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Research Article

Structural Properties of Zn-ZnO Core-Shell Microspheres Grown by Hot-Filament CVD Technique

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We report the hot-filament chemical vapor deposition (HFCVD) growth of Zn-ZnO core-shell microspheres in the temperature range of 350–650°C only using ZnO pellets as raw material. The samples were characterized by scanning electron microscope (SEM), energy dispersive spectroscopy (EDS), and X-ray diffraction (XRD) techniques. SEM micrographs showed the presence of solid microspheres and a Zn-ZnO layer in all samples. The observed heterogeneous morphology on each sample suggested two different growth mechanisms. On the one hand, solid microspheres were formed by means of gas phase nucleation of Zn atoms. The Zn-ZnO layer was formed on the substrate as result of surface reactions. It is possible that Zn microspheres condensed during the natural cooling of the HFCVD reactor as they were observed on the Zn-ZnO layer.

1. Introduction

Over the last few years, nanotechnology has emerged as an important research field of materials science, since nanostructures exhibit superior physical properties compared to their counterpart bulk materials. Nowadays, nanotechnology has focused on the understanding of the physical properties of nanomaterials and their consequent applications. The controlled fabrication of functional nanostructured materials is an important objective of fundamental and applied research. In addition to nanostructures, spherical-like structures such as hollow microspheres and hemispheres have attracted great interest due to their particular properties such as low density and distinct optical properties. The microspheres are technologically very important among nanostructures because of their large surface-to-volume ratio which is useful in gas sensors and drug delivery [1, 2]. For many years, ZnO has been recognized as a promising material. It is a compound that shows unique physical properties for direct application in varistors [3], optical devices [4], gas sensors [5], and so forth. ZnO has been extensively used as a gas sensing material due to its high electron mobility and good chemical and thermal stability under the sensors operating conditions [6]. Therefore, the synthesis of ZnO microspheres can be an alternative to gas sensing applications due to the interesting properties that exhibit the ZnO material and the microsphere structures.

Lately, various techniques have been employed to synthesize nano- and microstructures; however, some of them are complex and considerably expensive. The HFCVD technique is a low cost method with interesting properties. This technique has been a common method in the growth of diamond films due to its simple design and easy scaleup to deposit materials on substrates with large areas. The production of nanoscale materials by the HFCVD technique has focused on the carbon nanotubes synthesis [7–10]. In fact, the HFCVD technique has usually been more efficient in fast synthesis of long carbon nanotubes than other complex CVD techniques such as plasma-enhanced CVD [11–13]. One remarkable characteristic of using the HFCVD technique in the growth

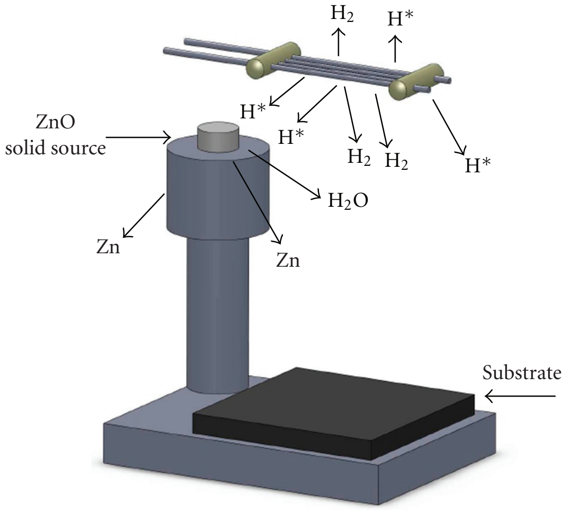


Figure 1: Schematic diagram of the experimental configuration of the filament, the ZnO pellet, and the substrate holder.

of diamond films and carbon nanotubes is that it uses atomic hydrogen as a volatile radical to generate gas-phase active species which, in large numbers, can lead into a possible increase in the growth rate. The above-mentioned advantages suggest this technique as an easy, reproducible, and low-cost alternative for the production of structures at the micro- or nanoscale. In the present work, Zn-ZnO microspheres were obtained by the HFCVD technique, but instead of using reactant gases, we used ZnO pellets as the only source in the formation of gas active species. We also used atomic hydrogen atoms in order to increase the decomposition rate of the ZnO pellet. We consider that this experimental setup can be a cheaper option to avoid the use of reactant gases that in some cases may be expensive.

