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ZnO Nanorods Array Synthesized by Chemical Bath Deposition: Effect of Seed Layer Sol Concentration

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Abstract

One-dimensional Zinc oxide is among the most promising nanostructures due to their exceptional properties in wide range of applications such as electronic, optoelectronic, electrochemical, and electromechanical devices. The ZnO nanorods are synthesized by the means of chemical bath deposition. Among all of the parameters affecting chemical bath deposition method, the seed layer properties are vitally important to control the structural, morphological, and optical features of the ZnO nanorods. In this study the effect of seed layer sol concentration is investigated. Zinc acetate dihydrate (ZAD) as precursor, triethylamine as an additive, and 1-propanol as an alcoholic solvent are used to provide the sol to synthesize the seed layers. X-ray diffraction patterns show that all the ZnO seed layers and nanorods have hexagonal wurtzite structure. The preferred orientation along (002) polar surface is enhanced by increasing the ZAD concentration. Field emission scanning electron microscope images show that the morphological properties of ZnO nanorods are strongly dependent on the seed layer sol concentration. As the ZAD concentration increases, the alignment of ZnO nanorods is enhanced. Furthermore, the diffuse reflectance spectroscopy analysis shows that the transmittance of nanorods is decreased by increasing the density of the ZnO nanorods.

Keywords: ZnO nanorods; Chemical bath deposition; Seed layers; Sol concentration.

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1. Introduction

One dimensional nanostructures such as rods, wires, and needles are among the most promising nanostructures for wide range of applications in electronic, optoelectronic, electrochemical, and electromechanical devices due to their unique features, Xia et al. (2003). Zinc oxide (ZnO) is one of the most applicable material due to its outstanding properties such as wide direct bandgap (3.37 eV), large exciton binding energy (60 meV) at room temperature, Özgür et al. (2005), and high electron mobility (100 cm²V⁻¹s⁻¹) (Könenkamp et al. 2002). In addition, the low symmetry of the wurtzite structure in ZnO caused piezoelectric properties, Wang (2008). ZnO semiconductor nanorods are the key parts of many applications including solar cells, Tian et al. (2014), photocatalytic properties, Zhang et al. 2014, ultraviolet photodetectors, Keem et al. (2004), sensors, Wan et al. (2004), and Schottky diodes, Park et al. (2003) due to their special structural, morphological, electrical, and optical properties.

There are several methods to synthesize ZnO nanorods such as vapor-liquid-solid, Klimovskaya et al. (1996) and vapor-solid, Yamai and Saito (1978) mechanisms, laser ablation-catalytic growth, Duan and Lieber (2000), metal organic chemical vapor deposition, Yazawa et al. (1992), pulsed laser deposition, Guo et al. (2001), hydrothermal, Wu et al. (2008), and chemical bath deposition (CBD) method, Tian et al. (2003), Xu and Wang (2011). Recently, CBD method has been largely used because it does not need high temperature or vacuum system. Moreover, it is cost-effective and can provide different morphologies and hence different properties in ZnO nanostructures. There are several parameters including solution and process parameters, which affect the properties of ZnO nanorods synthesized by CBD method. Type of precursor, type of additives, and type of solvent, time and temperature of CBD, and type of substrate are some of the important parameters of CBD method.

Type of substrate is one of the most important parameters, which has exceptional influence on the properties of ZnO nanorods. Deposition of seed layer on the bare substrate before CBD process is inevitable because it decreases the activation energy of ZnO nanorods growth and lattice mismatch between substrate and nanorods. Guillemin et al. proved that the structural morphology of the seed layer plays a significant role on the structural properties of ZnO nanowires, Guillemin et al. (2012). In addition, it is concluded that presence of the seed layer is crucial for the formation of well aligned ZnO nanorods, Kenanakis et al. (2009). The relationship between seed layer properties and the growth rate of ZnO nanorods is also shown, Song and Lim (2006).

There are several methods such as sol-gel to synthesize ZnO seed layer. In this paper, seed layers were deposited in sols with different precursor concentration and the influence of seed sol concentration on structural, morphological, and optical properties of ZnO nanorods has been investigated by means of X-ray diffraction (XRD), field emission scanning electron microscope (FESEM), and diffuse reflectance spectroscopy (DRS).

