Piezo-phototronic Effect Enhanced Responsivity of Photon Sensor Based on Composition-Tunable Ternary CdS$_x$Se$_{1−x}$ Nanowires

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ABSTRACT: The piezotronic effect and piezo-phototronic effect on materials and devices have been widely studied in binary semiconductors. Wide-band ternary semiconductors are a great class of materials with potential application in nano/microdevices, because of their continuously tunable physical properties with composition. Here, we first demonstrate the piezo-phototronics effect of ternary wurzite structured nanowires (NWs), opening an innovative materials system. Single-crystal ternary CdS$_x$Se$_{1−x}$ ($x = 0.85, 0.60$, and $0.38$) NWs were synthesized with site-controlled compositions via a chemical vapor deposition process, and high-performance visible photodetectors (PDs) with fast response speed (<2 ms), high photosensitivity, high responsivity, and broadened photoresponse region (than CdS NW) were fabricated based on these ternary materials. By introducing an external tensile strain, the performance of PDs is enhanced by 76.7% upon 0.2 mW/cm$^2$ 442 nm light illumination for CdS$_{0.85}$Se$_{0.15}$ by the piezo-phototronic effect. The composition effect of materials in ternary materials on light detecting and piezo-phototronics was also first investigated systematically. The results indicate that in the CdS$_x$Se$_{1−x}$ system, as the value of $x$ decreases, the photocurrent and responsivity experience an increase, while the enhancement of the piezo-phototronic effect was weakened. The change in piezoelectric coefficient and carrier screening effect are proposed for the observed phenomenon. This study reports a high-quality ternary CdS$_x$Se$_{1−x}$ NWs system used for high-performance PDs, broadens the family of piezotronic materials, offers an innovative material for high-performance visible PD, and provides a new pathway to modulate the performance of piezo-phototronic devices by tuning the atomic ratios of ternary wurzite semiconducting materials. This is essential for developing a full understanding of piezotronics on a broader scope, and it also enables the development of the better performance of optoelectronic devices.

KEYWORDS: piezo-phototronic effect, photodetector, nanowire, CdS$_x$Se$_{1−x}$

Investigations on the coupling among mechanical, optical, and electrical properties of semiconductor materials have explored an interdisciplinary field of piezo-phototronics, which has attracted more and more research interest in the past several years. Up to now, most of these works on piezo-phototronics are limited to binary semiconductor materials in binary semiconductors. The piezo-phototronic effect has been demonstrated to take this responsibility to work on devices constructed with traditional piezoelectric material. For example, ZnO and GaN have been studied extensively in piezotronic and piezo-phototronic devices, since a strong piezopotential can be created in the crystal by externally applying a strain due to the polarization of ions. Up to now, most of these works on piezo-phototronic effects are limited to binary semiconductor materials in ternary materials on light detecting and piezo-phototronics was also first investigated systematically. The results indicate that in the CdS$_x$Se$_{1−x}$ system, as the value of $x$ decreases, the photocurrent and responsivity experience an increase, while the enhancement of the piezo-phototronic effect was weakened. The change in piezoelectric coefficient and carrier screening effect are proposed for the observed phenomenon. This study reports a high-quality ternary CdS$_x$Se$_{1−x}$ NWs system used for high-performance PDs, broadens the family of piezotronic materials, offers an innovative material for high-performance visible PD, and provides a new pathway to modulate the performance of piezo-phototronic devices by tuning the atomic ratios of ternary wurzite semiconducting materials. This is essential for developing a full understanding of piezotronics on a broader scope, and it also enables the development of the better performance of optoelectronic devices.

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nanostructures. Exploration of new piezoelectric materials and the study of their doping/composition or structure on the modulating effect of device performance are equally important for the development of the piezo-photonics field.

One-dimensional (1D) wide-band ternary semiconductors are a great class of materials with potential application in nano/microdevices,24–27 because of their continuously tunable physical properties with composition. Among them, the ternary CdS$_{1-x}$Se$_x$ nanowires/nanobelts have attracted more research interest since its band gap can be tuned by means of the composition between $\sim$2.42 eV (for CdS) and $\sim$1.72 eV (for CdSe), almost covering the entire visible spectral range.28–35 Liu’s group has studied the strain-modulation behavior of a ternary MgZnO film PD by introducing the piezo-photonotronic effect.36 In this case, a ZnO thin film is alloyed with Mg to investigate how the alloying process and Mg content work on the piezoelectric effect and therefore how the corresponding piezo-photonotronic effect affects the performance improvement of PDs. However, as an effective polarized system to produce piezoelectric charges, 1D nanostructures based on ternary semiconductor nanowires have not been reported so far.

