



RESEARCH ARTICLE

A TWO STEP GROWTH TECHNIQUE FOR THE FORMATION OF ZnO NANORODS

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ABSTRACT

ZnO nanorods are grown on quartz substrates by metal organic chemical vapor deposition using diethylzinc (DEZn) and tert-butyl alcohol. Nanorods are grown basically by controlling the temperature and duration of growth at various steps. X-ray diffraction confirms the formation of ZnO nanorods. FESEM images show the uniform distribution of nanorods on the substrate. The mechanism of formation of ZnO nanorods is proposed.

INTRODUCTION

One-dimensional nano structured materials such as, nanorods, nanoflowers, nanospheres and so on, have received now-a-days a considerable attention in various applications owing to their peculiar properties (Guo *et al.*, 2012; Zeng *et al.*, 2012). Nanorods of various materials including ZnO have been reported by several researchers. ZnO is a promising semiconducting metal oxide as it has a wide band gap of 3.37 eV at room temperature, a large free exciton binding energy of 60 meV, high thermal and mechanical stability, and so on (Pati *et al.*, 2014; Pati *et al.*, 2014). As ZnO is prone to form nanorods, several methods have been developed for the growth of ZnO nanorods (Jung *et al.*, 2008; Jia *et al.*, 2010; Kim *et al.*, 2005). Although various substrates are used for the growth of ZnO nanorods (Jung *et al.*, 2008; Jia *et al.*, 2010; Kim *et al.*, 2005; Wu *et al.*, 2009), there are few reports on the growth of ZnO nanorods on fused quartz substrates using metal organic chemical vapor deposition. In this work, ZnO nanorods are grown on fused quartz substrates by metal organic chemical vapor deposition technique using diethylzinc (DEZn) and tert-butyl alcohol as zinc and oxygen precursor materials, respectively. The structural properties of the grown nanorods are investigated and a possible mechanism for the formation of nanorods is proposed.

Experimental

A two-step growth technique was followed for the growth of ZnO nanorods. Diethylzinc (DEZn) and tert-butyl alcohol were used as zinc and oxygen precursors, respectively. In the first step a buffer layer of ZnO was grown on the pre-cleaned quartz substrates at a lower temperature of 400 °C which acts as nucleation sites and facilitates the growth of nanorods. During buffer layer growth the flow rates of diethylzinc (DEZn) and tert-butyl alcohol were maintained at 10 sccm and 40 sccm respectively for 30 minutes. Then the flow of precursor materials was stopped for 20 minutes and the temperature was raised to 600 °C.

In the second step the flow rate of DEZn was increased to 30 sccm while the flow rate of tert-butyl alcohol was maintained at the same rate and the same growth temperature of 600 °C was also maintained for one hour. After one hour the flow of precursor materials was stopped and the sample was left for annealing at 600 °C for 20 minutes. Amano *et al.* (1986) was the first to develop the two-step MOCVD growth method for GaN (Amano *et al.*, 1986). The crystalline structure of the grown samples was characterized by X-ray diffraction (XRD) (Rigaku Ultima III Xray diffractometer) using Cu K α radiation. The surface morphologies were characterized by field emission scanning electron microscope (FESEM) (CARL ZEISS SUPRA-40).

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RESULTS AND DISCUSSION

The structural characteristics of the grown ZnO nanorods are investigated from the x-ray diffraction analysis using Cu K α radiation.

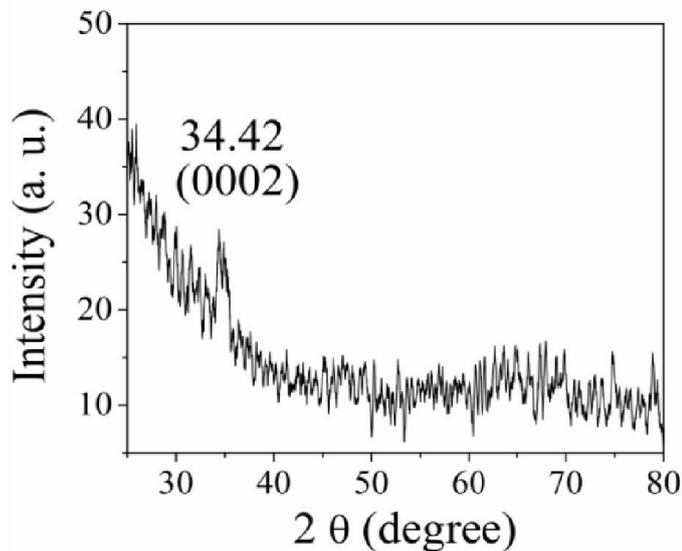


Fig. 1. X-ray diffraction pattern of ZnO nanorods grown by MOCVD using a two-step growth technique on fused quartz substrates

Figure 1 shows the XRD pattern of ZnO nanorods grown by MOCVD using a two-step growth technique. XRD pattern confirms the formation of hexagonal phase of ZnO nanorods with one diffraction peak at $2\theta = 34.42^\circ$ corresponding to (0002) plane of ZnO. This peak corresponds to the JCPDS-ICDD 36-1451 card of ZnO Zincite (Crystal system: Hexagonal, space group P63mc, $a = 3.24982$ and $c = 5.20661$) (Anh *et al.*, 2009). The lattice parameters estimated from the XRD pattern ($a = 0.3250$ and $c = 0.5207$ nm) is consistent with the reported values (Kim *et al.*, 2005). The micro structural characteristics of the grown ZnO nanorods are studied from FESEM micrographs. Figure 2 represents FESEM images of the top view of ZnO nanorods grown by MOCVD method.

