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FABRICATION OF $Zn_xCd_{1-x}Se$ NANOWIRES BY CVD PROCESS AND PHOTOLUMINESCENCE STUDIES

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$Zn_xCd_{1-x}Se$ alloy nanowires with composition $x = 0.2, 0.5$ have been successfully synthesized by a simple thermal evaporation on the silicon substrate coated with a gold film of 20 Å thickness. The as-synthesized alloy nanowires, 70 - 150 nm in diameter and several tens of micrometer in length. The nanowires are single crystalline revealed from Transmission electron microscopy (TEM) and XRD measurement. The structure of $Zn_xCd_{1-x}Se$ nanowires are hexagonal wurtzite with [01-10] growth direction. Energy gap of the $Zn_xCd_{1-x}Se$ nanowires are determined from micro photoluminescence measurements. The energy gap increases with increasing Zn concentration.

Keywords: $Zn_xCd_{1-x}Se$ NANOWIRES, CVD, PHOTOLUMINESCENCE, SEMICONDUCTOR NANOWIRES, II-VI NANOWIRES, TEM, XRD.

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1. INTRODUCTION

The ternary semiconductor compounds $Zn_xCd_{1-x}Se$ due to their excellent optical properties and fast response times [1, 2] have a wide range of potential applications, especially in optical switching, optical communications, optical signal processing and photo voltaic devices [3, 4].

The processing advantages of II-VI materials compared with other semiconductors are their high photochemical stability and size-dependent optical properties due to confinement effect [5, 6]. Aside from choosing various semiconducting materials of different band gaps, it is now possible to control the band gap energy of a given semiconductor from lowering the dimensionality and or reducing its size to values comparable with or smaller than the corresponding excitonic Bohr diameter [5]. Alloying of semiconductors is another means that can be applied to achieve semiconductor materials for various band gap energies. Among all groups, II-VI materials are a good representative example in laser photonics to generate coherent blue-green light. The recently developed ZnSe based laser diodes have a potential coverage of the whole green spectral region (490 - 590 nm). The $Zn_xCd_{1-x}Se$ alloy is used as a quantum well materials in ZnSe based diodes grown on InP substrate which can effectively reduce the compressive strain.

Alloyed nanowires of ternary II-VI semiconductors with elementary compositions of $Cd_xZn_{1-x}Se$ and $ZnCdS$ [7, 8], successfully fabricated by MBE, MOCVD and laser assisted deposition [9]. Chang et al. [10] synthesized $Zn_xCd_{1-x}Se$ nanowires by MBE technique to photodetector applications. $ZnSe/ZnCdSe$ heterostructures were grown on Si substrate [11] for luminescence applications.

2. EXPERIMENTAL STUDIES

Many methods have been developed to synthesize one dimensional nanostructures of II-VI semiconductors. Among these are thermal evaporation [12-14], laser ablation [16-17], arc discharge [18] and chemical synthesis methods [19]. The most common deposition based synthesis methods are physical and chemical vapor deposition [20-22]. Both methods consist of physical transport of the vapor species to the deposition site. To prepare $Zn_xCd_{1-x}Se$ ($x = 0.2$ and 0.5) nanowires a simple vacuum tube furnace is used (Fig. 1).

