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Effects of disk rotation rate on the growth of ZnO films by low-pressure metal-organic chemical vapor deposition

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Abstract

ZnO films were grown at low pressure in a vertical metal-organic vapor deposition (*MOCVD*) reactor with a rotating disk. The structural and morphological properties of the ZnO films grown at different disk rotation rate (*DRR*) were investigated. The growth rate increases with the increase of *DRR*. The ZnO film grown at the *DRR* of 450 revolutions per minute (rpm) has the lowest X-ray rocking curve full width at half maximum and shows the best crystalline quality and morphology. In addition, the crystalline quality and morphology are improved as the *DRR* increased but both are degraded when the *DRR* is higher than 450 rpm. These results can help improve in understanding the rotation effects on the ZnO films grown by MOCVD.

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Keywords: X-ray diffraction; Metal-organic chemical vapor deposition; Zinc oxide; Structural properties

1. Introduction

Zinc oxide (ZnO) is a semiconductor material with a band gap of 3.36 eV at room temperature [1]. ZnO has strong excitonic emission in the ultraviolet range even at room temperature due to its large exciton binding energy of (~ 60 meV) and has been receiving extensive attention for short-wavelength optoelectronic application, such as light emitting diodes (LEDs) and laser diodes (LDs) [2–4].

Recently, ZnO films have been grown by various techniques including pulsed laser deposition, magnetron sputtering, molecular beam epitaxy, sol–gel, metal-organic chemical vapor deposition (MOCVD), etc. [5–8]. Among them, MOCVD may be one of the most suitable deposition processes for mass-productively producing ZnO epilayers, taking into account the GaN-based films. They are currently used in LEDs and LDs and are prepared mainly by MOCVD. Many authors have reported the high-quality ZnO films grown on Al_2O_3 or Si substrates by MOCVD [8–11]. In the research of ZnO films grown by MOCVD, many previous papers have reported the growth parameters including growth temperature [12,13], VI/II molar ratio [14–16], total gas velocity [17] and buffer layer [18,19]. There already have been some theoretical calculations on the effects of disk rotation rate (DRR) in vertical MOCVD for the growth of GaN-based materials [20,21], however, the effects of DRR on the growth of ZnO films have not been reported.

In the present work, the growth rate, structural and morphological properties of the ZnO films were also investigated as a function of DRR. Finally, the growth mechanisms at different DRR are discussed and reasonable explanations are given to elucidate the phenomena observed in the study.

2. Experimental details

Undoped ZnO films were grown on sapphire (0001) substrates in a vertical low-pressure MOCVD reactor. Fig. 1 shows a schematic diagram of the reactor. The MOCVD system was home-designed and made with a disk rotating subsystem. The DRR can be kept between 0 rpm and 800 rpm steadily to

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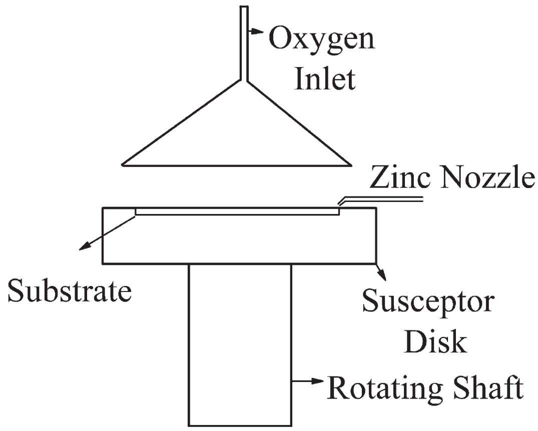

Fig. 1. Schematic diagram of the reactor.

get a good uniformity of the films. To reduce the pre-reaction, the reactor was designed to that diethylzinc (DEZn) is delivered from a side of the susceptor and oxygen (O_2) is delivered from the upside above a susceptor. Two inch (0001) sapphires were used as substrates. DEZn and high-purity O_2 gas (99.999%) were used as the precursors, respectively. Nitrogen gas (N_2) (99.999%) was used as the carrier gas. The flow rates of N_2-carried DEZn and pure O_2 were set at 49 standard cubic centimeters per minute and 1 standard liter per minute, respectively. The growth temperature was kept at 625 °C and the chamber pressure was maintained at 1.013×10^4 Pa. The substrates were degreased in trichloroethylene, and then cleaned ultrasonically with acetone, rinsed in deionized water before being sent to the reactor. The growth time of all the samples is 30 min.

