This is a pre-published version

ZnSep26a4.doc 8/24/2005

9 Aug 2005 version

Self-catalytic ZnSe nanorods on grains synthesized using thermal evaporation method

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Abstract

In this paper, ZnSe nanorods grown on in-situ synthesized ZnSe grains are reported. The ZnSe products are synthesized through thermal evaporation of elementary materials of Zn and Se powders in a horizontal resistance furnace. It is interesting to note that the ZnSe nanorods of nearly the same diameter and length are obtained and they grow in the same direction on a facet of the ZnSe grain. The ZnSe grains are random in shape with well-defined bounded facets. The ZnSe grains can be synthesized in various growth conditions while the ZnSe nanorods can be synthesized on the ZnSe grains with the fulfillment of the Zn enriched condition. The growth of ZnSe nanorods can be described by the self-catalytic Vapor-Liquid-Solid (VLS) mechanism.

Keywords: ZnSe, nanorods, nano-embryos, vapor growth, secondary growth, aligned nanostructure.

PACS no.: 73.21.-b, 78.55.Et, 61.10.Nz, 61.46.+w, 68.65.-k

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I. Introduction

Zn based nanostructures have recently been widely investigated particularly on ZnO [1-4] and ZnS [5-7]. However, there are relatively fewer reports on other Zn based nanostructures such as ZnSe [8, 9] and ZnTe [10]. In fact, since the first demonstration of the blue-green laser on ZnSe based material structures in 1991 [11, 12], ZnSe and its pseudomorphic ternary and lattice matched quaternary alloys have been considered as useful II-V compound semiconductors for optoelectronic devices covering the energy range from visible to ultraviolet. A typical ZnSe based ternary compound semiconductor of $Zn_xMg_{1-x}Se$ can tune the bandgap energy from 2.67eV for ZnSe to 3.6eV for MgSe. Apart from ZnSe substrate [13], ZnSe has been grown on GaAs [11] and Si [14] substrates for integrating ZnSe based optical devices to electronic devices of other semiconductors. For example, various ZnSe/Si-based devices such as electroluminescent cells [15], photoelectric cells [16] and visible sensitive emitter bipolar transistors [17] have all been demonstrated.

Recently, various ZnSe nanostructures such as nanowires, nanoribbons, quantum dots and nanograins have been synthesized. For one-dimensional (1-D) ZnSe nanostructures, the synthesis methods ranging from sophisticated molecular-beam epitaxy (MBE) [18] and metalorganic chemical vapor deposition (MOCVD) [19] to relatively simple thermal evaporation method [8, 20, 21] and electrochemistry with template [22] have been utilized. In the evaporation method, Au has been commonly used as one of the catalysts to synthesize the nanostructures. The Au film (or clusters) is usually of a thickness of a few nanometer formed by in-situ laser ablation in the reaction chamber of the evaporation method [23], or other typical thin film coating technologies such as sputtering. However, there are only a few reports on selfassembled 1-D ZnSe nanostructures [8, 9]. In addition, most of the reported 1-D ZnSe nanostructures grown by the evaporation method are nanowires.

In this article, self-catalyst ZnSe nanorods on in-situ synthesized ZnSe grains with a pure composition have been successfully synthesized by simply using elementary powder sources of Zn and Se through the thermal evaporation in a tube furnace. To simply the description, the nanorods on in-situ synthesized grains are hereafter named as the products. It is interesting to note that the nanorods generally grow in the same direction on a facet of ZnSe grain and the length and diameter of the nanorods are uniform. In section II, we will discuss the details of the experiments for the synthesis and characterization of the ZnSe products. The morphology, crystal structure and optical properties of the ZnSe products will be addressed in section III. The growth mechanism of the products will also be analyzed. Finally, conclusion will be drawn in section IV.

II. Experiments

The nanorods on grains were grown using thermal tube furnace. Zn and Se elementary powder sources were separately housed in two alumina crucibles. The two alumina crucibles with the sources were loaded into the quartz tube which was inserted into the furnace. The Se powder crucible was at an up-stream position with a temperature of 100^{o}C lower than that of Zn powder crucible where thermal couple was positioned. The quartz tube was then sealed and pumped down to 10^{-2} torr using a typical mechanical pump and was flushed with N_2 gas twice. After feeding the reaction chamber with N_2 gas at a flow rate of 150sccm for 30 minutes, the pressure was continuously maintained at 300 torr and the temperature of the furnace was increased to 650^{o}C. The temperature was then maintained at the same level for synthesis of ZnSe structures. After the process, the system was cooled down gradually to room temperature by simply turning off the power supply of the furnace. The samples were then collected from the inner-wall of the crucible of the Zn source.