2. Experimental Procedure

Zn-ZnO microstructures were synthesized in a home-made HFCVD system in the temperature range of 350–650°C. Commercial ZnO powder (Mallinckrodt) was compressed to obtain ZnO pellets (0.3 g), which served as raw material. Molecular H was used as reactant gas. P-type (100) oriented silicon wafers (area 4 cm^2) and resistivity $\rho = 1 - 3\,\Omega$-cm were used as substrates. The ZnO pellets were loaded into the center of the HFCVD reactor (diameter 60 mm, length 350 mm) and under of the tungsten filament. The scheme of the configuration of the filament, the ZnO pellets, and the substrate is shown in Figure 1. Using an AC voltage of 83.4 V, the filament was heated up to 2000°C and kept parallel to the substrate holder with a distance of 9, 7, and 5 mm on each experiment to reach substrate temperatures of 350, 500, and 650°C, respectively. The process time was 10 seconds in all samples. The ZnO pellets were placed 2 mm away from the filament and kept at a temperature of 1500°C. The filament and the ZnO pellet temperature zones were monitored by an infrared optical pyrometer. The substrate temperature was measured using a K-type thermocouple. During the microstructures formation, H_2 gas is introduced into the reactor, and it is then activated by contact with the hot filament. This generates a quantity of atomic H (H^*) [14], which is able to decompose the ZnO pellet into Zn gas and water vapor precursors that diffuse towards to the substrate where the reaction takes place.

After the end of the growth process, the HFCVD reactor was naturally cooled down to room temperature. The XRD diffractograms were measured with a Bruker D8 Discover diffractometer using Cu Kα radiation (1.5418 Å). The morphology and elemental analysis of the products were characterized using a scanning electron microscopy (SEM) Phillips XL-30.

3. Results and Discussion

3.1. SEM and EDS Measurements

3.1.1. Sample Grown at 350°C. Figure 2 shows the SEM images of the sample grown at 350°C by the HFCVD technique. We can see in Figure 2(a) a fibrous-like morphology with localized surface formation of dispersed micrometer clusters. High-magnification image (Figure 2(b)) clearly shows a heterogeneous morphology. Clusters located at the top of the structure show a sphere-like morphology. The surface under spheres presents a porous and nonuniform structure. The formation of spherical particles suggests that the material was liquid (droplet-like) before solidification. However, the growth process for this sample (350°C) was carried out at lower temperature than the melting point of Zn (419°C); therefore, the liquid assisted growth mechanism is ruled out since liquid droplets are not formed onto substrate surface at this temperature [15]. Thus, homogeneous nucleation of Zn during gas diffusion and its condensation is a strong argument to justify the obtained morphology. Besides, the formation of sphere particles seems to be independent from the substrate because the spheres were observed on the fibrous structure which grows onto the substrate surface, suggesting that they condensed during the natural coolingdown stage. Figure 2(c) shows that the spheres have a mean diameter around 10 micrometers. It can also be seen that they have an irregular surface. High magnification image (Figure 2(d)) shows that the fibrous morphology consists of entangled wire-like structures with irregular surface, and that they are connected with each other. The mean thickness of the wires was about 500 nanometers. Considering the one-dimensional vapor-solid (VS) growth of the wires [16] at 350°C, their irregular surfaces are ascribed to the formation of clusters that grow by nucleation of some species that do not reach the end of the wire because of their mobility drastically decreases with the natural cooling of the HFCVD reactor.

