NEW INSIGHTS ON THE MECHANISM OF SEMICONDUCTOR
NANOSTRUCTURES FORMED DURING VAPOR TRANSPORT AT
ATMOSPHERIC PRESSURE

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ABSTRACT

Co-deposition of two types of high aspect ratio nanostructured ZnO involving nanowires and nanotetrapods with a uniform structure were carried out through thermal evaporation and vapor transportation of a mixture of highly pure ZnO and graphite powders in 1:1 weight ratio. The mixture was heated at 1100 °C under various flow rates of N2 and air mixture. The surface morphology and structural characteristics of synthesized ZnO nanostructured materials revealed a highly crystalline structure with an average diameter of about 30 nm and length of several micrometers. The mechanism of co-deposition of ZnO nanowires and nanotetrapods during vapor transport at atmospheric pressure was proposed.

Keywords: ZnO nanowires, nanotetrapods, high aspect ratio, co-deposition, vapor phase.

1. INTRODUCTION

Among the various classes of one-dimensional nanostructures, semiconductor nanowires are a result of anisotropic nanostructure having the diameter in the order of a nanometer, usually constrained to several tens of nanometers or less and an unconstrained length. These one-dimensions that can be advantageous are the small diameters, large surface area and smooth surfaces of the nanowire materials, then they offer unique opportunities to control the density of states of semiconductors, and in turn their electronic and optical properties. Then semiconductor nanowires possess several unique characteristics. Their ability to be integrated into electronic devices, novel sub-wavelength optical phenomena, their large tolerance for mechanical deformations, their ability to interface with other microscopic and nanoscopic systems in nature, the decoupling of length scales associated different physical phenomena in the radial and axial directions, and their high surface-to-volume ratio, have led to an explosion of applications utilizing these structures. Indeed, since the first report of Radushkevich and Lukianovich, in 1952, on the formation of carbon fibrils by thermal decomposition of carbon oxide during
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contact with iron, to date a concept “Semiconductor Nanowires” is became a platform for nanoscience and nanotechnology where numerous studies have been carried out to explore nanowires as new building blocks in electronics and photonics [1 – 5], solar cells [6 – 9] sensors/biosensors [10 – 14], and energy applications [15, 16].

In all the mentioned literatures, the method either physical vapor deposition or chemical vapor deposition that were used to synthesize the nanowire materials was obeyed to the vapor–liquid–solid (VLS) mechanism. As to vapor transport depositions, there exist two different processes which either involve metal catalyst for the nanowires (NWs) growth or not. For both just mentioned above, the process consists of mass transfer of the material to the reaction zone in the form of the gas flux of components, their diffusion or molecular beam, adsorption on the surface and surface diffusion of the components to more favorable sites. In case if the mass transfer is sufficient and there is supersaturation of the vapors, the limiting factor of NWs growth is the nucleation rate at the surface. The metal catalyst facilitates growth by introducing a catalytic liquid alloy phase which can rapidly absorb components to supersaturation levels, and from which crystal growth can subsequently occur from nucleated seeds at the liquid–solid interface by the vapor–liquid–solid (VLS) mechanism. In case of the absence of metal catalyst, the growth of a crystal takes place through direct adsorption of gaseous components onto crystal defects of a solid surface, then aggregated into seeds that act as catalyst. In this situation, the formation and growth of nanowires from these seeds are considered as self-catalyzed process and similar to the one of the vapor-solid mechanism [17]. However the nucleation conditions at the interface are often not so favorable as compared with liquid catalyst.

Beside that almost vapor transport depositions to form semiconductor nanowires were carried out in high vacuum of about 10 Torr or in ultimate vacuum of several 10⁻³ Torr, the formation of semiconductor nanowires by the vapor transport deposition have been carried out at atmospheric pressure [10, 18]. Different from almost the mentioned literatures, in our work the nanowires growth was fully carried out in vapor phase and at atmospheric pressure, as represented in figure 1. Now we focus on the comparing the nanowires growth with VLS mechanism and the one of the nanowires growth in our work.