In this work, the piezo-photonotonic effect on PDs of ternary CdS$_{1-x}$Se$_x$ nanowires (NWs) is demonstrated for the first time. The piezo-photonotronic effect enhanced photoresponsivity of the single NW photodetector has been studied for different NWs of compositions CdS$_{0.85}$Se$_{0.15}$, CdS$_{0.60}$Se$_{0.40}$ and CdS$_{0.36}$Se$_{0.62}$. The devices show excellent photoresponse ability to visible light with fast response time, high photosensitivity, and photoresponsivity. Significantly, the photoresponse of this kind of device can be modulated under different strains and by the atomic composition of the ternary wurtzite semiconducting materials. The change in piezoelectric coefficient and carrier screening effect are proposed for explaining the observed phenomenon. Also, the energy band diagrams are presented to illustrate the piezo-photonotronic process on the Schottky contacted metal—semiconductor. This work offers an innovative candidate and provides a new perspective to study NW-based piezo-photonotronic PDs, which are all very important for the in-depth understanding of the physical mechanism of piezophotonotronic effects, and enables the development of high-performance piezo-photonotronic devices.

RESULTS AND DISCUSSION

Ternary CdS$_{1-x}$Se$_x$ NWs with site-controlled compositions were fabricated via a simple one-step CVD process in the presence of Sn catalyst. Figure 1a shows a low-magnification SEM image of the CdS$_{1-x}$Se$_x$ NWs, showing the diameters of about 500 nm and lengths of about several hundred micrometers. The inset is an enlarged SEM image of a CdS$_{1-x}$Se$_x$ NW, with a Sn particle located at the tip, which indicates a typical vapor–liquid–solid (VLS) growth mechanism of the NW terminating at a catalyst metal particle. It should be noted that a Sn ball at the tip of the NWs working as a catalyst can be found on most of the longer NWs, especially for the NWs with a length close to a millimeter. However, in many cases, such as NWs with lengths less than about 300 μm, the catalyst particles will fall off the NWs due to the thermodynamics of the growth process. TEM image and the high-resolution electron microscope (HRTEM) image of the corresponding area of a typical CdS$_{1-x}$Se$_x$ are given in Figure 1b1 and Figure 1b2. Combining with the corresponding selected area electron diffraction (SAED) pattern in Figure 1b3, it revealed that the as-synthesized CdS$_{1-x}$Se$_x$ NW is single crystalline and grows along the c-axis. Figure 1c shows the normalized X-ray diffraction (XRD) patterns of three representative CdS$_{1-x}$Se$_x$ NWs obtained at different growth temperatures. The composition x of the nanowire can be determined from Vegard’s law using the lattice parameters deduced from the XRD data.26,37 After careful observation, the diffraction peaks can be indexed to the typical wurtzite structure of ternary CdS$_{0.85}$Se$_{0.15}$, CdS$_{0.60}$Se$_{0.40}$ and CdS$_{0.38}$Se$_{0.62}$, respectively. Figure 1d shows the normalized PL spectra of the ternary CdS$_{1-x}$Se$_x$ NWs obtained at room temperature. The spectra of all the samples show a single emission band, located at $\sim$550 nm (2.258 eV), $\sim$609 nm (2.036 eV), and $\sim$656 nm (1.891 eV), respectively, which can be attributed to the near-band-edge emissions of ternary CdS$_{1-x}$Se$_x$ NWs. The single emission band with an absence of a defect-related band confirms the highly crystallized quality of the ternary alloy NWs.

