

Chemical vapor deposition growth of CdSSe nanowires for high-performance photodetector

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Abstract: In this paper, CdSSe nanowires with high crystal quality were growth through a chemical vapor deposition method, which used different temperature to control material evaporation rate. Scanning electron microscopy characterization found that these nanowires have a smooth surface structure. Fluorescence microscopy images showed that the nanowires were uniformly distributed in composition, and micro-PL showed that they have high crystalline quality. Photodetector constructed by single nanowire demonstrated a high responsivity of up to $2081\text{A} \cdot \text{W}^{-1}$, a fast rise time of 0.191s and a fall time of 0.192s at bias of 1V. These convincing results indicate that CdSSe nanowires will have a brilliant future in smart optoelectronics.

Keywords: CdSSe nanowires, High crystal quality, Photodetector

1. Introduction

Benefitting from the one-unique dimensional semiconductor nanowires structure and physical characteristics, nanowires are widely used in various optoelectronic devices such as high mobility transistors^[1], semiconductor lasers^[2], resonant tunnel diodes^[3], photodetectors^[4], solar cells^[5], etc. It is precisely because one-dimensional nanowires have the advantages of strong light absorption, high carrier separation and collection efficiency, high mechanical flexibility, rich surface state control functions, and good compatibility, they are widely used in the electrical research of devices, photoelectric and mechanical properties.

II-VI semiconductors, such as CdS, CdSe and their alloy nanowires, their direct band gap and other characteristics make them have the advantages of high absorption and high emission efficiency. It is not only used in nanophotonics, such as optical waveguides, nanolasers, optical interconnection and other fields, but also has potential applications in optoelectronic devices. Although the synthesis and application of II-VI semiconductor nanowires have made progress in many fields, there is still a great improvement in the low-cost method of growing high-quality nanowires.

In this work, homogeneous composition CdSSe nanowires with high crystal quality and optical performances were successfully grown by a chemical vapor deposition(CVD) method that uses different temperature zones to precisely control different materials evaporation rate. In the micro-PL image, it is shown uniform fluorescence of a single alloy nanowires and the micro-PL spectrum indicated high crystallinity of nanowires. The single nanowire photodetector, that manufactured by electron beam lithography(EBL) exhibited low power consumption and excellent light photoresponses.

2. Experiments

2.1. Growth of high-quality CdSSe nanowires

The samples were grown on Si(100) substrates by a metal-catalyzed physical evaporation method, and the evaporation rate and growth of different materials were controlled by a tube furnace with controlled dual temperature zones (the experimental setup is shown in Figure 1). Typically, two quartz boats filled with equimolar commercial-grade CdS and CdSe powders, respectively, were placed in the

center of different temperature zones, and several silicon wafers coated with $\sim 10\text{nm}$ Au film were placed downstream of the gas flow for deposition of the samples. Before heating, high-purity N_2 was introduced into the system at a rate of 150sccm for 40mins to purge the O_2 inside, and the pressure was maintained at 3Torr . The tube furnace was then rapidly heated the left temperature zone to 830°C , while the right temperature zone heated to 800°C . After 60mins of growth, the furnace was naturally cooled down to room temperature. Sponge-like products were deposited on the surfaces of the silicon wafers.

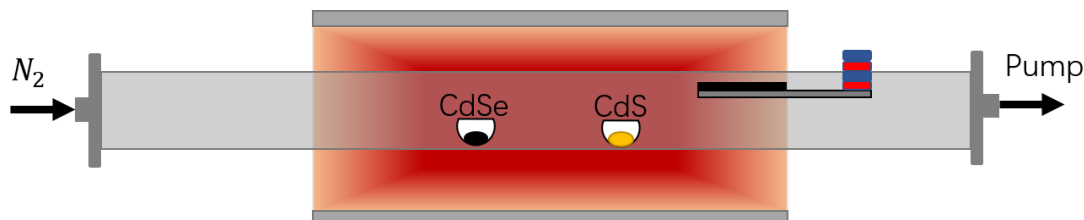


Figure 1: Schematic diagram of the experimental process of growing alloy CdSSe nanowire samples.

