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Few layers graphene as thermally activated optical modulator in the visible-near IR spectral range

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We report the temperature modulation of the optical transmittance of a few layers of graphene (FLG). The FLG was heated either by the Joule effect of the current flowing between coplanar electrodes or by the absorption of a continuous-wave 532 nm laser. The optical signals used to evaluate the modulation of the FLG were at 633, 975, and 1550 nm; the last wavelengths are commonly used in optical communications. We also evaluated the effect of the substrate on the modulation effect by comparing the performance of a freely suspended FLG sample with one mounted on a glass substrate. Our results show that the modulation of the optical transmittance of FLG can be from millihertz to kilohertz.

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Graphene is a material with unique physical properties that has attracted attention because of its high electron mobility [1–3] and thermal conductivity [4–7]. Upon combining it with other carbon structures, such as the fullerene C_{60}, for example, it is also possible to obtain new properties such as a negative photoconductive response [8]. The optical absorption of graphene is almost constant throughout the visible and infrared regions [9,10] and interestingly, this feature can be controlled by electric gating [11]. Electrical control of the electronic transitions in graphene has allowed the fabrication of electro-optical modulators operating at frequencies up to the gigahertz range [12]. Higher modulation frequencies have been achieved upon all-optical modulation schemes, based on fiber optic devices incorporating a graphene cladding layer [13]. In a previous work we showed that the optical transmittance through a few layers of graphene (FLG) can be modulated by an electrical signal via Joule heating [14]. This was demonstrated for the visible spectral region and for very low modulation frequencies [millihertz (mHz) range]. In this work, we studied the modulation capabilities of a FLG optical modulator, operating at modulation frequencies up to the kilohertz (kHz) range and working with near-infrared photon frequencies commonly used for optical communications. Furthermore, we also show that heating of the FLG can be achieved by absorption of a moderate power (250 mW CW, 532 nm) optical illumination, therefore providing an all-optical modulation of the FLG device. The FLG samples were synthesized by chemical vapor deposition (CVD) using copper foils (Alfa Aesar, 99.999% purity and 25 μm thick), and methane as the carbon precursor at atmospheric pressure. After dissolving the copper foil and the cleaning process, the FLGs were transferred to glass slides of 0.15 mm of thickness and finally two silver electrodes separated by 4 mm were deposited by thermal evaporation. Figure 1(a) shows a typical Raman spectrum (enSpectr Model 532/20/1800) of the samples fabricated with our CVD process. Note that the intensity of the G band is larger than that of the 2D band, which is characteristic of the few layer graphene samples. The existence of the D band indicates structural disorder in the samples [15,16].

A detailed analysis of the shape of the 2D band showed that the samples mainly consisted of four layers of graphene, which

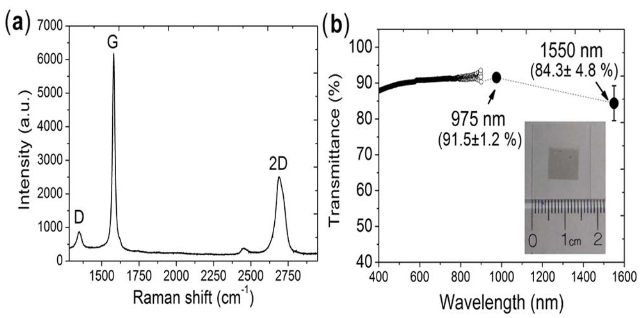

Fig. 1. (a) Raman spectra of FLG on SiO_2 using an excitation wavelength of 532 nm. (b) Visible spectra of a similar sample on a glass substrate (open circles) and the measured transmittance for the two wavelengths used in our experiments (closed circles); the inset shows FLG on glass.

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is consistent with the value of the measured transmittance (Shimadzu Model UV-2600) in the visible range using the general rule of 2.3% of absorbance per graphene layer [17,18]; this is illustrated in Fig. 1(b), which shows the transmission spectrum of the sample.

