Graphene light modulators working at near-infrared wavelengths

D. E. AZNAKAYEVA,* F. J. RODRIGUEZ, O. P. MARSHALL, AND A. N. GRIGORENKO

School of Physics and Astronomy, Manchester University, Manchester, M13 9PL, UK
*diana.aznakayeva@manchester.ac.uk

Abstract: We demonstrate a graphene-based electro-absorption modulator with extremely small modulation volume that can be controlled by low gating voltages 1-3 V and shows light modulation at wavelengths as short as 900 nm. Our choice of hafnium oxide dielectric separator gives the possibility to obtain significant electro-optical effect in a simple optical heterostructure. Having low power consumption, our devices could find a wide range of applications in telecom industry.

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References and links

1. Graphene based low-voltage modulators

Fast electro-optical modulators with small area footprints, low operating voltages, and low power consumption are in great demand by the optoelectronic industry. Such modulators can be created using the unique optoelectronic properties of graphene combined with high-\(k\) dielectrics [1]. High-\(k\) metal oxides are promising materials for dielectric spacer in graphene-based optical modulators due to their electrical and optical properties, as well as their compatibility with the fabrication of CMOS devices. HfO\(_2\) is the most promising dielectric to replace SiO\(_2\) due to its high \(k\) value, large band gap energy (5.68 eV) [2], thermal stability and ease of fabrication and integration. Furthermore, HfO\(_2\) is an ionic crystal which has low potential of ionization [3]. Through strong ionic bonding and high Madelung energy, pure stoichiometric HfO\(_2\) is stable and unlikely to engage in chemical reactions. On the other hand, graphene is increasingly being considered an extremely useful material, which can help in the creation of efficient electro-optical modulators [4–13]. Graphene shows tunability of its optical conductivity by gating over a broad range of wavelengths, from mid-infrared to near-infrared [14]. Other significant advantages of graphene include its chemical inertness, mechanical stability, durability and ease of integration into optical devices. The simplicity of graphene monolayer fabrication, the possibility of direct assessment defect densities using Raman spectrometry, high transfer precision and integration with arbitrary structures, all pave the way toward graphene based low loss electro-optical modulators. In this letter we demonstrate a planar electro-optical modulator where light modulation is achieved using a single layer of graphene. The modulator itself is a simple heterostructure, consisting of a thin layer of metal (copper in our case), a hafnium oxide and graphene. It possesses a small modulation volume \(~5\,\mu\text{m}^3\) (potentially as small as \(\lambda^3/10\)), works at low gating voltages (~1-3 V), has low power consumption (~1 nW), low insertion losses (~10\%) and shows broadband light modulation down to a wavelength of \(\lambda = 900\,\text{nm}\). Our devices are CMOS compatible and could find a range of applications in the optoelectronic industry. Therefore, to the best of our knowledge, this is the first time where the operating parameters listed above have been achieved in a free space modulator with a solid dielectric (light modulation at near-infrared and visible wavelengths was only previously achieved with the help of an ionic liquid spacer, see [15] and [16]).

Figure 1(a) shows a schematic view of the free space graphene broadband electro-optical modulator. The modulator is essentially a parallel plate capacitor where the light modulation is performed by electrical control of graphene optical conductivity via applied bias. The graphene modulator consists of a quartz substrate, a reflective copper mirror, a quarter wavelength thick high-\(k\) HfO\(_2\) dielectric layer (the thickness \(d\) was chosen to be \(\lambda/(4n)\), where \(\lambda\) is the desired working wavelength of the modulator and \(n = 2\) is the refractive index of HfO\(_2\) at telecoms wavelengths) and a high quality, defect-free, mechanically exfoliated graphene monolayer. Figure 1(b) provides a microscope image of a fabricated modulator. Devices were fabricated as follows. The quartz substrate was cleaned in acetone and isopropanol (IPA) to ensure a clean surface and complete removal of dust particles, which could cause additional optical losses due to Rayleigh scattering. Prior to photolithography a chromium adhesion layer and the copper layer were deposited on the substrate using a Moorfield electron beam evaporator. The primary advantages of using copper as the bottom electrode are the good quality flat surface, high optical and electrical conductivity and low cost. As copper is a highly reactive material the hafnium oxide dielectric layer with quarter wavelength thickness was deposited on top of it immediately in order to protect it and increase electromagnetic fields at graphene location. The copper layer serves two main functions in the operation of the electro-optical modulator: it forms a reflective metal mirror and also works as a back gate electrode for graphene electrostatic doping. Graphene flakes were obtained from graphite by an exfoliation technique onto a SiO\(_2\)/Si substrate. Flake thickness and quality were assessed by optical microscopy and Raman spectroscopy. A
polymethyl methacrylate (PMMA) layer was spin-coated onto the Si-SiO$_2$-graphene structure in order to perform a wet transfer of the flake to the HfO$_2$ dielectric. The device was subsequently cleaned using acetone, IPA and water in order to fully remove the PMMA and any residue. The electrical contacts to the graphene surface were made by laser-writer optical lithography, followed by chromium (2 nm thickness) and gold (30 nm) electron beam deposition and lift-off. During the electrical measurements it was found that the graphene flakes were $p$-doped, which could be explained by hydrocarbon contamination and water adsorption.

