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Journal of Solid State Chemistry 177 (2004) 3830–3834
JOURNAL OF SOLID STATE CHEMISTRY
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Preparation, structure and ultraviolet photoluminescence of ZnO films by a novel chemical method

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Received 21 June 2004; accepted 22 July 2004
Available online 27 August 2004

Abstract

A novel and simple chemical method was developed for the deposition of ZnO films from aqueous solution, integrating the merits of successive ionic layer adsorption and reaction with the chemical bath deposition technology. By this new method, dense and continuous ZnO thin films with good crystallinity can be prepared in a very short time, e.g., in about 20 min. Results show that as-deposited ZnO films on glass and Si (1 0 0) exhibit hexagonal wurtzite crystalline structure and the preferential orientation along (0 0 2) plane. With a dense and continuous appearance, the film is composed of ZnO particles in even size of 200–300 nm. The strong and sharp emission at 391 nm and several weak emissions at the wavelength band of 440–500 nm indicate the high optical quality and the stoichiometrical nature of obtained film. Mechanism analysis shows that the reaction duration in hot water and the drying process are vital important factors affecting the deposition process and the crystallization behavior of the film prepared via the aqueous solution route.
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Keywords: ZnO film; Chemical syntheses; Microstructure; Photoluminescence

1. Introduction

As an important II–VI group semiconductor with versatile properties, ZnO possesses wide applications in various fields such as transducers, gas sensors, transparent conduction electrodes, and surface acoustic wave devices etc. [1–3]. Especially, the recent successful demonstrations of ZnO film and nanowire array film with excellent ultraviolet (UV) photoluminescence [4–6], the realization of p-type ZnO film and p–n junction [7–9], and their great potential applications in such optoelectronic devices as UV light detectors, UV light-emitting diodes, and semiconductor lasers [4–6,10,11], have greatly stimulated the research interests on the photoelectric properties of ZnO film.

Many methods can be used to prepare ZnO films, including sputter [12], pulse laser ablation [13], chemical vapor deposition [14], sol–gel [15], chemical bath deposition (CBD) [16], and successive ionic layer adsorption and reaction (SILAR) [17]. Compared with the technologically demanding vapor deposition techniques, the deposition of ZnO film from aqueous solution represents a simple and effective route. In addition, the solution route is also suitable to prepare the stoichimetrical ZnO film because of its oxygen-rich deposition environment, which will help to suppress the deep-level defects in ZnO and enhance the UV photoluminescence.

Among various technologies preparing ZnO film via solution route, CBD and SILAR are two commonly adopted methods. In CBD method, the film is deposited on substrate through the controlled precipitation of objective material, i.e., the heterogeneous precipitation. However, because all the precursors are present in one reaction vessel, the bulk precipitation in the precursor

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0022-4596/$ - see front matter © 2004 Elsevier Inc. All rights reserved.
doi:10.1016/j.jssc.2004.07.030

solution (i.e., the homogeneous precipitation) is inevitable, which makes it very difficult to control the deposition process precisely and to obtain high quality films. In SILAR method, a thin layer of precursor ions is adsorbed on the substrate first, and the solid film is formed via the chemical reaction between adsorbed ions and precursor ions with opposite charge. The features of SILAR include the layer-by-layer growing mode and the separate precursor of anionic and cationic solutions, which makes the control over the deposition process fairly convenient. However, the very slow growth rate and the great difficulties involved in the deposition of oxide films have greatly limited its application [18]. Therefore, it is meaningful to develop novel solution techniques for the deposition of high quality semiconductor films in higher growth rate.

In a previous study, we have reported the synthesis of porous ZnO film by a modified SILAR method [19]. However, we found that the same procedure is not effective to create a dense and continuous ZnO film, e.g., by simply increasing the deposition cycles or the concentration of precursors. To further extend the SILAR method to the preparation of dense and continuous ZnO films, which possess much more important optical and electric properties than porous films, we have explored the underlying deposition mechanism of ZnO particles on substrate, and developed a simple and novel method to prepare dense and continuous ZnO films based on the heterogeneous precipitation principle in solution. Compared with the previous method, the newly developed method is characterized by the much higher deposition rate, the dense and continuous feature of the obtained film, and most important, the essentially different deposition mechanism. In this paper, the specific formation mechanism of the new method for the growth of ZnO films with dense and continuous structure was presented. Results on structure, morphology analysis and photoluminescence properties at room temperature were provided.