The optical transmission of the FLG samples was evaluated using the setup shown in Fig. 2. As illustrated in the figure, the FLG sample with electrodes was placed on a glass substrate and this arrangement was mounted in an optical minibench. The bench contained two collimating lenses with optical fiber receptacles; hence, transmission measurements could be readily performed by placing the sample within the light path. Two fiber-coupled laser diodes were used as probe beams in these experiments: at 975 nm (JDSU, 220 mW max. output power), and at 1550 nm (JDSU, 120 mW output power). The light transmitted through the sample was measured using an InGaAs detector (THORLABS, Model D400FC, 1 GHz bandwidth) connected to an oscilloscope (Tektronix TDS 3032B). Modulation of the FLG transmittance was achieved by applying a voltage signal to the electrodes ($V = V_0 \sin(2\pi\nu_m t)$) using a function generator (Wavetek, Model 22). We also explored all-optical modulation of the sample using a continuous-wave (CW) laser (LASEVER Model LS532NL500, wavelength of 532 nm) modulated with an optical chopper, as illustrated in Fig. 2(c). The modulation schemes were tested over a frequency range of mHz to kHz. The steady-state temperature obtained with the modulation signals, either electrical or optical, were measured at the center of the sample using a thermographic camera (Fluke Ti300, 9 Hz refresh rate).

Figure 3 shows the fast Fourier transform (FFT) spectra of the transmitted light detected for two modulation frequencies and for the two wavelengths used in our experiments; the inset shows the time signal as registered in the oscilloscope. For these measurements, the power of the lasers was set to 876 and 832 μW for the 975 and the 1550 nm wavelengths, respectively. Note that the transmitted light registered by the detector shows a modulated component with a main frequency that is twice the frequency of the modulation signal.

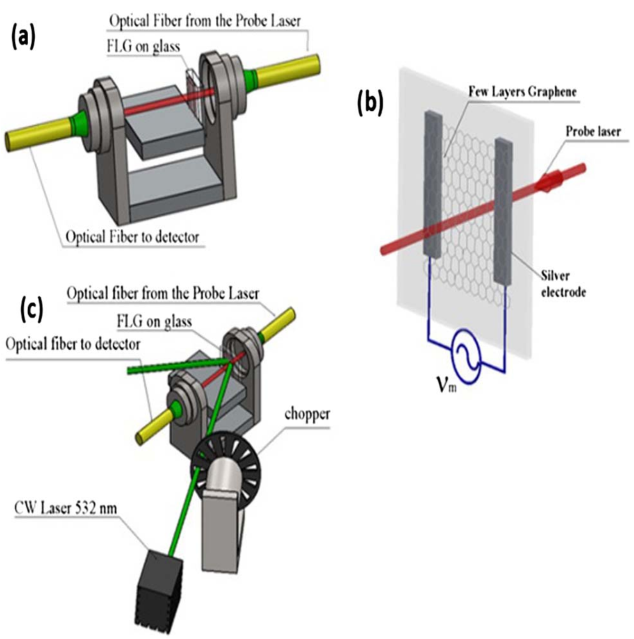

Fig. 2. (a) Experimental setup for the optical measurements; (b) diagram of the FLG sample placed on a glass substrate with electrical connections; (c) setup for all-optical modulation tests: the CW laser is modulated with an optical chopper.

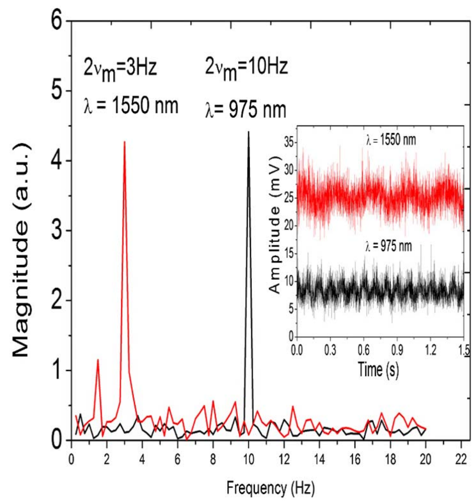

Fig. 3. FFT spectra of the transmitted light; the inset shows the measured signal as a function of time. The frequency of the modulation signal applied to the FLG device was $\nu_m = 5$ Hz and $\nu_m = 1.5$ Hz, for the 975 nm and 1550 nm lasers, respectively. An amplitude of 7.9 V was used as the modulating voltage in both cases.

