Research Article

Fast Formation of Surface Oxidized Zn Nanorods and Urchin-Like Microclusters

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Entangled Zn-ZnO nanorods and urchin-like microstructures were synthesized by the hot filament chemical vapor deposition technique at 825 and 1015°C, respectively. X-ray diffraction results showed a mixture of ZnO and Zn phases in both nanorods and urchin-like structures. The presence of Zn confirms the chemical dissociation of the ZnO solid source. The Zn-ZnO nanorods with diameter of about 100 nm showed dispersed-like morphology. The urchin-like structures with micrometer diameters exhibited porous and rough morphology with epitaxial formation of nanorods.

1. Introduction

Several techniques have been employed in obtaining nanostructured materials due to their potential applications in electronics, optoelectronics, and chemical gas sensing [1–4]. Recently, micro- and nanoscale composite materials with core-shell structure have stimulated a lot of attention due to their interesting properties such as large surface area and quantum confinement effects. Zn-ZnO core-shell structures are of special interest since heterojunctions can be formed at the interface. These structures offer great promise for fabrication of devices as nanotransducers [5], in solar energy conversion [6], and field emission [7], among others. Nowadays several methods are commonly applied to prepare Zn-ZnO core-shell structures such as urchin-like [6], nanoparticles [8], and nanorods [9].

Chemical vapor deposition (CVD) and its different experimental configurations such as metal organic CVD, plasma enhanced CVD, laser enhanced CVD, low pressure CVD, and HFCVD have shown versatility and reliability in obtaining a large variety of films, coatings, and recently nanostructures. The HFCVD method requires only a filament

and a current source to decompose hydrogen molecules into atomic hydrogen (H^*). These radicals assist the fast decomposition of several types of gas phase and solid raw materials. In the present work is reported the formation of Zn-ZnO nanorods and urchin-like microclusters by the HFCVD technique, using catalytic produced hydrogen atoms as reducing agent.

2. Materials and Methods

Zn-ZnO nanorods and urchin-like microclusters were fabricated by the HFCVD technique by using ZnO powders as reactant material. Although the main characteristic of the HFCVD system is that it uses a metallic filament, it is known that by contact with SiH_4 or H_2 it yields hydrogen atoms when it is heated at 1600°C and above [10, 11]. The aim of using hydrogen atoms was to produce Zn and OH gases from a ZnO solid source in a short period of time in relation to other methods. Actually, the amount of hydrogen atoms in HFCVD is in some cases by one or two orders larger than in PECVD system [12]. Since the hydrogen atoms concentration

depends upon the distance from the filament [13], the ZnO solid source was placed around 2 mm under the filament. ZnO powders were compressed in order to obtain a tablet of 0.2 g. The ZnO tablet with cylindrical shape was loaded into the center of a quartz tube (diameter 60 mm, length 350 mm) and under of a tungsten filament. The filament has a parallel array to minimize thermal gradients between individual wires and offer uniform heating over the substrate. The substrates were placed 6 and 4 mm on each experiment below the filament during five minutes, reaching substrate temperatures of 825 and 1015°C (Figure 1), respectively. P-type (100) oriented silicon wafers and resistivity $\rho = 1-3 \Omega \cdot \text{cm}$ were used as substrates. By applying an AC voltage of 83.4 V the filament was heated up to 2000°C. The vapor precursor production and the substrate chemical reactions are proposed as follows:

Reaction (1) is produced on the ZnO tablet and reaction (2), onto the substrate surface. The XRD diffractograms were measured with a Bruker D8 Discover diffractometer using Cu K α radiation (1.5418 Å). The morphology of the products was characterized by using a scanning electron microscopy (SEM) Phillips XL-30.

