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GROWTH MECHNISM OF ZnO NANO-STRUCTURE USING CHEMICAL BATH DEPOSITION

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Uniformly distributed ZnO nanorods with diameter 80 nm-1200 μm and several micrometers long have been successfully grown at low temperatures on different substrates by using chemical bath deposition. The size of the ZnO nanorods can be controlled on the different substrates by tuning growth parameters. The mechanism of the nanorod growth on the different substrates is proposed. The effect of substrate on the ZnO nanorods morphology was also investigated. the morphology of the ZnO nanorods changed from rods to wire or pie. By investigation on growth characteristics of ZnO on the different substrate, these kinds of structure are useful in laser and solar cell application

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1. Introduction

Znic oxide (ZnO) is a very important II-VI semiconductor material with a direct bandgap of 3.37eV at room temperature and a large exciton binding energy of 60meV [1]. ZnO increasingly attracted attention due to its excellent chemical stability, non-toxicity, good electrical, optical and piezoelectric property. Since the properties of ZnO strongly depend on its morphology and microstructure, it is essential to precisely control the size, shape and microstructure of ZnO for its application as optoelectronic materials used in solar cells [2], photocatalysis [3], and light emitting diodes, gas sensors. For these applications, it is essential to have a thorough understanding of the growth mechanism and morphology controlling of ZnO nano-structures fabricated by chemical bath deposition techniques.

Chemical bath deposition (CBD) is extremely attractive due to its advantageous features over other thin film deposition techniques, such as its simple, low temperature, low cost, low evaporation temperature and easy coating of large surfaces.[4] Lin *et al*. investigated that ZnO nanorod arrays were effectively selective-grown on a p-type GaN:Mg layer through CBD at a low temperature hydrothermal synthesis (85 degrees) with a ZnO seed layer.[5] Hari *et al*. reported that properties of ZnO nanorods grown on indium tin oxide coated glass substrates by heating an equimolar solution of zinc (II) nitrate and hexamethylenetetramine solution.[6] Well-aligned ZnO nanorod arrays with different sizes in diameter were fabricated on Si substrates by two-step chemical bath deposition method CBD, and The effects of substrate pre-treatments, pH, angel between substrate and beaker bottom and growth time on the structure of ZNAs were investigated in detail.[7] Obviously, the size of ZnO nanorods play important role in optimizing the optical prosperties ZnO nanorod array films.

In this paper, ZnO nanorods films were prepared by chemical bath deposition. Effect of the concentration of Zn^{2+} on the morphology prosperties of ZnO nanorods films were investigated

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by SEM. A sol-gel method was applied to deposite ZnO film on the glass substrate as a seed layer to deposition at the low temperature of 90℃. The morphology of characteristics of the as-grown ZnO nanorods were studied in detail. The mechanisms of the forming of ZnO nanorods were further analyzed.

2. Experiments

All reagents were used as received. Commercial glass (16mm×76mm) were thoroughly cleaned by detergent solution, acetone, ethanol washed, and deionized water. The glass substrates were first immersed in a 3mol/L sodium hydroxide solution for 3h, and then washed by deionized water (DI), followed by ultrasonicating for 15 min, after that they were immersed in the mixed solution of hydrogen peroxide and concentrated sulfuric acid (1:3) for 10h, washed by deionized water and ultrasonicating again, then dried in air. Before doing the experiment, the glasses were kept in a $SnCl_2$/HCl mixed solution for at least 1h in order to show hydrophilic properties. 0.03M $Zn\left(CH_3COO\right)_2 \cdot 2H_2O$ and 0.03M methenamine ($C_6H_{12}N_4$) were mixed together. The pretreated glass substrates were immersed into the aqueous solution for 2h at a required temperature (90℃), The glass substrates were removed from the beaker after reaction, and washed in running tap water, and then dried in air before characterization or the next step deposition. ZnO nanorods were also grown on glass slide via a two-step process. In the first step, a thin seed layer was prepared on glass substrate by sol-gel technology. The samples were further deposited by chemical bath deposited. After deposition, the substrates were taken out of the bath, rinsed with deionized water, dried in air and preserved in an airtight plastic container. Scanning electron microscopy (SEM, JSM-5600) was used to characterize the morphology of the films.