Three PD devices with a similar channel area (200 μm × 500 nm) based on the single ternary CdS$_{1-x}$Se$_x$ NW with different compositions (device #1: $x = 0.85$, CdS$_{0.85}$Se$_{0.15}$, device #2: $x = 0.60$ CdS$_{0.60}$Se$_{0.40}$, and device #3: $x = 0.38$, CdS$_{0.38}$Se$_{0.62}$) were fabricated by a standard procedure, which has been described in the Experimental Section. In order to avoid the uncertainty of the introduction of a metal Sn catalyst on the device interface electronic properties, the NW with no catalyst particles at the
tip is selected to fabricate the device. The schematic of the measurement setup and the digital image of the as-fabricated NW device are illustrated in Figure 1e and the corresponding inset. The schematic diagram and the typical optical image of the PD device under strain-free conditions are also shown in Figure 1f and Figure 1g, respectively, which can more clearly illustrate the structure of the devices.

Figure 2. (a–c) Typical I–V characteristics of the single CdS$_{x}$Se$_{1-x}$ NW PD as a function of excitation light intensity. Curves (a)–(c) for $x = 0.85$, 0.60, and 0.38, respectively. The inset in (a)–(c) is the photocurrent of the NW PD without strain under different illumination intensity with the periodical changing of light irradiation on and off. (d) Typical response time of a single CdS$_{x}$Se$_{1-x}$ NW PD. (e) Absolute photocurrent and (f) derived photoresponsivity relative to excitation intensity on the three NW devices at bias = 2.0 V. Excitation wavelength = 442 nm.

Figure 3. (a–c) Typical I–V characteristics of device #1 (CdS$_{0.85}$Se$_{0.15}$) under different tensile and compressive strains, with excitation light intensity of (a) 0.2 mW/cm$^2$, (b) 3.5 mW/cm$^2$, and (c) 44 mW/cm$^2$. The inset in (a)–(c) is the corresponding absolute photocurrent at bias = 2.0 V. (d) Changes of photocurrent derived from (a)–(c). $I_0$ is set as the photocurrent under zero strain for this illumination power. (e) Derived change in SBH as a function of strain using the thermionic emission diffusion model. (f) Changes of responsivity derived from (a)–(c). $R_0$ is set as the responsivity under zero strain. Excitation wavelength = 442 nm.
drifting from the interface and thus produced a larger photocurrent. The insets in Figure 2a–c show the corresponding time-resolved photocurrent response curves of device #1, #2, and #3, respectively. (d, e) Dependences of responsivity (R) and relative increases of responsivity (ΔR/R0) on excitation light intensity under 0.4% tensile strain and at a bias of 2 V, derived from (a)–(c). R0 is set as responsivity under zero strain. Excitation wavelength = 442 nm. (f) Simulation of the piezopotential distribution in the wire of typical CdS0.85Se0.15 with x = 0.85, 0.6, and 0.32 under tensile strain.

Figure 4. (a–c) Column graph of absolute photocurrent under different tensile strains and different excitation intensity at bias = 2 V. Graphs (a)–(c) for device #1 (CdS0.85Se0.15), device #2 (CdS0.60Se0.40), and device #3 (CdS0.38Se0.62), respectively. (d, e) Dependences of responsivity (R) and relative increases of responsivity (ΔR/R0) on excitation light intensity under 0.4% tensile strain and at a bias of 2 V, derived from (a)–(c). R0 is set as responsivity under zero strain. Excitation wavelength = 442 nm. (f) Simulation of the piezopotential distribution in the wire of typical CdSxSe1−x with x = 0.85, 0.6, and 0.32 under tensile strain.

Figure 5. Schematic energy band diagram for illustrating the piezophototronic effect on a Schottky contacted metal–semiconductor interface when (a) only illumination, (b) tensile strain and illumination, and (c) compressive strain and illumination are applied to the single CdSxSe1−x NW device.

Figure 6. Schematic energy band diagram for illustrating the piezophototronic effect on a Schottky contacted metal–semiconductor interface when (a) only illumination, (b) tensile strain and illumination, and (c) compressive strain and illumination are applied to the single CdSxSe1−x NW device.

Figure 7. (a) Column graph of absolute photocurrent under different tensile strains and different excitation intensity at bias = 2 V. Graphs (a)–(c) for device #1 (CdS0.85Se0.15), device #2 (CdS0.60Se0.40), and device #3 (CdS0.38Se0.62), respectively. (d, e) Dependences of responsivity (R) and relative increases of responsivity (ΔR/R0) on excitation light intensity under 0.4% tensile strain and at a bias of 2 V, derived from (a)–(c). R0 is set as responsivity under zero strain. Excitation wavelength = 442 nm. (f) Simulation of the piezopotential distribution in the wire of typical CdSxSe1−x with x = 0.85, 0.6, and 0.32 under tensile strain.

