Photon-generated carrier transfer process from graphene to quantum dots: optical evidences and ultrafast photonics applications

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Graphene/Ill–V semiconductor van der Waals (vdW) heterostructures offer potential access to physics, functionalities, and superior performance of optoelectronic devices. Nevertheless, the lack of a bandgap in graphene severely restricts the controllability of carrier properties and therefore impedes its applications. Here, we demonstrate the engineering of graphene bandgap in the graphene/GaAs heterostructure via C and Ga exchange induced by the method of femtosecond laser irradiation (FLI). The coupling of the bandgap-opened graphene with GaAs significantly enhances both the harvest of photons and the transfer of photon-generated carriers across the interface of vdW heterostructures. Thus, as a demonstration example, it allows us to develop a saturable absorber combining a delicately engineered graphene/GaAs vdW heterostructure with InAs quantum dots capped with short-period superlattices. This device exhibits significantly improved nonlinear characteristics including <1/3 saturation intensity and modulation depth 20 times greater than previously reported semiconductor saturable absorber mirrors. This work not only opens the route for the future development of even higher performance mode-locked lasers, but the significantly enhanced nonlinear characteristics due to doping-induced bandgap opening of graphene by FLI in the vdW heterostructures will also inspire wide applications in photonic and optoelectronic devices.

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The SSL structure serves as a carrier reservoir to effectively adjust the carrier transfer dynamics, and the QDs are the final absorber of the photon-generated carriers. An Er-doped fiber laser constructed with the graphene/GaAs/SSL/QD SA exhibits continuously stable modelocking, which is vastly superior to reported mode-locked lasers based on conventional QD-SESAMs, graphene, or other two-dimensional material-based SAs. The development of the doped-graphene/III–V semiconductor heterostructure SAs paves a way towards the realization of robust and high-performance ultrafast lasers which are of key importance for applications of all-optical clocking recovery, optical frequency comb, and coherent optical communication systems.

RESULTS

Carrier transfer process in vdW heterostructures

Figure 1a shows the optical image of the graphene/GaAs vdW heterostructures, which were fabricated by wet-chemical transfer of graphene layers onto the surface of a GaAs substrate and the cross-sectional transmission electron microscope (TEM) image of the graphene/GaAs heterostructure after a 740 nm femtosecond Ti:sapphire laser irradiation, where the closed contact at the interface can be observed clearly. Upon irradiating the graphene/GaAs vdW heterostructure with ultrashort laser pulses, the exchange between C and Ga or As atoms at the interface results in the doping of exotic atoms into the graphene lattice, as depicted in Fig. 1b. This doping induces the opening of an energy gap in the electronic structure of graphene, which could promote the transfer of photo-generated carriers from graphene to GaAs. The detailed comparison of these effects on the carrier transfer, including the power density of irradiating laser and the layers of graphene coated in the vdW heterostructures, are schematically presented in Fig. 1c–f. By comparing Fig. 1c, d, although enhanced photon harvesting and carrier generation are expected with graphene, the direct coating of graphene onto the InGaAs/GaAs QD structure can hardly result in the efficient transfer of carriers to reach the QDs, due to the severe carrier loss at the interface. As illustrated in Fig. 1e, the FLI treatment modifies the graphene/GaAs vdW interface and effectively enhances the carrier transfer, which leads to an adjustable transfer efficiency (L1–L5) of carriers across the heterostructures. In addition, as represented by the geometry size of the funnel top in Fig. 1f, the effects of optical absorption and carriers harvesting (A1–A5) could be controlled by varying the number of graphene layers in the graphene/GaAs vdW heterostructures, which is confirmed by the results of photo-luminescence (PL) and nonlinear reflection measurements.