2. Experimental details

2.1. Film preparation

Aqueous zinc-ammonia complex ions ($[Zn(NH_3)_4]^{2+}$) were chosen as the cation precursor, in which analytical reagents of $ZnSO_4$ (99.7%) and concentrated ammonia (25–28%) were used. The concentration of zinc solution is 0.1 mol/L and the molar ratio of $Zn:NH_3$ is 1:10 based on our optimal results. Normal microscope slides with the dimension of $75 \times 25 \times 1$ mm and Si (1 0 0) were chosen as substrates. While for Si (1 0 0) substrate, no etching in fluorhydric acid was applied to reserve the oxide layer on the substrate surface, the slide glass substrate was boiled in dilute sulfuric acid (1:10 by volume) for 30 min first. And then, both Si (1 0 0) and glass substrate were rinsed in ethanol, acetone and deionized water subsequently. After above rinsing procedures, both glass and Si substrates would exhibit good hydrophilic property, which is vital important to obtain a uniform ZnO film throughout the substrate. Double distilled water (resistivity $\sim 18\,M\Omega\,cm$) was used throughout the experiment.

Fig. 1 illustrates the experimental scheme of the proposed method for the deposition of ZnO film on substrate. Four successive steps comprise a full deposition cycle, i.e., the immersion of substrate in the precursor solution for 15 s to cover a thin liquid film containing $[Zn(NH_3)_4]^{2+}$ on the substrate, the instant immersion of withdrawn substrates in hot water (95 °C) for 7 s to form a solid ZnO layer, the drying process of substrate in air for 30 s, and the ultrasonic rinsing of substrate in a separate beaker to remove larger and loosely bonded ZnO particles. After four to five deposition cycles, a dense and lustrous ZnO layer can be visibly detected. In this experiment, totally ten deposition cycles were deposited prior to the film characterization.

The above-mentioned procedure for the deposition of ZnO film is distinguished from the previously reported method [19] by three aspects. First, the substrate was immersed in the hot water for reaction immediately after it was removed from the precursor solution. It means that the decomposition of the precursor complex in the thin liquid film adsorbed on the substrate occurs in the hot water, which make it feasible to control the precipitation process of $Zn(OH)_2$. While in the previous method, the precipitation of $Zn(OH)_2$ was formed in the standstill process before the reaction step in hot water. Second, the reaction duration in hot water was precisely controlled to avoid the homogeneous precipitation of $Zn(OH)_2$ as far as possible. Third, the ultrasonic irradiation was performed after the drying process of substrate instead of before the reaction in hot water. So the function of ultrasonic rinsing in this experiment is

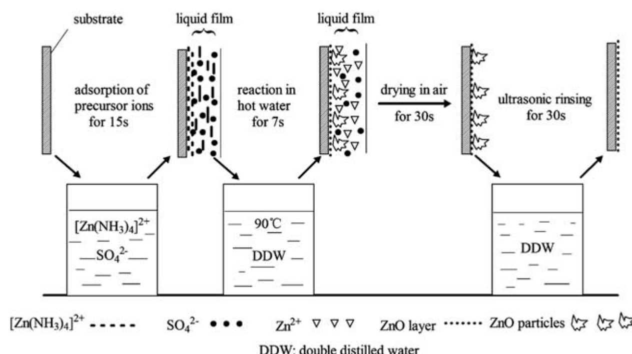


Fig. 1. Experimental scheme for the deposition of ZnO films.

merely to remove the loosely adsorbed large particles rather than to modify the microstructure of obtained film. Therefore, we believe that the difference in the experimental procedure is the basic reason that two similar modified SILAR methods follow intrinsically different deposition mechanism.

