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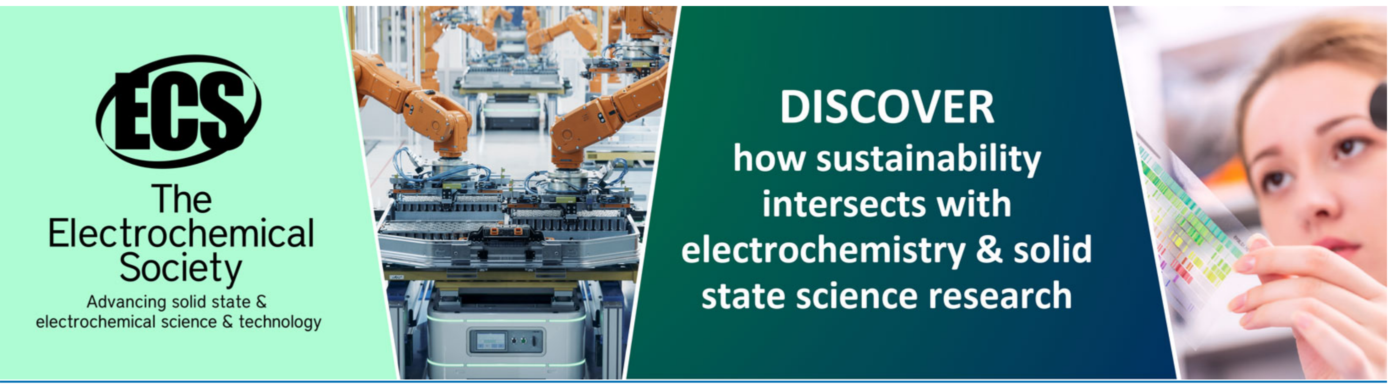

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Twinning modulation in ZnSe nanowires

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Abstract
ZnSe nanowires were grown on Si substrates by Au-catalyzed vapour phase growth at 725 °C. A detailed structural and microstructural investigation has been carried out using electron diffraction and high-resolution transmission electron microscopy (HRTEM). Modulated twins have been observed along the nanowire axial direction along the entire length of the nanowires. Faceting has been observed on the side surfaces of the wires with a larger twinning periodicity. The formation mechanism of these twinning-modulated nanowires is discussed. The optical properties are correlated with the microstructure of the nanowires. These twinning-modulated ZnSe nanowires might have great potential as building blocks for optoelectronic nanodevices.

1. Introduction

ZnSe is a wide-band-gap (E_g 2.7 eV at 300 K) II–VI semiconductor, which is suitable for blue and green light emission. With its large exciton binding energy (21 meV), ZnSe is an ideal candidate for efficient room-temperature exciton devices. Thus, in recent years, ZnSe-based microstructures have been widely investigated for their potential optoelectronic applications. Moreover, controlling the formation of different ZnSe nanostructures, as well as achieving well-confined interfaces induced by structural modulations, may lead to further novel properties and promising applications in nanoscale optoelectronic devices [1–6]. However, defects related to stoichiometric variations such as point defects, twins and stacking faults are commonly detected in nanomaterials including the II–VI materials [7, 8]. Twin boundaries in particular are expected to have significant effects on optical, electronic and mechanical properties [9–12]. Therefore, it becomes imperative to investigate the microstructure of one-dimensional ZnSe nanostructures.

In this paper, we report on the structure and correlated optical properties of twin modulations in ZnSe nanowires. The modulated twins are observed along the nanowire axial direction throughout the entire length. Faceting is observed on the side surfaces of the wires with a larger twin periodicity.

2. Experimental procedure

ZnSe nanostructures were grown on n-type (1 1 1) silicon wafers by vapour phase growth at 725 °C. The Si substrate was first cleaned and a thin layer of Au (50 nm) was deposited by thermal evaporation. The source material was pure ZnSe powder (99.999% purity). The Si substrates were placed at the downstream end of a flowing Ar gas furnace. The source temperature was rapidly raised to 1000 °C, while the substrate was maintained at 725 °C. The nanostructures were found to grow preferentially on the Au catalyst locations. Samples for transmission electron microscopy (TEM) examinations were prepared by scraping the products off the substrate, and dispersing them onto a copper grid coated with a lacy carbon film. Scanning electron microscopy (SEM) observation was carried out via a field-emission gun system. Selected-area electron diffraction (SAED), bright-field (BF) imaging, high-angle annular dark-field (HAADF) imaging, high-resolution transmission electron microscopy (HRTEM) and energy dispersive x-ray spectroscopy (EDS) analyses were performed using a field-emission gun, scanning transmission electron microscopy (STEM) operating at 200 kV. Photoluminescence (PL) measurements were performed at room temperature using second harmonic emission (380 nm) from a Coherent Mira 900 Ti-Sapphire laser. The laser beam diameter was 0.5 mm with an excitation pulse width of 200 fs, a repetition rate of 76 MHz and an average power of 40 mW.

