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Effects of high-dose Ge ion implantation and post-implantation annealing on ZnO thin films*

Xue Shu-Wen(薛书文)[a)b)], Zu Xiao-Tao(祖小涛)[a)†] Su Hai-Qiao(苏海桥)[a)], Zheng Wan-Guo(郑万国)[c)], Xiang Xia(向 霞)[a)], Deng Hong(邓 宏)[d)], and Yang Chun-Rong(杨春容)[d)]

[a)] *Department of Applied Physics, University of Electronic Science and Technology of China, Chengdu* 610054, *China*
[b)] *Department of Physics, Zhanjiang Normal College, Zhanjiang* 524048, *China*
[c)] *Laser Fusion Research Center, China Academy of Engineering Physics, Mianyang* 621900, *China*
[d)] *School of Microelectronics and Solid-State Electronics, University of Electronic Science and Technology of China, Chengdu* 610054, *China*

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This paper reports that ion implantation to a dose of 1×10^{17} ions/cm^2 was performed on *c*-axis-orientated ZnO thin films deposited on (0001) sapphire substrates by the sol-gel technique. After ion implantation, the as-implanted ZnO films were annealed in argon ambient at different temperatures from 600 − 900 °C. The effects of ion implantation and post-implantation annealing on the structural and optical properties of the ZnO films were investigated by x-ray diffraction (XRD), photoluminescence (PL). It was found that the intensities of (002) peak and near band edge (NBE) exitonic ultraviolet emission increased with increasing annealing temperature from 600 − 900 °C. The defect related deep level emission (DLE) firstly increased with increasing annealing temperature from 600 − 750 °C, and then decreased quickly with increasing annealing temperature. The recovery of the intensities of NBE and DLE occurs at ∼ 850 °C and ∼ 750 °C respectively. The relative PL intensity ratio of NBE to DLE showed that the quality of ZnO films increased continuously with increasing annealing temperature from 600 − 900 °C.

Keywords: ZnO thin films, thermal annealing, ion implantation, photoluminescence
PACC: 6180J, 7155G

1. Introduction

The developments of the blue, green, and red emission materials which can be of practical use have been widely studied in recent years. ZnO, a direct bandgap semiconductor, has received increasing interest in the research community for its large bandgap of 3.3 eV as well as free exciton energy of 60 meV. Up to now, many techniques have been employed to synthesize high-quality ZnO films, such as radio frequency (RF) magnetron sputtering, electrophoretic deposition, pulsed laser deposition and the sol-gel process.[1−4]

In order to develop materials for special application, doped ZnO films have been fabricated and investigated by many groups. Ion implantation, especially in the semiconductor industry, is a widespread tool for doping semiconductors. It can be used to fabricate doped ZnO films.[5−10] Advantages of ion implantation are the lateral selectivity of sample area and doping depth as well as an accurate dose control. In principle, every element from the periodic system can be implanted, which makes it a multipurpose and flexible tool for doping semiconductors. However, undesirable side effects are the implantation-induced damage and its effects on the optical and electrical properties of the semiconductor.

Up to now, many dopants have been implanted into ZnO films. However, few were reported on the fabrication of ZnO:Ge through ion implantation. Ge is an indirect bandgap semiconductor with smaller energy difference between indirect gap and the direct gap ($\Delta E = 0.12$ eV), and smaller effective masses for electron and hole pairs. These characteristics lead to the expectation that it is much easier to change the electronic structure around the band edge.[11] Gao *et al* observed an intense photoluminescence peaked at 396 nm from Ge-implanted SiO_2 films after annealing

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†E-mail: xiaotaozu@yahoo.com

in nitrogen at 600 – 900 °C, which was attributed to the transitions of excited electrons from triplet states to singlet states ($T_1 \rightarrow S_0$) in GeO centres.[12] The peak position is very close to that of near band edge (NBE) from ZnO films prepared by our group.[13] It is presumably expected that Ge incorporation into ZnO films through ion implantation may increase radiative efficiency of NBE. Yu *et al* prepared ZnO:Ge compound by the solid state reaction method.[14] Fan *et al* prepared ZnO:Ge by the alternate RF magnetron sputtering.[11] It is known that the growth process and post-growth treatment have pronounced influence on the properties of ZnO films. Jeong *et al* found that the crystallinity recovery of the as-implanted sample presents the optimum condition when it is annealed at 800 °C for 1 h.[8] For ZnO:Ge films fabricated through ion implantation, defects accumulated during ion implantation. To eliminate the unwanted influence of ion-implantation-induced defects on the quality of ZnO films while keeping or enhancing the desirable properties, it is necessary to understand the effects of post-implantation annealing on Ge-implanted ZnO films.