3. Results

Figure 2 shows XRD spectra measured from samples deposited at 825 and 1015°C. The analysis of each diffractogram shows that there is a mixture of ZnO and Zn phases in both samples. However, it seems that ZnO exhibits better crystallization characteristics than Zn since it shows stronger and sharper diffraction lines, including the overlapping Zn (002) and ZnO (101) peaks. The formation of Zn traces can be ascribed to the condensation of Zn vapor, which may confirm the reduction of the ZnO tablet by hydrogen atoms and molecules, as was suggested in (1). Several authors have reported a better crystallization of ZnO by increasing the growth temperature [14–16]. This has been attributed to increase of surface mobility of Zn and oxygen atoms in higher temperatures. However, these results were obtained in substrate temperatures lower than 600°C.

The morphology of the products obtained by the HFCVD technique at 825 and 1015°C is shown in Figures 3 and 4. Different morphologies can be clearly seen by changing the growth temperature from 825 to 1015°C. In Figure 3(a), the product deposited at 825°C exhibits a porous and nonuniform structure. Figure 3(b) shows a high magnification SEM image of this sample. A large quantity of nanoscale rod-like structures can be seen. The diameter of the nanorods is observed to be relatively uniform (100 nm approximately) and their lengths of several micrometers. The nanorods are not aligned and have a scattered distribution. From XRD spectra, we suggest that they are Zn-ZnO structures. The formation of the Zn-ZnO nanorods can be explained by

FIGURE 1: Heating rate and deposit temperature of ZnO nanorods and microclusters grown by the HFCVD technique.

FIGURE 2: XRD spectra of the Zn-ZnO nanorods and microclusters deposited at 825 and 1015°C, respectively.

the vapor-liquid-solid (VLS) mechanism. Zn vapor is quickly produced by reaction between atomic hydrogen and the ZnO solid source. Then, Zn vapor diffuses towards lower temperature region (substrate surface). The Zn species condensate and then nucleate at short time forming Zn nanodroplets. The surface of the nanodroplets provides many sites for adsorption and hence Zn atoms easily grow onto these liquid structures forming Zn nanorods. The water vapor produced by reduction of the ZnO solid source (1) oxidizes the surface of the Zn nanorods. Figure 4(a) is a low magnification SEM image of the sample deposited at 1015°C which shows that the substrate is covered with irregular shaped microclusters. It is observed that a great number of these clusters coalesced forming bigger structures. Also, some of them have partly opened mouth. Figure 4(b) is a SEM image of a single microcluster with diameter around 50 micrometers. A hollow

FIGURE 3: SEM images of ZnO nanorods: (a) low magnification image and (b) high magnification image. ZnO nanorods with diameters around 100 nm can be observed.

FIGURE 4: SEM images of ZnO microclusters: (a) low magnification, (b) individual ZnO microcluster, and (c) high magnification of the ZnO microcluster.

core is observed on this cluster. The surface of it is rough and porous and in some areas the presence of a lot of small rod-like nanostructures is observed (Figure 4(c)).

The proposed growth mechanism of the microclusters obtained at 1015°C is proposed as follows: the generated Zn gas diffuses toward the substrate surface where it nucleates forming many small nanodroplets. Some of these droplets may coalesce at 1015°C producing bigger structures than

those formed at 825°C. The surface of the Zn droplets quickly oxidizes, resulting in core-shell Zn-ZnO clusters. In some cases the interior of the clusters overpressures and cracks the outer shell and leaves the Zn vapor from the droplet. Thus, the solid Zn spheres transform into ZnO hollow microclusters. The reevaporated Zn vapor condensates and oxidizes, forming epitaxial ZnO nanorods on the surface of the ZnO hollow microclusters.

4. Conclusions

In summary, the HFCVD technique has been employed to fabricate Zn-ZnO nanorods and microclusters by using a ZnO tablet as solid source and hydrogen molecules and atoms as reducing species. XRD spectra showed a mixture of Zn and ZnO phases. However, ZnO showed better crystallization characteristics than Zn. On the other hand, it was suggested that the formation of the Zn-ZnO nanorods and microclusters follows a VLS mechanism, which starts from condensed Zn nanodroplets.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

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