2. EXPERIMENTAL

As the detailed description of the experiment set up was represented in a previous work [10], the ZnO nanowires were synthesized through thermal evaporation and vapor transportation of a mixture of extrapure ZnO powder (Merck, 99.99 %) and graphite powder (Merck) in 1:1 weight ratio that were carefully grounded and mixed. The mixed material was kept in a porcelain boat (with 1 cm diameter and 8 cm long) and loaded into the centre of a horizontal quartz tube furnace (with 100 cm long and 4 cm inner diameter). The tube furnace was heated to 1100 °C at a heating rate of 10 °C/min. One end of the tube was connected to the gas supply and flow control system. A mixture of highly pure nitrogen gas (99.99 %) and air in 1.7:1 volume ratio was flowed at a constant rate of 2880 sccm into the tube furnace. The flow rate was modulated with a digital mass-flow-control system (Aalborg, Model: GFC175-VALD2-A0200, USA). The reactions began within 2–3 min and continued for approximately 13–15 min, depending on the amount of initial materials. A striking point here is to use the ambient atmosphere as the oxygen source for the reaction. The tube furnace was preheated up to and kept at 1100 °C before loading the source material. The product was deposited onto a borosilicate glass cup positioned out of the tube furnace (Fig. 1). The as-synthesized product was observed in cotton-white color and very uniform in diameter and length. The collected ZnO NWs were ultrasonically dispersed in
ethanol for 48 h until a stable dispersion was obtained. The morphology, size distribution, crystallinity, and composition of as-synthesized products were characterized using field emission scanning electron microscope (FESEM 4800, Hitachi, Japan) operating at 10 kV. Transmission electron microscopy (TEM), selected area electron diffraction (SEAD), and high resolution transmission electron microscopy (HRTEM) examinations were conducted using a JEOL JEM-3010 system at an accelerating voltage of 300 kV. The X-ray diffraction (XRD) patterns were obtained using a Siemens diffractometer with Cu Kα1 radiation.

3. RESULTS AND DISCUSSION

Morphology and structure of as-synthesized ZnO

The as-synthesized product that was obtained in a borosilicate glass cup positioned at the outlet of the reactor (Fig. 1) was observed in cotton-white color. FE-SEM and TEM studies revealed that the as-synthesized ZnO product can be distinguished into two regions with two different morphologies, nanowires and nanotetrapods, as shown in Figures 3 and 4. In more detailed, it also revealed that structure of the part of the product positioned at the central of the borosilicate glass cup is consisting of ZnO nanowires. Meanwhile structure of the one positioned near by the wall of the cup is ZnO nanotetrapods. Figure 2 presents the XRD pattern of as-grown ZnO NWs, which are identified as hexagonal wurtzite ZnO phase (JCPDS 36-1451) from the XRD analysis results.

It is interesting to note that no diffraction peaks corresponding to other phases or impurities are observed. Thus, the XRD pattern clearly reveals the formation of ZnO NWs with wurtzite structure under the conducted experimental conditions.

The presence of well-defined diffraction peaks of (100), (002), (101), (102), (110), (103), (200), (112), and (004) clearly reveals that the aggregates of vapor ZnOx molecules are converted into ZnOx cluster form that are then oxidized into ZnO through absorption of oxygen atoms by these surfaces. The strong and sharp ZnO peaks with a narrow spectral width indicate that the synthesized nanowires are highly crystalline.
The overall morphologies of the as-synthesized ZnO nanomaterials were studied with FE-SEM technique. Figure 3(a) shows the low magnification image of the as-synthesized ZnO NWs in high aspect-ratio structure and heap up together. High magnification image of ZnO NWs (Fig. 3(b)) revealed very uniform ZnO NWs with a diameter of approximately 30 nm and a length of several micrometers. Additional structural characterizations were conducted using HRTEM technique. Figure 3(c) shows a low magnification image of a single ZnO nanowire. No voids or tubular structures were observed, which reveals that the growth of ZnO NWs may occur immediately in vapor transportation.

For the ZnO product positioned near by the wall of the cup, FE-SEM studies (Fig. 4a) revealed that as-synthesized ZnO materials have structural morphology of nanotetrapods in high aspect-ratio structure and heap up together. A higher magnification image (Fig. 4b) the surface morphology and structural characteristics of synthesized nanotetrapods revealed a high uniform and highly crystalline structure with an average diameter of about 30 nm and length of several micrometers, 3÷5 µm.