3. Results and discussion

First, we consider the growth mechanism of ZnO nanorods thin film by CBD. The following chemical equations are involved in the reaction process.

$$(CH_2)_6N_4 + 6H_2O \rightarrow 6HCHO + 4NH_3 \tag{1}$$

$$NH_3 + H_2O \rightarrow NH_4^+ + OH^- \tag{2}$$

$$Zn^{2+} + 2OH^- \rightarrow ZnO(nuclei) + H_2O \tag{3}$$

$$Zn^{2+} + 4OH^- \rightarrow Zn(OH)_4^{2-} \tag{4}$$

$$Zn(OH)_4^{2-} \longrightarrow ZnO + H_2O + 2OH^- \tag{5}$$

As the decomposition of zinc acetate dihydrate and hexamethylenetetramine at elavated temperature, the concentration of Zn^{2+} and OH^- increases correspondingly (equ. 1and 2) [10,11]. When the $Zn^{2+,}$ OH- and $Zn(OH)_4{}^{2-}$ concentration reaches a supersaturated degree, it leads to the rapid nucleation of ZnO (equ.3) and forming of ZnO nanostructures (equ.4 and 5) in the reactive solution with an appropriate temperature[12]. In the process of the formation of ZnO nanorods, the ZnO crystalline grains were formed as the nuclei for the growth of ZnO nanorods. The size of ZnO nanorods can be mainly dependent on the size of crystalline grains unclei, which can result in the nanorods with different diameters. As for the growth direction of ZnO nanorods, the nanorods grew preferentially along [0001] directions due to the high surface energy of (0001) facets.

Here, we simple the process of preparing ZnO nanorods film, directly grow the nanorods on the glass substrate by CBD method. Fig. 1 shows SEM images of ZnO thin films deposited on glass substrate by chemical bath deposition methods. As can be seen from the figure, the ZnO nanorods are disorderly, and have a wide size distribution. It can be convinced that some defects can be formed in ZnO nanorods due to disengaged growth on the solution. First, the formation of nanorods in solution, and then absorbed at surface of the glass slide substrate. Polycrystalline glass cannot provide the nucleation of ZnO and influence nanorods growth, which leads to disordered growth of nanorods.

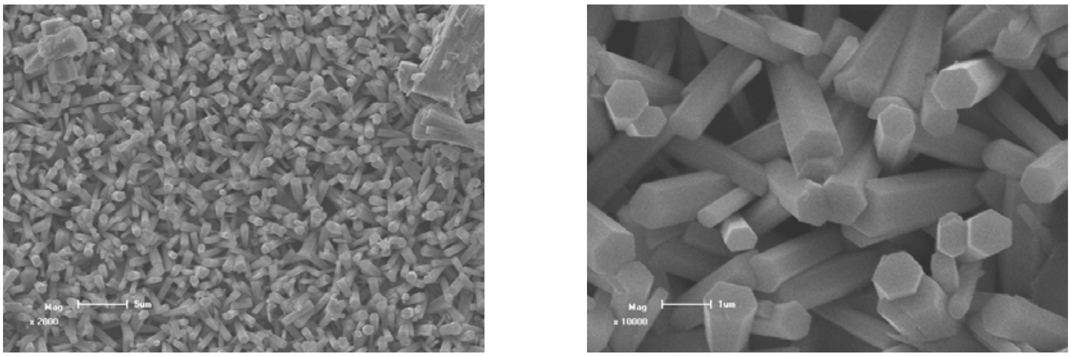
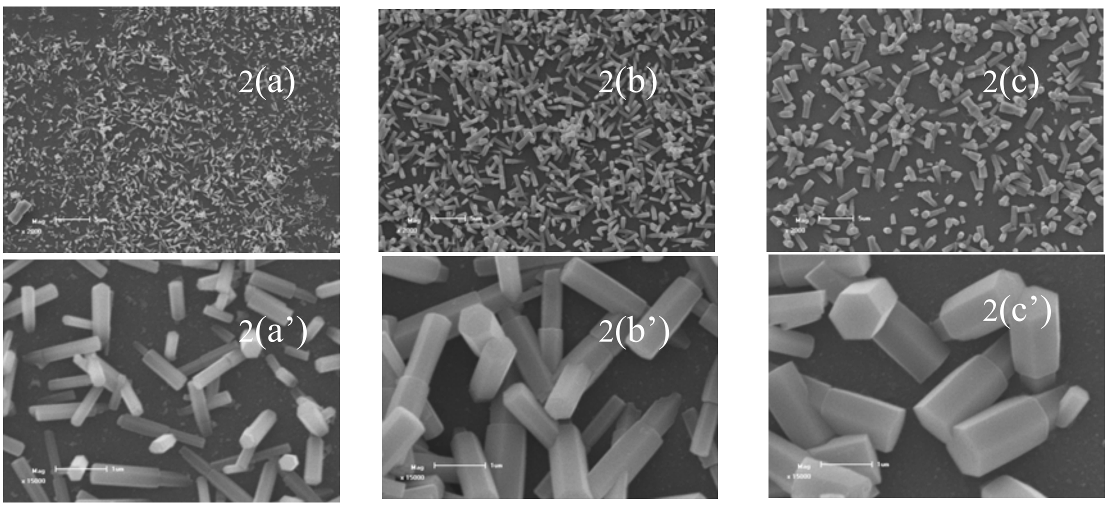