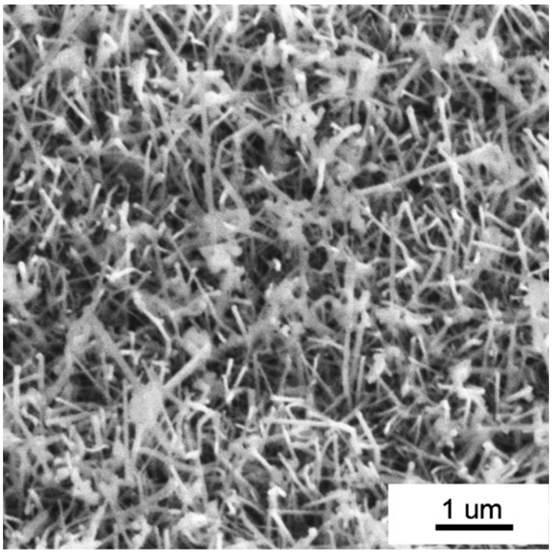

Figure 1. A typical SEM image of the ZnSe nanowires investigated.

3. Results and discussion

The products were extensively examined using STEM. Three different types of ZnSe nanostructures were observed: nanowires, nanoribbons and nanosaws. Their estimated areal fractions found in the TEM samples were 40%, 20% and 40%, respectively, which also reflected the approximate ratio of these structures as seen in SEM images. We have investigated the microstructure of ZnSe nanosaws [13], and here we focus on the microstructural investigation of the nanowires. SEM observations (figure 1) show that the diameters range from 30 to 250 nm. TEM examinations indicate that the nanowires have a zinc-blende structure, and most of them have periodic twins along their growth direction $\langle 1\,1\,1\rangle$. The particular polarity of the growth was not determined but was likely $\langle 1\,1\,1\rangle$B, similar to observations in GaAs and other III–V [6, 14]. Quantification of EDS spectra revealed that the nanowires contain only Zn and Se of equal atomic ratio, while the tip is an alloy from the system Au–Zn–Se. No evidence of Au migration away from the tip was detected.

Figure 2(*a*) shows a BF image of a single ZnSe nanowire with a diameter of about 230 nm. From figure 2(*a*), it can be clearly seen that alternating black/light contrast appears along the growth direction [1 1 1], with a periodicity around 16 nm. Figure 2(*b*) shows a HRTEM image from the rectangle-enclosed region in figure 2(*a*). From the HRTEM image, we can clearly see that the alternating contrast corresponds to periodical twins. The twin periodicity is the same as that of the alternating contrast shown in the bright-field image. In this nanowire, faceting is not very evident although it begins to be apparent on the side surface. There are also some kinks on the side surfaces of the wire. However, the wire has a more or less cylindrical shape.

For wires with a larger twin periodicity, faceting appears on the side surfaces. Figure 3(*a*) shows an example of an individual ZnSe nanowire with a larger twin periodicity. The wire has a diameter of about 200 nm, and the twin periodicity is about 50 nm. From figure 3(*a*), it is very clear that this zigzagged nanowire consists of many subunits, and each subunit has a projected shape of a parallelogram along $[0\,\bar{1}\,1]$. The turning points in general coincide with the twin boundaries and yield a series of parallelogram-shaped nanounits. It is well known that the $\{1\,1\,1\}$ twinning angle between two adjacent twin variants in equilibrium is 70.53° [15]. The zigzag angle between two twinning nanounits is measured to be 141°, which is in good agreement with the theoretical estimation. From the energy point of view, it is known that the $\{1\,1\,1\}$ planes are the most densely packed and thus the most stable. As in figure 3(*a*), all facets on the side surfaces can be indexed as $\{1\,1\,1\}$ planes, which reduces the surface energy drastically. Figure 3(*b*) shows the $[0\,\bar{1}\,1]$ zone-axis diffraction pattern from this ZnSe nanowire confirming the existence of twinning in the wire. HRTEM images (figures 3(*c*) and 3(*d*)) from the rectangle-enclosed regions in figure 3(*a*) prove that the angle between two subunits is 141°. A similar structure in GaP and ZnO has been recently analysed to consist of octahedral segments between the twin planes [6, 11].

