

MORPHOLOGICAL CHANGES IN VAPOR GROWN Zn AND ZnO NANO- AND MICROSTRUCTURES

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Abstract

Zn-based crystalline nano- and micromaterials were synthesized by the pyrolytic technology at 410°C. The powders of ammonium chloride, ZnO and Zn served as source materials. At first, while the Si substrate temperature was rising up to 410°C, the ZnO microcrystals were produced by the interaction of ZnCl₂ vapor with water molecules. After the consumption of ammonium chloride and the formation of an oxygen deficient environment, the metallic Zn was providing the Zn vapor to the substrate. The hexagonal ZnO microcrystals with prismatic habit were produced, together with hexagonal crystalline Zn platelets. Finally, when the metallic Zn in the source was also completely consumed, the hollow ZnO microspheres were formed.

Introduction

As it is well known, the properties of nanomaterials strongly depend on their morphology [1 – 3]. The new shape of nanomaterials can give rise to some new properties, thus increasing their functionality. In some cases, the morphological changes may also alter even their toxicity and biocompatibility [4].

ZnO is a well-studied semiconductor, which attracts great attention because of its unique properties, including a wide direct band-gap, piezoelectric and lasing ability, high thermal and chemical stability. Besides, ZnO is an environmentally friendly material, because it has low toxicity and high biocompatibility [5 – 8]. ZnO has an inherent ability to form nanomaterials with a variety of morphologies. The number of shapes that can get ZnO nanomaterials is compatible with the well-established large number of morphologies that can take the carbon-based nanostructures.

Recently, we have developed the new pyrolytic technology for the vapor growth of nanomaterials. The novelty of this technology is based on the application of gaseous products formed after thermal decomposition of ammonium chloride (NH₄Cl). Work aims to synthesize the Zn-based nano- and micromaterials using this technology and to study their morphology.

Experimental

The developed technology was described in our previous work [9]. Here, we will briefly consider some of its details.

The nanomaterials were produced in the vertical quartz reactor, heated by an external furnace up to 550°C. The mixture of NH₄Cl, ZnO and Zn powders was done on its bottom. The Si substrate was located at 2 cm distance from the source powders and was heated by the convective flow. NH₄Cl decomposed beginning from 195°C, forming gaseous HCl and ammonia [10]. Starting from 260°C the chemically aggressive hydrogen chloride reacted with ZnO producing volatile ZnCl₂ and water molecules, which served as oxidizing species.

During the first growth stage, which lasted 40 min, the substrate temperature was gradually increased up to 410°C and then stabilized. During this time the ammonium chloride in the source was completely consumed. Until NH₄Cl was completely depleted, the ZnO crystals were produced on the Si substrate due to the gas-phase reaction between ZnCl₂ and H₂O, or residual oxygen. In the second growth stage the Zn powder in the source was the only Zn supplier to the substrate and the residual oxygen molecules were the only oxidizing species in the reactor. In these oxygen-deficient conditions the Zn rich material was growing on the substrate. In approximately 30 min the Zn powder in the source was also depleted and the process was transformed in to the annealing of grown product in the residual oxygen. This third growth stage lasted for 20 min. All three growth stages were performed in one closed technological cycle without interruption of the process.

The morphology and composition of synthesized material was analyzed using the SEM (Scanning Electron Microscope) Tescan Vega-3 XMU equipped with EDS (Energy Dispersive Spectroscopy) and PCL (Panchromatic CathodoLuminescence) imaging methods. The structure was studied by XRD (X-Ray Diffraction) method on Rigaku SmartLab-10 instrument.

Results and discussion

As outlined in the previous section, in the first growth stage, the water vapor and residual oxygen served as oxidizing species for ZnCl₂ vapor. The former is thermodynamically favorable at temperatures below 270°C, and the latter – below 470°C. According to [11], 91.3% of the chemical reaction between ZnCl₂ and oxygen occurs in the gas environment and then adsorbs on the substrate. Zn atoms can be produced at the substrate also by the interaction of Si with ZnCl₂, yielding Zn and highly volatile SiCl₄. This reaction may proceed spontaneously, as it has a negative Gibbs energy ranging from –37 kJ/mol at 300°C to –21 kJ/mol at 410°C. The produced Zn may be oxidized, forming ZnO.

Figure 1a shows the SEM image of the synthesized ZnO granular layer. The sizes of crystals vary in a wide range and the size of the longest one was 5 μm. As is known, ZnO has a direct band-gap and high luminescence ability. **Figure 1b** represents the PCL image of the same region. All crystals that are shown in **Figure 1a** are luminescent, indicating the formation of microcrystals with the same composition and structure. XRD pattern in **Figure 1c**, also confirmed the synthesis of hexagonal ZnO microcrystals.