X-ray diffraction (XRD, Bruker CCD X-ray diffractometer with CuKα radiation) and field emission scanning electron microscopy (FESEM, LEO 1530) have been applied, respectively, to study the crystallinity and morphology of the products. The detail structures were investigated using transmission electron microscopy (TEM, Philips Tecnai 20). The crystal structures and compositions were studied using the selected area electron diffraction (SAED) and energy dispersive X-ray spectroscopy (EDS) attached to the TEM system. The photoluminescence (PL) of the ZnSe products were studied in a cryostat. The temperature of the sample-under-test was controlled by a liquid He closed cycle cooling system. The excitation source was He-Cd laser with a wavelength of 325nm. The signal was detected by GaAs based PMT with a response time of 2ns.

III. Results and discussions

After the synthesis at a temperature of 650^{o}C, yellowish products were obtained from the inner wall of the crucible with Zn powders. When the growth time is 20 minutes, the products are nano-embryos on in-situ synthesized grains as shown in Figure 1 (a). The grains have random shapes bounded with well-defined facets. When the growth time is increased to 1 hour, the nanometer-scale structures on the in-situ synthesized grains become nanorods as shown in Figure 1(b). The TEM pictures and EDS spectrum of the nanostructures are shown in Figure 2. From the EDS results, we find that the nanorods generally composites of Zn and Se without other impurities while the C and Cu signals are from the carbon coated Cu grid used for TEM. The TEM pictures of the nanorods show that the contrast of the nanorod is quite uniform. In other reports [18-20], clear contrast difference at the tip is easily observed in the synthesis of nanostructure using metal catalysts such as Au. Figure 3 shows one set of TEMs and SAEDs of ZnSe nanorods. The typical pattern index determined from SAED (Figure 3b) indicates that the nanorod is cubic ZnSe with a growth direction of [111]. This is consistent with the hexagonal shape of the cross section of ZnSe nanorods as shown in Figure 1(b). From the results of EDS, SAED, TEM and SEM, we can conclude that the nanorods are ZnSe.

The overall crystal structure and phase purity of the nanorods on in-situ synthesized grains have been investigated using XRD as shown Figure 4. The sharp diffraction peaks in the XRD pattern can be indexed to show that the products are ZnSe with zinc blende structure. Since the grains are generally in micrometer size and the nanorods are only few tens nanometers for their diameter and less than few micrometers for their lengths, the XRD results provide the information of the grains and not likely the nanorods. As a result, the XRD shows that the grains are ZnSe. Meanwhile, the XRD spectrum of the products at other growth temperature from 600^{o}C to 800^{o}C is similar to that of the 650^{o}C case. This means that the diffraction pattern and thus the zinc blende structure of ZnSe products do not change with the growth temperature. Consequently, the XRD results show that the grains are mainly ZnSe. The PL spectrum of the products also confirms that the grain is ZnSe although the PL spectrum does not show here.

In the synthesis of the ZnSe nanostructures on ZnSe grains, we find that ZnSe grains can be obtained in the outer-wall of the Zn powder crucible and the inner-wall of the quartz tube near the down-stream end of the furnace. The ZnSe grains at the outer-wall of the crucible and the end of the quartz tube are also random in shape bounded by well-defined facets and similar to what we obtained in the inner-wall of the Zn powder crucible. The formation of the ZnSe grain can be described as homogenous vapor-phase nucleation [24]. The ZnSe grains then aggregates on the walls of the crucible and quartz tube. Consequently, ZnSe grains can be synthesized in a wide range of growth conditions. On the other hand, from the SEM studies of the products obtained from the inner-wall of the Zn powder crucible, we cannot obtain any stand alone ZnSe nanorods but ZnSe nanorods on facets of ZnSe grains. In addition, the ZnSe nanorods on ZnSe grains can only be obtained in the inner-wall of the Zn powder crucible where the vicinity is believed to be Zn enriched during the heating. Moreover, when the growth time increases from 15 minutes to one hour, the nanostructures change from nano-embryos to nanorods as shown in Figure 1. As a result, it is believed that the ZnSe grains will firstly form around the inner wall of the Zn powder crucible. With the Zn enriched condition in the crucible of the Zn powder, Zn and Se nucleates to form ZnSe nano-embryos and then nanorods on the lattice-matched facets of ZnSe grains. In this case, the small columnar growth of ZnSe nanorods on ZnSe grains can be considered as a secondary growth on crystal facets.