Figure 8. Schematic energy band diagram for illustrating the piezophototronic effect on a Schottky contacted metal–semiconductor interface when (a) only illumination, (b) tensile strain and illumination, and (c) compressive strain and illumination are applied to the single CdSxSe1−x NW device.

Figure 9. Schematic energy band diagram for illustrating the piezophototronic effect on a Schottky contacted metal–semiconductor interface when (a) only illumination, (b) tensile strain and illumination, and (c) compressive strain and illumination are applied to the single CdSxSe1−x NW device.

Figure 10. Schematic energy band diagram for illustrating the piezophototronic effect on a Schottky contacted metal–semiconductor interface when (a) only illumination, (b) tensile strain and illumination, and (c) compressive strain and illumination are applied to the single CdSxSe1−x NW device.
higher than that of the networks CdSe NWs PD.\textsuperscript{40} The photoresponsivity of all three devices decrease with increasing excitation intensity, which could be attributed to the hole-trapping saturation and the Schottky barrier being transparent at high light intensity, as has been observed from a ZnO NW-based UV light PD.\textsuperscript{15} However, the photosensitivity of the three devices, as shown in Figure S1a–c, displays a linear increasing with improving the excitation intensity. The maximum value of about 4462% in device #1 is obtained at a light intensity of 280 W/cm\textsuperscript{2}, which is much higher than a previously reported photoco nductive PD based on a single CdS nanobel t.\textsuperscript{41}

In addition to the excellent response to blue light, the ternary CdS\textsubscript{0.38}Se\textsubscript{0.62} NWs also exhibit a good response to green light. Figure S2a shows the real-time photo switching behavior of the CdS\textsubscript{0.38}Se\textsubscript{0.62} NW device performed under 532 nm with a power intensity of 2.48 mW/cm\textsuperscript{2} at a bias of 2.0 V. However, when the same excitation light was imposed on an individual CdS NW device (the CdS NW was fabricated in the same growth process as CdS\textsubscript{0.38}Se\textsubscript{0.62} NW, but obtained at a lower deposition temperature), it had no observable photocurrent response to 532 nm light, as shown in Figure S2b. Obviously, the ternary CdS\textsubscript{0.38}Se\textsubscript{0.62} NW exhibits a broader range of light detection, compared with CdS NW. Furthermore, the response range can extend to the entire visible spectrum, even the near-infrared, as the ratio of Se/S increases.\textsuperscript{42} It is attributed to the flexible band-gap tuning from CdS (x = 1 with a band gap of 2.42 eV) to CdSe (x = 0 with a bandgap of 1.72 eV) of ternary CdS\textsubscript{0.38}Se\textsubscript{0.62}, which indicated a prospective candidate for applications in optoelectronics.

To investigate the effects of the piezopotential on the performance of the ternary CdS\textsubscript{0.38}Se\textsubscript{0.62} NWs, the strain, coupled with light excitation, was imposed upon the single NW device to study the piezo-phototronic effect. Figure 3a–c show the typical I–V characteristics of device #1 (CdS\textsubscript{0.38}Se\textsubscript{0.62}) under illumination of 442 nm light, and the corresponding insets are plots of photocurrents as a function of strain upon different excitation light intensity at a bias voltage of 2.0 V. The asymmetric I–V curves show the rectification behavior under all strain conditions, which indicate the forming of the back-to-back Schottky barriers at the interfaces of the semiconductor NW and metal Ag electrodes. Obviously, in the positive voltage range, the photocurrent decreases upon the compressive strain and increases as the tensile strains increase from 0% to 0.4%. Figure 3a shows I–V curves measured in the weak light excitation intensity at about 0.2 mW/cm\textsuperscript{2}. From the inset in Figure 3a, the photocurrent at 2.0 V bias increases from 26.94 nA to 45.3 nA under tension strains up to 0.4% and down to 20.97 nA under compressive strains up to −0.4%. A similar tendency was also observed under the illumination of medium excitation intensity (3.5 mW/cm\textsuperscript{2}) and intense excitation intensity (44 mW/cm\textsuperscript{2}), as exhibited in Figure 3b and 3c. However, the change of photocurrent induced by strain at the negative bias side has no definite trend because of the accompanied piezoresistance effects.\textsuperscript{49} Figure 3d shows the photocurrent changes of the PD with and without strain (I\textsubscript{S}−I\textsubscript{O}) under different excitation intensity, which were extracted from Figure 3a–c. It can be seen clearly that compressive strain leads to a monotonic decreasing photocurrent and tensile strain induces a monotonic increasing photocurrent in the undegraded strains range. In addition, larger photocurrent changes are observed in intense excitation intensity with the same variation of strain. This is because more photogenerated carriers are exposed to the variation of the strain in a higher excitation intensity, thus inducing more obvious photocurrent changes.