Fig. 1 SEM images of as-prepared ZnO nanorods grew on glass substrate by chemical bath deposition methods.

The growth parameters and ions concentration play a critical role for tuning the morphology of ZnO nanostructures grown during CBD process. In investigation the effect of Zn^{2+} concentration on samples were prepared with different zinc acetate dihydrate molar ratio in the solution. Fig. 2 shows the evolution of the ZnO nano-structure as a function of Zn^{2+} concentration, and kept the other experiment condition constant. The results of SEM observation shows that the diameter and length increase with Zn^{2+} concentration increasing. It can clearly seen that the density of ZnO nanorods decrease with the increasing of Zn^{2+} ion concentration. All of ZnO nanorods have hexagon cross section. As the Zn^{2+} concentration is high, a lot of ZnO nuclei are generated and grow into closely packed ZnO nanorods. The length and diameter increase with the reaction time increasing of ZnO nanorods. The size of nanorods can be readily controlled by tuning the Zn ions concentration and growth time. It can be noted that the size and density of ZnO nanorods increased with the increasing of the Zn ions, which proved that the size of ZnO nanorod can be tuned by changing the rate of ions released in the solution, and the average size distribution was further improved. One can see that the density of ZnO crystallites decrease, while the size increase with decreasing of Zn ion concentration in the solution. The experiment results showed largely random and with relatively poor reproducibility. This implied that ZnO nuclei were formed in the solution, and ZnO nanorods mainly formed in the solution, then were adsorbed or deposited to the glass substrate.



0.02mol/L 0.03mol/L 0.04mol/L

Fig. 2. SEM images of as-prepared ZnO nanorods grew on glass substrate with different solution concentration.2(a)and 2(a')0.02mol/L ; 2(b)and 2(b')0.03mol/L; 2(c)and 3(c')0.04mol/L.

The investigation shows that the size, density, and preferred orientations of ZnO nanorods can be controlled using the two steps process by the CBD method. In order to understand the effect of substrate on the growth mechanism of ZnO nanorods, ZnO films were prepared by composing the sol-gel and chemical bath deposition. Fig. 2 shows the typical SEM images of the uniformly distributed and compact ZnO nanorods arrays synthesized by two steps method. The arrays of nanorods exhibit an improved arrangement and high orientation perpendicular to the substrates. The average diameters and length of nanorods by two steps method is much smaller than that of the thin films by directly chemical bath deposition, which makes it possible to produce high quality ZnO nanorods thin films. ZnO nanorods grow on the seed layer, as the growth continues, ZnO nanorods grow is almost with the same speed, this can not guarantee that each nanorod is perpendicular to the substrate. Nanorods squeezed each other and grow along the direction perpendicular to the substrate because of space limitations. As can be seen from the figure, the twins nanorods was formed.

