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The Optical and Electrical Properties of ZnO Films Grown on Flexible Substrate at Low Temperature by ALD

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Abstract: ZnO films were grown on flexible substrate by the atomic layer deposition (ALD) using diethyl zinc (DEZn) as a metal precursor and water as a reactant. AFM, XRD and HALL effect were used to investigate the morphology, structural and electrical properties of the films. PL spectrum was measured for optical property. With the increasing temperature, the crystal quality and optical property of the films were improved. When grown at 170 ℃, the films exhibited *c*-axis orientation, the electron concentration was 5.62×10^{19} and the electron mobility was 28.2 $cm^2 \cdot V^{-1} \cdot s^{-1}$.

Key words: ZnO; ALD; growth temperature; flexible substrate
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柔性衬底上 ALD 法低温制备的 ZnO 薄膜的光学和电学特性

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摘要: 以二乙基锌和水分别作为金属前驱体和反应物,利用原子层沉积方法(ALD)在柔性衬底上生长 ZnO 薄膜,讨论了生长温度对薄膜特性的影响。用 AFM、XRD 和 HALL 等对薄膜的表面形貌、晶体结构和电学性质进行表征,并且用 PL 光谱表征了其光学特性。实验结果表明,随着生长温度(低温下)的升高,薄膜的晶体质量和光学特性得到改善。当生长温度为 170 ℃时,薄膜呈现良好的 *c* 轴择优取向,且具有较高的电子浓度(5.62×10^{19} cm^{-3})和电子迁移率(28.2 $cm^2 \cdot V^{-1} \cdot s^{-1}$)。

关　键　词: ZnO; ALD; 生长温度; 柔性衬底

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1 Introduction

ZnO is a wide band gap semiconductor (E_g = 3.36 eV at room temperature) material with high thermal and chemical stability. The large exciton binding energy (about 60 meV, twice higher than exciton binding energy in GaN which is about 25 meV[1]) determines the optoelectronic applications[2-8] of ZnO, such as solar cells, gas sensors, light-emitting diodes and spintronics which has attracted rapidly increased attention in the past few years.

For the growth of ZnO films, metal-organic chemical vapor deposition (MOCVD)[9], pulsed laser deposition[10], molecular beam epitaxy (MBE)[11] and sputtering[12] are commonly method, and Si, sapphire are used as the substrates[13]. However, for the special substrates, such as PI (Polymide), PET (Polyethylene terephthalate)[14], flexible substrate, which can be decomposed at high temperature. The above methods are not suitable for the growth of ZnO films on these substrates. However, atomic layer deposition (ALD) is a unique technique for the deposition of thin films. With the advantages of simplicity, reproducibility, it appears to be a promising deposition technique. Especially for the low growth temperature, it's suitable for the growth of thin films on flexible substrate.

In this paper, ZnO films were grown on PET substrates by ALD at different temperature. The morphology, structure and optical properties of as-grown films were investigated. By changing the growth temperature, the optical and electronic properties of ZnO films were improved.

2 Experiments

In the ALD process, precursors are introduced sequentially into the growth chamber and cycles of precursor dosing are interrupted by perids of purging with an inert gas. We have grown the ZnO thin films in the ALD process at very low temperature using Lab NanoTM 9100 ALD system from Ensure Nanotech (Beijing). In the deposition processes, we used volatile metal-organic precursor diethyl zinc (DEZn) and de-ionized water. High-purity nitrogen gas was used as a purging gas and carrier gas.

In this study, we compare the results of obtained films by ALD at 120, 150, 170 ℃. The pulse time of the water precursor and the DEZn precursor were both 20 ms, the purging time after the H_2O precursor and the DEZn precursor were both 5 s. We performed deposition with 1 000 cycles and the thickness of ZnO films was about 200 nm. ZnO thin films were deposited on sapphires and PET substrates.

The samples were investigated by LabNano TM 9100 ALD system from Ensure Nanotech (Beijing). Photoluminescence (PL) measurements were performed using a He-Cd laser line of 325 nm as the excitation source.

3 Results and Discussion

The surface roughness of the films grown at different temperature was measured by AFM, as shown in Fig. 1. Fig. 1(a), (b) and (c) represent AFM images of the films grown at 120, 150, 170 ℃, respectively. From Fig. 1, the color of images at (c) is the most uniform in these three figures. With the growth temperature increasing, the surface roughness is not changed. Thus, we can conclude that the smooth of the films are not related to the growth temperature.

Fig. 2 shows the XRD pattern of as-grown samples. The (100), (002) and (101) diffractive peaks

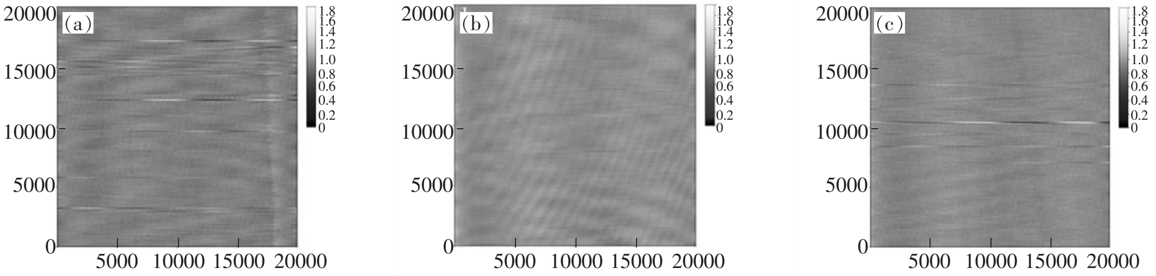

Fig. 1 AFM images of ALD ZnO thin films grown at 120, 150, 170 ℃

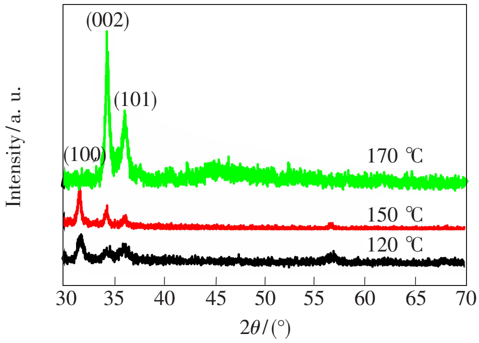

Fig. 2 XRD spectra of ALD ZnO thin films grown at 120, 150, 170 ℃, respectively.

