



## Letter

## High oriented ZnO films by sol–gel and chemical bath deposition combination method

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## ABSTRACT

Poly-crystalline ZnO films with high oriented columnar grains were deposited on ZnO-coated seed layers by chemical bath deposition (CBD) in an aqueous-solution bath containing zinc nitrate [Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O], and dimethylamineborane (DMAB) at 60 °C without pre-activation especially. Sol–gel ZnO films on glass substrates were used as the seed layers which the mean size of the crystals in seed layer increased from several to approximately 80 nm at temperature from 150 °C to 550 °C. The deposited ZnO films on the ZnO-coated seed surfaces are preferentially on the (0 0 2) plane and exhibit increased from several 10 nm to 150 nm with increasing seed layer grain size.

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## 1. Introduction

ZnO is an important material for the application in optoelectronics due to its unique physical and stable chemical properties, abundance in nature and absence of toxicity which make it very popular for use in solar cells [1], photo detectors [2], light-emitting devices [3], thin film transistors [4] and surface acoustic wave guides [5]. Presently, most of the practical devices of ZnO materials are based on the polycrystalline ZnO [6]. However, for the applications of optoelectronic devices, high-quality *c*-axis-oriented ZnO films are very favorable due to effective ionic charges between the alternating Zn and O layers [7]. Besides, crystal ZnO film with stronger [0 0 2] preferred orientation will increase the Hall mobility [8]. It is essential to grow high-quality *c*-axis-oriented ZnO films for crucial applications in the future.

Many different methods are used to deposit ZnO films, such as metal–organic chemical vapor deposition (MOCVD) [9], magnetron sputtering [10], and pulse laser deposition (PLD) [11]. Among them, the deposited ZnO films usually exhibit the good crystallinity and the *c*-axis-orientation due to high diffusivity of absorbed particles on the growth surface, and the defects in the ZnO films are less. However, these methods require expensive and complicated apparatus to attain high vacuum ambience. Generally, by a solution

method, ZnO films are prepared at the atmosphere, the orientation of the films strongly depends on the substrate materials, growth conditions, and especially difficult to obtain highly orientated crystallinity at low temperature [12,13]. Moreover, in order to grow a continuous ZnO films, pre-activation with metal ions is essential for room temperature chemical bath deposition (CBD) [14]. However, the influences of metal ion pre-activation on intrinsic properties of ZnO films are undetermined, therefore, the applications are limited.

Followed these backdrops, the purpose of this investigation is to demonstrate a strongly *c*-axis-oriented ZnO films which is grown under low temperature, ambient pressure without the need of metal ions pre-activation.

## 2. Experimental details

In the process of fabricating the ZnO films, the seed layer was firstly coated with spin-on sol–gel method [15], which has molar ratio of monoethanolamine (MEA) and zinc acetate Zn(CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O equal to 1.0, and the concentration of zinc acetate equal to 0.375 mol/L. The sol–gel layer was followed two steps heat treatment in order to optimize the seed layer properties which will improve the uniformity, grain structure, and grain orientation of the CBD ZnO layer. The pre-baking temperature was 100 °C, and the post-baking temperature varied from 150 °C to 550 °C on hotplate. The CBD solution contained 0.1 mol/L zinc nitrate and 0.03 mol/L dimethylamineborane, and the substrate was immersed in the soak solution. Regarding the ZnO growth using CBD, the crystalline growth was led by nucleation and propagation growth. The thickness of the ZnO film could be controlled by tuning the soak solution and immersing time for the film growth at 60 °C for 30 min [14].

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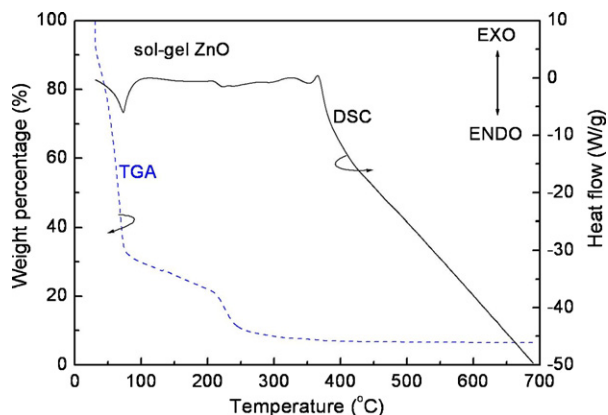


Fig. 1. TGA/DSC curves measured in air at a heating rate of 5 °C/min for ZnO sol-gel.

