Solid-state reaction synthesis of two-dimensional CuGaSe$_2$ nanosheets for high performance photodetectors†

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CuGaSe$_2$ is an important non-layered I–III–VI$_2$ compound with superior optical properties. In this work, monocrystal two-dimensional (2D) CuGaSe$_2$ nanosheets were successfully synthesized via a simple solid-state reaction. The electronic and optoelectronic properties of photodetectors based on 2D CuGaSe$_2$ nanosheets were investigated for the first time. 2D CuGaSe$_2$ FETs present a typical p-type conductance behaviour, and photodetectors based on 2D CuGaSe$_2$ show a sensitive response to the UV-visible spectrum. Under 490 nm light illumination, the responsivity and detectivity of photodetectors are as high as 10$^3$ AW$^{-1}$ and 8 × 10$^{11}$ Jones, respectively. Our results offer a new opportunity to use 2D CuGaSe$_2$ nanosheets for future nano-optoelectronic devices.

Introduction

Because of their unique structure and fascinating physical properties, two-dimensional (2D) materials have emerged as basic building blocks of future electronic and optoelectronic devices, such as transistors, diodes and photodetectors.$^{1-8}$ Although 2D compounds offer new opportunities for nanodevices, the species are still limited to layered compounds, such as transition metal dichalcogenides (TMDs).$^{1-8}$ It is a great challenge to fabricate 2D non-layered compounds, due to the difficulty in cleaving the bond of non-layered compounds, although 2D layered compounds can be fabricated by mechanical exfoliation,$^{1,9}$ CVD synthesis$^{10,11}$ and liquid exfoliation.$^{12,13}$

The colloidal template method is regarded as an effective way to produce 2D non-layered compounds, however nonvolatile organic solvents and templates are difficult to remove and the occurrence of aggregation during the solvent evaporation process makes their application in devices difficult. Photodetectors, which convert incident optical signals into electrical signals, are element building blocks used for space communication and chemical/biological detection.$^{7}$ Recently, 2D semiconductors have attracted great attention for application in photodetectors,$^{6-8,14-18}$ and optoelectronic devices have been demonstrated using various 2D compounds of MoS$_2$, GaSe, GaS, GaTe and InSe.$^{6-8,14-18}$ Photodetectors based on MoS$_2$ show tunable spectral photoresponse by channel thickness$^{6,14,15}$ and are ultrasensitive to visible light with responsivity reaching as high as 880 AW$^{-1}$.$^{16}$ UV-visible photodetectors based on few-layer GaSe and GaS nanosheets are investigated and exhibit responsivities of 2.8 AW$^{-1}$ and 19.2 AW$^{-1}$, respectively.$^{7,8}$

Multilayer GaTe photodetectors have been demonstrated to present a high photoresponsivity of 10$^3$ AW$^{-1}$ for UV-visible light.$^{17}$ Photodetectors based on multilayer InSe show a high responsivity of 104 AW$^{-1}$ and a wide spectral response from the UV to IR region.$^{18}$

Copper gallium selenide (CuGaSe$_2$), a typical I–III–VI$_2$ chalcopyrite compound, is an effective light-absorbing material due to its suitable direct band-gap of 1.67 eV and high optical absorption coefficients.$^{19}$ CuGaSe$_2$-based thin film devices have been impeded by widespread commercialization, due to limitations such as the complexity and high cost of fabrication processes or the difficulties in obtaining single crystals. Recently, a lot of attention has been focused on the synthesis and properties of CuGaSe$_2$ nanoparticles.$^{19-22}$ Colloidal CuGaSe$_2$ nanoparticles have been successfully synthesized in oleylamine, and the nanoparticle size and composition are tunable through manipulation of the reaction temperature and precursor concentrations.$^{19}$

