Low-Temperature Growth of ZnO Films on GaAs by Metal Organic Chemical Vapor Deposition

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Abstract: ZnO thin films were grown on GaAs (001) substrates by metal-organic chemical vapor deposition (MOCVD) at low temperatures ranging from 100 to 400℃. DEZn and H_2O were used as the zinc precursor and oxygen precursor, respectively. The effects of the growth temperatures on the growth characteristics and optical properties of ZnO films were investigated. The X-ray diffraction measurement (XRD) results indicated that all the thin films were grown with highly *c*-axis orientation. The surface morphologies and crystal properties of the films were critically dependent on the growth temperatures. Although there was no evidence of epitaxial growth, the scanning electron microscopy (SEM) image of ZnO film grown at 400℃ revealed the presence of ZnO microcrystallines with closed packed hexagon structure. The photoluminescence spectrum at room temperature showed only bright band-edge (3.33eV) emissions with little or no deep-level emission related to defects.

Key words: metal-organic chemical vapor deposition; ZnO film; GaAs; low-temperature
PACC: 6855; 7280E; 8115H
CLC number: TN304.2+5 **Document code**: A **Article ID**: 0253-4177(2008)01-0012-05

1 Introduction

Wide band-gap semiconductors are attracting attention because of the increasing need for short wavelength photonic devices and high-power, high frequency electronic devices. Remarkable progress has been achieved in GaN and SiC related materials. Wurtzitic ZnO is another wide band gap (3.37eV) semiconductor with a large exciton binding energy (60meV) that could lead to lasing action based on exciton recombination even at room temperature, which is expected to facilitate semiconductor lasers in the ultraviolet spectral region such as blue-, violet-, and ultraviolet laser diodes (LDS)[1~6] with low-threshold current density and high efficiency. These applications, however, require the realization of high quality ZnO epitaxial films.

A number of studies on ZnO films have been performed on sapphire substrates by pulsed-laser deposition and oxygen plasma-assisted molecular-beam epitaxy. Epitaxial films on sapphire with good quality have been obtained by many research groups[7~9] taking advantage of its hexagonal wurtzite structure, which is the same as ZnO. But, since it is an electrically insulating material, it makes the optoelectronic devices more complicated in actual application. ZnO film deposited on GaAs allows the combination of ZnO with other optoelectronic devices and the research of ZnO on GaAs also plays a key role in fabricating the p-type ZnO film by As diffusion. However, there are few reports about ZnO films deposited on GaAs[10~12] and the film quality is low, mainly due to the different crystal structure and the large lattice mismatch (19%) between the wurtzitic ZnO and GaAs.

ZnO thin films have been grown using many different techniques, including magnetron sputtering[13], molecular beam epitaxy[14], metal organic chemical vapor deposition[15~17], and pulsed laser deposition[18]. Among them, the molecular beam epitaxy method is used the most for research. The optical UV lasing emission from ZnO film has been demonstrated for the first time by using the MBE method[1,2]. MOCVD has been used for high-quality epitaxial growth of various semiconductors and it is the ideal production technology for the mass production. Recently, ZnO electrical homo-structural light-emitting diode has been obtained[19,20] by MOCVD. However, unlike the relatively mature MOCVD technique for Ⅲ-Ⅴ compound semiconductor growth, research into MOCVD growth of ZnO is still in its early stage. There are a lot of growth parameters that affect the film growth process such as the substrate temperature, chamber pressure, Ⅵ/Ⅱ ratio, and gas flow rate. The growth temperature is one of the most important parameters determining the quality of the films. But, there are only a few

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Received 10 July 2007, revised manuscript received 10 September 2007

reports on the temperature dependence of the properties of the ZnO films grown on GaAs by MOCVD and the effects of growth temperature on the crystalline, optical, and surface properties of ZnO films, especially at lower temperatures[21~23].