It has been reported that the SBH at the interface of a metal and semiconductor is an important factor in determining the transport property of the metal—semiconductor—metal structure.\textsuperscript{9} To understand the changes of the photocurrent with strain in Figure 3d, a thermionic field emission (TFE) theory was considered to describe the current transport with illumination. The changes of SBH (\(\Delta \Phi\)) with strain are calculated by \(\Delta \Phi = -k T \ln (I_i/I_o)\),\textsuperscript{43} where \(k\) is Boltzmann constant, \(T\) is temperature, and \(I_i\) and \(I_o\) are measured at a fixed bias \(V\) with and without strain, respectively. The relationship of changes of SBH on strains is calculated and plotted in Figure 3e, which indicate an increase/decrease of SBH under the compressive/tensile conditions. The changes of responsivity, inducing by applied strain, is a significant parameter to evaluate the degree of piezo-phototronic effect on the performance of PDs. We have the changes of responsivity as \(\Delta R/R_0 = (R_s - R_o)/R_o\) where \(R_s\) and \(R_o\) are set as the responsivity under applied strain and free strain, respectively. Figure 3f shows the relationship of \(\Delta R/R_0\) on applied strain at different excitation intensity. It can be seen that \(\Delta R/R_0\) increases with tensile strain and decreases with compressive strain, but the degree of variation is asymmetric, which is a typical feature of the piezo-phototronic effect.\textsuperscript{11} The responsivity of the PD under the 0.4% tensile strain was enhanced by 76.7%, 57.1%, and 40.2% upon the excitation intensity of 0.2, 3.5, and 44 mW/cm\textsuperscript{2}, respectively. The enhanced performance of the PD is attributed to the effective decrease of the SBH between the ternary CdS\textsubscript{0.38}Se\textsubscript{0.62} semiconductor and the metal Ag electrode due to the energy band modification caused by polarization charges, as will be discussed later. It is pointed out that the responsivity is much more enhanced for weak light detection than for strong light detection, which indicates a potential application in ultrasensitive light detection, as the detection of low-intensity light is practically desired.

To further investigate the piezo-phototronic effect on the ternary PD performance with different x composition, device #2 (CdS\textsubscript{0.38}Se\textsubscript{0.40}) and device #3 (CdS\textsubscript{0.38}Se\textsubscript{0.60}) are also studied by applied tensile strain. Figure S3 shows the typical I–V characteristics of (a–c) device #2 and (d–f) device #3 with excitation light intensity of (a, d) 0.2 mW/cm\textsuperscript{2}, (b, e) 3.5 mW/cm\textsuperscript{2}, and (c, f) 44 mW/cm\textsuperscript{2}, respectively, and the inset in (a–f) is the corresponding absolute photocurrent at a bias of 2.0 V. It can be seen that intense excitation intensity induced larger photocurrent changes by strain, as observed in device #1. In order to clearly show the performance improvement of the three devices under tensile strains at different illumination intensities, Figure 4 presents the compared results of (a–c) photocurrent, (d) responsivity \(R\), and (e) the relative increases of responsivity \(\Delta R/R_0\), respectively. It can be seen from the column graph in Figure 4a–c that the absolute photocurrents of the three devices increase as the tensile strain increases and improves as the excitation intensity rises. The maximum changes of photocurrent are from ∼5.6 nA (C1: strain free, dark) to ∼204 nA (C2: 0.4% tensile strain, 44 mW/cm\textsuperscript{2}) for device #1 (Figure 4a), from ∼150 nA (C1) to ∼1348 nA (C2) for device #2 (Figure 4b), and from ∼270 nA (C1) to ∼2265 nA (C2) for device #3 (Figure 4c), which have been enhanced by 36.43, 8.99, and 8.38 times, respectively. The larger improvement in device #1 is mainly attributed to the lower dark current, which can be seen from Figure 4a. As we
know, a Schottky junction will form between an n-type semiconductor material and a metal with higher work function. A lower electronic affinity will induce a higher SBH between the metal–semiconductor (M–S) junction if the carrier concentration is close in the semiconductor with a similar high crystal quality. Then, a high contact resistance will form and induce a low dark current. It has been reported that the affinity energy of the binary CdSe is higher than that in CdS, and the energy band of ternary CdS\textsubscript{1−x}Se\textsubscript{x} changes continuously between the band gap of binary CdS and CdSe.\textsuperscript{30} So the SBH between the semiconductor CdS\textsubscript{1−x}Se\textsubscript{x} and metal Ag electrode increases as x approaches 1. Then, a higher SBH of device #1 than that of device #2 and/or #3 with decreasing x will hinder the carriers from drifting on the M–S interface and therefore induce a lower dark current.

