A Quaternary ZnCdSeTe Nanotip Photodetector

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Received: 20 June 2009 / Accepted: 1 September 2009 / Published online: 16 September 2009
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Abstract The authors report the growth of needle-like high density quaternary Zn$_{0.87}$Cd$_{0.13}$Se$_{0.98}$Te$_{0.02}$ nanotips on oxidized Si(100) substrate. It was found that average length and average diameter of the nanotips were 1.3 μm and 91 nm, respectively. It was also found that the as-grown ZnCdSeTe nanotips exhibit mixture of cubic zinc-blende and hexagonal wurtzite structures. Furthermore, it was found that the operation speeds of the fabricated ZnCdSeTe nanotip photodetector were fast with turn-on and turn-off time constants both less than 2 s.

Keywords ZnCdSeTe · Nanotips · MBE · Photodetector

Introduction

ZnSe is an important II–VI semiconductor with wide direct bandgap energy of 2.67 eV and large exciton binding energy of 21 meV at room temperature. Two-dimensional (2-D) ZnSe-based epitaxial layers can also be grown directly on the closely lattice matched GaAs substrate. Other than the binary ZnSe, it is possible to grow strained and/or lattice matched ternary/quaternary epitaxial layers so as to achieve ZnSe-based heterostructures. Using these heterostructures, ZnSe-based light emitting diodes [1], laser diodes [2], and photodetectors [3] have all been demonstrated. Other than 2-D epitaxial films, one-dimensional (1-D) semiconductor nanostructures such as nanowires, nanorods, nanotips, and nanotubes have attracted great attention in recent years. With a significantly larger surface-to-volume ratio, 1-D semiconductor nanostructures exhibit unique optical and electronic properties that make them desirable for use in various novel devices. For example, it has been shown that 1-D ZnO nanowire photodetector exhibit extremely high photoconductive gain [4]. Very recently, we also reported the fabrication of a 1-D ZnSe nanowire photodetector [5].

Similar to devices based on 2-D epitaxial films, heterostructure also plays an important role in 1-D nanostuctured devices. For example, it is possible to couple the longitudinal confinement with radial confinement in heterostructure nanowires. This could provide more functionalities for heterostructure nanowires, as compared to homogeneous ones [6]. To realize ZnSe-based heterostructure nanowires, it is necessary to form ZnSe-based ternary/quaternary nanowires. The growth of ternary ZnCdSe nanowires has already been demonstrated by Colli et al. [7]. Compared to ternary ZnCdSe, the quaternary ZnCdSeTe provides an extra degree of freedom to control the bandgap energy and...
lattice constant. By controlling the composition ratio among Zn, Cd, Se, and Te carefully, we should be able to grow lattice matched ZnCdSeTe on ZnSe with adjustable bandgap energy [8]. Furthermore, it has been reported that binding energy of Te bound excitons in related II–VI compound semiconductors is very large. Extremely strong room temperature photoluminescence (PL) and electroluminescence (EL) signals were also observed from localized excitons bound to Te atom (Te₁ emission) and Teₙ (n ≥ 2) cluster (Teₙ cluster emission) in 2-D ZnSeTe films [9–11]. It has also been shown that the extrinsic self trapping of excitons (STE) formed in Te-related emission in ZnSeTe films could provide a much higher luminescence efficiency, as compared to free excitons [11–16]. These observations suggest that Te-containing II–VI nanowires are potentially useful for various applications. If we can grow 1-D ZnCdSeTe nanowires successfully, we should also be able to achieve ZnSe-based heterostructure nanowires with improved optical properties. This will be important in realizing ZnSe-based nanodevices. In this work, we report the growth of quaternary ZnCdSeTe nanotips on oxidized Si(100) substrate. A ZnCdSeTe nanotip photodetector was also fabricated. Structural, physical, electrical, and optical properties of ZnCdSeTe and the fabricated photodetector will also be discussed.