High-resolution TEM studies of ZnO nanowires (Figs. 3(d)–(f)) and ZnO nanotetrapods (Figs. 4(d)–(f)) also reveal that ZnO nanostructures are clean, atomically sharp and without any sheathed secondary phases or stacking faults. In the lattice-resolved scale, the HRTEM images of ZnO nanowires (Figs. 3(e), (f)) and ZnO nanotetrapods (Figs. 4(f), (h)) show that the length of the lattice fringe of ZnO nanowire is approximately 0.52 nm, corresponding to the (0001) fringes perpendicular to the growth direction, which is consistent with that of the bulk wurtzite ZnO crystal. In addition, SEAD patterns of ZnO nanowires (Figs. 3(d), (f)) and ZnO nanotetrapods (Figs. 4(d), (f)) reveal clearly visible bright spots corresponding to the crystal planes of the hexagonal for 1-D wurtzite ZnO nanostructure.
Figure 3. Typical SEM (a), (b), TEM (c), and HRTEM (d)–(f) micrographs of the as-synthesized nanowires ZnO.
Figure 4. A typical SEM (a), TEM (b) and HRTEM (d)-(h) micrographs of the as-synthesized ZnO nanotetrapods.
4. MECHANISM OF CO-DEPOSITION OF ZNO NANOWIRES AND NANOTETRAPODS

Because of using catalyst-free synthesis method in our work, the growth mechanism of ZnO NWs could not be based on VLS model, involving in a catalyzed-tip or base growth mode, depending on the metal-support interaction to be strong or weak. In our synthesis method, the tube furnace was preheated to 1100 °C. The obtained product was with a white cotton color and very uniform in diameter and length, suggesting that the nucleation and growth of ZnO nanostructures (nanowires and nanotetrapods) may begin during vapor transportation. Indeed, the melting temperature of ZnOx is approximately 419 °C (when x < 1), which is much lower than that of ZnO (1975 °C) [17,19]. ZnOx is produced through the reactions (1) and (2) [17]:

\[
\begin{align*}
\frac{3}{2}\text{ZnO}(s) + (1-x)\text{C}(s) & \rightarrow (1-x)\text{CO}(g) + \text{ZnO}_x(g) \quad (1) \\
\text{ZnO}(s) + \left(\frac{1-x}{2}\right)\text{C}(s) & \rightarrow \left(\frac{1-x}{2}\right)\text{CO}_2(g) + \text{ZnO}_x(g) \quad (2)
\end{align*}
\]

For more detailed reactions, it is not treated in this work and we refer the reader to our previous work [12]. The ZnOx molecules aggregates are converted into ZnO clusters as revealed in reaction (3):

\[
\text{ZnO}_x (\text{clusters}, x < 1) + \left(\frac{1-x}{2}\right)\text{O}_2 \rightarrow \text{ZnO (clusters)} \quad (3)
\]

The ZnO clusters are ideal nuclei centers to form ZnO nanostructures, as discussed below. In this situation, the formation and growth of ZnO nanostructures are considered as self-catalyzed and similar to that of the vapor-solid mechanism [17].

![Diagram explaining the formation mechanism of ZnO nanowires under lamina flow conditions.](image)

Figure 5. Diagram explaining the formation mechanism of ZnO nanowires under lamina flow conditions.
A possible growth mechanism of ZnO nanostructures in our synthesis method can be explained using a heating curve. As shown in Figures 4 and 5, for the formation of ZnO nanowires and nanotetrapods respectively, it takes 110 min for the tube furnace to reach the process temperature of 1100 °C. During the reaction time, the ZnO vapor, gases CO and CO₂ are formed via reactions (1, 2), and after vaporization into separated flows, they are transported in side by side by the supporting gas mixture of nitrogen and air (Fig. 5). A mixture containing a large quantity of graphite with ZnO powder ensures the availability of sufficient concentration of ZnO vapor and high super saturation condition in the central region of the furnace. However the hydrodynamic regime is under different flow conditions, lamina flow for the supporting gas flows running along the axis of the tube reactor and turbulent flow for the ones running close to the wall (see Figs. 5 and 6).

