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Gas-phase supersaturation effects on morphology properties of ZnO nano and microstructures grown by PVT

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Abstract. A systematic study of the morphology evolution of ZnO nanostructures grown by physical vapour transport was carried out. The evolution of the shape with the growth time is shown to depend on the different gas-phase supersaturation and temperature conditions encountered in the crystallization zone of the tube furnace. The observed morphology transitions are discussed, and a growth model for ZnO nanostructures is given.

1. Introduction

The synthesis of ZnO at nanoscale has paid a renewed interest during the last decade due to the potential applications of this material. Indeed, ZnO nanostructures are viewed as potential candidates for application in biomedical nanodevices thanks to the non-toxic and biocompatible character of this semiconductor [1,2]. In addition, ZnO nanostructures can be applied in numerous technology devices due to the unique combination of physical properties exhibited by this material [1,2]. Nanostructured ZnO has been achieved to grow by using several methods involving in most cases the transport of precursors in the vapour phase [3,4] and wet chemistry processes [5,6]. Despite the efforts made during the last years, the growth mechanisms of ZnO nanostructures and the control of their physical properties are no totally understood. Low-cost growth methods have attracted intensive interest due to the requirements of the crystal growth technology. Physical vapour transport (PVT) has shown to be well-adapted for the growth of nanostructures with good quality and physical properties [4]. Unlike other vapour phase methods with industrial character, PVT does not offer an accurate and direct control of the richness of gas-phase precursors during the growth process. This aspect makes difficult the control of nanostructure properties. Considering that studies on PVT growth mechanisms are still needed, we have investigated in this work the role of gas-phase supersaturation. We have also emphasized the influence of growth time on the behaviour of the gas-phase supersaturation along the crystallization region and their effect on morphological characteristics of ZnO nanostructures.

2. Experimental details

Catalyst-free ZnO nano and microstructures were grown on c-sapphire substrates by physical vapour transport method under atmospheric pressure. The experiments were carried out into a horizontal tube furnace with two temperature control zones. An argon flow (100l/min) and a mixture of ZnO and graphite powder [100:1] were used as carrier gas and material source, respectively. The temperature gradient was obtained by setting the temperature of the evaporation zone (material source) at $1015^{\circ}C$ while the temperature of the crystallization zone (substrates) was set at $400^{\circ}C$. The morphology of

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ZnO nanorods was assessed by using scanning electron microscopy (SEM Jeol 840) and the structural properties of the samples were determined by powder X-ray diffraction (BrukerD8Advance).

3. Results and discussion

Several sets of samples were grown by employing different growth times (5, 15, 30 and 60 minutes) and using the same temperature gradient as illustrated in Figure 1(a). The analysis of each set of samples evidenced substantial changes such as the grown material quantity on the substrates and the nanostructures morphology, depending on the position in the crystallization zone. The Figure 1(b) shows the typical behaviour of the grown material quantity of our sets of samples as a function of the distance along the crystallization zone, measured from the material source. The corresponding graph exhibits an asymmetric bell shape with a maximum centred in the zone corresponding to $420-450^{\circ}C$.



Figure 1. (a) Temperature gradient (temperatures of controllers: $1015^{\circ}C$ (evaporation zone) and $400^{\circ}C$ (crystallization region)). (b) Estimation of grown material quantity along crystallization region.

Crystal growth fundamentals emphasize the primordial importance of parameters such as supersaturation of precursors and surface energies of crystal facets because they tend to govern the morphological development of crystals [7,8]. Regarding nanostructures it was previously reported that the final morphology is governed by the competition between the processes of adsorption and incorporation of atoms on the different crystal surfaces under a particular supersaturation conditions [9]. It is commonly admitted that the anisotropic growth is favourable under low supersaturation conditions [10] while some studies carried out on whiskers growth have shown that rich supersaturation conditions favour the lateral growth of the structures [11]. Indeed Ye et al. [9] have particularly studied the behaviour of gas-phase supersaturation of precursors along the crystallization region during a growth process using a CVD system. These authors showed that gas-phase supersaturation exhibits a decreasing behaviour along the crystallization region when the growth is made without carrier-gas flow, while it exhibits a curving behaviour with an asymmetric bell shape when a carrier-gas flow is used. According to our results, the behaviour of the grown material quantity on our samples seems to be well-correlated with the above described behaviour of gas-phase supersaturation using a carrier-gas flow. Therefore, and similarly to the procedure done by these authors [9], we have divided the crystallization region into 4 different zones regarding their gassupersaturation level associated to a grown material quantity: zone I, low supersaturation (480-500°C); zone II, high supersaturation ($420-480^{\circ}C$); zone III, intermediate gas-phase supersaturation (380-400°C) and zone IV, low gas-phase supersaturation $(300-370^{\circ}C)$, as shown in Figure 1(b).

