Electromagnetic Applications of

Graphene and Graphene Oxide

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Abstract

Since the isolation of graphene in 2004, a large amount of research has been directed at 2D materials and their applications due to their unique characteristics. This thesis delivers pioneering developments on the applications of graphene and graphene oxide (GO) on electromagnetic ranges such as radio frequency, microwave frequency and THz bands, and specifically 2D materials based antennas, absorbers, sensors and etc.

This thesis focuses on exploring electromagnetic applications of monolayer graphene, printed graphene and graphene oxide. In study of monolayer graphene applications, the theoretical and simulation studies are carried out to design tunable terahertz (THz) absorbers, tunable microwave wideband absorbers, and reconfigurable antennas, etc. These studies on the applications of monolayer graphene have proved prospective potentials of graphene in THz sensing, RCS reduction, and reconfigurable antennas.

This thesis also presents pioneering advances on electromagnetic applications of printed graphene. Among these works, low-cost highly conductive and mechanically flexible printed graphene is developed for radio frequency (RF) applications. For the first time, effective RF radiation of printed graphene is experimentally demonstrated. Based on these results, applications of printed graphene including RFID (radio frequency identification) tags, anti-tampering RFID, EMI shielding, flexible microwave components such as transmission lines, resonators and antennas, conformable wideband radar absorbers, graphene oxide based wireless sensors, etc. are developed and experimentally demonstrated. This work significantly expands applications of graphene in electromagnetic areas.
Declaration

No portion of the work referred to in this thesis has been submitted in support of an application for another degree or qualification of this or any other university or other institute of learning.
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# Acronyms

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
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<tbody>
<tr>
<td>2D</td>
<td>Two dimensional</td>
</tr>
<tr>
<td>3D</td>
<td>Three dimensional</td>
</tr>
<tr>
<td>AFM</td>
<td>Atomic force microscopy</td>
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<tr>
<td>AgNW</td>
<td>Silver nanowire</td>
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<td>CNTs</td>
<td>Carbon nanotubes</td>
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<td>CPW</td>
<td>Coplanar waveguide</td>
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<tr>
<td>CuNW</td>
<td>Copper nanowire</td>
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<tr>
<td>CVD</td>
<td>Chemical vapor deposition</td>
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<td>DC</td>
<td>Direct current</td>
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<tr>
<td>DMA</td>
<td>Dimethylacetamide</td>
</tr>
<tr>
<td>DMF</td>
<td>Dimethylformamide</td>
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<tr>
<td>DUT</td>
<td>Device under test</td>
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<tr>
<td>EC</td>
<td>Ethyl cellulose</td>
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<tr>
<td>EM</td>
<td>Electromagnetic</td>
</tr>
<tr>
<td>EMC</td>
<td>Electromagnetic compatibility</td>
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<td>EMI</td>
<td>Electromagnetic interference</td>
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<td>FSS</td>
<td>Frequency selective surface</td>
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<td>GO</td>
<td>Graphene oxide</td>
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<tr>
<td>HOPG</td>
<td>Highly oriented pyrolytic graphite</td>
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<tr>
<td>Abbreviation</td>
<td>Definition</td>
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<tr>
<td>IC</td>
<td>Integrated circuit</td>
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<tr>
<td>ICP</td>
<td>Intrinsically conducting organic polymers</td>
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<tr>
<td>IOT</td>
<td>Internet of things</td>
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<td>ITO</td>
<td>Indium tin oxide</td>
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<tr>
<td>LED</td>
<td>Light emitting diode</td>
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<tr>
<td>LNA</td>
<td>Low-noise amplifier</td>
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<td>LPE</td>
<td>Liquid phase exfoliation</td>
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<td>M2M</td>
<td>Machine to machine</td>
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<td>MC</td>
<td>Micromechanical cleavage</td>
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<td>MEMS</td>
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<td>PCB</td>
<td>Printed circuit board</td>
</tr>
<tr>
<td>PDMS</td>
<td>Polydimethylsiloxane</td>
</tr>
<tr>
<td>PEC</td>
<td>Perfect electronic conductor</td>
</tr>
<tr>
<td>PET</td>
<td>Polyethylene terephthalate</td>
</tr>
<tr>
<td>RCS</td>
<td>Radar cross section</td>
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<tr>
<td>RF</td>
<td>Radio frequency</td>
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<tr>
<td>Acronym</td>
<td>Description</td>
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<tr>
<td>RFID</td>
<td>Radio frequency identification</td>
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<tr>
<td>RGO</td>
<td>Reduced graphene oxide</td>
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<tr>
<td>SE</td>
<td>Shielding effectiveness</td>
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<tr>
<td>SEM</td>
<td>Scanning electron microscope</td>
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<td>SLG</td>
<td>Single layer graphene</td>
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<td>SMA</td>
<td>Subminiature version A</td>
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<tr>
<td>SRR</td>
<td>Split ring resonator</td>
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<td>SSA</td>
<td>Specific surface area</td>
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<td>TE</td>
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<td>THz</td>
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<td>TL</td>
<td>Transmission line</td>
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<tr>
<td>TM</td>
<td>Transverse magnetic</td>
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<tr>
<td>UHF</td>
<td>Ultra high frequency</td>
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<tr>
<td>UWB</td>
<td>Ultra-wideband</td>
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<tr>
<td>VNA</td>
<td>Vector network analyzer</td>
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<tr>
<td>WLAN</td>
<td>Wireless local area network</td>
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Chapter 1: Research Background

Introduction

1.1 Graphene and Graphene Oxide

1.1.1 Graphene

Graphene is a one-atom-thick layer of carbon atoms arranged in a hexagonal lattice [1]. It is the building-block of graphitic materials of all other dimensionalities as shown in Figure 1.1. 2D graphene can be wrapped up into 0D fullerenes, rolled into 1D nanotube or stacked into 3D graphite [2]. But graphene itself is a remarkable material with a multitude of astonishing properties which repeatedly earn it the title “wonder material” [3-4].

Figure 1.1 2D graphene is the mother of all carbon materials in other dimensionalities. It can be wrapped up into 0D fullerenes, rolled into 1D nanotube or stacked into 3D graphite [2].

What makes graphene so distinguished is its sp2 hybridization and atomic thickness of 0.345 nm [1,2,4]. These properties enable graphene outstanding performances in terms of
electricity, mechanical strength, and heat conduction, etc. [5-12]. Its electron mobility at room temperature is proved to be as high as 200,000 cm²/(V·s) [6]. Graphene is also the lowest resistivity substance at room temperature [1,4]. The resistivity of graphene sheet is 1×10⁻⁶ Ω·cm, less than the resistivity of silver with 1.59×10⁻⁶ Ω·cm [7-10]. The high conductivity (low resistivity) of graphene results from its zero-overlap semimetal, which has both holes and electrons as charge carriers [13]. Carbon atoms have a total of 6 electrons, and 2 of them are in the inner shell and the other 4 in the outer shell. The 4 outer shell electrons in an individual carbon atom are available for chemical bonding. However, each carbon atom is connected to 3 other carbon atoms on the two dimensional plane of graphene, leaving 1 electron freely available in the third dimension for electronic conduction. These highly-mobile electrons are called pi (π) electrons which are located above and below the graphene sheet. These pi (π) orbitals overlap and help to enhance the bonds between carbon atoms in graphene [13-14].

The mechanical property of graphene is also extraordinary [1,7,12]. Graphene is believed to be the strongest material, which is around 200 times stronger than structural steel [12]. Also, graphene has a theoretical specific surface area (SSA) of 2630 m²/g [15-16]. This is much larger than that reported for carbon black (typically smaller than 900 m²/g) or for carbon nanotubes (in range of 100 to 1000 m²/g) [17].

Graphene is an extremely diverse material, which can be combined with other elements such as gases and metals, etc., to create different materials with superior properties in many aspects [18-28]. Researchers continue and persevere to explore graphene’s properties and possible applications, which includes flexible displays [18], high-speed transistors [19-20], batteries [21-22], supercapacitors [23-24], DNA sequencing [25], water filters [26], antennas [27], solar cells [28], and so on.
Fabrication of graphene is the foundation of its property study and applications. People have developed many techniques to fabricate graphene for different purposes. The followed Figure 1.2 summarizes the main fabrication methods [29].

Figure 1.2 Schematic illustration of the main graphene production techniques. (a) Micromechanical cleavage; (b) Anodic bonding; (c) Photo-exfoliation; (d) Liquid phase exfoliation; (e) Growth on SiC; (f) Segregation or precipitation from carbon containing metal substrate; (g) Chemical vapor deposition. (h) Molecular beam epitaxy; (i) Chemical synthesis using benzene as building blocks [29].

Among these methods, micromechanical cleavage (MC), also known as micromechanical exfoliation, is now optimized to yield high quality graphene layers. As illustrated in Figure 1.2a, using an adhesive tape, the single layer graphene (SLG) was firstly isolated from MC by Novoselov et al. [30]. The size of graphene produced from MC is limited by the single crystal grains in the starting graphite, which is in the order of millimetres [4,5]. The number of layers of graphene from MC method can be readily identified by elastic [31] and inelastic light scattering [32]. Raman spectroscopy can also
be used for fast and non-destructive monitoring of graphene’s doping, defects, strain, disorder, chemical modifications, and edges [29, 33-36], as seen in Figure 1.3.

Figure 1.3 Optical micrograph of graphene flake from MC method. (a) The optical micrograph of graphene flakes consisting of different layers; (b) Evolution of Raman spectra with the different numbers of graphene layers, and the spectra are normalized to have the same G peak intensity [29,32].

Even though the MC method can produce high quality SLG, its size limitation and low efficiency make it unsuitable for mass production and industrial applications. Instead, chemical vapor deposition (CVD) is a method suitable for mass production of large area hetero-structures, though it requires the large investment and effort in terms of identifying the precursors, system design and process development [37-38]. Besides, in order to get high-quality graphene, it is important to strictly adhere to guidelines set concerning pressure, temperature, gas volumes, and time duration, etc. [29, 39].
Simply put, CVD is a way of depositing gaseous reactants onto a substrate. The way CVD works is combining gas molecules in a reaction chamber which is typically set at ambient temperature. When the combined gases come into contact with the substrate within the reaction chamber (which is heated), a reaction creating a material film on the substrate surface occurs. The waste gases are then pumped out from the reaction chamber. The temperature of the substrate is a primary condition that defines the type of reaction, so it is critical to guarantee the correct temperature, etc. [40][41].

Figure 1.4 CVD preparation of graphene. (a) Thermal CVD set-up for the fabrication of graphene [42]; (b) grown CVD graphene on copper foil [43].

The advantage of using CVD method to deposit materials onto a substrate is the high quality of the resulting materials. Other common characteristics of CVD coatings include imperviousness, high purity, fine grained and increased hardness over other coating methods [38-39]. It is a common solution for the film deposit in semiconductor industry, and optoelectronics, due to the lower costs compared with other methods creating high-purity films [38].

CVD graphene is still expensive to synthesize and not user friendly because of the supporting metal substrates [39,41,43]. Liquid phase exfoliation (LPE) is believed to be an alternative route to give low cost, medium quality, large area and mass production of graphene. By this method it is possible to get defect-free, un-oxidized graphene flakes.
which can be deposited on the desired substrate. The exfoliation of graphite in different organic solvents is based on the matching between solvents’ surface energies and the energy required for exfoliating graphene [29,47]. The hi-boiling point solvents such as NMP (N-Methyl-2-pyrrolidone) and DMA (Dimethylacetamide) are suitable for exfoliating graphene flakes with help of surfactants. Also, some volatile solvents like Isopropanol and Chloroform are also effective for making graphene flakes [44-47]. The schedule of making liquid phase exfoliation graphene is shown in Figure 1.5. The highly oriented pyrolytic graphite (HOPG) is sonicated in solvents, and through centrifugation fewer layer graphene nano-flakes can be obtained [29]. The graphene ink can be further deposited on substrate to form uniform films.

As seen from the above schedule, the LPE is cheap and easily scalable, and does not require expensive growth substrates. Furthermore it is an ideal method to produce graphene based inks [49], thin films [50], composites [51], as in Figure 1.6(a)-(c) respectively. The resulting materials can be deposited on different rigid or flexible substrates by drop and dip casting [52], rod coating, spray coating [53], screen and ink-jet printing [49], corresponding to Figure 1.6 (d)-(g) [29].
Figure 1.6 Graphene from LPE and its deposition with various methods. (a) Graphene ink produced via LPE of graphite [49]; (b) Graphene-based transparent and flexible conductive film [50]; (c) Graphene polymer composite produced via LPE of graphite in water and mixed with Polyvinyl alcohol [51]; (d) Dip casting of LPE graphene. The substrate is immersed in the graphene dispersion/ink to obtain a uniform coverage [52]; (e) Rod coating of LPE graphene. In this coating process, a wire-covered metal bar (Meyer bar) is used to apply in a controlled way the graphene dispersion onto the substrate; (f) Spray coating. The graphene dispersion/ink is deposited through the air onto the substrate by a device sprays (e.g. spray gun) [53]; (g) Ink-jet printing is used to deposit droplets of graphene inks on substrates with higher precision [29].

1.1.2 Graphene oxide

As graphene is expensive and relatively hard to produce, great efforts are made to find effective yet inexpensive ways to make and use graphene derivatives or related materials [54]. Graphene oxide (GO) is one of such materials. Due to the presence of oxygen functionalities, GO can easily disperse in organic solvents, water, and different matrixes. This is a major benefit when combining it with polymer or ceramics to enhance mechanical and electrical properties [55]. GO is a single-atomic layered material, made by the
powerful oxidation of graphite, which is cheap and abundant. Graphene oxide is an oxidized form of graphene with abundant oxygen-containing groups, as seen in the Figure 1.7. These groups make GO possible to be functionalized with chemical alteration. With GO and GO derivatives such as GO-based composites, GO-based coating and thin films, as well as GO-based nanoparticles, many applications have been developed in sensors [57], nanocomposite materials [58], polymer composite materials, energy storage, biomedical applications, etc. [56,59-61].

![Figure 1.7 Graphene oxide](image)

Figure 1.7 Graphene oxide [62].

With respect to electrical conductivity, GO is an electrical insulator. It could however work as an intermediary in the production of conductive graphene sheets. In mass production of graphene, the method through chemical reduction of graphene oxide is one of the most viable cheap and easy methods. As displayed in the following Figure 1.8, to make graphene from graphene oxide reduction method, an oxidization and reduction process should be developed so that carbon layers can be isolated and separated without changing their structure.

After oxidation of graphite with strong oxidizing agents, oxygenated functionalities are introduced in the graphite structure which not only help to expand the layer separation, but also makes the material hydrophilic (meaning that they can be dispersed in water) [63-64].
This property enables the graphite oxide to be exfoliated in water or ethyl alcohol using sonication and ultimately single or few-layer graphene oxide are produced [46,]. The main difference between graphite oxide and graphene oxide is the number of layers. In graphene oxide dispersion, both few-layer flakes and monolayer flakes can be found. In order to recover the honeycomb hexagonal lattice, and restore it electrical conductivity, the reduction of the graphene oxide has to be achieved [67-70]. After reduction, most of the oxygen groups on GO are removed, and reduced graphene oxide (RGO) is left. It should be noted that currently no method can remove the oxygen groups completely to make pure graphene. However, RGO is very conductive due to the removal of most the oxygen groups, as discussed later in Figure 1.10.

Figure 1.8 GO synthesis and reduction [66]. Graphite can be oxidized with different procedures in the presence of strong acids. The GO flakes are functionalized with epoxy and hydroxyl groups both above and below, and at the edges [64-65]. A recovery of the electronic properties can be reached with a reduction treatment [67-71]. However, none of the current approaches can completely remove all the defects.

With the superior hydrophilic property and good compatibility with various substrates, GO solution is developed in market. The following Figure 1.9 gives the graphene oxide aqueous solutions with various weight percentages of GO. As seen, GO solution with low weight percentage is light tallow, while its color turns to darker when the GO percentage is higher.
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Figure 1.9 Graphene oxide aqueous solutions in market [72].

Except for aqueous solutions, GO can also be printed as membrane on transparent PET (Polyethylene terephthalate) substrate. As seen in following Figure 1.10 (a), the coated GO is yellow and non-conductive. However, after reduction, the RGO is black and has sheet resistance of around 30-40 Ω/Sq.

Figure 1.10 Graphene oxide and reduced graphene oxide on PET. (a) Graphene oxide membrane; (b) Reduced graphene oxide.

1.2 CVD Graphene EM Application Research

As introduced in above Section 1.1, graphene and graphene oxide have been explored in wide range applications such as flexible displays, high-speed transistors, batteries, energy storage, supercapacitors, DNA sequencing, water filters, sensors, composite
materials, energy storage, biomedical applications, etc. Besides, graphene has also been widely researched in electromagnetic applications. The proposed research and potential applications have covered wide frequency band from optical frequency to THz, infrared to microwave band. In the following parts, the main applications of graphene in EM are introduced with some typical published works.

1.2.1 EM characterization of graphene

To better apply graphene for EM field, it is critical to understand its electromagnetic properties. The study of the graphene’s response on EM waves can provide reference for graphene modeling in simulations, so that further graphene related designs can be conducted. The characterization of graphene is mainly done using two methods, transmission line method and free space method.

In the early stage of graphene EM characterization research, the size of available graphene sheet was quite small as they were exfoliated graphene or small-sized CVD graphene. The transmission line method is suitable for the small-sized graphene measurement. As seen in Figure 1.11 (a), graphene sheet with size of 38 µm×190 µm is inserted in the gap of CPW (coplanar waveguide) signal trace to measure the resistor of graphene sheet. Also, in Figure 1.11(b), another two graphene sheets with size of 700 µm×20 µm are placed in between signal trace and CPW grounds for the graphene’s equivalent inductance measurement. Simulations and experiments show that graphene has almost constant sheet resistance in frequency band under 110 GHz, and the equivalent resistance is around 1100 Ω [73].
Figure 1.11 The simulated (dashed lines) and measured (solid lines) performance of graphene transmission lines [73]. (a) Graphene is inserted in conductor gap to characterize the resistance; (b) Graphene shunt in TL to characterize inductance.

A similar work has also been conducted as shown in Figure 1.12 to characterize the SLG (single layer graphene) and MSG (multi-layer graphene), and build up their equivalent circuit models in microwave bands [74].

As seen in the Figure 1.12, the equivalent circuit model of graphene based TL is extracted and the characteristic impedances of SLG and MLG are obtained and a consistency of simulation and experiments is achieved. Also, in this work, the attenuation and phase constants of the graphene based CPW lines are measured, which explored the possibility of graphene based TL.
Figure 1.12 Characterization of SLG and MLG in transmission line structure. (a) Measurement principle and equivalent circuit model; (b) Extracted impedance of SLG and MLG; (c) The measured performance of graphene based transmission lines [74].

The TL characterization of graphene sheet requires transfer of graphene, which is easy to bring damage to graphene sheet. The free space method is a non-contact measurement, which protects the sample well. As seen in Figure 1.13(a), a non-contact measurement is setup in waveguide measurement system, and graphene sheet is placed between several...
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layers of dielectric. The transmission and reflection of the layered sample was measured, and the measurement data was used to calculate the impedance of graphene sheet with transfer matrix method [75,76]. From this calculated surface impedance of graphene sheet shown in Figure 1.13(b), it can be seen that the graphene sheets have around 2-4 kΩ resistance, and the imaginary part of surface impedance is negative. Besides, the surface impedance is also almost frequency-independent at microwave band [75].

![Figure 1.13 Characterization of graphene sheet of space method. (a) Measurement setup of stacked layer sample in waveguide; (b) Calculated surface impedance of graphene sheet [75].](image)

1.2.2 Graphene based circuit/components

Graphene has attracted much research interest on electronic circuit applications due to its high conductivity and tunability. Researchers have studied graphene’s possibility in microwave circuit design like phase shifter, and filters, etc.

In Figure 1.14, a THz switch was studied and used for THz phase shifter [77]. As seen in the phase shifter structure, the phase shift can be tuned by selecting switch on/off. When the external voltage is applied on the graphene, the conductivity of graphene increase to the proper level and the switch is on, otherwise it is off. This switch is then used in phase shifter to change the effective length, so that the phase shift can be tuned [77].
Besides, with similar principles, graphene based tunable low-pass filters were studied [78-79]. As seen in the design of Figure 1.15 (a), several gating pads locate beneath monolayer graphene sheet. From the simulated performance in Figure 1.15 (b), the working band of low-pass filter can be tuned with different statues of graphene sheet [79].

Except for bandpass filter, a band-stop THz filter was also proposed as in Figure 1.16 with similar designs. The graphene Plasmon is used to design the filter, and the performance in Figure 1.16 has shown more than 20 THz tunability when the chemical potential of graphene is tuned from 0.3 eV to 0.6 eV [80].
Figure 1.16 Band-stop THz filter with tunable working frequency [80]. (a) Band-stop filter design based on graphene; (b) Performances of the frequency-tunable band-stop filter under different chemical potentials of graphene.

Moreover, graphene was also investigated in tunable microwave attenuator as in Figure 1.17. The measurement setup is shown in Figure 1.17(a), and the measured insertion loss in Figure 1.17(b) has shown more than 5dB tunability with only 5.5 V external voltage [81].

Figure 1.17 Graphene based tunable microwave attenuator [81]. (a) Measurement setup for the tunable attenuator; (b) Measured tunable insertion loss of the graphene based attenuator under various external voltages.

### 1.2.3 EMI shielding

As graphene can be regarded as a transparent conductive sheet, it is a suitable candidate for EMI (electromagnetic interference) shielding in some applications requiring transparency. Figure 1.18 gives the measurement setup and the result for EMI shielding of
graphene sheet. It was demonstrated that several layers of epitaxial graphene at 12–18 GHz can obtain an average of -15 dB rejection with above 70% visible transparency [21]. This result proves that graphene has much potential values in applications requiring both light transparency and high shielding effectiveness [82].

![Graphene EMI Rejection at Ku-band](image)

Figure 1.18 The test and result of graphene sheet for EMI shielding [82].

### 1.2.4 THz modulator

In THz frequency band, the reactance of graphene sheet can also be tuned with external voltage, which fuels the research of tunable THz modulator. Figure 1.19 gives the design and working principle of the THz modulator. As seen, the layered graphene sheet can be tuned by external voltages, which changes their sheet resistance and responses to THz beams. Ideally, when the applied voltages are all 0 V, then the THz transmission is 1. However, when the voltages are properly tuned, the transmission is 0. From the principle and performances, it can be seen that the modulator can response differently to THz beam with external voltage control [83].
Another developed THz modulator is shown in Figure 1.20. In this design, a graphene sheet is placed under a patterned metal resonance structure. The transmission of the modulator under incident waves can be tuned as sheet resistance of graphene can be controlled. As seen in the principle, when external voltages are applied, the fermi level of the graphene layer is changed [84].

Figure 1.20 THz modulator with hybrid of graphene sheet and metal structure [84]. (a) Arrayed structure of the graphene based modulator; (b) Structure of the modulator unit cell; (c) Effects of graphene’s Fermi level on transmission of modulator.
The magnitude and phase modulation of the THz modulator is shown in Figure 1.21. From the performance, the surface conductivity of the graphene sheet can be tuned, which can be used to modulate the magnitude and phase of the transmission. It should also be noticed that the combination of resonance structure and graphene can enhance the modulation function of graphene, as the interaction of field and graphene is stronger at resonance frequency [84].

![Graph](image)

Figure 1.21 The tunability of magnitude and phase of transmission with voltage controlled conductivity of graphene. (a) Transmission of the modulator under various sheet conductivity of graphene; (b) Transmission phase of the modulator under various sheet conductivity of graphene [84].

### 1.2.5 Graphene based absorber

As graphene is proved to have frequency-independent sheet resistance in microwave and low THz band, it is suitable for designing THz and microwave absorbers. Figure 1.22
shows the design of graphene based THz metamaterial absorber. This absorber is based on graphene fishnet pattern, and both THz narrow band and wideband absorbers are designed for THz sensing. As can be seen from Figure 1.22 (b), due to the tunability on graphene’s sheet resistance, the narrow-band absorber has tunable working band when different chemical potentials is applied, while the absorption decreases, so as the case of the wideband absorber design [85]. However, for THz sensing applications, the absorption is preferred to be constant when the frequency is scanned, so that the detected signals are easier to be measured and characterized. In Chapter 2 of this thesis, a working frequency tunable THz absorber is designed with constantly maintained absorption peak, which is highly desirable in THz sensing applications.

![Design of tunable THz narrow band absorber and wideband absorber](image)

Figure 1.22 Design of tunable THz narrow band absorber and wideband absorber. (a) Fishnet graphene pattern based absorber structure; (b) Absorption and tunability of narrow-band absorber; (c) Absorption and tunability of wide-band absorber [85].

Also, researchers have studied graphene’s possibility in microwave band absorbers. The following work uses the multi laid graphene to imitate the case of different chemical potentials. As can be seen in Figure 1.23, the absorption is tuned under different chemical potentials and the working frequency is fixed. With the multi-laying graphene sheet method, the potential of graphene in tunable microwave absorber is proved [86].
Figure 1.23 The simulated and measured absorption of the graphene based microwave absorber. (a) Simulated reflections of the graphene based absorber under various chemical potentials; (b) Measured reflections of the graphene based absorber with different layers to imitate chemical potential changes; (c) Simulated absorptions of the graphene based absorber under various chemical potentials; (d) Measured absorptions of the graphene based absorber with different layers to imitate chemical potential changes [86].

1.3 Conductive Nanomaterials and Their Applications

Conductive nanomaterials are widely used in many practical applications such as printed electronics, touch screen, flexible display, etc. [87-89]. In this section, conductive nanomaterials including metal nanoparticles, nanowires, conductive polymers, carbon nanotubes, and graphene, are briefly introduced and compared. Besides, the applications of these conductive nanomaterials are introduced. From this introduction, it can be seen that printed graphene has its advantages in high conductivity, low cost, and mechanical flexibility. These superior characteristics boot graphene’s application in RF radiation, wearable electronics, as well as EMI shielding, etc. which are introduced in the following several chapters respectively.
Currently, Indium tin oxide (ITO) is a transparent conductor of choice for most electronic screens (such as smart phone screens) because of its high light transmittance and conductivity, but it is scarce, brittle, and expensive [90-91]. The cost of ITO films is relatively high due to not only the fact that indium is a rare and costly material, but also ITO must be deposited in an inefficient, low-throughput, vapor-phase coating process that, at 0.01 m/s, which is 1000 times slower than wet-coating processes such as newspaper printing [92]. These limitations of ITO have hindered further cost reduction of widely used screens, which has motivated a worldwide search for flexible, low-cost alternatives that can be deposited at rates orders of magnitude greater than vapor-phase coating processes. Here these possible competitors are listed and compared.

1.3.1 Metal nanoparticles

Metal based nanoparticles, such as nano-silver inks, which are widely used today for conductive printing, enable obtaining printed patterns with high conductivity. The followed Figure 1.24 gives the SEM of conductive grid lines made of silver nanoparticles. The grids have balanced both required light transparency and conductivity [93].

![Figure 1.24 SEM images of the transparent grid composed of silver NPs. (a) A 2x2 mm section of the sintered silver grid; (b–d) SEM observations at various magnifications [93].](image-url)
Even though metal based nanoparticles offer high conductivity, it is however normally expensive, and some challenges are needed to overcome. Firstly, nanoparticles in the ink should be stable against aggregation and precipitation in order to provide reproducible performance. Therefore, stabilizing agents are required, which are normally non-conductive polymeric materials or surfactants. In conductive inks with high metal loading, stabilizer is critically important to make uniform dispersions. The presence of stabilizer usually poses a major problem when aiming at high conductivity, as they are isolators [94].

Secondly, silver nanoparticles is widely utilized in industrial applications, it is however expensive as silver is scare and costly. Due to their high cost, researchers are exploring to replace silver with cheaper alternatives, such as copper and aluminum. This would depend on the success in avoiding their oxidation at ambient conditions. For example, aluminum undergoes rapid oxidation in air (within around 100 picoseconds) forming a dense thin amorphous Al₂O₃ layer with a thickness of 2–6 nm [95], which results in the loss of electrical conductivity and makes aluminum NPs inapplicable for conductive ink formulations.

Another challenge in using metallic nanoparticles is the need for post-processing in order to sinter the NPs for obtaining continuous metallic phase. The printed nanoparticles are independently isolated and much less conductive. After sintering, the nanoparticles are connected to form a uniform surface and conductivity can be significantly enhanced [96]. The conventional approach for sintering metallic NPs is heating. However, in the case of heat-sensitive substrates (e.g. paper, plastics), heating at temperatures above 120-150 °C is not applicable and, therefore, non-destructive methods of sintering are required [94].

Highly conductive metal based nanoparticles have many applications such as electroluminescent device as in followed Figure 1.25 [93].
Figure 1.25 Silver nanoparticles for flexible transparent film. (a–c) Images of electroluminescent device printed with conductive silver nanoparticles, under different magnifications. (d) Demonstration of the flexibility and transparency of the conductive silver grid [93].

Another approach is given in Figure 1.26. A transparent conductive screen is achieved with gold network printed with Au NPs. As seen from Figure 1.26(b), the conductive screen has demonstrated high transparency and flexibility. It should be noticed that the gold network formed by Au NPs requires sintering temperature at 425 °C on glass first, and then transferred to PET film [97].