From our results, one can suppose that vapor phase Zn exists at the growth temperature of ~650°C and molten Zn forms on the ZnSe grains in the crucible with Zn source. During the formation of nanorods, the molten Zn not only acts as the reactant but also provides an energetically favored site for the absorption of Se.

Continual feeding of Zn and Se into the molten Zn results into the formation of the ZnSe nanorods. The molten Zn may continuously react with the Se vapor to form ZnSe when the temperature of the reaction chamber is gradually decreased after the heating process of the synthesis. In fact, the initiation of nanostructure formation by the rich Zn has also been described in ZnO nanostructures [25-28] but no trace of Zn at the top of the nanowires [27, 28]. Consequently, we believe that a self-catalytic Vapor-Liquid-Solid (VLS) mechanism [29, 30] plays an important role in the growth of the ZnSe nanorods.

IV. Conclusion

ZnSe nanorods on ZnSe grains have been successfully grown through thermal evaporation method using horizontal tube furnace. The ZnSe products are synthesized using elementary powders of Zn and Se. The results show that the ZnSe products have a pure composition. ZnSe grains can be synthesized in a wide range of growth conditions while ZnSe nanorods can be synthesized in the Zn enriched region with the presence of ZnSe grains. The growth of ZnSe nanorods on ZnSe grains is considered to be a secondary growth of columnar nanostructures on crystal facets. It is interesting to note that with the suitable growth conditions, ZnSe nanorods with uniform size and length can be obtained and their growth directions are the same on a facet of the ZnSe grain. The growth mechanism has also been analyzed and the growth of ZnSe nanorods can be explained using self-catalytic Vapor-Liquid Solid (VLS) mechanism.

Acknowledgement: W.C.H. Choy would like to acknowledge the support of the UDF grant and seed funding from the University of Hong Kong. T.I. Yuk would like to acknowledge the support of the small project funding. G.Z Wang would like to thank the support of the William Mong Visiting Research Fellowship held at the University of Hong Kong.

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Figure Captions

Figure 1. (a) SEM of ZnSe products obtained from the furnace maintained at growth temperature of 650°C for 20 minutes, and (b) SEM of ZnSe products obtained from the same condition as (a) but the growth time increases to one hour. Figure (b) is the enlarged part of the inset ZnSe picture.

Figure 2 (a) TEM picture of typical nano-embryos (b) TEM picture of typical nanorods, (c) the EDS of a nanorod body, and (d) the EDS of a nanorod tip.

Figure 3 (a) TEM and (b) the SAED of ZnSe nanorods.