Panthani et al. reported that high-yield CuGaSe$_2$ nanocrystal “inks” were obtained through arrested precipitation in solution. The nanocrystals readily disperse in various nonpolar solvents and can be deposited as uniform crack-free micrometer-thick films onto glass and metal substrates.$^{20}$ Syntheses of CuGaSe$_2$ quantum dots have been demonstrated,$^{21}$ and the size of quantum dots could be tuned by growth temperature, reaction time and precursor concentration. Li and co-workers
successfully synthesized CuGaSe₂ nanocrystals by a hot-injection process using TETA assisted diethylene glycol solution under air pressure conditions with advantages of processing safety and manipulation facility. To the best of our knowledge, there is no report on the synthesis of 2D CuGaSe₂ nanosheets and investigation of 2D CuGaSe₂ photodetectors.

In this letter, monocrystal 2D CuGaSe₂ nanosheets were successfully fabricated via a simple solid-state reaction for the first time. The field effect transistors (FETs) based on 2D CuGaSe₂ nanosheets exhibit a typical p-type transistor behaviour. 2D CuGaSe₂ photodetectors show a broad range of spectral response from UV (254 nm) to visible (700 nm). Under 490 nm light illumination, the responsivity and detectivity are 103 AW⁻¹ and 8 × 10¹¹ Jones, respectively, which is comparable to or higher than those of other 2D layered semiconductors, such as MoS₂, GaSe, GaS.

Experimental

The entire synthesis process of 2D CuGaSe₂ nanosheets by the templated solid-state reaction from GaSe nanosheets is illustrated in Fig. 1a. The 2D GaSe nanosheets were fabricated by mechanical exfoliation and transferred to the n⁺ Si substrate coated 300 nm SiO₂ as shown in Fig. 1a (left image) and Fig. 1b. Then suitable GaSe nanosheets were identified using an optical microscope and were covered with a 50 nm Cu film by thermal evaporation, and the violet balls represent copper film as shown in Fig. 1a middle image. These copper coated GaSe nanosheets were annealed in a tube furnace at a temperature of 350 °C for 30 min with 100 sccm of Ar. After annealing, there is residual Cu on the nanosheets, and in order to evaluate the electronic and optoelectronic properties of 2D CuGaSe₂ nanosheets, it is necessary to remove excess Cu. A simple cleaning step of 5 min submersion in 3 M aqueous FeCl₃ is sufficient for this goal. Optical images of 2D GaSe nanosheets (Fig. 1b), after annealing and copper cleaning (Fig. 1c), show that the overall nanosheet morphology is preserved during the templated solid-state reaction and cleaning steps.

The structure and morphology were characterized by transmission electron microscopy (TEM), selected area electron diffraction (SAED) and energy dispersive X-ray spectroscopy (EDS) (FEITECNAL High Resolution TEM operated at 300 kV). The substrates with CuGaSe₂ nanoflakes were immersed in 1% HF solution for 5 s to etch silica. Then CuGaSe₂ nanoflakes in solution were fished up using carbon films supported on Au grids for TEM tests. Optical images of CuGaSe₂ nanoflakes were taken using an OLYMPUS BX41. The thickness of synthesized CuGaSe₂ nanoflakes was determined by using atomic force microscopy (AFM) in tapping mode with a commercial multimode Nanoscope IIIa (Veeco Co. Ltd). Raman spectra and photoluminescence spectra (PL) were measured using a Lab-RAM Xplora laser Raman spectrometer (Horiba JobinYvon CO. Ltd) at room temperature. The wavelength and intensity of the laser used for Raman spectroscopy and PL is 532 nm and 1 mW, respectively. To investigate electronic and optoelectronic properties of 2D CuGaSe₂ nanoflakes, field-effect transistors (FETs) were fabricated and Cr/Au electrodes were deposited by thermal evaporation with shadow masks. Monochromatic wavelengths of 254 nm, 365 nm, 490 nm, 550 nm, 610 nm and 700 nm were obtained using optical filters with a 500 W xenon lamp. All optical intensities are measured behind the filter using a power and energy meter (Model 372, Scienteck). The electronic and optoelectronic properties were characterized using a Keithley 4200-SCS on the Lakeshore probe station at room temperature in an ambient environment.