Figure 1.26 Transparent conductive screen fabricated with Au nanoparticles on PET. (a) Au grids transferred to PET film; (b) Image of the transparent and flexible film [97].
1.3.2 Metal nanowires

Except for metal based nanoparticles, metal nanowire is another catalogue for providing high conductivity, taking advantages of superior conductivity of metals. As seen in Figure 1.27, the SEMs of silver based nanowires are shown, under different coating density and thickness. From the figure, it can be seen that when density of silver nanowire coating increase, the transparency decrease. As seen, when the film is coated with 780 mg/m², the substrate is fully covered and low transparency can be provided. Naturally, the sheet resistance of the film decreases with denser coating. For the less thick coating with M/A (Metal/Area) of 70 mg/m², the sheet resistance is $R_s=3.4 \ \Omega/$Sq. When the coating increase to M/A= 230 mg/m², its sheet resistance decreases to 0.5 $\Omega/$Sq [98].

![Figure 1.27 Films deposited with varying coating thickness of silver nanowires [98].](image)

To replace expensive silver, researchers have also developed copper nanowires, to provide high conductivity at lower cost. As seen in the following Figure 1.28, the SEMs of copper nanowires are given. Similarly, with denser nanowires coating, lower sheet resistance can be obtained. However, as seen in the figure, thicker coating gives lower
sheet resistance but also lower transparency [92]. In real applications, the sheet resistance and transparency should be balanced.

Figure 1.28 Optical and SEM observation of copper nanowires based films. (a) Optical microscope images of an uniformly dispersed films of CuNWs with providing 90% transparency with sheet resistances of 186 $\Omega$/Sq; (b) Optical microscope images of CuNWs films providing 85% transparency with sheet resistances 30 $\Omega$/Sq; (c) SEM of the CuNW films from sample in (a); (d) SEM of the CuNW films from (b) [92].

Moreover, Researchers have applied these metal based nanowires to wearable antennas and flexible circuits. Figure 1.29 illustrates how the AgNWs based antenna is fabricated, by embedding AgNWs in flexible material polydimethylsiloxane (PDMS, known as silicone). The final fabricated sample has thickness of 3 mm and the sheet resistance of the embedded AgNWs was measured to be lower than 5 $\Omega$/Sq [99].
Figure 1.29 Fabrication process of embedding AgNWs in PDMS; (a) AgNWs were firstly deposited on a silicon wafer and etched with a mask; (b) Liquid PDMS was poured on the silicon wafer after the removal of the mask; (c) After peeling off the PDMS, the embedded AgNWs were revealed [99].

Figure 1.30 Measured $S_{11}$ of the AgNWs based flexible RF antenna under different applied forces [99].

In Figure 1.30, the $S_{11}$ of the flexible antenna is given, and also different forces were applied to push the antenna. As can be seen, proper impedance matching of the RF antenna was achieved, and also a notable shift of working frequency to lower band were observed with increasing applied force [99].

Also, the CuNWs were incorporated into an ink that could be coated onto a clear plastic substrate to give a flexible, transparent conducting film with properties close to films of AgNWs. As seen in Figure 1.31, CuMWs is coated on transparent film as conductive line connection to bulb, showing its potentials in transparent electronics [92].
Figure 1.31 CuNWs based ink is coated on flexible film to form conductive and transparent film. (a) CuNW ink before coating; (b) The CuNWs is coated on PET with a Meyer rod. (c) The transparent CuNW film (25 Ω/Sq and 83% transparency) is bent in completing an electrical circuit with a battery pack and a LED [92].

1.3.3 Conductive polymers

Conductive polymers are intrinsically conducting organic polymers (ICPs). Such compounds can have metallic conductivity or can be semiconductors [100]. Conductive polymers normally have low conductivity, so that they can hardly be used for microwave radiation. However, they are widely studied for wearable electronics like sensors.

Figures 1.32 1.33 show the applications of conductive polymer in flexible strain sensors. In Figure 1.32, the conductive polymer is printed on the Nylon fabric for strain sensing [101]. Also in Figure 1.33, the strain sensors based on conductive polymers are used on parachute to monitor the working statues [102]. In these applications, the conductivity requirement is not that high, while mechanical flexibility is essential. In some applications requiring high conductivity and low cost, conductive polymers are not in the options. Except for the low conductivity, applications of conductive polymers are also limited by their chemical and thermal instability [103].
1.3.4 Carbon nanotubes/Carbon black

Carbon based conductive materials provide a good alternative to metal NPs, due to their advantageous electrical and mechanical properties. CNTs are cylindrical nanomaterials. Researchers have constructed CNTs with length-to-diameter ratio up to 132,000,000:1, which is significantly larger than any other materials [104]. The intrinsic electrical conductivity of individual CNTs is close to the conductivities of metals [105].
However, because of their large aspect ratio, van der Waals forces cause them to stick together, thus forming large bundles or ropes [106]. Therefore, the major challenge in formulating CNTs based conductive inks is the preparation of dispersions composed of separated CNTs without chemical modification, mechanical damage (e.g. buckling, bending), which is important for high electrical conductivity [107-109].

Although the intrinsic electrical resistivity of individual CNTs is as low as $10^8 \Omega \cdot m$ [110], the resistivity of CNT films is however higher, and the reported values from experimental data is in a wide range of $7.8 \times 10^8 \Omega \cdot m$ to $2.3 \times 10^3 \Omega \cdot m$. The applications of CNTs are limited by its relatively high sheet resistance, which is in range of 0.05-100 kΩ/Sq [105,111]. This high resistance is mainly from the high contact resistance between overlapped nanotubes (due to van der Waals as explained in above paragraph) in the random network (junction resistance). Usually, longer CNTs lead to more conductive films, as it reduces the number of CNT junctions per unit area [112].

![Figure 1.34 CNTs conductive film and its SEM. (a) CNTs film floating on the water surface; (b) releasing from the glass substrate; (c) The film is transferred to filter paper; (d) SEM images of CNT films [113].](image)

Figure 1.34 shows morphologies of CNT conductive films. A film of single-walled carbon nanotubes (SWCNT) is spin coated on a glass slide to form uniform film. The film is then transferred to a filter paper. The CNTs film is characterized with sheet resistance of
59 Ω/Sq [113]. From the SEM of the film as in Figure 1.34 (d), the carbon nanotubes are randomly cross-lapped and stacked.

Another widely used carbon material is carbon black. Carbon black is composed of fine particles consisting mainly of carbon [114]. Its applications cover black coloring pigment of inks, resin and film coloring agents, electric conductive agent, etc.

Carbon black is widely applied as conductive filler, as carbon black particles have the graphite-type crystalline structure which provides excellent electric conductivity. Therefore, it is normally mixed in paints, plastics, elastomer, adhesives, films, and pastes. For example, in fuel caps or fuel-introducing pipes of automobiles, the rubbers are required to be conductive to prevent static. These rubbers are normally filled with carbon black as excellent antistatic agent.

Carbon black also works as conductive agent in conductive inks. In industry, it is normally combined with other conductive agents such as silver, graphite, to reduce the cost [115]. Carbon black conductive ink can hardly provide high conductivity, due to the high contact resistance between particles. As seen in Figure 1.35, the carbon black particles are gathered together, and high contact resistance is introduced.

Figure 1.35 SEM of carbon black [116].
The property of carbon black based conductive ink is mainly determined by its particle size. The diameter of spherical carbon black particles determines the blackness and dispersibility when it is filled in ink. Generally, smaller carbon black particle size based ink has higher blackness. However, its dispersion becomes more difficult due to an increase of coagulation force. Beside, larger carbon black particles provide higher conductivity of ink if it can be uniformly and stably dispersed [117].

1.3.5 Printed graphene

Graphene, an allotrope of carbon nanotube, is a very promising material for conductive ink owing to its high conductivity and unique properties. The basic property and preparation methods of graphene have been introduced in the above Section 1.1. Here some published works about printed graphene are displayed.

To facilitate printing of graphene, normally graphene conductive inks are needed. The two main methods to prepare graphene ink are liquid phase exfoliation and RGO method. Graphene conductive ink can be printed through many printing methodologies such as inkjet printing, screen printing, gravure printing, stencil sputtering, etc.

The following Figure 1.36 gives the graphene based highly conductive ink for dipole antenna application. In this work, the graphene ink was prepared through RGO method, and the inkjet-printed micro-pattern offers sheet resistance of 65 $\Omega$/Sq. A dipole antenna was inkjet-printed to explore possibility in RF radiation, and a good impedance matching was achieved [118]. However, due to the high sheet resistance, effective RF radiation cannot be achieved because of the high ohmic loss from conductive materials. Obviously, more study is needed to improve the conductivity and demonstrate its effective radiation.
Figure 1.36 Optical microscopy images of the inkjet-printed graphene lines with different widths, and return loss of the printed dipole antenna. (a) Optical microscopy images of printed line with width of 70 μm; (b) Optical microscopy images of printed line with width of 100 μm; (c) Optical microscopy images of printed line with width of 200 μm; (d) Multi-meter electrical measurement of the full line and dash line with gaps of 70 μm to show the printing resolution; (e) Measured return loss of printed graphene dipole antenna [118].

A higher-resolution inkjet-printed graphene is achieved as shown in Figure 1.37. The graphene based conductive ink is prepared with liquid phase exfoliation. From the edge of the lines, it can be seen that the inkjet-printed graphene has high printing resolution. Besides, the inkjet-printed graphene shows conductivity of $2.5 \times 10^4$ S/m after a thermal anneal at 250 °C for 30 min, and uniform morphology, compatibility with flexible substrates, and excellent tolerance to bending stresses are demonstrated [119]. This work proves that graphene is a quite promising in flexible electronics.
Figure 1.37 Morphology of high-resolution inkjet-printed graphene lines. (a) SEM of multiple printed lines; (b) SEM of a single printed line and a drop in inset to illustrate the uniformity of the printed features pattern; (c) SEM image of a graphene line printed with multiple passes; (d) Cross-section thickness measured by AFM, with 1, 3, and 10 printing passes separately [119].

Except for inkjet printing, the graphene based conductive inks can also suit other printing methods. For example, Figure 1.38 shows the printing procedure of graphene conductive ink through stencil printing. A stencil made of 120 µm thickness silicon wafer is patterned. To print the pattern, a substrate is placed on a vacuum plate, and spacers around 2 mm thickness were inserted between the stencil and the substrate. The graphene ink, prepared with liquid phase exfoliation, was placed on top of the stencil and pushed by a squeegee. The ink was transferred through the opening on stencil to make patterns on the substrate [120].

The printed sample using the above described stencil printing is shown in Figure 1.39. As can be seen from printed graphene lines in Figure 1.39(a)-(c), the stencil printing of graphene ink has demonstrated high resolution on patterning both gaps and lines with resolution from 5 µm to 40 µm. Besides, in Figure 1.39 (d), two inks with shear viscosity of 1 Pa.s and 10 Pa.s were prepared and printed in 2 directions (A and B) with the same
printing method. From the comparison in Figure 1.39(d), it can be seen that this printing method has tolerance on ink viscosity and printing direction [120].

![Stencil printing of graphene ink](image)

Figure 1.38 Stencil printing of graphene ink. (a) Schematic process of screen printing using the silicon stencil and graphene ink. (b) Cross-sectional illustration of the screen printing method with the flexible silicon stencil during printing [120].

![High-resolution printed graphene lines](image)

Figure 1.39 The high-resolution printed graphene lines. (a) Optical microscopy image of lines with gaps of 20 μm, 30 μm, and 40 μm; (b) Printed line with width of 20 μm; (c) Printed line with width of 5 μm; (d) Printed lines from two inks of different viscosities (Ink 1 and 2), with two different printing directions (A and B) [120].

From the above introduction of various conductive nanomaterials, one can find the uniqueness of printed graphene by comparing with its competitors. In summary, silver
based nanomaterials are highly conductive and also expensive. Other metal nanomaterials such as copper nanoparticle have high conductivity and lower cost, but easy to be oxidized in high-temperature annealing. Conductive polymers are much less conductive for RF radiation and also unstable. Carbon nanomaterials such as CNTs and carbon black are initially highly conductive, low-cost and anti-oxidant. However, the contact resistance between nanoparticles and nanowires are high, making the printed samples less conductive for radiation. Graphene, which has advantages of high conductivity, low cost and resistance to oxidation, offers much lower contact resistance between nano-flakes owing to its 2D structure. These properties make printed graphene a promising candidate for printed RF applications.

1.4 Important Concept and Basic Theory

1.4.1 Skin depth

In practical problems, loss or attenuation are involved due to imperfect conductors. In a good conductor, the conductive current is much greater than the displacement current, which means $\sigma \gg \omega \varepsilon$. Metals can be categorized as good conductors. By ignoring the displacement current term, the propagation constant of the plane wave in the medium can be adequately approximated as [121]:

$$\gamma = \alpha + j\beta \cong j\omega\sqrt{\mu\varepsilon} \sqrt{\frac{\sigma}{j\omega\varepsilon}} = (1 + j)\sqrt{\frac{\omega\mu\sigma}{2}} \quad (1.1)$$

The skin depth, or characteristic depth of penetration, is defined as:

$$\delta_s = \frac{1}{\alpha} = \sqrt{\frac{2}{\omega\mu\sigma}} \quad (1.2)$$
From Equ. (1.1) and Equ. (1.2), the amplitude of the fields in the conductor decays by amount of $1/e$, or 36.8%, after traveling a distance of one skin depth, as $e^{-\alpha z} = e^{-\alpha \delta_s} = e^{-1}$. It should be noticed that at microwave frequencies, this distance is very small for a good conductor. For instance, at 10 GHz, the skin depth of silver is calculated to be $6.4 \times 10^{-7} \text{ m}$. The practical importance of this estimation is that only a thin plating of a good conductor (e.g., silver or gold) is necessary for low-loss microwave components.

### 1.4.2 Sheet resistance

Bulk resistivity ($\rho$) is a property that is independent of frequency and geometry. In microwaves engineering, thin films of conductors are normally dealt with. For thin films, the more convenient property to deal with is sheet resistance. The sheet resistance of a metal film is often expressed in $\Omega/\text{Sq}$ [122].

Recall the equation for calculating resistance from bulk resistivity as:

$$ R = \frac{\rho L}{wt} \quad (1.3) $$

where $R$ is the resistance, $\rho$ is the bulk resistivity in $\Omega \cdot \text{m}$, $w$ is the width of the resistor, $L$ is the length of the resistor, and $t$ is the thickness. The quantity $L/w$ can be taken as square numbers the conductor or resistor has.

The sheet resistance $R_s$ is equal to bulk resistivity divided by thickness. Namely:

$$ R_s = \frac{\rho}{t} \quad (1.4) $$

Combine (1.3) and (1.4), the resistance can be conveniently calculated from square numbers and sheet resistance as:

$$ R = R_s \frac{L}{w} \quad (1.5) $$
For example in Figure 1.40, a thin-film resistor with length 6 cm and width of 1 cm has 6 squares. Suppose the sheet resistivity of the thin-film resistor is 50 Ω/Sq, the resistor has value of 300 Ω.

### 1.4.3 Surface impedance

In many applications, attenuation or conductor loss of an imperfect conductor must be taken into account. The surface impedance concept is a very convenient and accurate manner to do it in an approximation [124]. As in Figure 1.41, considering a good conductor in the region z > 0, a normally incident plane wave on this conductor is mostly reflected, and the power transmitted into the conductor is dissipated as heat within a very short distance from the surface.
The power dissipated (or transmitted into) 1 m² area of conductor surface can be calculated as [124]:

\[
P_t = \frac{\sigma |E_0|^2 |T|^2}{4\alpha}
\]

(1.6)

where transmission

\[
T = \frac{2\eta}{\eta + \eta_0}
\]

(1.7)

and intrinsic impedance of a conductor is

\[
\eta = (1 + j) \frac{1}{\delta_s}
\]

(1.8)

Combine (1.7) (1.8) and \(\alpha = 1/\delta_s\), then:

\[
\frac{\sigma |T|^2}{\alpha} = \frac{\sigma \delta_s |\eta|^2}{|\eta + \eta_0|^2} \approx \frac{8}{\sigma \delta_s \eta_0^2}
\]

(1.9)

where \(\eta \ll \eta_0\) is assumed, which is true for a good conductor. Then the dissipated power in a lossy conductor can be written as:

\[
P_t = \frac{\sigma |E_0|^2 |T|^2}{4\alpha} = \frac{2|E_0|^2}{\sigma \delta_s \eta_0} = \frac{2|E_0|^2 R_s}{\eta_0^2}
\]

(1.10)

Then we can have:

\[
R_s = Re\{\eta\} = Re\left(\frac{1+j}{\sigma \delta_s}\right) = \frac{1}{\sigma \delta_s} = \frac{\omega \mu}{2\sigma}
\]

(1.11)

\(R_s\) is the surface resistance of the metal. Also from above (1.11), we can get [124]:

\[
R_s = \frac{1}{\sigma \delta_s} = \frac{\rho}{\delta_s}
\]

(1.12)

By comparing the surface resistance in (1.12) with DC sheet resistance in (1.4) \(R_s = \rho/t\), it can be seen that these two are quite similar in expression.
1.4.4 Three-antenna gain measurement method

For antenna gain or radiation pattern measurements, the ideal condition is an illumination of uniform plane wave. In practice, the transmitting antenna generates far fields which are approximately close to plane wave, when the observation point is far enough from the source. In antenna gain and radiation pattern measurements, the distance between transmitting and receiving antennas must be bigger than the any far-field zone of these two antennas, so that two antennas are in each other’s far-field zones. The minimum distance of far-field zone to source can be calculated as [125]:

\[ R_{\text{min}} = \frac{2D_{\text{max}}^2}{\lambda} \]  

(1.13)

\( D_{\text{max}} \) is the maximum dimension of the source antenna. It should be noticed that the above (1.13) suits electrically small antenna only.

![Antenna gain measurement system setup](image)

Figure 1.42 Antenna gain measurement system setup [126].

The three-antenna gain measurement method setup is shown in the above Figure 1.42. Three antennas are used in the whole measurement, and any two antennas are measured in pairs as in Figure 1.42. It does not matter whether an antenna is in a transmitting or in a receiving mode. There are three measurements involved with possible pairs of antennas:
antenna #1 and antenna #2; antenna #1 and antenna #3; antenna #2 and antenna #3. The calculations are based on Friis transmission equation as in Equ. (1.14), assuming that the antennas are well matched in terms of impedance and polarization,

\[
\frac{P_r}{P_t} = \left(\frac{\lambda}{4\pi R}\right)^2 G_t G_r
\]  

(1.14)

where \(P_r\) is the power transmitted from source antenna, and \(P_t\) is the received power, \(R\) is the distance between two antennas. In the case of two different antenna pairs (antenna \(\#i\) and antenna \(\#j\)) measured during experiment \(\#k\) (\(k=1,2,3\)), the Equ. (1.14) can be rewrite in dB format as [126,127]:

\[
G_{i \, dB} + G_{j \, dB} = 20 \log_{10} \left(\frac{4\pi R}{\lambda}\right) + 10 \log_{10} \left(\frac{P_r}{P_t}\right)^{(k)}
\]  

(1.15)

The whole measurement involves three experiments, and the Equ. (1.15) can be expanded as:

\[
G_{1 \, dB} + G_{2 \, dB} = 20 \log_{10} \left(\frac{4\pi R}{\lambda}\right) + 10 \log_{10} \left(\frac{P_r}{P_t}\right)^{(1)}
\]  

(1.16)

\[
G_{1 \, dB} + G_{3 \, dB} = 20 \log_{10} \left(\frac{4\pi R}{\lambda}\right) + 10 \log_{10} \left(\frac{P_r}{P_t}\right)^{(2)}
\]  

(1.17)

\[
G_{2 \, dB} + G_{3 \, dB} = 20 \log_{10} \left(\frac{4\pi R}{\lambda}\right) + 10 \log_{10} \left(\frac{P_r}{P_t}\right)^{(3)}
\]  

(1.18)

The right-hand sides of the Equ. (1.16), Equ. (1.17), Equ. (1.18) are known if the distance \(R\) (keep \(R\) the same in all three experiments) and the ratios received-power/transmitted-power are known (from measured S parameters). Then the above three equations can be simplified as:

\[
G_{1 \, dB} + G_{2 \, dB} = A
\]  

(1.19)

\[
G_{1 \, dB} + G_{3 \, dB} = B
\]  

(1.20)

\[
G_{2 \, dB} + G_{3 \, dB} = C
\]  

(1.21)
The solution of the antenna gains are:

\[ G_{1dB} = \frac{A+B-C}{2} \]  
(1.22)

\[ G_{2dB} = \frac{A-B+C}{2} \]  
(1.23)

\[ G_{3dB} = \frac{B+C-A}{2} \]  
(1.24)

From the above solutions of three antenna gains, it can be seen that this method can measure gain of three antennas simultaneously with three experiments.

### 1.4.5 Electromagnetic wave absorption

Several mechanisms can be used to explain EM absorption, which may involve the dielectric and/or magnetic properties of the materials. The primary mechanism of the loss is the conversion of microwave energy to heat dissipation [128]. The optimum absorber is normally required to have high absorption over a wide frequency range and a wide incident wave angle, as well as some mechanical requirements and robust adaptiveness to application environment. To minimize the reflection, proper structure and material arrangement is required to achieve appropriate impedance matching.

![Absorber structure and equivalent circuit model](image)

Figure 1.43 Typical absorber and its equivalent circuit model. (a) Absorber structure; (b) Transmission line equivalent circuit model of absorber [129].
As in Figure 1.43(a), a typical dielectric layer coated metallic surface can act as an absorber (frequently referred as Salisbury absorber when $t=\lambda/4$). Its transmission line equivalent circuit is shown in Figure 1.43(b), and the input impedance can be calculated with:

$$\frac{1}{Z_{in}} = \frac{1}{R_s} + \frac{1}{jZ_c \tan \beta t} \tag{1.25}$$

When the thickness $t=\lambda/4$,

$$\frac{1}{Z_{in}} = \frac{1}{R_s} + \frac{1}{Z_\infty} = \frac{1}{R_s} \tag{1.26}$$

Namely, $Z_{in} = R_s$ for the Salisbury screen. The reflection coefficient of the absorber is:

$$\Gamma = \frac{Z_{in} - Z_0}{Z_{in} + Z_0} \tag{1.27}$$

Clearly, if $Z_{in} = Z_0$, then the reflection $\Gamma = 0$, namely no reflected wave from the absorber. The purpose of the absorber design is to find the proper structure and materials to construct the absorber, and meet the conditions to obtain $\Gamma \to 0$ in wide frequency band and incident wave angles.

For the Salisbury screen, if the $R_s = 377 \, \Omega$, then the input impedance of the absorber $Z_{in} = R_s = Z_0$, the screen has perfect absorption when the thickness is quarter wavelength or $\lambda/4 + n\lambda/2$ [129].

To increase the bandwidth, the Jaumann absorber was proposed, which can be regarded as multi-layered Salisbury absorbing screen [130-132]. Jaumann absorber consists of two or multi equally spaced reflective surfaces and grounded plane, as seen in the following Figure 1.44. More layers of the resistive films bring more resonance and the absorption bandwidth can be expanded [133].
To have more design freedom, the resistive FSS based absorbers were designed to have better performances on bandwidth, wide-angle performances, lower profiles, etc. [134-136]. As seen in Figure 1.45, the resistive FSS based absorber has patterned resistive films, spacer and grounded planes. Also, the resistive FSS layers can be multi-stacked to extend the bandwidth.
The Figure 1.46 gives an example of the resistive FSS based absorber to have wideband absorption. As can be seen, a patterned resistive film, which brings resistor and paralleled capacitance and inductance in equivalent circuit to have more resonance, seen in Figure 1.46(b). The simulated and experimental measurements of the absorber in following Figure 1.47 shows good consistency, and the absorber is demonstrated to have 5-18 GHz wideband effective absorption [137].

Figure 1.46 Resistive FSS based wideband absorber. (a) Absorber design, (b) Equivalent circuit model [137].

Figure 1.47 The comparison of the experimental and simulation results of the absorber [137].
1.5 Thesis Organization

The thesis organization is summarized here. The Chapter 1 is the background introduction of 2D materials, including graphene and graphene oxide. The basic properties, fabrication and applications of them are introduced. As this thesis focuses on EM applications of 2D materials, the previous work on characterizing CVD graphene and graphene applications are introduced in 1.2. The main advantage of using graphene in EM applications is the tunability of graphene, so the review mainly focuses on the tunable devices developed with graphene. In following Chapter 2, 3, 4, the tunability of monolayer graphene has been employed in THz/microwave absorbers and reconfigurable antennas, etc. Because the later Chapters 5, 6, 7, 8 work on printed graphene and graphene oxide, the other conductive materials are introduced in the first chapter to have a clearer view of their competitors. These works in each chapter are relatively independent, and they can roughly categorized into two parts, EM applications of CVD graphene (Chapter 2, 3, 4) and EM applications of printed graphene and graphene oxide (Chapter 5, 6, 7, 8). The research work in each chapter is introduced below.

Chapter 2 proposes an equivalent circuit method to model, analyze and design graphene metasurface based terahertz absorbers. Broadband and tunable graphene based absorbers can be easily designed based on the derived formulas. This work was published as "Design of broadband and tunable terahertz absorbers based on graphene metasurface: equivalent circuit model approach." IET Microwaves, Antennas & Propagation 9, no. 4 (2015): 307-312.

Chapter 3 applies graphene in tunable microwave broadband absorbing screen, and explores its design, performances and working principles, etc. This work was published as

Chapter 4 works on the graphene based reconfigurable antennas, including frequency reconfigurable, radiation pattern reconfigurable and beam-scanning antennas. This chapter is the summary of three published conference papers (Conference papers listed as 1, 4, 8 in Publication).


Chapter 6 demonstrates the flexibility of printed graphene based antennas and microwave components. This chapter was published as "Highly Flexible and Conductive Printed Graphene for Wireless Wearable Communications Applications." Scientific Reports 5 (2015). and "Graphene radio frequency and microwave passive components for low cost wearable electronics." 2D Materials 3, no. 2 (2016): 025021.

Chapter 7 demonstrates experimentally the wideband absorption of printed graphene, and flexibility of the absorber is proved. This work is published on Scientific Reports with
the title "Experimental Demonstration of Printed Graphene Nano-flakes Enabled Flexible and Conformable Wideband Radar Absorbers".

Chapter 8 combines printed graphene and graphene oxide to make RFID based wireless sensors. The ultrathin graphene oxide coating is characterized in GHz bands, and a addressable wireless sensing is demonstrated experimentally. This work is under review of Scientific Report at the time of this thesis submission, titled "Graphene Oxide Dielectric Properties at GHz and Its Application for Wireless Humidity Sensing".

Chapter 9 summaries the whole work and gives the prospective of the possible future research.

1.6 Chapter Summary

In this chapter, the 2D materials graphene and graphene oxide have been introduced in terms of basic property, preparation and applications. The applications of graphene combining with the EM applications and theory have been introduced. In these EM applications, the tunability of graphene is widely used to introduce flexibility in various areas. Besides, the competitors of conductive graphene ink, such as metal nanoparticles, conductive polymers, carbon materials, etc., have also been reviewed. To help the understanding of later work, some basic concepts used in following chapters have been given. From this chapter, one can see that applications of graphene and its derivatives have expanded to more and more areas. 2D materials are changing the world with their unique properties, and many more can be expected.
Electromagnetic Applications of Graphene and Graphene Oxide

Xianjun Huang

References


Electromagnetic Applications of Graphene and Graphene Oxide
Xianjun Huang


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Chapter 2: Tunable Terahertz Absorbers Design Based on Graphene Metasurface: Equivalent Circuit Model Method

2.1 Introduction

Terahertz technology has attracted intensive research interests for its growing application areas in security, medical imaging, food quality control and communications [1]-[4]. However, THz radiation cannot be detected and measured using traditional microwave sensors, resulting to tremendous research on THz sensor technology. In THz detection, a THz absorber is an indispensable sensing device [3]. In the past decade, metamaterials and metasurface have been utilized to develop THz absorbers [5]-[7]. More recently, due to its tunability of surface conductivity and high THz absorption, graphene has been demonstrated as an alternative in realizing THz absorbers [8]-[10]. With tunable surface conductivity of graphene sheet, absorption and propagation of electromagnetic wave on graphene can be electronically controlled [10]-[14].
Graphene based absorber researches have been conducted in various groups. In reference [15], far-infrared graphene micro-ribbon based absorber, characterized with wide-angle high absorption was reported. A stack of graphene-dielectric-metal ground was used to verify the tunability of graphene absorber in [16]. However, these works are often characterized with narrow operation bandwidth. To expand its bandwidth for wideband applications, multi-layer structures were designed to obtain multiple resonances [17]-[19].

Besides, tunable graphene absorbers have also been proposed taking advantages of graphene’s tunability [13] [15]-[17] [20]-[24]. Nevertheless, in all these works, resulting from impedance mismatch, the absorption peak dramatically degraded when the absorber’s working frequency was tuned. For practical applications such as THz detector, it is highly desirable to maintain the absorption peak constantly when operating frequency is tuned.

It is a challenging task to design graphene absorbers, and most reported design were based on 3D commercial full-wave electromagnetic simulators, which is time consuming to get well-tuned structure parameters. Although transfer matrix and multiple interference theories were used in the graphene absorber analysis in [15][16][18][23], they provide no accurate guidelines on designing absorber’s material and dimensional parameters. In my work, equivalent circuit model method was utilized to analyze and design graphene metasurface based THz absorbers. The conditions for perfect absorption have been analytically derived and a set of closed-form designing equations formulated. Given design specifications, the key material and geometrical parameters of the THz absorber can be directly calculated from the proposed formulas. To validate the proposed approach, narrowband absorber with one resonance, broadband absorber with two resonances, as well as tunable absorber, have been designed and studied. The calculated results from this method have been compared with those obtained from simulations in CST Microwave Studio. Excellent agreements have been achieved. Moreover, distinctively different to
previously reported tunable graphene absorbers, the proposed design in this work has constant absorption peak when resonant frequency is electrostatically tuned, which is highly desirable in THz sensing applications.