In this paper, we report ZnO film growth on GaAs (001) substrate at low temperatures ranging from 100 to 400℃, while the other deposition temperatures of ZnO/GaAs are usually above 500℃. The results indicate that the crystalline and optical quality become much better as growth temperatures increase. But, as temperature increases, the grain's size increases, resulting in a relatively rough surface. Since ZnO films grown at a low temperature exhibit smooth surface morphology while ZnO films grown at high temperature obtain good crystalline quality, we may produce high crystalline quality by introducing a thin ZnO buffer layer at a low temperature before the high temperature epitaxial growth.

2 Experiment

Diethyl zinc (Zn $(C_2H_5)_2$, DEZn) and H_2O were used as precursors. Nitrogen gas was used as the carrier gas. GaAs (001) substrates were chemically cleaned with enchants of HCl ∶ H_2O (1 ∶ 1) for 5min and then treated in 5% HF solution and blown in dry nitrogen gas before the GaAs substrate was put into the growth chamber. The substrate was first heated to 500℃ to remove contaminate before the epitaxy and the pressure was controlled to be 1.33kPa. Then, the substrate temperature was reduced and became stable at the set growth temperature for 10min. H_2O was introduced into the chamber about 1min before the introduction of DEZn. During growth, the flows of H_2O and DEZn were set to be 20 and 200sccm, respectively. Four samples were grown at different temperatures ranging from 100 to 400℃. The temperature of the bubble was 30℃. After growth, the samples were cooled for 2h in an atmosphere of nitrogen with a pressure of 1.33kPa. X-ray diffraction (XRD) was used to characterize the crystalline quality. The surface morphology was examined by using scanning electron microscope (SEM) and AFM. The optical characteristics of ZnO films on GaAs were evaluated by photoluminescence (PL) spectra at room temperature.

3 Results and discussion

3.1 Crystalline properties

The crystal quality of ZnO films deposited on GaAs (001) substrates and the surface morphology of the films were evaluated by X-ray diffraction and scanning electron microscopy, respectively.

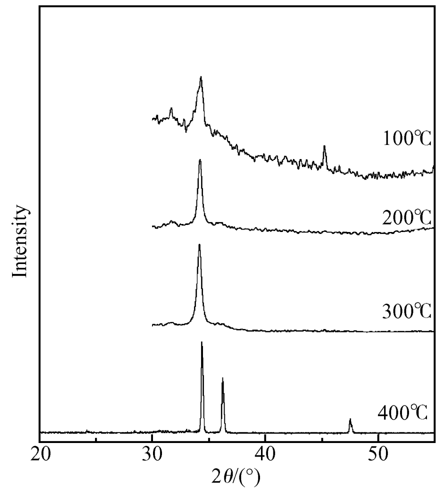

Fig. 1 XRD spectra of the ZnO films grown on GaAs substrate at different temperatures

Figure 1 shows the structural properties of ZnO films as a function of the growth temperature. The film thickness was about 200nm. All of the films exhibited the preferred ZnO (002) orientation, suggesting that most grains have a *c*-axis orientation perpendicular to the substrate surface, due to the largest surface free energy of (001) plane. The intensity of the (002) peak increased as the growth temperature increased, indicating better crystal quality. For the film grown at 100℃, the microstructure was polycrystalline. The intensity of the peaks was very weak because the grain size was too small to cause enough XRD intensity. For the films deposited at 200 ~ 300℃, the ZnO film exhibited the preferred (002) orientation along the *c*-axis with some trace of (100) and (101) peaks, which means that the ZnO *c*-axis direction was not well aligned for all of the films. The intensity of the (002) peak was strong and the FWHM was large with a value of about 0.4°, which was believed to be a result of the large lattice mismatch (19%) between the ZnO film and GaAs substrate. No big shift of the (002) diffraction peak was observed, indicating that the residual stress and associated strain may not have significant influence on the structural properties of the films. For the film grown at 400℃, the intensity of the (002) peak became quite high. Although the (101) peak became relatively strong at the same time, it was believed that the film crystal quality had been improved because the FWHM value improved to 0.18°, while the surface morphology became much rougher at the same time.

