Growth and luminescence of zinc-blende-structured ZnSe nanowires by metal-organic chemical vapor deposition

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Zinc-blende-structured single-crystalline ZnSe nanowires and nanoribbons were grown on (001) silicon substrates by metal-organic chemical vapor deposition. The as-synthesized nanowires were characterized by x-ray powder diffraction and scanning electron microscopy. The diameters of the nanowires range from a few tens to 100 nm and the typical length is in the tens of micrometers. Individual strands of the nanowires were examined by transmission electron microscopy and cathodoluminescence spectroscopy. They were found to be single crystals elongated along the $\langle 11\bar{2}\rangle$ crystallographic direction. Strong and narrow room-temperature band-gap light emissions indicate that their optical and electronic properties rival those of the epitaxial layers employed in diode lasers. A possible growth mechanism of the ZnSe nanowires is also discussed. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1638633]

One-dimensional nanometer-sized semiconductor structures, such as nanowires, nanoribbons, and nanorods, have attracted considerable attention due to their interesting fundamental properties and potential applications in nano-scale opto-electronic devices.[1] The growths of group IV, III–V, and II–VI semiconductor nanowires have recently been demonstrated by various methods.[2] Most studies have focused on semiconductor systems, such as Si, Ge, GaN, GaAs, ZnO, ZnS, CdSe, and CdS. The few on ZnSe include nanorods obtained by a solovthermal method, quantum wires by lithography and electrodeposition, and, very recently, short nanowires by vapor phase growth.[3–6] As far as we know, growing one-dimensional nanostructured II–VI semiconductors by metal-organic chemical vapor deposition (MOCVD) has not been reported, although there exists a considerable literature on the growth of epitaxial layers,[7] quantum wells,[8] and quantum dots.[9] MOCVD growths of a few kinds of III–V nanowires have been reported,[10] but the nanowires obtained are quite different in morphology from those reported here. They are much shorter and tend to taper significantly from the base to tip, while ours have a uniform diameter along the entirely length.

ZnSe is a wide-band-gap semiconductor that is used in the fabrication of blue and green light emitting devices. Room-temperature continuous-wave operations of ZnSe-based laser and light-emitting diodes have been demonstrated in the past. In this article, we report the success of synthesizing ZnSe nanowires on Si (001) substrate using Ag colloids as a catalyst by MOCVD, a technique with demonstrated value in the commercial production of light-emitting devices. By its design, MOCVD is capable of growing very high quality semiconductors at lower temperatures than most methods.

The Si substrate was steamed in 1-1-1 trichloroethane vapor for 30 min, rinsed with deionized water, and blown dry with N_2 gas. Ag colloids were spread on the substrate just before it was loaded into the MOCVD reactor. Diethylzinc and diisopropylselenide at a flow ratio of 1.7:1 were used as precursors and 7N hydrogen as the carrier gas. The reactor pressure was kept at 100 torr and growth temperature at 450 °C. Control samples grown without Ag colloids were also carried out under the same conditions. The general morphology of the as-synthesized nanowires was examined by scanning electron microscopy (SEM) and atomic force microscopy (AFM). Their structure was determined by x-ray diffraction (XRD) using the Cu K_α radiation, selected area electron diffraction (SAED), and high-resolution lattice imaging in a transmission electron microscope (TEM). Their composition was determined by an energy dispersive x-ray (EDX) spectrometer attached to the TEM. Luminescent spectra of individual nanowires were measured at room temperature by a cathodoluminescence (CL) system installed on the SEM.

The general morphologies of the ZnSe nanowires are shown in Fig. 1(a). As can be seen from the low-magnification SEM image, a dense carpet of nanowires, having a typical length of tens of micrometers and an average diameter of ~80 nm, covers the substrate. Most of the nanowires appear to have a relative uniform and circular cross-section. Besides the round nanowires, nanoribbons with a single saw-tooth edge are also observed [Fig. 1(a), inset]. For comparison, the AFM image [Fig. 1(b)] of the sample grown without Ag colloids shows only small faceted ZnSe grains. An XRD diffractogram of the nanowires is shown in Fig. 2. All of the diffraction peaks can be indexed to zinc-blende-structured ZnSe. The cubic structure of the nanowires is also confirmed by SAED on many individual nanowires. Figure 3(a) shows a TEM bright field image of a single nanowire of diameter ~50 nm, which is consistent with the SEM observations. The contrast along the nanowire is caused by the sample grid and the bending strains. The inset is an EDX spectrum taken from this nanowire that identifies the presence of only Zn and Se (Cu peaks are from the sample grid) at an approximate atomic ratio of 1:1. The high-resolution image shown in Fig. 3(b) demonstrates the single

