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Ga-catalyzed growth of ZnSe nanowires and the cathodoluminescence and electric transport properties of individual nanowire

M. Lei\textsuperscript{a,b,*}, X.L. Fu\textsuperscript{a,b}, H.J. Yang\textsuperscript{b}, Y.G. Wang\textsuperscript{b}, P.G. Li\textsuperscript{c}, Q.R. Hu\textsuperscript{b}, W.H. Tang\textsuperscript{b}

\textsuperscript{a} State Key Laboratory of Information Photonics and Optical Communications, Beijing University of Posts and Telecommunications, Beijing 100876, China  
\textsuperscript{b} School of Science, Beijing University of Posts and Telecommunications, Beijing 100876, China  
\textsuperscript{c} Institute of Electronic structure & Laser, Foundation for Research and Technology-(FORTH), Heraklion, Crete, Greece

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A B S T R A C T

We developed a facile thermal evaporation method to fabricate zinc-blende ZnSe nanowires on GaAs substrates by using Ga as catalyst. The Ga catalyst originates from the reduction of the amorphous Ga\textsubscript{2}O\textsubscript{3} layer pre-oxidized on surface of GaAs substrates. The cathodoluminescence (CL) spectra of an individual nanowire reveal a weak near-band-edge emission centered at 468 nm and a strong deep-level emission at 593 nm. The deep-level emission is assigned to self-activated luminescence induced by donor–acceptor pairs that are associated with intrinsic point defects: Zn vacancies and Zn interstitials. The electrical transport property of individual nanowire reveals that the current versus voltage curve remains linear relation even at high applied voltage, indicating that the conventional electric power dissipation cannot affect the electric transport properties of the nanowire.

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1. Introduction

Vapor–liquid–solid (VLS) process [1–3] has been the most effective to synthesize one-dimensional (1D) inorganic nanostructures such as nanotubes and nanowires. In the VLS process, metal catalyst, typically as Au, is rationally chosen from the phase diagram by identifying metal that is in liquid state at the growth temperature and serves as the site for adsorbing the incoming molecules [3–9]. During the growth, the metal droplet directs the growth direction of 1D nanowires and defines their diameter. Except conventional Au, some transition metals are effective in synthesis of specific nanowires such as Sn/ZnO [10], Mn/GaN [11], Co/SiO\textsubscript{2} [12], and Ni/Ga\textsubscript{2}O\textsubscript{3} [13]. ZnSe nanowires are potential candidates as photodetectors, light-emitting diodes and laser diodes due to its wide bandgap of ca. 2.7 eV (460 nm) and large exciton binding energy of 21 meV [14–17]. Among various synthesis routes to ZnSe nanowires, Au-catalyzed vapor–liquid–solid (VLS) process has been the most effective to synthesize ZnSe nanowires. Up to now, Au-analyzed methods, e.g. chemical vapor deposition (CVD) [18–24], metalorganic chemical vapor deposition (MOCVD) [25,26], molecular beam epitaxy (MBE) [27–29] and pulsed-laser deposition (PLD) [30] have been successfully applied in the controllable growth of ZnSe nanowires and nanowire arrays. The morphologies and diameters of the 1D ZnSe nanostructures can be controlled by the size of Au. Except Au, other transition metals were also used as catalysts to initiate the growth of 1D ZnSe nanostructures. Ohno et al. [31,32] used Fe as catalyst to synthesize ZnSe nanowire arrays via a MBE method. Hu et al. [33] reported a facile Sn-catalyzed thermal evaporation synthesis of ZnSe tetrapods. Recently, Liang et al. [34,35] reported a MOCVD route to 1D ZnSe and ZnS nanowire arrays by using metal Ga as catalyst and demonstrated that Ga is highly effective for catalyzing these nanowires. In this work, we extend the insight to synthesize well crystalline ZnSe nanowires with zinc-blende structures on GaAs substrates via a facile thermal evaporation method. The microstructure, cathodoluminescence and electric transport properties of individual nanowire are investigated, which reveals some new features on the ZnSe nanowires.

2. Experimental details

2.1. Synthesis

The ZnSe nanowires were grown on GaAs substrates by a facile thermal evaporation method. Commercial ZnSe powders were used as source materials. GaAs substrates were first annealed at 400 °C in air for two hours. Thus the surface of GaAs substrates was oxidized to a thin film of amorphous Ga\textsubscript{2}O\textsubscript{3}. In a typical synthesis procedure,
a quartz boat containing ZnSe powder was placed in the center of an alumina tube. Then the GaAs substrates with a thin film of amorphous GaOₓ were placed at the downstream end. The furnace was first heated to 350 °C in pure H₂ atmosphere with a flow rate of 150 sccm and held at the peak temperature for half an hour. Then, the furnace was heated to 950 °C and kept the temperature for an hour. Mixture atmosphere of Ar and H₂ (molar ratio is 9:1) with flow rate of 80 sccm instead of pure H₂ was introduced in the furnace at the second step. The products were deposited on the GaAs substrates in the local temperature region of 600–650 °C.