2. Experimental

2.1. Sol formation and seed layer preparation

The thin seed layers of ZnO were deposited on soda lime glass substrate by means of sol-gel method followed by dip-coating process. Zinc acetate dihydrate (Zn(CH₃COO)₂·2H₂O – ZAD) as precursor, triethylamine (N(CH₂CH₃)₃ – TeA) as additive and stabilizing agent, and 1-propanol (nPrOH) as an alcoholic solvent are used to synthesize the seed layers. All the reagents were purchased from Merck KGaA and utilized without further purification. ZAD was dissolved in 1-PrOH by means of magnetic stirrer for 30 min at room temperature. TeA was added to the sol with TeA/ZAD mole ratio equal to one. The soda lime glass substrates were pre-cleaned with deionized water and ethanol. The dip coating process was carried out with withdrawal speed of 120 mm/min. All the films were dried after each dip coating process at 300 °C for 10 min. Ten layers were deposited on each substrate to achieve the desired thickness. Finally, all the films were calcined at 500 °C for 1 h. Since the effect of seed layer sol concentration on the properties of ZnO nanorods is desired, ZAD concentration of 0.1, 0.2, and 0.4 M are considered.
2.2. Formation of ZnO nanorods

CBD method was used to synthesize ZnO nanorods. ZAD as precursor, hexamethylenetetramine (C₆H₁₂N₄ - HMT) as complexing agent and pH buffer, and deionized water as solvent are blended to achieve the solution. All the reagents were purchased from Merck KGaA and utilized without further purification. 0.02 M of ZAD and 0.02 M of HMT were dissolved separately in deionized water and then mixed together. This solution was placed in a bath at 90 °C and seeded substrates were placed into the bath for 4 h. After CBD process, substrates were rinsed with deionized water and dried at 90 °C in ambient atmosphere. Finally all substrates were annealed at 500 °C for 1 h.

2.3. Characterization methods

X-ray diffraction method (XRD, Rigacu Ultima IV diffractometer with Cu Kα radiation, λ= 1.5418 Å) was used to investigate the structural properties of ZnO seed layers and ZnO nanorods. Mira 3-XMU field emission scanning electron microscope (FESEM) was applied to study the influence of seed sol concentration on morphological properties of ZnO nanorods and Avaspec-2048TEC equipped by Avalamp-DHS was used for diffuse reflectance spectroscopy (DRS) in order to investigate the optical properties of ZnO nanorods on different seed layers.

3. Results and Discussion

3.1. Relationship between structural properties of seed sol concentration and nanorods

The XRD patterns of the ZnO seed layers prepared with 0.1, 0.2, and 0.4 M sol concentration and the corresponding nanorod arrays are shown in Figure 1a and 1b, respectively. XRD patterns of all ZnO seed layers and ZnO nanorods show formation of hexagonal wurtzite structure (JCPDS No. 36-1451). Fig. 1a shows all the ZnO thin films are oriented along c-axis. In addition, the relationship between ZAD concentration in sol and the crystallographic properties of ZnO seed layers is clarified by these XRD patterns. It is revealed that the intensity of (002) polar surface is enhanced by increasing the ZAD concentration from 0.1 M to 0.4 M, which is attributed to a couple of reasons. As it is posited by the Landau–Levich model (equation 1), the viscosity (η) of the sol is increased by increasing ZAD concentration and the thickness of the thin films is increased by increasing the viscosity of the sol (Table 1).

\[
h = 0.94 \frac{(\eta u)^{2/3}}{\gamma^{1/2}(\rho g)^{1/2}}
\]  

(1)

where \( \gamma \), \( \eta \), \( \rho \), \( g \) and \( u \) are the surface tension, the viscosity, the density of the fluid, the acceleration of gravity, and the withdrawal speed, respectively, Kuznetsov and Xiong (2002).

