Band-tunable photodetectors based on graphene/alloyed \( \text{Zn}_x\text{Cd}_{1-x}\text{S} \) film hybrids

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Graphene/semiconductor film hybrid-based photodetectors have attracted extensive attention because of their ultra-high performance. However, only the photoconductive behavior of binary semiconductors with fixed bandgap was studied since achieving tunable optoelectronic properties is significant for the practical applications of semiconductors. Herein, alloyed \( \text{Zn}_x\text{Cd}_{1-x}\text{S} \) \((0 \leq x \leq 1)\) films with complete compositional tunability were successfully prepared by an e-beam evaporation method via changing the molar ratio of \( \text{ZnS} \) to \( \text{CdS} \) in the target. UV-visible optical absorption measurements showed that the composition-dependent band-edge absorption is generated in the as-prepared alloyed \( \text{Zn}_x\text{Cd}_{1-x}\text{S} \) films, with the energy gaps continuously shifted from 2.41 eV \((x = 0, \text{CdS})\) to 3.67 eV \((x = 1, \text{ZnS})\). After graphene is transferred on the alloyed \( \text{Zn}_x\text{Cd}_{1-x}\text{S} \) films, band-tunable photodetectors are achieved based on graphene/alloyed \( \text{Zn}_x\text{Cd}_{1-x}\text{S} \) film hybrids with the cut-off wavelength in the spectral response gradually changing from 410 nm to 580 nm. Obviously, the method introduced in this study can be extended to fabricate other graphene/alloyed ternary film hybrid-based photodetectors with band tunability in the visible and infrared region.

However, achieving tunable optoelectronic properties is significant for the practical applications of semiconductors. Therefore, it is desirable to achieve band-tunable graphene/semiconductor film hybrid-based photodetectors.

Alloying of binary semiconductors is an important approach to achieve tunable optoelectronic properties via composition modulation. Our previous study illustrates that \( E_g(\text{AB},C_{1-x}) \) \((\text{the energy gap of the binary compound AB to } E_g(\text{AC})) \) and \( E_g(\text{AB}) \) \((\text{the energy gap of the binary compound AB})\) can be continuously tuned from \( E_g(\text{ZnS}) \) to \( E_g(\text{ZnS}) \) as the composition \( x \) varies. This approach has been widely utilized to obtain tunable optoelectronic properties including photoluminescence, lasing, and photocatalysis. However, only few studies have reported nanowire-based band-tunable photodetectors based on the abovementioned bandgap engineering.

To the best of our knowledge, graphene/semiconductor film hybrid-based photodetectors with band tunability have never been reported.

In view of the tunable photoconductive properties of graphene/alloyed film hybrids, ternary \( \text{Zn}_x\text{Cd}_{1-x}\text{S} \) \((0 \leq x \leq 1)\) is a good candidate. As a wide-gap II–VI semiconductor, \( \text{ZnS} \) and \( \text{CdS} \) have a bandgap of 3.67 eV and 2.41 eV, respectively, which implies that \( \text{ZnS} \) and \( \text{CdS} \) are potentially excellent photoactive materials for photodetectors. Several studies have investigated the photocatalytic activity and photoelectrochemical performance of the graphene/alloyed \( \text{Zn}_x\text{Cd}_{1-x}\text{S} \) hybrids. In this study, we prepared alloyed wide bandgap \( \text{Zn}_x\text{Cd}_{1-x}\text{S} \) \((0 \leq x \leq 1)\) films by e-beam evaporation method by changing the molar ratio of \( \text{ZnS} \) and \( \text{CdS} \) compositions.
to CdS in the target, and for the first time, examined the band-tunable photoconductive properties of graphene/allloyed Zn$_x$Cd$_{1-x}$S film hybrids.

2. Experimental

2.1. Preparation of the Zn$_x$Cd$_{1-x}$S film

ZnS (99.99% purity) and CdS (99.99% purity) powders with different molar ratios were mixed and ground in a grinding dish for 30 minutes. After this, the mixed powders were sintered at 950 °C for 1.5 hours with 10 sccm H$_2$ and 20 sccm Ar. With the sintered Zn$_x$Cd$_{1-x}$S powders as targets, the Zn$_x$Cd$_{1-x}$S film with a thickness of 60 nm was deposited on a 300 nm SiO$_2$/Si substrate by e-beam evaporation. The vacuum remained at 2 x 10$^{-4}$ Pa during the entire deposition process. Before the graphene transfer, the Zn$_x$Cd$_{1-x}$S film on the Si/SiO$_2$ substrate was annealed for 30 min at 300 °C under low pressure with 10 sccm H$_2$ and 20 sccm Ar, enabling the film adhesion to the substrate as it was placed in water to pick up the graphene films.

