

Luminescence of ZnSe nanowires grown by metalorganic vapor phase deposition under different pressures

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Quasi-one-dimensional ZnSe nanowires have been synthesized by metalorganic chemical vapor deposition on Si (001) substrates, sputter coated with gold catalyst, at various pressures using diethylzinc and diisopropylselenide. The nanowires appear to be randomly oriented on the substrate and some are slightly bent along their length. X-ray diffraction and scanning electron microscopy studies show that the nanowires are zincblende in structure and have a uniform cross section along its length, and an average diameter about 30 nm, regardless of growth pressure. Individual strands of the nanowires were examined by high-resolution transmission electron microscopy and were found to be single crystals elongated along the $\langle 112 \rangle$ crystallographic direction. Gold particles at the tips of the nanowires identified by transmission electron microscopy and atomic force microscopy indicate that the nanowires grow via the vapor-liquid-solid process. Room-temperature photoluminescence spectra of the ZnSe nanowires grown under different pressures show variations in their optical properties, despite their similarity in morphology and crystalline structure. At the optimal pressure of growth, strong near band-edge emission and very weak deep-level emissions are observed, indicating the low level of nonstoichiometric defects in the resulting ZnSe nanowires.

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I. INTRODUCTION

Since the discovery of carbon nanotubes by Iijima,¹ one-dimensional (1D) nanostructured materials, such as nanotubes,² nanowires,^{3–8} and nanobelts,⁹ have become an intriguing field of research. Extensive studies on their synthesis have been carried out by various methods⁷ because of their fundamentally interesting mesophysical phenomena and potential nanodevice applications. Many semiconductors of interest have now been synthesized into nanoscale forms. Among these, ZnSe has attracted a fair share of attention because of its promising potentials in fabricating blue- and green-emitting optoelectronic nanodevices. Compared to the extensive studies of quantum wells and dots,^{10,11} studies on wires have been rather limited for this important semiconductor. Electron-beam lithography and wet etching techniques were used to laterally pattern ZnSe quantum wires on chalcogenide substrates.^{12,13} However, these methods are limited by the resolution of the lithography and the complexity of processes involved.

Alternatively, ZnSe nanowires have also been directly synthesized by a solvothermal route,¹⁴ laser-assisted catalytic growth,¹⁵ atomic layer deposition process,¹⁶ and vapor phase growth.^{17–19} As far as we know, growing ZnSe nanowires by metalorganic chemical vapor deposition (MOCVD) has not been reported. MOCVD is a technique with a demonstrated track record in the commercial production of light-emitting devices. The purity of precursors used and the lower temperatures of growth ensure that the nanowires grown contain very low concentration of impurities. The reductive environ-

ment of hydrogen gas in the reactor also significantly lowers the likelihood of oxidation of their surface. To realize their potential, optical, in addition to the structural and morphological, properties of the nanowires grown under different conditions have to be studied. Nonoptimal conditions of growth often yield nanowires that contain too many detrimental defects to be useful in optoelectronic applications. In this article, we report the synthesis of ZnSe nanowires on Si (001) substrates sputter coated with gold by MOCVD under different reactor pressures. Photoluminescence (PL) studies of nanowires allow us to identify an optimal pressure for the growth of ZnSe nanowires that emits predominantly via band-edge exciton transitions.

II. EXPERIMENTAL DETAILS

ZnSe nanowires were grown on (001) Si substrate in a horizontal reactor using diethylzinc and diisopropylselenide as precursors and 7N hydrogen as carrier gas. The substrate was steamed in 1-1-1 trichloroethane vapor for 30 min, rinsed with deionized water, and blown dry with N₂ gas. It was sputtered with a thin layer (~1 nm thick) of Au just before being loaded into the reactor. Before growing the nanowires, diethylzinc at a flow rate of 5.6 sccm was introduced into the reactor at 350 °C. A Zn thin film was first initiated on the surface of Si substrate. Then, the reactor temperature was raised to 550 °C and the flow ratio of II to VI precursor was maintained at 1:9 to grow ZnSe nanowires. Growths were carried out at reactor pressures of 100, 250, 500, and 760 Torr for 2200 s, respectively.