2.2. Characterization

The morphologies of the products were characterized by field emission scanning electron microscope (FE-SEM, FEI XL30 S-FEG) equipped with energy-dispersive X-ray spectroscopy (EDS). The crystal structures of the products were analyzed by using a rotating anode Rigaku (Tokyo, Japan) D/max-2400 X-ray diffractometer with Cu Kα radiation. The microstructures of the product were examined by transmission electron microscopy (TEM, Tecnai 20 at 100 kV) and high-resolution TEM (HRTEM, Tecnai 20 at 200 kV). The cathodoluminescence (CL) studies of individual nanowire were performed in the scanning electron microscope equipped with an Oxford Instruments MonoCL2 spectrometer at room temperature. The focused electron beam was scanned over the surface, and the emitted light was collected with a parabolic aluminum mirror and guided to the slit of a grating monochromator. The working voltage and current for CL measurement are 15 kV and 500 pA, respectively. To further characterize electrical transport properties of single ZnSe nanowire, four-terminal electrodes were contacted on the nanowires by using electron beam lithography followed by metal deposition and standard lift off process. After Ti/Au (5/50 nm) electrodes were fabricated, rapid thermal annealing was performed at 550 °C with the aim of improving ohmic contact between electrodes and nanowires. To further observe the variation of the electrical transport properties of the ZnSe nanowire under UV illumination, the nanowire-based device was exposed to the UV illumination for an hour. The intensity of UV is relative high, up to 200 W, and the wavelength of the UV light is 365 nm.

3. Results and discussion

The morphology of the product deposited on the GaAs substrate is first characterized by SEM measurement, as shown in Fig. 1a. The product consists of a large amount of straight nanowires with uniform size. The nanowires are ultralong, up to tens of micrometers in length. Fig. 1b shows the EDS spectrum of the nanowires grown on the GaAs substrate. Ga, As, Zn and Se elements are detected in the products. The Ga and As signals maybe come from the GaAs substrates, irrelevant to the chemical composition of the nanowires.
**Fig. 2.** (a) TEM image of an individual ZnSe nanowire. The inset is the DF-STEM image of the nanowire. (b–c) The EDS spectra of the nanowire and the nanoparticle attached on the tip of the nanowire, respectively. (d–e) HRTEM images of the nanoparticle and the nanowire, respectively.

**Fig. 1c** is the XRD pattern of the nanowires. All diffraction peaks can be indexed as (1 1 1), (2 2 0) and (3 1 1) on the basis of zinc-blende ZnSe (ICDD-PDF No. 37-1463), and no other peaks from impurities are observed. Combined the EDS spectrum and XRD pattern, the nanowires are confirmed as zinc-blende ZnSe.

**Fig. 2a** shows a typical TEM image of an individual nanowire. The nanowire is straight along growth direction and has smooth surface. A spherical particle with a diameter of 100 nm, slightly larger that of 80 nm of the wire body, can be clearly seen at the tip of the nanowire. Dark-field scanning transmission electron microscopy (DF-STEM) is employed to exactly determine the chemical composition of the nanowire and nanoparticle. The DF-STEM image was shown in the inset of **Fig. 2a**. **Fig. 2b** and c shows the EDS results of the line scan analysis of the nanowire and nanoparticle along the “black line” as marked in the inset of **Fig. 2a**, respectively. The EDS spectrum (**Fig. 2b** and c) indicates that the wire body mainly consists of Zn and Se elements, and the spherical nanoparticle is composed of Ga element. The Zn and Se elements distribute uniformly along the scanning line direction. The atomic ratio of Zn to Se is fixed at 1:1.092, revealing that Se...
is a trace of excess compared with the stoichiometric composition of ZnSe. It should be pointed out that the EDS here just present a semi-quantitative analysis result and the value does not reflect the exact atomic ratio of the nanowire. Fig. 2d shows the HRTEM image of the nanoparticle. The parallel fringes with a spacing of 0.238 nm is observed, corresponding to the (1 0 1) planes of tetragonal Ga (ICDD-PDF No. 71-1835). It is concluded from the EDS spectrum (Fig. 2b) and the HRTEM measurement (Fig. 2d) that the nanoparticle is identified as tetragonal Ga, revealing that the growth process is initiated by the Ga-catalytic vapor–liquid–solid (VLS). According to the literature [34,35], a thin film of amorphous GaOₓ was formed on the surface of GaAs substrates by annealing in air. Then the amorphous GaOₓ was continuously reduced into Ga droplets by H₂ above 350 °C. Finally, the Zn and Se vapors originating from thermal decomposition of ZnSe source are continuously dissolved in Ga droplets. If Zn and Se in the Ga droplets reach the supersaturation, they co-precipitate as ZnSe nuclei on GaAs substrates. Continuous absorption of Zn and Se vapors and precipitation of ZnSe nuclei result in the final ZnSe nanowires. Fig. 2e shows the HRTEM image of the nanowire, revealing that the nanowire is well crystalline ZnSe with zinc-blende structure and the growth direction is determined to grow along [1 1 1].