2.2. Graphene growth and transfer

The details of graphene growth and transfer can be found in our previous studies, except that the PMMA carrier for graphene transfer was removed by annealing for 2 hours at 400 °C under low pressure with 10 sccm H$_2$ and 20 sccm Ar. This method enables the crackless transfer of graphene.

2.3. Transistor fabrication

After PMMA was removed, devices with a channel length of 20 μm and width of 500 μm were fabricated with a shadow mask. The doped Si substrate served as a global back gate. Cr/Au (10 nm/100 nm) was used as the electrical contact metal for the source and drain electrodes were deposited using a high-vacuum thermal evaporation system.

2.4. Characterization and measurement

The composition of Zn$_x$Cd$_{1-x}$S films was characterized via energy dispersive X-ray spectroscopy (EDX) using a Hitachi SU8020 scanning electron microscope and via X-ray photoelectron spectroscopy (XPS) (ESCALAB250Xi). XRD patterns of the samples were obtained using an X-ray diffractometer (X’Pert Pro MPD) with λ = 1.54056 Å. UV-vis absorption (UV-3600) was conducted on the samples after they were transferred on a quartz substrate. The microstructure of Zn$_x$Cd$_{1-x}$S was characterized by transmission electron microscopy (TEM) (Tecnai G2 F20). The electrical and photoconductive properties of the graphene/CdS film and graphene/Zn$_x$Cd$_{1-x}$S film hybrid devices were measured by a semiconductor parameter analyzer system (Keithley 2636B) at room temperature using light emitting diodes with the corresponding wavelength as the incident light.

3. Results and discussion

3.1. Surface information and composition

To investigate the surface information and determine the composition x of the as-deposited ternary Zn$_x$Cd$_{1-x}$S films, EDX mapping and XPS analysis was carried out. The uniform distribution of Zn, Cd, and S in the EDX mapping shows that the as-deposited film is Zn$_x$Cd$_{1-x}$S (Fig. 1a–c). Fig. 1d–f show the XPS survey spectra of the alloyed Zn$_x$Cd$_{1-x}$S films obtained by e-beam evaporation with the targets having various ZnS/CdS molar ratios of 2 : 8, 5 : 5, 7 : 3, 8 : 2, and 9 : 1. The XPS peaks of Zn 2p$_3/2$, Zn 2p$_1/2$, Cd 3d$_{5/2}$, Cd 3d$_{3/2}$, and S 2p for the alloyed Zn$_x$Cd$_{1-x}$S films are located at around 1022.5 eV, 1045.5 eV, 405.2 eV, 412.0 eV, and 162.7 eV, respectively, which are all in agreement with the corresponding binding energies of Zn$_x$Cd$_{1-x}$S. The radii of the Zn$^{2+}$ ions (0.74 Å) are smaller than those of the Cd$^{2+}$ ions (0.97 Å), leading to shorter bond lengths of Zn–S than those of Cd–S. The local environment around Cd$^{2+}$ ions would be changed due to the substitution of Zn$^{2+}$ ions in place of Cd$^{2+}$ ions in the CdS lattice. Therefore, the variation of the coordination environments around the S$^{2-}$ ions would affect the position of the binding energy of S 2p, leading to a shift of the binding energy to high values as the number of Zn$^{2+}$ ions increases. The area under the peaks was calibrated to obtain the Zn/Cd ratio, namely composition (x) values. The compositions of the ternary Zn$_x$Cd$_{1-x}$S films obtained by e-beam evaporation with the targets having various ZnS/CdS molar ratios of 2 : 8, 5 : 5, 7 : 3, 8 : 2, and 9 : 1 were calculated to be x = 0.23, 0.59, 0.72, 0.82, and 0.95, respectively, as shown in Table 1.

