Enhanced photogating via pyroelectric effect induced by insulator layer for high-responsivity long-wavelength infrared graphene-based photodetectors operating at room temperature

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Infrared (IR) sensors have attracted significant interest in both industrial and academic fields, due to their wide range of applications in security, surveillance, enhanced vision systems, military operations, fire fighting, gas detection, maintenance, vehicles, and medical care. In particular, the long-wavelength IR (LWIR) region from 8 to 15 μm is important because this corresponds to human body temperature. IR detectors are typically categorized into thermal and quantum types. The former are used commercially because of their low-cost, but suffer from low responsivity and poor response speed. In contrast, quantum-type detectors exhibit higher performance but require cooling to reduce thermal noise, which increases the system size and cost. In addition, the majority of detector materials are compound semiconductors such as HgCdTe, which are both hazardous and expensive.

Graphene is an atomically thin 2D carbon film that exhibits excellent optoelectrical properties, including a broadband photoreponse and high carrier mobility. Graphene can be fabricated by chemical vapor deposition (CVD) at a much lower cost than compound semiconductors. Graphene photodetectors are expected to allow broad operation over wavelengths ranging from the ultraviolet to the terahertz region, to be capable of a rapid response, and to be cheap to manufacture, none of which are possible using present-day technology. However, the optical absorbance of graphene is only 2.3%, which results in low responsivity, and this value must be increased to allow the practical application of such devices. Various techniques have been proposed to enhance the responsivity of graphene-based photodetectors, including the use of two different electrodes, pn-junctions, bolometer, thermopile, optical cavities, plasmonic resonance, tunneling structures with two graphene sheets, nanoribbons, and photogating. Photogating is an especially promising approach because it results in extraordinarily high-responsivity that cannot be achieved by conventional methods such as quantum efficiency enhancement. This effect is obtained by situating photosensitizers around a graphene channel. Incident light couples with these photosensitizers to produce electrical changes that in turn modify the gate voltage of the graphene channel. As a result, extraordinarily large variations in the carrier density and the electrical signal from the graphene are obtained. Quantum dots, n-type or p-type Si substrates, and other carbon materials have typically been used as the photosensitizers in such devices. Recently, our own group demonstrated high-responsivity visible, near-IR, and middle-wavelength IR (MWIR) graphene photodetectors based on photogating with Si or InSb substrates. However, the wavelength range was limited by the cutoff wavelength of Si and InSb. In addition, MWIR graphene photodetectors incorporating InSb still require cooling. In fact, a high-responsivity, non-cooled LWIR graphene photodetector using photogating has not yet been demonstrated, so it would be useful to develop a photosensitizer for use in the LWIR region that is capable of operating at room temperature.

In the present study, to address this challenge, we employed a pyroelectric material as a photosensitizer. In a pyroelectric material, changes in surface charge can be induced by temperature variations. For example, pyroelectric crystals such as lithium niobate (LiNbO3), lithium tantalate, and lead zirconate titanate are capable of undergoing significant spontaneous polarization at room temperature. The IR radiation absorbed by a pyroelectric substrate is converted into heat, and the change in temperature causes spontaneous polarization of the substrate, which creates an internal electric field. It can therefore be expected that a high-responsivity LWIR graphene photodetector capable of operating at room temperature could be obtained by taking advantage of the pyroelectric effect to produce gate voltage modulation in conjunction with photogating.

Several graphene photodetectors using ferroelectric substrates have been reported, all of which have incorporated graphene and a ferroelectric substrate in direct contact with one another. The performance of these detectors was therefore limited by the polarizability and pyroelectric coefficient of the ferroelectric component. Obtaining a sufficiently high pyroelectric effect in such devices would...
require changing the composition of the substrate, which would be costly because tuning the composition of ferroelectric substrates is highly complex. To address this challenge, we envisioned a structure incorporating an insulator layer inserted between the graphene and the pyroelectric substrate. This insulator layer, composed of a material such as silicon nitride (SiN), would absorb LWIR radiation to ensure a temperature increase, and the resulting heat would enhance the pyroelectric effect and thus increase the photogating effect. In this manner, it should be possible to fabricate higher-responsivity, low-cost graphene LWIR photodetectors without the necessity of controlling the composition of the ferroelectric material.