Thermo gravimetric analysis and differential scanning calorimeter (TGA–DSC, TA Instrument, STD 2960) were used to identify the evaporation, decomposition and crystallization points of the ZnO sol precursor. The deposited crystal structure was identified by X-ray diffractometry (XRD) (Mac Science M18XHF-SRA) over a range from 10° to 80°. Further structural characterization of the CBD ZnO grains was performed by high-resolution transmission electron microscopy (HRTEM; FEI/Philip Tecnai F20) and selected area electron diffraction (SAED). Scanning electron microscopy (SEM; Hitachi 4700) was employed to characterize the device structure and morphology of the prepared films.

### 3. Results and discussion

Three weight variation zones were showed in TGA curve (dash line) of Fig. 1, in which low boiling point solvent evaporated at 40–90 °C, water evaporated and organic compounds decomposed at 90–230 °C. One large and two small endothermic peaks, and two exothermic peaks were found in DSC curves of ZnO sol. The two exothermic peaks, one (imperceptible peak) was presented at about 325 °C and the other was at 360 °C. The last peak of the DSC curve, the exothermic peak, results from the crystallization of ZnO materials.

In fact, ZnO nanocrystalline seeds were preformed under 150 °C gradually, which were verified in XRD spectra of Fig. 2. As shown in Fig. 2, curves (a)–(c) are the XRD spectra of ZnO seed layers which post-baked at 150, 250, and 550 °C, respectively. Crystallized ZnO seed layers have a hexagonal crystal structure which was confirmed by the main diffracted peaks for the (100), (102), (200), and (202) planes [16]. The XRD spectra of ZnO films grown by CBD method on

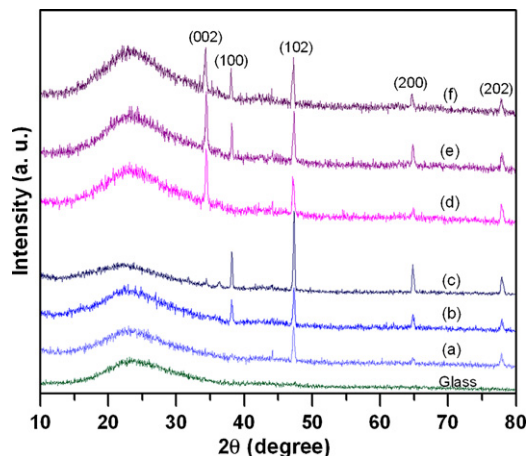


Fig. 2. X-ray diffraction patterns of ZnO films; seed layers post-baked at: (a) 150 °C, (b) 250 °C, and (c) 550 °C; combination ZnO films of CBD ZnO films grown on post-baked seed layers at: (d) 150 °C, (e) 250 °C, and (f) 550 °C.