3.2. Crystallinity and microstructure

The crystallinity and microstructure of Zn$_x$Cd$_{1-x}$S films were characterized by TEM. The TEM images in Fig. 2a, c, and e show the film morphology after the deposited Zn$_x$Cd$_{1-x}$S films on 300 nm SiO$_2$/Si substrate were dispersed in ethanol. The selected-area electron-diffraction (SAED) patterns (insets in Fig. 2a, c, and e) confirm that the as-deposited films are polycrystalline. Combining the high-resolution TEM (HRTEM) images with the corresponding Fourier transform images in Fig. 2b, d, and f, the as-deposited Zn$_x$Cd$_{1-x}$S films with x = 0.23 and 0.59 are characterized to have the hexagonal wurtzite structure, whereas Zn$_x$Cd$_{1-x}$S films with x = 0.82 have the zinc blende structure. This phenomenon that the structure of the alloys is related to the composition was also reported by another group. Furthermore, the interplanar distances of {100} for hexagonal Zn$_x$Cd$_{1-x}$S with x = 0.23 and 0.59 are 3.56 Å and 3.35 Å, respectively, confirming that the interplanar distances of Zn$_x$Cd$_{1-x}$S films vary with the composition x.

3.3. Crystal structure

The X-ray diffraction (XRD) measurements were further conducted to investigate the structure of all Zn$_x$Cd$_{1-x}$S samples with different x values, as shown in Fig. 3. Curves (a) and (g) are for the pure ZnS and CdS films, respectively, which correspond to the respective bulk zinc blende ZnS (JCPDS 77-2100) and wurtzite CdS (JCPDS 70-2553) crystals. Curves (b)–(f) are for the samples obtained by e-beam evaporation with the targets having various ZnS to CdS molar ratios of 9 : 1, 8 : 2, 7 : 3, 5 : 5, and 2 : 8, respectively. The XRD patterns revealed that the
ternary Zn$_{x}$Cd$_{1-x}$S films over the compositions of $x = 0.95, 0.82, \text{and } 0.72$ have the zinc blende structure, whereas the ternary films with the composition of $x = 0.59$ and 0.23 have the wurtzite structure. It can be observed that the XRD peaks of zinc blende structured and wurtzite structured Zn$_{x}$Cd$_{1-x}$S ternary films continuously shift to smaller angles from curves (a) to (d) and from curves (e) to (g), respectively, indicating that the lattice parameters of the films increase with of the decreasing composition $x$. The continuous peak shift further indicates that alloyed Zn$_{x}$Cd$_{1-x}$S films with modulated compositions between ZnS and CdS were successfully achieved by an e-beam evaporation method via changing the molar ratio of ZnS to CdS in the target, which may also rule out the phase separation of ZnS or CdS.

### Table 1

| Molar ratio of ZnS/CdS | Atomic percentage% | Film composition |
|-----------------------|--------------------|------------------|
| 2/8                   | 11.35 39.51 49.15  | Zn$_{0.95}$Cd$_{0.05}$S |
| 5/3                   | 13.37 9.58 21.25   | Zn$_{0.82}$Cd$_{0.18}$S |
| 7/3                   | 37.77 14.8 47.42   | Zn$_{0.59}$Cd$_{0.41}$S |
| 8/2                   | 27.54 6.09 28.99   | Zn$_{0.82}$Cd$_{0.18}$S |
| 9/1                   | 30.62 1.70 28.30   | Zn$_{0.95}$Cd$_{0.05}$S |

#### 3.4. Energy gap

The UV-visible optical absorption spectra were acquired at room temperature to obtain the variation of light absorption for Zn$_{x}$Cd$_{1-x}$S films with different values of $x$, as shown in Fig. 4a. The spectra clearly show that the absorption edge is gradually shifted towards a longer wavelength with the decreasing value of $x$. As is known, the optical absorption is related to the electron excitation from the valence band to the conduction band. Therefore, the shift towards a longer wavelength indicates a decrease in the energy gap ($E_g$). Moreover, $E_g$ can be attained by extrapolating the straight line plot of $\alpha h \nu$ versus $h \nu$ to the energy axis. The absorption coefficient ($\alpha$) and the incident photon energy $h \nu$ are related by the following equation:

$$\alpha h \nu = A (h \nu - E_g)^n$$  \hspace{1cm} (1)

where $A$ is a constant, $E_g$ is the band gap of the material, and the exponent $n = 1/2$ for the material with direct band gap. The variation of $\alpha h \nu$ as a function of $h \nu$ is shown in Fig. 4b. Obviously, the obtained $E_g$ of Zn$_{x}$Cd$_{1-x}$S films with different values of $x$ continuously decreases with the decreasing value of $x$.