This chapter is organized as follows. Section 2.2 gives the modeling of graphene, which is also used in later chapters in this thesis. Section 2.3 derives the equivalent circuit model method. Section 2.4 discusses the numerical validation of the accuracy and effectiveness of the equivalent circuit method. Finally, chapter conclusions are drawn in Section 2.5.

2.2 Modeling of Graphene

As graphene is 2D material with one-atom layer thickness, the modeling of graphene can be expressed with surface conductivity $\sigma$. With Kubo’s equation, the surface conductivity of graphene is the sum of inter-band and intra-band contributions, and the intra-band term $\sigma_{\text{intra}}$ reads [20]:

$$\sigma_{\text{intra}}(\omega) = \frac{e^2 k_B T \mu_c}{\pi h^2 (1 + j \omega \tau)} \left[ \frac{\mu_c}{k_B T} + 2 l_n \left( e^{-\mu_c/k_B T} + 1 \right) \right]$$  \hspace{1cm} (2.1)

The inter-band conductivity can be approximated for $k_B T \ll |\mu_c|$ as [20],

$$\sigma_{\text{inter}}(\omega) \approx -\frac{je^2}{4\pi h} ln \left( \frac{2|\mu_c| - (\omega - j2\Gamma)\hbar}{2|\mu_c| + (\omega + j2\Gamma)\hbar} \right)$$  \hspace{1cm} (2.2)

$$\sigma = \sigma_{\text{inter}} + \sigma_{\text{intra}}$$  \hspace{1cm} (2.3)

where $e$ is the electron charge, $\hbar$ is the reduced Planck’s constant, $k_B$ is Boltzmann’s constant. $\mu_c$ is the chemical potential, $T$ is the temperature, $\omega$ is operation frequency and $\Gamma = 1/\tau$ is the carrier scattering rate with being $\tau$ is the electro-phonon relaxation time.
In the low THz region and microwave band discussed in this thesis, the inter-band transition threshold $\hbar \omega < 2|E_F|$, so the intra-band contribution dominates $\sigma_{\text{intra}}$ over $\sigma_{\text{inter}}$, therefore the sheet conductivity of graphene can be explicitly calculated as [9][20],

$$
\sigma \approx \sigma_{\text{intra}} = \frac{\sigma_0}{1+j\omega\tau} = \frac{e^2k_BT}{\pi\hbar^2} \left\{ \frac{\mu_c}{k_BT} + 2l_n\left(e^{-\mu_c/k_BT} + 1\right) \right\}
$$

(2.4)

where

$$
\sigma_0 = \frac{e^2k_BT}{\pi\hbar^2} \left\{ \frac{\mu_c}{k_BT} + 2l_n\left(e^{-\mu_c/k_BT} + 1\right) \right\}
$$

(2.5)

As seen, the surface conductivity of graphene is complex, including real and imaginary part.

Let $f(\mu_c) = \frac{\mu_c}{k_BT} + 2l_n\left(e^{-\mu_c/k_BT} + 1\right)$, then,

$$
\sigma_0 = \frac{e^2k_BT\tau}{\pi\hbar^2} f(\mu_c)
$$

(2.6)

and the surface conductivity is

$$
\sigma = \frac{\sigma_0}{1+j\omega\tau} = \frac{e^2k_BT\tau}{\pi\hbar^2(1+j\omega\tau)} f(\mu_c)
$$

(2.7)

The surface impedance of graphene can be calculated as:

$$
Z_s = 1/\sigma
$$

(2.8)

From the above Equ. (2.7), the surface conductivity of graphene is the function of $\mu_c$, which means $\sigma$ and $Z_s$ of graphene can be tuned with various chemical potential $\mu_c$. The changes of $\mu_c$ can be achieved with external voltages [9][25]. The numerical relationship between external voltages and chemical potentials is included in Chapter 3, part 4.

As in Figure 2.1, taking typical values $T = 300 K$ and $\tau = 0.2 ps$ as example, the complex surface conductivity of graphene under various chemical potentials is calculated and displayed in wideband ranging from microwave, THz band, and infrared bands. From
the figure, the surface conductivity of the graphene sheet changes dynamically with varies of chemical potentials. Focus on the microwave band below 100 GHz, as $\omega \tau \ll 1$, the imaginary part of the surface conductivity is quite small and almost frequency independent in this band. However, the real part is quite sensitive to changes of $\mu_c$. In THz band from 0.1 THz to 10 THz, both the real and imaginary parts of surface conductivity can be obviously tuned by $\mu_c$, which poses more tunability of graphene based components. In the following sections, the tunability of graphene in THz band is utilized for flexible absorbers.

Figure 2.1 Complex surface conductivity of graphene with various chemical potentials.

### 2.3 Equivalent Circuit Model Method

To present the equivalent circuit model method for designing graphene metasurface based absorber, a simple structure is taken as example and shown in Figure 2.2. As seen, the absorber structure consists of stacking layers of metasurface and metal-backed dielectric. The metasurface is constructed with two monolayer graphene layers separated by ultra-thin silicon dioxide isolator. The above graphene layer is typical patch array, and
the second layer is continuous graphene sheet. The silicon dioxide is extremely thin (0.5μm in simulations) compared with the operation wavelengths (less than λ/200).

Figure 2.2 Schematic diagram of graphene metasurface based absorber.

As described in above section, the graphene sheet can be modelled with surface impedance. Here in this chapter, the temperature is assumed to be 300 K, and τ = 0.1 ps [23][26].

Under the incident plane wave as depicted in Figure 2.2(a), the patch array provides extra capacitor with gaps. The surface impedance of the above layer patch graphene is sum of effective area resistance and gap capacitance, which can be calculated as [12][27]:

\[
Z_{s1} = \frac{D}{(D-g)\sigma} - j \frac{\pi}{\omega \varepsilon_0 (\varepsilon_r + 1) D t_n \{\csc(\pi g/2D)\}}
\] (2.9)

In the equation, D is the patch array period, g is the gap distance between graphene patches (D > g), and \(\varepsilon_r\) is relative permittivity of the supporting silicon dioxide. Equ. (2.9) can be re-arranged as

\[
Z_{s1} = \frac{D}{(D-g)\sigma_0} + j \left[\frac{\omega D}{D-g}\frac{\sigma_0}{\sigma_0} - \frac{1}{\omega C_{eff}}\right]
\] (2.10)
where $C_{eff} = (1/\pi)\varepsilon_0(\varepsilon_r + 1)Dt_n[\csc\left(\frac{\pi g}{2D}\right)]$, determined by the supporting material and geometrical dimension of the graphene patches. $\sigma_{01} = \frac{e^2k_BT}{\pi h^2}f(\mu_{c1})$ is the surface conductivity of graphene patch and $\mu_{c1}$ is its chemical potential. From (5), it can be seen that this patch array surface can be modeled by $R - L - C$ series circuit. The $R$ and $L$ are created by the graphene material itself. The capacitor $C$ is induced by the gaps between graphene patches. $C_{eff}$ in (5) represents the effective capacitance introduced by the gaps.

Besides, the character of above layer can be tuned by chemical potential of graphene.

The surface impedance of second-layer continuous graphene sheet can be described as:

$$Z_{s2} = \frac{1}{\sigma} = \frac{1+j\omega\tau}{\sigma_{02}}$$

(2.11)

where $\sigma_{02} = \frac{e^2k_BT}{\pi h^2}f(\mu_{c2})$, and $\mu_{c2}$ is the chemical potential of the continuous graphene layer. From Equ. (2.11), it can be seen that the continuous graphene sheet can be modeled by $R - L$ series circuit, and also tunable with changes of chemical potential.

From transmission line theory, the input impedance of the metal-backed dielectric layer can be calculated as:

$$Z_d = jZ_c \tan(\beta l) = \frac{1}{j\omega C_d}$$

(2.12)

where $Z_c$ and $\beta = \omega \sqrt{\varepsilon_r l}/c$ are the characteristic impedance and wave number, respectively. As in Figure 2.2(b), $l$ is the dielectric thickness, $\varepsilon_r$ is the relative dielectric constant of the dielectric material, $c$ is the free space light speed, and $C_d$ is the effective capacitance raising from the dielectric. From Equ. (2.12), the metal grounded dielectric can be modelled as capacitor $C_d$.

With the aforementioned analysis, Figure 2.3 gives the derived equivalent circuit model. The above-layered graphene patch array contributes a $R - L - C$ series circuit (as
section (A)) and the continuous graphene sheet together with the metal grounded dielectric provides parallel circuit (as section (B)). The extremely thin silicon dioxide layer has ignorable influence, as its thickness is incomparably small to the wavelength at the working band.

![Figure 2.3 Equivalent circuit of graphene metasurface based absorber.](image)

From Figure 2.3 and Equ. (2.10), it can be calculated that the series $R - L - C$ circuit (section (A)) can resonate at frequency $\omega_{01}$

$$\omega_{01}^2 = \frac{D-g}{D} \frac{\sigma_1}{\tau_{eff}}$$  \hspace{1cm} (2.13)

At the resonant frequency $\omega_{01}$, the surface impedance of the graphene patch array is,

$$Z_{s_{1,\omega_01}} = \frac{D}{(D-g)\sigma_01}$$  \hspace{1cm} (2.14)

Similarly, the parallel R-L-C circuit (section (B)) has self-resonance frequency $\omega_{02}$. The resonance frequency $\omega_{02}$ meets condition in Equ. (2.15) to produce resonance, and its input impedance at resonance is given in Equ. (2.16).

$$\omega_{02}^2 \tau^2 + Z_c \tau \sigma_{02} \omega_02 \tan(\omega_{02} l \sqrt{\varepsilon_r f} / c) + 1 = 0$$  \hspace{1cm} (2.15)

$$Z_{s_{2,d,\omega_02}} = \frac{1+\omega_{02}^2 \tau^2}{\sigma_{02}}$$  \hspace{1cm} (2.16)
From transmission line theory, the total input impedance $Z_{\text{in}}$ of the absorber can be calculated with Equ. (2.17),

$$\frac{1}{Z_{\text{in}}} = \frac{1}{Z_{s1}} + \frac{1}{Z_{s2}} + \frac{1}{Z_d}.$$  \hspace{1cm} (2.17)

The reflection coefficient $S_{11}$ from the interface of absorber and free space is,

$$S_{11} = \frac{Z_{\text{in}} - Z_0}{Z_{\text{in}} + Z_0}.$$  \hspace{1cm} (2.18)

Then the absorption of the absorber is,

$$\text{Absorption} = 1 - |S_{11}|^2 \hspace{1cm} (2.19)$$

Assuming sections (A) and (B) resonate at the same frequency and the input impedance of absorber matches the characteristic impedance of free space $Z_0$, i.e.,

$$\omega_0_1 = \omega_0_2.$$  \hspace{1cm} (2.20)

And

$$\frac{1}{Z_{\text{in}}} = \frac{1}{Z_{s1,\omega_0_1}} + \frac{1}{Z_{s2,d,\omega_0_2}} = \frac{1}{Z_0}.$$ \hspace{1cm} (2.21)

Then a perfect absorption can be obtained at frequency $\omega_0_1$. The conditions for this to happen can be summarized as:

$$\begin{align*}
\omega_0_1^2 &= \frac{D - g}{D} \frac{\sigma_{01}}{\varepsilon_{\text{eff}}} & \text{(1)} \\
\left(\frac{D - g}{D}\right)\frac{\sigma_{01}}{\varepsilon_{\text{eff}}} + \frac{\sigma_{02}}{1 + \omega_0_1^2 \tau_2^2} &= \frac{1}{Z_0} & \text{(2)} \\
\omega_0_1^2 \tau_2^2 + Z_c \tau \sigma_{02} \omega_0_1 \tanh(\omega_0_1 l \sqrt{\varepsilon_{\text{eff}} / c}) + 1 &= 0 & \text{(3)}
\end{align*}$$

Equ. (2.22) gives the designing process and conditions of the graphene metasurface based absorber. From the equation, it can be found that for a given resonance frequency $\omega_0_1$, corresponding $\sigma_{01}$ can be obtained from condition (1). $\sigma_{02}$ can be calculated from condition (2) which is the matching condition at resonance frequency $\omega_0_1$. After getting required $\sigma_{01}$ and $\sigma_{02}$, chemical potentials $\mu_{c1}$ and $\mu_{c2}$ can be obtained from
above Equ. (2.5). Condition ③ makes sure the parallel section (B) resonates, and its resonance frequency at $\omega_{01}$ as well. With the results from ①②, the desired dielectric thickness $l$ can be calculated directly from ③. In a word, all key graphene parameters and dimensional designs of the absorber can be analytically obtained from (17).

2.4 Method Verification and Tunable Absorbers

In this section, graphene metasurface based tunable absorbers are designed using the method on 2.3, and they are catalogued as narrowband absorber, wideband absorber and tunable peak-maintained absorber. The designed absorbers are simulated with both CST simulation and equivalent circuit model method. The comparison of these two methods verifies the accuracy of proposed equivalent circuit model method for graphene based absorbers.

2.4.1 Narrowband absorbers

With the help of the analytical equations presented in Section 2.3, graphene metasurface based narrowband absorbers were designed. The performances of the designed absorbers were simulated with CST MWS. The dimensional parameters of the designed absorber are: $D = 10 \, \mu m$, $g = 1 \, \mu m$, and silicon layer $\varepsilon_r = 3.9$. The grounded dielectric substrate has $\varepsilon_{r_l} = 5$. Given the working frequency, the chemical potential $\mu_{c1}$ of the graphene patch array can be obtained from condition ① in Equ. (2.22) and Equ. (2.5), and with matching condition from Equ. (2.22)(2) and Equ. (2.5), $\mu_{c2}$ can also be calculated. Thickness of dielectric layer $l$ was calculated from condition ③ in Equ. (2.22). With these procedures, a narrow band absorber is designed, and its absorption is calculated from the equivalent circuit model method using Equ. (2.19). The results from equivalent circuit model method are compared with those obtained from CST, as shown in Figure 2.4. From
Figure 2.4, it can be found that absorptions calculated by the equivalent circuit model and CST simulations are very close, demonstrating the equivalent circuit model method is accurate and effective.

To make the comparison clear, the parameters of the absorbers, as well as resonance frequencies extracted from curves in Figure 2.4, are listed in following Table 2.1. In the table, \( f_{c,cir} \) and \( f_{c,cst} \) are resonant frequencies, namely peak absorption frequencies, from equivalent circuit method and CST simulation separately. The listed \( f_{0,cir} \) and \( f_{0,cst} \) are frequency points of the first Fabry-Perot resonances obtained from both methods. From the numerical comparison in Table 2.1, it is clearly illustrated that equivalent circuit method results agree well with the CST simulated ones, in both absorption peak and Fabry-Perot resonant frequencies.

From the above analysis, with equivalent circuit model method, the narrowband absorber design can be easily achieved by calculating parameters from formulas with given design requirements. The absorbers performance can also be accurately predicted with simple equations. These two points demonstrate that equivalent circuit model method can speed up the absorber design and analysis significantly, as numerical calculation using equations are much faster than complicated structure parameter tuning and repeating simulations in CST.
Figure 2.4 Comparison of absorption simulated by CST and calculated by the equivalent circuit.

Table 2.1 Comparison of theoretical and simulated resonant frequencies (THz) under different parameters

<table>
<thead>
<tr>
<th>No.</th>
<th>Parameters (µm/eV)</th>
<th>( f_{c,\text{cir}} )</th>
<th>( f_{c,\text{cst}} )</th>
<th>( f_{0,\text{cir}} )</th>
<th>( f_{0,\text{cst}} )</th>
</tr>
</thead>
</table>
| 1   | \( l = 24.7 \)  
\( \mu_{c1} = 0.20 \)  
\( \mu_{c2} = 0.10 \)     | 1.45   | 1.43   | 2.72   | 2.64   |
| 2   | \( l = 29.2 \)  
\( \mu_{c1} = 0.15 \)  
\( \mu_{c2} = 0.15 \)     | 1.25   | 1.24   | 2.29   | 2.25   |
| 3   | \( l = 36.4 \)  
\( \mu_{c1} = 0.10 \)  
\( \mu_{c2} = 0.20 \)     | 1.03   | 1.02   | 1.84   | 1.83   |

2.4.2 Broadband absorbers

The above analysis has verified the equivalent circuit method and designing procedure of a narrowband absorber with one resonance. Here wideband absorber design is conducted to verify the accuracy and effectiveness of the proposed method. Introducing more resonances is a well-known and effective way to enhance absorber bandwidth. The above narrowband absorber meets condition to make sections (A) and (B) in Figure 2.3 resonate at same frequency. Imaging resonant frequencies of these two sections are separated, two
resonances poles can be obtained, leading to a wider absorption bandwidth. In graphene based absorber, this can be achieved by taking advantages of graphene’s tunability. In this work, two independent parameters of graphene $\mu_{c1}$ and $\mu_{c2}$ can be properly set, as shown in Figure 2.5. For simplicity $\mu_{c2}$ has been set to be zero, and $\mu_{c1}$ ranges from 0.3 to 0.5 eV. In Figure 2.5, it can be seen that results from equivalent circuit model method and CST simulation are agreeing very well, which proves the proposed method is also accurate and effective in designing and analyzing graphene based broadband absorbers. Furthermore, when $\mu_{c1} = 0.3$ eV, the absorption peak locates at 1.68 THz and the effective absorption (above 90%) bandwidth is from 1.2 THz to 2.05 THz, indicating a relative bandwidth of 52.3%. When $\mu_{c1}$ increases, two resonances emerge and separate further, leading to a broader absorption bandwidth. When $\mu_{c1} = 0.5$ eV, the effective absorption bandwidth covers from 1.34 THz to 2.8 THz and the relative bandwidth is 70.5%

![Figure 2.5 Variation of absorption bandwidth for various $\mu_{c1}$ in case $\mu_{c2} = 0$ eV.](image)

With the equivalent circuit model method, the double resonances phenomenon can be easily analyzed. When $\mu_{c1} > 0.3$ eV, from Equ. (2.10), the resistance of $Z_{s1}$ becomes lower
than 377 Ω. In this case, the condition for perfect matching in Equ. (2.21) cannot be satisfied. Take $\mu_{c1} = 0.5$ eV, $\mu_{c2} = 0$ eV absorber as an example, the impedances of sections (A) and (B) are depicted in Figure 2.6 respectively. It can be seen that at 2.28 THz (dash line pointed), the imaginary parts of impedances for both section (A) and (B) becomes zero, revealing resonance occurring in both sections. In this case, the input impedance of absorber at this frequency point consists of two paralleled resistors, namely $7200/190 \approx 190\Omega$, which is obviously not matched with 377 Ω of free-space character impedance, leading to an absorption minimum as shown in Figure 2.5 (blue curve). As seen from the impedance in Figure 2.6, for frequency band lower than 2.28 THz, section (A) is capacitive, whereas section (B) is inductive. The real part of input impedance of the absorber falls between 190 Ω and 377 Ω, contributing to an absorption peak in this region. In contrast, above 2.28 THz frequency band, section (A) turns to inductive while section (B) becomes capacitive. Similar analysis can be applied to explain the absorption peak above 2.28 THz.

![Impedance Diagram](image)

Figure 2.6 The impedance of two resonant sections; above one is for section (B) and bottom one is for section (A).
To clearly show the effective tunability in bandwidth of the graphene based wideband absorber, useful information are gathered from Figure 2.5 and listed in Table 2.2. As seen from the Table, the relation between the chemical potential and absorption bandwidth is obviously revealed. When $\mu_{c1}$ increases from 0.1 eV to 0.5 eV, the absorption bandwidth can be widened from 34.5% to 70.5%. Combined with the narrowband absorber in above section, the conclusion for bandwidth transfer can be drawn. When the two sections in equivalent circuit resonate at same frequency, the absorber is relatively narrowband. When $\mu_{c1} > 0.3$ eV, two nearby resonances are induced, resulting to a wideband absorption. Broader bandwidth up to 70% can be achieved by increasing $\mu_{c1}$.

Table 2.2 Absorption bandwidth with different $\mu_{c1}$ with $\mu_{c2} = 0$ eV.

<table>
<thead>
<tr>
<th>No.</th>
<th>$\mu_{c1}$ (eV)</th>
<th>Bandwidth (THz/%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.10 eV</td>
<td>0.34 THz 34.5%</td>
</tr>
<tr>
<td>2</td>
<td>0.20 eV</td>
<td>0.51 THz 36.1%</td>
</tr>
<tr>
<td>3</td>
<td>0.30 eV</td>
<td>0.85 THz 52.3%</td>
</tr>
<tr>
<td>4</td>
<td>0.40 eV</td>
<td>1.18 THz 63.6%</td>
</tr>
<tr>
<td>5</td>
<td>0.50 eV</td>
<td>1.46 THz 70.5%</td>
</tr>
</tbody>
</table>

2.4.3 Tunable absorbers

In this part, the design and performance of a tunable absorber characterized with maintained absorption peak is presented using the equivalent circuit model. In above broadband absorber, the chemical potential of the second layer graphene is set to be zero and unchanged. If we make use of this additional flexibility to design tunable absorber, the absorption peak might be maintained when frequency is tuned. Figure 2.7 shows how the absorption peak can be tuned to different frequencies. By properly adjust the chemical potential value sets of two graphene layers, the frequency of peak absorption can vary from 1.5 THz to 2.5 THz. The most distinguish property of this absorber is its ability to keep almost constant absorption peak value within the tuning range, highly desirable for THz
sensing applications. Besides, from the comparison in Figure 2.7, it is shown that results from equivalent circuit model method and CST simulation are almost identical at absorption peak, as well as performance within the whole operation band, proving that this proposed circuit method can also be applied in tunable absorber design and analysis.

![Graph showing the tunability of resonant frequency with constant absorption peak.](image)

Figure 2.7 The tunability of resonant frequency with constant absorption peak.

To further verify the frequency tunability of the graphene metasurface based absorber, the corresponding reflection coefficients simulated by CST are given in Figure 2.8. It can be seen that the reflection minimum point alters when the chemical potential of the graphene varies. Furthermore, the minimum reflection coefficient precisely corresponds to absorption peak in Figure 2.7, demonstrating that the frequency tunability has been achieved without absorption peak recession.
2.4.4 Wide-angle performance

As an effective absorber, the absorption under different incident angle is an important criterion. Figure 2.9 and Figure 2.10 give the absorption and reflection under different incident angles \( \theta \), which is the angle of wave vector \( \vec{K} \) and axis \( \vec{Z} \). As the absorbing structure in Figure 2.2 is symmetric, the performances under vertically and horizontally polarized incident waves are the same. From Figure 2.9, it can be seen that the absorption maintains higher than 90% in most frequency range when incident angle varies from 0° to 50°, revealing that the absorber is angular-stable. When the incident angle keeps increasing, the absorption decreases. The absorption is still above 60% when the angle is 70°. Furthermore, the resonance frequency shifts to higher frequency band when the incident angle increases, as displayed in Figure 2.10. The wide-angle effective absorption is mainly results from the relatively small size of the units. The unit length is 10 um, only around \( \lambda/20 \) when the working frequency is 1.7 THz.
2.5 Chapter Summary

In this chapter, an equivalent circuit model method has been proposed and validated numerically for graphene metasurface based THz absorber design. This approach significantly simplifies the design and analysis of graphene THz absorbers. Based on the rigorous derivations, equivalent circuit model have been built up, and a set of close-form formulas that can be easily used to design narrow band, broadband and tunable graphene
absorbers have been presented. Graphene metasurface based absorbers of high performances have been designed using the proposed approach and the results have been compared with 3D full-wave electromagnetic simulations. Excellent agreements have been achieved in the comparison. It can be summarized that the proposed equivalent circuit model method can provide an accurate and effective alternative to design and analyze graphene metasurface based THz absorbers.

References


Chapter 3: Graphene Based Tunable Fractal Hilbert Curve Array Broadband Radar Absorbing Screen for Radar Cross Section Reduction

3.1 Introduction

Currently, the applications of graphene have covered wide frequency bands ranging from optical frequency to THz [1-9], infrared frequency to microwave band [10-12]. Among these works, tunable cloaks [4], metasurface and polarizers are designed with advantage of electrically tunability of graphene [9,11,12]. Also, graphene has been studied in reconfigurable optical and THz antennas [5-7].

Even though graphene has been widely investigated from lower THz to optical spectrums, its microwave band applications are much less cultivated. The reported works in microwave bands have focused on the characteristics of graphene based transmission lines [13-15], and exploring the possibility of antenna applications, etc. [16]. The slow development is mainly due to the relatively higher loss of graphene in the microwave band, as well as size limitation of available graphene sheet. In microwave bands, the wavelength
was relatively large compared with available graphene sheet, as it was very challenging to produce high-quality and large-size graphene [13-15]. However, this is changing. Nowadays qualified large-area CVD (above 300 inch) graphene sheets are commercially available [17]. It is timely to do research on the potential of graphene in tunable microwave applications.

In this chapter, a graphene base tunable broadband microwave absorbing screen design is proposed for RCS reduction. Previously, graphene has been studied in tunable optical and THz absorbers [18-21]. Complete optical absorptions were proved with periodically arranged graphene pattern [19], as well as ribbon graphene metamaterials [18]. In THz band, graphene based Salisbury screen was demonstrated for absorption [20]. These works proved that graphene can be used in designing narrowband absorber, which can be used for optical/THz sensors. Moreover, Salisbury screen is limited by one quarter wavelength thickness [22-23], even though it is easy to design. To reduce thickness limitation, very thin FSS based absorbers and ultra-thin metamaterial absorbers have been developed [24-25]. It should be mentioned that, in microwave bands, absorbers are mainly applied in RCS reduction applications (rather than for sensor applications as in THz band), in which high absorption, wide bandwidth and low profile are generally required simultaneously. This work explores the possibility of graphene in meeting these requirements, and a hybrid metasurface made of Hilbert metal strips and graphene is put forward.

For implements of tunable absorbers, several methods were previously studied and reported. Dynamical control of THz band absorption was obtained with conductivity controllable semiconductor substrate under optical doping using high intensity laser [26]. As in the reference [27], combining metamaterials with MEMS (microelectromechanical systems) is another option proved to tune the absorber. The more preferable choice in tunable microwave absorbers design for RCS reduction is conducted by embedding
semiconductor devices like diodes in metamaterial structures [28-30], which is several orders faster than MEMS, and no external bulky optical components needed [26,30]. However, the switchable microwave absorbers/reflectors based on diodes normally have narrow working band [28-30]. This is because the junction impedance of diodes is highly frequency-dependent, which brings extraordinary challenges in wide-band impedance matching [30,31]. However, graphene is perfect to solve above problems. For one, graphene can provide ultrafast tuning when external electrostatic voltages are applied [32,33]. For another, the frequency-independent surface impedance of graphene at microwave band suits greatly for wide-band impedance matching [14-16, 34]. Moreover, CVD graphene’s sheet resistance is around 400 $\Omega$ to 3 $k\Omega$ [13,14,35], making it easy to match with free space characteristic impedance of 377 $\Omega$.

In this work, graphene’s tunability and frequency-independent surface impedance in microwave band are fully utilized for broadband frequency tuning, impedance matching and microwave power absorption. The following Section 3.2 gives the design of performances of the graphene based absorber. Section 3.3 focuses on the function of graphene in the absorber, and analysis of working principle and influential factors to guide design. Chapter conclusion is given in 3.4.

### 3.2 Design and Performances

In this design, the modelling of graphene is based on Section 2.1 in Chapter 2. In this work, graphene has typical value of $\tau=0.2$ ps [36,37]. It is known that the surface conductivity of graphene is almost frequency-independent in microwave region [34]. Also, it is worthy to point out that, at microwave band, the real part of the graphene surface conductivity changes significantly from 0.9 mS to above 9 mS as chemical potential varies from 0 to 0.4 eV, whereas the imaginary part of it barely changes in magnitude. Besides,
the inductive reactance is negligibly small in microwave band since $\omega \tau \ll 1$. With the data above, surface resistance of the graphene is calculated to be around 1.2 k$\Omega$ when chemical potential is 0 eV, which is consistent with reported experimental results [13,14]. The surface resistance reduced to 420 $\Omega$ and 110 $\Omega$ at chemical potential of 0.1 eV and 0.4 eV, respectively. These values are comparable with free space characteristic impedance 377 $\Omega$, thus impedance matching and broadband tuning can be easily achieved. Therefore graphene can be a proper candidate for designing tunable broadband microwave radar absorbing screen.