Figure 4. XRD of ZnSe products obtained from various growth temperatures

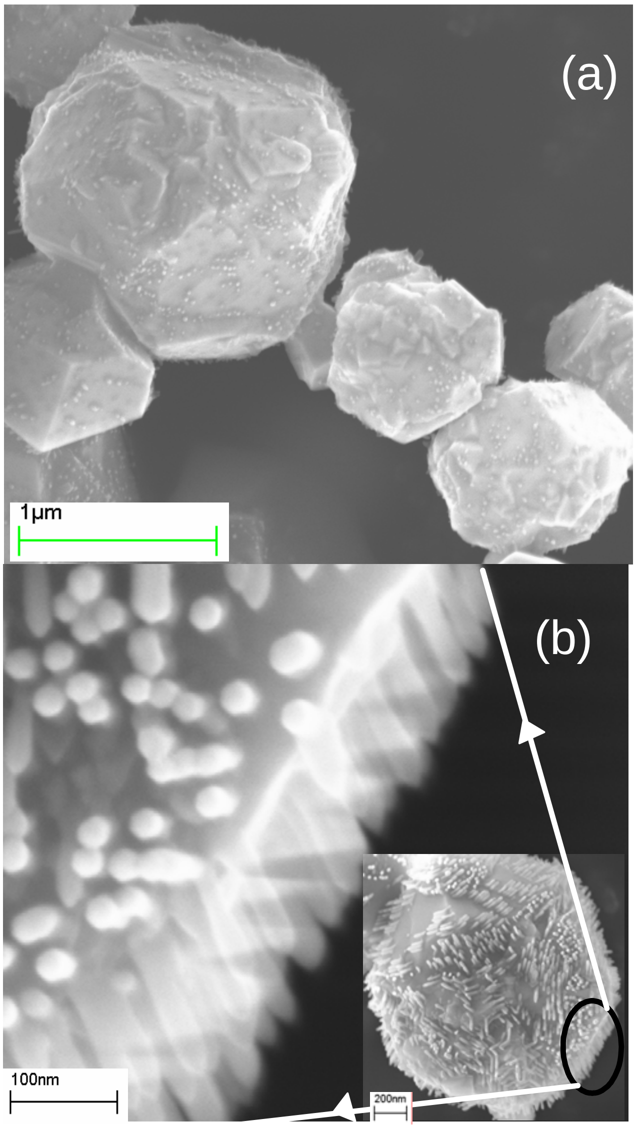

Figure 1. (a) SEM of ZnSe products obtained from the furnace maintained at growth temperature of 650°C for 20 minutes, and (b) SEM of ZnSe products obtained from the same condition as (a) but the growth time increases to one hour. Figure (b) is the enlarged part of the inset ZnSe picture.