Photoresponsivity (R) under strain is an important parameter in evaluating the effects of piezo-phototronics on the performance of a PD. Figure 4d shows the R values of the three devices by 0.4% tensile strain under different excitation light intensity at a bias of 2.0 V. It can be seen that the responsivity of device #3 is higher than that of device #2 and is much higher than that of device #1. The trend is similar to the compared result of the photocurrent, which indicates device #1 has fewer photogenerated carriers than those in device #2/#3 when applying the same strain and illumination conditions. Figure 4e presents the changes of responsivity of the three PDs at a fixed tensile strain of 0.4%. The maximum value of enhancement for device #1 is 76.7%, larger than that of device #2 enhanced by 59% and device #3 enhanced by 41.9% upon an excitation intensity of 0.2 mW/cm\textsuperscript{2}. It was reported that the effect of the piezopotential on the SBH can be described as $P = \epsilon_{xx}c_3$ for an axial polarization, where $\epsilon_{xx}$ is a constant strain along the length of the wire and $c_3$ is the piezoelectric tensor.\textsuperscript{15}

In our case, the piezoelectric coefficient of CdS is 0.440, which is larger than 0.347 for CdSe.\textsuperscript{44} For the ternary CdS\textsubscript{1−x}Se\textsubscript{x} with similar wurtzite crystal structure of binary CdS and CdSe, the ratios of lattice parameters c/a that reflect the asymmetry of crystals increase from CdS to CdSe as x decreases.\textsuperscript{26} So the potential drops resulting from the changes of piezoelectric coefficients will increase from CdS to CdSe. By the finite element method, we calculated a piezopotential distribution in the wire of typical CdS\textsubscript{1−x}Se\textsubscript{x} with x = 0.38, 0.6, and 0.85, as shown in Figure 4f. It can be seen that a positive potential drop will be induced along the length of the wire under tensile strain and the potential drops will increase from CdS\textsubscript{0.38}Se\textsubscript{0.62} (~0.53 V) to CdS\textsubscript{0.60}Se\textsubscript{0.40} (~0.57 V) and further to CdS\textsubscript{0.85}Se\textsubscript{0.15} (~0.62 V). For quantitative comparisons, the calculated results of piezopotential drops for binary CdS (~0.47 V) and CdS (~0.72 V) are demonstrated in Figure S4. Therefore, the SBH is decreased with x increasing at a fixed tensile strain. Thus, a more obvious piezopotential drop will be produced in device #1 and induce a more pronounced enhancement of photoresponsivity in ternary CdS\textsubscript{1−x}Se\textsubscript{x} with a larger x. In addition, the screening effect induced by the photogenerated carriers is another possible reason for the performance of the PDs.\textsuperscript{15} An increased carrier density speeds up the possibility of a screening effect on the polarization charges, which weakens the function of the piezo-phototronic effect on the performance of the PD. In our three devices, carrier density and photocurrent are increasing with Se/S value of the ternary CdS\textsubscript{1−x}Se\textsubscript{x} NW based PD upon the same excitation light and applied strain. Therefore, a larger enhancement of photoresponsivity in device #1 is observed.