2. Experimental demonstration of graphene based light modulators

Optical characterization of the graphene based free space modulators was performed using a Bruker Vertex 80 Fourier transform infrared (FTIR) spectrometer with a Hyperion 3000 microscope, operating in reflection mode. Figure 2 highlights the main results of this work, where the solid state dielectric has been employed to achieve significant modulation using small bias voltages. Modulators with small operational voltages have already been reported for supercapacitors, where the modulation effects were achieved with the help of an ionic liquid electrolyte. For conventional solid state dielectrics much higher voltages of around 50-150 V are usually necessary to observe modulation effects at near infrared wavelengths. By taking advantage of the electrochemical supercapacitor effect observed in the HfO$_2$ dielectric we were able to produce solid state modulators working at small operation voltages. The modulation mechanism can be explained in the following way. The change in reflectance of the devices is produced by the change in the graphene conductivity due to electrostatic doping. Interference between the incident electromagnetic wave and the wave reflected by the bottom copper mirror maximizes the optical field on the graphene layer, increasing the contrast. Figure 2(a) shows the results from a modulator in which the thickness of copper is 35 nm while the thickness of HfO$_2$ is $d = 156$ nm. The relative reflectance $R(V_g)/R(0)$ is the reflectance of the modulator with an applied gate voltage $V_g$ relative to the reflectance of the unbiased modulator. A modulation depth of 3% was obtained at the telecom wavelength of 1500 nm with an applied bias of 2 V. In fact, the device produces significant modulation across a large wavelength range (from $\lambda = 1200$ nm to $\lambda = 2000$ nm). By reducing the thickness of HfO$_2$, the operational wavelength range of the modulator can be blue shifted. As an example, Fig. 2(b) demonstrates light modulation in the wavelength range from 900 nm to $\lambda = 2000$ nm for a second device, this time with a smaller thickness of HfO$_2$ ($d = 100$ nm). It is worth noting that simple capacitance model for graphene gating [1] suggests that much larger voltages are required in order to observe the measured modulation depths due to optical Pauli
blocking (for the studied thicknesses of HfO₂). Indeed, the Fermi energy of the graphene $\varepsilon_F$ that has central neutrality point at a gating voltage of $V_g = V_{CNP}$ can be estimated at zero temperature as:

$$\varepsilon_F = \hbar v_F \text{sign}(V) \sqrt{\frac{e|V|}{4de}},$$

where $V = V_g - V_{CNP}$, $v_F$ is the graphene Fermi velocity, $\varepsilon$ is the permittivity of dielectric and $e$ is the electron charge. Taking $d = 100\text{nm}$ and $\varepsilon = 18$ for HfO₂ at low frequencies, we obtain the gate voltage $V$ required to achieve significant modulation at $\lambda = 1000\text{ nm}$ due to optical Pauli blocking as $V = (\pi c / \lambda v_F)^2 \times (4de / \varepsilon) = 30V$, which is an order of magnitude larger than observed experimentally. To elucidate the reason for the discrepancy between theory and experiment we measured the temperature dependence of the gating characteristics. Figure 3 shows the electrostatic gate effect on the graphene electrical resistance at low and high temperatures. These measurements were performed in a Linkam temperature controlled, liquid nitrogen cryostat at reduced pressure.

