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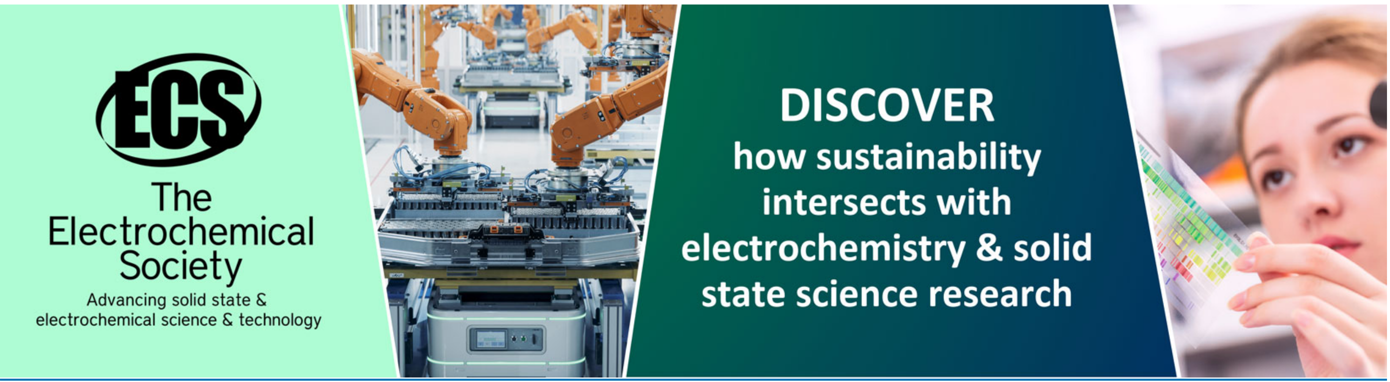

Low temperature growth of Zn-ZnO microspheres by atomic hydrogen assisted-HFCVD

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Abstract. Using ZnO pellets and molecular hydrogen as solid source and reactant gas respectively, Zn-ZnO microspheres were grown by hot filament chemical vapor deposition in low temperature growth regime. The presence of Zn-ZnO microspheres was confirmed by scanning electron microscopy (SEM) technique. It is suggested that microspheres formed in the gas phase by nucleation of Zn atoms. Energy dispersive spectroscopy (EDS) and X-ray diffraction (XRD) measurements suggest that microspheres were only superficially oxidized by water vapor species.

1. Introduction

Nowadays, various methods are commonly used for preparation of micro- and nanostructured materials because of their potential applications in electronics, optoelectronics, and chemical gas sensing [1-3]. Among them, chemical vapor deposition (CVD) technique with its experimental configurations such as metal-organic CVD, plasma-enhanced CVD, and low-pressure CVD, have been shown to be reliable methods in obtaining thin films, coatings, and recently nanostructures. Nevertheless, there are some CVD configurations such as hot-filament CVD (HFCVD) technique that have not been much explored. This technique shows some interesting characteristics such as low cost and easy scale-up for the growth over substrates with large areas. Zinc oxide (ZnO), an important wide band gap (3.37 eV) semiconductor, has the prospect of wide variety of applications in many fields due to its interesting optical and electronic properties. ZnO nanostructures with various morphologies, including nanowires, nanorods, and nanotubes, have been successfully fabricated by electrochemical methods, evaporation methods, among others. Recently, synthesis of ZnO hollow microspheres has attracted particular interest because of potential applications in many areas [4, 5]. For example, microspheres are suitable for medical applications since they can serve as small containers for encapsulation on drug delivery. In the present work, we report the formation of Zn-ZnO solid microspheres by the HFCVD technique in low temperature growth regime. It was observed that microspheres not directly growth on the substrate surface, which rules out the vapor-liquid-solid growth mechanism.

2. Experimental

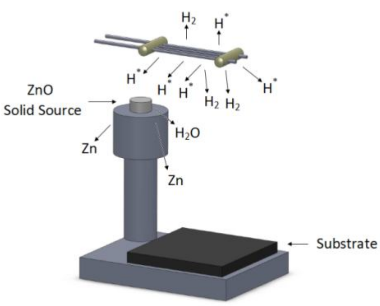
Zn-ZnO microspheres were synthesized by the HFCVD technique in low temperature range of 300-600 ^{0}C. The regime of low temperature for ZnO was determined by using the homologous temperature parameter T_h defined as follows:

$$T_h = \frac{T_p}{T_f}$$

where T_p and T_f are the substrate temperature and the melting point of the grown material respectively. The low temperature regime is considered if the T_h parameter is 0.3 and below. By considering that ZnO has a melting point of 1975 ^{0}C, the substrate temperatures were limited to 600 ^{0}C as the maximum value. Commercial ZnO powder (Mallinckrodt) was compressed to obtain ZnO pellets (0.3 g) which served as raw material. Molecular hydrogen (H_2) was employed as reactant gas. Polished p-type (100) oriented silicon wafers (area 4 cm^2) were used as substrates. The ZnO pellet was loaded into the center of the HFCVD reactor (diameter 60 mm, length 350 mm) and under of a tungsten filament. The scheme of the configuration of the filament, the ZnO pellet, and substrate is shown in figure 1(a). Using an AC voltage of 83.4 V, the filament was heated up to 2000 ^{0}C. The filament-substrate distances were fixed at 9.5, 7.5 and 5.5 mm on each experiment to reach during the process, maximum substrate temperatures of 300, 450, and 600 ^{0}C respectively. The heating rate of the substrate is shown in figure 1(b). The ZnO pellet was placed 2 mm away from the filament and kept at a temperature around 1500 ^{0}C. H_2 gas is introduced into reactor during the experiment and then is activated by contact with the hot filament. This generates a quantity of atomic hydrogen (H*) [6] atoms which are able to decompose the ZnO pellet, forming the gas precursors. After the end of the experiment, the HFCVD reactor was naturally cooled down to room temperature. The chemical reactions on the ZnO pellet and the substrate surface are proposed as follows:

$$ZnO_{(s)} + 2H^*_{(g)} \rightarrow Zn_{(g)} + H_2O_{(g)} \quad (1)$$
$$ZnO_{(s)} + H_{2(g)} \rightarrow Zn_{(g)} + H_2O_{(g)}$$
$$Zn_{(g)} + H_2O_{(g)} \rightarrow ZnO_{(s)} + H_{2(g)} \quad (2)$$

Therefore, Zn gas and water vapor precursors are quickly produced (equation (1)) and then, they diffuse to substrate surface where chemical reaction takes place (equation (2)). The XRD diffractograms were measured with a Bruker D8 Discover diffractometer using Cu Kα radiation (1.5418 Å).The morphology and the elemental analysis of the products were characterized using a scanning electron microscope Phillips XL-30.



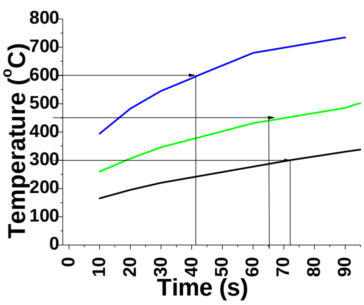


Figure 1. (a) schematic diagram of the Zn-ZnO microspheres growth zone; (b) heating rate of the substrate during deposition process from samples grown by HFCVD technique in low temperature regime.

3. Results and discussion

Figure 2 shows the XRD patterns of the products obtained by HFCVD technique in the temperature range of 300-600 °C. It is observed that a mixture of the Zn (04-0831 JCPDS Card Number) and ZnO (36-1451 JCPDS Card Number) phases in all samples is obtained independently of the substrate temperature. The strongest Zn peak at 2Θ=42.89 ° in the XRD pattern of the sample grown at 300 °C indicates a low contribution of ZnO crystals. The intensity of the Zn peaks decreases with further increase in the substrate temperature, suggesting that Zn crystals are gradually oxidized. The gradual oxidation of Zn has been ascribed to the increase in the surface mobility of Zn and oxygen atoms [7], which induces the nucleation and island growth of ZnO crystals.

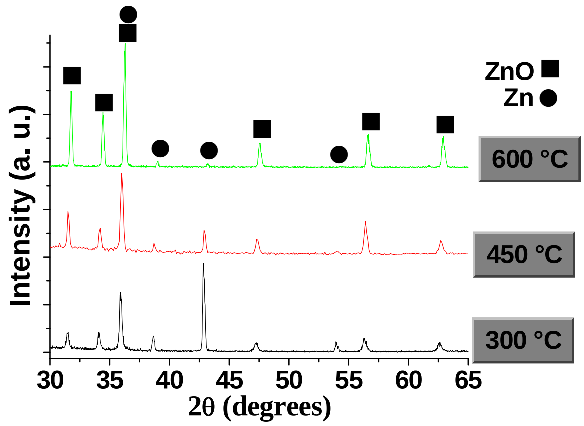


Figure 2. XRD spectra of products grown at 300, 450, and 600 ^{0}C by the HFCVD technique.