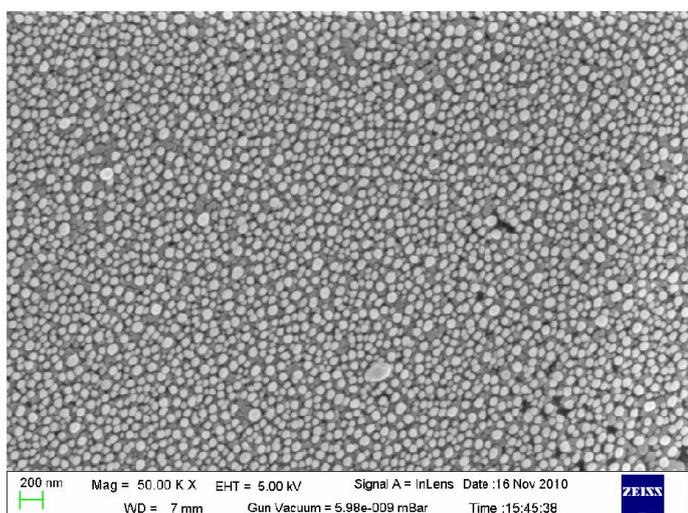
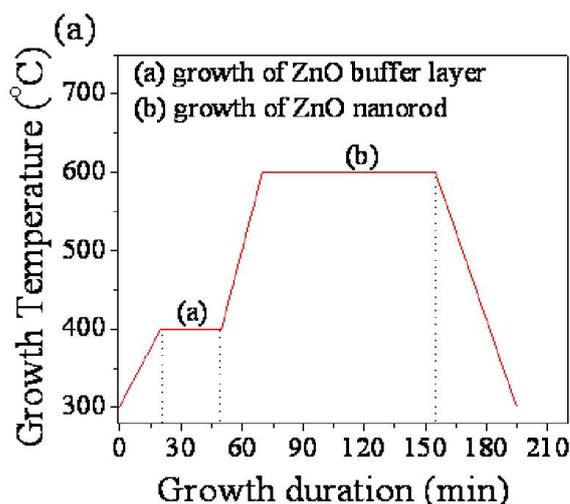


Fig. 2. FESEM images of the top view of ZnO nanorods grown by MOCVD using a two-step growth technique on fused quartz substrates

As observed from the figure, initially a thin layer (two-dimensional grains) of ZnO has been formed on the top of the fused quartz substrates. Subsequently, some of the grains of ZnO promote the three-dimensional growth (nanorod) owing to its lesser free energy. As reported in the literature some nuclei of ZnO facilitates the growth of ZnO nanorods along the preferential c -axis ((0001)) direction (Jung *et al.*, 2008). From the top view image (Figure 2) it is inferred that nanorods are grown in a direction perpendicular to the substrate i. e. along (0002) directions.



(b)

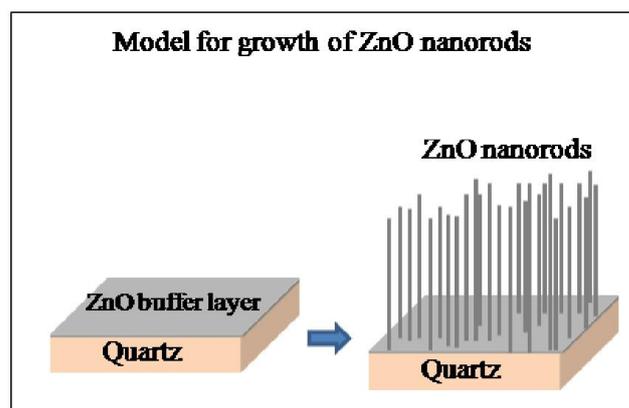


Fig. 3. (a) A graph showing the variation of growth temperature and growth duration for the formation of nanorods, (b) A model for the growth of ZnO nanorods

Figure 3 shows the graphical representation of the experimental procedure for the growth of ZnO nanorods. As illustrated in the experimental section growth temperatures are varied at various intervals for the two-step growth of ZnO nanorods. This is represented in the Figure 3(a). Figure 3(b) shows the schematic of the mechanism for the formation of ZnO nanorods. It can be said that ZnO nanorods are considered as one of the most promising structure for the applications of gas sensors owing to its large specific surface area.

Conclusion

In summary, we have successfully grown ZnO nanorods on fused quartz substrate using MOCVD growth technique.

Initially a buffer layer is grown at a substrate temperature of 400 °C which acts as nucleation sites and subsequently nanorods are grown on it at a higher temperature of 600 °C. The mechanism for the growth of ZnO nanorods is proposed schematically.

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