Results and discussion

The synthesized CuGaSe₂ samples were characterized by Raman spectra, AFM, PL spectra and TEM. The contrast colours of as-synthesized nanosheets are obviously different from the initial GaSe as present in Fig. 1b and c, suggesting that this reaction could be preliminarily judged by this simple and convenient way. Fig. 2a shows Raman spectra of GaSe nanosheets and annealing nanosheets, which are entirely different. The Raman peaks of GaSe all disappear in the annealing samples, and all three Raman peaks can be primarily indexed to CuGaSe₂, suggesting that GaSe nanosheets were completely transformed into CuGaSe₂. The main peak is the A₁ mode of 184 cm⁻¹ and there is no shift compared with the value of bulk CuGaSe₂, which suggest the good crystallinity of CuGaSe₂ nanosheets. And the other weak peaks (247 cm⁻¹ and 270 cm⁻¹) belonged to the E mode, and there is obvious shift compared with the values (239 and 261) of bulk CuGaSe₂, which can be attributed to low defect state densities introduced during the synthesis process. The PL spectra of GaSe shows a peak value of 2.05 eV, which is consistent with the bandgap of GaSe. After annealing, the PL peak value of the 2D CuGaSe₂ nanosheet (16 nm) shifts to 1.71 eV and takes a
blue-shift compared with 1.67 eV of CuGaSe₂ film as shown in Fig. S1 (ESI†), which is attributed to planar quantum confinement of photo-excited carriers by the external surfaces of the flakes. The differences in PL also indicate that the solid-state reaction completely proceeded. The thickness of CuGaSe₂ nanosheets is identified by AFM. As shown in Fig. S2 (ESI†), the thinner 2D CuGaSe₂ nanosheet is 6 nm, and the surface is rough. The rough surface can be ascribed to two following reasons: (1) the CuGaSe₂ nanosheets are synthesized at a solid-state reaction at 623 K for 30 min. The reaction temperature will aggravate lattice vibration and introduce some defects. (2) The solid-state reaction is a replacement reaction:

\[2\text{GaSe} + \text{Cu} = \text{CuGaSe}_2 + \text{Ga}\]

The generated Ga will escape from the nanosheets and also produce some defects. All these can make the CuGaSe₂ nanosheet surface rough. The structure and morphology of 2D CuGaSe₂ nanosheets are further characterized by TEM. Fig. 2c presents a low magnification TEM image. The surface of the CuGaSe₂ nanosheet is clean, suggesting that unreacted copper is cleaned. In Fig. 2c inset, the selected area electron diffraction (SAED) pattern shows that the as-synthesized 2D CuGaSe₂ nanosheets are monocrystal. The monocrystal structure of CuGaSe₂ nanosheets is further confirmed by the high-resolution TEM (HRTEM) pattern as shown in Fig. 2d. The chemical compositions of the CuGaSe₂ sample were detected by the energy-dispersive X-ray spectroscopy (EDS) (Fig. S3, ESI†), showing the CuGaSe₂ with a Cu/Ga/Se atomic ratio close to 1:1:2. All the above evidence confirms that the synthesized CuGaSe₂ nanosheet has a good and uniform crystal structure.