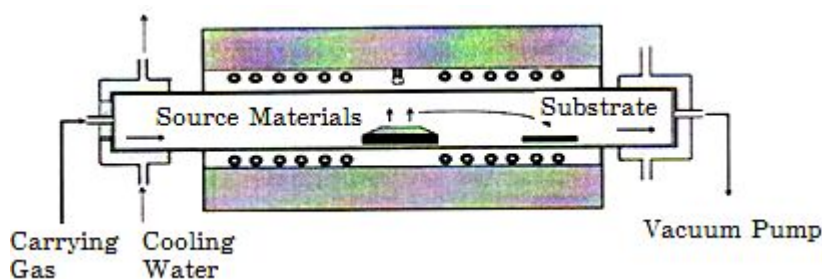


Fig. 1 – Schematic of Single-zone tube furnace vapor-solid growth

For the preparation of source material high purity $ZnSe$ and $CdSe$ (99.999 purity) were used. It was prepared by physical mixing the desired quantities of ($x = 0.2$ and 0.5) of $ZnSe$ and $CdSe$ and then sintering the mixture at $1000\text{ }^\circ\text{C}$ in a vacuum sealed quartz tubes for 18 hours. The sintered mixture was slowly cooled to room temperature in 5 hours and then used as a source material for the fabrication of $Zn_xCd_{1-x}Se$ alloy nanowires. The source materials are put in the alumina boat and placed in the centre of a single – zone horizontal tube furnace where the atmosphere, evaporation time, pressure and temperature are controlled. The Au film (20 \AA thickness) coated on a Si substrate ($20 \times 10\text{ mm}$) was used as a product collection substrate and located down stream in a lower temperature region in the furnace which kept at a reasonable vacuum. The substrate was vacuum annealed at $550\text{ }^\circ\text{C}$ to recrystallize into Au nanoparticles. Then the temperature in the furnace is elevated to a controlled temperature of $900\text{ }^\circ\text{C}$ at a specific rate. A carrier gas mixture of Ar (90 %), and H_2 (10 %) with flow rate of 220 sccm was frequently introduced into the quartz tube till the pressure was 250 torr. The furnace temperature was kept at $900\text{ }^\circ\text{C}$ throughout the experiment.

The nanowires were characterized by XRD, SEM, TEM and Photoluminescence studies. X-ray diffraction (XRD) spectra of the as-synthesized nanowires were recorded using scintag X1 diffractometer with

CuK_α ($\lambda = 1.5418 \text{ \AA}$) radiation at scanning speed of $2^\circ/\text{min}$ in 2θ ranging from 20° to 60° . Composition were measured by energy dispersive X-ray spectroscopy (EDS). TEM was recorded from JEOL JEM 2010 analytical at 200 kV. Room temperature photoluminescence was measured in a confocal microscope (Jobin Yvon, MFO) using 325 Ar-Kr ion laser (coherent, Innova 70 °C) as an excitation source with laser intensity of $\leq 3.8 \text{ kW/cm}^2$.

2.1 Growth Mechanism

In this study the formation of $\text{Zn}_x\text{Cd}_{1-x}\text{Se}$ ($x = 0.2$ and 0.5) nanowires follow a vapour-liquid-solid (VLS) growth mechanism as evidenced by the eutectic tips containing Au, Zn, Cd and Se. At an early reaction stage in the formation of $\text{Zn}_x\text{Cd}_{1-x}\text{Se}$ nanowires, a vapour mixture of Zn, Cd and Se was carried by the Ar and H_2 gases and deposited onto catalytic Au nanodroplets. When the dissolution of Zn, Cd and Se in the Au nanodroplets became supersaturated, $\text{Zn}_x\text{Cd}_{1-x}\text{Se}$ nanowires extruded from the liquid eutectic Au nanodroplets and precipitated at the liquid-solid interface. This process complies basically with an ordinary VLS growth model proposed originally by wagner et al. [23], in which a liquid cluster of metal catalyst provides energetically favored sites for the absorption/adsorption of gas-phase reactants. The sizes of the catalysts are considered to be responsible for the diameter of resultant nanowires. Growth directions of the $\text{Zn}_x\text{Cd}_{1-x}\text{Se}$ nanowires are [01-10]. These results suggest that the $\text{Zn}_x\text{Cd}_{1-x}\text{Se}$ alloy nanowires prefer a specific crystalline structure with a particular growth direction at certain composition ratio and growth temperature.

3. RESULTS AND DISCUSSION

General SEM morphologies of the as synthesized $\text{Zn}_x\text{Cd}_{1-x}\text{Se}$ ($x = 0.2$ and 0.5) nanowires orienting randomly on the Si substrate are shown in figures 2a and 2b respectively. The diameter of the $\text{Zn}_x\text{Cd}_{1-x}\text{Se}$ nanowires are distributed in the range of 70 - 150 nm. While the lengths of the nanowires are several tens of micrometer and respond sensitively to the synthetic reaction time. Chemical contents of the $\text{Zn}_x\text{Cd}_{1-x}\text{Se}$ nanowires were analyzed from EDS spectra and their data shown in Figures 3a and 3b being listed in Table 1.