As described in previous work, the internal piezoelectric field formed inside a wurtzite semiconductor NW can tune the charge transport/photocurrent process at the contact and thus optimize the photoresponse of a single semiconductor wire.\textsuperscript{9} To further understand the piezoelectric potential on the performance of our PDs under illumination, a theoretical model by analyzing the energy band diagram is proposed to illustrate the piezo-phototronic effects on the CdS\textsubscript{1−x}Se\textsubscript{x} NW, as shown in Figure 5. The conduction band (CB) and valence band (VB) of the n-type CdS\textsubscript{1−x}Se\textsubscript{x} are located between the corresponding band-edge of CdS and CdSe.\textsuperscript{3,45} Two back-to-back contacts, with SBH at the drain side and at the source side, would be created between semiconductor CdS\textsubscript{1−x}Se\textsubscript{x} and a Ag electrode. In our case, when a relatively large positive voltage was applied at the drain side, the voltage drop occurred mainly at the reversely biased Schottky barrier at the source side. So the SBH at the source side is much higher than that at the drain side. When the Schottky barrier photosensitive device is under illumination of 442 nm light, as shown in Figure 5a, the incident photons give rise to electron–hole pairs in the semiconductor. Under an external electric field, the electron–hole pairs are separated and induce plenty of excess electrons and excess holes. The photogenerated electrons in the CB are inclined to move close to the interface of the drain side, and the holes in the VB are inclined to move toward the source side and therefore induce the photocurrent to flow from the drain side to the source. Usually, the photocurrent depends on the effective separation and transport of both holes and electrons at the vicinity of the contacts and strongly affects the SBH as a result of the TFE theory.\textsuperscript{46,47}

When tensile strain is applied along the c-axis direction of the semiconductor NW, positive polarization charges were introduced at the vicinity of the source side to reduce the SBH (Φ\textsubscript{Se} < Φ\textsubscript{Ag}). The decreasing SBH at local contact will facilitate electron transport across the M–S interface and induce an increasing photocurrent, as shown in Figure 5b. Furthermore, a larger tensile strain will result in a greater decrease in SBH and induce a greater photocurrent, as observed in Figure 3a and Figure S3. In addition, the function of the polarization charges on the SBH is affected by the excitation intensity on the device. An increased excitation intensity will induce a larger carrier density, which will increase the screening effect on the polarization charges and weaken the function of strain on the photocurrent enhancement. Therefore, the piezo-phototronic effect can help enhance the responsivity of the device at low light intensity, but does not necessarily have a significant effect for strong light intensity. Conversely, if compressive strain is applied on the device, negative polarization charges will be introduced at the interface and increase the SBH (Φ\textsubscript{Se} > Φ\textsubscript{Ag}), as shown in Figure 5c. In this case, the higher SBH is not favorable for the photogenerated electron–hole transfer, therefore reducing the photocurrent, leading to a low responsivity of the detection.

As discussed above, although the photocurrent and responsivity of device #1 with lower Se content (CdS\textsubscript{0.85}Se\textsubscript{0.15}) are lower than those of device #2 (CdS\textsubscript{0.60}Se\textsubscript{0.40}) and device #3 (CdS\textsubscript{0.38}Se\textsubscript{0.62}), with higher Se content, the enhanced responsivity is larger due to the enhancing of the piezoelectric coefficient and the decreasing screening effect of the polarization charges. According to the fundamental theory, carrier transport behavior can be controlled by piezopotential, which is achieved by external strain and the photoexcitation process, whereas the present...
study demonstrates that the piezopotential can also be tuned by the composition of the Se/S ratio in the ternary CdS$_{x}$Se$_{1-x}$. The performance of the PDs can be regulated by changing the Se/S ratio to manipulate the optical–electrical process through the piezo-phototronic effect, which provides a novel way to study piezo-photoelectronic effects.