The graphene LWIR detectors were fabricated using single-crystal LiNbO$_3$ substrates. A 100 nm thick SiN layer was deposited on the LiNbO$_3$ substrate by catalytic CVD. The source and drain electrodes consisted of a 10 nm thick Cr layer and a 30 nm thick Au layer formed by vacuum evaporation on the SiN layer, respectively. A single-layer of graphene was prepared by CVD and transferred onto the substrate with the source and drain electrodes using a conventional transfer technique. A graphene channel (15 μm in width and 5 μm in length) was fabricated using photolithography and O$_2$ plasma etching. This process, in which the graphene is transferred to the electrodes, reduces damage that might otherwise occur to the graphene during the resist removal process in the manufacture of the electrodes.

The photoresponse of each unit was measured with a vacuum probe at a pressure of 10$^{-4}$ Pa, using a quantum cascade laser with a wavelength of 7.9 μm as the light source. Quasi-continuous wave irradiation of the entire top side of the device was performed at a frequency of 0.5 Hz and a duty ratio of 0.4. The change in the source–drain current, $I_d$, for each device was monitored using a semiconductor device analyzer (B 1500 A, Keysight) with the lower part of the substrate electrically grounded.

Figure 1(a) presents a schematic diagram of an LWIR graphene photodetector incorporating a LiNbO$_3$ substrate with a SiN layer inserted between the graphene and the LiNbO$_3$ substrate. Figure 1(b) illustrates the pyroelectric effect resulting from incident LWIR radiation, while Fig. 1(c) shows a Fourier transform IR absorbance spectrum of the LiNbO$_3$ substrate used in this study, as determined from transmittance and reflectance data obtained at an incident angle of 15°. From this spectrum, the LiNbO$_3$ substrate exhibits greater than 80% absorbance over the LWIR region from 8 to 11 μm. Figure 1(d) shows a Raman spectrum of a graphene layer transferred onto a LiNbO$_3$/SiN substrate. The 2D peak at 2700 cm$^{-1}$ is more than twice the intensity of the G peak at 1580 cm$^{-1}$ as expected for single-layer graphene. The peaks at 1300 and 1750 cm$^{-1}$ are attributed to the LiNbO$_3$ substrate. These results confirm that a graphene monolayer was formed on the SiN/LiNbO$_3$ substrate.

Graphene-based LWIR photodetectors with and without a SiN layer were fabricated in this study. Figure 2(a) shows the photoresponse of both devices to LWIR radiation at a wavelength of 7.9 μm and a power level of 88.3 mW. The photoresponse was measured at a source–drain voltage, $V_d$, of 1 V and a back-gate voltage, $V_{bg}$, of 0 V at room temperature. The results demonstrate that a maximum photocurrent, $\Delta I_d$, of approximately 60 and 10 μA was obtained with and without SiN, respectively. In contrast, the $\Delta I_d$ values obtained from conventional graphene photodetectors without photogating are approximately 10 nA below 14 K. These results clearly demonstrate that the photogating effect induced by a LiNbO$_3$ substrate with a SiN layer strongly enhances the photoresponse by a factor of approximately 600 at $V_d = 0.1$ V, while the presence of the SiN layer increases the photoresponse by a factor of more than 6. Figure 2(b) plots the LiNbO$_3$ substrate photocurrent, $\Delta I_{bg}$, generated by devices with and without a SiN layer. A negative $\Delta I_{bg}$ appears under LWIR radiation, while a positive $\Delta I_{bg}$ is observed without illumination, regardless of the presence of the SiN layer. In addition, $\Delta I_{bg}$ for the device with a SiN layer is 100 times greater than that for the device without a SiN layer. This demonstrates that the change in the polarization of the LiNbO$_3$ substrate is increased by the presence of the SiN layer, because SiN absorbs at wavelengths of 8–15 μm, thus imparting an additional temperature increase to the LiNbO$_3$. In order to confirm this, the temperature variation of $\Delta I_d$ at two different wavelengths was investigated. Figure 2(c) plots the time variation of $\Delta I_d$ for the device with a SiN layer irradiated at wavelengths of 7.9 and 9.6 μm at an intensity of 20 mW. It can be seen that $\Delta I_d$ at 9.6 μm is approximately 20% greater than that at 7.9 μm, in good agreement with the wavelength dependence of SiN absorbance.