EDS spectrum of the microspheres (Figure 3(a)) shows only Zn signals, which may confirms the gas phase nucleation of Zn. In the case of the wires, EDS spectrum (Figure 3(b)) reveals the presence of Zn and a very little concentration of oxygen. This suggests that wires have Zn core with a thin ZnO

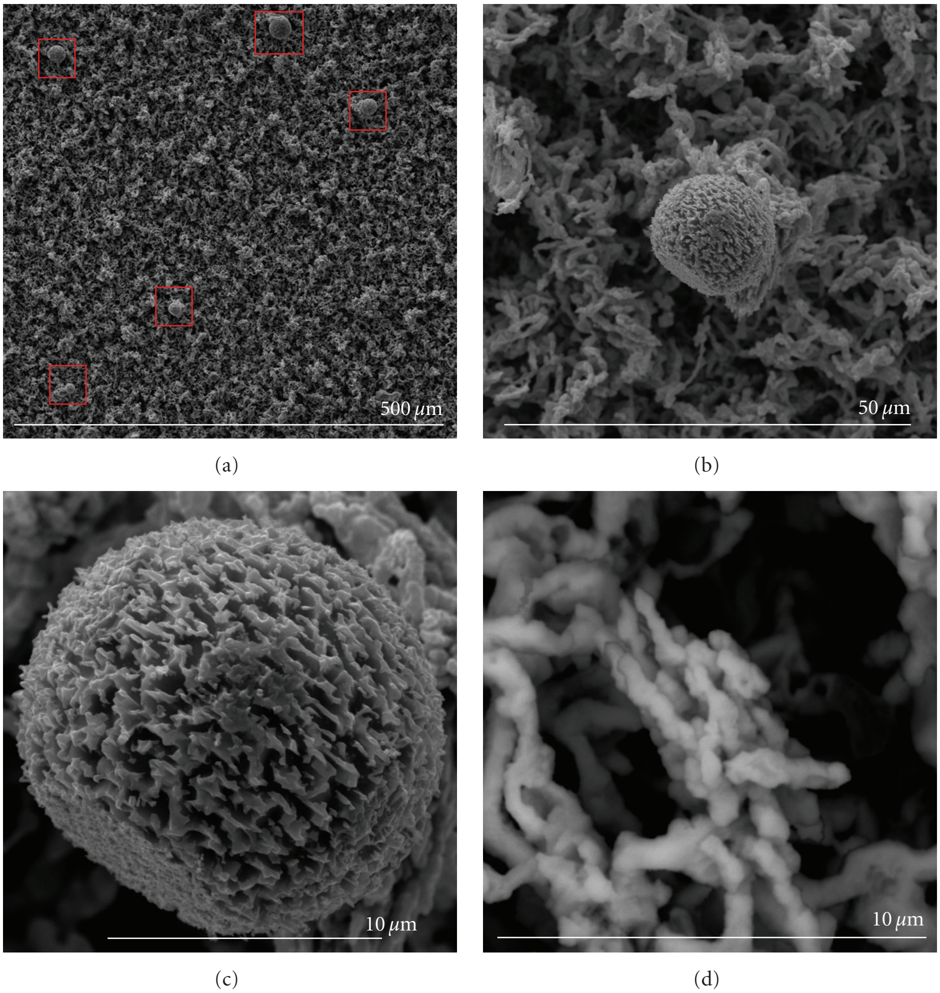


Figure 2: SEM micrographs of the sample grown at 350°C; the Zn microspheres on a Zn-ZnO layer composed by wire-like structures are observed in this figure.