In this work, we reported the preparation of ZnO:Ge films by the sol-gel process and ion implantation techniques. Our focus was on the effects of post-implantation annealing on the structural and luminescent properties of Ge-implanted ZnO films.

2. Experiment

2.1. Preparation of ZnO films and Ge ion implantation

ZnO thin film deposited on sapphire substrates was prepared by the sol-gel method. Zinc acetate dehydrate ($Zn(CH_3COO)_2{\cdot}H_2O$) was used as a starting material. Monoethanolamine (MEA) and 2-methoxyethanol were used as stabilizer and solvent respectively. Zinc acetate dihydrate was first dissolved in a mixture of 2-methoxyethanol and MEA solution at room temperature. The molar ratio of MEA to zinc acetate ($Zn(CH_3COO)_2$) was maintained at 1.0 and the concentration of zinc acetate was 0.35 mol/L. The solution was stirred at 60 °C for 2 h to yield a clear and homogeneous solution, which served as the coating solution after cooling to room temperature. The coating was usually made 24 hours after the solution was prepared. The solution was dropped onto sapphire substrates, which were rotated at 4000 rpm for 30 s. After depositing by spin coating, the films were dried at 300 °C for 10 min over a hot plate to evaporate the solvent and remove organic residuals. The procedures from coating to drying were repeated twelve times until the thickness of the sintered films were approximately 800 nm which was measured by an OLYMPUS BX51 interference/transmission microscope. The films were then put into a quartz tube furnace and annealed in air at 550 °C for 1h.

After annealing, the as-prepared films were subjected to ion implantation. Ge ions were implanted into the ZnO films at 56 keV to a dose of 1×10^{17} ions/cm^2.

2.2. Measurements

To characterize the structural and optical properties of ZnO and Ge-implanted ZnO films, the crystal orientation was investigated by using a BEDE-D1 x-ray diffractometer (XRD) with the radiation source of Cu$K\alpha$. The surface morphology was investigated by using a SPA-300HA atomic force microscope (AFM). Transmittance spectra were measured by using a SHIMADZU UV2550 spectrophotometer. Room temperature (RT) photoluminescence spectra (PL) were recorded by a SHIMADZU RF5301PC spectrophotometer with excitation wavelength of 345 nm.

3. Results and discussion

3.1. Characteristics of as-prepared ZnO films

Figure 1 shows typical AFM images of as-prepared films deposited on (0001) sapphire substrates by the sol-gel process. The minimum root-mean square of surface roughness is about 5 nm. The average grain size is 41 nm. Compared with RF sputtered ZnO films,[15] the surface of as-prepared films is very smooth. X-ray diffraction patterns of as-prepared ZnO films are shown in Fig.2. It shows that as-prepared ZnO films exhibit the hexagonal wurtzite structure (JCPDS 36-1451) with *c*-axis preferred orientation. Figure 3 shows the optical transmittance of the as-prepared films. It can be seen that the average transmittance in the visible region is $\sim$ 80%. The calculated optical bandgap of as-prepared films from $(\alpha h\nu)^2$ vs. photon energy plot is about 3.2 eV as shown in the inset of Fig.3.

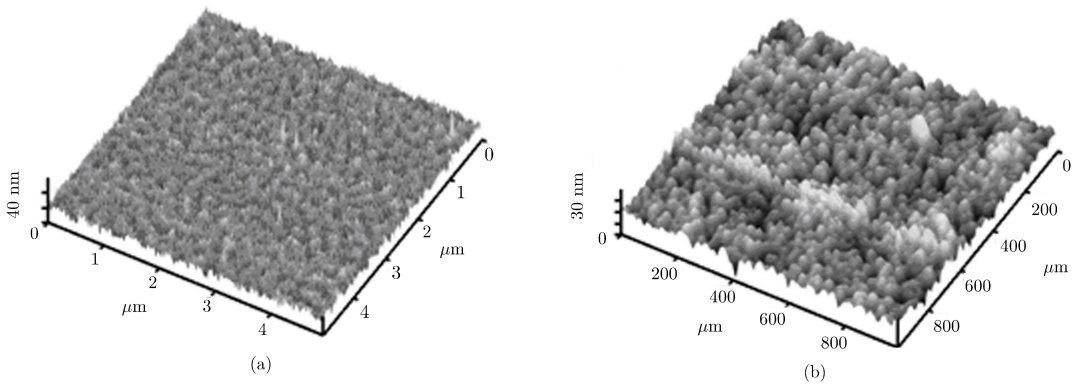


Fig.1. AFM images of as-prepared ZnO films: (a) $5\times5\mu m^2$; (b) $1\times1\mu m^2$.