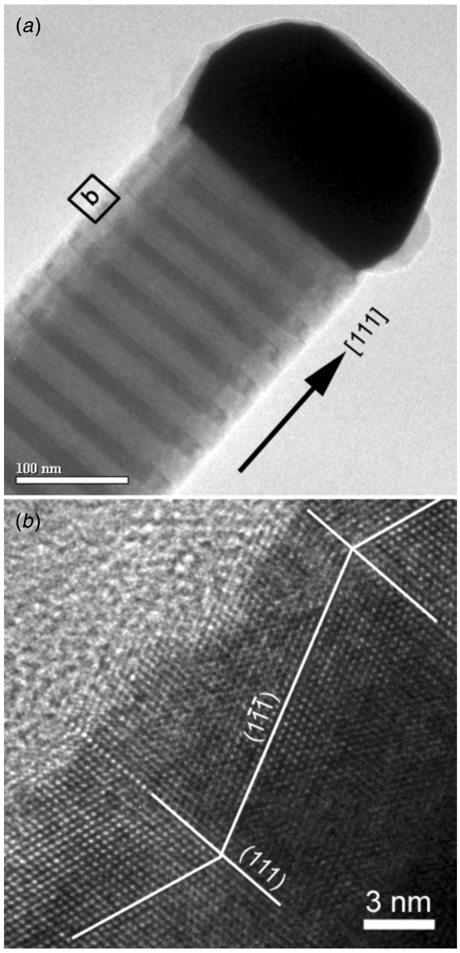

Figure 2. (*a*) A typical bright-field (BF) TEM image of a ZnSe nanowire with alternating black/light contrast; (*b*) HRTEM image from the square-enclosed region in (*a*).

From TEM examination, it is clear that the diameter of the nanowires is determined by the Au particle size at the tip. In addition, the different morphologies of ZnSe nanowires are associated with different shapes of gold particles and different interfaces between the gold catalyst and the wire. For the cylinder-shaped nanowires, the gold particles have

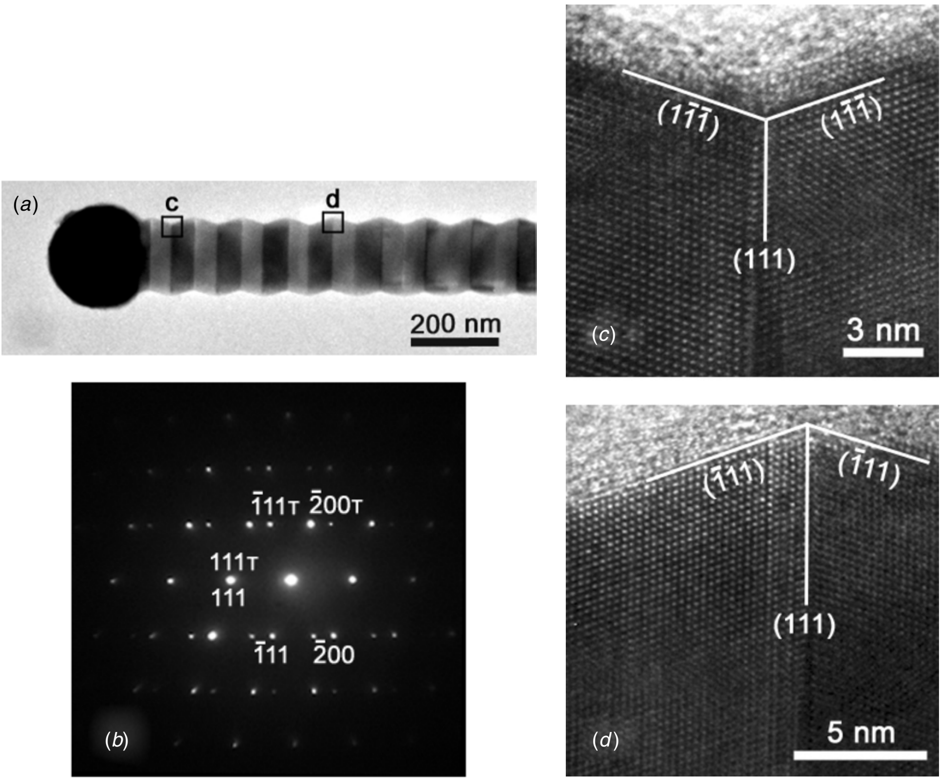

Figure 3. BF images (*a*) and (*b*) of a ZnSe nanowire with a large twinning periodicity and the corresponding electron diffraction pattern; HRTEM images (*c*) and (*d*) from the square-enclosed regions in (*a*).

a hemispherical shape, and the interface between the gold particle and ZnSe nanowire is flat. However, for the zigzagged wires, the gold nanoparticles are more spherical, and the interfacial region is not flat. The influence of interfacial lattice mismatch between the catalyst and nanostructure on nanostructure shape has been reported in other systems [16]. The twin periodicity is crucial for the appearance of faceting on-side surfaces. And for nanowires with a larger twin periodicity, the faceting is more evident, consistent with having more time to adjust and to adopt a more energy-favourable side surface.