$E_g$ of the alloyed Zn$_{x}$Cd$_{1-x}$S films are plotted in Fig. 4c as a function of the composition $x$. It can be seen that the variation of $E_g$ with composition $x$ slightly deviates from linear dependence, displaying a downward bowing. This character has also been reported for many alloyed films,\textsuperscript{41-43} alloyed nanocrystals,\textsuperscript{44} and alloyed 1D nanostructures.\textsuperscript{19,21} In the case of the Zn$_{x}$Cd$_{1-x}$S system, the nonlinear variation of $E_g$ can be represented as a quadratic function of the composition $x$:\textsuperscript{19,45,46}
\[ E_g(x) = xE_g(ZnS) + (1 - x)E_g(CdS) - x(1 - x)b \]  

(2)

where \( E_g(x) \) is the energy gap of \( Zn_xCd_{1-x}S \), \( E_g(ZnS) \) is the energy gap of ZnS, \( E_g(CdS) \) is the energy gap of CdS, and \( b \) is the bowing parameter. The second-order polynomial fitting of the experimental results, as shown in Fig. 4c (solid line), gives the following quadratic expression:

\[ E_g(x) = 2.43 + 0.68x + 0.50x^2 \]  

(3)

which yields the bowing parameter of \( b = 0.50 \text{ eV} \). The obtained bowing parameter is similar to the value reported in the previous studies on \( Zn_xCd_{1-x}S \).

3.5. Photoconductive properties

After graphene films are transferred on the alloyed \( Zn_xCd_{1-x}S \) films on the 300 nm SiO\(_2\)/Si substrate, band-tunable photodetectors based on graphene/alloyed \( Zn_xCd_{1-x}S \) film hybrids can be achieved. To fabricate graphene/alloyed \( Zn_xCd_{1-x}S \) film-based field effect transistors, Cr/Au (10 nm/100 nm) electrodes with a length of 20 \( \mu \text{m} \) and width of 500 \( \mu \text{m} \) were deposited by e-beam evaporation through a shadow mask. After light was focused on the channel, the photoconductive properties of graphene/\( Zn_xCd_{1-x}S \) film hybrids could be investigated, schematically shown in the inset of Fig. 5a. Typical transfer characteristics of the back-gated transistors for graphene transferred on the \( Zn_xCd_{1-x}S \) films show a hole-dominated transport without the appearance of a Dirac point. This probably arises from the p-doping of oxygen in air.\( ^{9,14,15} \)

Upon 365 nm light irradiation, the source-drain current \( (I_{sd}) \) obviously increases regardless of the gate bias \( (V_g) \) for all \( Zn_xCd_{1-x}S \) films with different compositions (Fig. 5). The increase in the hole-dominated current in the graphene channel means that the holes transfer from the \( Zn_{0.5}Cd_{0.5}S \) film to graphene.\( ^{9,14,15} \)

Therefore, the working mechanism for a graphene/\( Zn_xCd_{1-x}S \) film hybrid photodetector is the same as for...
a graphene/ZnS film hybrid photodetector, which was illustrated in a previous study.\textsuperscript{17} Fig. 6 depicts a time-dependent response of graphene/alloyed Zn\textsubscript{1-x}Cd\textsubscript{x}S film hybrid-based device by switching light illumination with different wavelength yet at the same power of 1 mW cm\textsuperscript{-2} on and off periodically at a fixed voltage of 1.0 V. The current increases to a stable value of certain mA upon illumination, and then decreases to the initial value when the light is turned off, which shows good stability for the devices based on graphene/alloyed Zn\textsubscript{1-x}Cd\textsubscript{x}S film hybrids. The responsivity and response time of the graphene/II-VI semiconductor film-based photodetectors can be observed in a previous study,\textsuperscript{17} and we only focus on the band tunability of the devices based on graphene/alloyed Zn\textsubscript{1-x}Cd\textsubscript{x}S film hybrids in this study. All the photodetectors show that the photocurrents depend on the incident wavelength, with the largest values for the detectors with all values of \(x\) being located at around 365 nm (Fig. 6). In addition, the values of the largest photocurrent for the ternary Zn\textsubscript{1-x}Cd\textsubscript{x}S (0 < \(x\) < 1) films are all higher than those of the binary compound CdS (\(x = 0\)) and ZnS (\(x = 1\)) films. Ren \textit{et al.} also reported a similar phenomenon that the largest photocurrents of the ternary In\textsubscript{1-x}P\textsubscript{x} (0 < \(x\) < 1) nanowires are larger than those of the InP (\(x = 0\)) and InAs (\(x = 1\)) nanowires.\textsuperscript{28}

To attain the detailed wavelength related spectral response for the photodetector based on graphene/alloyed Zn\textsubscript{1-x}Cd\textsubscript{x}S films, wavelength-dependent photocurrents of the devices were measured with the incident light wavelength scanned from 365 to 585 nm under a bias voltage of 1 V and a light intensity of 1 mW cm\textsuperscript{-2}, as shown in Fig. 7. Note that the photocurrents calculated from the detectors based on graphene/alloyed Zn\textsubscript{1-x}Cd\textsubscript{x}S films with different compositions are normalized. Two types of variation tendency of the spectral response for graphene/alloyed Zn\textsubscript{1-x}Cd\textsubscript{x}S film hybrids are clearly observed.