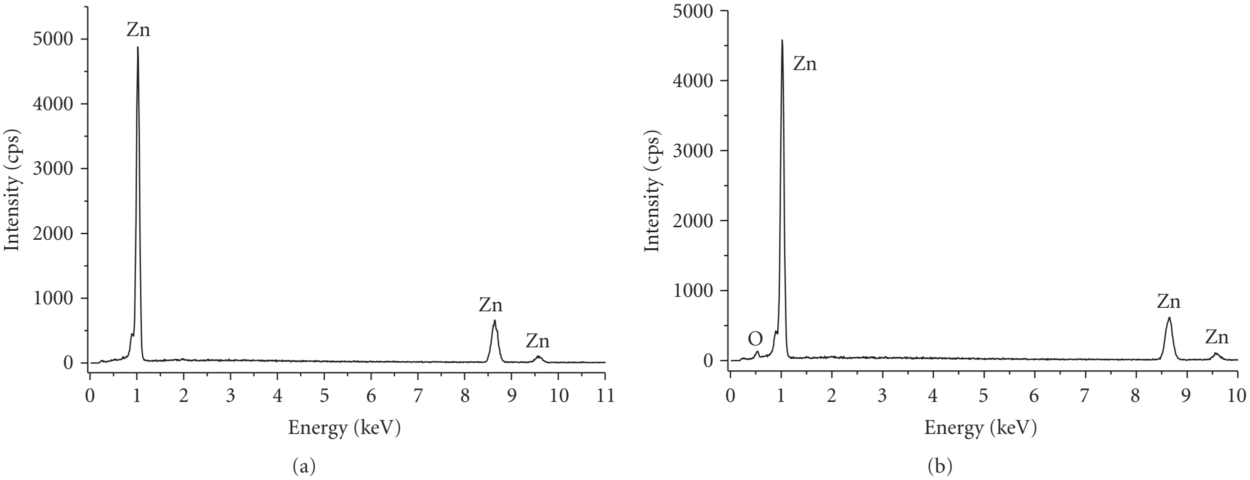
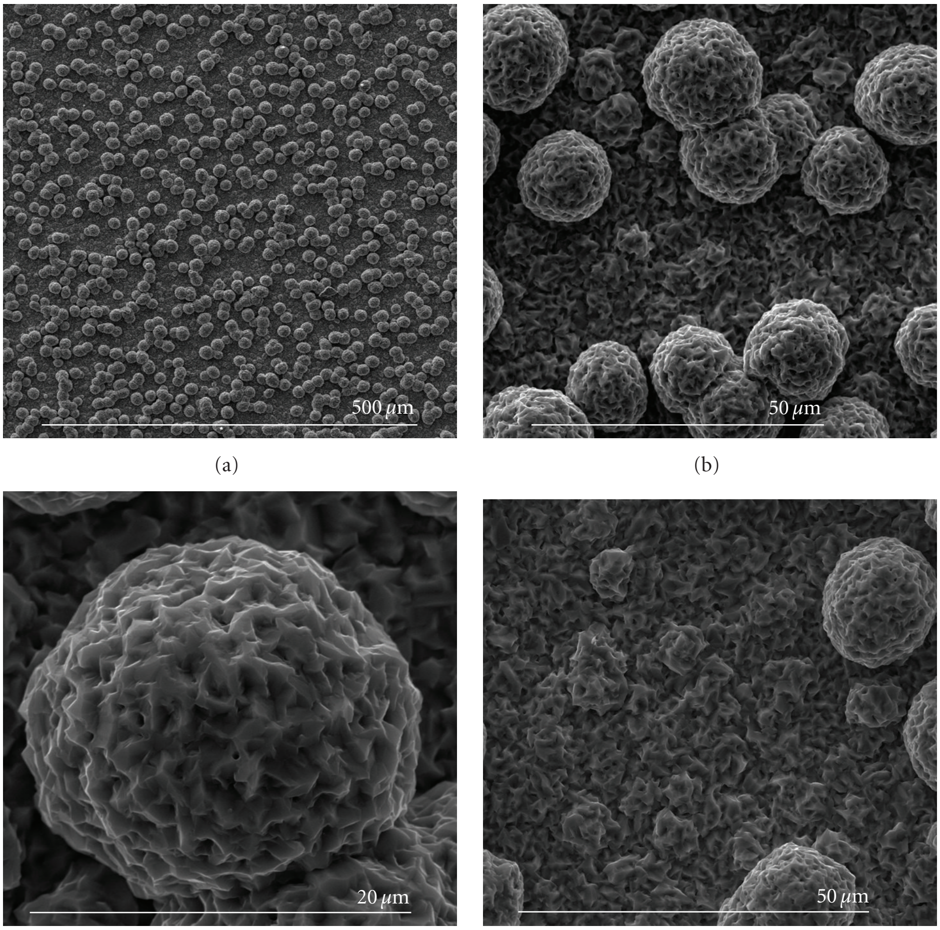
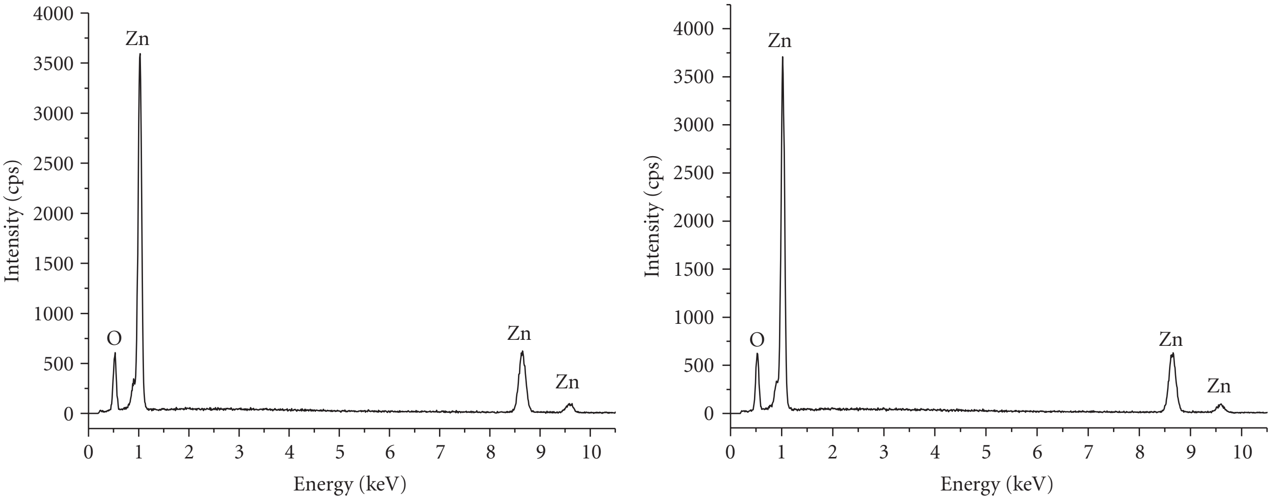