Figure 3 shows SEM micrographs of samples grown at 300, 450, and 600 ^{0}C by the HFCVD technique. It can be seen in Figure 3(a) that a little number of microspheres were formed at 300 °C. The microspheres can be observed on the surface of a layer with fibrous-like morphology, which is quite different from that of silicon substrate. The observation of two morphologies suggests different growth mechanisms. The formation of the fibrous layer is proposed as a result of surface reactions since this layer can be observed at the bottom of the image which shows the top-view of the sample. A similar morphology composed by Zn nanowires was previously observed [8], where the growth of such Zn nanowires was attributed to the so-called vapor-solid process. The presence of Zn and a weak oxygen signal in the EDS results measured from the fibrous layer (not shown here) indicates the formation of a superficially oxidized Zn fibrous layer. Moreover, the formation of Zn microspheres (see inset in Figure 3(a)) suggests that the material was liquid before solidification and that the condensation of these microspheres takes place before they reach the surface of the Zn fibrous layer [9]. Thus, it seems that the Zn microspheres condensed during the natural cooling of the HFCVD reactor as they are observed on the surface of the Zn fibrous layer, which grows during the experiment. Higher growth temperatures lead to an increase in the number of Zn microspheres (Figures 3(b) and 3(c)). EDS spectra (see insets in Figures 3(b) and 3(c)) suggest that the Zn microspheres have been partially oxidized into ZnO at 450 and 600 °C. This could be attributed to the higher number of oxidant species present in the gas phase during the natural cooling of the HFCVD reactor since the substrate surface is closer to the hot filament.

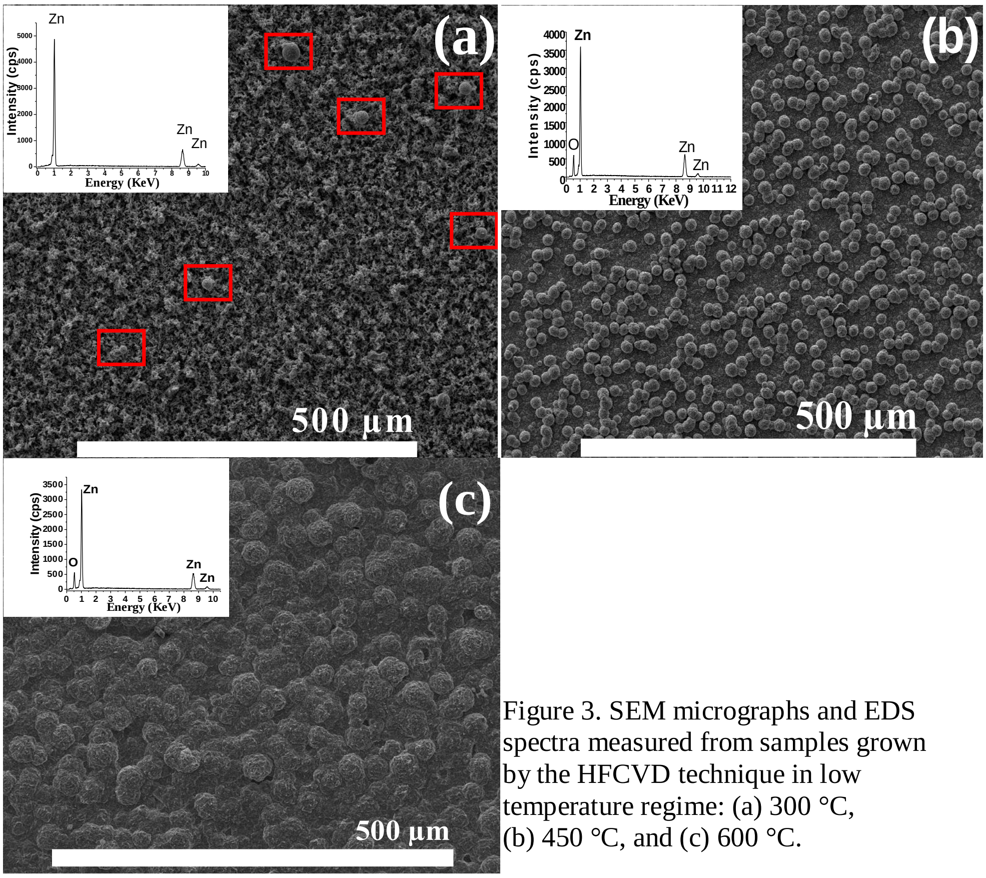


Figure 3. SEM micrographs and EDS spectra measured from samples grown by the HFCVD technique in low temperature regime: (a) 300 °C, (b) 450 °C, and (c) 600 °C.

4. Conclusions

Zn-ZnO microspheres were grown by HFCVD technique. XRD results showed a mixture of Zn and ZnO crystalline phases in all samples. The Zn crystals were gradually oxidized as the substrate temperature was increased. SEM and EDS results showed the formation of Zn microspheres at 300 ^{0}C and Zn-ZnO microspheres at 450 and 600 ^{0}C. We suggested a gas formation and subsequent condensation of Zn microspheres during the natural cooling of the HFCVD reactor as they were observed on the surface of a layer which was formed on the substrate surface during the experiment.

5. References

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