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# Contact printing of compositionally graded $CdS_xSe_{1-x}$ nanowire parallel arrays for tunable photodetectors

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**Abstract**
Spatially composition-graded $CdS_xSe_{1-x}$ ($x = 0$–1) nanowires are grown and transferred as parallel arrays onto $Si/SiO_2$ substrates by a one-step, directional contact printing process. Upon subsequent device fabrication, an array of tunable-wavelength photodetectors is demonstrated. From the spectral photoconductivity measurements, the cutoff wavelength for the device array, as determined by the bandgap, is shown to cover a significant portion of the visible spectrum. The ability to transfer a collection of crystalline semiconductor nanowires while preserving the spatially graded composition may enable a wide range of applications, such as tunable lasers and photodetectors, efficient photovoltaics, and multiplexed chemical sensors.

(Some figures may appear in colour only in the online journal)

## 1. Introduction

The ability to spatially tune the bandgap of semiconductors enables new applications such as tunable-wavelength optoelectronic devices. Bandgap controllability by alloying crystalline semiconductors of different band gaps with existing thin film growth techniques is, however, severely limited by the lattice matching required for epitaxial film growth. Recently, it has been demonstrated [1, 2] that these restrictions are dramatically relaxed by the use of nanowires (NWs) [3]. Various compositionally graded NWs grown on a single substrate have been reported for material systems such as $In_xGa_{1-x}N$ [1], $CdS_xSe_{1-x}$ [2, 4], and $Zn_xCd_{1-x}S_ySe_{1-y}$ [5, 6]. This approach to semiconductor alloying has led to the first growth of quaternary alloy nanostructures in the form of ZnCdSSe nanobelts, and composition grading over the entire visible spectrum on a single substrate [6]. Specifically, for the ternary $CdS_xSe_{1-x}$ alloy, the full composition range from CdS ($x = 1$, bandgap: 2.44 eV) to CdSe ($x = 0$, bandgap: 1.72 eV) covers an important range of the visible spectrum (500–700 nm). Spatially composition-graded CdSSe NWs with optically pumped lasing behavior over a broad wavelength tuning range have been reported [2]. Due to the random orientations of the as-grown nanowires, the fabrication of electrical devices is challenging without subsequent re-alignment. Here, compositionally graded $CdS_xSe_{1-x}$ NWs are combined with a previously reported contact printing method [7–9] in which as-grown NWs are directly transferred to any arbitrary substrate (p + $Si/SiO_2$ substrate in this work) by directional

 

