Broadband THz Modulators Based on Multilayer Graphene

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ABSTRACT

THz modulators are key components for the improvement of THz technology. However, it has been proved to be challenging to fabricate simple devices to obtain high modulation depth across a broad bandwidth. In this study, four different CVD grown multilayer graphene (MLG) modulators based on MLG/ionic liquid/gold sandwich structures have been investigated. Flexible substrates (PVC and PE) were chosen as host materials, and devices were fabricated at three different thicknesses: 30, 60, and 100 layers. The resultant MLG devices can be operated at preferentially low voltages ranging from 0 to 3.5 V and provided nearly complete modulation between 0.2 THz and 1.5 THz at ca. 3.5 V with low insertion losses. Even at such low gate voltages the devices have been doped significantly inducing an enormous improvement in their sheet conductivities ranging between 7 to 11 times depending on the thickness of the device. In addition, sheet conductivity has been improved more than 3 times with change in the layer number from 30 to 100. With the demonstration of promising device performances, the proposed modulators can be potential candidates for applications in THz and related optoelectronic technologies.

Since its discovery in 2004, graphene has attracted intense attention in many fundamental areas due to its remarkable electronic and mechanical properties.¹ With its gapless nature and symmetrical band structure, graphene has extraordinary physical properties such as room-temperature quantum Hall effect and micrometer long mean free path.²,³ Its massless carriers result in an extremely high carrier mobility exceeding 200000 cm²/V·s⁴ and graphene becomes a unique material in applications of high speed electronics. Single layer graphene’s fairly low (ca. %2.3) absorption of visible and IR radiation⁵ makes it utilizable in the application of transparent electrodes, photodetectors, and broadband infrared electro-optical modulators.⁶ Exploration of graphene carrier dynamics has shown that electronic structure of graphene is more sensitive to the THz region of the electromagnetic spectrum rather than IR and optical range.⁷ THz beams allow characterization of carrier dynamics near the Fermi level.⁸,⁹ Therefore, graphene is recognized as a potentially active material for photosensitive THz devices in the application of active filters, switches and modulators. These optical devices are urgently needed by THz technology in order to advance a diverse range of applications such as nondestructive imaging,¹⁰,¹¹ spectroscopy,¹² biomedical diagnosis,¹³ ultrahigh wireless communication,¹⁴ and security.¹⁵

Conventional THz modulators that are based on semiconductor materials¹⁶ and hetero-structure containing 2D electron gas¹⁷ showed low modulation depths. Metal gates used in the structures can limit the working range of carrier density and Fermi energy tuning.¹⁸ Compared to those, single layer graphene based THz modulators have higher carrier mobilities with an electrically tunable carrier density and offer very low insertion loss (0.2-0.5dB).⁶,¹⁹ However, theoretically expected high modulation depth and broadband performance is difficult to achieve due to its strong dependence on quality of graphene ⁶ and unforeseen component effects of the devices such as substrate effects.²⁰ In order to improve THz modulation by single layer graphene different methods such as integrating graphene with photonic cavities ²¹ and metamaterials ²²,²³ have been reported. In their study Kakenov et al. have demonstrated a flexible active THz surface constructed with a large-area single graphene layer, a metallic reflective electrode, and an electrolytic medium in between that provides complete modulation in the THz reflectivity at 2.8 THz. ²¹ 50% amplitude modulation at low voltages is reported by Gao et al using a gated single-layer graphene modulator with metallic ring aperture.²² However, the modulation is limited to a quite narrow bandwidth.

Increased modulation depth can be obtained by use of multilayer graphene (MLG) alone or MLG with ionic liquids.¹⁰,²⁴-²⁶ Shen et al. presented a metamaterial based modulator with a multilayer stack of alternating patterned graphene sheets with 75% modulation depth.²² However, the narrowband operational range and polarization dependent response of metamaterial based modulator may limit their future applications.²⁹ In their study Baek et al. has shown improvement in THz modulation with production of high quality MLG.²⁶ In that study the optical sheet conductivity increase has also been demonstrated as the layer number increase from 1 to 12. The dielectric substrates can cause change in the fermi level of a single layer graphene due to band gap opening and this situation could mislead optical results.³⁰ Whereas in MLG, optical response is dominated by the layers that do not interact with substrate. In their study Wu et al. investigated a graphene/ionic liquid/graphene device where ionic liquid forms interfaces with the graphene electrodes.²⁵ As the

