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2006 Chinese Phys. 15 2710

(http://iopscience.iop.org/1009-1963/15/11/041)

Vol 15 No 11, November 2006
1009-1963/2006/15(11)/2710-03

Chinese Physics

Induced growth of high quality ZnO thin films by crystallized amorphous ZnO*

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(Received 9 March 2006; revised manuscript received 22 April 2006)

This paper reports the induced growth of high quality ZnO thin film by crystallized amorphous ZnO. Firstly amorphous ZnO was prepared by solid-state pyrolytic reaction, then by taking crystallized amorphous ZnO as seeds (buffer layer), ZnO thin films have been grown in diethyene glycol solution of zinc acetate at 80 °C. X-ray Diffraction curve indicates that the films were preferentially oriented [001] out-of-plane direction of the ZnO. Atomic force microscopy and scanning electron microscopy were used to evaluate the surface morphology of the ZnO thin film. Photoluminescence spectrum exhibits a strong ultraviolet emission while the visible emission is very weak. The results indicate that high quality ZnO thin film was obtained.

Keywords: amorphous ZnO, Induced growth, ZnO thin films

PACC: 6855, 7360P, 7865K

1. Introduction

As a wide and direct band-gap II–VI semiconductor material, ZnO has an energy gap of 3.37 eV at room temperature that is suitable for ultraviolet optoelectronic applications.[1] In the past decade, a particularly large volume of research has been devoted to ZnO films. Previous reports on ZnO films have described a variety of deposition techniques, molecular beam epitaxy,[2] electron plasma sputtering, spray pyrolysis, pulsed laser deposition,[3] atmospheric pressure chemical vapour deposition,[4] radio-frequency magnetron sputtering,[5] etc. For the use of ZnO in optoelectronic applications,[6,7] high-quality thin films need to be grown.[8,9] Normally, an additional high-temperature ($\geq$ 400 °C) processing is often required for ZnO films. This high-temperature step can always lead to considerable constraints (vacancies, heat-defects, etc.) in combining the desirable characteristics of ZnO films. High-temperature processing also adds considerable costs to manufacturing. So far, the fabrication of such ZnO thin films has remained to be experimental challenges.

In this paper, amorphous ZnO is prepared by solid-state pyrolytic reaction firstly. Then crystallized amorphous ZnO is taken as seeds (buffer layer). Finally, ZnO thin films have been grown in diethyene glycol solution of zinc acetate.

2. Experimental details

2.1. Low temperature growth of ZnO thin films

C-plane (001) sapphire substrates were purchased from Shanghai Institute of Optics and Fine Mechanics. All of other high pure materials were purchased from Beijing Beihua Fine Chemicals Co. Ltd. There are three main steps to prepare ZnO film. First, prepare amorphous ZnO. An equal mass of $Zn(CH_3COO)_2\cdot$

*Project supported by the "863" High Technology Research Program in China (Grant No 2001AA311120), the National Natural Science Foundation of China (Grant No 60278031), the Innovation Project of Chinese Academy of Sciences, the Jilin Province Science and Technology Development Program Project of China (Grant No 20040564) and the Young Innovation Function of the Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences (Grant No Q03M23Z).
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$2H_2O$ and $NaHCO_3$ is mixed at room temperature, then the solid mixture is pyrolyzed at 160 °C for 2 h. Consequently, amorphous ZnO powder is prepared.[10,11] Second, plant seeds. The sapphire substrate is degreased by successive supersonic cleaning in acetone, methanol and deionized water, then chemically etched in hot solution of 3:1 (H_2SO_4:H_3PO_4) for 10 min and blowed in dry nitrogen.[2] 0.03 mL of a 1×10^{-6} M/mL ($1\,M=10^{-3}\,mol \cdot cm^{-3}$) amorphous ZnO ethanol solution is uniformly filmed on a 1 cm × 1 cm sapphire surface by spin-coat, then the substrate is annealed at 200 °C for 2 h and washed by deionized water. Because of the metastable characteristics of amorphous ZnO, the amorphous ZnO are crystallized along the direction of substrate due to the substrate-traction effect when it is heated. As a result, highly oriented ZnO seeds (or buffer layer) are planted on the sapphire substrate. Last, induce grow ZnO thin films. The substrate with buffer layer is immersed in a 1×10^{-5} M/mL $Zn(CH_3COO)_2 \cdot 2H_2O$ diethyene glycol solution at 80 °C for 30 h. This process is completed by rinsing with ethanol, by this way, ZnO thin films are prepared.

2.2. Characterization

X-ray diffraction (XRD) data are collected at room temperature by a RU-200 b XRD spectrometer (Rigaku) equipped with a quartz monochromator ($\lambda_{CuK_\alpha} = 0.154059$ nm).

The surface morphology of the films is evaluated by means of scanning electron microscopy (SEM) (KYKY-1000 B) and atomic force microscopy (AFM) (Digital Instruments, Dimension 3100).

A Hitachi MPF-4 fluorescence spectrophotometer is used for the optical characterization of the ZnO thin film. The resolution is 2 nm. The sample is excited by the 325 nm line of He–Cd laser with a power of 50 mW. The laser beam is focused to a spot of 30 μm^2.