Within every supporting gas flow running under lamina flow conditions, the ZnOₙ molecules vapor are transported to the low temperature region. During that time they are oxidized further and aggregated into nanoclusters of ZnO via reaction (3) due to the reduction of the transported vapors rate and absorption of ZnOₙ molecules and aggregates together (Fig. 5). Meanwhile, a slight flow of CO₂ prevents aggregation of the vapor ZnOₙ; therefore, uniform and high aspect ratio ZnO NWs are formed.

In parallel to the lamina supporting gas flows running along the central axis of the tube reactor, the vapors were transported by the supporting gas flows that running along and close to the wall (see Fig. 6) are under turbulent flow conditions. In general, turbulent flow is time-dependent, rotational, and three dimensional. Therefore there usually exist small perturbations imposed on the flow originated from the roughness of a quartz tube reactor, from small variations in the supporting gas flows caused by presence of CO, CO₂, ZnOₓ, ZnO vapors, ZnO clusters (suspended solids) having different mass, etc. These make advantages for oriented connects of ZnO clusters to form some aspects of nanotetrapods in the way to achieve minimum free energy of the system (tetrapod nuclei and ZnO vapor clusters). Figure 5 represents diagram explanation of the formation mechanism of nanotetrapods. As seen the vapor ZnOₓ molecules that were transported in the supporting gas flow were oxidized further into ZnO vapors and aggregated into ZnO nanoclusters. Under turbulent flow conditions, in the initial stages of the
growth of ZnO nanotetrapods, the ZnO molecules were connected together to form ZnO nanotetrapod nuclei having eight tetrahedral crystals named the octa-twin model as proposed by Takeuchi et al. [20]. As FE-SEM and HR-TEM studies revealed that the ZnO nanotetrapods that were synthesized successfully are characteristic of structure of very uniform in diameter and length. It revealed that the adsorption of ZnO molecular vapors and connections of ZnO clusters with a ZnO nanotetrapod nucleus in the way to achieve minimum free energy of the system. This growth is different the growth by VLS or/and VS mechanism that occurred under static conditions with high or ultimate high vacuum where some growth facets of a ZnO nucleus can achieve faster growth rates, while inhibiting the growth rates in other directions [1].

5. CONCLUSION

Using thermal evaporation and vapor transport method, the produced ZnO: nanowires and nanotetrapods were co-deposited under atmospheric pressure. FE-SEM and HRTEM studies revealed that both structure are very uniform and high aspect ratio structure and a diameter of approximately 30 nm and a length of several micrometers. The XRD examinations revealed that the produced ZnO are identified as hexagonal wurtzite ZnO phase and have highly crystallized structure with strong and sharp ZnO peaks of narrow spectral widths but without characteristic peaks of the impurities. The new insights on the mechanism of co-deposition of ZnO nanowires and nanotetrapods during vapor transport were proposed.

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REFERENCES

Tóm tắt

GIẢI THÍCH MỚI VỀ CƠ CHẾ HÌNH THÀNH CẦU TRÚC NANO CỦA VÁT LIỆU BÁN DÂN TRONG QUÁ TRÌNH VÀN CHUYÊN PHA HƠI Ở ÁP SUẤT KHÍ QUYỀN

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Trong quá trình bốc bay nhiệt hình thành đồng thời hai dạng nano ZnO là dây nano và nano tetrapod có tỉ số chiều dài/dường kính lớn với cấu trúc đơn nhất. Trong quá trình bốc bay là quá trình vận chuyển pha hơi của hỗn hợp bột ZnO và Các bon với tỉ lệ khối lượng 1:1 tại nhiệt độ 1100 °C bằng dòng hơi khí không khí và N2 có lưu lượng khác nhau. Đặc trưng cấu trúc và hình thái bề mặt của vật liệu cấu trúc nano ZnO được tổng hợp có cấu trúc hình thể cao với đường kính trung bình cỡ 30 nm, chiều dài vài micromet. Báo cáo này chúng tôi đưa ra cơ chế hình thành đồng thời hai dạng vật liệu trong quá trình vận chuyển pha hơi ở áp suất khí quyển.

Từ khóa: dây nano ZnO, nanotetrapod, ti só doc-ngang cao, dòng ngung tụ, hơi.