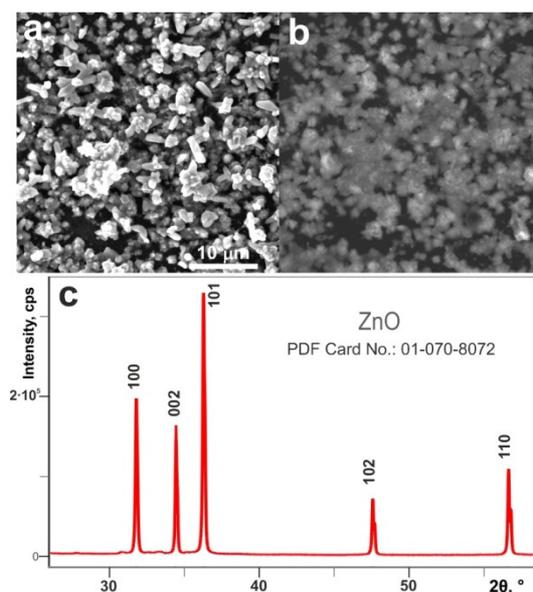


Figure 1. ZnO nanocrystals produced in first growth stage (a), corresponding PCL image (b) and XRD pattern of same granular layer (c).

It should be mentioned that the seeding of ZnO crystals on a solid surface from the vapor is quite difficult due to thermodynamic restrictions and it is common practice to form the initial ZnO seeds on a substrate [12]. No seeding layer was used in our technology. A high nucleation rate of ZnO crystals can be explained by the initial treatment of a substrate in HCl vapor during the growth and by the formation of Zn atoms on the Si surface, which are ideal sites for the nucleation of ZnO vapor [13]. In the second growth stage, the metallic Zn powder served as a source of Zn vapor. In this stage, the ammonium chloride was consumed and hence the oxidizing water molecule concentration was low.

The crystalline Zn and ZnO both have hexagonal structures. However, there is a great difference in the surface properties of their facets. The Zn terminated basal (0001) facet of ZnO has the highest surface energy and chemical activity [13]. ZnO crystals usually grow along c-axis, which is perpendicular to Zn (0001) surface. In contrast to this, the {0001} facets of metallic Zn have a lowest surface energy. They are chemically inert, more stable, and resistive to oxidation [14]. Accordingly, the metallic Zn nano- and microcrystals naturally grow laterally by expanding their chemically active $\{10\bar{1}0\}$ or $\{11\bar{2}0\}$ facets and forming plate-like layers.

Figure 2 represents images of material formed on Si substrate in the second growth stage. In the oxygen-deficient atmosphere, the spherical particles were produced with maximum sizes reaching tens of μm . The spheres were growing on the granular ZnO layer, which was produced in the first growth stage. The detailed analysis revealed that the spheres had a layered structure. The thicknesses of layers vary in the range of 100 – 200 nm. They were composed of Zn plates with embedded ZnO nanocrystals having the same lateral sizes. The enlarged view of a stack of such layers with spherical shapes is shown in **Figure 2b**. It should be emphasized that according to the phase diagram of Zn–ZnO system [14], the solubility of oxygen in Zn is very low. Accordingly, in the oxygen-enriched Zn layer at a substrate temperature of 410°C (which is close to the Zn melting point), the spontaneous segregation of Zn and ZnO phases is expected. The XRD pattern confirmed the presence of both Zn and ZnO phases (**Figure 2c**). The growth of pure Zn and ZnO nanocrystals was observed on the surfaces of spheres.

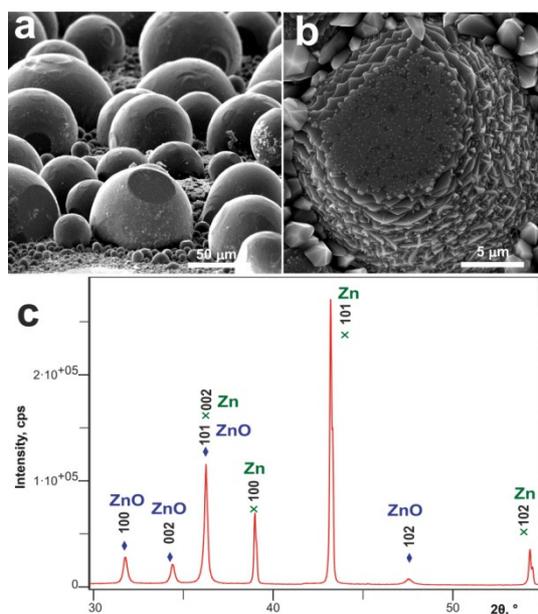


Figure 2. SEM images of layered microspheres produced in second growth stage (a and b) and XRD pattern of grown microspheres (c).