Raman spectra of the vdW heterostructures treated with FLI

Raman spectroscopy is an efficient method for the characterization of graphene, doped graphene, and graphene-based vdW heterostructures due to the sensitive dopant and carrier effects on Raman vibrational modes. The Raman spectra of the fabricated graphene/GaAs vdW heterostructures with different graphene layers are presented in Supplementary Fig. 1. The pristine mono-layer graphene exhibits two clear Raman peaks at ~1584 and 2676 cm⁻¹ corresponding to the G band and 2D band, respectively. Mono-layer, tri-layer, and five-layer graphene in our samples were identified by the intensity ratio between G band and 2D band, respectively. To realize a closed contact of graphene with the GaAs substrate, the graphene/GaAs heterostructure was irradiated with a Ti:sapphire femtosecond pulsed laser at different power densities varied from 38.2 to 61.6 MW cm⁻². Figure 2a illustrates the irradiating power density at selected positions, and the corresponding optical image of the irradiated areas is shown in Fig. 2b. The distance among the areas irradiated with the same power densities of the femtosecond laser is about 2 μm, and the...
distance among the areas irradiated with the different power densities of the femtosecond laser is about 3 μm.

The Raman spectra of the graphene/GaAs heterostructure treated with FLI at different power densities are presented in Fig. 2c. The Raman spectra of the mono-layer graphene/GaAs heterostructure remain the same as the non-irradiated sample until the irradiation laser power density exceeds 43.6 MW cm⁻². With the increase of the power density from 43.6 to 60.2 MW cm⁻², the third Raman peak at 1344 cm⁻¹ gradually appears and becomes stronger. In addition, the linewidths of the D band become narrower, while those of the G band and 2D band become wider, and the intensity ratio between the D band and G band increases with the increased laser power density, as shown in Fig. 2d, e. Further increasing the FLI power density above 60.2 MW cm⁻², no obvious change in the Raman peaks can be observed, which can be attributed to the serious thermal damage to the graphene. It is well known that the D band of the graphene is related to the breathing mode of the six-atom rings; the G band is associated with the in-plane stretching mode of C–C bonds, and the 2D band corresponds to a phonon resonance mode. In this work, when the power density is lower than 43.6 MW cm⁻², the energy of the femtosecond laser pulses is below the threshold to break the C–C bonds. As a result, the D band is not observed and the G band and 2D band are similar to those of the non-irradiated graphene. When the power density gets higher than 43.6 MW cm⁻², the C–C bonds are broken, leading to the quick broadening of the G band and 2D band, and the observation of the breathing mode-related D band. When the laser power density is much higher than 43.6 MW cm⁻², the decomposition of the underlying GaAs even occurs, which is confirmed by the energy-disperse spectroscopy (EDS) characterizations shown in Fig. 2f, manifested as the gradual decrease of the As elements with the increased FLI power density. This result suggests the possibility of intermixing C atoms with the atoms from GaAs.

FLI-induced bandgap opening in graphene

To investigate the graphene doping behavior as well as the carrier generation and transfer characteristics at the graphene/GaAs interface, a Schottky infrared photodetectors (SIPs) were fabricated with a single layer of graphene transferred onto the GaAs (Fig. 3a). A built-in electric field exists at the graphene/GaAs interface leading to the bending of the GaAs electron bands near the interface. Upon light illumination, electrons are excited in the graphene and migrate to GaAs driven by the built-in electric field to produce photocurrent and the holes accumulate at the surface of graphene. The I–V curves of the device illuminated with 1550 nm light ranging from 0 to 197 μW are presented in Fig. 3b. An efficient rectifying behavior with applied bias is observed and the direction of photocurrent from GaAs to graphene is confirmed by the negative circuit current. According to the I–V curve obtained in darkness, the conduction band offset (ΔE_C) is calculated to be 0.61 eV by using the thermionic-emission theory. The SIP device with the graphene/GaAs heterostructure was irradiated with a Ti:sapphire femtosecond pulsed laser at different power densities. It is found that, below 43.6 MW cm⁻², the photocurrent density (J) and ΔE_C remain the same as the non-irradiated samples, indicating the existence of a “threshold” of the graphene doping. As described in Fig. 1e, for the device treated with increased power density above 43.6 MW cm⁻², the J increases gradually, indicating enhanced carrier transfer efficiency. Irradiation densities of larger than 60.2 MW cm⁻² lead to thermal damage to the vdW heterostructure. Figure 3c shows I–V curves of the SIP device irradiated at a 56.4 MW cm⁻², revealing a ΔE_C value of 0.51 eV which is much smaller than the non-irradiated heterostructure. It should be noted that, at the incident power of 197 μW and at zero bias voltage, the obtained J of the irradiated graphene/GaAs heterostructure is about 20 times larger than the non-irradiated sample, confirming a significantly enhanced light harvesting and carrier transfer due to the bandgap opening in the graphene.