Fig. 2. Light modulation by the graphene-based heterostructures. (a) Spectral dependence of the relative reflection with a HfO₂ thickness $d = 156\text{ nm}$ and gate voltages of $-1\text{ V}$ (the blue curve) and $-2\text{ V}$ (the red curve). (b) Relative reflection spectra for $d = 100\text{ nm}$, at gating voltages of $-1\text{ V}$ (the blue curve), $-2\text{ V}$ (the red curve), $-3\text{ V}$ (the green curve). (c) and (d) Numerical simulations based on Fresnel theory, corresponding to the spectra presented in (a) and (b) respectively.
Figure 3(a) shows the graphene resistance as a function of gate voltage. Sweeps were made at a rate of 3 V/min, while limiting the voltage range to keep the gate current below 10 nA. The broadening of the $R(V_g)$ peak at low temperatures indicates that the low values of modulation voltage are most probably connected with ionic conductivity of HfO$_2$. The width of the $R(V_g)$ peak increased by a factor of three when the temperature was lowered from 80°C to −80°C, which implies that the effective capacitance of the device decreased by the same order.

The decrease of leakage current with the decrease in temperature, shown in Fig. 3(b), also indicates that it is the ionic conductivity of HfO$_2$ that is responsible for the supercapacitance effect observed in our devices. At room (and higher) temperatures the ionic conductivity of HfO$_2$ is relatively large and the electrostatic doping of graphene is governed by a double layer near the graphene sheet. This results in the supercapacitance effect and hence the low modulation voltages. However, at lower temperatures the ionic conductivity drops and gating is governed by the “normal” capacitance of the structure. Further modelling also supports the presence of a supercapacitance effect. Figure 2(c) and (d) show the results of Fresnel modelling for our heterostructures. The optical conductivity of graphene was taken in the following form [17]:

$$\sigma = \frac{e^2}{4h} \left[ \frac{1}{\pi} \arctan \left( \frac{\hbar \omega - 2\mu}{2k_BT} \right) - \frac{i}{2\pi} \ln \left( \frac{(\hbar \omega + 2\mu)^2}{(\hbar \omega - 2\mu)^2 + 4k_BT^2} \right) + \frac{i}{\pi} \frac{8k_BT}{\hbar \omega + i\gamma} \ln(2 \cosh \frac{\mu}{2k_BT}) \right],$$

where $\mu$ is the chemical potential of graphene, $T$ is the temperature, $k_B$ is the Boltzmann constant and $\gamma$ is the electron collision rate. The last term in the expression represents the Drude contribution to graphene’s optical conductivity and is negligible at near-infrared and visible frequencies. The optical constants of copper and HfO$_2$ thin films were extracted by spectroscopic ellipsometry from test samples deposited on a glass substrate as explained in Ref [18].

It is worth noting that graphene layer can effectively safeguard the excellent plasmonic properties of the underlying copper layer [18] and keep the electrical properties of the dielectric separator intact. The model provides a good qualitative fit to the measured reflection spectra; compare Fig. 2(a) and (b) with Figs. 2(c) and (d) respectively. However, in order to achieve this fit we had to assume that the chemical potential of graphene changes with gating much faster than is predicted by a simple capacitance model. For example, in order to achieve a chemical potential of 0.5 eV in a heterostructure with $d = 100$ nm one would need to apply a gate voltage of 18 V, whereas the experimental data suggest that this
value is reached at $V_g = -2V$, see Fig. 2(b) and (d). This again indicates the presence of a supercapacitance effect, where the effective thickness of the dielectric separating the charges is an order of magnitude smaller than the actual physical thickness. A detailed study of the HfO$_2$ supercapacitance effect will be reported elsewhere.

3. Summary

To summarize, we have fabricated, characterized and tested simple, efficient and low-loss graphene-based electro-optical modulators working at near infrared wavelengths. A modulation depth of 3% was achieved at $\lambda = 1.5$ µm (and 1.5% at $\lambda = 1$ µm), with gate voltages of just a few volts applied to the graphene heterostructure. The unexpected supercapacitance effect observed in the high-$k$ HfO$_2$ gate dielectric allowed us to create extremely simple free space, CMOS compatible, telecom modulators with significant electro-optical modulation effect, low power consumption and small modulation volume. This supercapacitance effect could be useful for other optoelectronic applications.

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