To design a broadband absorber, wide-band impedance matching is the primary requirement for eliminating reflection. Moreover, proper power consumption by the structure has to be carefully considered. Wide-band impedance matching can be achieved by introducing multi-resonance with fractal structures [38,39]. In this design, a typical third-order Hilbert metal strip is chosen as unit structure, and the units are placed in array, as shown in Figure 3.1 (a) and Figure 3.1 (b) respectively. The strips are made of copper with conductivity of $5.96 \times 10^7$ S/m. The graphene sheet is directly placed under copper strips. When resonances occur, electrical field near metal strips are intensive, so that power dissipation can be enhanced in underneath lossy graphene sheet. It should be mentioned that, wide-band impedance matching can be obtained for this structure as surface impedance of graphene is frequency-independent in microwave band. To facilitate tuning of graphene, two extremely thin layers, silicon dioxide layer with thickness of t=50 nm and 50 nm thick polysilicon layer, are placed under graphene in sequence, as shown in Figure 3.1 (c). The silicon layer works as isolator, and polysilicon as electrode. External voltage VDC is connected between the metal strips on the top of the graphene and polysilicon layer. As the metal strips are in electrical contact with graphene in large area, surface conductivity of graphene can be effectively tuned [33,40]. These layers are sandwiched
with two dielectric layers (D1 and D2) having thickness of h1 and h2, and both D1 and D2 have dielectric constant of $\varepsilon_r = 4.3$. Here D2 works as supporter of above layers, and also provides space for destructive interference [5]. The placed top layer D1 helps to improve angular performances and provides more flexibility for design [41,42]. The whole structure is grounded typically with PEC to eliminate transmission. It should be pointed out that, effects of the extremely thin silicon dioxide layer and polysilicon layer can be safely neglected in simulation [33,40]. This is because the thickness of these two layers (around 100 nm) is only $0.5 \times 10^{-5} \lambda$ (at 15 GHz), and the relative dielectric constant of silicon dioxide ($\varepsilon_t = 3.9$) and polysilicon ($\varepsilon_p = 3$) [43] are quite close to the nearby dielectric layer D2 ($\varepsilon_r = 4.3$) [33,40].

As Hilbert curve strip is a conventional fractal structure applied in designing multi-resonance antennas, etc., the relationship between working frequency and its dimensions were studied and is used for initial estimation in this work [44,45]. For dielectric thickness, the general principle is: higher dielectric constant of upper cover layer results to higher surface capacitance, whereas larger substrate thickness brings increases on inductive load impedance yielded by the metal-grounded dielectric slab.

After the initial design, the structure is optimized using CST MWS [46]. The final optimized dimensional parameters of the screen are: $l=2$ mm, $w=0.1$ mm, $h_1=1.2$ mm, $h_2=2.2$ mm, the metal thickness is 5 $\mu$m, so the total thickness of the screen is around $h_1+h_2=3.4$ mm. As the structure is with a PEC ground, which blocks any transmission, the absorption can be calculated with:

$$A(\omega) = 1 - R(\omega) = 1 - |S_{11}|^2$$  \hspace{1cm} (3.1)
Figure 3.1 Schematic diagram of graphene based Hilbert curve metal strip array tunable radar absorbing screen. (a) Hilbert curve unit cell; (b) Hilbert curve array; (c) Structure of the radar absorbing screen.

Under incidence of a vertically polarized plane wave as shown in Figure 3.1, the performance of the absorbing screen is simulated when the chemical potential is 0 eV ($V_{DC} = 0$ V). The absorption and reflection are depicted in Figure 3.2. It can be found that the -10 dB reflection bandwidth is from 8.9 GHz to 18.1 GHz. The effective absorption (above 90%) bandwidth is 9.2 GHz, i.e., a relative bandwidth of 68.1%. Considering that the screen has thickness of 3.4 mm or 0.15λ at central frequency of 13.5 GHz, the absorbing screen has demonstrated high absorption and wide bandwidth.
Figure 3.2 Simulated reflection and absorption of the radar absorbing screen under normal incidence when graphene’s chemical potential is 0 eV.

To fabricate an absorber as shown in Figure 3.1, the following procedure could be followed. A metal grounded dielectric D2 is firstly prepared, and then it is covered with ultra-thin conducting polysilicon and silicon dioxide through sputtering fabrication process. Between the steps of sputtering polysilicon and sputtering silicon dioxide, the metal contact (gold) should be evaporated and etched on the edge of polysilicon to make an electrode for tuning purpose. After these two layers are fabricated, graphene can be transferred on stacks. Then the copper strips structure can be patterned on graphene using e-beam lithography. Next, the second electrode is connected to the metal strips, which is easy to connect with silver epoxy. At last, the upper layer dielectric slab D1 can be bonded together with the stack using adhesive bonding film with thickness less than 1 mil under thermal compression, as commonly used in fabricating sandwich FSS [41,47].
3.3 Analysis and Discussion

The design and performance of graphene based absorbing screen have been given above. This section studies the absorbing principle and important role of graphene sheet in the absorbing screen. More analysis on effects of the dielectric layers, metal patterns and incident angles will also be conducted to help the design and principle understanding.

3.3.1 Function of graphene sheet

(a) Tunability

In Equ. (2.4) and Figure 3.1, conductivity of graphene can be changed by tuning chemical potentials, which can be achieved with external DC bias. With the setting in Figure 3.1, the carrier density on graphene \( n_s \) can be modified by \( V_{DC} \) between graphene and polysilicon layer as

\[
n_s = \varepsilon_0 e t V_{DC} / \varepsilon_t e
\]

where \( \varepsilon_0 \) is permittivity in space, \( e \) is the electron charge, and \( \varepsilon_t \) is the relative permittivity of silicon dioxide layer with thickness \( t \). The carrier density has a relationship with graphene’s chemical potential as [40,48]:

\[
n_s = \frac{2}{\pi \hbar^2 v_f^2} \int_0^\infty \epsilon [f_d(\epsilon - \mu_c) - f_d(\epsilon + \mu_c)] d\epsilon
\]

In Equ. (3.3), \( \epsilon \) is the energy, \( v_f \) is the Fermi velocity (around \( 10^6 \) m/s for graphene), and \( f_d \) is the Fermi-Dirac distribution:

\[
f_d(\epsilon) = \left( e^{(\epsilon - |\mu_c|)/k_B T} + 1 \right)^{-1}
\]

From, Equs.(3.2), (3.3) and (3.4), the chemical potentials of graphene can be tuned through external voltage \( V_{DC} \). The relationships between chemical potential of graphene
and required external voltage $V_{DC}$ are depicted in Figure 3.3 in cases $t=20$ nm, 50 nm, 100 nm. As seen, corresponded with these three different thicknesses $t$, when $\mu_c=0$ eV, $V_{DC}=0$ V for all cases; when $\mu_c=0.2$ eV is required, $V_{DC}=3.2$ V, 7.9 V, 15.9 V are needed, when $\mu_c=0.4$ eV is required, the applied voltages are $V_{DC}=12.2$ V, 30.7 V, 61.3 V respectively.

![Graph](image.png)

Figure 3.3 Relationship between chemical potential ($\mu_c$) and externally applied voltage ($V_{DC}$) under different silicon dioxide layer thicknesses.

From Figures 3.1 and 3.3, the surface conductivity of graphene can be changed with externally applied voltages. This property is utilized in the absorber to tune the performance of the absorbing screen. Figure 3.4 shows the absorption of the screen when applied voltage $V_{DC}$ changes from 0 V to 7.9 V and 30.7 V, in case $t=50$ nm, namely graphene sheet’s chemical potential varies from 0 eV to 0.4 eV. To clearly illustrate the tunability of the absorbing screen, the tuning performance in terms of central frequency and bandwidth is summarized in Table 3.1. As can be seen from Figure 3.4 and Table 3.1, when applied voltage increases from 0 V to 30.7 V, the absorber’s central frequency shifts from 13.5 GHz to 19.0 GHz, and the relative effective absorption bandwidth reduces from
68.1% to 41.1%. These results demonstrate that with tunability of graphene sheet, both central frequency and bandwidth of the screen can be tuned.

![Graph showing absorption vs frequency for various applied voltages](image)

Figure 3.4 Working frequency shift of the graphene based tunable absorbing screen with various applied voltages ($V_{dc}$) when $t=50 \text{ nm}$.

Table 3.1 Tunability of central frequency and effective absorption bandwidth ($t=50 \text{ nm}$).

<table>
<thead>
<tr>
<th>External Voltage</th>
<th>Chemical Potential</th>
<th>Central Frequency</th>
<th>Effective Bandwidth</th>
<th>Relative Bandwidth</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0 V $\mu =0.0 \text{ eV}$</td>
<td>13.50 GHz</td>
<td>9.2 GHz</td>
<td>68.1%</td>
<td></td>
</tr>
<tr>
<td>7.9 V $\mu =0.2 \text{ eV}$</td>
<td>16.65 GHz</td>
<td>8.5 GHz</td>
<td>51.1%</td>
<td></td>
</tr>
<tr>
<td>30.7 V $\mu =0.4 \text{ eV}$</td>
<td>19.00 GHz</td>
<td>7.8 GHz</td>
<td>41.1%</td>
<td></td>
</tr>
</tbody>
</table>

(b) Broadband matching

It is well known that properly designed metal strips and perfect electrical conductor (PEC) backed dielectric hybrid structure can bring high absorption. What is the role of the graphene sheet in the proposed structure for broadband absorption? To investigate this, the cases without and with graphene sheet are simulated (at chemical potential of 0 eV, and in
both cases the dielectric layers are assumed to be lossless). As in Figure 3.5, when graphene sheet is absent, the screen has multiple absorption peaks with very narrow absorption bandwidth. This is because the metal Hilbert curve strip array only matches to the free space at discrete frequency points and the incident power can only be consumed by ohmic loss in metal (dielectric has been assumed lossless). However, in the proposed graphene based absorbing screen, the one-atom thick graphene sheet laid directly underneath the metal strips. It not only provides broadband impedance matching to the free space, but also dissipates the incident power much more efficiently. The remarkable difference between cases with and without graphene sheet shown in Figure 3.5 unambiguously demonstrates that the graphene sheet has significantly improved the performance of the radar absorbing screen.

From these two parts, the role of graphene in the absorber is studied. It can be concluded that graphene is an indispensable part in the absorber, providing tunability and broadband impedance matching.

![Graphene Absorption](image)

Figure 3.5 Absorption of the graphene based radar absorbing screen without and with graphene sheet.
3.3.2 Effects of other parameters

In this part, the other elements in the absorbing screen are studied to explore further the working principle and performances. It is believed that design rules can be concluded from this study.

(a) Dielectric losses

So far, the dielectric layers are assumed to be lossless in above analysis. To further examine the necessity of the graphene sheet for efficient RF power dissipation, it is necessary to investigate how lossy dielectric layers affect the absorbing performance. Here two different cases are analyzed. In one case, the dielectric layers are lossless, but metal and graphene losses are taken into consideration. In the other case, all materials in the structure are assumed lossy. The lossy dielectric has loss tangent of 0.025, the conductivity of metal strips is 5.96×10⁷ S/m and surface impedance of graphene sheet is 1.2 kΩ. Figure 3.6 shows the simulation results for both cases at when μ|=0 eV. As can be seen, the absorption and reflection in both cases are rather similar. Combining results in Figures 3.5 and 3.6, it is clearly demonstrated that it is the graphene that works as broadband absorbing element, not the dielectric layers.
Figure 3.6 Reflection and absorption of the graphene based absorbing screen with and without dielectric layers’ losses.

**(b) Hilbert Curve Strips**

It is worthy to point out that the Hilbert curve fractal strip array is also critical for the broadband absorption. As it can be seen in Figure 3.1, the Hilbert curve metal strip array has been designed to introduce multiple resonances, which makes it possible for broadband impedance matching. Given that surface impedance of graphene barely changes in microwave band, the hybrid combination of these two properties in fractal array and graphene makes wide-band impedance matching and absorption achievable. To verify this assertion, electric field distributions at resonance frequencies of 11.19 GHz, 13.44 GHz, and 16.64 GHz have been simulated and displayed in Figure 3.7.
Figure 3.7 Electric field distribution at three resonance frequencies for the graphene based absorbing screen, when $\mu_c = 0$ eV.

From the electric field distributions in Figure 3.7, it is apparent that three resonances occur at different part of the structure separately. Besides, the field at resonance frequency is intensive in the vicinity of metal strips, posing strong interaction with the graphene laid underneath, hence strong absorption in graphene. From Ohmic loss theory, the power dissipation density $P_d$ can be calculated with [49]:

$$P_d = \frac{1}{2} \iiint_S \sigma |E|^2 \, d\mathbf{v}$$  \hspace{1cm} (3.5)

From Equ. (3.5), it can be observed that, with both intensive field distribution and moderate conductivity of graphene sheet, the energy is absorbed effectively and thermally dissipated in the screen.

From the aforementioned analysis, the working principle of the graphene based absorbing screen can be concluded and simply put as: the impedance of the absorber is tuned to match the free space in wide band, and the electric field is intensively concentrated nearby metal strips and dissipated in graphene due to strong interaction.

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(c) Bandwidth optimization

For nonmagnetic absorbers, Rozanov proposed a method to calculate the thickness limit for a required absorber. It is proved that the infinite integral of natural logarithm of reflection coefficient is the theoretical thickness limit of the absorber [23,50]. This theory is usually employed to check whether the absorber is low-profile enough with the performance, by comparing the designed thickness with theoretical limit. Rozanov thickness limit for a nonmagnetic absorber can be calculated with [23],

\[
d \geq \left| \int_{0}^{\infty} \ln|R(\lambda)| \, d\lambda \right| \frac{1}{2\pi^2}
\]  

(3.6)

where \(d\) is the absorber thickness, \(R\) is the reflection, and \(\lambda\) is the wavelength.

Figure 3.8 A fitted curve with same bandwidth is applied to calculate the theoretical thickness limit for the graphene based absorbing screen.

With the methodology proposed in reference [23], some straight lines are used to fit the performance of proposed absorber design, as shown in Figure 3.8. This fitted curve has -10 dB bandwidth from 8.9 GHz to 18.1 GHz, same as the designed absorber. The fitted curve is used to calculate the theoretical thickness limit. With Equ. (3.6) and programming, the
theoretical limit is calculated to be 3.1 mm, which means an absorber with this performance has a minimum thickness 3.1 mm. In comparison, the whole thickness of the proposed absorbing screen is 3.4 mm, only 0.3 mm thicker than theoretical limit.

(d) **Shift of frequency bands and Influence of incident angles**

In the proposed absorbing screen, dielectric layers also play an important role. The dielectric layer D2 provides not only supports for graphene and metal strips, but also space for destructive interference as in the cases of metamaterial or FSS based absorbers [4]. On the other hand, the top dielectric layer (D1) protects the fragile graphene and metal strips, and extra degree of design freedom is offered for lower band impedance matching. Simulated results are displayed in following Figure 3.9 and Figure 3.10, to verify how the dielectric constant and thickness of D1 affect the absorbing screen’s performance.

From Figure 3.9 and Figure 3.10, it is clear that the absorption band of the screen shifts to lower frequency with the increase of the dielectric constant or the dielectric thickness. This is because increase on epsilon increases the surface capacitance of FSS, while the substrate height increase brings higher inductive load impedance yielded by the metal-backed dielectric slab. Meanwhile, the relative bandwidth of effective absorption almost maintains the same, indicating that this absorber can be applied in different frequency bands with further optimization. The above parameter changes only help to shift working band slightly. The working band can be dynamically shifted with dimensional scalability [51], even though optimization is required due to variety of graphene’s character in different frequency bands.
Figure 3.9 Reflections of the absorbing screen under different dielectric constants of layer D1.

Figure 3.10 Reflections and absorptions of the absorbing screen under various height of D1.

The dependence of the absorption on incident wave angles is an important criterion for radar absorbing screens. Figure 3.11 shows the absorption at different incident angles \( \theta \), the angle between \( Z \) axis and wave vector \( \vec{K} \). It can be seen that both absorption rate and the bandwidth decrease with increment on incident angle, whereas the central working
frequency band is almost fixed. When the incidence angle varies from $0^\circ$ to $20^\circ$, the absorption bandwidth (>90%) is barely changed. With further incident angle increment, the bandwidth drops slightly, especially at lower frequency end. However, the radar absorbing screen still have about 90% absorption within reasonable frequency band when the incident angle becomes as large as $50^\circ$. When the incident angle turns to $70^\circ$ and higher, the absorption becomes below 80%. Also, the absorptions of this absorber under vertically and horizontally polarized incident waves are the same due to the structural symmetricity as in Figure 3.1. The wide-angle stability and polarization insensitivity of the absorber are very useful in radar absorbing material applications, to absorb detecting radar waves with different incidence directions and polarizations.

![Absorption of the absorbing screen under various incidence angles theta.](image)

**3.4 Chapter Summary**

In this chapter, a novel graphene based tunable broadband radar absorbing screen for RCS reduction application has been proposed and investigated in details. This screen has been demonstrated being broadband, tunable, and with high absorption. Both the central
frequency and absorption bandwidth of the screen have been proved to be tunable when the applied DC voltage on graphene sheet changes. The working principles and functions of each part of the screen have been fully investigated. In the structure, the Hilbert curve metal strips introduce multiple resonances and graphene sheet is responsible for tuning, wide-band impedance matching, as well as RF power dissipation. Moreover, the absorbing screen is still functional when the incident wave angle is as wide as 50°. In summary, this work extends the graphene’s application to tunable broadband radar absorbing screen, which can be potentially promising for RCS reduction and broadband microwave sensing.

Reference


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Chapter 4: Graphene Enabled Reconfigurable Antennas

4.1 Introduction

Reconfigurable antenna is an antenna capable of modifying its frequency and radiation to adapt the antenna performance in changing scenario or to meet changing working requirements [1,2]. Reconfigurable antennas can be classified according to the adjusted antenna parameters, typically as frequency, radiation pattern, polarization reconfigurable antennas [2-4].

Researchers have proposed many novel concepts to achieve adaptable antenna properties, and they are mainly realized by using two ways. One way is to integrate electronic switches, tunable devices or materials to get re-configurability, such as MEMS, Pin diodes, varactor, etc. [5-8]. Another type is using UWB or multiband antennas combining with tunable filters [4,9]. Recently developed liquid antennas have demonstrated tunability by changing effective radiation element [10-13].
Graphene, a new electrically tunable 2D material, has attracted intensive research interest in electromagnetic and optical applications such as tunable cloaks, metasurface, reflective array, etc. [14-16]. However, these works mainly focus on higher bands such as THz/infrared applications, and the microwave band applications are rarely reported. One of the main reasons is that the available high quality graphene is small compared with wavelength in this band. For another, the loss of graphene in microwave band is large, as the one-atom thickness is incomparably smaller than skin depth in microwave band [17]. In previous studies, graphene has been used as a radiation unit of tunable antenna [18]. However, the radiation efficiency is very low because of large loss; therefore effective radiation can hardly be achieved [18]. Considering that the CVD technology nowadays can provide economical and large-size graphene sheet, the size issue is no longer the main obstacle for microwave applications of graphene. It is timely to utilize graphene’s electronically tunable conductivity in microwave applications, and graphene based reconfigurable antenna is among the options.

In reconfigurable microwave antenna applications, even though graphene is highly conductive and electrically tunable, the loss of one-atom structure hinders effective radiation [18]. To achieve both re-configurability and high radiation efficiency in graphene based antenna, a hybrid method combining typical metal antennas with graphene based reflectors is proposed in this chapter. The metal antenna radiates effectively and graphene sheet introduces agility by changing its conductivity under external voltages. In this work, both frequency-reconfigurable antennas, radiation pattern reconfigurable antennas are designed utilizing this concept.

In reconfigurable THz antenna applications, the conventional lumped elements such as capacitor and diodes are too large in dimension for THz system. Graphene suits reconfigurable THz antenna perfectly due to its low profile, high conductivity and
tunability. In this chapter, I also apply the hybrid method to design a graphene strip array based beam-scanning antenna in THz band, maintaining both high radiation efficiency and re-configurability.

To sum up, this chapter works on the graphene based reconfigurable antennas based on hybrid method. Section 4.2 presents a frequency reconfigurable microwave antenna design based on graphene reflective sheet. The radiation pattern of the antenna is almost fixed when the frequency is tuned. Section 4.3 introduces radiation pattern reconfigurable microwave antenna enabled by graphene based frequency selective surface. The working frequency of the antenna is almost fixed when the radiation pattern is tuned. Section 4.4 presents the beam-scanning THz antenna based on graphene strip array. The radiation beam can be scanned while maintaining the fixed working frequency. A summary is given in Section 4.5.

4.2 Frequency Reconfigurable Antenna Based on Graphene

4.2.1 Frequency reconfigurable antenna enable with reflective graphene sheet

This section presents a hybrid design of frequency tunable antenna based on metal CPW monopole and graphene reflective sheet. In this design, metal CPW monopole works as main radiation unit, whereas graphene is a complementary part for tunability.

The modelling of graphene in design running in CST MWS is based on the theory in Section 2.2, Chapter 2. Here we set the parameters $T=300$ K, and $\tau = 0.1$ ps[19]. As previously concluded in Chapter 2, in microwave band, graphene behaves as a sheet with
frequency independent sheet resistance, and its sheet resistance can be tuned by changing chemical potentials with external voltages.

The proposed structure of the tunable antenna is shown in Figure 4.1. As seen, the main part is a normal CPW monopole antenna placed on FR4 dielectric layer (dielectric constant of 4.3). Under the dielectric layer, a complete graphene sheet is attached as backed reflector. The dimensional parameters of the antenna is as follows, \(w=10\ \text{mm}\), \(l=5\ \text{mm}\), and \(h=1.6\ \text{mm}\), the dielectric layer is with dielectric constant of 4.3.

![Proposed structure of the graphene based frequency-tunable antenna.](image)

Figure 4.1 Proposed structure of the graphene based frequency-tunable antenna.

![Frequency tunability of the proposed antenna.](image)

Figure 4.2 Freuency tunability of the proposed antenna.
With the help of simulation tool CST Microwave Studio the $S_{11}$ of the tunable antennas under various chemical potentials ($\mu_c$) are given in the Figure 4.2. As seen in Figure 4.2, without graphene, the antenna works at 9.29 GHz and the radiation efficiency is 71%. After the graphene sheet is applied, when no external voltage is applied, namely the chemical potential $\mu_c=0$ eV, the antenna works at 9.45 GHz with a radiation efficiency of 58.3%. Compare the cases of $\mu_c=0$ eV, and without graphene, it is easy to find that the resonance frequency is mainly determined by the metal radiation component. Besides, the radiation frequency decreases with the introduction of graphene and the loss on it. Moreover, when the chemical potential is increased from 0 eV to 0.8 eV, the frequency decreases to lower band, indicating that the graphene sheet has the function to tune the working band of antenna.

To study the function of graphene further, an equivalent circuit model of the graphene based antenna is given in Figure 4.3. In the circuit, $Z_S$ is the source impedance, $Z_A$ is the antenna impedance of the CPW monopole antenna, and paralleled $Z_g$ is the impedance introduced by graphene sheet. From the equivalent circuit, it is clear that when $Z_g$ is changed, the total antenna impedance changed, resulting to shift of working band.

![Figure 4.3 Equivalent circuit of graphene based antenna.](image)

Another important property, the radiation patterns at the resonance frequencies are given in Figure 4.4 and Figure 4.5 separately with $\mu_c=0$ eV and $\mu_c=0.2$ eV. Compare these
two figures, it can be found that the radiation pattern is hardly changed with vary of chemical potentials. This is because the graphene reflector is small-sized, and the sheet resistance is still high (ranging from 100 $\Omega$ to 2.3 $k\Omega$ when $\mu_c$ varies from 0 eV to 0.8 eV) so that the reflection is not comparable with metal ground. In a word, when the chemical potential is changed, the radiation pattern is almost fixed even the working frequency is tuned, which is an advantage aimed in some practical applications.

Figure 4.4 Radiation patterns in two planes when $\mu_c=0$ eV.

Figure 4.5 Radiation patterns in two planes when $\mu_c=0.2$ eV.
This section proposes a design of tunable CPW monopole antenna with graphene sheet, and explored the working principles and performances of it. With simulations, the proposed antenna is proved to be with tunability of resonance frequency, whereas the radiation pattern is almost fixed. The working principle of the antenna is also studied with equivalent circuit model. Even though the radiation efficiency reduces from 71% to 58.3% with the introduction of graphene, it is still an effective radiation structure. In summary, this antenna is equipped with high radiation efficiency and tunability, which provides a valuable reference for tunable antenna design and application.

### 4.2.2 Frequency reconfigurable antenna with graphene based tunable FSS

For frequency reconfigurable antennas, except for integrating tunable devices as in 4.2.1, using UWB or multiband antennas combining with tunable filters is another option [4]. In this section, a tunable frequency filter in space, frequency tunable FSS is designed with graphene based SRR (split ring resonator) structure. The hybrid antenna system is shown in Figure 4.6. As seen, the radiated wideband signal transmits to a closely placed FSS, a narrow-band signal is produced with the selective function of in-space frequency filter FSS.

As described in Section 2.2, Chapter 2, the sheet resistance of graphene is frequency-independent in microwave region, and changes significantly under different chemical potentials. For graphene with $\tau=0.1$ ps, sheet resistance is calculated to be around 2.3 k$\Omega$ when $\mu_c$ is 0 eV. Under external voltage, the sheet resistance changes to 420 $\Omega$ and 100 $\Omega$ when chemical potential is tuned to 0.2 and 0.8 eV, respectively [20,21]. As graphene can be tuned continuously with externally applied voltage, the sheet resistance can be achieved
at any value between 100 $\Omega$ to 2.3 k$\Omega$. Here in this section, some typical values are used to design and characterize graphene based FSS.

![Diagram of Frequency Tunable Antenna System Based on FSS](image)

Figure 4.6 Frequency tunable antenna system based on FSS.

To take advantages of tunability introduced by graphene, a typical metamaterial unit split ring resonator is adopted to design tunable FSS. To enhance the performance tunability brought by graphene, the graphene sheet is placed between the gaps of the resonator, seen in Figure 4.7. As the field intensity is the highest in slot at resonance frequency, changes of graphene property can pose more influence on SRR performance.

![Unit Cell of Tunable FSS Based on Graphene](image)

Figure 4.7 Unit cell of tunable FSS based on graphene.
The structural parameters of the unit metal resonator in Figure 4.7 are: $l_1 = 5.7\,\text{mm}$, $l_2 = 3.3\,\text{mm}$, $w_1 = w_2 = 0.4\,\text{mm}$, and the gap distances $g_1 = g_2 = 0.3\,\text{mm}$. The supporting dielectric has dielectric constant of $\varepsilon_r = 3$, and height $h = 0.6\,\text{mm}$. The above units are arrayed periodically with distance of $p = 5.8\,\text{mm}$. Using the CST MWS array simulation template [22], the performance of the array is simulated. By changing the sheet resistance of graphene, the $S_{11}$ of the array is simulated and shown in following Figure 4.8. As can be seen, under several $R_S$ of graphene, the resonance frequency of the graphene based FSS can be tuned from 7.73 GHz to 8.42 GHz, which demonstrates the feasibility of graphene in making tunable FSS.

![Figure 4.8 Frequency tunability of graphene based FSS under different sheet resistance of graphene layer.](image)

Besides, the polarization selectivity of the array is studied by applying both TE and TM polarized incident waves. From Figure 4.9, it can be seen that when the graphene sheet is tuned to $R_s = 100\,\Omega$, its responses to TE/TM waves are quite different. At around 7.72 GHz band, the $S_{21}$ of TE polarized wave reaches its minimum point of $-55.9\,\text{dB}$, which means the wave is completely blocked. However, at this frequency, TM polarized wave
has insertion loss of only 1.2 dB, revealing good transmission. The polarization isolation is as high as 54.7 dB.

![Graphene Based SRR](image)

Figure 4.9 Polarization selectivity of the graphene based SRR.

### 4.3 Radiation Pattern Reconfigurable Antenna Based on Graphene

The above 4.2.2 gives graphene based frequency tunable FSS. Here in this section, a switchable FSS is designed based on similar SRR unit structure. Furthermore a radiation pattern reconfigurable antenna is designed by combining the switchable FSS with dipole antenna. Simulation results have proved radiation pattern reconfiguration of the hybrid antenna.

#### 4.3.1 Switchable FSS based on graphene

As seen in the structure of Figure 4.10, graphene sheets are placed in both slots of the SRR unit. The structural parameters are \( l_1 = 5.7\text{mm}, \ l_2 = 3.3\text{mm} \), width of metals are \( w_1 = w_2 = 0.9\text{mm} \), and gap distances are \( g_1 = g_2 = 0.3\text{mm} \). The sizes of graphene
sheets are both 0.3mm×0.5mm, and the supporting dielectric layer has dielectric constant of $\varepsilon_r = 3$, and height of $h = 0.6$mm.

Similarly, the response of the array under TE/TM incident waves are simulated in CST MWS, and the $S_{11}$ is given in Figure 4.11. From the figures, when incidence is TE polarized, the $S_{11}$ keeps the same, no matter how the sheet resistance of graphene changes, indicating that the array is insensitive to TE waves.

![Unit cell of reconfigurable metamaterial array based on graphene.](image)

However, when the incident wave is TM polarized, the performances vary with graphene property. When graphene is tuned to $R_s = 2000 \Omega$, with no external voltage applied, the array has resonance of -9.55 dB on its $S_{11}$ at around 7.89 GHz, revealing little reflection. In contrast, when the graphene is tuned to $R_s = 100 \Omega$, the reflection is -1.1 dB, providing a high reflection. This property means the graphene based array has tunable reflection under external voltage control, which poses possibility of designing reconfigurable arrays based on graphene metamaterials.
Figure 4.11 Performances of graphene metamaterial array under TE and TM polarizations, and different sheet resistances.

4.3.2 Radiation pattern reconfigurable antenna based on graphene switchable FSS

The above section has proved the tunable reflection based on graphene metamaterials array. Here this property is used to design reconfigurable antennas. In following Figure 4.12, a typical dipole antenna is designed and its reflection is given. The dipole antenna in the insert of Figure 4.12 is designed to work at same frequency band of array in Figure 4.11, and it has dimensions of: \( l_a = 8.05 \text{ mm}, g = 1 \text{ mm}, w = 0.5 \text{ mm} \). From the \( S_{11} \), the dipole antenna works at around 7.89 GHz with -30 dB resonance, same with working frequency of array in Figure 4.11.