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layer number of the graphene electrodes increased an increased modulation is observed, which is explained by elimination of boundary defects during multilayer formation. Kakenov et al. presented another ionic liquid based THz amplitude modulator. Due to efficient mutual gating of graphene electrodes and ionic liquid more than 50% modulation depth was obtained. Furthermore, Liu et al. used ionic liquid in their THz modulator device and achieved a modulation depth of 22%. In this study, high flexibility of THz modulator has been demonstrated by the great flexibility of graphene, ionic gel and also the host material, polyethylene terephthalate.

A compromise between modulation depth, polarization dependence, ease of fabrication, design flexibility, large area production, and operational bandwidth exist in most of the studies reported in literature. In this study we present large area MLG devices on flexible substrates that do not compromise on the modulation performance. The study experimentally demonstrates an excellent performance on THz amplitude modulation by devices made from ionic liquid doped MLG structures on Polyvinyl chloride (PVC) and Polyethylene (PE) substrates. The modulation depths were investigated at a broadband frequency range from 0.2 to 1.5 THz with application of very low voltages ranging between 0 V and 3.5 V. To our knowledge, this is one of the highest modulation depth achieved by graphene based THz modulators with such a broad THz range at such low gate voltages.

A sketch of THz-TDS system is given in Figure 1(a). The spectrometer has an effective working range of 0.2-1.5 THz with the sample. An amplified femtosecond laser is the light source that is centered at 800 nm and has 180 fs pulsewidth and a repetition rate of 1 kHz. A <110> ZnTe crystal was used to generate coherent THz radiation via optical rectification. Through the Pockells effect, phase of the detection pulse is retarded by the oscillating electric field of the THz radiation. Change in the polarization is monitored by quarter wave plate and Wollaston prism. Voltage from the balanced detector is synchronously detected using a lock-in amplifier. The water vapor attenuation effect is minimized by enclosing the system in an atmosphere controlled box with dry air.

Multi-layer graphene samples were grown on nickel foils using chemical vapor deposition method. Due to high solubility of carbon atoms on Ni surface, highly crystalline MLG with varying layer numbers can be grown on nickel foils. The growth process takes place in quartz chamber at the presence of argon, hydrogen and methane gases. The temperature in the chamber determines the layer number of synthesized graphene samples. Our samples were grown at 850 °C, 900 °C and 1000 °C corresponds to nearly 30, 60 and 100 layers of MLG, respectively. The layer numbers are estimated from optical measurements.

After the growth, MLG samples with 30, 60 and 100 layers were transferred on PVC (labelled as MLG850, MLG900 and MLG1000) and 100 layers on PE (MLG1000PE) by lamination, and nickel was removed with iron chloride (FeCl$_3$·6H$_2$O) solution.

Inset of Figure 1(a) demonstrates the fabricated MLG structure. The device consists of MLG and gold electrodes sandwiching ionic liquid [deme][Tf2N] (Diethylmethyl(2-methoxyethyl) ammoniumbis (trifluoromethylsulfonyl) imide). The gold electrode has a circular opening of 5 mm through which terahertz transmittance was measured. At zero bias the transmittance through the MLG device is maximum (Figure 1(b)) suggesting very low doping level,
if any. Upon application of bias voltage, the ions of the same polarity intercalate through layers of graphene by inducing charge carriers in layers of graphene resulting in attenuation of THz transmission\textsuperscript{33,34} (Fig. 1(c)).