The optical properties of the nanowires are studied by cathodoluminescence (CL) which is an effective tool to study the optical properties of an individual nanowire. The nanowires are first dispersed on Cu grid for TEM characterization and then the Cu grid is further attached in the SEM system for CL measurement. Fig. 3a and b shows the SEM image and the panchromatic CL image of the nanowires dispersed on the Cu grid, respectively. The light intensity of the emission along the length of all nanowires does not decrease from their tip to bottom, as confirm by the panchromatic CL image (Fig. 3b). To avoid the effects of some impurities deposited on the
substances on the optical properties of the nanowires, here we choose representative CL spectra of an individual nanowire rather than a large area of nanowires to reveal optical properties of the ZnSe nanowires. Fig. 3c and d shows the spectra taken from the “1” and “2” region denoted in Fig. 3b, respectively. A weak near-band-edge (NBE) emission centered at 468 nm and a strong deep-level (DL) emission at 593 nm are detected in the two spectra, and only the intensity of emission is slightly different, which indicating the optical property along the nanowires is similar. Generally, DL emission is related to bulk defects and intrinsic point defects such as Zn vacancies and interstitial states [20,33,36–38]. The bulk defects e.g. dislocations and stacking faults are not detected by HREM measurements (Fig. 2e), indicating the bulk defects are not related to the DL emission. Theoretical calculations demonstrated the Zn vacancies and Zn interstitials rather than Se vacancies are the most probable point defects due to their low formation energy [36,37]. We deduce that DL emission is assigned to “self-activated” luminescence, probably as a result of some donor–acceptor pairs that are associated with Zn vacancies and Zn interstitials. Zn vacancies and Zn interstitials act as the acceptor species and the donor species, respectively. In the case, all carriers excited to the conduction band instantaneously decay to shallow donor levels and recombine with acceptor states, which finally results in the strong DL emission. To characterize electrical transport properties of individual nanowire, four-terminal Ti/Au (5/50 nm) electrodes were contacted on the nanowires by using electron beam lithography followed by metal deposition and standard lift off process. The inset of Fig. 4 shows the SEM image of individual ZnSe nanowire in diameter about 120 nm contacted by four-terminal electrodes, the separation of inner two electrodes is 2 μm. A typical electrical transport property of individual nanowire, current versus voltage (I–V) curves, as shown in Fig. 4. In the voltage range between −5 and 5 V, the I–V remains linear relation, revealing the ohmic contacts between electrodes and nanowire. The resistivity (ρ) of the nanowires is ca. 3100 Ωcm calculated by formula \( \rho = RA/L \), where \( R \) is resistance of nanowire, \( A \) is the cross sectional area and \( L \) is the channel length. I–V curve is not deviated from linearity even at higher applied voltage, indicating the conventional electric power dissipation does not have influence on the I–V properties of the nanowire. Similar I–V curves are also found when the device was exposed to UV illumination, indicating the I–V property is insensitive to the relative high temperature and strong illumination. 

### 4. Conclusions

We grew the ZnSe nanowires on GaAs substrates using Ga catalysts by means of conventional thermal evaporation method. The ZnSe nanowires are of well crystalline zinc-blende structure and smooth surface. The nanowires are free of bulk defects and grown along [1 1 1]. The growth mechanism follows a Ga-catalyzed VLS process. Ga catalysts originate from the reduction of Ga2O3 layer pre-oxidized on GaAs substrates assisted by H2 vapor. The CL spectra taken from two regions in individual nanowire show almost same optical properties: a weak NBE emission centered at 468 nm and a strong DL emission at 593 nm. The DL emission originates from “self-activated” luminescence induced intrinsic Zn vacancies and Zn interstitials which act as the acceptor species and the donor species, respectively. The electrical transport property of individual nanowire reveals the resistivity (ρ) of the nanowires is ca. 3100 Ωcm and that the I–V remains linear relation even at high applied voltage, indicating conventional electric power dissipation do not have influence on the I–V properties of the nanowire.

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### References


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**Fig. 4.** A typical current versus voltage (I–V) curves measured at room temperature. The inset is the SEM image of individual ZnSe nanowire in diameter of ~120 nm contacted by four-terminal electrodes on the top of SiO2/Si substrate.