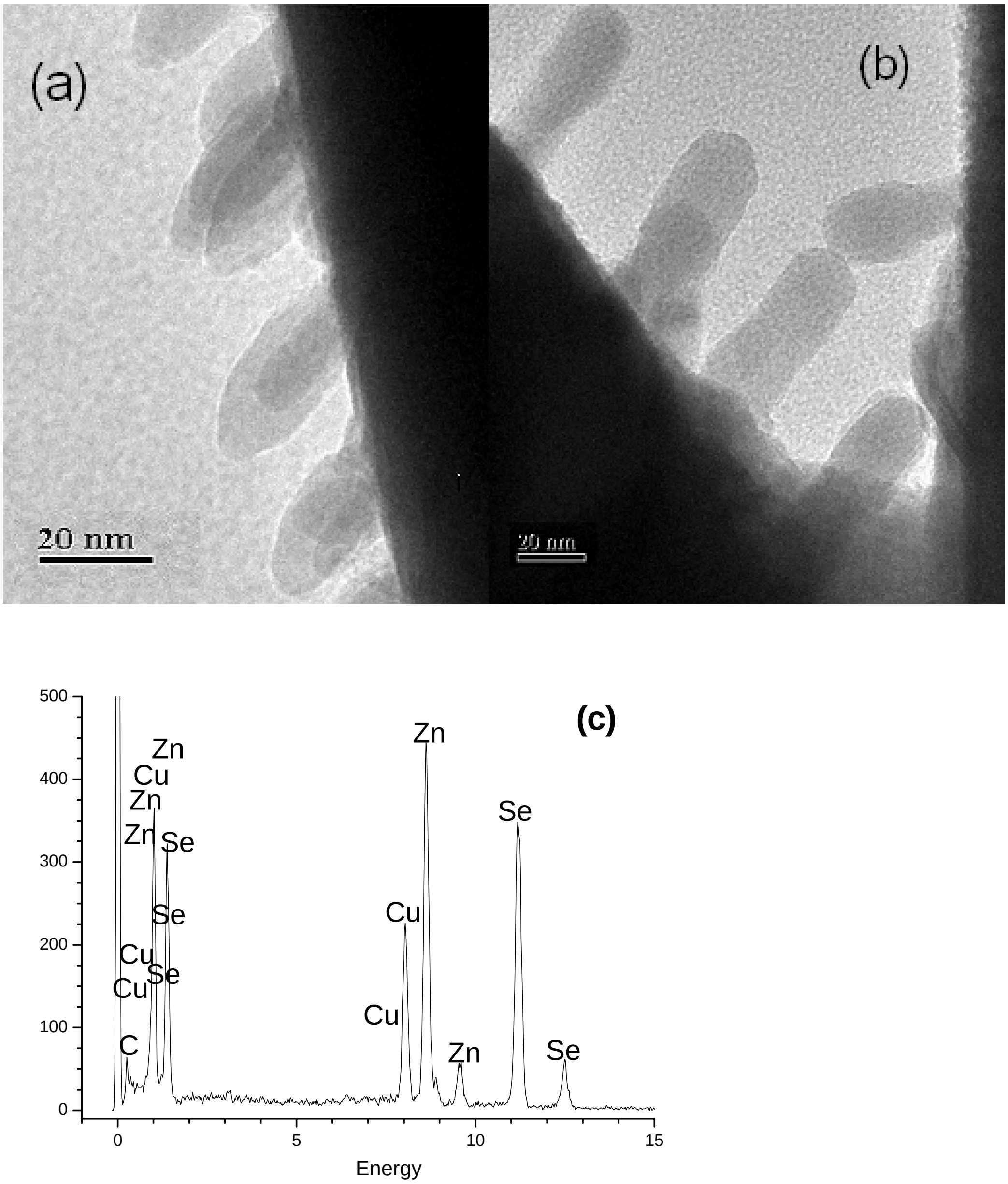

Figure 2 (a) TEM picture of typical nano-embryos (b) TEM picture of typical nanorods, and (c) the EDS of nanorod.

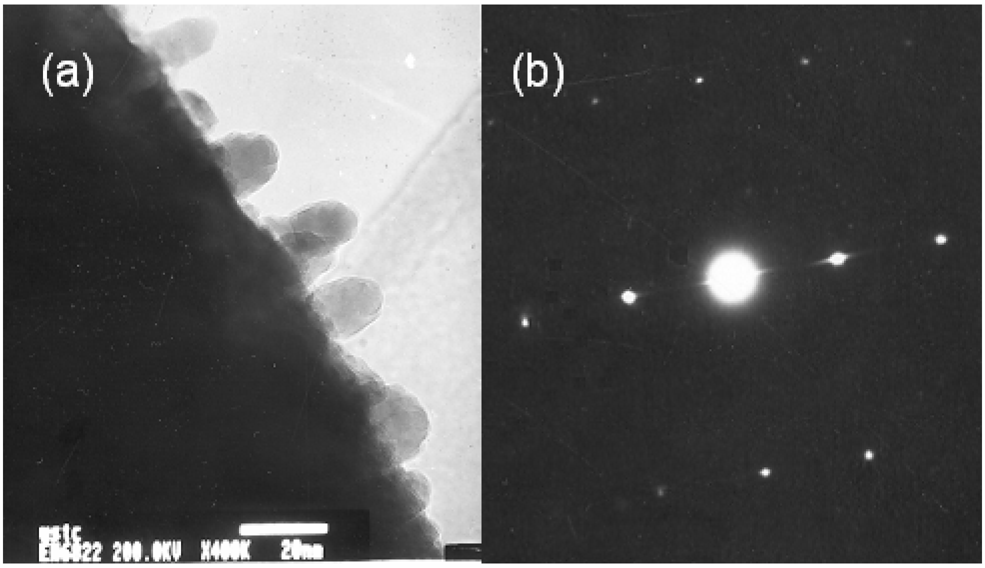

Figure 3 (a) TEM and (b) the SAED of ZnSe nanorods

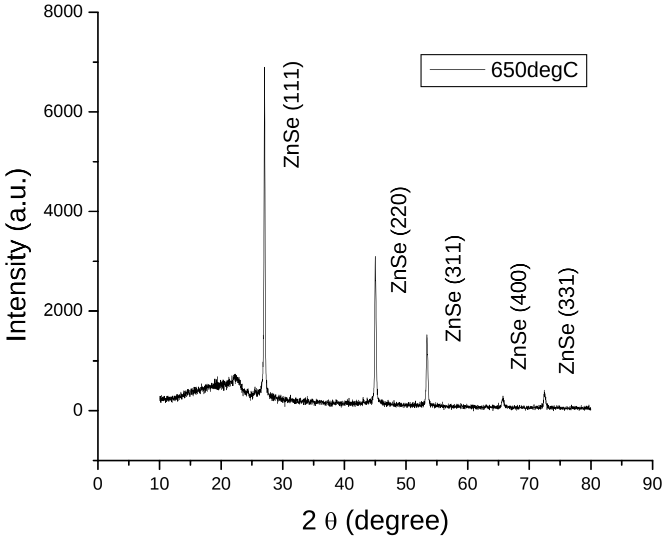

Figure 4. XRD of ZnSe products obtained at the growth temperature of 650^oC.