could be detected, no impurities diffractive peaks can be observed which means the samples had the ZnO wurtzite structure. In addition, with the growth temperature increasing, the above diffractive peaks became sharper and narrower. When the growth temperature was 170 ℃, the ZnO (002) diffraction peak was strongest and dominant which indicated the sample had a preferred orientation along the *c*-axis. From the XRD results, 170 ℃ could be a suitable temperature for the growth of *c*-axis orientation ZnO.

In order to further evaluate the properties of samples grown at different temperature, we measured photoluminescence (PL) as shown in Fig. 3(a). All the samples exhibited a strong ultraviolet (UV) emission located at about 380 nm which was attributed to the near band gap exciton emission, meanwhile a weak visible emission related to the defect can also be observed. And the UV emission of the films grown at 170 ℃ was the strongest of all the samples. The type and width of the PL bands, intensity of excitonic peaks and defect-related luminescence not only show the quality of obtained layers but also yield information on defects present in as-grown films. As already mentioned, the observation of strong and sharp excitonic peaks suggested good quality of the films. Likewise, the lack of PL related to deep defects suggests a low concentration of such defects in our samples. The ratio of the intensity of deep level emission (I_{DLE}) to that of the UV emission (I_{UV}) has been plotted as shown in Fig. 3(b). It is clear that the $I_{\mathrm{DLE}}/I_{\mathrm{UV}}$ increased with the increase of growth temperature. From the PL measurement, with the increase of growth temperature, optical properties of the films were improved, too. This is consistent with XRD results.

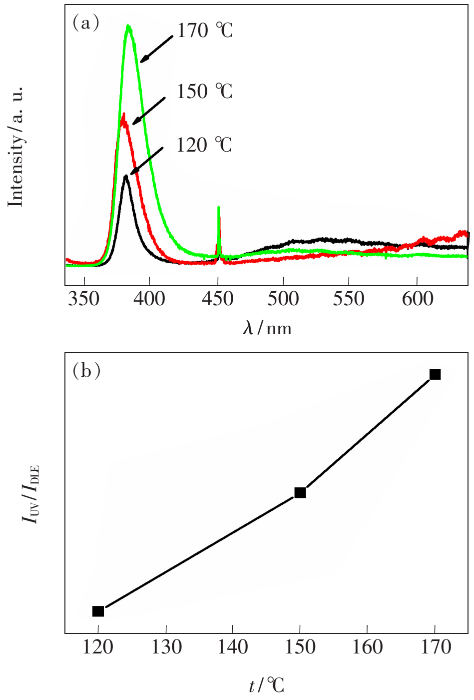

Fig. 3 (a) Photoluminescence spectra of ZnO sample grown at 120, 150, 170 ℃. (b) The ratio $I_{\mathrm{UV}}/I_{\mathrm{DLE}}$ as a function of the temperature at 120, 150, 170 ℃.

Table 1 The results of Hall measurements for ZnO films grown at different temperature

Sample	Carrier type	Carrier density/ cm^{-3}	Mobility/ $(\mathrm{cm}^2 \cdot \mathrm{V}^{-1} \cdot \mathrm{s}^{-1})$
120 ℃	n	–	0
150 ℃	n	2.75×10^{18}	7.05
170 ℃	n	5.62×10^{19}	28.2

Electrical parameters of ZnO films were obtained from the Hall effect measurements, which were measured with a Hall measurement system at room temperature. Table 1 displayed Hall measurement data. The results show that the films grown at 120 ℃ was n-type conduction, carrier density and mobility couldn't be measured which means the sample was a high resistance film. The films grown at 150 ℃ was still n-type conduction with the carrier density of 2.75×10^{18} and the mobility of 7.05 $\mathrm{cm}^2 \cdot \mathrm{V}^{-1} \cdot \mathrm{s}^{-1}$. For the films grown at 170 ℃, the electron concentration was 5.62×10^{19} and the electron mobility was 28.2 $cm^2 \cdot V^{-1} \cdot s^{-1}$.

4　Conclusion

In summary, by changing the growth temperature, ZnO films were grown on PET substrate by ALD. From the XRD results, growth temperature would affect the quality of crystallization and orientation of the films. And UV emission intensity would also be enlarged. At room temperature, the electrical properties of as-grown films were measured, at low growth temperature, the films exhibited a high resistance. And at relatively high temperature (at 170 ℃), the electron concentration was 5.62×10^{19} and the electron mobility was 28.2 $cm^2 \cdot V^{-1} \cdot s^{-1}$.

The quality of ALD samples depends on growth parameters such as deposition temperature. When the temperature is too high, metal organic precursor could be decomposition or evaporation on the surface of the substrate. These effects may produce some defects in samples[9]. At too low deposition temperature, we may have uncompleted reaction or condensation on the surface of the substrate. These effects also may produce crystal defects[9]. In our experiment, when the growth temperature was lower, the crystal quality of obtained ZnO films was poor (based on XRD result). With the growth temperature was rising, crystal quality and electrical parameters of the films can be also improved. So in our experiment condition, 170 ℃ was a suitable temperature for the growth of ZnO films.

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