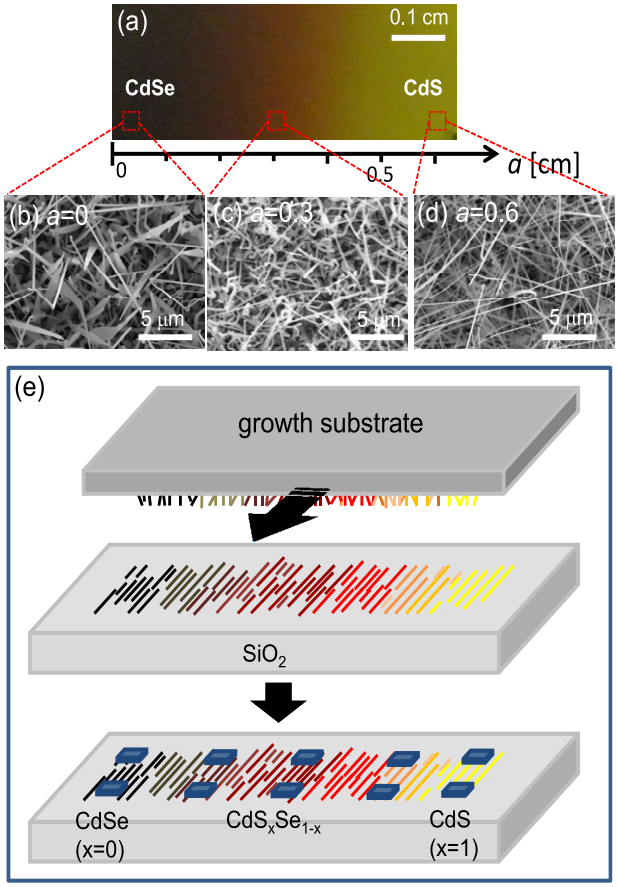


**Figure 1.** Compositionally graded $CdS_xSe_{1-x}$ NWs. (a) Real-color photograph of as-grown spatially composition-graded $CdS_xSe_{1-x}$ NWs. (b), (c), (d) SEM images taken from three different locations, the Se-rich, middle, and S-rich regions, respectively. (e) Schematic of the contact printing method, and the final device configuration for CdS/Se-based photodetectors.

sliding, thus preserving the spatial compositional grading. With this simple one-step printing method, an organized collection of parallel NW-arrays with different bandgaps is assembled for subsequent device fabrication, which is otherwise unobtainable by conventional methods.

## 2. Experimental details

$CdS_xSe_{1-x}$ alloy NWs spanning the full composition range are synthesized on a $Si/SiO_2$ substrate by the dual gradient method which combines a temperature gradient and spatial gradient of the source materials across the substrate for optimal growth of each material composition [5]. Commercially available CdS and CdSe powders (Alfa Aesar, 99.995% purity) are each loaded into individual source dispersion tubes within a quartz tube furnace. The $Si/SiO_2$ substrate with 2 nm thick Au catalyst film is placed downstream facing the openings of the source dispersion tubes. The substrate orientation is vertical with a slight angle such that its two ends are at different axial locations within the temperature gradient region near the exit of the furnace. With

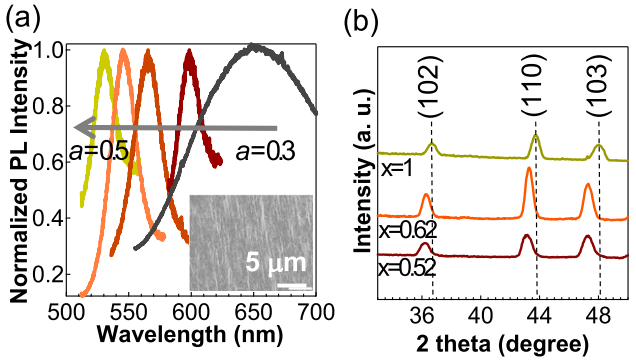


**Figure 2.** (a) Micro-photoluminescence spectra of contact-printed compositionally graded NW-arrays ($0.3 < a < 0.5$). An SEM image of printed NWs from the $a = 0.4$ region is shown in the inset. (b) The normalized x-ray diffraction patterns (XRD) of three different printed NW regions. The dashed lines correspond to (102), (110), and (103), respectively (CdS: JCPDS 41-1049).

a 100 sccm gas flow of 5% $H_2$ in Ar, the pressure is maintained above 600 Torr to prevent source material diffusion while the furnace is heated slowly to 700 °C. The pressure is reduced to 5 Torr and held for 30 min of growth.

A real-color photograph of the as-grown spatially composition-graded $CdS_xSe_{1-x}$ NWs substrate is shown in figure 1(a). It is confirmed from photoluminescence (PL) that the bandgaps of the as-grown NWs cover most of the visible spectrum range (data not shown here). Figures 1(b)–(d) show scanning electron microscopy (SEM) images of as-grown NWs taken from three different positions: $a$ (cm) = 0, 0.3 and 0.6, with $a = 0$ corresponding to the Se-rich region. As the composition becomes Se-rich, the morphology of the NWs becomes tapered and short (<5 $\mu$m) due to the involvement of the vapor–solid growth mechanism in addition to vapor–liquid–solid growth. The NWs are transferred as parallel arrays onto a $Si/SiO_2$ substrate using a contact printing method [7, 8]. Next, Ti (5 nm)/Au (40 nm) is deposited with electron beam evaporation to form source/drain contact electrodes. With this simple one-step printing, photodetectors made of compositionally graded parallel NW-arrays are readily achieved (figure 1(e)).