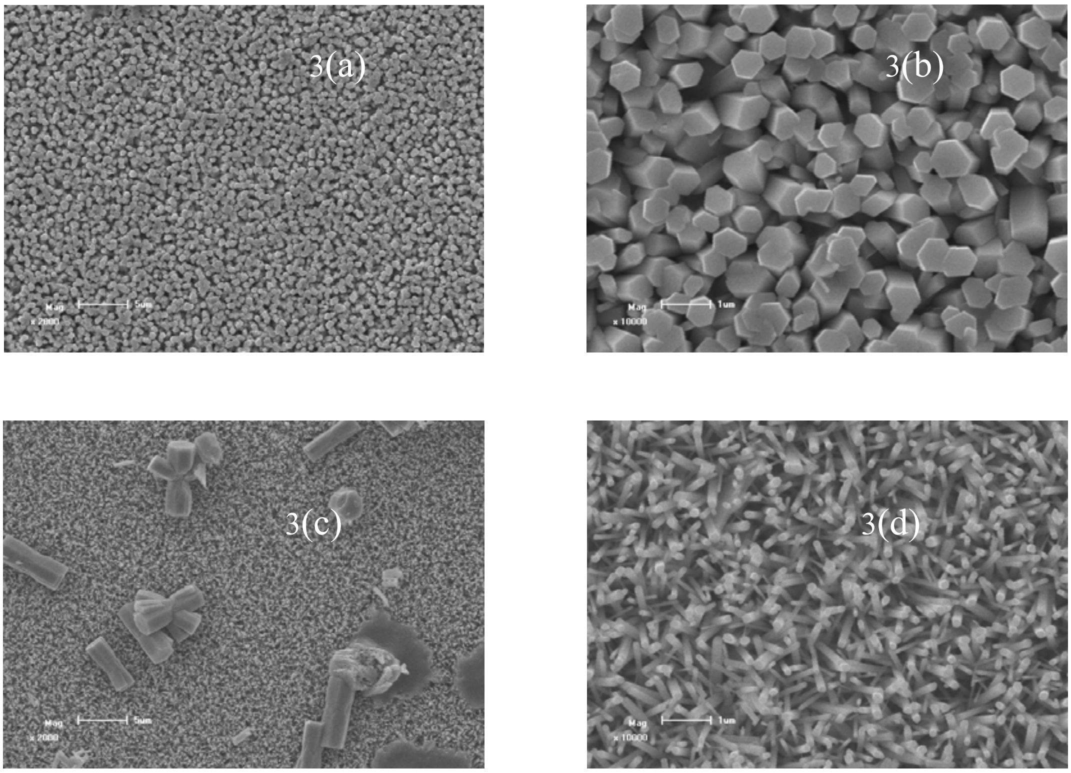


Fig. 3 SEM images of as-prepared ZnO nanorods grew on glass substrate using the two-step method with different diping times (a) and (b) 3 times; (c) and(d) 1h

The more diping membrane times are, the more thick seed layer is, the greater ZnO nano-crystalline grain size is formed after annealing. Pre-preparing ZnO thin film served as seeds layer oriented along the c-axis. At high diping times, large size ZnO seeds were formed. The density of ZnO nanorods can be estimated according to the top-view images shown in Figs. 3(a) and 4(c). It was about 180 and 130 nanowhiskers/μm^2 with a concentration of 0.025, 0.05 and 0.1 M, respectively. In other words, a pre-existing ZnO seed layer improved the growth of ZnO whiskers along the c-axis; weak solution is beneficial for obtaining individual, smaller-diameter and high-density ZnO nanowhiskers without the dense middle layer.

4. Conclusions

In summary, uniformly distributed ZnO nanorods with diameter 80nm-1200 µm and several micro meters long have been successfully grown at low temperatures by using chemical bath deposition. The mechanism of the nanorod growth on the different substrates is proposed. The effect of substrate on the ZnO nanorods morphology was also investigated. the morphology of the ZnO nanorods changed from rods to wire or pie. In addition, the growth mechanism of the ZnO nanorods had also been discussed. Zn^{2+} ion concentration play a key role during the process of regulating the growth rate and forming the ZnO nanorods semiconductor films by CBD.

Acknowledgments

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