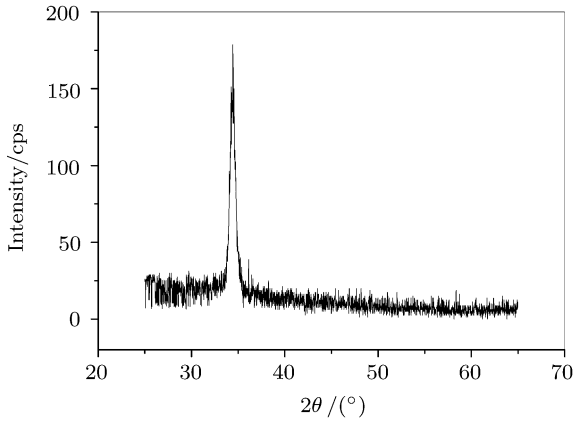


Fig.2. XRD pattern of as-prepared ZnO films.

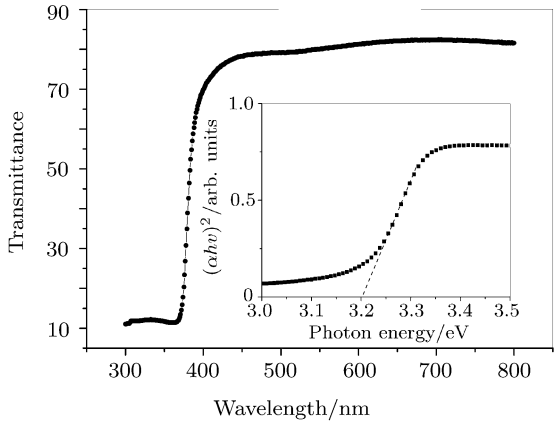


Fig.3. Optical transmittance spectrum of ZnO films.

3.2. Influence of post-implantation annealing on Ge-implanted ZnO

To investigate the effects of annealing on the structural properties of Ge-implanted ZnO films, the films were annealed in argon ambient at different temperatures from $600-900$ °C after ion implantation. Figure 4 shows XRD patterns of ZnO films after ion implantation and annealing at different temperatures. It can be seen that all films still show the hexagonal wurtzite structure with *c*-axis preferred orientation after ion implantation and annealing. No evidence of any other secondary phases and impurities is found in the XRD patterns. As ZnO is a radiation-hard material, it is not surprising to see that even under heavier-ion bombardment at high dose ZnO remains crystalline.[16] However, the intensity of (002) peak evidently decreases by ion implantation and the full width at half maximum (FWHM) of (002) is found to be narrowed. Kono *et al* observed that little changes were seen in HWFM of (002) for Cu-ion-implantation to a dose of 1×10^{16} ions/cm^2, which was defined as tolerance limit.[17] Earlier results showed that dynamic annealing takes place below the tolerance dose. The dpa at the threshold dose of ZnO is 19 for Zn and 12 for O at maximum which are determined by using SRIM2000 at the tolerance dose of 1×10^{16}ions/cm^2.[18] In our work, the total dose is above the tolerance limit for ZnO. So, (002) peak distinctly decreases and the FWHM is narrowed after ion implantation.

Furthermore, it can be seen that (002) peak increases gradually with increasing annealing temperature from $600-900$ °C. Similar results were obtained on the RF sputtered ZnO films annealed in oxygen ambient at different temperatures from $600-900$ °C.[19] However, Fang *et al* found that the intensity of (002) peak decreases quickly after annealing temperature exceeds 600 °C.[20] The discrepancy may be attributed to different growth conditions. It also can be seen

that significant recovery of the FWHM and intensity of (002) peak occurs after annealing at 600 °C.