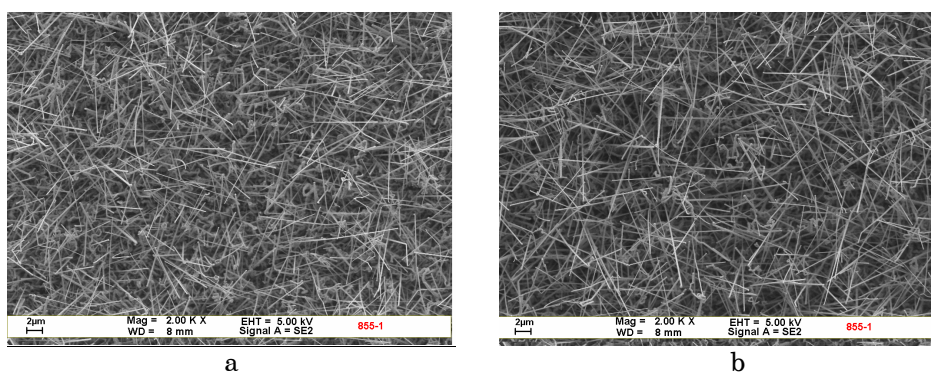


Fig. 2 – SEM image of $\text{Zn}_x\text{Cd}_{1-x}\text{Se}$ nanowires (a) $x = 0.2$, (b) $x = 0.5$

Table 1 – Chemical contents in the $Zn_xCd_{1-x}Se$ nanowires with various compositions

Composition (x)	Chemical contents from EDS		
	Zn	Cd	Se
0.2	9.95	39.80	50.25
0.5	25.25	25.37	49.37

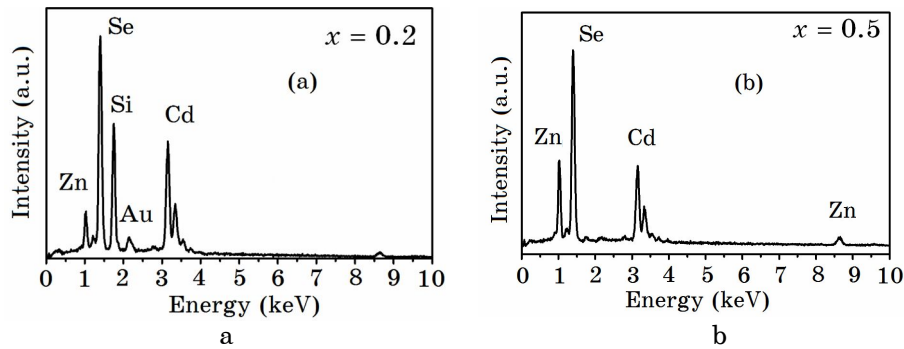


Fig. 3 – EDS spectra of $Zn_xCd_{1-x}Se$ nanowires (a) $x = 0.2$ (b) $x = 0.5$

Fig. 4 displays typical XRD pattern for the $Zn_xCd_{1-x}Se$ nanowires with $x = 0.2$ and 0.5 respectively. From the figure it is obvious that for both the compositions the structure is hexagonal wurtzite. The XRD spectra of nanowires of CdSe and ZnSe, CdSe and ZnSe nanopowders were recorded to compare the lattice parameters. We have calculated $a/c = 4.271/6.898 \text{ \AA}$ (CdSe nanowires) and $4.293/6.998 \text{ \AA}$ for (CdSe powders), $a = 5.646$ (ZnSe nanowires) and 5.679 (ZnSe powder) for the zinc blende, reveal that there exist lattice contractions in both of the as synthesized CdSe and ZnSe nanowires.