Figure 2(a) presents change in terahertz waveforms around the peak amplitude for MLG850 as the applied gate voltage is increased. The inset of Figure 2(a) presents a full profile at 0 V as an example. Corresponding frequency domain data of the device is given in Figure 2(b). Full waveform in time domain for all devices and their corresponding frequency domain data are given in Supplementary Material, Fig. S1 and S2. The gate voltage applied appears to be low enough that no observable phase change was noticed neither in time domain nor in phase data. No observed change in phase might be because of graphene’s robust nature under electrolyte gating\textsuperscript{35} and having a thickness much less than the THz wavelength. Figure 2(c) shows the change in THz peak amplitude of all four devices as the bias voltage was varied from 0 V to 3.4 V. The maximum transmission was at 0 V while the minimum is at 3.4 V. As the gate voltage increased almost linear decrease in the amplitude was observed up to ca. 2 V. Beyond 2 V, a sharp nonlinear decrease with the voltage was observed. Approximately 2.5 V appeared to be turning point where the decrease slowed down and reached to a minimum at 3 V. The observed change in THz field amplitude is controlled by mobile carrier density that is being tuned by doping level or by the applied potential in effect. The voltage dependent behavior of the MLG devices is very similar to each other except the thinnest device which requires slightly higher voltage (ca. 0.5 V), which might be due to thickness dependent diffusion limit of the ions. Voltage dependent sheet resistance behavior of MLG850 device measured with four probe method is given in inset of Figure 2(c) and shows a very similar behavior. In Figure 2(d) THz transmission of MLG850 is given between 0.2 THz and 1.5 THz at all applied voltages. (For other thicknesses please see supporting material) The observed modulation with the set voltage appears to be independent of the THz frequency and, thus, limited by the instrument response. Up to 1.5 V less than 20 % modulation is observed. A modulation between 20 and 30% at ca 2 V can be achieved depending on the MLG thickness (Supplementary Material, Fig. S3). While the thinnest layer showed the lowest modulation at 2.6 V as approximately 50%, the remaining MLG devices had more than 80% modulation. Almost full power modulation has been achieved with all MLG devices at voltages beyond 3 V. The modulation depth is significantly improved compared to single\textsuperscript{7} and multilayer\textsuperscript{26} devices over a very broad range. Among all devices MLG850 provided a more controllable modulation change with increased voltage.

Optical conductivity of graphene appears to follow its electrical conductivity at the THz frequencies and, thus, follows the Drude model.\textsuperscript{35–39} With its high quantum efficiency and electron-phonon interaction beyond 7 THz all the changes observed in sheet conductivity is expected to be due to a change in carrier density and/or change in scattering time.\textsuperscript{10} Therefore, THz sheet conductivities ($\sigma_{sh}$) of MLG devices is proportional to the amplitude ratio of reference (PVC or PE) substrate and MLG sample as given in equation (1).\textsuperscript{41}

$$\sigma_{sh} = (n_1 + n_2)(A_{\text{Substrate}}/A_{MLG}) \cdot 1/Z_0$$

here, $Z_0$ is the impedance of free-space, $n_1$ and $n_2$ is the refractive index of air and substrate, respectively. The sheet conductivities of the MLG850 device at all voltages are given in Figure 3(a). The sheet conductivities of MLG devices at the Dirac point are featureless and inherently broadband between 0.3 to 1.5 THz and increase with increase in layer number as expected (Supplementary Material, Fig. S4). The conductivity values of MLG850, MLG900, MLG1000 and MLG1000PE are derived to be 4.4 mS, 7.5 mS, 17.8 mS and 10.3 mS respectively. The device with PE substrate appears to be lower than the PVC counterpart. The observed difference in conductivity is most likely due to the quality of the graphene, crystalline size,\textsuperscript{42} since it will affect the scattering time of the carriers. The calculated DC conductivities of the devices as inverse of the sheet resistance, which is measured with four probe method, are 3.3 mS for MLG850, 5.8 mS for MLG900, 31.2 mS for MLG1000. Our conductivities measured with THz are close to the DC conductivities measured and are
consistent with the ones reported for the similar devices in literature.19,26,32,39,40

Recent studies have shown quite high scattering time for well grown multilayer graphene ranging from 100 fs to 300 fs.43 Considering an average value of 200 fs and using experimental sheet resistance values carrier densities are estimated as ca. 1.5 x 10^{11}/cm² for MLG850, ca. 4.5 x 10^{12}/cm² for MLG900, and ca. 1.3 x 10^{13}/cm² for MLG1000. The carrier densities are comparable to ones reported in literature.26,40,44,45