2.2. Morphology and characterization

Figure 2(a), (b) and (c) are low, middle and high magnification scanning electron microscope (SEM) images of the obtained sample, which indicates that the nanowires are clean and smooth and free of visible particles and impurities, except for the existence of Au catalyst tips. And the Au catalyst tips indicate that the growth of nanowires followed the vapor-liquid-solid (VSL) mechanism. The nanowires have diameters in the range of $50\text{--}250\text{nm}$ and lengths from several tens of micrometres up to hundreds of micrometres. In order to further study the growth quality of nanowires, Figure 2(d)-(f) are the TEM images we observed. From the STEM images, it can be seen that the nanowire axis is vertical and uniform, with smooth edges. The inset image in Figure 2(e) shows that the nanowires present a good single crystal structure without obvious defects.

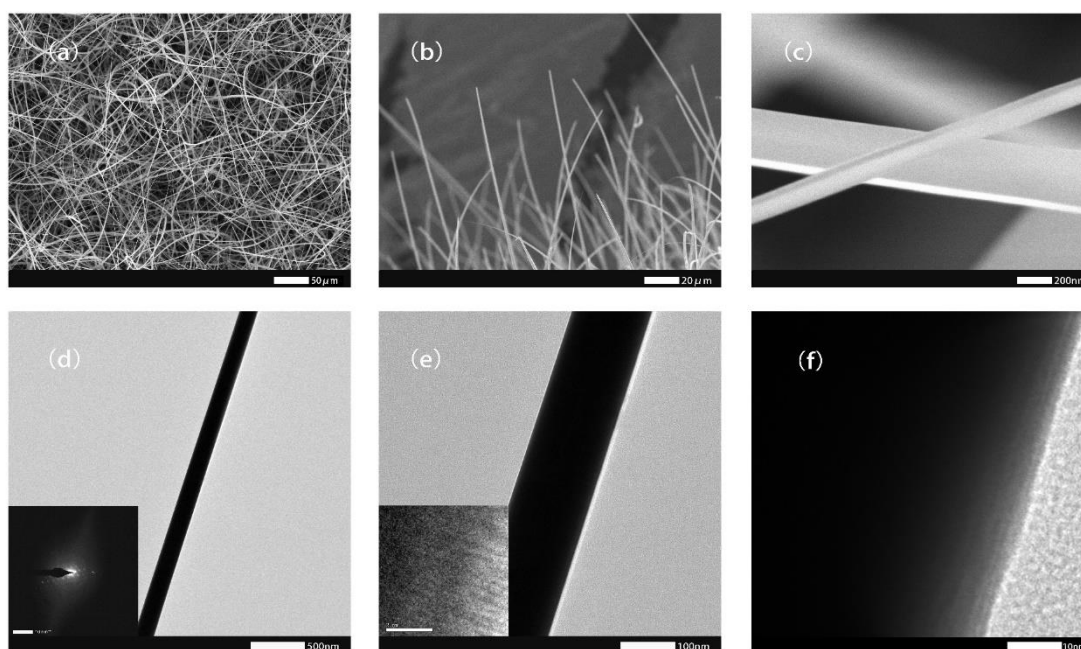


Figure 2: (a-c) The SEM morphology images in low, middle and high magnification of the nanowires obtained, respectively; (d) a typical TEM image of a single nanowire; the inset shows its selected area electron diffraction (SAED) pattern; (e) the TEM morphology images in middle magnification of the nanowire obtained; the inset shows its high magnification TEM at the edge of nanowire; (f) the corresponding high magnification TEM image.

The in-situ energy dispersive X-Ray (EDX) spectra (Figure 3d) collected from a representative part of a single nanowire along the length direction of the wire reveal that the nanowires are mainly formed by Cd, S and Se elements, with about 2:1 ratio of Se/S. The detailed spatial element distributions were

obtained by STEM-EDX elemental mapping and are shown in Figure 3(a-c), which further demonstrate clearly that S is located along the full wire(Figure 3b), and Se is obviously distributed higher than S(Figure 3c), while Cd has an uniform distribution across the whole scanning area(Figure 3a). The elemental analysis results confirm these grown nanowires are composed of pure CdSSe alloy, which is also consistent with the observations in real color photographs and the micro-PL spectra in Figure 4.