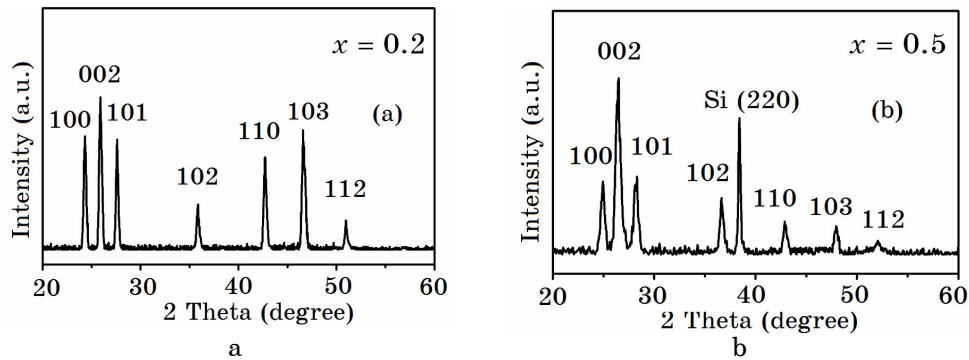


Fig. 4 – XRD pattern of $Zn_xCd_{1-x}Se$ nanowires (a) $x = 0.2$ (b) $x = 0.5$

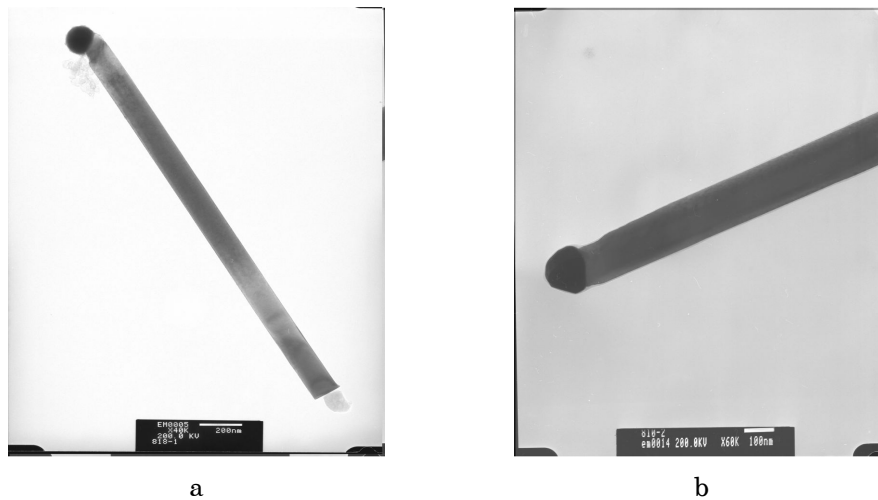


Fig. 5 – TEM image of single nanowire of $Zn_xCd_{1-x}Se$ (a) $x = 0.2$ (b) $x = 0.5$

The observed lattice contractions could have been induced by a surface tension along surface reconstruction in the growth of nanocrystallites, similar type of results were observed in CdSe nanocrystals [24] and CdSe nanobelts/nanosheets [25].

Typical TEM images of the $Zn_xCd_{1-x}Se$ ($x = 0.2$ and 0.5) are shown in Fig. 5a and 5b respectively. In any as-synthesized $Zn_xCd_{1-x}Se$ nanowires on Au-containing tip, composed of major Au and minor Zn, Cd and Se, was always found at one end suggesting that the nanowires compiled with a vapor-liquid-solid growth mechanisms.

3.1 Photoluminescence and energy gap

ZnSe and CdSe are direct band gap semiconductors. As synthesized $Zn_xCd_{1-x}Se$ alloy nanowires exhibit strong PL at room temperature. Fig. 6a and b shows the PL spectrum of $Zn_xCd_{1-x}Se$ nanowires. It is obvious from the figure that as Zn concentration increases the luminescence peak position shifted to higher energy, it is shown in Fig. 6a and b. The band gap was calculated from the strong peak and the band gap increases with Zn concentration.

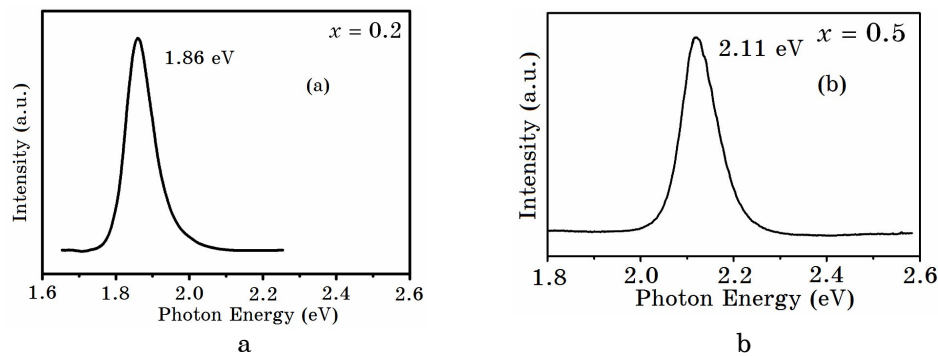


Fig. 6 – Room temperature PL spectra of $Zn_xCd_{1-x}Se$ nanowires (a) $x = 0.2$ and (b) $x = 0.5$

4. CONCLUSIONS

$Zn_xCd_{1-x}Se$ alloy nanowires have been fabricated by CVD method. XRD studies confirmed that the crystal structure is hexagonal wurtzite. The synthesized nanowires exhibited photoluminescence, with increasing Zn concentration luminescence peak shifted to higher energy side. The band gap also calculated from luminescence peak. Band gap increased with Zn concentration.

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