The observed changes in the optical transmittance were related to the temperature dependence of the optical conductivity [19–21]. Measurements of the optical transmittance as a function of temperature are presented in Fig. 4(a). These were obtained by heating the sample via the Joule effect by applying a constant bias voltage. These measurements were made with the thermographic camera once a steady-state temperature was reached. Clearly, the transmittance increased as a function of the temperature.

Calculations of the transmittance of the FLG were made using the following model for the interband optical conductance

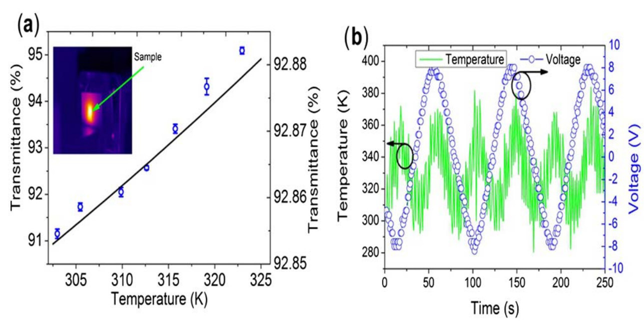

Fig. 4. (a) Measured transmittance of the FLG sample as a function of temperature T (open circles). The sample was heated via Joule effect applying a constant bias voltage and T was determined using a thermal image obtained with the thermographic camera (shown in the inset). The continuous line is the result of the calculation using Eqs. (1) and (2) (using $N = 4$ layers graphene, $\varepsilon_{F0} = 0.52$ eV, and $\lambda = 975$ nm). (b) Temperature variations registered with a thermocouple placed near the sample. The heating was produced by applying a modulated bias voltage with frequency, $\nu_m = 11.5$ mHz; note that the frequency of the modulated temperature is twice that of the modulation voltage.

[Eq. (1)], for a sample of graphene at temperature T and irradiated with a photon energy $\hbar\omega$ [21,22]:

$$\sigma^{\text{inter}}(\omega, T) = \frac{e^2}{4\hbar}\frac{\text{Sinh}\left(\frac{\hbar\omega}{2k_BT}\right)}{\text{Cosh}\left(\frac{\varepsilon_F}{k_BT}\right) + \text{Cosh}\left(\frac{\hbar\omega}{2k_BT}\right)}. \quad (1)$$

The temperature dependence of the Fermi energy is considered as $\varepsilon_F = \varepsilon_{F0} - \frac{\pi}{6}\frac{(k_BT)^2}{\varepsilon_{F0}}$.

The optical transmittance (Tr) can be obtained using the following relation [23,24],

$$\text{Tr} = \frac{1}{\left(1 + \frac{NZ\sigma^{\text{inter}}(\omega,T)}{1+n}\right)^2}, \quad (2)$$

where N is the number layers of graphene, Z the free-space impedance, and n the refractive index of the substrate. The results of the calculated transmittance are presented in Fig. 4(a), where a qualitative agreement with the experimental measurements can be seen.

When the bias voltage was varied at a frequency of ν_m, the temperature changed at frequency of $2\nu_m$ due to the Joule effect [see Fig. 4(b)]. Hence, the spectrum of the modulated optical signal showed a main peak centered at twice the frequency of the modulation bias voltage, see Fig. 3 [14].