Figure 3: EDS spectra of sample grown at 350°C: (a) elemental analysis from a single microsphere and (b) from the wires.



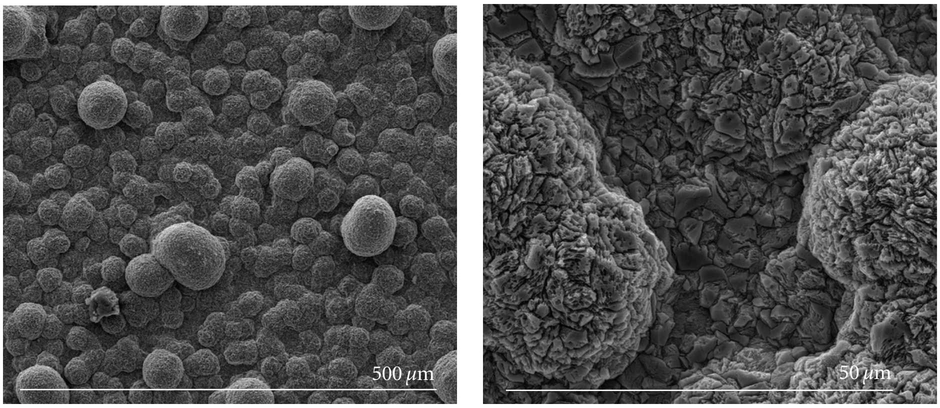
(a) (b) (c) (d)

Figure 4: SEM micrographs of the sample grown at 500°C; the Zn-ZnO microspheres on a compact layer are observed in this figure.



(a) (b)

Figure 5: EDS spectra of sample grown at 500°C: (a) elemental analysis from a single microsphere and (b) from layer under microspheres.



(a) (b)

Figure 6: SEM micrographs of sample grown at 650°C. The large number of microspheres covers the layer grown onto the substrate surface completely.

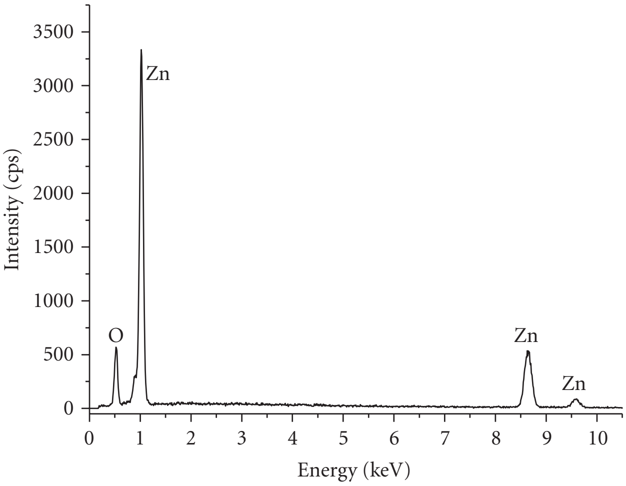


Figure 7: EDS spectra of sample grown at 650°C.