The typical morphology characteristics of the samples grown into zones II, III and IV, with different growth times (5, 15, 30 and 60 minutes) are shown in Figure 2. Samples grown into zone I (polyhedrons structures) are not shown here due to the very low material quantity found on these samples. The SEM images reveal three principal features: (i) nanopolyhedrons with well-defined hexagonal facets are synthetized into all crystallization zones during the early growth stages (5

minutes); (ii) depending on the crystallization zone, these nanopolyhedrons exhibit different morphological evolution as the growth time is increased: zone II, nanopolyhedrons evolve to a rough layer composed by coalesced polyhedrons (Figures 2(c), (f), (i), (l)); zone III, nanopolyhedrons to isolated micropolyhedrons (figures 2(b), (e), (h), (k)) and zone IV, nanopolyhedrons to needles (Figures 2(a), (d), (g), (j)); (iii) the number of structures/area seems to be constant as the growth time is increased. The last observation suggests that, under our conditions, the nucleation process is not continuous during the growth, i.e. once a number of seeds have been nucleated during the early growth stage, the subsequent atoms will tend to be incorporated into different crystal planes of the nucleated seeds instead of creating new ones on the substrate surface. The morphological transitions agree with what is usually admitted, i.e. isolated polyhedrons with well-defined hexagonal crystal facets are obtained under intermediate gas-phase supersaturation conditions, while under low gas-phase supersaturation conditions our structures develop into needles (IV zone).



Figure 2. SEM images of the samples grown into the three zones, II (420-500 C), III (380-400°C) and IV (300-370°C) with different growth times: (a-c) 5min, (d-f) 15 min, (g-i) 30min and (j-l) 60min.

Otherwise, SEM images of zone II samples show that polyhedrons exhibit a faster lateral growth as time growth is increased. As it was mentioned, previous studies have shown that high supersaturation conditions favour the lateral growth of the structures [11]. This aspect can explain the morphology transition exhibited by our samples in this zone, i.e. polyhedrons to a rough layer. Under high gasphase supersaturation, the lateral growth ("m" and "a" planes) of our ZnO polyhedrons is enhanced, thus favouring the coalescence of the structures and the subsequent development of a rough layer. Moreover, higher magnification SEM images of needles structures (zone IV) show that they tend to develop from some pyramidal or basal plane of a polyhedron structure previously synthetized, Figure 3(a). Into the BCF (Burton, Cabrera and Frank) theory [7] and the studies developed by Sears [8], a screw dislocation is proposed to be at the origin of the whisker growth. However, reported studies have associated the anisotropic growth of ZnO nanostructures to another kind of crystal defect, such as stacking faults [12] or twin planes [13]. Recently, Perillat et al. have focused on the growth of ZnO nanorods grow by MOCVD [14]. These authors suggest an inversion domain boundary (IDB) to be at the origin of the nanorod growth. The IDBs could come from the segregation of aluminium impurities; nevertheless the occurrence of such a polarity inversion is still to be fully understood. In our study, the same kind of mechanism could explain the development of needles, emerging from the polyhedrons. According to our experimental results, a growth model which summarizes the morphology evolutions observed for our ZnO nanostructures, can be drawn when the growth time is increased, depending on the gas-phase supersaturation conditions in each crystallization zone, Figure 3.



Figure 3. (a) and (b) SEM images of needles structures; (c) proposed model of the morphology development of ZnO structures, as the growth time increases under different gas-phase supersaturation of precursors.

4. Summary and conclusions

Several ZnO structures were grown at low temperature range by varying the growth time using a well selected value of the carrier gas flow and temperature gradient. The study carried out has allowed correlating the morphology transitions observed in our ZnO structures with the level of gas-phase supersaturation along the crystallization zone. The results show that: (i) under low supersaturation conditions, the anisotropic growth is more favourable. The needle shape structures tend to develop from the basal o pyramidal facets of a nanopolyhedron synthesized during the early growth stages; (ii) under high supersaturation conditions, rough layers tend to be formed, due to the coalescence of polyhedrons. This latter case can be explained by the enhanced lateral growth of the polyhedrons.

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