3.2 Surface morphology

The SEM images of the ZnO films are shown in

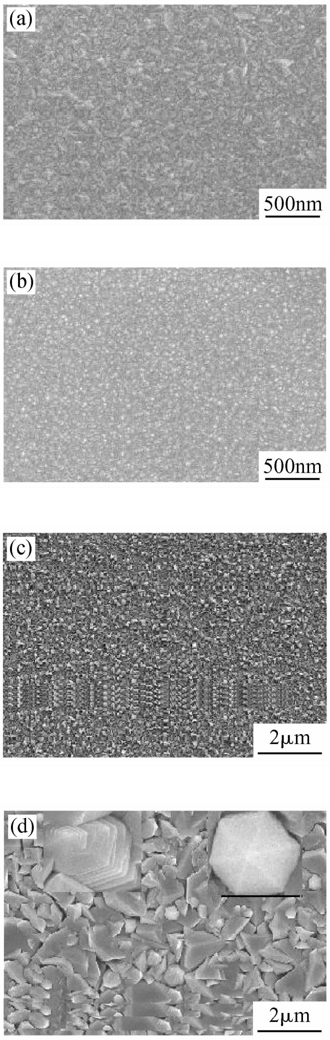

Fig. 2 Surface morphology of ZnO films grown at 100℃ (a), 200℃ (b), 300℃ (c), and 400℃ (d) The inset images are enlarged images of hexagonal and multiplayer-tower structure grains with a bar of 500nm.

Fig. 2. The surface morphologies of the films were critically dependent on the growth temperatures, as presented in Fig. 2. When the growth temperature was lower than 300℃, a smooth surface with very small fine grains was observed, while as the growth temperature increased, large, grains were observed. The tetra-pod-like grains shown in Fig. 2 (a) were a result of self-textured growth, which is preferable and important in the epitaxial growth of ZnO films[24]. The temperature dependence of the surface morphology of thin films can be explained mainly by the mobility of the atoms on the surface at different temperatures. In the initial stage of ZnO growth, the crystals do not have a specific preferred orientation to follow and competition among different crystals growth orientations occurs. As the growth rate is the highest along the c-axis of ZnO, the crystal growth with this orientation will grow faster and tend to dominate. At lower growth temperatures, the energy required for thermal diffusion is not enough for atoms on the surface to diffuse to the fit lattice site, which has smaller strain and mismatch, resulting in a lot of independent, small grains and, thus, poor crystal properties. When the temperature increases slightly (200～300℃), the in-plain atom diffusion will increase and the grain size becomes larger, forming a relatively smooth surface. But, when the temperature gets even higher, there is enough energy available for thermal diffusion and the films will end up with a rough surface morphology.

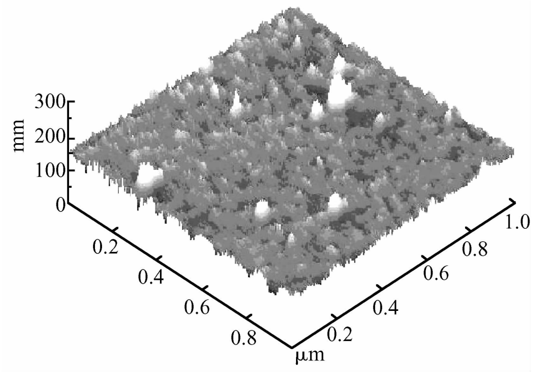

Fig. 3 AFM image of ZnO film grown at 300℃

The columnar grains were relatively uniform with a typical grain size of 50nm. However, as the growth temperature reached 400℃, there was enough energy available for atoms to occupy the correct site in the crystal lattice and grains with lower surface energy became larger. The films ended up with a rough surface morphology. Both hexagonal structure grains and multiplayer-tower grains can be observed with a typical size of 500nm.