Figure 3d, g show the valence band spectra of highly oriented pyrolytic graphite (HOPG) and the GaAs substrate, whose VBM values are determined to be 0.81 and 0.29 eV, respectively, by extrapolating a linear fit of the leading edge of the valence band photoemission to the baseline. Figure 3e, h reveal the binding energy of 284.74 eV for C 1s core level and 1118.56 eV for Ga 2p core level in the heterostructures treated with FLI. In order to further demonstrate the doping of Ga atoms into the graphene lattice, further XPS analysis results, of the high-resolution spectra of C 1s core levels in a series of graphene/GaAs heterostructures treated with different laser power densities are presented in Supplementary Fig. 2, where the binding energy of 283.51 eV corresponding to the C–Ga bond is observed. This characteristic for C–Ga bonds has been reported by Lee et al.4 and Maa and

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**Fig. 2 Raman measurements of the vdW heterostructure.** a Power density distributions of the femtosecond laser for irradiating the graphene/GaAs vdW heterostructure. b Power density distributions of the femtosecond laser on the surface of the irradiated graphene/GaAs vdW heterostructure. The scale bar used is 3 μm. c Raman spectra of the graphene/GaAs vdW heterostructure irradiated by femtosecond laser with different power densities. d, e The irradiation power density-dependent linewidths and intensity ratio of Raman spectra for the irradiated graphene/GaAs vdW heterostructure. f The irradiation power density-dependent content ratio of As and Ga for the irradiated graphene/GaAs vdW heterostructure measured by EDS.
Dapkus$^{15}$, which confirms that Ga atoms are doped into the graphene lattice and C–Ga bonds are created. The graphene in the femtosecond laser-irradiated heterostructure exhibits a much larger bandgap value of 0.31 eV compared to the non-irradiated structure, as illustrated by the band alignment diagrams depicted in Fig. $3f$, $i$, which were obtained using the method referred in the “Methods” section. The parameters for calculating the band alignment of the graphene/GaAs heterostructures are listed in Supplementary Table 1. The calculated band structures of the monolayer graphene doped with respective Ga and As of the content varying in the range of 0.7–12.5% are shown in Supplementary Fig. 3. The Ga-doped graphene exhibits a bandgap ranging from 0.26 to 0.45 eV, while the As-doped graphene has a bandgap lower than 0.14 eV. We have found that the graphene bandgap in the graphene/GaAs heterostructure irradiated with 56.4 MW cm$^{-2}$ is about 0.31 eV, which lies in the range of the calculated bandgap of the Ga-doped graphene, confirming the doping of Ga atoms into the graphene lattice. To exclude the influence of the water residues between the graphene and the GaAs on the bandgap opening of the graphene after the FLI, the atomic force microscopy (AFM) images of the graphene/GaAs heterostructure before and after the FLI are presented in Supplementary Fig. 4.