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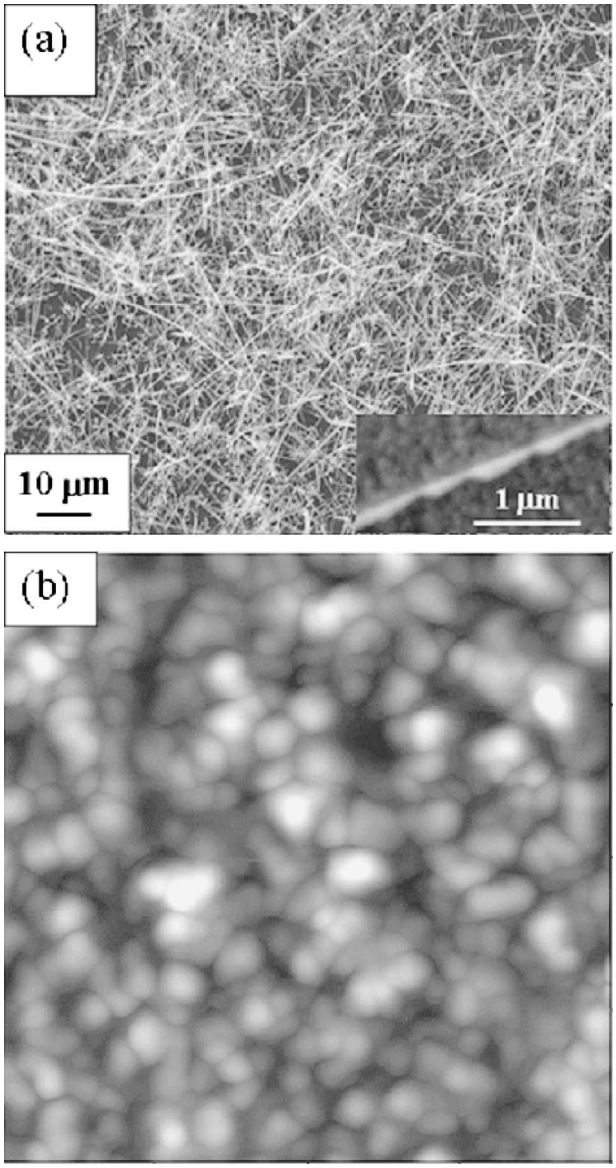

FIG. 1. (a) Low magnification SEM image of ZnSe nanowires and a magnified view (inset) of a ZnSe nanoribbon with a saw-tooth edge; (b) AFM image (1 μm×1 μm) of a control sample grown without Ag colloids.

crystalline nature of the nanowires and shows that it grows along the ⟨112⟩ direction.

A representative room temperature CL spectrum from an arbitrarily chosen spot on a single nanowire is shown in Fig.

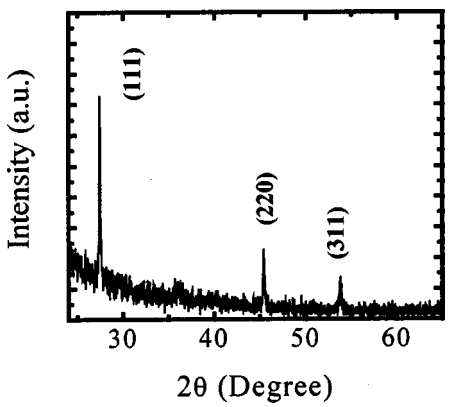

FIG. 2. X-ray diffractogram of the as-synthesized ZnSe nanowires.

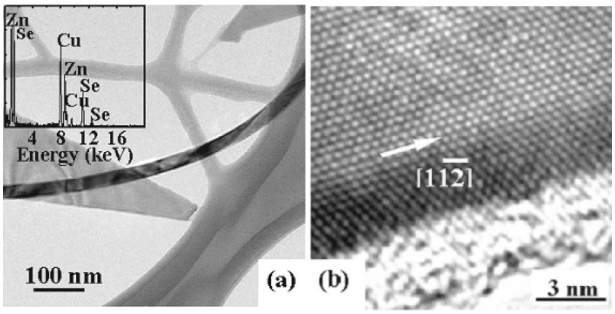

FIG. 3. (a) Bright field TEM image of a single ZnSe nanowire; inset is its EDX spectrum and (b) high resolution image of the nanowire.