With the successful synthesis of high-quality monocrystal 2D CuGaSe₂ nanosheets, it is possible to carry out nano-device fabrication. The 2D CuGaSe₂ field-effect transistors (FETs) were fabricated on 300 nm SiO₂/Si substrates using a shadow mask combined with metal thermal evaporation. Fig. 3a shows the 3D schematic of CuGaSe₂ FETs. An optical image of CuGaSe₂ FETs is shown in Fig. 3b, and the corresponding AFM image and AFM height profile is presented in Fig. S4 of ESI†. The channel thickness is 16 nm (Fig. S4b, ESI†). The electrical characteristics of CuGaSe₂ FETs with Cr/Au contacts were
measured under the ambient environment. Fig. 3c presents a transfer curve measured at $V_{ds} = 1$ V. The current drops with increasing gate voltage, indicating that a p-type conductance is produced as desired. The mobility of CuGaSe$_2$ FETs can be extracted from the linear region in Fig. 3c using the following equation: $\mu = \frac{L}{W(C_i/V_{ds})} \times \frac{d(I_{ds}/dV_{g})}{dV_{g}}$, where $L$ is the channel length of 35 $\mu$m, $W$ is the channel width of 10 $\mu$m, $C_i = \varepsilon_0 d/e$, $\varepsilon_0 = 8.854 \times 10^{-12}$ F m$^{-1}$ is the vacuum permittivity, $e_i$ is 3.9 for SiO$_2$ and $d$ is 300 nm for the thickness of SiO$_2$. The calculated mobility value is 0.21 cm$^2$ V$^{-1}$ s$^{-1}$, which is comparable to that of monolayer or few layer GaSe FETs. Similar to other 2D semiconductors, the mobility of CuGaSe$_2$ nanosheets is lower than that of CuGaSe$_2$ films. This is attributed to the stronger scattering effects from the interface between the substrate and materials in ultrathin 2D systems. The output characteristic of CuGaSe$_2$ FETs is shown in Fig. 3d. The source-drain current linearly depends on bias voltage, suggesting that the CuGaSe$_2$/Cr contact is ohmic contact. The output current also degrades with gate voltage increasing, demonstrating a p-type conductance.

To investigate the optoelectronic behaviour of 2D CuGaSe$_2$ nanosheet photodetectors, monochromatic light illumination was directed vertically onto devices. Optoelectronic properties of 2D CuGaSe$_2$ nanosheet photodetectors were measured under various light wavelengths and light intensities (shown in Fig. 4a and Fig. S5, ESI†). Our photodetector exhibits a wide spectral response from the ultraviolet to visible spectrum as shown in Fig. 4a, which is similar to CuGaSe$_2$ bulk films as shown in Fig. S5a (ESI†). The photocurrents $I_{ph}$ ($I_{ph} = I_{illumination} - I_{dark}$) increase with the bias voltage $V_{ds}$, due to the increase in carrier drift velocity and the related decrease of carrier transit time $T_i$ under high bias voltage.

Responsivity ($R_i$) is a critical parameter to evaluate the performance of a photodetector. The $R_i$ is defined as the photocurrent generated per unit power of the incident light on the effective area of a photodetector. The $R_i$ can be calculated using the following equations: $R_i = I_{ph}/P.S$. Here, $I_{ph}$ is the generated photocurrent, $P_i$ is the incident light intensity, $S$ is the effective illuminated area. Fig. 4b presents the wavelength dependent responsivity, confirming that our 2D CuGaSe$_2$ nanosheet photodetectors are responsive to a broad spectral range from UV to visible. Responsivity measured under broadband illumination of ultraviolet (254 nm), visible (490 nm), and 700 nm are $R_{254\text{nm}} = 123.7$ AW$^{-1}$, $R_{490\text{nm}} = 102.7$ AW$^{-1}$ and $R_{700\text{nm}} = 73$ AW$^{-1}$, respectively. The responsivity of 2D CuGaSe$_2$ nanosheet photodetectors even largely surpass most presently reported values for other 2D materials based photodetectors including MoS$_2$, GaSe, GaS, GaTe and InSe. Photodetectors based on 2D CuGaSe$_2$ nanosheets present a higher photo-responsivity than CuGaSe$_2$ films as shown in Fig. S6b (ESI†). The higher photo-responsivity of 2D CuGaSe$_2$ nanosheets is attributed to a larger surface-to-volume ratio.