Figure 2(d) shows the effect of $V_d$ on $\Delta I_d$ at an incident light intensity of 88.3 mW for devices with and without a SiN layer. In both cases, $\Delta I_d$ increases in proportion to $V_d$, although the slope for the device with a SiN layer is 8 times larger than that for the device without a SiN layer. This confirms that the enhanced photoresponse is attributed to the SiN layer and occurs at all $V_d$ values. Figure 3(a) shows the effect of the incident light intensity on $\Delta I_d$ for devices with and without a SiN layer for $V_d = 0.1$ V. For the device with a SiN layer, $\Delta I_d$ abruptly decreases at 65.5 mW. Figures 3(b) and 3(c) plots $\Delta I_d$ and $\Delta I_{bg}$ as a function of time for the device with a SiN layer for two different light intensities at $V_d = 0.1$ V. It can be seen that negative and positive $\Delta I_d$ values are obtained at light intensities of 65.5 and 88.3 mW, respectively. On the other hand, only negative $\Delta I_{bg}$ values are obtained at both light intensities of 65.5 and 88.3 mW. These results indicate that the nature of the charge carriers in the graphene changes in response to the light intensity. Figure 3(d) presents a schematic illustration of the associated mechanism. A negative $\Delta I_d$ is produced at low light intensity, but as the intensity increases, the photogating effect shifts the Dirac point to longer wavelengths, changing the charge carriers from electrons to holes. This phenomenon was not observed for the device without a SiN layer, due to the small photogating effect.

To further clarify the carrier switching mechanism, the temperature dependence of $\Delta I_d$ and $\Delta I_{bg}$ was investigated. Figure 4(a) shows the time dependence of $\Delta I_d$ at temperatures from 12 to 300 K (room temperature) at $V_d = 1$ V for the device with a SiN layer at irradiation wavelengths of 7.9 μm at 88.3 mW. It can be seen that the sign of $\Delta I_d$ switches at around 100 K. On the other hand, as shown in
Fig. 1. (Color online) Schematic diagram of (a) graphene LWIR photodetector incorporating LiNbO₃ substrate and (b) polarization change induced by LWIR radiation. (c) Absorbance spectrum of LiNbO₃ substrate. (d) Raman spectrum of graphene on LiNbO₃/SiN substrate.

Fig. 2. (Color online) Time variation of (a) $\Delta I_d$ and (b) $\Delta I_{bg}$ in response to irradiation at 7.9 μm with an intensity of 88.3 mW. (c) Time variation of $\Delta I_d$ in response to irradiation at 7.9 and 9.6 μm with an intensity of 20 mW. (d) $\Delta I_d$ as function of $V_d$ at an incident light intensity of 88.3 mW.
Fig. 4(b), there is no change in the sign of $\Delta I_{bg}$. It is evident from the fact that $\Delta I_{bg}$ is enhanced with increasing temperature. These results indicate that the graphene carrier type switches with increasing temperature, which can be explained by the mechanism as shown in Fig. 3(d). Therefore, the photogating effect due to the polarization change in the LiNbO$_3$ substrate is enhanced at higher temperatures.

In conclusion, a high-responsivity LWIR graphene photodetector capable of operating at room temperature was demonstrated. The detector is based on an enhanced photogating effect due to a LiNbO$_3$ substrate with a SiN layer. At an optical wavelength of 7.9 $\mu$m, the photoresponse was improved by a factor of approximately 600 compared to that for a conventional graphene photodetector using a Si/SiO$_2$ substrate, where no photogating occurs. The SiN layer between the graphene and the LiNbO$_3$ absorbs LWIR radiation, which increases the device temperature and enhances the polarization change in the LiNbO$_3$. As a result, an approximately 8-fold increase in responsivity was achieved by inserting the SiN layer. A change in the charge carrier type also occurred, and this was attributed to a large shift in the Dirac point due to the strong photogating effect. This phenomenon could potentially be applied to devices other than photodetectors, such as memory devices and optical circuits.

The results obtained in this study are expected to contribute to the future realization of high-responsivity, low-cost LWIR photodetectors for applications such as thermal imaging, medical care, and gas analysis.

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Fig. 4. (Color online) Time dependence of (a) $\Delta I_d$ and (b) $\Delta I_{bg}$ at various temperatures for $V_d = 1$ V.

Fig. 3. (Color online) (a) $\Delta I_d$ as function of light intensity at $V_d = 0.1$ V. (b) $\Delta I_d$ and (c) $\Delta I_{bg}$ as function of time for device with SiN at light intensities of 65.5 and 88.3 mW, and $V_d = 0.1$ V. (d) Schematic illustration of carrier change mechanism due to presence of SiN layer.

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