2.2. Characterization

The structural characterization of as-deposited ZnO films was carried out by X-ray diffraction (XRD) patterns obtained from D/max 2550 V diffractometer (Rigaku Ltd., Japan, Cu K_α radiation, $\lambda = 1.54056$ Å). The morphology measurement was carried out by field emission scanning electron microscope (SEM) (JSM-6700F) and atomic force microscope (SEM) (SPA 400, Seiko Inc., Japan). The film thickness was determined by direct SEM observation, and the nominal growth rate was calculated through dividing the film thickness by the number of deposition cycles. The photoluminescence was measured by RF-5301PC fluorescence spectrophotometer (Shimadzu Ltd., Japan) at room temperature excited by photon of 340 nm. A Xe lamp with a filter was used as the excitation light source.

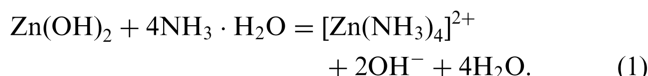
3. Results and discussion

3.1. Mechanism of film deposition

For zinc ions aqueous solution, when the ion product (IP) of the solution is higher than solubility product (SP), the precipitation $Zn(OH)_2$ occurs. It is commonly accepted that the degree of supersaturation (S), defined as the ratio of ion product to solubility product, is an important parameter to evaluate the precipitation process in aqueous solution. When S is lower than 1, no precipitation is formed in solution. When S is higher than 1 but lower than a critical value S_c, the heterogeneous precipitation occurs on the wall of vessel and substrate because the value of S is not sufficient to induce nuclei in the bulk solution. When S is higher than S_c, a large quantity of nuclei is formed in the bulk solution and the homogeneous precipitation occurs. Based on this theory, the deposition of high quality film from aqueous solution is to control the value of S, to induce the heterogeneous precipitation on substrate, and to suppress the homogeneous precipitation in the bulk solution.

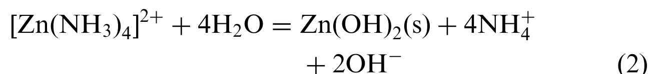
In this paper, we have made full use of the thermal decomposition nature of $[Zn(NH_3)_4]^{2+}$ in neutral aqueous solution, which will release ions of Zn^{2+} and OH^- into solution and result in the formation of $Zn(OH)_2$ or ZnO particles. Eqs. (1)–(3) illustrate the chemical reactions related to the process.

A dynamic equilibrium exists in the precursor under the presence of excessive ammonia:



$$Zn(OH)_2 + 4NH_3 \cdot H_2O = [Zn(NH_3)_4]^{2+} + 2OH^- + 4H_2O. \quad (1)$$

During the reaction process in hot water, $[Zn(NH_3)_4]^{2+}$ complex decomposes and $Zn(OH)_2$ precipitation forms:



$$[Zn(NH_3)_4]^{2+} + 4H_2O = Zn(OH)_2(s) + 4NH_4^+ + 2OH^- \quad (2)$$

As-deposited $Zn(OH)_2$ will transform to ZnO in aqueous solution at the temperature of over 50 °C [20]:

$$Zn(OH)_2(s) = ZnO(s) + H_2O. \quad (3)$$

Above analysis indicates that the chemical reaction process in hot water occurred in the thin liquid film adsorbed on substrate is vital important for the deposition of ZnO layer, and is extremely complicated as well. With the elapse of time starting from the initial immersion of substrate in water, three stages will occur subsequently within the liquid film, i.e., the solution stage, the heterogeneous precipitation stage, and the homogeneous precipitation stage. By adjusting the reaction time, the chemical reaction within the liquid film can be terminated in the second stage when solid $Zn(OH)_2$ is deposited on the substrate. Thus the homogeneous precipitation and the corresponding "ostwald" ripening process may be prevented. Then ZnO film with certain thickness and high quality can be produced after a series of successive deposition cycles.

3.2. Crystalline structure

Fig. 2 illustrates XRD patterns of ZnO films on glass and Si (1 0 0) substrate. It can be seen that as-deposited ZnO films exhibit good crystallinity corresponding to the hexagonal wurtzite structure (JCPDS 36-1451). No diffraction peak of $Zn(OH)_2$ or other materials was detected, illustrating that most of formed $Zn(OH)_2$ has been converted to ZnO. For both films on slide glass and Si (1 0 0) substrate, the preferential orientation along (0 0 2) plane were observed clearly, with the higher orientation degree for film on glass, illustrating the obvious effect of substrate on the film crystallinity.