The synthesized products were characterized by x-ray diffraction [(XRD) Rigakau, Japan, RU300 with Cu $K\alpha$ radiation]; scanning electron microscope [(SEM) LEO, 1450

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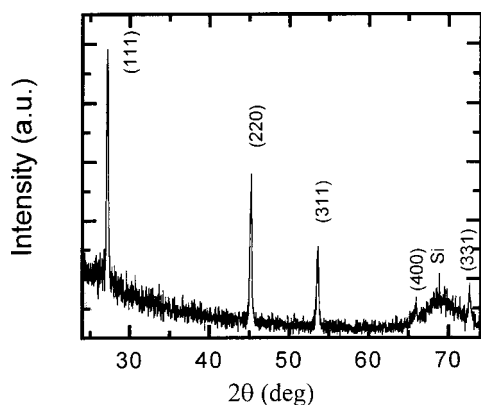


FIG. 1. XRD pattern of the synthesized products.

VP, UK], with an energy-dispersive x-ray [(EDX) Oxford Link II, UK] spectrometer attached; and high-resolution lattice imaging and selected area electron diffraction (SAED) in a transmission electron microscopy [(TEM) Philips CM200, USA]. PL spectra of the synthesized nanostructures were measured at room temperature using the 325 nm line of a He–Cd laser as the light source. The excitation power density is estimated to be ~ 500 W/cm².

III. RESULTS AND DISCUSSION

Depending on the growth pressure, different hues of yellow coating were seen on the surface of the substrates after growth. Under an optical microscope, and more clearly in a SEM, one can see that the length and density of weedlike nanowires are influenced by the pressure of growth. XRD of all the samples gave patterns similar to the one shown in Fig. 1. All of the peaks in the pattern can be indexed to a zincblende-structured crystal having a lattice constant $a = 5.673$ Å, which agrees with the standard bulk value of a ZnSe lattice parameter within experimental errors ($a = 5.667$ Å in the JCPDS file, No. 05-0522). It should be noted that no diffraction peaks from other phases, except the substrate Si peak, has been found in our samples.

The low-magnification SEM image of Fig. 2(a) shows that the nanowires have lengths ranging from several to tens of micrometers. The high-magnification SEM image of Fig. 2(b) shows a nanowire that is uniform in length, with a cross-sectional diameter of about 30 nm. The atomic force microscopy (AFM) image of Fig. 3 shows another nanowire of similar dimension, but with a spherical particle, most likely Au, at its tip. TEM observations also corroborate the observations of AFM and SEM in that the diameters of the nanowires range from a few to tens of nanometers, with an average diameter about 30 nm. Some of nanowires are very uniform but others are slightly tapered along the growth direction; and some are capped with a small particle. The high-resolution TEM (HRTEM) image of Fig. 4 clearly reveals that the particle at a tip of nanowire is mainly composed of Au and the direction of growth of the nanowire is $\langle 112 \rangle$, which is rather uncommon, as zincblende-structured semiconductors tend to grow along either the $\langle 111 \rangle$ or $\langle 110 \rangle$ direction in most other methods.^{17,18} The SAED pattern (Fig. 4, inset) recorded along the $\langle 111 \rangle$ zone axis of a typical nano-

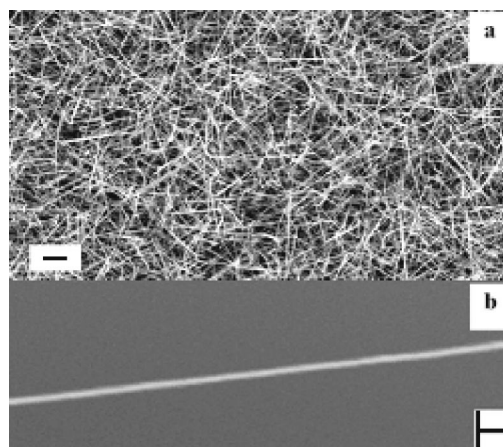


FIG. 2. (a) SEM image of the synthesized products. Large amounts of the nanowires are distributed homogeneously on the Si substrate. The scale bar corresponds to 2 μ m. (b) A high-magnification SEM image of a long nanowire of uniform cross section, the scale bar corresponds to 200 nm.