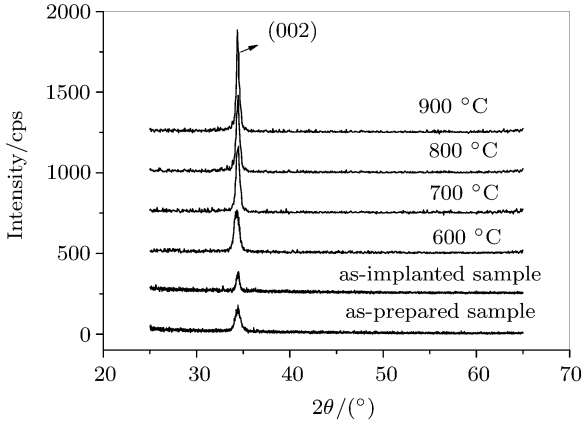


Fig.4. XRD patterns of ZnO films after ion implantation and annealing at different temperatures.

Figure 5 shows RT PL spectra of ZnO films after ion implantation and annealing at different temperatures from 600 − 900 °C. It has been known that ZnO has three PL bands centred around 390, 510 and 640 nm,[21] labelled NBE emission, defect related deep level emission (DLE) and orange emission respectively. In this work, all the as-prepared films show a NBE emission at 389 nm and a DLE emission centred at about 500 nm in the visible region. Recent studies revealed that only Zinc vacancy (V_{Zn}) and oxygen vacancy (V_O) are the two possible defects that are involved in DLE emission.[22] V_{Zn} has the lowest formation energy among the native point defects in n-type ZnO and is easier to form. In contrast, the formation energy of V_O is quite high and its concentration is very low in n-type material.[23] It is expected that V_{Zn} concentration is higher than that of V_O in our as-prepared samples.

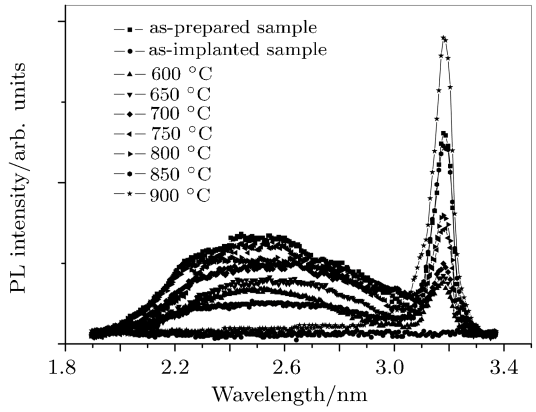


Fig.5. RT PL spectra of ZnO films after ion implantation and annealing at different temperatures (Excitation wavelength: 345 nm).

Figure 5 shows that NBE and DLE disappear after ion implantation. The disappearance of NBE and DLE can be mainly attributed to the structural damages induced by ion implantation, which can act as non-radiative defects.[6] On the other hand, it is expected that some Ge ions may occupy the sites of V_{Zn} because the ionic radius of Ge^{2+} (0.73 Å) or Ge^{4+} (0.53 Å) are smaller than that of Zn^{2+} (0.74 Å). This could lead to a decrease of V_{Zn} concentration in ZnO films, which could also result in a decrease of DLE.

To eliminate the unwanted influence of ion-implantation-induced defects on the quality of ZnO films while keeping or enhancing the desirable properties, the as-implanted films have been annealed at different temperatures from 600 − 900 °C in argon ambient. Figure 6 shows the dependence of NBE intensity on the annealing temperatures. It can be seen that NBE intensity increases gradually with increasing annealing temperature from 600 − 900 °C. At about 850 °C, the recovery of the intensity of NBE occurs. After that, the intensity of NBE continues increasing with increasing annealing temperature up to 900 °C. It is known from our previous study[13] that NBE of ZnO increases with increasing annealing temperature 600 − 900 °C due to the continuous improvement of the quality of ZnO films. In this work, however, NBE distinctly increases especially after annealing at 900 °C compared with previous results. This may be due to the incorporation of Ge into the ZnO matrix. During ion implantation, heavier-ion bombardment may destroy Zn–O bonds, and many Ge–O bonds are formed. With increasing annealing temperature from 600 − 900 °C, GeO content increases as confirmed in Ge-implanted SiO_2 films.[12] PL intensity originated from GeO centres also increases. This may result in a distinct increase of the intensity NBE after Ge-implanted ZnO films annealed at high temperatures.

Figure 7 shows the dependence of DLE intensity on annealing temperatures. We can see from the figure that the change of DLE is much different from NBE with increasing annealing temperature. At temperatures from 600−750 °C, the intensity of DLE increases with increasing annealing temperature. However, the intensity of DLE decreases quickly with increasing annealing temperature when it exceeds 750 °C. Figure 7 shows that the intensity of DLE recovers at about 750 °C. This is somewhat different from that of NBE. This indicates that DLE recovers more easily than NBE. The decrease of DLE can be attributed to a

continuous improvement of the quality of ZnO films with increasing annealing temperature from 750 – 900 °C.