## 3. Results and discussion

Figure 2(a) shows the normalized PL spectra measured at room temperature from the printed $CdS_xSe_{1-x}$ NW-arrays. The PL peaks vary between ~525 and ~650 nm as a function of location (figure 2(a)), and the spectra show no midgap emission bands. In the inset, a representative SEM image of the printed NWs from the $a = 0.4$ region is shown. Further growth optimization is required for the printing of NW-arrays with the full composition range. Figure 2(b) shows the x-ray diffraction (XRD) data taken from three different locations on the printed substrate. The diffraction peaks are in good agreement with typical bulk wurtzite crystal structures (CdS: JCPDS 41-1049). The results are consistent with previously reported transmission electron microscope studies of the

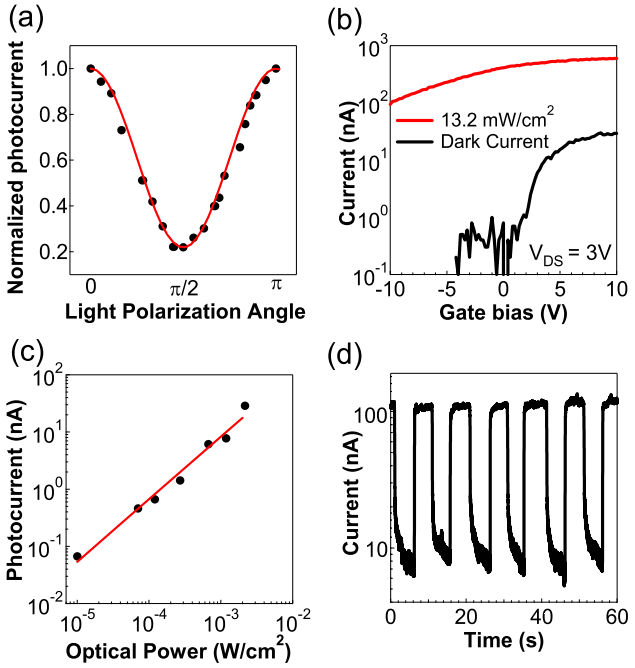


**Figure 3.** (a) The normalized photocurrent of $CdS_{0.5}Se_{0.5}$ NWs as a function of the angle of light polarization. The photocurrent is measured with $V_{GS} = 0$ V and $V_{DS} = 3$ V, and normalized with the current at $\theta = 0°$. (b) The transfer characteristics of a $CdS_{0.5}Se_{0.5}$ NW-array device as a function of the back-gate voltage at $V_{DS} = 3$ V in the dark (black line) and under white light illumination at 13.2 mW $cm^{-2}$ (red line). (c) The photocurrent with $V_{GS} = 0$ V and $V_{DS} = 3$ V as a function of the optical power intensity. (d) The time response under illumination at 2 mW $cm^{-2}$ with $V_{GS} = 0$ V and $V_{DS} = 3$ V.

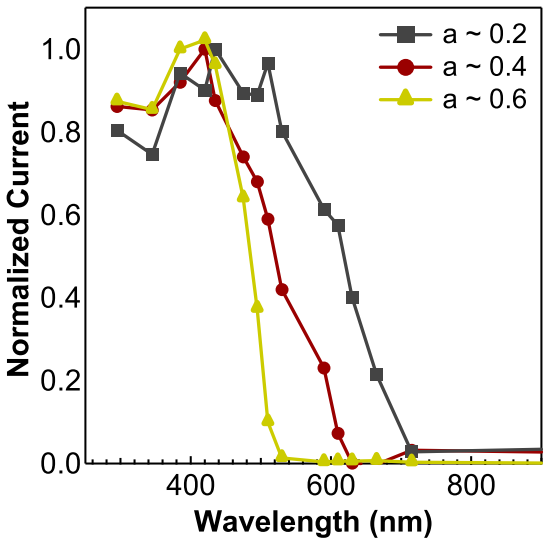


**Figure 4.** The spectral response of the photocurrent obtained from three different NW-array devices corresponding to S-rich, middle, and Se-rich regions.

as-grown $CdS_xSe_{1-x}$ NWs [4]. The diffraction peaks from bottom to top gradually shift toward higher angles, indicating that the lattice constant gradually decreases as the NWs become S-rich. With the extracted lattice cell parameters, the composition $x$ is determined to be in the range between $x = 1$ (CdS) and $x = 0.52$ ($CdS_{0.52}Se_{0.48}$) [4, 5].