AFM measurements were also performed to study the growth process of the film. The image shown in Fig. 3 is over a scale of 500nm × 500nm. We can see that the ZnO film was deposited in a column-by-column growth process and mainly grown along the c-axis orientation, which agrees with the results shown in XRD patterns. The crystal structure for ZnO is hexagonal, while that of GaAs is cubic. ZnO film on GaAs was therefore primarily grown with the self-texture preference and experienced a column-by-column growth process.

3.3 Optical properties

Figure 4 shows the room-temperature PL spectra of the ZnO films. The broad band edge emission at ～3.33eV was observed for all of the films. The RT peak is a combination of many multiple peaks, including the free excitons; donor bound exciton and their coupling LO-phonon replica with the line broadening[25]. Though the expected position is 3.31eV, if the mostly accepted band gap of 3.37eV and the

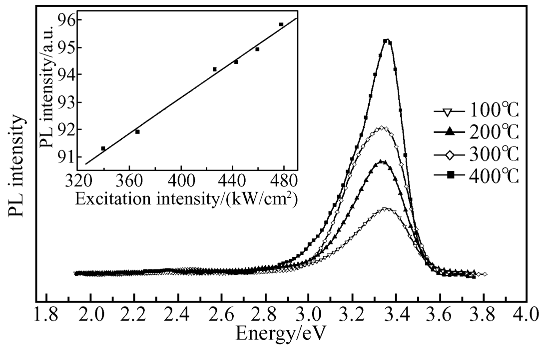

Fig. 4 Normalized PL spectra of ZnO films grown at different temperatures measured at room temperature

measured exciton binding energy of 60meV were used, a free exciton emission peak at 3.3eV is reasonable. Little or no deep-level emission was observed due to the radioactive emission from the conduction band to shallow acceptors or the emission from shallow donors to the valence band. We also found that the PL intensity increases linearly as the excitation intensity increases as shown in the inset image.

4 Conclusions

ZnO films were grown on GaAs (001) substrates by MOCVD at temperatures from 100 to 400℃. DEZn and H_2O were used as the zinc and oxygen source, respectively. All the ZnO films show a preferred (002) orientation, while the ZnO films grown below 150℃ exhibit polycrystalline with multi-orientations. The crystal quality and optical properties became better as the growth temperature increased, while the surface morphology became rougher at the same time. The minimum value of the FWHM was 0.18° and was obtained at a growth temperature of 400℃. The PL spectral of the ZnO films demonstrates only the UV emission peak at 370nm and the FWHM value of the peak is about 200meV.

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用 MOCVD 方法在 GaAs 衬底上低温生长 ZnO 薄膜

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摘要： 采用二乙基锌(DEZn)和水(H_2O)作为生长源，利用金属有机化学气相沉积(MOCVD)的方法，在 100～400℃ 低温范围内，在 GaAs (001)衬底上制备了 ZnO 薄膜. 利用 X 射线衍射(XRD)，室温 PL，AFM，SEM 研究了薄膜的晶体结构特性、发光特性及表面形貌特性. XRD 分析表明 ZnO 薄膜具有很强的 c 轴取向，(002)峰的 FWHM 平均值为 0.3°. 当生长温度达到 400℃ 时从 SEM 测量结果可以观察到薄膜表面呈六角状结晶. 随着生长温度的升高，薄膜的晶粒尺寸变大，结晶质量得到提高但同时表面变粗糙. 室温 PL 测量显示薄膜在 370nm 附近有强的近带边发射，没有观测到深能级发射峰.

关键词： MOCVD；ZnO 薄膜；GaAs；低温

PACC： 6855；7280E；8115H

中图分类号： TN304.2+5 **文献标识码：** A **文章编号：** 0253-4177(2008)01-0012-05

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2007-07-10 收到，2007-09-10 定稿