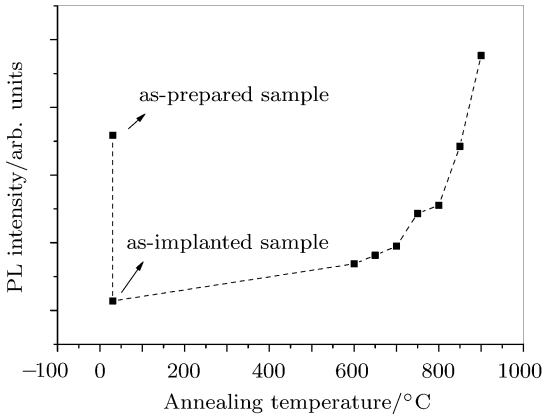


Fig.6. Dependence of NBE intensity on annealing temperature.

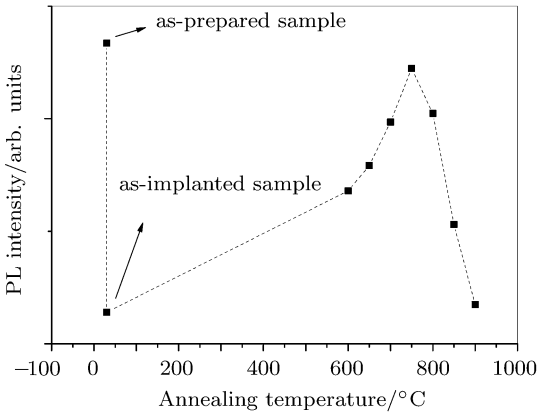


Fig.7. Dependence of DLE intensity on annealing temperature.

PL spectroscopy is a powerful tool in characterizing the optical quality of semiconductor materials, such as PL intensity correlates directly with the defect densities in material. One way to evaluate the concentration of structural defects in ZnO is to compare the relative PL intensity ratio of the NBE to the DLE.[24–26] To evaluate the quality of the ZnO films, R defined as the ratio of the intensity of the NBE to that of the DLE ($R = I_{389\ \mathrm{nm}}/I_{500\ \mathrm{nm}}$) was used. The bigger the ratio R, the higher the quality of ZnO films. Figure 8 shows R values as a function of annealing temperature. It is evident from this figure that post-implantation annealing treatment enhances the ZnO film quality significantly. Moreover, for the sample annealed at 900 °C, the FWHM of NBE is ∼70 meV, which suggests a clear evidence of quality improvement of ZnO films.[27,28]

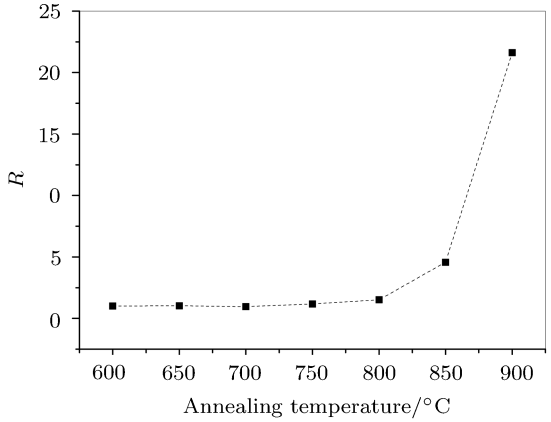


Fig.8. The relative PL intensity ratio (R) of NBE to DLE at different annealing temperatures.

4. Conclusion

Ge doped ZnO thin films are prepared by the sol-gel and ion implantation techniques. Ge ion implantation to a dose of 1×10^{17} cm^{-2} has caused structural and optical changes for ZnO thin films. After Ge ion implantation, ZnO films still remains single phase and hexagonal wurtzite structure with c-axis preferred orientation while NBE and DLE are distinguished. Through post-implantation annealing, ion-implantation induced non-radiative defects can be effectively annealed out, which can lead to the recovery of the structural and optical properties of ZnO films. With increasing annealing temperature, the intensities of (002) peak and NBE increases. DLE firstly increases with increasing annealing temperature from 600 – 750 °C, and then decreases quickly with increasing annealing temperature. The intensities of NBE and DLE recover at ∼ 850 °C and 750 °C respectively.

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