Optical properties of hybrid SAs

As depicted in Fig. 4a, InGaAs capped and SSL capped InAs QD SESAM structures were grown by molecular beam epitaxy (MBE) and a dot density of about $4 \times 10^{10}$ cm$^{-2}$ has been revealed by the AFM image. SA samples including graphene SAs, QD SAs, and hybrid SAs combining InAs QDs and graphene/GaAs heterostructures were fabricated. The test samples which had identical structures as to the SAs except for the bottom DBR were also prepared to allow comparison of PL spectra. Both the test samples and SAs were irradiated for 2 min with the Ti:sapphire laser at the...
average power density of 56.4 MW cm$^{-2}$. Figure 4b shows the PL spectra measured at room temperature with the excitation laser of 633 nm. All the samples exhibit two emission peaks corresponding to the capping and QD layers, respectively. A slight redshift of the 1332 nm emission peaks in the TestQDSSL sample can be observed, which can be attributed to the weaker quantum confinement effect of QW structure composed of the capping and GaAs layers due to the thicker SSL capping layer. Strikingly, the TestQD sample capped with InGaAs layers exhibits a weaker QD emission than the capping layer emission, while a much stronger QD emission than the capping layer is observed with the TestQDSSL sample capped by SSL layer. The main reason responsible for the enhanced QD PL emission lies in high-quality SSL capping layer with the uniform distribution of indium and the indium content decreased to 25%, which effectively modulates the carrier relaxation behaviors and enhances the capture of carriers by the QDs. Moreover, in the TestQD sample, it is harder for the photon-generated carriers to relax from the capping layer to the QDs, owing to the phonon bottleneck effect, which leads to much weaker radiative recombination of the carriers in QDs. In addition, as expected for the hybrid SAs with graphene/GaAs heterostructures, obviously increased modulation depth and decreased saturation intensity have been achieved. Taking the SAQDSSL-G3 as an example, a saturation intensity <1/3 and a modulation depth 20 times greater than conventional SESAMs have been obtained as shown in Fig. 5a and Supplementary Table 2.

SA properties and mode-locking characteristics

As described in Supplementary Fig. 5, the nonlinear saturable adsorption properties of the SAs were acquired with a typical balanced twin-detector setup. The characteristics of the mode-locked EDF lasers measured with the representative SAs are listed in Supplementary Table 2. The obtained modulation depth of the SAQDSSL is four times larger than that of the SAQD, indicating the important impact of the SSL structure on the photon-generated carriers participating in the saturable absorption, i.e., the greatly enhanced carrier scattering and energy relaxation efficiency. In addition, as expected for the hybrid SAs with graphene/GaAs heterostructures, obviously increased modulation depth and decreased saturation intensity have been achieved. Taking the SAQDSSL-G3 as an example, a saturation intensity <1/3 and a modulation depth 20 times greater than conventional SESAMs have been obtained as shown in Fig. 5a and Supplementary Table 2.

When the SAQDSSL-G3 is irradiated by a 1550 nm continuous wave or pulse laser, the electron–hole pairs are separated in graphene...
and InAs QD layers. The generated electrons in the layer of graphene are transferred through the GaAs and SSL layers into the InAs QD layers, which effectively promote the bleaching process of SA. Therefore, the SAQDSSL sample exhibits lower saturation intensity than SAQDSSL. Extensive work was carried out to demonstrate SESAMs as a mature and highly functional component in stable mode-locked lasers. However, obtaining a low saturation intensity and a large modulation depth simultaneously is challenging for conventional SESAM designs. Mode-locked fiber ring lasers in the configuration depicted in Supplementary Fig. 6 have been constructed with different SA samples and mode-locked behavior has been observed in all cases. Mode-locking pulse train in the mode-locked laser based on SAQDSSL-G3 is shown in Fig. 5b. With the SAQDSSL sample, the pulse width of ~1.1 ps is obtained, while a narrower pulse width of ~680 fs is observed with the SAQDSSL-G3 sample at the central wavelength of 1559 nm with an associated bandwidth of 5.4 nm at 3 dB as shown in Fig. 5c, d. The radio frequency spectrum recorded at a span of 100 MHz is shown in Fig. 5e. The fundamental peak is located at 11.1 MHz, exhibiting a signal-to-noise ratio higher than 62 dB. Long-time stable mode-locking tests were carried out at a continuous pump current of 200 mA, and over 2 weeks stable operation was achieved. Figure 5f presents the result of the SAQDSSL-G3 sample, revealing an almost unchanged output power over the extended time period, which is a crucial feature for practical applications.