In order to evaluate the effect of the substrate and the surrounding media on the optical response of the FLG, experiments on free-standing samples and under vacuum conditions (~10^{-4} Torr) were performed. The FLG was mounted on a Bakelite plate with 0.6 mm diameter holes and two coplanar silver electrodes were evaporated on the sample [see Fig. 5(a)]. Heating of the sample was performed via Joule effect as described for the previous experiment. As before, the transmitted light showed a modulated component at twice the frequency of the electrical signal [Fig. 5(b)]. We therefore conclude that modulation of the optical transmittance of the FLG through temperature changes was an intrinsic property of the FLG material. In this case, the probe signal was within the visible region of the spectrum (633 nm) showing that the transmittance of the sample could be effectively modulated over a wide spectral range.

We explored higher modulation frequencies by heating the sample on the glass substrate using a CW laser (LASEVER

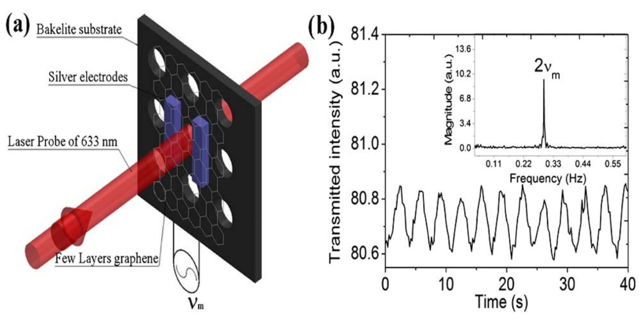

Fig. 5. (a) Diagram of the free-standing FLG on a Bakelite substrate with electrical connections and (b) modulated transmitted signal of a free-standing FLG sample as a function of time using a modulation voltage at a frequency of $\nu_m = 150$ mHz. The inset shows its corresponding FFT. The probe optical signal was from a He–Ne laser ($\lambda = 633$ nm) and the measurement was made in vacuum at a pressure of around 10^{-4} Torr.

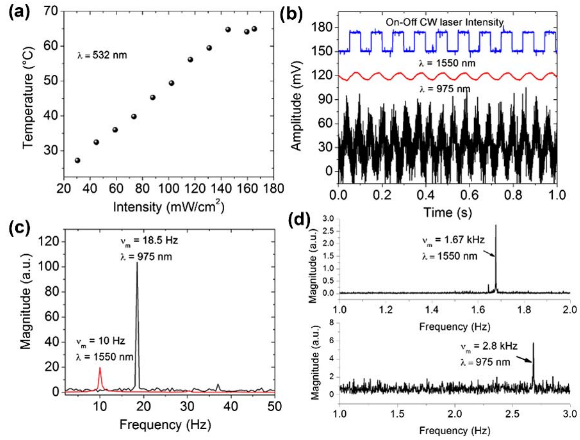

Fig. 6. (a) Temperature of the FLG as a function of the incident CW laser intensity; (b) transmitted optical intensity modulated at 10 Hz for the 1550 nm laser diode, and at 18.5 Hz for the 975 nm laser. The upper trace shows the registered waveform of the optical signal modulated by the chopper where the maximum intensity is 159.6 mW/cm^2 (0.05 s width, nominal chopper frequency of 10 Hz). (c) FFT spectrum of the transmitted signals and (d) shows the FFT spectrum of similar measurements at KHz frequencies.