To form reconfigurable antenna, 4×4 units array is periodically placed and the designed dipole is placed above the array with distance of \( h_d = 3 \text{ mm} \). To reduce the influence of edge diffraction, four metal walls with height of 3mm are placed to form a rectangular surround. The configuration is shown in Figure 4.13.
Figure 4.12 Designed dipole antenna and its reflection.

Figure 4.13 Dipole antenna hybrid with graphene metamaterials array to form a reconfigurable antenna system.

The performances of the hybrid antenna are simulated under various sheet resistance of graphene. As shown in Figure 4.14, when graphene has $R_s = 100 \, \Omega$, the hybrid antenna resonates at 7.964 GHz with return loss of -8.15 dB. When it is tuned to 2000 $\Omega$, the resonance shifts to 8.15 GHz with return loss of -17.59 dB. A small resonance frequency shift is obtained. However, frequency shift here is not the main concern. The radiation
patterns of the hybrid antenna under these two cases are further studied to show its flexibility.

Figure 4.14 Reflections of the reconfigurable hybrid antenna, when sheet resistance of graphene is tuned to $R_s = 2000 \, \Omega$ and $R_s = 100 \, \Omega$.

Figure 4.15 Radiation pattern reconfiguration of graphene metamaterials array based antenna system. (a) Radiation pattern when graphene sheet resistance is 2000 $\Omega$, at 7.964 GHz. (b) Radiation pattern when graphene sheet resistance is 100 $\Omega$, at 7.964 GHz.
Figure 4.16 Reconfiguration of graphene metamaterials array based antenna system. (a) 2D Radiation pattern when graphene sheet resistance is 2000Ω, at 7.964 GHz; (b) 2D Radiation pattern when graphene sheet resistance is 100 Ω, at 7.964 GHz.

The 3D radiation patterns at 7.964 GHz are shown in Figure 4.15, and corresponding 2D polar patterns are given in Figure 4.16. From the 3D patterns in Figure 4.15(a), the main lobes of the hybrid antenna are in two directions in Z axis, while only one main lobe direction in Figure 4.15(b). The negative Z direction radiation is blocked by the array when $R_s = 100 \Omega$. This effect can be more clearly seen in 2D radiation pattern in Figure 4.16. When $R_s = 2000 \Omega$, the two radiation lobes in Figure 4.16 (a) are almost symmetric, while in Figure 4.16 (b), the back radiation lobe is below -5dB, while main lobe is 3.55 dB, above 8dB difference. Besides, this graphene based antenna has simulated radiation efficiency of 65.7% (-1.821 dB) and 44.6% (-3.503 dB) when graphene sheet resistance is 2000 Ω and 100 Ω respectively as in Figure 4.15.

To conclude this section, applications of graphene in reconfigurable microwave applications have been demonstrated. Typical SRR metamaterials unit is used to hybrid with graphene to form working frequency tuneable frequency selecvtive surfaces, and its
polarization selectivity is proved. Based on these results, the unit is further employed for reconfigurable graphene metamaterials. The performances of the array show reconfiguration under voltage tuning, which is applied for reconfigurable hybrid antenna design. From the radiation pattern at working frequency under various tunings of graphene, the graphene based hybrid antenna shows flexibility on radiations.

4.4 Beam-Scanning THz Antenna Based on Graphene Strip Array

Beam-scanning antenna is among the category of the reconfigurable antennas. Here in this section, the concept and design of beam scanning terahertz antenna based on graphene arrays are presented. The main lobe direction is verified to be scannable with tunability introduced by graphene. The working principle of the beam scanning is further studied.

Figure 4.17 shows the antenna proposed. As can be seen, a straight dipole antenna is placed above graphene strip array. The distance between dipole and graphene array is \( h = 9 \mu m \), and graphene strip arrays are divided into two groups as graphene array 1 and graphene array 2, as seen in Figure 4.17(b). The arrays are connected with external voltage \( V_{DC1} \) and \( V_{DC2} \) separately to tune the chemical potentials. To facilitate the tunability of graphene, an ultrathin layer of silicon dioxide with thickness \( t \) is placed between graphene layer and doped silicon. The dipole length is \( l = 37 \mu m \), and gap between two arms is \( g = 0.75 \mu m \). The size of graphene strips is \( 120 \mu m \times 12.4 \mu m \), and the gap between strips is \( 3 \mu m \).

In this simulation, graphene is also modelled with complex surface conductivity as studied in Section 2.2 of Chapter 2. The relationship between chemical potential (\( \mu_c \)) of graphene and required external voltage \( V_{DC} \) under different isolation layer (silicon dioxide
in Figure 4.17(b)) thickness can be found in Figure 4.3 of above Section 3.3.1. From the figure, when $\mu_e = 0.4$ eV, around 60 V voltage is needed when $t = 100$ nm.

![Figure 4.17 Structure of graphene array based antenna.](image)

As described in Figure 4.17(a), the graphene strips are grouped to two arrays. When array 1 is with $\mu_{c1} = 0$ eV, namely $V_{DC1} = 0$ V, and apply $V_{DC2}$ to tune graphene in array 2 to different chemical potentials, the reflection can be found in Figure 4.18.

![Figure 4.18 Reflection of the antenna with different $\mu_{c2}$.](image)
From the reflection in Figure 4.18, the resonance frequency of the antenna is around 1.91 THz, at which the dipole is half-wavelength. The working frequency under different $\mu_{c2}$ is hardly changed, namely the resonance frequency mainly determined by straight dipole dimensions.

From above analysis, graphene introduces no tunability on resonance frequency here. It however brings beam scanning performance. When the external voltages of two graphene arrays are the same with $V_{DC1} = V_{DC2} = 0$ V, the 3D radiation pattern of antenna is shown in Figure 4.19 (b). It is a typical radiation of dipole antenna with backed PEC, and the main lobe direction is in Y axis.

![Figure 4.19 Radiation patterns of antenna.](image)

Figure 4.19 Radiation patterns of antenna. (a) 2D radiation pattern in theta plane when $\mu_{c1} = \mu_{c2} = 0$ eV; (b) 3D radiation pattern of the antenna at 1.91 THz.

To clearly show the beam scanning effect brought by graphene array, the 2D pattern of frequency 1.91 THz at theta plane when phi=90 is displayed in Figure 4.20. As can be seen from Figure 4.19(a), when $\mu_{c2} = 0$ eV, the main lobe direction is at theta=90, which means Y direction in Figure 4.19(b). From Figure 4.20, when tuned to $\mu_{c2} = 0.2$ eV ($V_{dc2} = 15$ V), $\mu_{c2} = 0.4$ eV ($V_{dc2} = 61$ V) separately, the main lobes are at theta=81 and 77 degree, which
mean main lobe rotation of 9 degree and 13 degree respectively. Due to the symmetry, when keep \( \mu_{c2} = 0 \) eV, and applied \( \mu_{c2} = 0.2 \) eV, 0.4 eV, the beam can be scanned to -9 degree and -13 degree separately. From the results, the scanning angle of the main beam can be ±13 degree, namely 26 degree in both sides, when the voltages applied up to 61 V.

The principle of the beam scanning effect can be easily explained. The dipole antenna here is the source antenna, which is the reason why working frequency is hardly affected as shown in Figure 4.18. The graphene array and PEC backed dielectrics works as secondary radiation, with induced currency from dipole antenna radiation. The whole antenna radiation is the addition of dipole radiation and secondary radiation. However, the secondary radiation is not symmetrical because of the different external voltage added (which changes graphene’s complex surface conductivity), making the current on graphene array unsymmetrical, and main lobe direction rotated away form 90 degree. Obviously, various current strengths make the rotation angles different.

This rotation demonstrates that the introduction of graphene array here make the antenna flexible and enabled with beam scanning characters. The beam scanning angle is expected to be further enhanced if the antenna above graphene has narrow main lobe.
Figure 4.20 2D radiation pattern of antenna at different $\mu c_2$ when $\mu c_1 = 0$ eV. (a) $\mu c_2 = 0.2$ eV; (b) $\mu c_2 = 0.4$ eV.

This section presents a design of graphene based beam-scanning antenna. Graphene array here introduces flexibility to the antenna, and the main lobe of radiation is demonstrated to be scannable with external voltages applied to graphene array. Higher scanning angle can be expected with narrow lobe source antenna, and more flexibility can be introduced when graphene array is replaced with metasurface.

### 4.5 Chapter Summary

In this chapter, frequency and radiation reconfigurable microwave antennas, as well as THz band beam-scanning antenna have been designed with a hybrid method. In all those designs, graphene is introduced for its tunability on sheet resistance, and normal antennas work as main radiator. With this method, those antennas have both high radiation efficiency and tunability. The outstanding characters of those graphene based antennas are not only on the tunability, but also on fixing other parameters unexpected to be tuned. For
frequency reconfigurable antennas, the radiation patterns are fixed when frequency is tuned. Similarly, radiation pattern reconfigurable antenna, and beam-scanning antenna, keep working frequency unchanged while altering radiation patterns. The working principles of these reconfigurable antennas have also been investigated. This work has covered the main types of reconfigurable antennas, and explores possibilities of applying graphene in flexible antenna areas.

References


Chapter 5: Highly Conductive Screen Printed Graphene for Low Cost Radio Frequency Electronics

5.1 Introduction

Printed electronics is a rapidly growing technology due to its spreading applications in flexible display screen [1,2], chemical/biomedical sensors [3-5], wearable electronics [6], radio frequency identification (RFID) [7,8], energy harvesting and storage, etc. [9,10]. As electrical conductor is the core element in printed electronics, the main research has been focused on providing highly conductive inks, along with other characteristic in transparency, flexibility, adhesion and cost, etc.

As introduced in Chapter 1, conductive inks can be catalogued into several classifications, such as metal nanoparticles [11], metal nanowires [12], conductive polymers [13], and carbon nanomaterials [14,15] to name a few. Metal nanoparticles and nanowires normally have high conductivity. Among them, silver based nanoparticles/nanowires are popular and not easy to be oxidized, but it is too expensive for wide applications. For example, to get around 0.5ohm/sq sheet resistance, 230 mg/m²
AgNWs coating is needed [16-17], which costs too much for mass produced electronics [18]. Besides, migration issue of silver nanoparticles makes it unsuitable to be printed on normal papers [19-20]. Researchers tried to replace silver with copper or aluminum nanoparticles, but they are prone to become oxidized, especially during high-temperature annealing [11,21]. A more challenging issue for metal based inks is the compatibility with other heat-sensitive components as high-temperature annealing treatments are normally essential [15].

As to conductive polymer, it is less conductive to meet RF or microwave radiation requirement [13]. Conductive polymer is also limited by its thermal and chemical instability [22]. Carbon nanomaterials, such as carbon nanotubes or carbon black, are difficult to be oxidized even in high temperature environments. However, with typical sheet resistance above 50 \( \Omega /\text{Sq} \), they are still not conductive enough for radiation purpose [23-25]. The high junction resistance in overlapped carbon nanotubes [23-24], and high contact resistance between nearby carbon black particles, hinder their improvement in conductivity [25,26]. In contrast, graphene, the new 2D carbon materials, is proved to be quite competitive in providing high conductive ink along with advantages in cost, chemical stability, and mechanical flexibility, etc. [23-24].

Graphene conductive inks are generally prepared in two ways. One is to disperse graphene in solvents without binder, typically N-Methyl-2-pyrrolidone or Dimethylformamide (NMP/DMF) [24,27], and the other is to add binders like ethyl cellulose (EC) in solvents to increase linkage between components [23,28]. To date, graphene conductive ink containing binder (EC) was reported to reach conductivity of \( 2.5 \times 10^4 \text{S/m} \) through method of reduced graphene oxide (RGO) [23]. However, binders are electrical insulators which reduce the conductivity of inks. To increase the conductivity, thermal annealing at 250°C for 30min is required to decompose binder (EC) and reduce
graphene oxide after printing procedure [23]. However, thermal annealing makes it incompatible with heat-sensitive substrates like paper, plastics and etc. [15]. In contrary, binder-free ink has reduced requirement of post-processing. For instance, a typical 70°C treatment was conducted in preparing binder-free graphene patterns with conductivity of 3×10³ S/m [27]. Despite its advantages in low temperature processing, conductivity of binder-free graphene ink is low and needs further improvement.

Herein, a straightforward but effective technique is presented to enhance the conductivity of binder-free graphene ink for large scale screen printing. A rolling compression is applied to replace function of absent binder, and improve conductivity significantly. The conductivity of prepared printed graphene laminate is improved by more than 50 times and reaches 4.3×10⁴ S/m, which is almost double of 2.5×10⁴ S/m of previously reported RGO with binder [23] and 10 time higher than that of binder-free [27]. The achieved conductivity makes the ink suitable for RF radiations. A simple dipole antenna was printed with graphene ink on a paper substrate. The measurements have demonstrated its effective radiation in aspects of impedance matching, realized gain and far-field radiation pattern. Based on the effective radiation demonstration, the practical RFID tag, novel-concept anti-tampering tag, EM shielding applications are characterized and experimentally proved in this chapter. These results reveal its valuable commercial prospective in RFID and other printed RF applications.

In this chapter, the preparation of graphene conductive ink and followed rolling compression method for conductivity improvement are presented in Section 5.2. Characteristic of fabricated dipole antenna to demonstrate the effective radiation is given in Section 5.3. The printed graphene based commercial RFID tags are designed and measured in Section5.4. Section 5.5 presents the novel-concept anti-tampering RFID tag utilizing
unique breakable property of printed graphene. An additional EM shielding of the printed graphene in C band is given in Section 5.6, and a conclusion is made in Section 5.7.

5.2 Preparation of Highly Conductive Printed Graphene

Screen printing is widely used in printing industry due to its advantages in low cost and high throughout. To achieve both high conductivity and low temperature processing, a binder-free strategy combining with followed rolling compression to enhance printed graphene conductivity is developed. Here in this section, both the graphene conductive ink preparation and conductivity enhancement are introduced.

Normally, conductive ink for screen printing contains binders such as polymeric, epoxy, siloxane, or resin binders because granular powders cannot form a continuous film without linkages of them [29-30]. However, binders need to be decomposed or evaporated through high-temperature thermal annealing. This high-temperature process prevents graphene ink from printed on flexible substrates such as papers and textiles. Furthermore binders are insulators that degrade ink conductivity. To achieve both low temperature processing and high conductivity, a binder-free graphene ink has been developed, and rolling compression was conducted to enhance printed graphene conductivity.

In this work, the graphene conductive ink is commercially available Gra-ink 102E from BGT Materials Ltd, UK. This binder-free graphene ink contains graphene nano-flakes, dispersants and solvents. Graphene nano-flakes were dispersed in solvent N-Methyl-2-pyrrolidone (NMP) with help of ultrasonic processing, to form a uniform 10wt% graphene ink. Less than 1wt% non-ionic polymer-type surfactants were added to the ink. The presence of surfactants helps to improve the dispersion of graphene flakes and viscosity of ink. More dispersion of graphene nano-flakes improves the percentages of conductive items in ink, and adjusted viscosity helps to get uniform deposition of film in printing. The
following Figure 5.1(a) gives the picture of the graphene conductive ink. As seen, the graphene ink is black and uniform due to excellent dispersion of graphene nano-flakes. The more clear suspensions of the nano-flakes can be found in Figure 5.1(b), the optical image of the ink under 1000× magnification observation.

Figure 5.1 Graphene conductive ink and graphene nano-flakes dispersion. (a) Graphene ink; (b) Optical image of graphene nano-flake with 1000× magnification.

The graphene ink, prepared as described was used to print designed patterns. The patterned stainless-steel screen with 150×150 mesh was used in the screen printing. The printing procedure is presented in the following Figure 5.2. As seen in Figure 5.2, the conductive ink containing graphene nano-flakes, dispersants and solvents, is coated on substrate. After drying process at 100°C for 10 minutes, part of solvents is volatilized, and graphene nano-flakes coating is left on the substrate. It is worthy to mention that, the low temperature drying is compatible with substrates like papers and textiles. Even without binders, the free-standing graphene coating is robust and flexible, due to the good film-forming ability 2D graphene nano-flakes [31]. However, the graphene coating at this stage is the highly porous stacking of graphene nano-flakes, as illustrated in inserted SEM of Figure 5.2(b), leading to high contact resistance between nano-flakes and unsmooth pathways for electron transport. To enhance the conductivity and the adhesion of graphene
nano-flakes, a further rolling compression is adopted. After compression, the graphene coating becomes highly dense and the printed graphene laminate forms, as seen in Figure 5.2 (c).

![Figure 5.2 Schematic illustration of preparing graphene laminate and its characteristics.](image)

To check the effectiveness of the rolling compression on conductivity of the printed graphene, the conductivity and sheet resistance of the printed graphene were measured under various compression ratios. The sheet resistance of the printed graphene laminate was measured with the 4-point probe (RM3000, Jandel, UK). The thicknesses of samples were measured with digital thickness gauge (PC-485, Teclock, Japan). The roller used to compress the samples was Type. SERP02 from Shining Energy LTD, Taiwan. The different compression ratios were controlled by adjusting space between two rollers. To
reduce the measurements error, 10 measurements at different spots were carried out to obtain the average value of each sample.

The measured surface resistance and conductivity of the printed graphene samples under various compression ratios are shown in both Figure 5.2 (d) and Table 5.1. Here the compression ratio is defined as the ratio of the thickness decrement of compressed sample over un-compressed sample thickness. The thickness and the sheet resistance were measured, and other properties listed in Table 5.1 were calculated with these two measured data. As shown in Figure 5.2 (d) and Table 5.1, when the compression ratio is 0%, namely the graphene coating without compression, its thickness $t$ is 31.6 µm, and sheet resistance $R_s$ measured to be 38.0 Ω/Sq. The bulk conductivity of the uncompressed sample is $\sigma = \frac{1}{t \times R_s} = 8.3 \times 10^2$ S/m. From the Figure 5.2 (d), with the increase of compression ratio, the conductivity rises and sheet resistance decreases accordingly. The exact values of the printed graphene sample under 4 different compression ratios can be found in Table 5.1. When the compression ratio is 81%, the thickness of printed graphene is 6 µm, and its conductivity increases to $4.3 \times 10^4$ S/m, which means the conductivity is improved by more than 50 times with rolling compression, compared with the un-compressed sample. Also, the sheet resistance under 81% compression is decreased to 3.8 Ω/Sq, one tenth of uncompressed sample.
Table 5.1 Measured property of printed graphene under various compression ratios.

<table>
<thead>
<tr>
<th>Samples</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compression ratio (%)</td>
<td>0%</td>
<td>30%</td>
<td>73%</td>
<td>81%</td>
</tr>
<tr>
<td>Thickness (µm)</td>
<td>31.6</td>
<td>22.1</td>
<td>8.4</td>
<td>6.0</td>
</tr>
<tr>
<td>Sheet Resistance R_s (Ω/Sq)</td>
<td>38.0</td>
<td>28.5</td>
<td>8.2</td>
<td>3.8</td>
</tr>
<tr>
<td>Normalized R_s^a (Ω/Sq/mil)</td>
<td>48.0</td>
<td>25.0</td>
<td>2.7</td>
<td>0.9</td>
</tr>
<tr>
<td>Resistivity ρ (Ω.m)</td>
<td>1.2×10^{-3}</td>
<td>6.3×10^{-4}</td>
<td>6.9×10^{-5}</td>
<td>2.3×10^{-5}</td>
</tr>
<tr>
<td>Conductivity σ (S.m^{-1})</td>
<td>8.3×10^{2}</td>
<td>1.6×10^{3}</td>
<td>1.4×10^{4}</td>
<td>4.3×10^{4}</td>
</tr>
</tbody>
</table>

^a Normalize sheet resistance to 1 mil = 25.4 µm.

To make the compression process more visible, the top SEM views and the cross-sectional SEM images of 4 samples with different compression ratios (as in Table 5.1) are given respectively in Figure 5.3. Figure 5.3 (a) and Figure 5.3 (e) shows the uncompressed case, with top and cross-sectional views. Similarly SEM of three more samples with compression ratios of 30%, 73% and 81%, corresponding to thicknesses of 22.1 µm, 8.4 µm and 6.0 µm respectively, are shown. Figure 5.3 (b), (c), (d) illustrate their top views, and Figure 5.3 (f), (g), (h) present cross sectional views accordingly. The top SEM views are under 1000× magnification. For cross sectional views in Figure 5.3 (e) to Figure 5.3 (h), magnifications of 500×, 1000×, 2000×, 3000×, are used respectively to have better observation and fit the scope. The Obviously from Figure 5.3 (e) to (h), with the increase of compression ratio, graphene laminate thickness decreases. By comparing the top views in Figure 5.3 (a)-(d), it can be seen that the surface of graphene nano-flake film becomes denser and smoother with higher compression ratio. From Figure 5.3 (e)-(h), one can see that the thickness decreases correspondingly with higher compression ratios.
Figure 5.3 SEM images of top and cross sectional views of printed graphene samples with various compression ratios. (a) Top view of un-compressed porous sample; (b) Top view of sample with compression ratio 30%; (c) Top view of sample with compression ratio 73%; (d) Top view of sample with compression ratio 81%; (e) Cross sectional view of un-compressed porous sample; (f) Cross sectional view of sample with compression ratio 30%; (g) Cross sectional view of sample with compression ratio 73%; (h) Cross sectional view of sample with compression ratio 81%.
With the above method of preparing printed graphene laminate samples, some rectangular patterns were printed on normal paper and compressed, as shown in Figure 5.4. It can be found that the printed graphene have good adhesion with paper, which enables the flexibility of the printed graphene laminate on paper as seen in Figure 5.4 (b). The characteristics of high conductivity, superior flexibility, low cost and light weight of the printed graphene make it quite competitive for applications in RFID, flexible electronics, wearable communications, EMI shielding, etc.

![Figure 5.4 Printed graphene laminate sample on paper and its flexibility.](image)

### 5.3 Effective RF Radiation from Printed Graphene

From the above analysis, it should be pointed out that the compression not only increases the conductivity significantly, but also reduces the sheet resistance of graphene laminate 10 times from 38 Ω/Sq to 3.8 Ω/Sq. In radio frequency antenna applications, sheet resistance matters more. In previous reported work, a printed graphene antenna with sheet resistance of 65 Ω/Sq has proved good impedance matching, while no demonstration of effective radiation is given as the sheet resistance is too high [8].

To study whether the binder-free printed graphene laminate can be used for RF radiation, a typical half-wavelength dipole antenna was designed. The antenna is printed on a normal paper for possible flexible applications. Following the same process in above Figure 5.2, dipole pattern was printed on paper and its sheet resistance was measured to be
3 Ω/Sq. Its final thickness after compression was 7.7 µm, measured with digital thickness gauge (PC-485, Teclock).

In the antenna fabrication, no high temperature thermal annealing or any vacuum condition is required. The entire screen printing and heating procedure are widely used in printing industry. These characters not only make printing compatible with paper/plastics, but also lower the manufacturing costs significantly. Moreover, the screen printing is ideal for low-cost and high-throughput mass commercial production.

The designed antenna made of graphene laminate was printed on paper, as shown in Figure 5.5. The length of one antenna arm is \( l = 68.82 \text{mm} \), the arm width and gap distance are \( w = 3.53 \text{mm} \) and \( g = 3.53 \text{mm} \), respectively. The paper substrate has dielectric constant of 2.3 and 50µm in thickness.

![Figure 5.5 Printed graphene dipole antenna. (a) Structural dimension of the dipole antenna; (b) Screen printed graphene laminate dipole antenna; (c) Graphene laminate antenna attached on foam and connected with a SMA for measurement.](image)

Due to the mechanical flexibility of graphene laminate, the graphene antenna is flexible if printed on paper, plastic and PET, which is very important for flexible electronics like wearable communications and RFID applications. To facilitate the experiment, thin foam
layer (RS 554-844) having dielectric constant of 2.6 and thickness of 0.8 mm is laid under the paper for support. A 50 $\Omega$ SMA connector is connected with graphene laminate antenna arms with conductive epoxy (Circuit works CW2400), as displayed in Figure 5.5 (c).

The following Figure 5.6 gives the reflection coefficient ($S_{11}$) of the graphene laminate antenna measured with Vector Network Analyzer (VNA Agilent E5071B). As it can be seen, the minimum reflection occurs at 0.96 GHz with -11.6 dB, indicating that the antenna is well impedance matched. The -10 dB bandwidth of the dipole is from 0.89 GHz to 1.02 GHz, which indicates that more than 90% power is transmitted to the antenna in this frequency band.

![Figure 5.6 Measured reflection coefficient of the graphene laminate dipole antenna.](image)

However, good impedance matching, i.e., low reflection coefficient ($S_{11}$), only means effective power transmission from the source to the antenna. It does not tell whether the transmitted power to antenna is effectively radiated to the free space. The transmitted power from the source can be partly or mostly dissipated due to the ohmic loss of the antenna [32-33]. The higher the sheet resistance is, the less the RF power can be radiated to free space. As one of the most important criteria of antenna performance evaluation, the realized gain is necessary to show the effectiveness of radiation. In this work, the graphene
laminate antenna’s realized gain was measured with three antenna method [34]. As shown in Figure 5.7, the realized gain peaks to -0.6 dBi at 962 MHz, and it is above -1 dBi between 930 MHz to 990 MHz. Although it is well known that the gain of an ideal (made of PEC) half-wavelength dipole antenna is 2.14 dBi in theory, here the gain achieved is good enough for many applications, especially RFID. Take commercial RFID chip Ucode 7 (NXP Semiconductors) as an example, in case the conjugate impedance matching between chips and antenna is satisfied, the theoretical maximum reading distance can exceed 10 meters with antenna of -1 dBi gain.

Figure 5.7 Measured realized gain of the graphene laminate dipole antenna.

As the dipole antenna radiation pattern is well known, the effective radiation of printed graphene dipole can be judged by the pattern measured in far field. If the measured pattern is same as dipole, then the RF radiation from printed graphene antenna is verified, and vice versa. To further verify the radiation, the radiation pattern of the printed graphene was measured at 962 MHz in anechoic chamber as shown in Figure 5.8. Vivaldi antenna was used as source radiator and DUT (graphene laminate antenna) was placed on a rotary table.
as receiver. These two antennas were connected with VNA (Agilent E5071B), and radiation pattern was recorded with antenna radiation measurement system (Antenna Measurement Studio 5.5, Diamond Engineering). The data was recorded for every 10 degree rotation of the DUT. Combining with the realized gain value at 962 MHz shown in Figure 5.7, the radiation pattern is displayed Figure 5.9.

![Image of measurement setup](image)

**Figure 5.8** Measurement of radiation pattern in anechoic chamber. (a) Elevation plane pattern measurement; (b) Azimuth plane pattern measurement.

As can be seen in Figure 5.9, the radiation pattern of the printed graphene antenna shows a typical dipole pattern. In Figure 5.9 (a), a bit smaller radiation on the left side radiation results from the influence of the pasted foam layer. At 0 degree, the gain is at its
peak (-0.6 dBi). When it comes to direction at around 90° and 270°, the gain turns to the lowest. From Figure 5.9 (b), the azimuth plane radiation is a typical circle, which matches theoretical radiation pattern of a dipole antenna. The radiation pattern again proves that the printed graphene dipole antenna can radiate to far field effectively.

![Figure 5.9 Measured gain radiation patterns. (a) Elevation Plane and (b) Azimuth Plane.](image)

### 5.4 High-Performance Printed Graphene UHF RFID

The aforementioned graphene dipole antenna has proved the effective radiation from printed graphene laminate with graphene BGTM 102E ink. To achieve better RFID tag performance, especially reading range, the company has developed ink 102A, which has higher conductivity. With the same fabrication procedure as described in Section 5.2, the final compressed sample with 102A ink has conductivity of $1.33 \times 10^6$ S/m, and sheet resistance of 77 mΩ/sq. In this section 5.4, the designs for commercial purpose RFID applications use ink 102A to get competitive performance compared with products in market are presented.
5.4.1 Printed graphene tag designs and performances

A RFID system consists of RFID reader antenna, RFID tags, signal processing and user interference, etc. In this part, printed graphene is used for passive RFID tags aiming for commercialization. As known, the most important criteria of RFID tag is its reading range, and the reading range \( r \) can be calculated using Friis free space formula [35,36].

\[
 r = \frac{\lambda}{4\pi} \sqrt{\frac{P_t G_t G_r \tau}{P_{th}}}
\]  

(5.1)

where \( \lambda \) is the wavelength, \( P_t \) is the transmitted power from reader antenna, \( G_t \) is the gain of reader antenna, \( G_r \) is the gain of tag antenna, \( P_{th} \) is the minimum threshold of the power needed to active the RFID chips. \( \tau \) is the matching factor, which describe the conjugate impedance matching between tag antenna and IC. The impedance matching factor \( \tau \) is given as:

\[
 \tau = \frac{4R_c R_a}{|Z_c + Z_a|^2}
\]  

(5.2)

As seen in the equivalent circuit of tag in Figure 5.10, \( Z_c = R_c + jX_c \) is the impedance of chip, and \( Z_a = R_a + jX_a \) is the antenna impedance.

Clearly, impedance matching factor \( \tau \) in Equ. (5.2) has range of \( 0 \leq \tau \leq 1 \). The best impedance matching for maximum power transmission to IC is conjugate impedance matching between RFID antenna and chip, when \( R_c = R_a \) and \( X_c = -X_a \), having \( \tau = 1 \). Take a typical design for commercial IC NXP Ucode 7 as an example. Figure 5.11 gives the model of impedance for the IC. The chip impedance is modelled as parallel of resistor and capacitors. The tag chip part \( R_p \) and \( C_p \) are from the impedance of the IC circuit, and the \( C_{mount} \) is the additional capacitance brought by chip assembly [39].
Figure 5.10 Equivalent circuit of RFID tag [37,38].