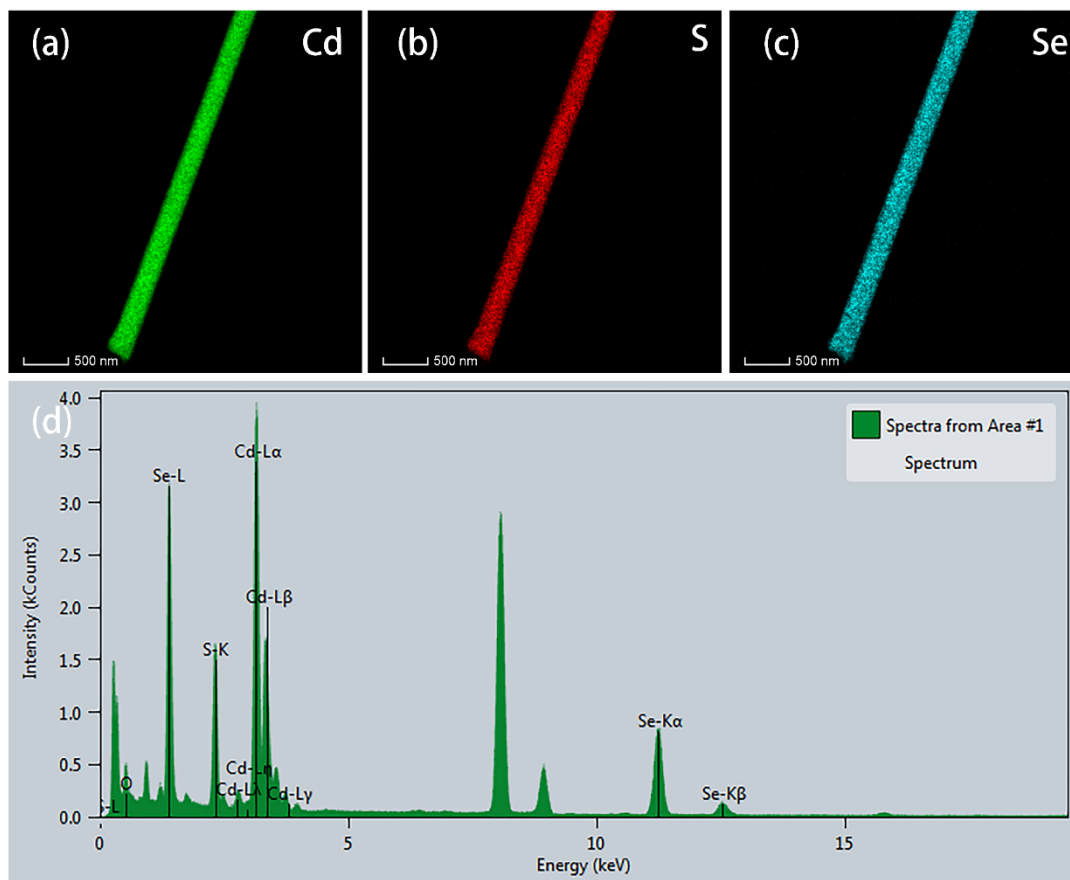


Figure 3: ((a)-(c))2D elemental mapping for the three detected elements(Cd, S, and Se);(d)the in situ energy dispersive x-ray spectrum(EDS)of the nanowires.