Next, the photoresponse of printed parallel NW-arrays is investigated. The composition used in the representative device is $CdS_{0.52}Se_{0.48}$ ($a \sim 0.3$). Figure 3(a) shows the angle dependent photocurrent measurement taken under a halogen lamp (1 mW $cm^{-2}$). The photocurrent was measured by rotating the polarization direction of the incident light from $\theta = 0°$ (maximum) to 90° (minimum), where $\theta$ is the angle between the NW orientation and the polarization direction of the incident light, and normalizing with the current at $\theta = 0°$ [10, 11]. The photocurrent shows a harmonic response and can be fitted to a $\cos^2\theta$ function. The polarization anisotropies are extracted to be ~0.67 according to $\rho = (I_{\parallel} - I_{\perp})/(I_{\parallel} + I_{\perp})$, where $I_{\parallel}$ ($I_{\perp}$) are the photocurrents obtained from light illumination parallel (perpendicular) to the NW direction. The $\rho$ value of ~0.67 is comparable with previously reported results where CdSe NWs are aligned either with dielectrophoresis (~0.75) [10] or a contact printing method (~0.54) [11].

Figure 3(b) shows the back-gated transfer characteristics ($I_{DS} - V_{GS}$) at $V_{DS} = 3$ V with and without illumination (halogen lamp, 13.2 mW $cm^{-2}$). This clearly indicates that the $I_{ph}/I_{dark}$ (photocurrent/dark current) ratio can be modified depending on the back-gate bias, and a high ratio (>100) is obtained for $V_{GS} = 0$–1 V. Figure 3(c) shows the dependence of the photocurrent amplitude on the optical power. The amplitude is expressed with a simple power law ($I_{photo} = c_1 P^{c_2}$), where $P$ is the optical power, $c_1$ is a proportionality constant, and $c_2$ is an empirical value. By fitting, $c_2$ is 1.09. This superlinearity is due to the complex combination of electron–hole generation, trapping, and recombination processes [12]. Figure 3(d) shows the time response of the photocurrent measured under chopped light illumination (halogen lamp: 1 mW $cm^{-2}$). The response time and recovery time, defined as the time between 10% and 90% of maximum photocurrent, are 200 ms and 800 ms, respectively. The time constant for response ($\tau_{resp}$) is 130 ms, and those for slow and fast recovery ($\tau_{rec,slow}$, $\tau_{rec,fast}$) are 80 ms and 350 ms, respectively, which are obtained by fitting the equations $I = I_0(1 - e^{-t/\tau})$ and $I = I_0 e^{-t/\tau}$ to the leading and trailing edges of a single pulse. The biexponential behavior of the recovery is consistent with previous studies of CdS nanoribbons (NRs) [13] and CdSe NRs [14] and NWs [15].

Finally, the spectral response is investigated from representative devices chosen at three different locations ($a$ (cm) = ~0.2, ~0.4, and ~0.6, corresponding to, respectively, the Se-rich, middle, and S-rich regions). The normalized photocurrent at $V_{DS} = 3$ V, illuminated with light through a low pass filter with various cutoff wavelengths, is shown in figure 4. The transition wavelengths extrapolated for the $a = 0.2$, 0.4, and 0.6 devices are ~690 nm (1.8 eV), ~600 nm (2.1 eV), and ~510 nm (2.4 eV), respectively, demonstrating NW-array photodetectors based on different bandgap materials. This result proves that the proposed concept of optical–electrical conversion with various wavelengths on a chip can be achieved. To estimate

the bandgap of a ternary alloy, interpolation of the bandgaps from its two binaries with additional nonlinear bowing can be used.

## 4. Conclusions

In summary, we demonstrate the capability to controllably assemble an organized collection of semiconductor nanomaterials with tunable bandgap by a simple but versatile one-step contact printing process. Eventually, this concept can be extended to other material systems to obtain orthogonal response in optical and chemical sensors.

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