High repetition rate pulse fiber lasers have attracted considerable attention due to the widely practical applications in fields such as fiber communication system and astronomical frequency combs. Harmonic mode locking of a fiber laser can be usually utilized to obtain high repetition rate pulse. As pump current increases from 295 to 600 mA, the harmonic pulse train of different orders (3rd, 11th, 18th, 21st, 27th, and 34th) with the span of 70 ns are obtained by employing the irradiated SAQDSSL-G3, as shown in Fig. 6a, respectively. At the same time, the output power increases from 2.1 to 7 mW and the repetition rate of the harmonic mode-locked fiber laser gradually increases from 33.3 to 377.4 MHz (34th harmonic of fundamental repetition frequency), as shown in Fig. 6b–d. Moreover, the long time stable harmonic mode-locked pulses can also be observed at different pump powers. The stable 377.4 MHz harmonic mode-locked fiber laser based on the irradiated SAQDSSL-G3, indicating these hybrid SESAMs have great potential in optical communication systems.

**DISCUSSION**

In this work, we have demonstrated the enhancement of both the photon harvesting and carrier transfer efficiencies in the graphene/III–V semiconductor vdW heterostructure due to the bandgap opening of graphene induced by the method of FLI. To verify the carrier transfer characteristics and bandgap opening of graphene, SIP devices were fabricated by transferring the graphene onto a GaAs substrate. The measured photocurrent density of the SIP device irradiated with a Ti:sapphire femtosecond pulsed laser at power density of 56.4 MW cm$^{-2}$ is 20 times larger than the non-irradiated device, which can be ascribed to the bandgap opening of 0.31 eV in graphene due to the FLI-induced C and Ga atoms exchange at the graphene/III–V semiconductor. Fully benefitting from the bandgap opening of graphene, we have developed a SA combining a delicately engineered graphene/GaAs vdW heterostructure with InAs QDs capped with SSLs. By controlling the layer number of graphene, the saturation intensity is tuned from 3.3 to 13.7 MW cm$^{-2}$ and the modulation depth is...
Graphene plasma-enhanced chemical vapor deposition method as shown in Fig. 3a. Deposited on the thinned semi-insulation (SI)-GaAs substrate by using SAQDSSL was capped with a 10 nm InGaAs layer. The high-quality SSL capping layer with uniform distribution of indium can effectively modulate the carrier relaxation behaviors and enhance the capture of carriers by the QDs, which is critical for the transfer behaviors of the photo-generated carriers.

Before wet-chemical transfer process of graphene, a 200 nm SiO2 layer was deposited on the thinned semi-insulation (SI)-GaAs substrate. The water bubbles in the graphene and SiO2/ST-GaAs interface were removed by slow air blowing. After that, two rectangle metal electrodes including a Ti/Au electrode with an area of 0.04 cm2 and an Au/Ni/Ge/Au electrode with an area of 0.1 cm2 were deposited to form the top and bottom ohmic contacts, respectively.

The asymmetric DWELL structure with different types of capping layers. As shown in Fig. 4a, the InAs QDs in the SAQD sample were grown on 1 nm In0.18Ga0.82As layer with a capping layer of 6 nm In0.35Ga0.65As, while SAQDSSL was capped with a 10 nm InGaAs layer. The high-quality SSL capping layer with uniform distribution of indium can effectively modulate the carrier relaxation behaviors and enhance the capture of carriers by the QDs, which is the main factor responsible for the enhanced QD PL emission.

MBE growth of the SESAM structures

Two QD SESAM samples comprising a single QD absorption layer and a bottom GaAs/AlGaAs DBR were grown with solid-source MBE, which have an asymmetric DWELL structure with different types of capping layers. As shown in Fig. 4a, the InAs QDs in the SAQD sample were grown on 1 nm In0.18Ga0.82As layer with a capping layer of 6 nm In0.35Ga0.65As, while SAQDSSL was capped with a 10 nm InGaAs layer. The high-quality SSL capping layer with uniform distribution of indium can effectively modulate the carrier relaxation behaviors and enhance the capture of carriers by the QDs, which is the main factor responsible for the enhanced QD PL emission.