The mean size of crystallites of ZnO film can be estimated from Scherre's formula. For ZnO films on glass and Si (1 0 0) substrate, the average crystallite size is 32.5 and 32.2 nm, respectively. So it can be inferred that the crystallite size of ZnO film may be primarily controlled by the deposition parameters.

It is both fundamentally interesting and technologically important to deposit thin film with good crystallinity from aqueous solution free from surfactant or organic additive. In examining the effects of different

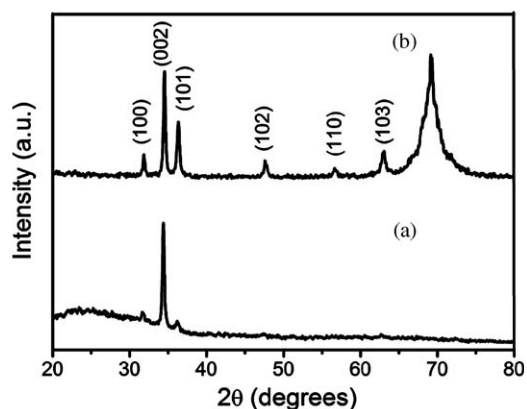


Fig. 2. XRD patterns of ZnO films on (a) glass substrate, and (b) Si (1 0 0).

experimental parameters on the deposition process, we found that the drying process after the reaction in hot water is very important to the crystallization process of ZnO films. For the ZnO film deposited with similar procedure but without the drying process, only an amorphous structure was obtained, which is also consistent with results of previously reported porous ZnO film [19]. However, the underlying mechanism for how the drying process determines the crystallization process of solid particles deposited from aqueous solution should be investigated further.

3.3. Morphology

From visual observation, the as-deposited film is smooth, bright, and reflective, possessing uniform red luster and strong adherence with the substrate. Fig. 3 shows results of AFM and SEM analysis of ZnO film on Si (1 0 0). It can be seen from SEM images that as-deposited ZnO film is dense and uniform throughout the substrate, without any cracks or pores. ZnO particles are distributed evenly on the whole, with the mean size of 200–300 nm. A close view of particles also reveals that most ZnO particles are closely accumulated aggregation of smaller ZnO crystallites in size of 30–50 nm, which is consistent to results of XRD analysis. However, these smaller crystallites are so closely interfused together that no clear boundary between neighboring crystallites can be observed. In addition, on the substrate surface, a spot of relatively large and irregular ZnO particles can also be observed. AFM measurement gave the consistent result with SEM about the film morphology, and the root mean square roughness of film was calculated to be 47.5 nm, which agrees well with the particle size of 200–300 nm.

It should be noticed that the growth rate of ZnO film is much higher than that by SILAR method. Based on the film thickness of 300 nm after ten deposition cycles from the direct observation of the cross section of film

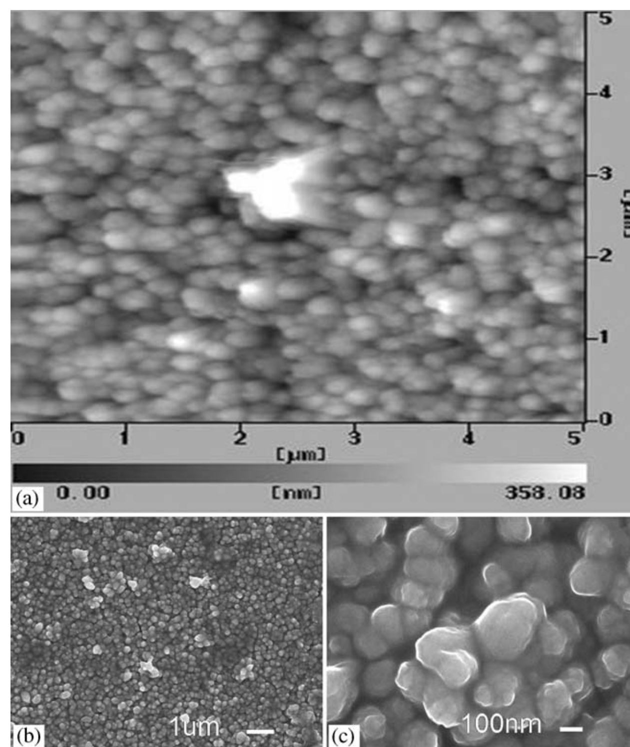


Fig. 3. Morphology of ZnO films on Si (1 0 0) substrate: (a) AFM image; (b) SEM image; (c) image of individual ZnO particles.