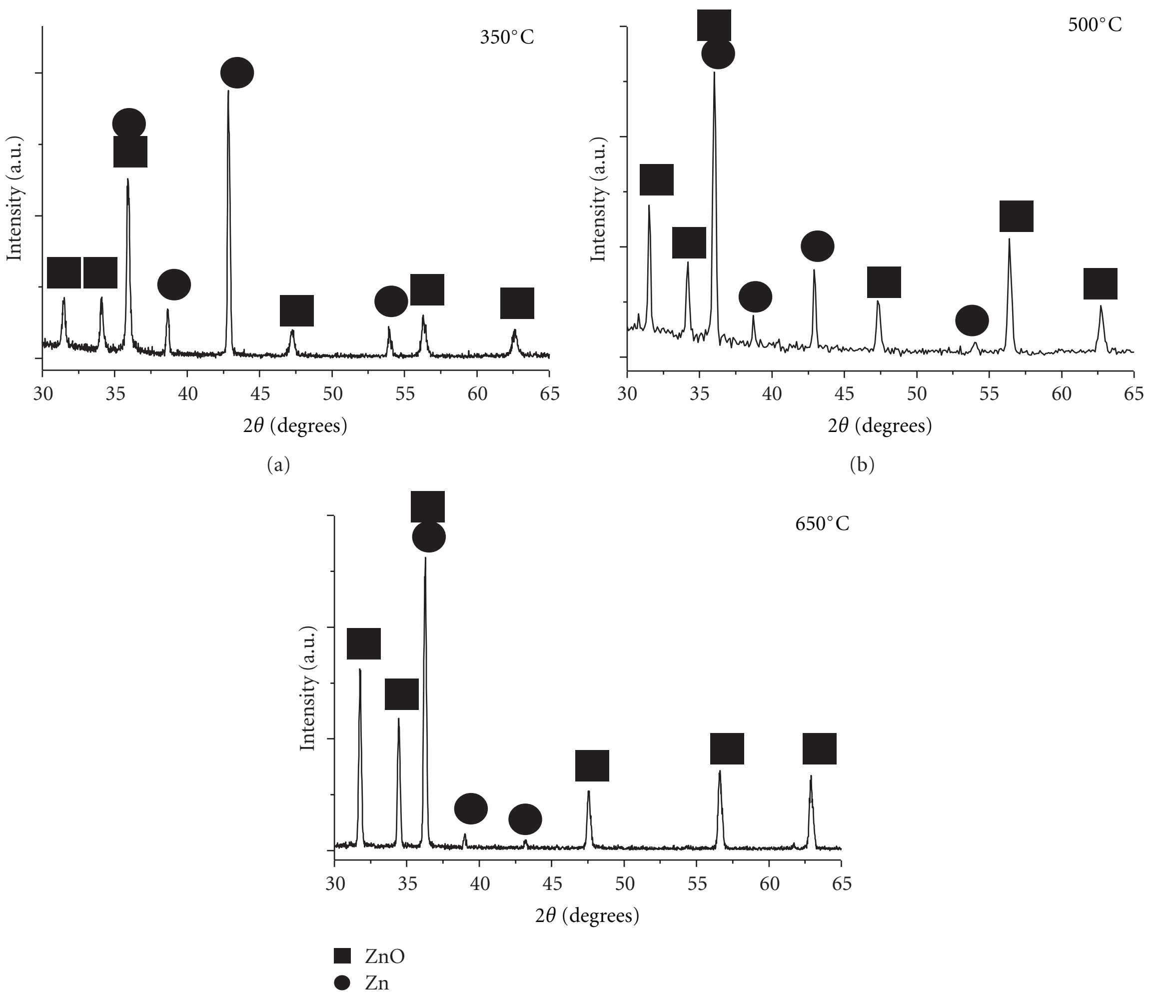
surface layer as was observed by some previous authors [17]. The wires are only partially oxidized due to its surface oxide layer that inhibits the oxidation of the bulk Zn by forming a protective layer, leading to a very slow oxidation.