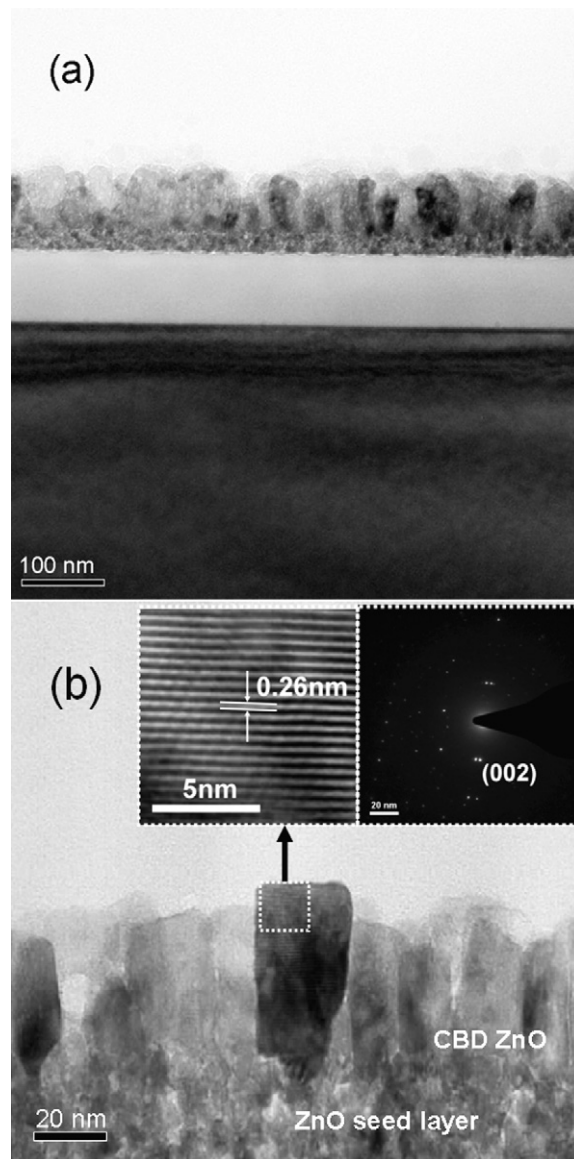
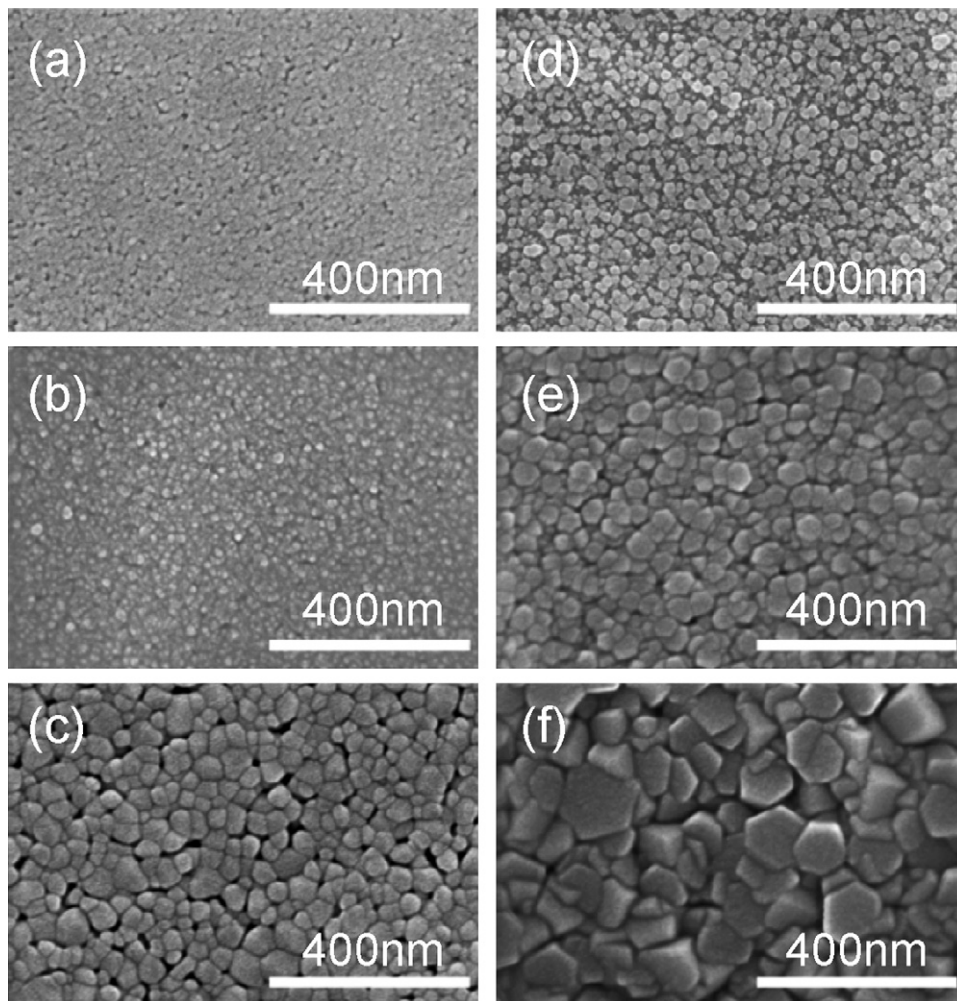