wire again demonstrates its cubic nature. The EDX spectrum shown in Fig. 5 determines that the nanowires contain only Zn and Se of equal atomic ratio. The pressure does not appear to have any effect on the diameter, composition, and structure of the nanowires. The only apparent effects of pressure seem to be on the length and the density of nanowires, until one measures their PL.

We note that some of the nanowires shown in Fig. 2(a) are slightly curved in shape and have a radius of curvature of a few microns. Such a large curvature does not seem to be the result of bending by an external torque, such as that caused by their weight. The curvature is more likely a result of internal strains associated with dislocations. We estimate²⁰ that to display a curvature of 10 μ m a typical bent nanowire may contain about 2.8×10^{10} dislocations per cm³.

For cubic crystals to display 1D growth habits, a certain symmetry breaking mechanism is required to account for the large anisotropy. Many such mechanisms have been proposed, one of the better known ones are found in the vapor–liquid–solid (VLS) model. For the effective operation of the VLS mechanism, the presence of a supersaturated liquid

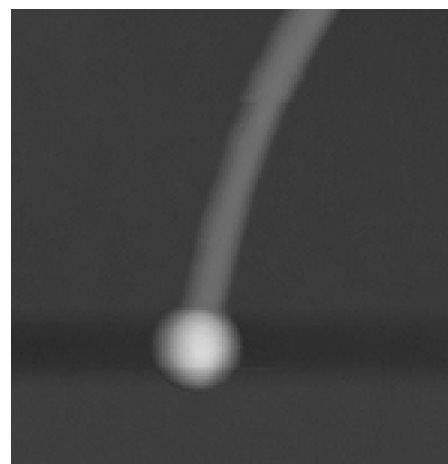


FIG. 3. AFM image (900×900 nm²) of ZnSe nanowire adorned with a particle.

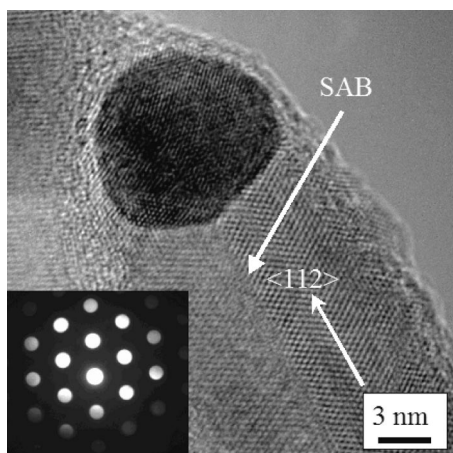


FIG. 4. HRTEM image and SAED pattern of a typical nanowire near its tip. The image shows the lattice planes of Au particle {111} and ZnSe nanowire {110}, the $\langle 112 \rangle$ direction of growth, and a small angle grain boundary. The SAED pattern (inset) is obtained with the electron beam directed along the nominally $\langle 111 \rangle$ zone axis, showing its cubic structure.

phase during growth is essential. One way to adjust the supersaturation in MOCVD is through the growth pressure. Also essential are the small molten particles that collect and concentrate the vapors. Particles found at the tips of the nanowires are commonly considered to be the evidence for the VLS mechanism.^{21–23} In our case, molten droplets containing Au are the growth sites of ZnSe nanowires.