3.1.2. Sample Grown at 500°C. SEM micrographs shown in Figure 4 illustrate the morphology of product grown at 500°C. Figure 4(a) shows the formation of a large number of microspheres distributed on a compact layer. The number of the microspheres is considerably higher than that for sample grown at 350°C. It is observed that surfaces of both microspheres and the compact layer are very similar and relatively rough (Figure 4(b)). Also, the microspheres have relatively uniform sizes with a mean diameter about 20 micrometers (Figure 4(c)), and some of them are self-assembled leading to spherical packing. The layer under microspheres (Figure 4(d)) exhibits a film-like structure, which is different than the wires formed at 350°C.

EDS analysis of the microspheres shows Zn and O peaks (Figure 5(a)). Although microspheres principally formed in the gas phase and condensed at the slow cooling-down stage at the end of the process, it is possible that some water vapor species oxidizes their surface because the substrate is closer from the hot filament. Therefore, a Zn microsphere with a ZnO shell can be obtained by increasing the substrate temperature at 500°C. EDS measurements of the compact layer formed under the microspheres (Figure 5(b)) show Zn and O peaks, indicating again that substrate surface reaction includes Zn layer formation and a postsurface oxidation process. Additionally, this result suggests that this compact layer is sufficiently thick to prevent the silicon substrate contribution.

3.1.3. Sample Grown at 650°C. Figure 6 shows SEM micrographs of the sample grown at 650°C. The obtained product exhibits a dense structure composed by solid microspheres (Figure 6(a)). The microspheres have uniform sizes of approximately 50 μm. This image shows no further layer under microspheres as seen for samples grown at 350 and 500°C. It could be suggested that the large number of condensed microspheres and its coalescence lead the microspheres to cover the layer grown onto the substrate completely. High magnification SEM image of the microspheres is shown in Figure 6(b). It is observed that the shape of some microspheres is lost by coalescence with the tendency to integrate to the under layer. EDS spectrum (Figure 7) of this sample shows Zn peaks with a low contribution of oxygen, which confirms the presence of a Zn-ZnO structure.

3.2. XRD Measurements. Figure 8 shows the XRD spectra of the microspheres grown at 350, 500, and 650°C by the HFCVD technique. The observed diffraction peaks in all recorded XRD patterns are in agreement with the



(a)

(b)

(c)

Figure 8: XRD spectra of samples grown at 350, 500, and 650°C by the HFCVD technique.

JCPDS 00-035-1451 and 00-004-0831 cards corresponding to ZnO and Zn hexagonal crystal structures, respectively. No peaks of any other phase were detected; this rules out the possibility of sample contamination by the tungsten filament. The presence of ZnO and Zn phases in all XRD spectra corroborates the fact that both microspheres and the layer that grow on the substrate are only superficially oxidized independently from the substrate temperature. It is observed that peak at 43.10° corresponding to Zn (101) plane in the XRD diffractogram of sample grown at 350°C is the strongest. We suggest that the main contribution of Zn crystals on this sample comes from the bulk Zn of the wires due to the low number of Zn microspheres placed at the top of the structure. At higher substrate temperatures, the intensity ratio of the Zn peaks to the ZnO peaks decreases, suggesting a better oxidation characteristic. It is known that in Zn-ZnO structures, the bulk oxidation is controlled by the outdiffusion of Zn through the surface ZnO layer [18, 19]. Thus, the increase of the substrate temperature enhances the mobility of Zn, leading to the outdiffusion of these atoms across of the thin ZnO layer from the microspheres and from the layer under microspheres. This results in bigger Zn-ZnO microspheres as a result of this physical mechanism.

4. Conclusion

Zn microspheres and Zn-ZnO core-shell microspheres were obtained in the temperature range of 350–650°C by HFCVD technique. The Zn microspheres were observed on a Zn-ZnO surface layer, which is formed on the silicon substrate surface during the experimental process. XRD and EDS results suggested that all grown Zn microspheres are only partially oxidized independently of the substrate temperature. We suggest that the Zn-ZnO microspheres condensed during the natural cooling of the HFCVD reactor, and they are not formed as a result of the vapor-liquid-solid growth mechanism. The formation of Zn-ZnO microspheres by the HFCVD technique could be an easy and low cost way to produce these structures at the large scale.