4. It clearly displays a sharp and strong band edge emission at 2.68 eV. The measured 83 meV width of the peak is a result of temperature broadening convoluted with an instrument resolution of 64 meV. The peak is only about 53 meV wide after the latter is removed. A weak and broad deep level emission centered at 1.80 eV is also seen.[7] The strong band edge luminescence shows that the nanowires contain very few, if any, dislocations or stacking faults, as these defects tend to quench band edge radiative recombinations. The weakness of the deep level emissions also suggests that the nanowires have stoichiometric composition, with perhaps a low density of point defects. It is interesting to note that there is no evidence of Ag causing any harm to the luminescence properties of the nanowires. The fact that the luminescence property of ZnSe nanowires grown by MOCVD is superior to those grown by other methods suggests that using a catalyst to induce one-dimensional growth need not result in detrimental effects on their electronic properties. This is perhaps related to the low growth temperature and the high purity of materials used in MOCVD.

It is interesting to speculate on how the ZnSe nanowires are formed. There exist several models to explain the growth of crystalline whiskers, including the (VLS) mechanism.[11,12] However, none of the above mechanisms seems to be appropriate for the present MOCVD growth of ZnSe nanowires. The role of Ag is interesting, but we do not think it is playing the role of typical catalysts in the VLS mode of growth. First of all, Ag was not found at the bottom or the tip of the nanowires. They should be readily detectable in TEM, for

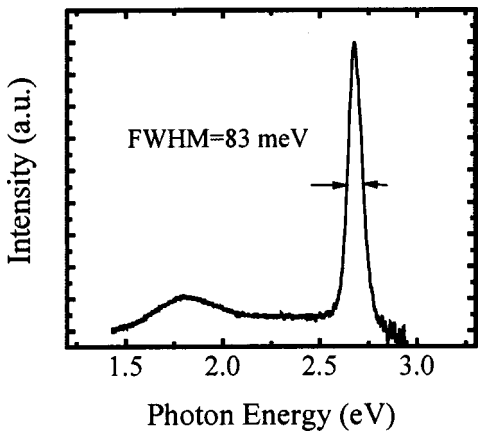

FIG. 4. Room-temperature cathodoluminescence spectrum of a single ZnSe nanowire obtained with a focused electron beam at an accelerating voltage of 20 kV and current of 1 nA.

their average diameter is about 9 nm.[13] The colloidal particles are perhaps buried under the layer of ZnSe grains. The low growth temperature of 450 °C suggests most of the Ag colloids could not have melted. Significant depression of the melting temperature of Ag occurs only for particles of diameter less than 1 nm.[14] Second, high magnification SEM examinations of the area near the roots of the nanowires indicate they grew out of small ZnSe crystal grains. Short buds of growth were seen sprouting up from the grains at the early phase of growth; these buds would eventually grow into long nanowires. Third, the high density of nanowires far exceeds the estimated density of colloidal Ag particles on the substrate. The simultaneous presence of more than one morphological distinct nanowire suggests that there are perhaps several complex mechanisms in operation. We think the spiral growth mechanism,[15] in which a screw dislocation emerging from a crystal face, can best describe what we observe. The mechanism also accounts for the exceedingly fast rate of growth of the nanowires, as compared with the undergrowth grains. The absence of axial dislocations in the nanowires is perhaps a result of them gliding out of the crystal structure during annealing or during deformation associated with the inevitable bending of the very long nanowires. How Ag promotes the formation of screw dislocations in the small ZnSe grains is not fully understood at this time. Investigations of the detailed mechanism are in progress.

In conclusion, long single-crystalline zinc-blende-structured ZnSe nanowires are successfully grown on Si substrate coated with Ag colloid by MOCVD. The high structural and electronic quality of the nanowires, as demonstrated by the strong and sharp room temperature band edge luminescence, shows the promising potential of MOCVD in the fabrication of nanoscale opto-electronic devices. A spiral growth mechanism involving Ag-induced screw dislocations is also suggested.

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