Experiment

The quaternary ZnCdSeTe nanotips used in this study were grown by a Riber 32P solid source molecular beam epitaxy (MBE) system using vapor–liquid–solid (VLS) mechanism with Au nanoparticles as the catalyst [5]. The source materials for the MBE system were elemental Zn(6 N), Cd(6 N), Se(6 N), and Te(6 N). Prior to the growth of quaternary ZnCdSeTe nanotips, a Si(100) substrate was first immersed in boiled acetone for 10 min, in boiled isopropyl alcohol for 10 min, and in hydrofluoric acid solution for 30 s. The chemically cleaned substrate was then rinsed in deionized water and dried with nitrogen flow. The substrate was then thermally oxidized to form a 150-nm-thick SiO₂ film. A 0.6-nm-thick Au film was subsequently sputtered onto the oxidized substrate. The substrate was then loaded onto the preparation chamber and annealed at 280 °C for 10 min to form Au nanoparticles [17]. Subsequently, the substrate was transferred into the growth chamber to grow the quaternary ZnCdSeTe nanotips at 280 °C for 1 h. During the growth, the beam equivalent pressures of Zn, Cd, Se, and Te were kept at 1.7 × 10⁻⁷, 5.1 × 10⁻⁸, 1.5 × 10⁻⁶, and 2.5 × 10⁻⁷ Torr, respectively. With careful calibration and precise control of growth parameters, we can thus control the composition ratio of our nanotips at Zn₀.₈₇Cd₀.₁₃Se₀.₉₈Te₀.₀₂.

Surface morphology of the sample was then characterized by a Hitachi S-4700I field-emission scanning electron microscope (FESEM) operated at 15 kV. A Philips FEI TECNAI G² high resolution transmission electron microscopy (HRTEM) operated at 200 kV and a Siemens D5000 X-ray diffractometer (XRD) system were used to evaluate crystallographic and structural properties of the as-grown quaternary ZnCdSeTe nanotips. The micro-Raman measurements were also performed using a 532 nm laser excitation. Photoluminescence (PL) properties of the nanotips were then measured at 20 K. The excitation source of the PL measured was a chopped continuous wave (CW) He–Cd laser operated at 325 nm. The luminescence signal emitted from the sample was then recorded by a lock-in amplifier.

For the fabrication of the quaternary Zn₀.₈₇Cd₀.₁₃Se₀.₉₈Te₀.₀₂ nanotip photodetector, we sputtered a thick Au film through an interdigitated shadow mask onto the nanotips to serve as the contact electrodes. The size of the shadow mask was 1950 × 4000 µm. Figure 1a shows schematic diagram of the fabricated nanotip photodetector. The electrode pattern was designed to have a spacing of 150 µm between the neighboring fingers. Dark current–voltage (I–V) characteristic of the fabricated photodetector was then measured by a Keithley 4200 semiconductor parameter analyzer. We subsequently illuminated the photodetector with a 1 mW ultraviolet light and measured its I–V characteristic again.