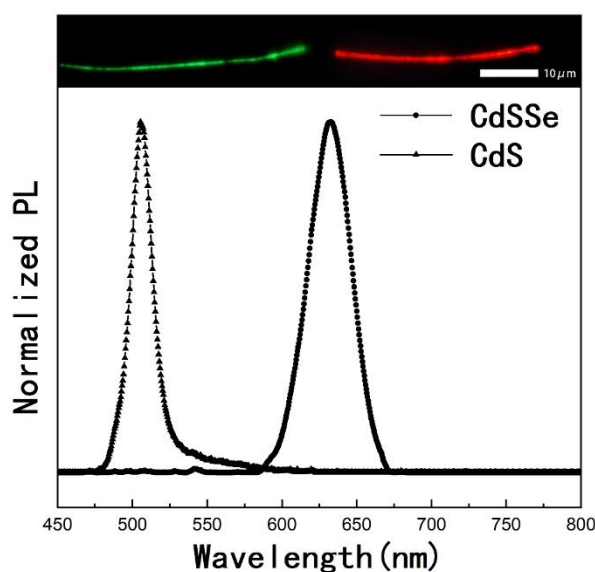


Figure 4: Real-color photo-luminescence(PL)image of a single CdS nanowire and a typical CdSSe alloy nanowire and its micro-PL spectra.

2.3. Optical properties

Figure 4 shows the real-color photograph of the as-grown CdS and CdSSe nanowires, respectively, the single nanowire were dispersed to a clean Si substrate though nano-transfer method and illuminated with a 405nm laser, which further indicates that CdS wire is green fluorescence and CdSSe is red fluorescence. The upper part of Figure 4 shows the corresponding micro-PL spectra detected from two different dispersed nanowires. From the PL results, the CdS nanowire exhibit emissions band with the peak wavelengths at 505nm, and the CdSSe exhibit emission peak at 632nm with FWHM at 32nm, which further indicates that CdSSe exhibit clean bandedge emission with no obvious trap/defect states emission demonstrating the high crystallinity and electronic quality wires.