As the gate voltage is varied, change in sheet conductivity \( \Delta \sigma_{sh} \) with respect to 0 V were calculated using equation 2, which is derived from equation 1.46

\[
\Delta \sigma_{sh} = \frac{\sigma_{sh,0} Z_0}{A_{gate}} \left[ 1 + \sigma_{sh,0} \left( \frac{Z_0}{n+1} \right) - 1 \right] \tag{2}
\]

where \( A_0, A_{gate} \) is the transmitted THz field amplitude of the MLG device at 0 V and gate voltages, respectively, and \( n \) is the refractive index of substrate. The results are given in Supplementary Material Fig. S4 for all the devices. As expected, sheet conductivities of the devices increased as the gate voltage increased and showed a saturation behavior at 3.4 V for all four samples. Figure 3(b) presents a comparison of the conductivities at representative voltages of 1.5 V, 2.8 V, and 3.4 V at 0.8 THz. Large increase in conductivity with doping can be seen when compared to their conductivities at 0 V by \( (\sigma_{3.4V} - \sigma_{0V})/\sigma_{0V} \). The conductivities were increased by 997% for MLG850, 716% for MLG900, 705% for MLG1000, and 1153% for MLG1000PE with an application of a comparably low gate voltage of 3.4 V. Similarly, Qi et al. observed increase in conductivity with doping due to increase in hole carrier concentration.40 Besides doping effect, growth temperature can also affect the conductivity drastically. When the thinnest and the thickest devices are compared to each other at 0 V \( [\Delta \sigma = (\sigma_{300 \degree C} - \sigma_{80 \degree C})/\sigma_{80 \degree C}] \) an enhancement of 304% was observed. The difference is still significant but less pronounced with an increase of 197% at 3.4 V for the same samples. The increase in layer numbers should not affect the THz conductivity of MLG devices or their carrier momentum scattering time40 since the sheet conductivity is defined as \( \sigma_{sheet} = \sigma_{THz} x d_{N-layer} \) where \( d \) is the thickness of N-layer \((N = 33, 64, 98)\) graphene. Thus only sheet conductivity should increase due to increased carrier density with thickness. Similarly, an increase in the sheet conductivity amounting to a 73% improvement was noted as the layer number increased from mono to 12 layers of graphene in the study by Baek et al.26 In addition, Wu et al. has also shown that the sheet resistance (and hence sheet conductivity) change with increase in layer number.28

In addition to being a preferential host material for flexible photonic devices PVC and PE are also preferred for their very low insertion losses; less than 1 dB at all frequencies (Supplementary Material, Fig. S5). The thinnest device had an average of 3 dB insertion loss though the loss increased with the layer thickness. The highest loss is observed for the thickest devices ranging from 8 dB to 12 dB. Figure 3(c) presents modulation of THz amplitude versus the insertion loss at 0.8 THz for 1.5 V, 2.8 V and 3.4 V. Here the insertion loss is the initial loss of the THz power when the device is inserted in the beam path and modulation represents the further change in the transmission of THz wave. The best performance is achieved with the thinnest MLG device with its much lower insertion losses and almost 100% modulation depth with an application of 3.4 V. Depending on the application type, devices with optimal numbers of graphene layers can be designed considering the trade-off between modulation depth and insertion loss at the preferred operational voltage.

In conclusion, THz modulators were fabricated using CVD-grown MLGs and change in the THz transmission with applied voltage due to the change in carrier density was investigated by THz time-domain spectroscopy. The thinnest device with 33 layers provided almost complete modulation of THz waves with an operation voltage of less than 3.5 V. The effect of increased number of layers on THz modulation was also investigated. Complete modulation was demonstrated at all the thicknesses; however, as the layer thickness increased an increase in the insertion loss was also observed. With the strong gating effect of dopant molecules, it was possible to achieve an extraordinary modulation depth with a very low operation voltage and broadband response over 0.2 and 1.5 THz. Here, bandwidth response appears to be limited only by the instrument. Sheet conductivities were also improved with doping and with increasing thickness, which is promising for new THz devices. Ionic liquid doped MLG devices are a promising platform to produce THz active filters with controlled modulation and expected to have a strong impact on improving THz optoelectronic devices in wide application areas.
See Supplementary Material for the results of all the devices.

The authors acknowledge the helpful discussions with Dr. Bulend Ortac. This research was supported by Scientific and Technological Research Council of Turkey (TUBITAK). E.K. and O.E. acknowledge funding from TUBITAK grant 111T393; H.A. and C.K. acknowledge funding from TUBITAK grant 114F379.

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Graphical Abstract