3. Results and discussion

It is easily known by a simple theoretical analysis[12] the decomposed ZnO molecules can easily turn into ZnO crystal at as low as 80 °C. The grown temperature is determined by the formation temperature of critical crystal nucleus concentration of ZnO in diethyene glycol solution. The absorption spectra are taken to detect the kinetically decomposition process. This method allows us to compute the $Zn(CH_3COO)_2 \cdot 2H_2O$ decomposition velocity in diethyene glycol at certain temperature, so we can expediently control the ZnO molecular concentration by controlling reaction temperature, the critical nucleation concentration will make the molecules to correct their position in developing ZnO thin films. To our knowledge, this is the first report of seed crystal induced growth of ZnO thin films at as low as 80 °C.

For consideration of the crystalline structure of the ZnO thin film, XRD curve is shown in Fig.1.

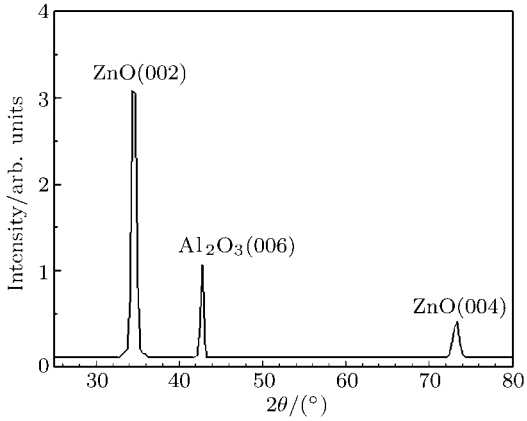

Fig.1. X-ray diffraction curves of ZnO thin film.

The two peaks are indexed [002] and [004] of the wurtzite structure of ZnO, indicating that the films are preferentially oriented [001] out-of-plane direction of the ZnO. The full-width at half maximum (FWHM) value is about 7 minutes (0.117°), while the substrate FWHM value is 2 minutes (0.033°). This feature is possibly related to structural defect, such as dislocation originating from the interface. Typical AFM images of ZnO thin films are shown in Fig.2.

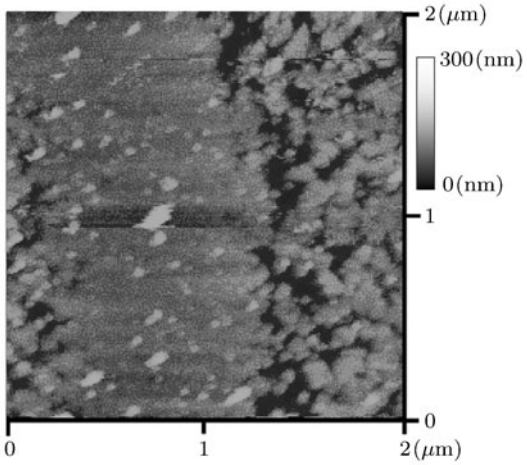

Fig.2. AFM images of ZnO thin films.

From the AFM image, we can clearly see that the

thickness is about 100 nm. The corresponding SEM image of the ZnO thin film is shown in Fig.3.

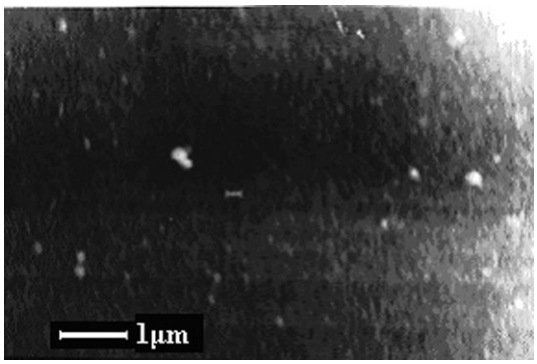

Fig.3. SEM images of ZnO thin films.

The micrograph shows that the structure of the film is smooth and uniform. This result is in agreement with the AFM image. According to the above discussion, the results have shown that the ZnO thin films have been deposited on sapphire substrate.

Photoluminescence (PL) is known as a sensitive method for examining the film quality, especially its optical properties. Figure 4 shows room temperature PL spectrum of ZnO thin film grown at 80 °C. The PL spectrum exhibits a strong near band emission at 383 nm, with a FWHM of 20 nm, while the visible emission band is very weak. We believe that the induced growth method should offer the advantage of improving crystal quality. The low temperature can greatly remove considerable constraints in combining the desirable characteristics of a ZnO thin film and decreases the native defects. The native defects, oxygen vacancies, also lead to visible emission.[13]

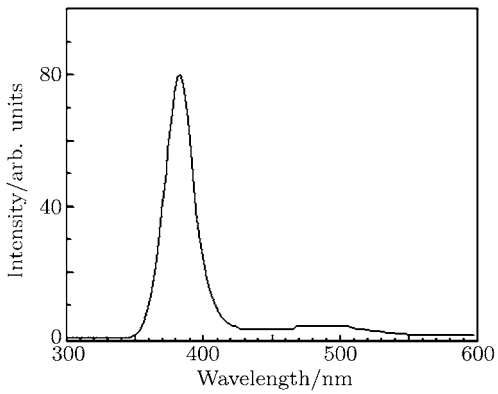

Fig.4. Room temperature PL spectrum of ZnO thin films.

4. Conclusions

We report induced growth of ZnO thin films by crystallized amorphous ZnO. The FWHM of XRD is $\sim$ 7 minutes (0.117°), AFM and SEM measurements show that the ZnO film surface is smooth and uniform, PL exhibits a strong ultraviolet emission while the visible emission is very weak at room temperature. At growth temperature as low as 80 °C, the heat induced native defects, oxygen or zinc vacancies can be dramatically reduced, the results indicate that the growth presented here is promising way for the preparation of high quality ZnO thin films, and may be potential for other metal oxide growth.

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