For graphene/Zn\textsubscript{1-x}Cd\textsubscript{x}S film with compositions \(x = 1, 0.95, 0.82\), and 0.72, the photocurrent increased with the decreasing excited wavelength, which is in good agreement with the results of the ZnS-based photodetector.\textsuperscript{3} However, for graphene/Zn\textsubscript{1-x}Cd\textsubscript{x}S film with compositions \(x = 0.59, 0.23\), and 0, the photocurrent increased with the decreasing excited wavelength as the wavelength is shorter than the value corresponding to the energy gap, and then decreased with the decreasing wavelength, and finally increased with the decreasing wavelength, namely presenting a peak and a valley. The different variation tendency of the spectral response was attributed to the different absorption behavior of the Zn\textsubscript{1-x}Cd\textsubscript{x}S film with different
compositions. For Zn$_x$Cd$_{1-x}$S film with composition $x = 0.59, 0.23,$ and 0, there is an obvious peak locating at $h\nu$ around the corresponding energy gap of Zn$_x$Cd$_{1-x}$S, whereas for Zn$_x$Cd$_{1-x}$S film with a composition $x = 1, 0.95, 0.82,$ and 0.72, the peak does not appear obvious (Fig. 4b). Choi et al. reported that the variation tendency of spectral response for CdSe$_x$S$_{1-x}$ nanowire-based photodetectors only includes a peak.\textsuperscript{27} This is because the absorption curve of CdSe$_x$S$_{1-x}$ nanowires only shows an absorption peak without an absorption edge, which exists in the absorption curve for the as-deposited Zn$_x$Cd$_{1-x}$S film with all values of $x$. Regardless of the variation tendency of the spectral response for the photodetector, the important point is that the cut-off wavelength is gradually blue shifted from 585 to 410 nm as the $x$ value increases from 0 (CdS) to 1 (ZnS). It is well known that the cut-off wavelength of the spectral response relates to the absorption wavelength at the band edge (band-to-band transition).\textsuperscript{47,48} The observed variation of the cut-off wavelength with the composition $x$ in the alloyed Zn$_x$Cd$_{1-x}$S films demonstrates the successful modulation of the optoelectronic response range of the devices by means of bandgap engineering of the Zn$_x$Cd$_{1-x}$S films.
Fig. 6  Time-dependent response of graphene/alloyed Zn$_x$Cd$_{1-x}$x/S film hybrid-based photodetectors with compositions (a) $x = 0$, (b) $x = 0.23$, (c) $x = 0.59$, (d) $x = 0.72$, (e) $x = 0.82$, (f) $x = 0.95$, and (g) $x = 1$, by switching light illumination with different wavelengths but the same power of 1 mW cm$^{-2}$ on and off periodically at a fixed voltage of 1.0 V. All the photodetectors show that the photocurrents depend on the incident wavelength, with the largest values for the detectors with all values of $x$ being located at around 365 nm.
4. Conclusions

In summary, alloyed Zn$_{x}$Cd$_{1-x}$S (0 ≤ x ≤ 1) films with complete compositional tunability were successfully prepared by e-beam evaporation by changing the molar ratio of ZnS to CdS in the target. The UV-visible optical absorption measurements show that the composition-dependent band-edge absorption is generated in the as-prepared alloyed Zn$_{x}$Cd$_{1-x}$S films with the energy gaps continuously shifted from 2.41 eV (x = 0, CdS) to 3.67 eV (x = 1, ZnS). After graphene is transferred on the alloyed Zn$_{x}$Cd$_{1-x}$S films, band-tunable photodetectors are achieved based on the graphene/ alloyed Zn$_{x}$Cd$_{1-x}$S film hybrids with the cut-off wavelength gradually changing from 410 nm to 580 nm. Obviously, the method introduced in this study can be extended to the fabrication of other graphene/alloyed ternary film hybrid-based photodetectors with band tunability in the visible and infrared region.

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