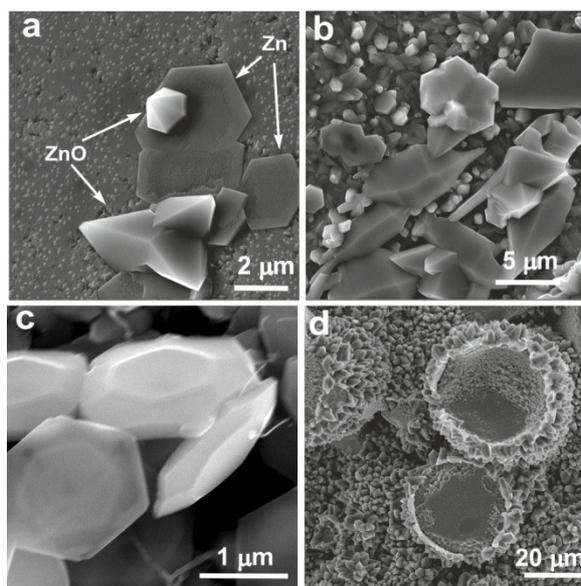


Figure 3. Zn and ZnO microcrystals synthesized in second stage (a and b), ZnO hexagonal microdiscs formed in same stage (c) and hollow microsphere produced by ZnO microcrystals in third stage (d).

ZnO and Zn crystals, that were growing on the layer of Zn with embedded ZnO nanocrystals, are shown in **Figure 3a**. They both have a hexagonal base. However, the lower crystal has a distorted hexagonal prism appearance, while the upper forms a regular shape. The prismatic habit indicates that the growth of ZnO was kinetically controlled and it was growing along the *c*-axis. In contrast to this, the Zn crystals had the shape of hexagonal planes. They were growing laterally and some of them merged during the in-plane growth. The pores and steps with smooth surfaces on Zn hexagon surfaces indicate that, at this temperature, Zn

evaporates from the plates. Some morphologies of ZnO microcrystals, which are grown on the granular ZnO layer, are shown in **Figures 3b** and **3d**. They include distorted hexagonal prisms and hexagonal discs with a thickness of ~ 500 nm. One of the interesting morphologies that were formed in the third growth stage is represented in **Figure 3d**. The hollow microspheres, with shells consisting of ZnO nanocrystals, were produced from layered spheres. The third growth stage was simple annealing of previously grown material in the residual oxygen-containing environment. At 410°C the vapor pressure of Zn is high reaching 0.12 Torr. This caused the out-diffusion of Zn from the core of the sphere to its surface, where it was oxidized producing ZnO nanocrystals. Gradually, the dense shell of ZnO nanocrystals was produced, which hermetically encapsulated the core. With time, the internal pressure of Zn vapor increased and, at a certain critical pressure, the shell exploded, producing the hollow microsphere.

Conclusions

The Zn and ZnO-based micromaterials were produced by the pyrolytic technology using NH_4Cl , ZnO and Zn powders as sources. The interaction of gaseous products formed after decomposition of NH_4Cl , with ZnO caused the synthesis of volatile ZnCl_2 and H_2O . The developed technology had three stages. In the first stage, the sources and substrate were heated up to 550 and 410°C respectively, during the first 40 min. Also, approximately at that time, the NH_4Cl powder was consumed and the following second stage proceeded in the oxygen-deficient environment in the presence of Zn vapor produced due to the evaporation of Zn source. The third stage was an annealing of produced material in the same oxygen-deficient ambient.

The layer of granular ZnO with sizes up to $5\ \mu\text{m}$ was formed in the first stage.

In the second stage, the layered microspheres were synthesized. The layers comprised $100 - 200$ nm thick merged Zn plates with embedded ZnO nanocrystals. The microsphere was a stack of these layers. On the surfaces of these spheres, the hexagonal ZnO microcrystals were growing, together with hexagonal Zn microplates.

At the end of the third stage, the hollow microspheres were produced from the microspheres. They were synthesized by the transformation of Zn-rich microspheres. The formation mechanism included Zn outdiffusion from the core, growth of ZnO crystalline shell around the Zn-rich spherical core, and its hermetic encapsulation. These processes were followed by the explosion of a core due to the increased Zn vapor internal pressure and formation of hollow ZnO microspheres.

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