Another important parameter to evaluate the performance of the photodetectors is the specific detectivity ($D^*$). The shot noise from the dark current is the major contributor to the total noise in this case, the detectivity can be calculated by the $D^* = R A^{1/2}/(2e I_d)$, where $R$ is responsivity, $A$ is the area of the photodetector channel, $e$ is the electronic charge, and $I_d$ is dark current. Fig. 4b shows the calculated $D^*$ of the photodetector at different wavelengths. For the whole responsive spectral range, the $D^*$ is in the range of $\sim 10^{11}$ Jones, which is compared to photodetectors based on MoS$_2$ and GaSe.

Fig. S5 (ESI†) shows $I_{ds}$-$V_{ds}$ curves of photodetectors measured under various light intensities at a constant illumination wavelength of 700 nm. The generated $I_{ph}$ increases with the light intensity increasing from 0.29 mW cm$^{-2}$ to 0.71 mW cm$^{-2}$. 2D CuGaSe$_2$ nanosheet photodetectors can generate a light intensity dependent photocurrent $I_{ph}$. To study the relationship between $I_{ph}$ and the light intensity, Fig. 4c shows the plot of $I_{ph}$ vs. light intensity at a bias voltage of 5 V, which is based on the results in Fig. S3 (ESI†). The $I_{ph}$ is linearly proportional to light intensity, and shows a power dependence with an exponent of 0.5 ($I_{ph} \sim P^{0.5}$). The good linear relationship between $I_{ph}$ and light intensity confirms that generated photocurrent is determined by the quantity of photogenerated carriers under illumination. However, as the illumination intensity is increased, both responsivity and detectivity are degraded, which is due to the trap states existing at CuGaSe$_2$ or at the interface between CuGaSe$_2$ and the dielectric substrate.

The stability and response speed are two other important parameters for evaluating a photodetector. Fig. 5a shows a transient photocurrent of our CuGaSe$_2$ nanosheet device measured under a bias voltage of 5 V at a light intensity of 0.29 mW cm$^{-2}$. With the light irradiation at 490 nm on and off, our CuGaSe$_2$ nanosheet photodetectors exhibit repeatable and stable response to incident light after five cycles from the “on” state to the “off” state. It is an obvious behavior that photocurrent rise and decay involves both a fast and a slow process. In order to show the rise and decay process clearly, we enlarge
the rise and decay edges (as shown in Fig. 5b). Response time is calculated by averaging the duration values between light-ON and light-OFF (corresponding to 90% increase or decay, the red line). We take the equations $I(t) = I_d + A \exp(t/\tau_1) + B \exp(t/\tau_2)$ for the rise process and $I(t) = I_d + A \exp(-t/\tau_1) + B \exp(-t/\tau_2)$ for the decay process to describe the rise and decay processes of transient photoresponse, where $t$ is the time of light which was turned on or off, $I_d$ is the dark current, $A$ and $B$ are the scaling constants, $\tau_1$ and $\tau_2$ are two time constants. The red solid lines are the fitting results, from which faster ($\tau_1$) and slower ($\tau_2$) times can be calculated to be 0.1 s and 1.5 s for the rise process, and 0.7 s and 5.9 s for the decay process, respectively. Two time constants of photoreponse indicate that two mechanisms control the whole process, and the fast decay process is attributed to direct band-to-band recombination of carriers and the slow decay process is attributed to the existence of hole trap states in CuGaSe$_2$ nanosheets. The hole trap states are attributed to introduced defects during the synthesis process as mentioned above.

Conclusions

In conclusion, 2D CuGaSe$_2$ nanosheets were successfully synthesized via a simple solid-state reaction without any template and the electronic and optoelectronic properties of 2D CuGaSe$_2$ nanosheet photodetectors were investigated for the first time. 2D CuGaSe$_2$ FETs present a typical p-type conductance behavior. The 2D CuGaSe$_2$ photodetectors show a sensitive response to the UV-visible spectrum. Under 490 nm light illumination, the responsivity and detectivity of photodetectors are as high as 103 AW$^{-1}$ and 8 x 10$^{11}$ Jones, respectively. Our results may pave the way for using 2D CuGaSe$_2$ nanosheets for future nano-optoelectronic devices.

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Notes and references