Acknowledgments

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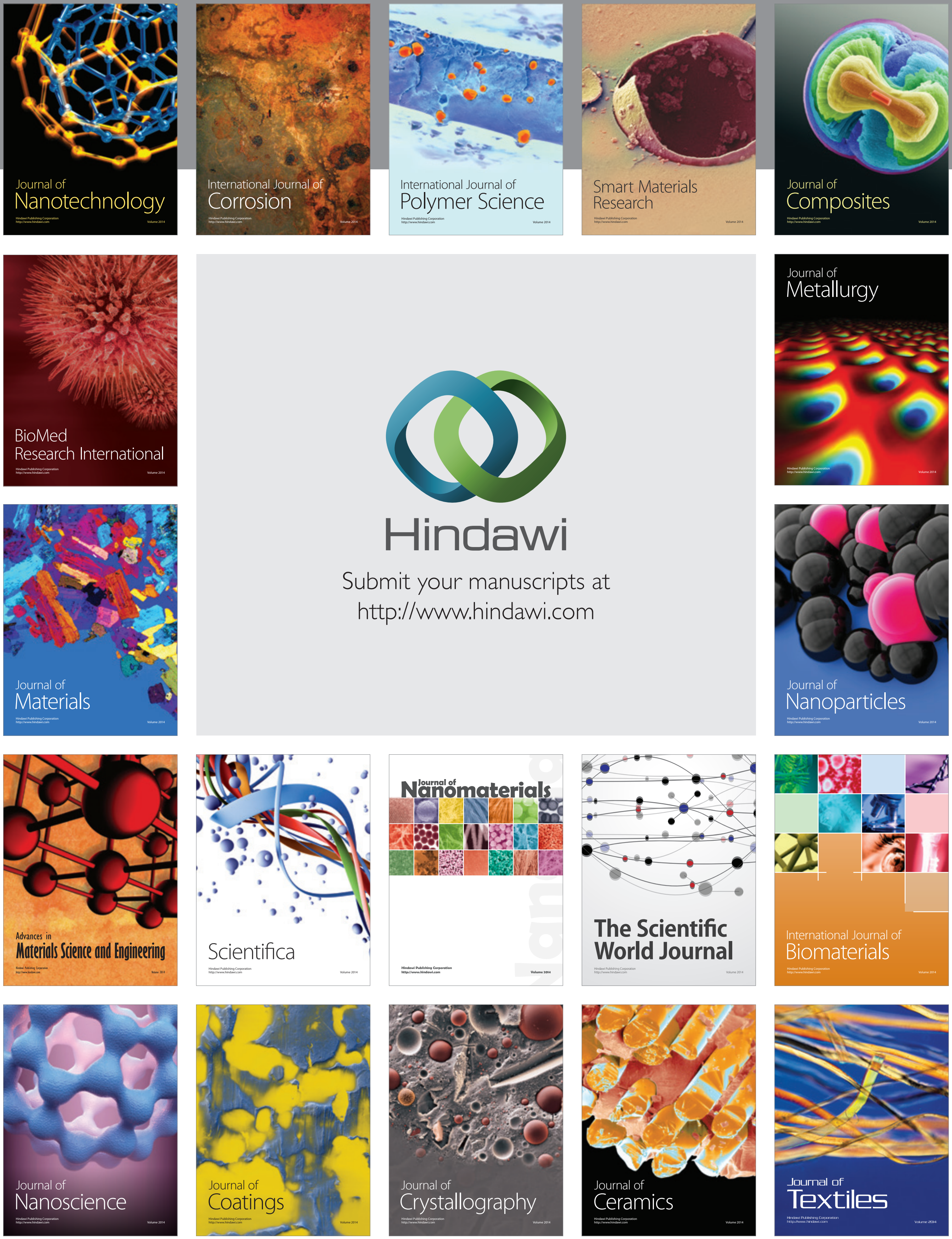

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