According to classical explanation, the existence of the catalyst (Au) particles at the tip of the nanowires observed by both SEM and TEM is considered as evidence for the operation of a vapour–liquid–solid (VLS) mechanism. During the growth at the interface between Au particle and ZnSe wires, the elastic energy and residual stress may be periodically released by the formation of coherent twin boundaries. Twins and stacking faults dominate only in the samples grown above a certain temperature. At lower temperature (650 °C), most nanowires are free of defects. Thus, higher growth temperature is also crucial for the formation of these twinning-modulated ZnSe nanowires. Fluctuations in mass transport or temperature influencing growth rates and twin formation would likely be more severe at higher temperatures.

To correlate the microstructure with the optical properties, we carried out photoluminescence (PL) measurements on ZnSe nanowires while still attached to the Si substrate. We have not measured individual wires but rather the ensemble of substrate plus grown material. At least four spots were

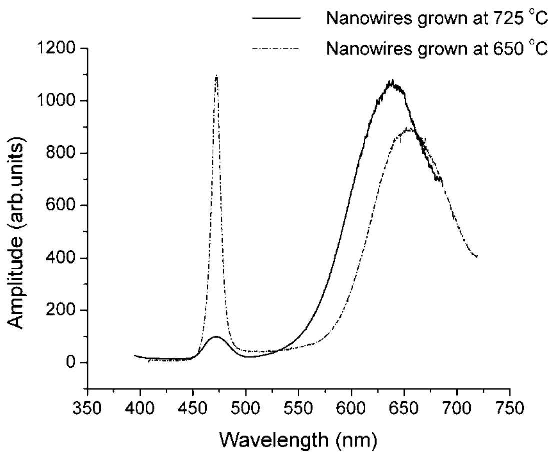

Figure 4. Typical PL spectra from ZnSe nanowires grown at 650 °C and 725 °C. The band edge emission intensity (∼463 nm) decreases with increasing growth temperature while the broad deep defect-related emission (extending from 500 to 680 nm) increases.

characterized on each sample. Typical PL spectra for samples grown at high and low temperatures are shown in figure 4. As can be seen, these spectra have two characteristic peaks corresponding to a narrow near band edge (NBE) emission at 465 nm and a broad defect-related deep level (DL) emission peak extending from 500 to 680 nm. The amplitude of these peaks varied from spot to spot depending on the density of wires, but the ratio did not. For samples with nanowires grown at 650 °C, containing few defects visible by TEM, the PL spectrum is dominated by NBE emission with a lower emission from the DL states. On the other hand, the PL spectrum from samples with nanowires grown at 725 °C containing a high density of visible structural defects including twins and stacking faults, is dominated by the DL emission with very weak NBE emission. These results suggest a strong anti-correlation between radiative band edge transitions and samples with visible structural defects in ZnSe nanowires. Samples with as-grown nanowires of poor structural quality tend to exhibit stronger DL transitions and smaller band edge emission.

This DL emission peak may be associated with point defects and/or with the visible planar defects seen in these wires [17]. The relative importance of point versus planar defects on the optical properties is not easy to determine. However, we suspect that it is point defects that are more important. Observations on the broad DL emission band as a function of post growth annealing environments find that it can be controlled, indicating that zinc point defects such as interstitials and vacancies are likely involved [17]. Thus, the presence of stacking faults may indicate an excess concentration of point defects invisible to TEM. Nanowires grown at the lower temperature of 650 °C with few stacking faults and with exciton-based PL emission dominant, likely had a more stoichiometric composition [17]. At higher growth temperatures including 725 °C non-stoichiometric point defects likely increased in concentration, participated in the generation of the observed stacking fault defects, and were primarily responsible for the resulting poorer PL properties.

4. Conclusion

In conclusion, modulated twins are observed along ZnSe nanowire axial directions throughout the entire length of wires grown at 725 °C by vapour–liquid–solid deposition. Faceting is observed on the side surfaces of wires with the larger twin periodicity. The presence of twins is correlated with a defect-related PL emission that likely indicates a large associated point defect concentration within the wires. This unique structure observed in ZnSe nanowires could lead to potential applications in nano-optoelectronics.

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