Results and Discussion

Figure 2a and b shows cross-sectional and top-view FESEM images of the as-grown quaternary ZnCdSeTe nanotips, respectively. It has been shown previously that ZnSe and ZnCdSe nanowires can be grown by MBE based
on Au-catalyzed VLS deposition [7]. Similar growth mechanism can be applied to our ZnCdSeTe nanotips and can be explained in Fig. 1b. With the Au nanoparticles dispersed on the oxidized Si substrate, eutectic Au–ZnCdSeTe alloy droplets were first formed [18, 19]. The deposited source atoms (i.e., Zn, Cd, Se, and Te) were then diffused along the nanotip sidewalls to form the ZnCdSeTe nanotips [20]. As shown in Fig. 2a, it was found that high density ZnCdSeTe nanotips were successfully grown on the oxidized Si(100) substrate with an average length of about 1.3 μm. It was also found from Fig. 2b that our nanotips were tapered with an average diameter of about 91 nm. Inset in Fig. 2b shows an enlarged FESEM image. It can be seen clearly that sawtooth-like stacking faults were formed at the sidewalls of the nanotips. On the other hand, it has been shown very recently that geometry of the ZnSe 1-D nanostructure grown by MBE depends strongly on temperature [21]. At high temperatures (i.e., 350–450 °C), nanowires with high aspect ratios were formed. Instead of nanowires, needle-shaped structures with wide base and sharp tip were formed at low temperatures (i.e., ~300 °C) due to the low migration speed of adatoms. The quaternary ZnCdSeTe nanotips observed in Fig. 2b should thus be attributed to the low growth temperature used in this study. Figure 3a shows a low-magnification bright-field (BF) TEM image of the as-grown sample. It was found that we can clearly observe an Au nano-particle at the tip. This indicates that our quaternary ZnCdSeTe nanotips were indeed grown via VLS mechanism. Inset in Fig. 3a shows an enlarged image taken from the top portion of one randomly selected nanotip. It can be seen again that sawtooth-like stacking faults were formed at the sidewalls of the nanotip. Similar sawtooth-like stacking faults were also observed from the sidewalls of 1-D ZnTe and InP nanostructures [22, 23]. Figure 3b and c shows high-magnification BF TEM images taken from the edge portion of two neighboring nanotips. Insets in Fig. 3b show selected area electron diffraction (SAED) patterns while insets in Fig. 3c show HRTEM images of the ZnCdSeTe nanotips. As shown in the SAED patterns, pairs
of reciprocal diffraction spots co-exist along cubic zinc-blende (ZB) structured phase and hexagonal wurtzite (WB) structured phase, respectively. It was also found from the HRTEM images that two different lattice constants (i.e., 0.325 and 0.354 nm) co-exist in different regions of our quaternary ZnCdSeTe nanotips. These results suggest that our nanotips are dual-phased.

Figure 4 shows energy dispersive X-ray (EDX) line-scanning of Zn, Cd, Se, and Te. Inset shows a scanning TEM image along the cross-section of a nanowire.

![Fig. 4 EDX line-scanning of Zn, Cd, Se, and Te. Inset shows a scanning TEM image along the cross-section of a nanowire.](image)

We keep the atomic percentage of Zn, Cd, Se, and Te around 43.5, 6.5, 49, and 1%, respectively. Figure 6 shows high angle annular dark field scanning TEM image and EDX elemental mapping of Zn, Cd, Se, and Te. It can be seen from Fig. 6 that the Te nanotip is not as sharp as others. This should be attributed to low Te concentration, as compared to Zn, Cd, and Se. From the intensities shown in Figs. 4 and 5 and from the EDX elemental mapping results shown in Fig. 6, it was found that composition ratio of the nanotips is $Zn_{0.87}Cd_{0.13}Se_{0.98}Te_{0.02}$, which agrees well with the designated composition ratio. It should be noted that the nanotips could not be grown successfully when the composition ratio is not reached exactly.

Figure 7 shows XRD spectrum measured from the as-grown sample. Table 1 lists the point group II–VI semiconductors, with various crystal structures and lattice constants, using Joint Committee on Powder Diffraction Standards. It was found that the diffraction peaks observed in Fig. 7 could all be exclusively indexed by the WZ and ZB crystal structures. It can also be seen that full-width-half-maxima of the observed XRD peaks were small. This suggests large grain size and reasonably good crystal quality of our ZnCdSeTe nanotips. Raman spectrum of the ZnCdSeTe nanotips measured at room temperature was shown in Fig. 8a. As shown in the figure, we observed a Si substrate related Raman peak at 521 cm$^{-1}$ [24]. Other than this peak, we also observed two strong Raman peaks at $\sim$241 and 482 cm$^{-1}$ and one much weaker peak at $\sim$189 cm$^{-1}$. The strong Raman peaks at $\sim$241 and 482 cm$^{-1}$ should be attributed to the longitudinal optical phonon mode while the weak Raman peak at $\sim$189 cm$^{-1}$ should be attributed to the transverse optical phonon mode of our ZnCdSeTe nanotips [25–27]. PL spectrum of the ZnCdSeTe nanotips measured at 20 K was shown in Fig. 8b. By Gaussian fitting, it was found that the measured PL spectrum composed of two emission bands, a narrow near band edge peak at 535 nm and a broad deep level related emission peak at 575 nm. It was also found that FWHMs were about 18 and 53 nm, respectively, for the near band edge peak and deep level peak. It should be noted that the deep level emission at 575 nm should be attributed to dislocations, stacking faults, and nonstoichiometric defects in our ZnCdSeTe nanotips [28].