Figure 5.11 Tag chip linearized RF model [39].

From the Ucode 7 datasheet, the impedances of the tag chip are 14.5-j293 and 12.5-j277 at 866 MHz and 915 MHz respectively. From this data, it can be calculated that $C_p = 0.625 \, \text{pF}$, $R_p = 5 \times 10^3 \, \Omega$. For the assembled chip, the impedance is 13.5-j195 from measurement as in the datasheet. With model in Figure 5.11, the additive capacitor introduced by bonding is calculated to be 262.4 fF, quite close to reference value 250 fF given in datasheet. So the total capacitor after assembly is $C_p + C_{mount} = 0.875 \, \text{pF}$. It should be noticed that $R_p$ is less accurate from the above model, concluded from the comparisons of calculated value and measured value given in datasheet. In the design, the input impedance of the chip is taken as constant, for instance Ucode 7, $\text{Real}(Z_c) = 13.5 \, \Omega$. The imaginary part of $Z_c$ is calculated with using the circuit model.
The tag design is the procedure of adjusting tag structural parameter to achieve high matching factor. The adjustment is based on the impedance calculation. As seen in Figure 5.12, the antenna input impedance ($Z_a$) and IC chip impedance ($Z_c$) are compared. The figure is the comparison of real part of the $Z_i$ and $Z_c$. It can be seen that at around 915 MHz, $\text{Real}(Z_a) = \text{Real}(Z_c)$. In Figure 5.12, the $\text{Imag}(Z_a)$ and $\text{Imag}(Z_c)$ are also shown, indicating $\text{Imag}(Z_a) = -\text{Imag}(Z_c)$ around 915 MHz. Combining these results, it can be seen that the perfect conjugate matching of antenna impedance and chip impedance has been achieved at around 915 MHz.

![Figure 5.12 Comparison of the antenna input impedance and chip impedance.](image)

The impedance matching factor $\tau$ from the above impedance can be calculated with Equ. (5.2) and displayed in Figure 5.13. As can be seen, the highest matching factor is at 915 MHz with almost perfect conjugate matching, corresponding to $R_c = R_a$ and $X_c = -X_a$ at 915 MHz in above Figure 5.12.
Figure 5.13 Calculated impedance matching factor.

From Equ. (5.1), the reading range is determined by factors from several aspects. To increase the range, the $P_t G_t$ can be increased, which means improve the reader antenna gain and its input power. However, there is a limit requirement to avoid interference to other systems according to regional EMC regulations. This limit is defined with $EIRP = P_t G_t$ (equivalent isotopically radiated power). Typically, EIRP=3.3 W.

Tag antenna gain $G_r$ also has influence on the reading range. However it cannot just be increased as practical tags have size limitation, which restricts the antenna gain. Another factor $P_{th}$, is the sensitivity of the RFID chips, which determined by IC itself. Clearly, lower $P_{th}$ means more sensitive and higher performance the IC is.

From the above analysis, the factors affecting RFID tag are mainly the frequency band, size limitation, EIRP, cost and reliability. The RFID tag design with given chips and EIRP is about how to achieve both high gain and high impedance matching factor under given size requirement.
In Figure 5.14, 9 antennas have been designed with help of CST simulations. In the simulation, the graphene sheet was modelled with $Rs=77 \, \text{mO/Sq}$. As seen, these designed tags were printed on papers.

![Figure 5.14 Fabricated 9 printed graphene RFID tags.](image)

To measure the reading range of these tags under commercial RFID reading system, the following setup in Figure 5.15 was made in anechoic chamber. Due to the size limit of the chamber, the transmitted power was not given as high as EIRP to reduce the required maximum length. Assume the maximum readable distance $d$ is obtained under transmitted power $P_{t0}$, then the maximum distance $r$ can be calculated with [35,37]:

$$r = d \sqrt{\frac{\text{EIRP}}{P_{t0}G_t}}$$  \hspace{1cm} (5.3)

With the above method, the reading ranges of 7 randomly selected tags were measured and calculated using the commercial RFID system. The reader antenna in these systems has gain of 8 dbi. The system can set the single working frequency in the frequency and the ranges under these frequencies were measured and listed in Table 5.2.
As seen from Table 5.2, all the samples have proved long distance. The distance between different tags is believed to be from design difference. The difference between same design tags is from the bonding. The longest range in this measurement is above 10 m, quite competitive in market.

Table 5.2 Measured reading range of randomly selected samples.

<table>
<thead>
<tr>
<th>Tags</th>
<th>Range-902 MHz (m)</th>
<th>Range-910 MHz (m)</th>
<th>Range-920 MHz (m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-1</td>
<td>10.6</td>
<td>10.0</td>
<td>9.24</td>
</tr>
<tr>
<td>2-1</td>
<td>9.56</td>
<td>9.56</td>
<td>8.43</td>
</tr>
<tr>
<td>2-2</td>
<td>9.46</td>
<td>9.46</td>
<td>8.43</td>
</tr>
<tr>
<td>3-1</td>
<td>9.13</td>
<td>9.13</td>
<td>8.05</td>
</tr>
<tr>
<td>3-2</td>
<td>8.53</td>
<td>8.43</td>
<td>7.43</td>
</tr>
<tr>
<td>4-1</td>
<td>9.03</td>
<td>8.62</td>
<td>7.78</td>
</tr>
<tr>
<td>5-1</td>
<td>8.83</td>
<td>8.53</td>
<td>7.69</td>
</tr>
</tbody>
</table>
To validate the superior performance of the printed graphene RFID tag, its performance was compared with the most popular aluminum long-range UHF RFID tag in market UPM Dogbone, as seen in the Figure 5.16. The size of the aluminum dog bone tag is 23 mm×93 mm, and the printed graphene tag has size of 30 mm×81 mm.

Figure 5.16 The commercial aluminum tag and printed graphene tag.

Figure 5.17 Printed graphene RFID tag performance measurement using Tagformance system.
The measurement was conducted using a professional RFID measurement system Tagformance, which can measure the reading range, backscattering signal, etc. in wide bandwidth from 800 MHz to 1000 MHz [40]. The measurement setup is given in Figure 5.17. A calibration using standard tag in system was conducted to eliminate influence from cables and environmental interference, etc.

Figure 5.18 The reading range comparison of the commercial aluminum tag and printed graphene tag.

Figure 5.18 gives the reading range comparison of commercial aluminum tag and printed graphene tag in frequency range of 800 MHz to 1000 MHz. The scanning space is 5 MHz. As seen, the reading range curve is flat in a wide frequency band from 850 MHz to 920 MHz, so that it can be applied in different regions. Besides, this wideband property makes sure the tag still works when attached to object (such as plastic bottles) and working frequency shifts. The longest reading range for the commercial tag is 8.5 m at 900 MHz, while the range for graphene tag goes to 9.9 m at 915 MHz. From 880 MHz, the printed graphene tag over commercial tag in reading range. The reading range above 9m is from 880 MHz to 930 MHz, which provides much space for attachment in different applications.
The central frequency of the designed graphene tag is at 915 MHz, as it is aiming for China market.

## 5.4.2 Cost-down RFID design and performance

The commercial aluminum tag is made with substration manufacturing method by lithographing and etching [41]. In contrast, the graphene RFID tag is made through additive manufacturing method screen printing. For the substration manufacturing, the material cost of a tag is a whole piece of complete aluminum, and the non-tag part of the aluminum is removed and wasted in etching. However, for additive manufacturing screen printing, the material used for every tag is just the tag section. If the tag pattern can be designed to be smaller while maintain the performance, the material cost can be reduced in manufacturing.

![Image of cost-down designs](image)

**Figure 5.19** Two cost-down designs for the printed graphene tags.

In Figure 5.19, two cost-down designs are shown. The tags were fabricated with the same screen printing methods of the above graphene tags, but they are characterized with some holes. These holes are made in pad sections of previous designs. By comparison, the
area of the cost-down designs 1 and 2 is reduced by around 30% and 45% respectively, compared with the design in above Figure 5.16.

The measured reading ranges of the cost-down tags in 800 MHz to 1000 MHz are shown in Figure 5.20. As can be seen, the design 1 (corresponding to Figure 5.19(a)) has maximum reading range of 8.3 m at 880 MHz, and from 875 MHz to 925 MHz, the reading range is above 8 m. The other cost-down design 2 has maximum range of 8.7 m at 920 MHz, and it has above 8m reading range in higher band from 885 MHz to 930 MHz. These results prove that the long reading range of the printed graphene RFID tag is maintained even with significant less material cost.

![Figure 5.20 Measured reading ranges of the cost-down designs.](image)

### 5.4.3 Printed graphene enabled RFID reader antenna

Since printed graphene can make RFID tags, its high conductivity has enabled its application for RFID reader antenna. The reader antenna design normally required to be wideband so that it can cover most RFID frequency bands in different regions [42].
Compared with conventional metal reader antennas, the printed graphene antenna has advantages in low cost, light weight and easy to fabricate, etc.

Figure 5.21 gives the antenna structure and assembly. As can be seen, this reader antenna is a grounded patch antenna fed with coaxial cable. The patch radiator and ground are made of highly conductive graphene, and a foam layer is placed as supporter and spacer.

Figure 5.21 Designed reader antenna based on printed graphene. (a) Antenna design and dimensions; (b) Antenna assembly.

Figure 5.22 Simulated reflection of the antenna.
The above designed antenna was simulated in CST, and the $S_{11}$ of the antenna is shown as in Figure 5.22. From the reflection, the -7 dB bandwidth is from 850 MHz to 950 MHz, which covers the worldwide RFID frequency bands. This wide bandwidth makes it suit all RFID systems.

From Equ. (5.1), the reading range of RFID is linear with the square root of reader antenna gain. To have longer range, the antenna gain is required to be higher. Figure 5.23 depicts the simulated 3D radiation pattern of the grounded patch antenna. As seen, the radiation pattern mainly focuses on half space due to the ground reflection. The total efficiency of the antenna is -0.35 dB at 920 MHz. Also, at this frequency, the realized gain is 8.55 dB, which is in the same level of the commercial RFID reader antennas.

![Simulated radiation pattern](image)

Based on the above design, the fabricated and assembled antenna is shown in Figure 5.24. The whole weight of the reader antenna is almost just weight of foam, which is
around 70 g. For this light weight, the printed graphene reader antenna can be easily placed in many places for many special applications such as security checking. It is also a huge advantage in portable reader applications.

Figure 5.24 Fabricated printed graphene reader antennas.

The $S_{11}$ of the graphene printed reader antenna was also measured with VNA. As seen in Figure 5.25, this reader antenna works in wide band from 850 MHz to 950 MHz. Also, the reading distance measured with the above RFID system and tag in Figure 5.16 is above 10m, verifying the efficiency of the reader antenna made with printed graphene.

Figure 5.25 Measured $S_{11}$ of the graphene printed reader antenna.
In the above part, the printed graphene has been proved effective in RFID reader antenna and RFID tags. Based on these results, a complete portable RFID system based on graphene is assembled as shown in Figure 5.26. As can be seen, the RFID system consists of RFID reader board, printed graphene reader antenna, printed graphene RFID tags and PC host. The RFID reader board processes signal and responsible for communication with interface on PC host, and PC host is the port for user to extract information from RFID system. As seen in the Figure 5.26, the RFID tag can also be placed or inserted in train ticket, or plastic tube tickets in real applications.

![Typical minimized RFID system based on printed graphene.](image)

5.5 Printed Graphene Anti-Tampering Tags

The above work has shown the RFID application of the printed graphene. As the graphene laminate is layered graphene nano-flakes, and the supporting material is a normal paper, so the whole printed sample can be teared up. This property is quite different compared with conventional aluminum etched tag. The aluminum etched tag is made of a
complete piece of aluminum sheet and the supporting materials are normally PET, etc. Both the conductive material and supporting materials for conventional tags cannot be easily broken. This difference endows printed graphene RFID tag unparalleled advantage in anti-tampering applications compared with its conventional competitors.

The basic idea of the anti-tampering RFID tag based on breakable property of printed graphene is shown in Figure 5.27. As can be seen in Figure 5.27 (a), the anti-tampering tag is the normal RFID tag connected with an addition part. The function of the addition part is to shift the working frequency of the RFID tag to frequency bands which RFID system cannot detect. This additional part can be connected on any part of the tag. Also, the addition part can be short lines, open lines, gaps, or those lines combined with lumped elements such as capacitors, inductors, etc. When the anti-tampering tag is complete, the tag cannot be read by RFID system. However, when the addition part is removed, the anti-tampering tag becomes a normal RFID tag, and it can be detected by RFID system. This concept can be used in sensing break actions wirelessly, and this detection can be a trigger signal to following response such as alarm, filming or photo shooting, etc. for security purposes and so on.
Figure 5.27 Working principle of the anti-tampering design. (a) Anti-tampering tag consists of normal tag and addition part. The addition part shifts the working frequency outside RFID band; (b) When the addition is removed, it turns to normal tag, and readable by RFID system.

The Figure 5.28 gives the equivalent circuit model of the anti-tampering tag before and after break. As can be seen, the additive part of the anti-tampering tag introduces $X_{add}$ to the antenna impedance, which helps to shift the working frequency. When it is removed, the antenna impedance matches well with the chip impedance as normal tag, same as the one shown in above Figure 5.10.

![Equivalent circuit of anti-tampering tag, before break and after.](image)

Based on the above anti-tampering tag principle, an anti-tampering tag was simulated in CST to verify its principle. The anti-tampering tag, shown in Figure 5.27 (a), is a normal RFID tag with short connection close to chips ports. From the chip port view, the shorted line is an equivalent parallel inductor connected as in above equivalent circuit in Figure 5.28.
Figure 5.29 Impedance matching factors of anti-tampering tag to prove the concept.

From the Figure 5.29, when the shorted line has length of l=20 mm, the impedance matching factor is lower than 0.02 within the RFID band from 820 MHz to 940 MHz. The highest matching factor is around 0.78 at around 1.45 GHz, which is out of RFID frequency band. When the length is l=10 mm, the impedance matching factor is even lower in RFID band, and the highest matching factor shifts to higher band above 1.7 GHz, further away from RFID band. However, when the additive short-circuited wire is all removed, the matching factor becomes close to 1. It works as a normal RFID tag. The matching factor jumps from 0.02 to 1 with the removal of addition part. This difference brings 7 times reading distance difference from Equ. (5.1). From the comparison, it can be seen that the RFID tag is inactive when the tag is short-circuited, as its impedance matching frequency shifts out of RFID bands and the matching factor is quite low in RFID band. However, the matching frequency shifts to RFID band once additive wire is removed and the tag turns to active.
In Figure 5.30, a practical anti-tampering tag is shown. This anti-tampering tag has a long additive whisker with length of 7.7 cm, so that it can be fit more application cases in commercial products. The additional area is combination of parallel lines and gapped ring. This structure brings extra paralleled inductance and capacitance to the RFID antenna.

![Design of anti-tampering tag](image)

Figure 5.30 Design of anti-tampering tag.

The designed anti-tampering tag was fabricated using the same of the above RFID tags. Figure 5.31 gives the fabricated sample. The whisker was removed step by step with cuttings. Its performances under different cutting were measured using frequency-scanning Tagformance measurement system, as shown in Figure 5.32.

As seen from the Figures 5.31 and Figure. 5.32, when the anti-tampering tag is complete and full, the reading range of the anti-tampering tag is around 0.5 m from 820 MHz to 900 MHz, and it goes up to 1m at 930 MHz. This is a short reading distance for UHF RFID tags. If the reader antenna is placed above 1m away from the tag, the anti-tampering tag is not readable. When the Cut 1 was conducted (Figure 5.31) the line length left is about 5 cm. The corresponding reading range increases as shown in Figure 5.32, compared with full tag. As seen, around 2 m reading range was measured in whole RFID bands. Similarly, when Cut 2 and Cut 3 were conducted, the reading range extends. By
comparing Cuts 3 and 4, the maximum ranges are all above 7.5 m. However the central frequencies are different. The tag after Cut 3 has highest reading range at around 920 MHz bands, which is Chinese RFID band. However, it moves to lower band to around 875 MHz (EU bands) when the whole whisker was cut. This comparison proves that the cutting of whisker shifts the working frequency.

Besides, from the data, it can be found that the maximum range difference can be as high as 15 times (7.5 m over 0.5 m) at 875 MHz band, and 13.5 times at around 920 MHz (8.1 m over 0.6 m at 920 MHz). Obviously, in applications, the reader antenna of the RFID system should have distance between lowest and highest reading range before/after breaking. For example, when the RFID system works at 920 MHz, the lowest reading range is 0.6 m before any break, while highest reading range is 8.1 m. In this case, the distance between reader antenna and anti-tampering tags should be within 0.6 m to 8.1 m, so that the tag is not readable when it is complete, while readable after breaking. From these analyses, the most important criteria for the anti-tampering tag are lowest reading range \( R_{\text{min}} \) (when tag is complete), and ratio of longest range \( R_{\text{max}} \) (after break) over lowest reading range \( K = \frac{R_{\text{max}}}{R_{\text{min}}} \). Clearly, in real applications, smaller \( R_{\text{min}} \) and higher \( K \) are preferred.
In Figure 5.33, a real application of the anti-tampering tag is shown. The anti-tampering tag was attached to a wine box, and the whisker strides the box cap so that it can be easily broke when the wine box was opened. The similar RFID reading system was setup as shown in Figure 5.15. The complete box was not readable when it is above 0.5m
away from the reader antenna. However, when the box was opened and the whisker was broke, the tag was read and shown in the system. Obviously, this anti-tampering tag can be used in alarming malicious damages on products in stores.

![Image](image_url)

**Figure 5.33** Practical application demo of anti-tampering RFID tag used on fine wine box.

## 5.6 Shielding Effectiveness of Printed Graphene in C Band

The highly conductive graphene laminate prepared above has been proved to radiate RF effectively. The achieved high conductivity is also expected to provide effective shielding in theory. As known, C band ranges from 4 GHz to 8 GHz, which includes applications of satellite communications, Wi-Fi devices, telephones, and some weather radar systems, etc. [43]. In these applications, EMI shielding is important to block interference of un-desired signals. In this part, the shielding effectiveness of screen printed graphene laminate is studied for EMI shielding applications. The graphene laminate was prepared as in section 5.2, and it was screen-printed on normal paper. The size of the sample was cut to fit C band waveguide size (34.85×15.80 mm²) for measurement.
The configuration of the shielding effectiveness measurement of the graphene laminate is displayed in Figure 5.34. Waveguides (WG14) working from 5.85 GHz to 8.20 GHz were connected to measure the transmission ($S_{21}$) using a VNA, HEWLETT PACKARD (85107A). A TRL (Thru-Reflect-Line) calibration was made for the cables to improve the measurement accuracy. After calibration, the waveguides were connected as in Figure 5.34(a).

![Figure 5.34 Shielding effectiveness measurement setup for the printed graphene on paper. (a) Transmission measurement setup; (b) Waveguide port without printed graphene; (c) Waveguide port pasted with printed graphene.](image)

The transmission without the printed graphene laminate sample (DUT, device under test) was firstly measured as shown in Figure 5.34(b). Then the DUT was tailored and pasted to cover the waveguide port (34.85 mm×15.80 mm), as in Figure 5.34(c). The transmission when the printed graphene was inserted between two waveguide ports was measured for comparison. Figure 5.35 shows the transmissions ($S_{21}$) measured with and without the DUT as described. When DUT is absent, it can be seen that a nearly full transmission was achieved from 6 to 7.2 GHz, and the transmission degrades to -2 dB approaching 8 GHz. This degradation results from the ohmic loss on waveguide walls.
However, the transmission with the DUT placed shows that severe decreases to -30 to -35 dB in 6–8 GHz band, revealing pretty low transmission through graphene laminate.

![Graphene Transmission Diagram](image)

Figure 5.35 Measured transmissions with and without printed graphene sample in waveguide.

![Graphene SE Diagram](image)

Figure 5.36 Calculated shielding effectiveness of the printed graphene laminate.

With the measured data above, the SE provided by the printed graphene laminate was calculated from the transmission difference with and without DUT. The calculated SE is shown in Figure 5.36, and around 32 dB shielding effectiveness throughout the entire
frequency 6-8 GHz is observed. It is worthy to notice that the sample thickness here is only 7.7 μm, much small compared with the skin depth 28.85 μm at central frequency 7 GHz. Increasing the thickness of printed graphene laminate can further improve its SE.

In this part, shielding effectiveness of screen printed graphene laminate for EMI applications has been studied. The shielding effectiveness of the highly conductive printed graphene laminate is measured to be above 32 dB from 6 GHz to 8 GHz, proving that printed graphene can be a viable alternative for EMI/EMC shielding.

5.7 Chapter Summary

In this chapter highly conductive graphene laminate has been proved to radiate RF signal effectively. The required ultra-low resistance of RF antenna is achieved by rolling compression of binder-free graphene laminate. With compression, the conductivity of graphene laminate is increased by more than 50 times compared to that of as-deposited one. Graphene laminate with conductivity of 4.3×10^4 S/m and sheet resistance of 3.8 Ω/Sq (with thickness of 6 μm) is presented. Moreover, the formation of graphene laminate from graphene ink reported here is simple and can be carried out in low temperature (100 °C), significantly reducing the fabrication costs. A dipole antenna based on the highly conductive graphene laminate is further patterned and printed on a normal paper to investigate its radio frequency (RF) properties. The performance of the graphene laminate antenna is experimentally measured. The measurement results have revealed that graphene laminate antenna can provide practically acceptable return loss, gain, bandwidth and radiation patterns, making it ideal for low cost printed RF applications, such as RFID tags and wearable wireless sensor networks.

Besides, the highly conductive printed graphene has been demonstrated in applications of RFID tag, RFID reader antenna and system, anti-tampering RFID tag, EMI shielding,
etc. From the work, with help of the more advanced graphene ink, the RFID tag with better performance compared with commercial ones in market has been achieved with printed graphene. Based on printed graphene RFID tag and reader antenna, a RFID system based on printed graphene has been synthesized. Moreover, with the breakable property, the printed graphene has extended its application in anti-tampering application, where the conventional ones cannot reach. The novel printed graphene anti-tampering tag has proved ‘break & active’ property, and a real application of security on fine wine has been developed to show its prospective future. As to its EMI shielding effectiveness, the highly conductive and flexible printed graphene has shown 35 dB shielding on C band, which widen the EM applications of the printed graphene.

In summary, this chapter has developed the highly conductive, low cost and light weight printed graphene, and explored its applications in RFID system, anti-tampering, EMI shielding, etc. This work has proven that the printed graphene is ready for commercial market applications, and much more can be expected from its future developments.

References


Chapter 6: Printed Graphene for Flexible Antennas and Microwave Components Applications

6.1 Introduction

Wireless wearable communications, machine to machine (M2M) and internet of things (IoT) are some of the emerging technologies that is potential to provide an enormous step forward for mankind in the next decade [1-3]. In these fields, RF and microwave components are indispensable to provide basic functional blocks to any communication systems. These components includes passive components such as transmission lines (TLs), impedance matching networks and antennas, as well as active circuits such as low-noise amplifier (LNA), power amplifier, frequency mixer and local oscillator, etc. [4]. Conventionally, a microwave circuit/components are mainly assembled using PCB technology, which poses a huge challenge in integration with flexible substrates like textiles and papers [5]. However, this kind of integration is highly desirable in many applications requiring mechanical flexibility and conformability, such as wearable communication/circuit, IOT, etc. [6-8].
To solve the integration issue, methods of coating or plating metal on textile yarns were proposed [9-10]. In these approaches, even though the metals were deposited on flexible substrates, the fabrication procedures were complicated and low-efficiency, and the materials used were expensive (silver or gold), not suitable for mass deployment in low cost wireless wearable applications. Silver nanowires (AgNWs), polymers, carbon nanotubes and carbon black based conductive inks have also been developed for wearable electronics applications. Although AgNWs is highly conductive [11], to obtain low enough sheet resistance for RF applications, a relatively thick AgNWs coating is required (230 mg/m² for nearly 0.5 Ω/Sq), which results in high cost for mass production because silver is scarce and high-cost [11-13]. As to conductive polymer, while it was used for flexible electronics such as sensors, solar cell, its conductivity is too low to be employed for RF signal transmission or radiation [14-15]. Conductive polymer is also limited by chemical and thermal instability [16]. Carbon nanotubes or carbon black based conductive inks, with typical sheet resistance above 50 Ω/Sq, due to high contact resistance between overlapped nanotubes or carbon nanoparticles [17-18], are still not less conductive to meet practical RF circuit requirements.

Graphene is a very promising material for constructing RF and microwave flexible passive components owing to its high conductivity and unique flexibility [6,19]. To date, researchers have intensively investigated the applications of monolayer graphene to make active devices such as diodes and transistors [20,21]. However, the application of graphene in RF and microwave passive components has far lagged behind. This is because, in spite of graphene’s high conductivity, both exfoliated and CVD (chemical vapor deposition) graphene sheets have very high surface resistance, hindering their RF and microwave applications [22,23]. Printed graphene has demonstrated with sheet resistance of 65 Ω/Sq, and was reported for a wideband dipole antenna application [24]. Even though good
impedance matching was proved in the work, the effective radiation was not successful as the ohmic loss in the printed graphene is too high.

As described in Chapter 5, the printed graphene in our work has achieved conductivity as high as $4.3\times10^4$ S/m (3.8 $\Omega$/Sq), combining screen printing technology and rolling compression. Moreover, the technique is characterized with low cost, high fabrication efficiency and low-temperature processing. It enables high-efficiency screen printing of graphene on heat-sensitive flexible substrate materials such as plastics, paper and textiles, etc. This development brings the possibility of practically printable graphene wearable electronics along with its advantages in high conductivity, mechanical flexibility, low cost and light weight [25,26].

In this chapter, this technique is further applied to fabricate flexible RF and microwave passive components such as coplanar waveguide transmission lines, quarter wavelength open/shorted circuited resonators and wideband antenna. The performances of these components, especially under different bending cases, are experimentally examined and characterized. The results demonstrate that graphene RF and microwave passive components have desired electrical and mechanical properties for low cost wearable electronics applications.

### 6.2 Flexible Printed Graphene Microwave Fundamental Components

#### 6.2.1 Transmission lines

Transmission lines are basic structures designed to carry signals and are essential for RF circuits in signal transmission, resonators, filters impedance matching network and etc. [27]. As a proof of concept, two kinds of basic TLs, parallel and CPW transmission lines,
are designed, screen printed and characterized to investigate their feasibility for RF signal transmission.

The performance of a TL is mainly determined by constructing material and geometrical parameters such as material losses, substrate material dielectric constant, line gaps, signal line thickness and etc. Two parallel transmission lines with different gaps between the lines are designed and fabricated as shown in insert of Figure 6.1 (a). As it can be seen, SMA connectors are connected at ports of the transmission line using conductive epoxy. The length of both lines is \( l = 50 \text{ mm} \), and the gaps are \( g = 1.0 \text{ mm} \) and \( g = 0.3 \text{ mm} \), respectively.

The scattering parameters of these two lines are measured with Agilent E5071B VNA and propagation constant can be calculated by the following equations [28],

\[
e^{-\gamma l} = \frac{2S_{21}}{1 - S_{11}^2 + S_{21}^2 \pm \sqrt{(1 + S_{11}^2 - S_{21}^2)^2 - 4S_{11}^2}}
\]

\[
\gamma = \alpha + j\beta
\]

where \( \alpha \) and \( \beta \) are attenuation constant and phase constant, respectively. To eliminate the effect of impedance mismatch on analyzing conductor loss, absorption attenuation, which is defined as the ratio of power entered into the input port of the network over the output power of the network, is calculated by [29].

\[
\text{Attenuation} = \frac{P_{\text{in}}}{P_{\text{out}}} = \frac{1 - |S_{11}|^2}{|S_{21}|^2}
\]

The attenuation is unitized to per \( \text{mm} \) and displayed in Figure 6.1 (a). It can be seen that the line with wider gap has lower attenuation. This is because the electromagnetic field is concentrated mainly at inner edges of the parallel lines; smaller gap results to more intensive field, thus brings more conductor loss. However, it should be pointed out that the
line gap is not to be set arbitrarily as it determines the characteristic impedance of the TL. As expected, the attenuation increases with frequency because the skin depth decreases at higher frequency.

Figure 6.1 Samples of the parallel transmission lines with various line gaps and their performances. (a) Attenuation of the transmission lines, and the insert is two samples with different line gaps, \( g = 0.3 \text{ mm} \) and \( g = 1.0 \text{ mm} \), respectively; (b) Phase constants \( \beta \) of the transmission lines.

The relatively high attenuation measured in these TLs is mainly due to the low thickness of the printed graphene. The printed graphene has thickness of \( t = 7.7 \mu\text{m} \) with conductivity of \( \sigma = 4.3 \times 10^4 \text{ S/m} \). Its skin depths, from 2 GHz to 8 GHz, are between 54 \( \mu\text{m} \)
to $27 \mu m$, which means the thickness of printed graphene is only $14.3\%$ to $28.5\%$ of its skin depth. In practical applications, generally conductor thickness is made 3-5 times of its skin depth to reduce attenuation. Increasing the thickness of printed graphene is an effective way to gain lower attenuation. Besides, the propagation constant in Figure 6.1 (b) is almost linear with frequency, demonstrating that there is little phase distortion in the printed graphene parallel lines, which is desirable for practical RF applications.