Fig. 3. (a) TEM images of bi-layer ZnO film (seed layer and CBD layer) on glass substrate and (b) TEM micrograph and SAED patterns of the ZnO film on glass substrate.

the sol-gel seed layers are shown in Fig. 2 also (curves (d)–(f)), from the recorded spectra, the main diffraction peak of (002) shown in curves (d)–(f), revealed the *c*-axis preferred orientation of the ZnO films.

The further structural characterization, Fig. 3 shows a TEM image (as shown insert (a) of Fig. 3) and the SAED patterns (as shown insert (b) of Fig. 3) of the CBD ZnO film on the seed layer which had been post-baked at 250 °C. It is clearly seen that the CBD ZnO film exhibits high-oriented columnar crystalline structure. As shown in HRTEM images (refer insert (b) of Fig. 3), the spacing between adjacent lattice planes is about 0.26 nm, which corresponds to the (002) plane distance of the hexagonal ZnO crystal.

Fig. 4 shows the SEM surface images of ZnO seed layers and ZnO thin films grown on seed layers by CBD. Fig. 4(a)–(c) are the images of seed layers post-baked at 150, 250, and 550 °C, respectively. It is clear that the seeds size increased with baking temperature increased and revealed that the size is from several to 80 nm. As shown in Fig. 4(d)–(f), hexagonal crystals with size increased as the seeds size increased and is from several 10 nm to 150 nm. The



**Fig. 4.** SEM images of ZnO film; seed layers post-baked at: (a) 150 °C, (b) 250 °C, and (c) 550 °C; combination ZnO films of CBD ZnO films grown on post-baked seed layers at: (d) 150 °C, (e) 250 °C, and (f) 550 °C.

high-oriented growth of the CBD film can be explained as Bauer [15] proposed a two-stage orientation mode, an initial nucleation orientation and a final growth orientation of the film, both of which result from the nucleation at the film–seed layer interface. In this case, the nucleation and grain growth behavior seems to be strongly affected by the grain size of the seed layer. As shown in Fig. 4, a finer and denser grain structure of the seed layer will lead to grow a finer and denser grain structure in CBD. We explain that the ZnO film grown by the CBD is typically controlled by the nucleation anchor and the propagation environment; this may indicate that the CBD grains prefer to nucleate on the grain boundary of the seed layer, which corresponds to the high-energy site for atoms adoption. The CBD nuclei then grow with [002] preferred orientation to minimize their surface energy and the final dimension of the CBD columnar grain is thus limited by the initial nuclei density simultaneously. According to the above results, we can recommend that the initial random orientated ZnO nuclei are catalyzed by the seed layer surface, especially on the grain boundaries. These nuclei provide the sites for ZnO to grow in the low temperature CBD bath. In order to minimize their surface energy, the grains growing in CBD bath are faster in the [002] direction than others. A columnar ZnO film with [002] preferred orientation perpendicular to the seed surface was then being formed through the merge/constraint of the adjacent grain of another orientation.

#### 4. Conclusion

A novel method for growing high orientated ZnO film with the combination of CBD and sol–gel process was demonstrated. The sol–gel ZnO seed layer can catalyze the nucleation and grain growth of the ZnO in the low temperature CBD bath without the aid of metal ion pre-activation. It was shown that the CBD ZnO film grown on the seed layer exhibited strongly [002] preferred orientation and was composed of close-packed columnar grain. In additions, the crystallinity, morphology, and grain distribution of the sol–gel seed layer depends strongly on its baking temperature, which directly affects the final morphology of the ZnO film grown in the CBD bath. The ZnO seed size increased with baking temperature increased and revealed that the size is from several to 80 nm. Also, the CBD ZnO films, that the (002) texture are observed; the size increased with the seeds size increased and range from several tens to 150 nm.

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