Figure 9 shows I–V characteristics of the fabricated ZnCdSeTe nanotip photodetector measured in dark and under ultraviolet illumination. It was found that measured currents increased nonlinearly with the applied bias which indicates that Schottky contacts were formed between the sputtered Au film and the ZnCdSeTe nanotips. With 5 V applied bias, it was found that dark current of the fabricated device was only $1.71 \times 10^{-7}$ A. The small dark current should be attributed to the fact that no dopant was introduced during the growth of these nanotips. Under illumination, it was found that measured current increased to $4.5 \times 10^{-7}$ A with the same 5 V applied bias. Figure 10 shows measured photo response as a function of time as we
switched the UV illumination on and off. With a 5 V applied bias, it was found that measured current increased rapidly as we shined UV light onto the fabricated photodetector. As we turned off the UV illumination, it was found that measured current decreased to its original value. As shown in Fig. 10, it can be seen that turn-on and turn-off time constants of the fabricated devices were both less than 2 s. The reasonably large photocurrent to dark current contrast ratio also suggests that the 1-D ZnCdSeTe nano-tips photodetector is potentially useful for practical detector applications. It should be noted that crystal quality of the ZnCdSeTe nanotips reported in this study was not optimized. By adjusting parameters such as growth temperature, catalyst, substrate surface quality/cleanliness, substrate oxidization, and BEP, we should be able to

Table 1 Crystal structure and lattice constants of group-II–VI semiconductors

| Material (II–VI) | Crystal structure | a (nm) | c (nm) | JCPDF card |
|------------------|-------------------|--------|--------|------------|
| c-ZnSe           | ZB                | 0.567  |        | 05-0522    |
| w-ZnSe           | WB                | 0.3996 | 0.655  | 15-0105    |
| c-CdSe           | ZB                | 0.6077 |        | 19-0191    |
| w-CdSe           | WB                | 0.430  | 0.702  | 02-0330    |
| c-ZnTe           | ZB                | 0.6102 |        | 15-0746    |
| w-ZnTe           | WB                | 0.431  | 0.709  | 19-1482    |
| c-CdTe           | ZB                | 0.6481 |        | 15-0770    |
| w-CdTe           | WB                | 0.458  | 0.750  | 19-0193    |
| c-ZnCdSeTe       | ZB                | 0.606  |        | 65-7966    |
minimize the number of stacking faults and thus improve performance of the 1D ZnCdSeTe nanotips photodetector.

Conclusions

In summary, we report the growth of high density quaternary Zn$_{0.87}$Cd$_{0.13}$Se$_{0.98}$Te$_{0.02}$ nanotips on oxidized Si(100) substrate using VLS mechanism by MBE with Au nanocatalyst. It was found that average length and average diameter of the nanotips were 1.3 μm and 91 nm, respectively. It was also found that the as-grown ZnCdSeTe nanotips exhibit mixture of cubic zinc-blende and hexagonal wurtzite structures. Furthermore, it was found that the operation speeds of the fabricated ZnCdSeTe nanotip photodetector were fast with turn-on and turn-off time constants both less than 2 s.

Acknowledgments This work was supported in part by the Taiwan Semiconductor Manufacturing Company, Ltd. (TSMC), in part by the Center for Frontier Materials and Micro/Nano Science and Technology, National Cheng Kung University (NCKU), Taiwan (D97-2700), and in part by the Advanced Optoelectronic Technology Center, NCKU, under projects from the Ministry of Education. This work was also in part supported by Ministry of Economic Affairs (MOEA) and NSC 98-EC-17-A-09020769. The authors would also like National Taiwan University of Science and Technology for the assistance in TEM measurements.

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Fig. 9 Dark and photo I–V characteristics of the fabricated ZnCdSeTe nanotip photodetector

Fig. 10 Measured photo response as a function of time as we switched the UV illumination on and off
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