**CONCLUSION**

In summary, we have fabricated high-quality single-crystal ternary CdS$_{x}$Se$_{1-x}$ nanowires. The application of the ternary alloyed CdS$_{x}$Se$_{1-x}$ NW for high-performance flexible visible photodetectors was first demonstrated. The devices exhibit an excellent photoresponse on visible light (442 nm) with high sensitivity, high responsivity, and fast response speed. By introducing external strain, the performance of the PDs was further improved by the piezo-phototronic effect. The responsivity of the PD (CdS$_{0.85}$Se$_{0.15}$) is enhanced by 76.7%, 57.1%, and 40.2% upon 0.2, 3.5, and 44 mW/cm$^2$ by introducing a 0.4% tensile strain. The piezo-phototronic effect under tensile strain reduces the SBH and facilitates the transport of photoexcited carriers, inducing the increase of photocurrent and responsivity. A theoretical model of the schematic energy band diagram is proposed to illustrate the enhancing mechanism. Significantly, the composition effect of materials in ternary materials on both light detecting and piezo-phototronic effects was also first investigated systematically. The results present that the performance of the ternary CdS$_{x}$Se$_{1-x}$ NW PD can be tuned by the S/Se ratio, and the piezo-phototronic effect was stronger as the ratios of S/Se increases. The unique piezo-phototronic properties of the ternary CdS$_{x}$Se$_{1-x}$ NW materials provide us with a versatile potential pathway to tune/control the performance of optoelectronic devices, enable the development of better performance of optoelectronic materials, and also broaden the family of piezotronic materials, demonstrating a promising candidate for further piezo-phototronic devices.

**EXPERIMENTAL SECTION**

**CdS$_{x}$Se$_{1-x}$ NW Synthesis and Characterization.** CdS$_{x}$Se$_{1-x}$ NWs were fabricated via a simple one-step chemical vapor deposition (CVD) process in the presence of Sn catalyst. Briefly, the mixed semiconductor powders of CdS (0.1 g, Alfa Aesar, 99.995% purity), CdSe (0.05g, Alfa Aesar, 99.995% purity), and SnO$_2$ (0.01g, 99.5% purity) were selected as source materials and were placed in the center of the tube furnace. Several pieces of Si wafers were placed separately about 6–10 cm from the center downstream. Typically, the temperature of the central site was raised to 1000 °C at a rate of about 50 °C/min, kept at this temperature for 60 min, and then naturally cooled to room temperature. During the growth process, the 40 sccm mixture of carrier gas (Ar+H$_2$ (10%)) was pumped into the tube. After the reaction, bright-yellow to brown-red products were deposited on the surface of silicon wafers and on the inner wall of the quartz tube at the deposition temperature of 600–800 °C downstream. Then, the morphology and composition of the product were characterized by a scanning electron microscope (SEM: Hitachi SU8010) and transmission electron microscope (TEM: FEI F30) with an energy dispersive X-ray spectrum. The structure was investigated by X-ray powder diffraction (Siemens D-5000). The room-temperature photoluminescence (PL) measurements were carried out by exciting the sample with a 488 nm Ar-ion laser within an optical cryostat.

**Device Fabrication and Measurements.** A typical single CdS$_{x}$Se$_{1-x}$ NW was transferred laterally onto the polyethylene terephthalate (PET) substrate (length of about 3 cm, width of about 8 mm, and thickness of 0.5 mm), with its c-axis in the plane of the substrate. Since the Sn catalyst is a very confusing part in the device configuration, we will try to choose the NW with no catalyst particles at the tip. If it is a long NW with a Sn catalyst ball at the tip, we will cut the ball before fabricating the device in order to avoid the uncertainty of the introduction of metal particles on the device interface electronic properties. Then, the silver pastes were applied to bond the two ends of the NW, serving as the two electrodes. Finally, a thin layer of polydimethylsioxane was used to package the device, which can prevent contamination or corrosion of the NW. A 3D mechanical stage with a movement resolution of 1 μm was used to fix one end of the substrate and keep the device in focus. Another 3D stage was used to bend the free end of the substrate to produce a tension or compression on the NW sample. For a detailed calculation of the applied strains, refer to ref 48. The device was excited by a He–Cd laser (442 nm) and green light (centered at 532 nm). The excitation intensity on the sample was varied by some neutral density filters and calibrated by a thermopile power meter (Newport 818 P-001-12). The $I$–$V$–$I$–$t$ characteristics of the device under different strains and different light intensity were measured by a low-noise voltage/current preamplifier (Stanford Research Systems, model SR560/SR570) in conjunction with a computer-controlled measurement system.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsphotonics.7b00724.

Figures S1–S4 showing further details of the ternary CdS$_{x}$Se$_{1-x}$ NW and the device performance (PDF)

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Notes

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