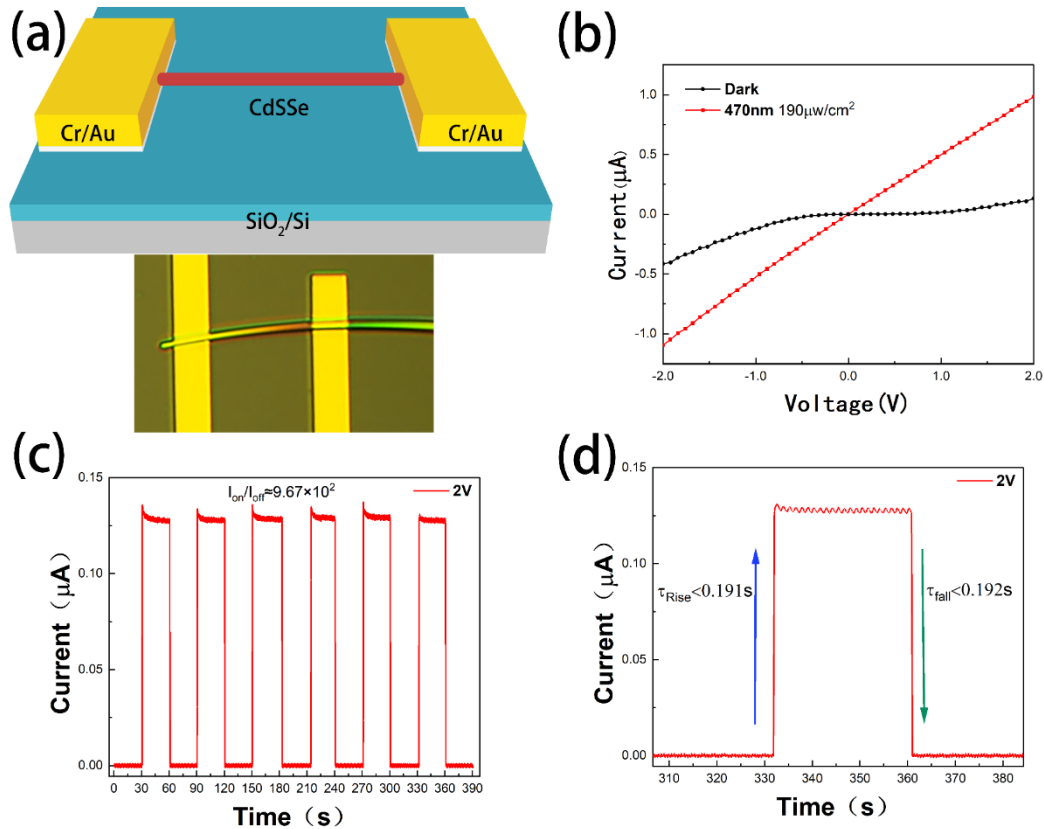


Figure 5: (a) Schematic and Optical microscope image of a nanowire photodetector; (b) I-V curves of the CdSSe nanowire photodetector illuminated with 470nm wavelength lights ($190 \mu W/cm^2$) or under dark conditions; (c) Time-resolved switching behavior of the device under laser intensity of $190 \mu W/cm^2$ at $V_{bia} = 1V$; (d) Enlarged rise and fall sides over round of 333 – 363s.

2.4. Fabrication of the photodetector

Figure 5(a) is the schematically and the optical microscope image of the as-grown single nanowires photodetector. For the construction, single nanowires were first dispersed on a p-type Si substrate with 300nm thickness SiO_2 layer. Then two Cr/Au (15nm/55nm) electrodes are thermal deposited on the ends of the nanowires. After the manufacturing process, we measured its photoresponse properties from $V_{bia} = -2V$ to $2V$ on the two-terminal structure as displayed in Figure 5(b) by turning 470nm laser illumination with $190 \mu W/cm^2$ power intensities. The spectral responsivity (R_λ) of the device can then be obtained by the following equations $R_\lambda = I_{ph}/PS$, where I_{ph} represents the photocurrent defined as the difference between light current and dark current ($V_{bia} = 1V$), P and S ($0.125 \mu m^2$) describe the corresponding light intensity and the effective illuminated area of the device. Excellent light responsiveness can reach $2081 A \cdot W^{-1}$ higher than Li's works⁰. The results that the electric conductance of device at dark condition is very small, but it increased dramatically under the light illumination at 470nm, indicating an excellent conversion ability of optical to electrical signals and a low power consumption of the device.

To explore the capability of the photodetector for fast-varying optical signals, the time-response cycles of the device were obtained by periodically turning on and off the laser at 30s intervals, under incident laser intensity of $190\mu W/cm^2$ at $V_{bia} = 2V$. As plotted in Figure 5(c), the device current sharply and reaches to a steady state about $0.13\mu A$ once the light switch is on, and falls down quickly to $0.0004\mu A$ when the light switch is off, demonstrating an excellent stability and reversible switching properties of the device. The rise time(τ_{Rise}) and fall time(τ_{Fall}), defined as the required time for the current rising to 90% and falling to 10% of the peak value, are about 0.191s and 0.192s, respectively, based on the enlarged curve Figure 5(d).

This high-performance visible-light photodetectors may be derived from two unique characteristics of our samples: (i) The high crystal quality. CdSSe nanowires with fewer defects are conducive to the transport of carriers, thereby increasing the photoconductive gain and promoting the photocurrent to quickly reach a steady state during the rising and falling process^{[6][7]}. (ii) The smaller diameter of the nanowire ($\sim 100nm$). On the one hand, the large specific surface area of nanowires ensures response speed of our device when the light source is turned on. On the other hand, when the light source is turned off, defects on the surface of the nanowires and dangling bonds can increase the recombination rate of carriers, meaning a shorter fall time^[9].

3. Conclusion

In summary, this work successfully growth CdSSe nanowires with excellent optical properties and high crystallinity by the method of controlling the evaporation rate of different material, with dual temperature zones. Micro-PL indicate all these nanowires have single crystalline phase structure without obvious defects. Benefitting from the high crystallinity and large specific area of CdSSe nanowires, the photodetector constructed by single nanowire demonstrates a high responsivity of $2081A \cdot W^{-1}$ and fast response speed ($\tau_{Rise} = 0.191s$, $\tau_{Fall} = 0.192s$). These works may accelerate the development of a new generation of high-performance optoelectronic devices.

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