The crystal structure of ZnO thin films was measured by X-ray diffraction (XRD) including θ–2θ scan and rocking curve on a Philips X'Pert X-ray diffraction apparatus with a Cu–Kα radiation source. The thicknesses of the films were characterized by cross-section scanning using an FEI Sirion-200 field-emission scanning electron microscope (FE-SEM) with an operating voltage of 5 keV. The morphologies were also observed in this FE-SEM. Atomic force microscope (AFM, SII SPI-3800) was used in tapping mode to investigate the surfaces of the films.

3. Results and discussion

Fig. 2 shows the dependence of the growth rate on DRR. By optimizing the reactor design and the growth conditions, the thickness nonuniformity of ZnO films is less than 5% within one wafer when DRR exceeds a value about 80 rpm. It is readily seen that the growth rate increases with the increase of DRR. This finding is consistent with Frolov et al.'s conclusion [23]. At 625 °C, the growth process is not controlled by surface reaction kinetics but by mass transport, in which molecules reaching the vapor–solid interface can react to each other quickly without any delay [22]. In vertical reactors, the gas flows downward impinging directly on the susceptor, which is oriented perpendicular to the direction of the gas flow, leading to the formation of boundary-layer [24]. In our case, with a rotating disk, the gas layer adjacent to the rotating disk is forced outward by centrifugal force. This flow is balanced by the axial flow toward the disk. Then the boundary-layer thickness on ideal conditions is given by the expression $\delta_o \cong 4\left(\frac{\nu}{\omega}\right)^{\frac{1}{2}}$, where ν is the kinematic viscosity, ω is the angular rotation rate of the disk and $\omega = \frac{\pi \times \mathrm{DRR}}{30}$ (radian/sec). The exact solution is for an infinite disk but is approximately obeyed for finite disk as long as the radius of the disk is much greater than [24]. Diffusive mass transportation is driven by gradients in the concentrations of the various species in the gas phase, or more accurately, by chemical potential gradients. Based on the theories mentioned above, it is easy to understand the phenomena in Fig. 2. At low DRR, the thickness is larger and molecules have to diffuse through a thick boundary-layer, so the growth rate is low. As the DRR increases in low region, it can be considered that the boundary-layer decreases and the changes are small. When the DRR is in the region of 330–520 rpm, the thickness of boundary-layers decreases greatly and chemical potential gradients become larger. The reactants then diffuse through the boundary-layer more easily and so the growth rate improves quickly. When the DRR is higher than 530 rpm, the gas flow begins to be affected by the hot susceptor greatly since the boundary-layer is very thin. The gas near the susceptor is suddenly heated and expands causing density gradients, which results in "buoyancy-driven convection" where the system attempts to respond to the force of the gravity. Finally, the gas flow reaches an equilibrium state. Therefore the growth rate also reaches a saturation state at the high DRR region.

Fig. 3 shows the typical XRD θ–2θ scan patterns of the ZnO layers grown with DRR at 90, 450, 750 rpm, respectively. Each XRD θ–2θ scan pattern was normalized at the maximum intensity. It is apparent that all the ZnO films consisted of a single ZnO phase oriented with its c-axis normal to the substrate surface, and no diffraction from randomly oriented grains or impurity phases can be observed from the XRD θ–2θ scan patterns. This c-axis preferential growth is accepted as a general habit of ZnO because the (0002) basal plane of ZnO has the highest surface energy [25]. It is also seen that with different DRR the ZnO (0002) peak slightly shifts from 34.425° to 34.410°, this indicates that the biaxial compressive stress gradually increases according to the calculation based on the

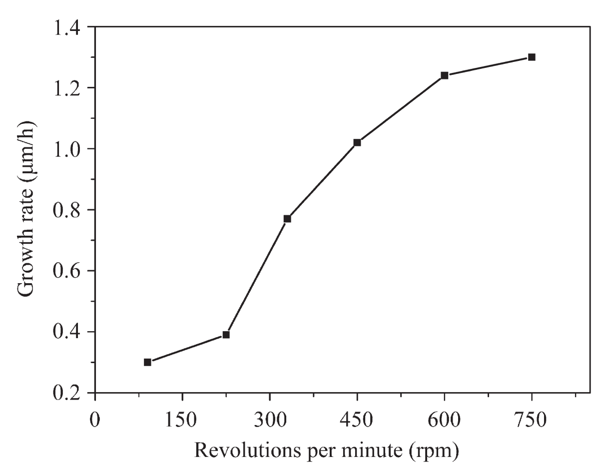

Fig. 2. Dependence of the growth rate on the disk rotation rate (DDR).