by SEM, the nominal growth rate of film is approximately 30 nm per cycle. In contrast, the film growth rate for SILAR usually remains at 0.1–1 nm per cycle [21,22]. Thus the growth rate has been increased by almost 30–300 times with no severe degradation in the film quality. With the much improved growth rate, the duration of the film depositing process can be reduced significantly. For example, for the growth of ZnO film with thickness of 300 nm, only 20 min are required.

3.4. Photoluminescence

Fig. 4 shows the photoluminescence spectra of ZnO films on slide glass and Si (1 0 0) substrate excited by photon of 340 nm. ZnO films on glass and Si (1 0 0) exhibit very similar emission properties throughout the investigated wavelength range (Fig. 4), indicating the good consistency of structure and composition in ZnO film irrespective of the substrate. A strong and sharp emission around 391 nm and relatively weak emissions in blue band (440–495 nm) were observed, and no green emission was detected, showing the stoichimetrical nature of obtained ZnO films. The full-width at half-maximum (FWHM) for emission peak at 391 nm was 8 nm (about 67.5 meV), significantly lower than the reported FWHM value of 100–120 meV [23,24]. This result shows that as-deposited ZnO films are in possession of evenly distributed crystallites.

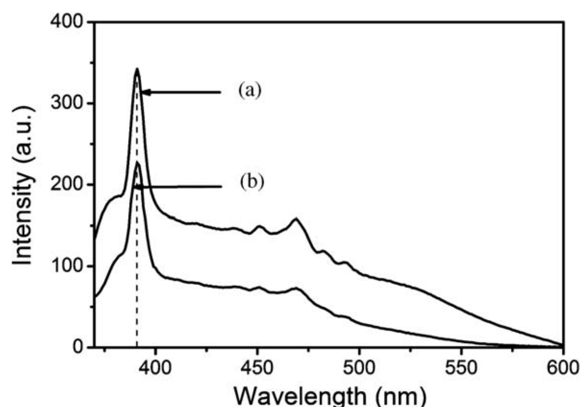


Fig. 4. Photoluminescence of ZnO films at the photon excitation of 340 nm: (a) glass substrate; (b) Si (1 0 0) substrate.

It is generally accepted that the near UV emission in ZnO film is closely related to the exciton transition from the localized level below the conduction band to the valance band [5,25]. The formation of this localized level is related to the breaking of lattice periodicity, which is often originated from the free impurity atoms, various defects, surface and interface. In the deposition process of ZnO film by this novel method, large quantities of ZnO particles are produced in the aqueous solution and deposited on the substrate in a very short period. Under the temperature as low as 95 °C and in the time slicing as short as several seconds, the deposited ZnO particles will have much less chance to agglomerate and interfuse together compared with the situation with higher temperature and longer time. So the ratio of surface and interface in as-deposited film will be much higher, which will in turn enhance the localized level significantly. Therefore, the strong and sharp near UV emission in obtained ZnO film was detected.

4. Conclusions

A novel and simple chemical deposition method was developed for the rapid preparation of ZnO film based on the heterogeneous precipitation principle in solution. Taking zinc-ammonia complex as the precursor, dense and continuous ZnO films can be coated on glass and Si (1 0 0) substrate in a fairly high growth rate of 30 nm per cycle. As-deposited ZnO film is composed of particles in even size of 200–300 nm, and exhibits hexagonal wurtzite structure with the preferential orientation along (0 0 2) plane. The strong and sharp near UV emission centered at 391 nm, and the suppression of deep-level defects related photoluminescence indicate the high optical properties of obtained film. Mechanism analysis shows that the reaction duration in hot water and the drying process are vital important factors affecting the deposition process and the crystallization behavior of the film prepared via the aqueous solution route.

Acknowledgment

This work is financially supported by the Ministry of Science and Technology of China through 973-project under Grant 2002CB613306.

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