The second reason is based on the reactions occur in sol preparation and calcination steps which expound that the amount of ZnO in final ZnO thin films is enhanced by increasing ZAD concentration. By comparing the scales in figure 1a and 1b, the correlation between ZnO seed layers and ZnO nanorods is deduced. Great difference between ZnO nanoparticles and ZnO nanorods is obvious in these XRD patterns. All ZnO nanorods are much more intensive along c-axis in comparison with ZnO seed layers, which is based on three crucial reasons. At first, these patterns prove that growth and alignment of ZnO nanorods are along [001] direction. In addition, it can be concluded that the length of nanorods have an important impact on the structural properties of ZnO nanostructures. Besides, figure 1b presents in order to show the effect of seed sol concentration on the structural properties of ZnO nanorods. It is just confirmed in the figure 1a that the intensity of (002) polar surface is enhanced by increasing ZAD concentration in sol, which means more (002) planes are available. Thus, there are more nucleation sites for ZnO nanorods to form and growth. Therefore, the intensity of (002) plane in ZnO nanorod patterns is enhanced by increasing ZAD concentration.
3.2. The influence of seed sol concentration on the morphological properties of ZnO nanorods

The FESEM images of ZnO seed layers and ZnO nanorods are presented in Fig. 2. As it is shown in figure 2a, 2b, and 2c all ZnO seed layers contain spherical nanoparticles and the mean grain size of ZnO nanoparticles is increased by increasing ZAD concentration in sol, which is attributed to Van der Waals forces in sol preparation step. Based on the Van der Waals forces, attractive forces between particles are enhanced by decreasing distances between particles or complexes; hence the size of colloids is increased in sol, resulting larger nanoparticles (Table 1).

Table 1. Seed layer thickness, NPs diameter on seed layer, and NRs length for various sol concentrations

<table>
<thead>
<tr>
<th>ZAD Concentration (M)</th>
<th>Seed Layer Thickness (nm)</th>
<th>NPs Diameter (nm)</th>
<th>NRs Length (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>100</td>
<td>30</td>
<td>700</td>
</tr>
<tr>
<td>0.2</td>
<td>250</td>
<td>40</td>
<td>800</td>
</tr>
<tr>
<td>0.4</td>
<td>700</td>
<td>90</td>
<td>1000</td>
</tr>
</tbody>
</table>
Figure 2d, 2e, and 2f reveal the close relationship between ZnO seed layers and ZnO nanorods. The length of ZnO nanorods is enhanced by increasing size of ZnO nanoparticles. These FESEM images confirm the conclusions from XRD patterns. As it is shown in XRD patterns of ZnO nanorods, one of the reasons explaining the enhancement of (002) polar surface by increasing seed layer sol concentration is the lengthening of nanorods. There are differences between diameters of nanoparticles and nanorods which prove the lateral growth along a-axis in addition to growth along c-axis in CBD process. However, the diameter of nanorods would not change significantly by changing ZAD concentration, which is attributed to HMT. HMT is a non-ionic and heterocyclic compound, McPeak et al. (2011) which plays three important roles. It is pH buffer and complexing agent. Furthermore, HMT is caped to non-polar facets of wurtzite structure and prevents its lateral growth along a-axis, Strano et al. (2014). Thus, anisotropic growth along [001] direction is induced by the use of HMT as an additive in CBD process.

3.3. Optical Properties of ZnO nanorods and the effect of seed sol concentration

The DRS curves of ZnO nanorod arrays with various sol concentrations are shown in Figure 3. All the ZnO nanorods have approximately the same bandgap. The absorption edge of all ZnO nanorods is about $\lambda=390$ nm which is equivalent to $E_g\sim 3.2$ eV. The DRS patterns also show the light trapping process, which occurs in visible region as the transmittance decreases by increasing the wavelength of spectra. The close relationship between morphological and optical properties of ZnO nanorods is deduced by comparing these patterns and the FESEM images. It can be concluded that the transmittance of this nanostructure is decreased by increasing the density of ZnO nanorods. For instance, the density of ZnO nanorods grown on the 0.4 M ZAD seed layer is more than that of other samples. Thus, the transmittance of this sample is less than that of other films.
4. Conclusions

The influence of seed sol concentration on the structural, morphological, and optical properties of ZnO nanorods has been investigated. The intensity of (002) polar surface is enhanced as a result of several reasons by increasing seed sol concentration from sol contains 0.1 M ZAD to 0.4 M ZAD. It is also shown that the morphology of ZnO nanorods strongly depends on the seed layer properties such as its grain size. Finally, it is shown that the bandgap of ZnO nanorods does not change significantly by increasing seed sol concentration. However, the transmittance and light trapping of ZnO nanorods have close relationship to seed layer properties. For instance, the density of ZnO nanorods is changed by changing seed sol concentration and it affects the optical properties of nanorods.

References