Calculations of band alignment for graphene/GaAs heterostructure

One of the key parameters in designing a heterojunction is the band offset which is critical for the transfer behaviors of the photo-generated carriers. To gain insight into the electronic structure of the irradiated and non-irradiated graphene/GaAs interfaces, high-resolution XPS analysis was performed and the spectra of the valence bands, C1s, and GaAs core levels were all measured on HOPG, the GaAs substrate, and the irradiated and non-irradiated graphene/GaAs heterostructures. Figure 3d, g show the valence band spectra of HOPG and the GaAs substrate, whose VBM values are determined to be 0.81 and 0.29 eV, respectively, by extrapolating a linear fit of the leading edge of the valence band photoemission to the baseline. The C1s spectra for HOPG and the non-irradiated graphene/GaAs heterostructure are shown in Fig. 3e, revealing the binding energies of 284.31 and 284.61 eV, respectively. The Ga 2p spectra in Fig. 3h exhibit the binding energies of 1118.35 and 1118.37 eV for the GaAs substrate and the non-irradiated graphene/GaAs heterostructure, respectively. The valence band offset (VBO) of the graphene/GaAs heterostructure can be determined according to the relation:

$$\Delta E_v = \Delta E_{CL} + \left( E_{VBM}^{HOPG} - E_{VBM}^{GaAs} \right) - \left( E_{VBM}^{HOPG} - E_{VBM}^{GaAs}\right) \left( VBM \right)$$

where $\Delta E_{CL}$ is the difference in the binding energy between Ga 2p and C 1s core levels at the non-irradiated graphene/GaAs interface, and $\left( E_{VBM}^{HOPG} - E_{VBM}^{GaAs}\right)$ and $\left( E_{VBM}^{HOPG} - E_{VBM}^{GaAs}\right)$ are the valence band maxima (VBM) energies with reference to the core level peaks in the single layer graphene and the GaAs substrate, respectively. Moreover, the bandgap ($\Delta E_{Graphene}^{GaAs}$) of the graphene transferred onto the GaAs substrate can be estimated by the formula:

$$\Delta E_{Graphene}^{GaAs} = E_{GaAs} - \Delta E_v$$

By using the room-temperature bandgap value ($E_{GaAs}$) of 1.43 eV, $\Delta E_{Graphene}^{GaAs}$ is calculated to be 0.02 eV. As a result, the schematic band alignment diagram of the graphene/GaAs heterostructure is depicted in Fig. 3f.

Femtosecond laser-induced doping treatment

The graphene/GaAs vdW heterostructures studied in this work were fabricated by wet-chemical transfer of graphene layers onto GaAs surface and then were irradiated for 2 min with a femtosecond Ti:sapphire laser (center wavelength: 740 nm, pulse duration: 130 fs, repetition rate: 76 MHz). The power density employed for the FLI treatment is in the range of 0–70.3 MW cm$^{-2}$.

DATA AVAILABILITY

The datasets generated during and/or analyzed during the current study are available from the corresponding author on reasonable request. All data generated or
analyzed during this study are included in this published article (and its Supplementary Information).

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AUTHOR CONTRIBUTIONS

Z.Y.Z conceived the original idea. Z.Y.Z., C.T.A.B., and J.Q.N supervised the project. X.W. and X.H.L. carried out the materials and devices characterizations. Z.Y.Z grew the QD-SESAMs, and X.W., Q.Y. and C.J. made the graphene-coating process. X.W., X.T.G., and J.Q.N. performed the laser irradiation annealing process and photoresponse characterization. X.W. performed the XPS measurements. X.W. and C.J. finalized the schematic images. All authors helped in analyzing and interpreting the data. Z.Y.Z., C.T.A.B., J.Q.N., X.W., X.H.L., and Q.J.W. wrote the paper and all authors commented on it.

COMPETING INTERESTS

The authors declare no competing interests.

ADDITIONAL INFORMATION

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