Moreover, the superior flexibility of the graphene laminate enabled TLs printed on paper is experimentally verified using the sample of 10 cm length and 1 mm gap. The samples in four cases were examined and shown in Figure 6.2, together with corresponded measurement results. The printed graphene TL was not bended in insert Figure 6.2 (a), bended in insert Figure 6.2 (b) but not twisted, bended and twisted in insert Figure 6.2 (c) and (d). It is clear from the measurements that the bending and twisting of the printed graphene TLs do not alter much on its transmission coefficients, highly desirable in flexible or wearable applications. The slight differences between these four cases results from the mutual coupling between different segments of the TLs. For instance, the un-bended case has least transmission than other three cases as no mutual coupling occurs between different parts of the straight line. TLs in Figure 6.2 (b) and (c) have less transmission than that in (d), because segments of the line in (d) are placed spatially closer and more mutual coupling is introduced. It should be pointed out that the TLs in Figure 6.2 have not been well optimized for impedance matching. Higher transmission coefficient can be obtained with better impedance matching. Moreover, the attenuation posed by ohmic loss as given in Figure 6.1 (a), is another factor for low transmission. Corresponding to incremental attenuation with frequency, the transmission coefficients for all four cases has decreasing trade with frequency increases.
A CPW transmission line is more practical, and it has one conducting track and two return conductors as ground. These three conductors are all placed on the same plane, resulting in low-profile advantage for CPW TL based components. This advantage makes CPW based components widely used in RF and microwave circuits. The performance of CPW TL is mainly determined by material and dimensional parameters such as constructing material losses, dielectric constant, line gaps, line widths and etc. Figure 6.3 shows the graphene CPW TL printed on paper substrate in different bending conditions. To facilitate the measurement of the performance, a SMA connector is connected to each port of the TL with conductive epoxy. The length of the TL is \( l = 50 \) mm, the central conductor width \( w = 1.7 \) mm and the gaps between ground and central line \( g = 0.5 \) mm.
Figure 6.3 Coplanar waveguide transmission lines (CPW TLs) and their performance under different bending. (a) Un-bended CPW TL with original length of 50 mm; (b) Bended CPW TL, port to port distance of 40 mm; (c) Bended CPW TL, port to port distance of 30 mm; (d) Bended CPW TL, port to port distance of 20 mm.

With measured S parameters and Equ. (5.3), the phase constant and attenuation (per mm) of the CPW TL can also be calculated and displayed in Figure 6.4. The two parameters, especially the phase constant, are almost linearly increasing with frequency, implying that there is little distortion in the printed graphene CPW TLs. Same as the above parallel lines, the attenuation is relatively high due to the low thickness of the printed graphene line compared with skin depth. Increasing the thickness of printed graphene is an effective way to obtain lower attenuation for both TLs.
Figure 6.4 Measured performance of bended CPW TL. (a) Attenuation and phase constant of the un-bended CPW TL; (b) Transmission coefficient of the CPW TL under different bending conditions (d is the port to port distance).

Moreover, the flexibility of the printed CPW TL is also experimentally verified with performances comparison under different bending cases. Figure 6.3(a)-(d) shows how the CPW TL with original length of 50 mm is bended. The port to port distances of 40 mm, 30 mm and 20 mm were studied respectively. The transmissions under these four bending cases are given in Figure 6.4 (b) correspondingly. It is evident that the bending alters little on the transmission coefficients, highly desirable for flexible applications. Higher
transmission coefficient can be expected under better impedance matching, as well as higher printing thickness.

6.2.2 Resonators

Resonator is one of the fundamental building blocks for RF and microwave signal processing [30]. In this part, the CPW resonators have been designed and printed through the same method as TLs. As seen in Figure 6.5, the printed graphene open-circuited (OR) CPW resonator and its performance are given. The effective length of the resonator is \( l = 30 \) mm, the width of central conductor \( w = 1.7 \) mm, and gap between central conductor and ground \( g = 0.5 \) mm. The resonator was connected with a SMA with conductive epoxy for measurement. The reflection coefficient \((S_{11})\) was measured using Agilent E5071B VNA. A numerical simulation was also carried out in CST Microwave Studio. In simulation, the printed graphene in modelled as ohmic sheet with \( R_S = 3.8 \) \( \Omega \), and the supporting paper has relative dielectric constant \( \varepsilon_r = 3 \) and thickness of 200 \( \mu \)m.

With measured \( S_{11} \), the input impedance of the resonator can be calculated with,

\[
Z_m = Z_0 \frac{1 + S_{11}}{1 - S_{11}}
\]  
(5.4)

where characterized impedance \( Z_0 = 50 \) \( \Omega \).

To facilitate the analysis of resonance, magnitude and phase of \( S_{11} \) are separately displayed. The magnitude of \( S_{11} \), both measured and simulated results are given in Figure 6.5 (a). The measured phase, as well as the calculated input impedance from Equ. (5.4), are presented in Figure 6.5 (b). From Figure 6.5 (a), the measurement and simulation result prove good match. As seen in Figure 6.5 (b), when the frequency infinitely approaches to zero, the phase of \( S_{11} \) is zero, and the magnitude of input impedance (\( \text{mag}(Z_m) \) in Figure 6.5 (a)) reaches almost infinite because the circuit is opened. At around 1.9 GHz, the phase
of $S_{11}$ becomes $180^\circ$, the imaginary part of $Z_{in}$ becomes 0 and the magnitude of $Z_{in}$ reaches minimum, indicating a fundamental open-circuited $\lambda/4$ resonator at this frequency.

![Figure 6.5](image)

**Figure 6.5** Printed graphene open resonator and its performance. (a) Photo of the CPW open-circuited $\lambda/4$ resonator printed on paper substrate and its reflection magnitude (dB); (b) Its input impedance (magnitude and phase) and reflection phase.

Even though the measured results show an effective resonator, the quality factor $Q$ of this open-circuited $\lambda/4$ resonator is only about 3. Again the low $Q$ is caused by ohmic loss originally resulting from small thickness of the printed graphene layer (14% of skin depth...
at 1.9 GHz). Much higher Q values can be obtained in case the thickness of printed graphene increases to 3-5 times of skin depth. Even though the Q value of the resonator is low, the potentials of printed graphene in constructing low cost flexible resonator are unambiguously demonstrated.

To demonstrate the flexibility, a short-circuited λ/4 resonator with effective length \( l \) =60 mm has been fabricated, as the above open-resonator is too wide to bend. As shown in Figure 6.6, the short resonator was bended under different cases. It is un-bended in Figure 6.6(a), and has total length of 65 mm. In Figure 6.6(b)-(c), the distances between the resonator end and port are 30 mm, 20 mm respectively. In Figure 6.6(d), the resonator is not just bended but also twisted, with distance 30 mm.

![Image](image.png)

Figure 6.6 Flexibility of printed graphene short-circuited λ/4 resonator. (a) Un-bended; (b) Bended; (c) Further bended; (d) Bended and twisted.

The corresponding measured reflection coefficients for these four cases are displayed in Figure 6.7. As it can be seen, little changes on reflection coefficients has been brought by the bending, which proves the resonator’s superior flexibility. Moreover, the minor difference on reflection minima intensities of bent and unbent samples is observed. This
can be explained by the minor coupling between segments in bent ones, while unbent device doesn’t have this coupling, same as analyzed in above flexible parallel lines.

Figure 6.7 Measured reflection coefficients under corresponding bending cases in Figure 6.6.

With successful experimental demonstration of printed graphene open/short-circuited resonators, more complex passive components such as filters and couplers can be constructed for RF and microwave signal processing. The work in this section reveals that graphene ink can be a cost-effective alternative to much more expensive competitors, such as silver nanoparticle based ink.

6.3 Flexible Printed Graphene Antennas and On-Body Communications

Antenna is essential element to send and receive RF/microwave signals in communications systems. For applications such as wearable communications systems, both mechanical flexibility and effective radiation of antennas are demanded. For the first time, effective radiation of flexible printed graphene enabled antenna is fabricated and experimentally demonstrated in communication bands, such as mobile cellular and WiFi
spectrums. For this purpose, a typical CPW fed slot antenna was designed [31]. The dimensional parameters of the antenna are included in the following Figure 6.8.

![Figure 6.8 Dimensional parameters of the antenna.](image)

The designed antenna was screen printed using the same way described in above Chapter 5.2. To prove its flexibility and radiation, the printed graphene antenna were bended and pasted on cylinders of different radius for flexibility and conformability tests. The cylinder was made of thin flexible paper boards, so that little influence on antenna performance was posed. Figure 6.9 (a) shows the un-bended antenna and (b), (c) and (d) illustrate the antenna attached on cylinders with radius of 5.0 cm, 3.5 cm and 2.5 cm, respectively.

The reflection coefficients of the antenna under these four different bending cases, shown in above Figure 6.9, were measured using VNA (Agilent E5071B). Also, the gain of the antenna under bending was measured with three-antenna method [32], displayed together with measured $S_{11}$ in Figure 6.10. From the curve (a) in Figure 6.10, corresponding to antenna un-bended in Figure 6.9(a), the reflection coefficient at 1.97 GHz is $-18.7$ dB, and another peak is at 3.26 GHz with $-19.2$ dB, revealing a good impedance matching. From 1.73 GHz to 3.77 GHz, the reflection coefficient is below $-8$ dB, showing
a wideband impedance matching. This frequency range covers the bands for Wi-Fi, Bluetooth, WLAN (wireless local area network) and mobile cellular communications [33]. The maximum realized gain is 0.2 dBi at 1.92 GHz, and from 1.82 GHz to 3.72 GHz the gain is above -1 dBi. The measured realized gain proves an effective radiation from the printed graphene antenna to the free space.

![Printed graphene enabled antenna](image)

Figure 6.9 Printed graphene enabled antenna bended on cylinders with various radius. (a) unbended, (b) bended with \( r = 5.0 \text{ cm} \), (c) bended with \( r = 3.5 \text{ cm} \) and (d) bended with \( r = 2.5 \text{ cm} \).

By comparing reflection coefficients at different bending cases, it can be found that the reflection coefficients are not sensitive to the bending. The wideband impedance matching is almost unchanged. However, the realized antenna gain in Figure 6.10 changes, especially in higher frequency bands. This is because the antenna gain measured from far-field is determined by current distribution on the antenna. When the antenna is bended, the current distribution is altered, resulting in variation on antenna gain performances. Despite that gain at higher frequency band near 3.26 GHz degrades visibly with increasing bending, the gain at lower band from 1.9 GHz to 2.2 GHz has much less variations. This lower frequency band is where wireless communications systems operate. The measured
reflection coefficients and gain data here demonstrate that the radiation can still be efficient at this frequency band even the printed graphene antenna is bended.

Figure 6.10 Measured reflection coefficients and realized gains of the printed graphene enabled antenna bended on cylinders with different radius, as shown in Figure 6.9. Accordingly, curves (a)-(d) correspond to un-bend, bended with radius of 5.0 cm, 3.5 cm and 2.5 cm, respectively.

A further detailed study on radiation patterns at lower band was conducted for antenna under bending cases (a)-(d) in Figure 6.9. The elevation plane radiation patterns at 1.97 GHz were measured using antenna measurement system (Antenna Measurement Studio 5.5, Diamond Engineering). The data were recorded for every 10 degree rotation, as shown in Figure 6.11. From the radiation patterns, it can be seen that patterns in cases (a)-(c) are quite similar despite of minor decrease in maximum gain. Pattern in case (d) is rather different from the other three because much severe bending poses more alteration in current distribution in space.
Figure 6.11 Measured radiation patterns of the printed graphene antenna at 1.97 GHz; Accordingly, curves (a)-(d) correspond to un-bend, bended with radius of 5.0 cm, 3.5 cm and 2.5 cm, respectively.

With the aforementioned verification for the flexibility and efficient radiation of the printed graphene enabled antenna, more investigation to prove its potentials in wireless wearable communications systems by giving a real life scenario shown in Figure 6.12(a). An on-body communications testing setup is presented. On-body communications transmit/receive signal between on-body networks and systems [10,34]. In this setup, the printed graphene antennas were bended and attached on mannequin’s hands to transmit/receive signals. The transmission coefficient between these two antennas is shown in Figure 6.12 (b). When the distance between the two graphene antennas is $d = 0.5 \text{ m}$, the transmission is above -32 dB from 1.67 GHz to 2.87 GHz, which is more than 20 dB higher than -55 dB observed out of band above 3.8 GHz. The measured results verify that RF/microwave signal can be effectively radiated and received by these two graphene antennas conformably attached to hands.
Figure 6.12 Measurement of transmission between two on-body printed graphene enabled wearable antennas. (a) Measurement setting of the wearable antennas on mannequin and (b) Transmission between two antennas attached on hands of mannequin with 0.5 m separation.

6.4 Flexible Printed Graphene UWB Antenna

Ultra-wideband antennas are used in many applications such as high speed data link, precise geolocation, microwave imaging and etc. [35-39]. With above analysis, printed graphene antennas are flexible and lightweight. An UWB antenna with efficient radiation and lightweight characters are always welcome. In this part, the UWB antenna based on printed graphene is studied. As shown in Figure 6.13 (d), a typical CPW-fed triangle slot antenna [40] is printed on paper with graphene conductive ink, and the CPW port is
connected to a SMA using conductive epoxy for measurement purpose. The dimensions of the antenna are: \( a = b = 26 \text{ mm}, \) \( l_1 = 22.65 \text{ mm}, \) \( c = 8.5 \text{ mm}, \) \( d = 3 \text{ mm}, \) \( w = 7 \text{ mm}. \) The CPW line has central electron width 3 mm and line gap 0.35 mm.

Figure 6.13 Printed graphene UWB antenna and its radiation patterns. (a) Radiation pattern at 4.94 GHz; (b) Radiation pattern at 5.97 GHz; (c) Radiation pattern at 7.07 GHz; (d) UWB antenna printed on paper.

The reflection coefficient (S\(_{11}\)) of the antenna was measured using VNA and shown in Figure 6.14 together with measured realized antenna gain which was obtained using three-antenna method. It can be found that the -10 dB bandwidth of the printed antenna is from 3.75 GHz to 12.88 GHz, i.e., 110% fractional bandwidth. This ultra-wide frequency band covers many important commercial applications such as wireless communication, navigation, satellite communications, etc. [41-43]. It can also be seen that a reasonably good gain within the wide band has been obtained. From the gain curve in Figure 6.14, the
maximum gain reaches 1.9 dBi at 10.06 GHz. To further verify its radiation in wideband, the radiation patterns of the printed graphene antenna at 4.94 GHz, 5.97 GHz and 7.07 GHz were measured in H-plane using antenna measurement system (Antenna Measurement Studio 5.5, Diamond Engineering). The radiation patterns are illustrated in Figure 6.13 (a), (b) and (c), respectively. The measurement data were recorded for every 10 degree rotation of DUT (antenna). These radiation patterns demonstrate the effective radiation of the antenna in wide band. It can be seen that the maximum radiation directions at all these frequencies are at 0° direction, i.e., normal direction to the antenna plane. Also, the radiation patterns in the wide band are very similar. Such consistent radiation patterns in wide frequency band are desirable for applications such as UWB detection/imaging, wideband wireless sensing and communications.

To verify the flexibility of the printed antenna, the performances for two bended cases were measured, as shown in Figure 6.15. The reflection coefficient of un-bended case is also given for comparison. The bending was made in two mutually perpendicular directions, as in insertion of Figure 6.15 (a) and (b). It is obvious that the reflection coefficients for all cases are quite similar and the -10 dB bandwidths are nearly the same, demonstrating excellent flexibility. The flexibility is highly expected in many applications, especially wearable electronics [44-46].
6.5 Chapter Summary

In this chapter, printed graphene RF/microwave passive components and antennas have been designed and fabricated by large-scale industrial screen printing technology. The
significant enhancement on printed graphene’s conductivity has made it feasible to construct printed graphene RF/microwave passive components. Together with the flexibility, the concepts of printed graphene flexible microwave components and antennas have been experimentally demonstrated with TLs (CPW and parallel lines), resonators (shorted and open resonators), wireless antennas, UWB antennas, etc. The TLs and resonators have shown the potentials of printed graphene in RF and microwave circuit applications, especially in which low cost and flexibility are required. The antenna has also shown the feasibility of using printed graphene to transmit/receive RF signals wirelessly, and an on-body communication has been demonstrated to verify the concept. The constructed UWB antenna also has proved flexibility and efficient radiation in ultra-wide band.

The screen printed graphene passive components in this chapter are characterized with high conductivity, high flexibility, light weight and low cost, making them ideal candidates for low cost wearable electronics. This work proves it prospective to manufacture RF and microwave passive components in mass production by screen printing in much lower cost to any other known techniques.

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Chapter 7: Experimental Demonstration of Printed Graphene Nano-flakes Flexible Wideband Radar Absorber

7.1 Introduction

Radar absorbers are widely used in civil and military applications such as EMI, EMC, antenna pattern shaping, stealth technology and etc. [1-3]. Premium absorbers are normally required to be of high absorption, wide bandwidth, light weight, low profile and flexibility [3]. Previously, Salisbury screen has been developed for absorption, while the narrow working band and quarter wavelength thickness limited its applications [3-4]. Recently, metamaterials inspired and resistive frequency selective surface (FSS) absorbers have been proposed. Metamaterials inspired absorber was first proposed in 2008. It was characterized with low profile but it has narrow bandwidth [5]. To increase the bandwidth, multi-resonances were introduced [6-10]. However, the bandwidth is further to be enhanced for practical applications as metamaterial absorbers were based on strong resonance. On the
other hand, advantages of combining metamaterials and resistive FSS to obtain wideband and low-profile absorbers were theoretically demonstrated [11-12]. The metamaterial resistive FSS absorber has 0.11λ thickness at lowest frequency and achieved 80% fractional bandwidth from 8 to 19 GHz [12]. Metamaterial structures combining with lump resistors to achieve enhanced absorption bandwidth were also demonstrated [13-15]. For all of these works, the absorbers typically consist of metal patterns photolithographed on PCB board, which means no flexibility is provided.

With the development of the printed electronics, many conductive inks were developed and can be used to replace conventional conductors [16-22]. Printable conductive inks have incomparable advantages over conventional metal sheet in radar absorber applications, considering its lightweight, flexibility and mass-production compatibility [16]. With the development of printed electronics, many options such as silver/copper nanoparticles/nanowires [17-19], conductive polymers [20-21], carbon black and carbon nanotubes [16,22], are possible candidates for constructing printed radar absorbers. Generally highly conductive inks are desirable for printed radar absorbers because non-conductive additives can be added to improve other printing properties such as adhesion, waterproof, flexibility, etc. [16]. Silver nanoparticle inks are advantageous in conductivity [17], and a flexible inkjet-printed metamaterial absorber was fabricated with it [23]. However, high costs of silver nanoparticles and low fabrication efficiency of inkjet printing have prevented their large-scale application [16,23]. Copper nanoparticle inks are much cheaper but very easy to be oxidized, especially during essential high-temperature annealing [19], which limits much on its applications. Conductive polymers are less conductive and its applications are hindered by chemical and thermal instability [20,21]. Carbon black and carbon nanotubes are cost effective and not easy to be oxidized. Their typical sheet resistance is above 50 Ω/Sq [16,22], which is slightly higher than desirable
value for a radar absorber. Graphene, the first isolated two dimensional carbon materials, has many super properties such as extraordinary high electron mobility, conductivity and thermal conductivity, to name a few [24]. With the conductivity and tunability of graphene, tunable microwave and THz absorbers were developed based on CVD graphene [25-28].

However CVD/exfoliated absorbers need clean room process and are low-efficiency and expensive for practically deployable radar applications. Graphene nano-flakes based ink and its printed products are obviously preferable alternative for practical absorber applications, due to its compatibility with mass-production printing procedure, high conductivity, low cost and flexibility [29-34]. In above chapters, graphene’s advantages in printing highly conductive patterns for antennas [31-32], microwave components and EM shielding [32-34], have been demonstrated. The high conductivity and flexibility of printed graphene were fully utilized in those works. In this work, a graphene nano-flakes based conductive ink was purposely developed for radar signal absorption. Designed FSS patterns were printed with this graphene ink on flexible substrate to demonstrate that printed graphene can provide desired absorption and wide operational bandwidth for flexible radar absorption applications.

7.2 Design and Fabrication of Wideband Screen Printed Graphene Based Radar Absorbers

A wideband radar absorber based on modified second-order Saltire cross structure and four H shape coupling additives have been designed, as shown in Figure 7.1. The absorber consists of printed graphene nano-flakes conductive pattern (dark part in Figure 7.1) for impedance matching, flexible silicone substrate (blue part in Figure 7.1), and a metal ground. The whole absorber was modeled and simulated with commercial software CST MWS [35]. In simulation, the printed graphene nano-flakes layer was modeled as resistive
sheet with desired sheet resistance $R_S=20\ \Omega/$Sq. The supporting silicone (Model: Polymax SILONA-Translucent Silicone Sheet 60ShA FDA, thickness 2mm) has dielectric constant of 2.9 and loss tangent 0.1, which were measured with Agilent probe (Model: 85070E Dielectric Probe Kit). The absorber was optimized to have as wideband absorption as possible for printed graphene sheet resistance of 20 $\Omega/$Sq. The geometrical parameters in Figure 7.1 are: $a_1=3.75$ mm, $a_2=2.8$ mm, $a_3=2.1$ mm, $b_1=3.2$ mm, $b_2=2.25$ mm, $d=1.25$ mm, $l_1=5.0$ mm, $l_2=4$ mm, $w_1=0.8$ mm, $w_2=0.75$ mm. The whole unit cell dimension is 15mm×15mm. Due to the symmetry of the structure, its responses to vertically and horizontally polarized incident waves are the same. In this work, the vertical polarization has been chosen for simulations and measurements.

Figure 7.1 Absorber unit structure and parameters

The simulated reflection coefficient ($S_{11}$) and absorption of the absorber with various silicone thickness $h$, can be found in following Figure 7.2. It can be seen that the broadest bandwidth can be achieved for $h=2$ mm. In this case, the optimized absorber has a wideband effective absorption (above 90%) from 8 GHz to 19 GHz, which covers both X band and Ku band. The absolute bandwidth is 11 GHz and relative bandwidth is 81.5%.
Figure 7.2 also gives the $S_{11}$ and absorption under different silicone thickness $h$ (other geometrical and material parameters were kept fixed). It can be found that the absorption band trends to lower frequency band with thicker supporting substrate and vice versa. In this work, the thickness of the optimized absorber is less than $0.1\lambda_0$ at central frequency 13.5 GHz, which is thinner in comparison with similar works [3,10].

![Graph showing $S_{11}$ and absorption under different silicone thickness](image)

**Figure 7.2** Simulated $S_{11}$ and absorption of graphene absorber with different silicone thickness.

To fabricate the printed graphene absorber, both graphene nano-flakes based conductive ink and a patterned stencil were developed. The preparation of the graphene nano-flakes ink is as followed: 3 g expanded graphite (EG) was added into a mixture solution of 15 ml ethylene glycol and 45ml ethanol. Non-ionic polymer-type surfactant was added to improve the dispersion of graphene nano-flakes. After stirring for 20 min, the dispersion was treated with sonication at 820 W with a cooling system for 24 hours. After that, the dispersion was heated on a hot plate with continuous stirring to remove the ethanol, yielding a final viscous ink of about 17% w/w solid in ethylene glycol. The well prepared graphene ink can be found in Figure 7.3(a).
Figure 7.3 Prepared graphene nano-flakes ink and absorber fabrication tools. (a) Graphene ink; (b) Stencil fabricated with laser cutting technology; (c) Absorber fabricating with air blaster and stencil.

To make patterns on silicone, a stencil was fabricated with laser cutting technology, as shown in Figure 7.3(b). The stencil was patterned according to the designed unit array as in Figure 7.1, and the to-be-printed part is left as through (dark part in Figure 7.1). In absorber fabrication, the stencil was placed on silicone sheet. Both stencil and silicone sheet were fixed on a vacuum absorption surface. The ready-made graphene nano-flakes ink was inserted into a commercially available air blaster (Clasohlson Air Tool Kit 30-9875, see Figure 7.3(c)), and it was sputtered on silicone through stencil holes. After the whole sputtering process was finished, the stencil was removed and the as-designed printed patterns were left on the silicone sheet. The well printed sample was then dried in oven for 15 min at 130 °C. The fabricated sample, with size of 300 mm×200 mm can be found in Figure 7.4. As both printed graphene and supporting silicone are flexible, the whole absorber is flexible. As in Figure 7.4(b), the absorber was conformably bended and
attached to a cylinder with radius of 5.9 cm. The mechanical flexibility of radar absorber is quite critical in applications to cover different shaped objects.

![Fabricated graphene absorber sample in planar (a) and bended cases (b).](image)

Figure 7.4 Fabricated graphene absorber sample in planar (a) and bended cases (b).

A further SEM (scanning electron microscope) characterization of the printed graphene nano-flakes sample was carried out, as shown in Figure 7.5. From the SEM, the printed graphene nano-flakes are stacked randomly and the layer is highly porous, similar as our previously screen printed sample [31,32]. The sheet resistance can be engineered by compression process to provide desired value to suit the applications [31,32]. This is a significant engineering approach as additive functional materials (such as binder, dispersant, surfactant, slip agent, coupling agent, etc.) can be added in the ink for better performances (such as adhesion, viscosity, waterproof, printability, etc.), meanwhile still achieving the desired sheet resistance. Namely, much more trading-off space is provided by highly conductive graphene nano-flakes compared with other options such as carbon nanotubes, etc.
Figure 7.5 SEM of top-viewed printed graphene.

7.3 Wideband Absorption and Flexibility Demonstrations of Printed Graphene Absorber

The following Figure 7.6 explains how the printed graphene absorber was measured in planar case. The printed graphene nano-flakes absorber in Figure 7.4(a) was attached to a reflective PCB board (Rogers 3015166) for measurement. As it can be seen, a pair of horn antennas working as transmitter/receiver, were connected to VNA (Vector Network Analyzer, Fieldfox N9918A, Keysight) to measure the reflection from the sample. Another PCB board with size of 300 mm×230 mm was inserted between two antennas for better isolation. The two antennas were slightly angled as seen to measure the reflection from the sample. The sample was placed vertically and 0.4 m away from antenna front face. As the horn antennas here have limited bandwidth, two pairs of horn antennas were utilized for lower (antenna pair: Standard Gain Horns QSH18, Q-par Angus Ltd) and higher band measurements lower (antenna pair: Stock No. 5985-99-914-6933, Marconi instruments Ltd).
With the aforementioned measurement setup in Figure 7.6, the measurements for planar case in both lower band (6-14 GHz) and higher band (13-20 GHz) were conducted, to demonstrate the RCS reduction for the printed graphene wideband absorber. As shown in Figure 7.7, the lower band 6-14 GHz reflections for 4 cases were measured to prove the mechanism of the absorber. Due to the cutoff effect of the waveguide, there is an obvious cutoff in the region of 7-8 GHz. Firstly the case without sample was measured and indicated as free space in Figure 7.7. It can be seen that the transmission between two antennas is lower than -50 dB. This transmission is mainly from the direct coupling between two nearby antennas, as well as minor reflection of the anechoic chamber walls. This low level transmission demonstrates that a good isolation was provided by the inserted PCB between two antennas. In the next step, the copper PCB board and the same
board attached with silicone (same used in absorber construction) were measured in the same position (0.4 m away, facing the antennas). As shown in the Figure 7.7, these two samples have almost the same reflections, revealing that the silicone itself can hardly act as absorber. The printed graphene nano-flakes absorber was then placed at same position and measured. By comparing the copper+silicone sample with the absorber (copper+silicone+graphene), It can be found that the reflection of the absorber is much lower than that of metal reflective samples, revealing a satisfactory absorption from the absorber. From the difference of the reflections, it can be concluded that it is the printed graphene nano-flakes pattern that has absorbed the electromagnetic wave, which leads to high RCS reduction.

![Figure 7.7 Measured reflection comparison of different samples in lower band.](image)

The same measuring process for planar absorber has been conducted in the higher frequency band from 13 GHz to 20 GHz, and the results are shown in Figure 7.8. As seen from Figure 7.8, when the absorber was placed, an obvious RCS reduction was observed in
the whole band. Similar conclusions can be drawn as those from Figure 7.7 of lower band measurements.

![Graph showing measured reflection comparison of different samples in higher band.](image)

Figure 7.8 Measured reflection comparison of different samples in higher band.

For a better view on the wideband property of the absorber, these two bands results were combined and shown in Figure 7.9. As it can be seen, the effective absorption bandwidth is from 10.4 GHz to 19.7 GHz, indicating an absolute bandwidth of 9.3 GHz, and 61.8% relative bandwidth. The measured results have been also compared with the simulated ones in Figure 7.9. As it can be seen, the simulation results show wider band absorption at lower band. This discrepancy is believed to be caused from the sheet resistance difference of fabricated sample and simulated one. The simulated sample has sheet resistance of 20 $\Omega$/Sq, whereas the fabricated one is lack of uniformity. The Figure 7.10 gives the sheet resistance among the central area of the absorber measured with four point probe system (Jandel Engineering Limited, RM3000). From measurements, the sheet resistance of the absorber is generally close to the expected 20 $\Omega$/Sq. However, it varies in
different sections due to the inconsistency of thickness in the manually sputtered graphene nano-flakes layer.

![Graphene Absorber Performance](image1)

Figure 7.9 Measured $S_{11}$ and absorption of graphene absorber in wideband, and comparison with simulated absorption.

![Sheet Resistance](image2)

Figure 7.10 Measured sheet resistance of the printed graphene nano-flakes in central area.