Model LS532NL500, 532 nm). Irradiation of the sample with the laser produced an increase in the temperature depending on the absorbed optical intensity, as shown in Fig. 6(a). For this measurement, the steady-state temperature was again measured using the thermographic camera. Modulation of the optical transmittance of the FLG was achieved upon varying the temperature of the sample by using an optical chopper to modulate the CW laser signal such as shown in Fig. 6(b). The measured transmitted signal as a function of time for the wavelengths of 975 and 1550 nm, and powers of 876 and 832 μW, respectively, for the low modulation frequencies are shown in Fig. 6(b); their corresponding FFTs are presented in Fig. 6(c). Figure 6(d) shows the corresponding FFT spectra obtained for higher modulation frequencies within the kHz range. In a similar manner to the electrical modulation scheme, the all-optical modulation scheme modified the transmission of the FLG via the heat generated due to the absorption of the laser beam. Thus, the modulated signal followed the characteristics of the modulation of the excitation laser beam. It is important to note that in these experiments, the optical power of the CW beam was kept at levels below those commonly used to obtain saturable absorption [12]. In our case, the transmittance is effectively modulated via heating of the FLG, whose optical properties are temperature dependent [19–21]. Hence, heating with an electrical or an optical signal can provide an effective means to modulate the optical transmittance of FLG samples.

A maximum modulation frequency close to 5.5 KHz on the glass substrate was attained using the proposed arrangement. We can also estimate a similar maximum frequency for the free-standing sample (see Fig. 7). For these experimental conditions, the FFT amplitude of the transmitted optical signal remains well above the noise level. The trend of the experimental data shown in Fig. 7 indicates that both kinds of samples (i.e., glass supported and free-standing) yield similar response times. Nonetheless, we believe shorter response times could be achieved owing to the intrinsic thermal properties of graphene [7].

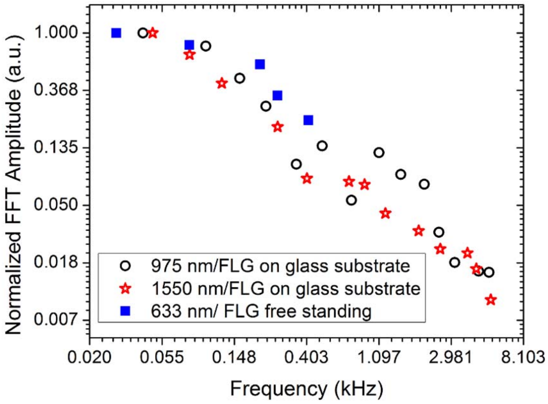

Fig. 7. Normalized FFT amplitude of the transmitted light as a function of the modulation frequency for FLG samples placed on a glass substrate and free-standing. The wavelength of the transmitted light is indicated with the corresponding symbol.

A rough estimate of the thermal response of the material can be obtained upon considering the so-called thermal time constant $\tau = \rho C d^2/\kappa = d^2/D$, where ρ is the density, C is the specific heat, κ the thermal conductivity, d the thickness of the film, and D the thermal diffusivity [25]. Using a recently reported experimental measurement of $D = 6.5 \times 10^{-4}\ \mathrm{m^2/s}$ [26] and $d = 1.36$ nm for four layers of graphene we obtain $\tau = 3 \times 10^{-15}$ s. Such a small ideal time is, however, increased due to the effect of the surrounding media. As an example, the Kapitza thermal resistance due to the thermal coupling between graphene and the supporting substrate may affect the thermal time constant [7].

In summary, in this work we have studied thermally activated optical modulation of FLG synthesized by CVD. The results showed that the optical transmittance, over wavelengths ranging from the visible to the near-infrared, could be successfully modulated in FLG films. Specifically, the optical transmittance of a few graphene layers was shown to increase as a function of temperature; this increase was in qualitative agreement with theoretical modeling of the optical conductivity of graphene. We demonstrated two convenient ways to change the temperature of the FLG: (1) using an electrical current to heat the film by the Joule effect, and (2) by means of the absorption of CW 532 nm laser light. In the first case modulation was achieved by varying the frequency of the AC current, and in the second case by using an optical chopper. While the former allowed frequencies in the Hz range, the latter could produce modulation in the kHz range. In addition, experiments on free-standing samples of FLG under vacuum conditions demonstrated that the variation of the optical transmittance due to heating was attributable to the intrinsic properties of few-layer graphene. We believe that our findings may have an impact on the design of optical devices used in telecommunications and other photonic-related applications.

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