Evidently, the particle size depression of the melting point and, possibly mixing with Zn and Se, allow the droplets to form at our growth temperature of 550 °C. Evidence of melting of nanosize Au particles at 530 °C was inferred from reflection high-energy electron diffraction (RHEED) patterns recently.¹⁸ In the VLS mode of growth, the three phases V, L, and S are intimately coupled, it is natural to expect changes in the vapor phase might have an effect on the solid phase. It is well known that it is difficult to obtain perfectly stoichiometric ZnSe and many other II–VI semiconductors. Unless the growth conditions are optimized to minimize the deviations from stoichiometry, the resulting crystals tend to contain too many defect complexes to be of use in light-emitting applications. Even minute deviations, too small for EDX to detect, may have a huge impact on the electronic properties. PL is one of the techniques that is sen-

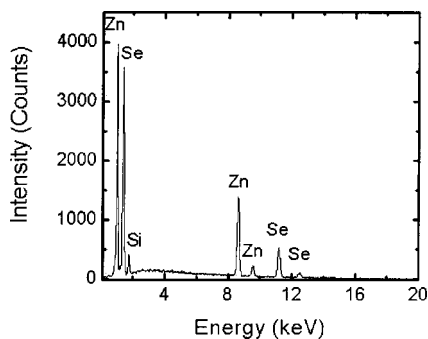


FIG. 5. EDX of the nanowires, showing the synthesized product is composed of Zn, Se. The Si signal is from the substrate.

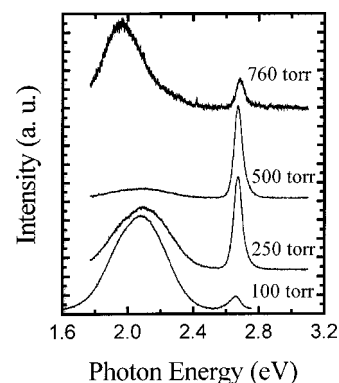


FIG. 6. PL spectra of ZnSe nanowires synthesized under different pressures.

sitive enough to detect the very low levels of stoichiometric deviations and other defects.

Figure 6 shows the room-temperature PL spectra of nanowires grown at different pressures. All spectra consist of two characteristic emission regions—the near-band-edge (NBE) emissions at 2.68 eV, usually associated with excitons, and the deep-level (DL) emissions at 2.2 eV, usually associated with dislocations, stacking faults, and nonstoichiometric defects.²⁴ As discussed earlier, the presence of dislocations is also implied by the curvature of the nanowires. We remark that the NBE emissions of ZnSe nanowires grown by other methods are not always as strong, relative to the DL emissions, as those shown here. In some cases, they were not even observed.^{17,19} It is apparent from Fig. 6 that the intensity ratio of the NBE to DL emissions of ZnSe nanowires depends strongly on the pressure of growth. The intensity ratio is largest at the optimal growth pressure of about 500 Torr. At this pressure, radiative recombinations mainly occur via band-edge states, indicating the low density of nonstoichiometric defects. We would like to point out that the optimal pressure for best quality is not also the optimal pressure for yield. Within the range studied, we found that the yield decreases with the pressure of growth.

IV. CONCLUSIONS

Long zincblende-structured ZnSe nanowires were grown on a Si (001) substrate sputter coated with a ~ 1 nm thick film of Au at the low temperatures of 550 °C and under various pressures by MOCVD using diethylzinc and diisopropylselenide as precursors. XRD and HRTEM results indicate that the nanowires have a zincblende structure, an average diameter of about 30 nm, and a uniform cross section. Particles at the tip of some of the nanowires show the nanowires most likely grown via the VLS process. Aside from the length and number density of the nanowires, there does not seem to be an obvious dependence of the structure and morphology on the pressure of growth. However, PL studies of the nanowires indicate that the pressure has a strong effect on their electronic properties. There is an optimized growth pressure at which the largest intensity ratio of NBE to DL emissions is obtained. The inherently low-temperature and high-purity chemical vapor deposition synthesis route, using metalorganic sources as precursors, may open up possibili-

ties for growing high-quality and ordered nanometer materials in the experimental studies of quasi-1D confined transport phenomena in nanomaterials and in the fabrication of optoelectronic nanodevices.

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