To further examine the cause of this discrepancy, simulations on the influence of sheet resistance variety of graphene nano-flakes layers were carried out. As it can be seen in
Figure 7.11, when the sheet resistance of graphene nano-flakes layer varies from 20 Ω/Sq to 30 Ω/Sq, the lower band absorption reduces. As the printed graphene pattern was designed for Rs=20 Ω/Sq, the larger the difference on sheet resistance, the more deterioration on lower band performance will be. From this analysis, it can be concluded that the difference on simulation and measured results was mainly caused by the non-uniformity of sheet resistance distribution of the printed graphene patterns.

![Figure 7.11 S11 and absorption of simulated absorber with various sheet resistances.](image)

For radar absorbers, it would be highly desirable that the absorbers can be mechanically flexible so to easily cover different shaped objects. For this purpose, flexibility of the printed graphene nano-flakes radar absorber has been investigated. The measurement setup for the bended case is explained in Figure 7.12. A Similar setup as in Figure 7.6 was made, while the absorber was bended and attached to a metal cylinder with radius of 5.9 cm. The distance of the cylinder (front point) to antenna front face is still 0.4 m. The same two bands were measured for the bended absorber.

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Figure 7.12 Measurement setup in anechoic chamber for bended graphene absorber, attached to metal cylinder.

The reflection coefficients of the metal cylinder as well as the metal cylinder covered with printed graphene nano-flakes absorber were measured and shown in following Figure 7.13 and Figure 7.14. The lower band and higher band reflections with and without absorber can be found in Figure 7.13 and Figure 7.14, respectively. As it can be seen that the absorber coverage brings much degrade on reflection, which means much reduction of RCS.
Figure 7.13 Reflection comparison of metal cylinder with/without absorber coverage in lower band.

Figure 7.14 Reflection comparison of metal cylinder with/without absorber coverage in higher band.
These two bands results again are combined and shown in Figure 7.15. It can be seen that the effective absorption bandwidth is from 9.8 GHz to 17 GHz and a relative bandwidth of 58.2% is obtained. Even though the absorption bandwidth reduces slightly by 3.6% compared with planar case, the wideband absorption is still maintained. From this comparison, it can be concluded that the printed graphene nano-flakes flexible absorber can be conformably adapted to objects and provide effective RCS reduction.

![Figure 7.15 Measured S11 and absorption of bended graphene absorber in 8 GHz to 20 GHz.](image)

7.4 Chapter Summary

To sum up, in this chapter graphene nano-flakes ink has been applied to microwave absorber for RCS reduction applications. A wideband absorber is designed with sandwich structure consisting patterned graphene nano-flakes layer, supporting silicone and backed metal. The absorber has been fabricated with stencil printing and the graphene nano-flakes are sputtered on silicone layer to form patterns through stencil, with help of air blaster. The absorber is experimentally demonstrated to provide effective absorption from 10.4 GHz to
19.7 GHz, a relative bandwidth of 61.8%, with thickness only around 2 mm. The graphene nano-flakes based absorber is also mechanically flexible, and its performances when bended to fit metal cylinder is measured to characterize its conformability. The measurement results have shown that only 3.6% reduction of the effective absorption bandwidth is brought by the bending. The maintained wideband absorption reveals the potential applications of the graphene absorber in providing RCS reductions for various objects. In conclusion, this work has demonstrated unambiguously that graphene can be used for wideband microwave absorption, and meanwhile providing flexibility.

Reference


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Chapter 8: Graphene Oxide Enabled Wirelessly Addressable Humidity Sensing Based on Printed Graphene RFID

8.1 Introduction

Graphene oxide (GO) is a chemical derivative of graphene functionalized with hydroxyl and epoxy groups. GO is a hydrophilic material and is capable to absorb a significant amount of water. Its water uptake depends strongly on the humidity of the environment and was previously studied by X-ray and neutron diffraction and in-situ electron microscopy. It was established that oxygen functional groups in GO drive intercalation of water molecules between individual GO sheets which results in an increase in the inter-layer spacing in GO thin films [1-5]. The presence of inter-layer water in GO films can be crucial for a number of its properties, such as electrical conductivity [6], molecular permeation [7,8], mechanical [9] and dielectric properties [10] (though the latter were studied only in the case of monolayer GO, where the water uptake is limited). Thus, at low humidity, GO films shows poor electrical conductivity and can be considered as an
insulator while at higher humidity the conductivity of GO films increases due to contribution of the ionic conductivity of the intercalated water [6].

Of particular interest would be the dielectric properties of multi-layered GO as a function of water uptake, considering the low intrinsic relative permittivity ($\varepsilon_r$) of GO and the high $\varepsilon_r$ for water at GHz frequencies. Thus, the permittivity of the GO-water composite material can be changed in a wide range depending on the water content. Moreover, as the GO water uptake depends on the humidity of the environment, such changes in $\varepsilon_r$ can be used for humidity monitoring. In this work both the real and imaginary parts of the permittivity of GO-water composite in GHz range are experimentally determined. It is found that in particular the imaginary part ($\varepsilon''$) changes by almost 200% depending on the water uptake, which is explained by a strong adsorption of RF waves by water. This property of GO-water composite is used to construct battery-less RFID humidity sensors for internet of things applications. Such sensors could be manufactured by printing technology.

### 8.2 GO Electric Property Characterization

GO is a nonmagnetic material [11], its electrical property can be completely characterized by its relative permittivity, $\varepsilon_r = \varepsilon' - i\varepsilon''$. There are several classical methods to measure permittivity in the microwave band, including transmission line (TL) method, free space method, resonator cavity and etc. [12]. However, all these methods do not suit permittivity measurement for ultrathin, fragile and small-sized GO under different humidity environment. The facilities of these methods are too large so that the humidity precisely controlled environment is hard to be prepared to contain all measurement setup. For coaxial probe method, TL method, resonant cavity and parallel plate methods, the fragile GO is easy to be harmed in contacts during measurements. Besides, those methods
prevent the sufficient exposure of GO to surrounding vapour. The non-contacting free space method requires large-sized GO sheet, which is very difficult to prepare.

![Resonator to characterize graphene oxide property.](image)

Figure 8.1 Resonator to characterize graphene oxide property. (a) Microstrip resonator without GO coating; (b) Microstrip resonator with GO coating. The GO layer was deposited on the capacitor area of the resonator, and the thickness of GO is 30 µm.

To measure the permittivity of small-sized ultrathin GO layer under various humidity, a resonator circuit as in the Figure 8.1(a) has been designed. To measure the GO permittivity with higher sensitivity, GO layer with size of 15 mm × 8 mm × 30 µm was coated on the capacitor area of the resonator, as in Figure 8.1(b). The PCB board to construct the microstrip resonator is chosen to have the low dielectric constant of 3 (Rogers R03003), so that EM field is closer to GO section. More interaction between EM field and GO layer brings higher sensitivity of the resonator responding to humidity changes. This is because higher dielectric constant makes the EM field constrained more within the dielectric area, while the field distributes more to space near the interface when PCB board dielectric constant is lower.
In this work, the GO is prepared as follows: A modified Hummers method was employed in order to prepare graphene oxide. Briefly, 4 grams of graphite was mixed with 2 grams of NaNO₃ and 92 mL of H₂SO₄. KMNO₄ was subsequently added in incremental steps in order to achieve a homogeneous solution. The temperature of the reaction was monitored and kept near 100 °C. The mixture was then diluted by 500 mL of deionized water and 3% H₂O₂. The resulting solution was washed by repeated centrifugation until the pH value of the solution was around 7. The GO was then diluted to the required concentration.

The above prepared GO was screen printed on the top of the resonator as in Figure 8.1(b). As the GO layer is in the capacitor area, when the electrical property of GO such as its permittivity changes with humidity, it alters the loading of the resonator and results in resonance frequency shift. The permittivity of GO under different humidity is expected to be extracted from the shift. Simulations were run in CST to investigate how the permittivity of coated thin GO layer may change the resonator performance. In simulations, GO layer was mimicked by coated thin dielectric layer, which has exactly the same size, thickness and location as that shown in Figure 8.1(b). If the simulated performance is the same with measured, it is persuadable to conclude that the GO layer has the same permittivity with the dielectric layer in simulation. Obviously, this assumption is based on the consistence between the simulations and measurements. To verify this consistence, the resonator in Figure 8.1(a) was taken as example. As in the following Figure 8.2, the simulated and measured transmissions of the resonator are given and compared.
Figure 8.2 The simulated and measured transmission coefficients of the resonator.

From the Figure 8.2, it can be seen that the simulation agrees well with the measurement results, proving that the simulation in CST can be a reference for measured results. Based on this verification, 5 more different sets of simulations were conducted to extract the relative permittivity \( (\varepsilon_r = \varepsilon' - i\varepsilon'') \) of GO at around 1GHz. As shown in Figure 8.3, the transmission coefficients of the dielectric layer coated resonator are given under 5 different relative permittivity \( (\varepsilon_r = \varepsilon' - i\varepsilon'') \). Each color set of the curves in the figure contains the same real part \( (\varepsilon') \) but various imaginary part \( (\varepsilon'') \) of the relative permittivity. It can be observed that for the same \( \varepsilon' \), the resonance frequency does not change much with \( \varepsilon'' \). This is because \( \varepsilon'' \), which is related to material loss tangent \( (\tan\delta = \varepsilon''/\varepsilon') \), mainly affects the Q factor of the resonator. The simulations reveal that the changes of relative permittivity pose obvious alteration on the resonator’s transmission performance. GO’s permittivity can be extracted by comparing the experimental measurements and full electromagnetic wave simulations.
Figure 8.3 Simulated transmission coefficients ($S_{21}$) of the resonator covered by dielectric layer of various relative permittivity ($\varepsilon'$ and $\varepsilon''$).

Figure 8.4 The relationship between dielectric constant and resonance frequency from simulations.
To clearly display how the permittivity, especially its real part $\varepsilon'$ (dielectric constant), poses an effect on the performance of resonator, the relationship between $\varepsilon'$ and resonance frequency is given in following Figure 8.4. As seen, the resonance frequency almost linearly decreases with increase of dielectric constant. This linearity makes it convenient to roughly estimate the dielectric constant of GO coating from measurements.

To study how the Go coating changes its electrical property under various humidity values and extract the GO permittivity in these cases, a sealed measurement box was designed and shown in Figure 8.5. Two resonators, same as shown in Figure 8.1, one with GO coating and the other one without, are placed and connected in a sealed plastic box (the top cover was removed in Figure 8.5(a) for better view). The GO layer was deposited on the capacitor area ($15 \text{ mm} \times 8 \text{ mm}$) of the resonator. The thickness of the GO layer is about 30 $\mu$m. To obtain stable, uniform and accurate humidity in the box, salt solution is placed to obtain the required humidity. A digital humidity meter (Fisher Scientific 116617D) is placed in the box for monitoring. Rubber-tight SMA connectors (RS Stock No.716-4798) are used to connect inside/outside microwave cables, making the box well sealed. The out-extended cables are connected to VNA (Agilent E5071B) for scattering parameter (S-parameter) measurements. Clearly, this method is much advantageous compared with conventional methods. For one, the GO layer is directly exposed in ambient vapour to make sure accurate and stable measurement of GO property under different humidity. For two, the sealed box is small and the humidity can be easily controlled and changed by placing different saturated salt solutions. Moreover, the whole measurement setup suits well for the fragile and small-sized GO layer, and it is quite cost-effective.
Figure 8.5 Sealed box setup for GO permittivity measurement (the top cover of the box has been removed for a better view).

The working principle of the measurement in above Figure 8.5 is briefly explained in the following Figure 8.6(a) with equivalent circuit model. As seen, the changes on GO poses tunable resistor and capacitor in the equivalent resonance circuit, which bringing frequency shift.

In the measurement, five salt solutions were used, which provided RH from 11% to 98%. The fives salts are LiCl (RH=11%), K₂CO₃ (RH=43%), Mg(NO₃)₂ (RH=55%), NaCl (RH=75%), and K₂SO₄ (RH=98%). To get accurate and stable RH as well as sufficient exposure of GO to vapour, the transmission coefficients of the two resonators are measured after the indication of humidity meter keeps unchanged for 24 hours.
Figure 8.6 Working principle explained with equivalent circuit model, and measured and simulated transmission coefficients ($S_{21}$) of the samples with/without GO coating. (a) Working principle explained with equivalent circuit model; (b) Measured and simulated transmission coefficients ($S_{21}$) of the samples with/without GO coating.

The measured transmission coefficients for the samples with and without GO coating are displayed in Figure 8.6 (b), together with the simulated results for permittivity extraction. From the measured results, it becomes clear that the sample with GO coating
has responded to the humidity changes, whereas the sample without GO coating hasn’t. The different responses of these two resonators can only be caused by the change of GO properties due to humidity. For the resonator with GO coating, it can be observed that the resonance frequency shifts to lower frequency and its fractional bandwidth increases as the RH rises. This reveals that not only the real part of the relative permittivity ($\varepsilon'$) of GO increases but its imaginary part ($\varepsilon''$) also rises as GO absorbs more vapour.

The simulated and measured resonance frequency as function of the RH is illustrated in Figure 8.7. Furthermore, by comparing simulated and measured results under different humidity, the relationship between the relative permittivity ($\varepsilon_r = \varepsilon' - i\varepsilon''$) of the GO (as well as loss tangent ($\tan\delta = \varepsilon''/\varepsilon'$)) and the RH can be obtained as shown in Figure 8.8. It can be seen that $\varepsilon'$ and $\varepsilon''$ of the GO change from about 11 to 17.6 and 2.3 to 6.4, respectively, as RH varies from 11% to 98%. Correspondingly, loss tangent $\tan\delta$ increases from 0.21 to 0.37.

![Figure 8.7 Resonance frequency as function of RH.](image.png)
Figure 8.8 Resonance frequency as function of RH and (b) Relative permittivity ($\varepsilon_r = \varepsilon' - i\varepsilon''$) and loss tangent ($\tan\delta = \varepsilon''/\varepsilon'$) of the GO under various RH.

### 8.3 Printed Graphene and GO Based Wireless Sensor

Passive sensing can find its ubiquitous applications for today’s life [13,14]. Sensing with ID provides not only the information about the parameters a sensor intends to sense but also the ID of the sensor, enabling us to monitor each individual object. From the above analysis, GO is sensitive to the change of humidity. As seen from Figure 8.8, GO’s real part of permittivity changes at rate of more than 0.5 per 10% change of RH. In this part, this property is combined with printed graphene RFID to make wireless humidity sensing system. This sensing system consists of a GO coated RFID tag as sensor, and a RFID reading system for signal processing.

The constitution and operating principle of the designed wireless humidity sensing system are shown in Figure 8.9. The photo of the GO coated RFID sensing tag is shown in the right top. For the purpose of coating the RFID tags with graphene oxide, ten grams per liter viscous GO solution was used. This allowed direct screen printing of the GO on the
paper tag, which was left to dry overnight in a fume hood under continuous air flow. The printed graphene RFID tag is made with screen printing and rolling compression as in Ref [15]. The lateral SEM view of the sample is shown in Figure 8.10. As seen, the three-layer structure is obvious and clear. GO coating, screen printed and compressed graphene layer, and supporting paper are stacked in sequence from above to bottom.

Figure 8.9 Operating principle of the GO based RFID sensor system. The GO coating thickness of the top right sensing tag is 15 µm.

The basic foundation of the sensing is that the input impedance of the GO coated RFID is tunable under different humidity. As explained in the Figure 8.9, when the GO coated on the printed graphene RFID antenna absorbs vapour, its permittivity changes, which alters the antenna impedance. The backscattering signal phase changes accordingly and can be detected by the reader. When the reader transmits an electromagnetic wave signal (also called ‘forward electromagnetic wave signal’) to the RFID antenna, the antenna draws energy from this forward signal and activates the RFID chip on the antenna. The backscattered signal is both amplitude and phase modulated by the RFID chip through varying the chip’s input impedance. Modulation occurs as the RFID chip rapidly switches
between two discrete impedance states [16-17], as shown in the equivalent circuit in bottom right corner of Figure 8.9.

In RFID antenna design, antenna impedance is typically conjugate matched to the higher impedance state of the chip in order to maximize the collected power. The equivalent Thevenin open source voltage $V_a$ on the antenna can be given as [18],

$$V_a = \sqrt{8P_{Ant}Re(Z_a)}$$  \hspace{1cm} (1)

where $P_{Ant}$ is the power available at the antenna port, $Z_a$ is the antenna impedance. The switching between the two input impedance states $Z_{C1}$ and $Z_{C2}$ generates two different currents at the antenna port, which can be calculated as [18]:

$$I_1 = V_a \left( \frac{1}{Z_a + Z_{C1}} \right)$$  \hspace{1cm} (2)

$$I_2 = V_a \left( \frac{1}{Z_a + Z_{C2}} \right)$$  \hspace{1cm} (3)

When the humidity changes, the electrical property (namely permittivity) of the GO layer coated on RFID antenna changes. This change alters the antenna impedance. As $Z_a$ changes, so do $I_1$ and $I_2$, causing the backscattered signal phase varies accordingly. The backscattered signal phase can be detected by the reader. In this work, the backscattered signal phase was measured using Voyantic Tagformance under different humidity and depicted in Figure 8.4 [19].

To have a better view of the printed graphene RFID and coated graphene oxide, the lateral SEM view of the GO sample is shown in Figure 8.10. As it can be seen, the three-layer structure is obvious and clear - GO layer, printed and compressed graphene layer and paper substrate, stacked in sequence from top to bottom.
Figure 8.10 Lateral SEM view of GO coated printed graphene RFID antenna on paper. (a) Large view; (b) Zoom in view, layers from top to bottom are GO, printed graphene and paper in sequence.

The following Figure 8.11 presents the experimental setup for the whole wireless sensing system based on GO coated RFID. As seen, the system consists of signal processing module, frequency scanning module and GO coated RFID tag in a sealed box. The saturated salt solution was placed in the sealed box to adjust humidity. The sealed box containing sensing tag was placed above the RFID reader antenna. 5 sets of salt solution providing humidity from 11% to 98% were used to feature the humidity system. To get stable and accurate results, the data under different humidity was harvested after the backscattering signal in processing system keeps unchanged for 24 hours. The phase of the backscattering signal was obtained with professional RFID processing system Voyantic Tagformance.
Figure 8.11 Experimental setup for the wireless RFID GO humidity sensing system.

The backscattering signal characterization was gathered and shown in following Figure 8.12. It can be seen that the humidity has clear effects on the backscattered signal phase at typical RFID frequency spectrum from 880 MHz to 920 MHz, which experimentally proves that the backscattered signal contains humidity information. Together with the ID information of the sensing tag, a wireless printed graphene enabled RFID GO humidity sensing system is presented. Enlarged phase information is given in Figure 8.12(b) and (c) at 910 MHz and 900 MHz, respectively, to illustrate the sensitivity of the GO sensor for detecting humidity changes. As it can be seen from Figure 8.12(b) and (C), the backscattered 910 MHz and 900 MHz signal phases increases by 44.6° and 39.5°, respectively, as RH rises from 11% to 98%. For 910 MHz signal, average phase change of 0.5° every 1% RH can be observed, unambiguously demonstrating the effectiveness of wireless printed graphene enabled RFID GO humidity detection.
Figure 8.12 Measured phase of backscattered signal for sensing. (a) Measured backscattered signal phases with various humidity as function of frequency, (b) enlarged backscattered signal phases at 910 MHz as function of humidity and (c) enlarged backscattered signal phase at 900 MHz as function of humidity.

8.4 Chapter Summary

The measurement results have clearly revealed that the GO dielectric properties, namely permittivity and loss tangent, changes with ambient humidity. The change of these parameters can be detected both wire and wirelessly. These parameters have been quantitatively estimated through experiments and simulations on resonators with printed GO layer on top. Besides, the printed GO graphene RFID tag experiences different backscattered signal phase shift when the humidity changes. This observation is very encouraging as it means that the humidity can be detected wirelessly through GO sensing. A RFID combined with its sensor-enabled tags having ambient environment sensing ability, as well as providing its own identification wirelessly, can find its wide applications in our daily life, such as IoTs, big data and digital economy. This work has proven much potential in simplifying the information gathering and collection infrastructures.
Reference

Chapter 9: The Conclusions and Future Plan

This work develops the applications of graphene and graphene oxide (GO) on electromagnetic ranges such as radio frequency, microwave frequency and THz bands, and specifically 2D materials based antennas, absorbers, sensors and etc.

In this thesis, the basic properties and preparations of graphene and graphene oxide are introduced. The electromagnetic applications of monolayer graphene initialized by its tunability, conductive nanomaterials, are reviewed. Some basic concepts and theory involved in this work are also included. The works on theoretical study on graphene based THz absorbers, microwave wideband absorbers and reconfigurable antennas are studied with analysis and simulations. The EM applications study of printed graphene, including designs, experimental demonstrations and analysis are conducted in printed graphene based RFID, wireless communication, flexible fundamental components, and radar absorbers. A further wireless sensor has been developed with printed graphene RFID and graphene oxide.

With the tunability of graphene’s conductivity, tunable terahertz (THz) absorbers, microwave absorbers, and reconfigurable antennas are designed to adapt flexible
applications. An effective method to model, analyze and design graphene metasurface based THz absorbers using equivalent circuit model approach is proposed. Broadband and tunable absorbers constructed with graphene metasurface have been designed based on the formulas derived from this approach and verified by full-wave electromagnetic simulation. By properly constructing the graphene metasurface, broadband absorption over 70% fraction bandwidth has been achieved, showing that graphene can provide a wideband absorption in low THz spectrum. Furthermore, tunability of the graphene metasurface has also been investigated. It is demonstrated that the absorption peak frequencies can be tuned while maintaining the peak absorption unchanged, which is highly desirable for THz sensing applications.

For graphene based tunable microwave absorber, a new design consists of Hilbert curve metal strip array and chemical vapor deposition (CVD) graphene sheet is presented. The graphene based absorbing screen is not only tunable when the chemical potential of the graphene changes, but also has broadband effective absorption. The absorption bandwidth is from 8.9 GHz to 18.1 GHz, i.e., relative bandwidth of more than 68%, at chemical potential of 0 eV, which is significantly wider than that if the graphene sheet had not been employed. As the chemical potential varies from 0 to 0.4 eV, the central frequency of the absorber can be tuned from 13.5 GHz to 19.0 GHz. The working principle of this absorbing screen is studied in details. This work extends applications of graphene into tunable microwave RCS reduction applications.

The tunability of graphene is fully utilized to design frequency reconfigurable, radiation pattern reconfigurable and beam-scanning antennas. To take advantages of graphene’s tunability, while overcome its high loss and gain high radiation efficiency, a hybrid method combining traditional antennas and graphene based reflectors, is proposed. In the frequency reconfigurable design, a design of tunable coplanar waveguide (CPW)
monopole antenna backgounded with graphene sheet is presented. Another concept of graphene based tunable FSS enabled reconfigurable antenna is also proved with simulations. In radiation pattern reconfigurable antenna, a graphene enabled switchable array is designed to change the radiation pattern is space, while keeping the working frequency unchanged. Another reconfigurable THz antenna is proposed to have the beam-scanning angle of up to 26° with graphene strip arrays. In all those reconfigurable designs, the introduction of graphene has brought flexibility on antenna performances, and the hybrid designing method helps to maintain the high radiation efficiency. When one parameter of the antenna is tuned (for example frequency), the other parameters (for instance radiation pattern) is fixed, highly desirable in practical applications.

Except for the monolayer graphene applications, this thesis also studies the electromagnetic applications of printed graphene in theory and experimental demonstrations. A method to make low cost highly conductive printed graphene is studied, and the effective radio frequency radiation is demonstrated for the first time. Based on the highly conductive printed graphene, printed RFID antennas have been designed and proved to have long distance reading range fitting well for commercial applications. Besides, with the unique breakable property of printed graphene, a novel-concept of designing anti-tampering RFID is proposed. The designing idea of the anti-tampering tag is to control the matching factor of the tag. Before break, the tag is un-readable as the impedance matching between IC and antenna is designed to be very low. In contrast, when the specific part of the tag is broken, the matching turns to the highest, and the tag has a long reading range. Based on this concept, anti-tapering tags are designed and experimentally characterized to verify the effectiveness. Moreover, the highly conductive printed graphene is also proved to provide above 30 dB shielding effectiveness in C band, quite promising in EMI shielding applications.
More applications of the printed graphene have been explored in constructing flexible microwave components such as TLs, resonators and antennas. From the measurements of the TLs and resonators, the graphene’s flexibility enables unchanged performances under bending. Besides, the printed graphene fabricated antennas is adopted to demonstrate its potentials on wearable wireless communications. More work on wideband flexible antenna has also been given to prove its possibilities in ultra-wideband (UWB) applications.

To adopt radar absorber application, another graphene nano-flakes conductive ink is developed. Based on this ink, a flexible wideband radar absorber have designed, fabricated and experimentally measured. The absorber covers both X band (8-12 GHz) Ku band (12-18 GHz) and is printed on flexible substrate using graphene nano-flakes conductive ink through stencil printing method. The measured results show that an effective absorption (above 90%) bandwidth spans from 10.4 GHz to 19.7 GHz, namely a 62% fraction bandwidth, with only 2 mm absorber thickness. The flexibility of the printed graphene nano-flakes enables the absorber conformably bending and attaching to a metal cylinder. The radar cross section of the cylinder with and without absorber attachment has been compared and excellent absorption has been obtained. Only 3.6% bandwidth reduction has been observed comparing to that of un-bended absorber. This work has demonstrated unambiguously that printed graphene can provide flexible and conformable wideband radar absorption, which extends the graphene’s application to practical RCS reductions.

This work also extends applications of graphene and graphene oxide to wireless sensing. First, electrical permittivity of GO, both its real and imaginary parts, have been measured under various humidity conditions. It is demonstrated that the electrical permittivity increases strongly with increasing humidity due to water uptake. This property is used to create RFID humidity sensor by coating printed graphene antenna with GO layer. The resonance frequency as well as the reflection phase of such antenna become sensitive
to the surrounding humidity due to water uptake by GO. This property can be used for wireless monitoring of the local humidity and paves the way for low cost efficient sensors for internet of things (IOT) applications.

In summary, this thesis has extended 2D materials’ applications in electromagnetic areas with study on tunable absorbers and antennas, as well as pioneering works on printed graphene based RFID, anti-tampering RFID, EMI shielding, flexible microwave components, printed flexible radar absorbers, and wireless sensors, etc. These applications prove that the potentials of 2D materials are much prospective in electromagnetic areas, and much more can be expected. The possible research in next step is listed as followed.

1. The fabrication and experimental verification of the absorbers and antennas designed in Chapter 2-4 can be the possible next step work. Especially the tunable THz absorbers with peak absorption when tuning frequency, it is very useful and promising in THz detection and sensing.

2. The printed graphene RFID has been proved to reach commercial application level performances. More study on solving practical problems in graphene RFID applications can be conducted, such as how to take advantage of flexibility of printed graphene on solving performance degrade problem when tag is near metal, and how to direct print the tags on objects.

3. The printed graphene based anti-tampering RFID tags has been demonstrated to be effective. To push forward its commercial applications, the difference before and after break is required to be bigger, so that the false alarm probability can be reduced.

4. The printed graphene has shown excellent advantages on making wideband, lightweight and flexible radar absorber. The research on the ultra-wideband
absorber, for example covering 1-18 GHz, is the priority for next step. Also, the multilayer printed graphene based absorbers are the possible topic.

5. Considering the limited absorption band and thickness issue in printed graphene radar absorbers, it is a possible solution to try hybrid materials of graphene and magnetic components, such as zinc oxide, ferroferric oxide, etc., for wider band absorption.

6. In the fabrication of printed graphene based absorbers, the uniformity of the printing is still required to be improved. Research on better graphene nano-flakes based inks is needed. Another method to improve the quality is combining 3D printing technology to fabricate the absorbers. New graphene ink compatible with 3D printer is demanded.

7. More study on GO based sensor can be done to improve the accuracy, and reduce the cost and complexity of the system for exploring possible commercial applications.
Publication

Journal paper list:


8. Ting Leng, **Xianjun Huang**, KuoHsin Chang, JiaCing Chen, Mahmoud A. Abdalla and Zhirun Hu, Graphene Nano-flakes Printed Flexible Meandere Line Dipole Antenna on Paper Substrate for Low Cost RFID and Sensing Applications, *IEEE Antenna and propagation letters*.


**Journal paper in preparation:**

1. **Xianjun Huang**, Ting Leng, Thanasis Georgiou, Jijo Abraham, Rahul Raveendran Nair, Konstantin Novoselov, Zhirun Hu. Graphene Oxide Dielectric Properties at

2. **Xianjun Huang**, etc. Printed Graphene for Low Cost Commercial RFID Applications. (*Preparing*).

**Conference paper list:**


2. **Xianjun Huang**, Ting Leng, Jia Cing Chen, Kuo Hsin Chang, Zhirun Hu, ‘Shielding Effectiveness of Screen Printed Graphene Laminate at C Band’, EuCAP’2016 in Davos, Switzerland.


8. **Xianjun Huang**, Abdullah Alburaikan, Ting Leng, Zhirun Hu, Jijun Huang, Yujian Qin, Peiguo Liu, Graphene Metamaterials Array Based Reconfigurable Antenna, ISAP 2016, Japan (accepted).


**Patent:**

1. Printed graphene oxide RFID sensors, Kostya S Novoselov, Zhirun Hu, **Xianjun Huang**. UMIP Ref.20150153 (Pending).

**Main media story:**

   
   [https://www.sciencedaily.com/releases/2015/05/150515174955.htm](https://www.sciencedaily.com/releases/2015/05/150515174955.htm).


