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Nitrogen binding behavior in ZnO films with time-resolved cathodoluminescence

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Abstract

ZnO film with (1 0 0) orientation was produced on silicon substrate and doped with nitrogen using plasma immersion ion implantation. The effects due to N doping were investigated using cathodoluminescence (CL). In the heavily nitrogen-doped ZnO film, the intensity of ultraviolet (UV) band decreases and that of the visible band increases as a function of the electron bombardment cycle i.e. time. Based on the X-ray photoelectron spectroscopy (XPS) analysis, the unstable Zn–N bond is responsible for the CL behavior and the experimental results agree well with the first-principle calculation. Our work is helpful to our understanding of the role of *p*-type dopants in ZnO.
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Zinc oxide (ZnO) films possess many interesting properties such as piezoelectric effects [1], conductive effects [2], acoustic characteristics [3], direct band gap (3.3 eV), and non-toxicity. The materials have thus attracted much attention because of their potential use in optoelectronic devices such as flat panel displays [4]. The fabrication of ZnO films by the filtered cathodic vacuum arc (FCVA) technique in conjunction with plasma immersion ion implantation (PIII) has aroused interest because of the readily adjustable deposition parameters, low growth temperature, and convenient in situ doping [5,6]. In this method, a zinc cathode is triggered to produce the zinc plasma and oxygen gas is simultaneously fed into the chamber [7]. The zinc plasma is guided through a curved magnetic duct to eliminate deleterious macro-particles and then transported to the processing chamber [8]. The zinc plasma reacts with oxygen in the vacuum chamber and dual zinc-oxygen plasma is formed to conduct deposition. Using this technique, highly (1 0 0) oriented ZnO films have been fabricated on silicon substrate at a DC bias of −500 V [6]. The results are of significance for large-scale optical-electronic integration in future devices. However, *p*-type doping of ZnO is not as easy and the feasibility has been studied extensively [9–14]. N is regarded to be the more soluble group-V impurity also having the shallowest acceptor level relative to P and As [14]. Cluster-doping has been investigated because of the stable bonds and low doping enthalpy [11]. The doping bottleneck is generally due to intrinsic defects, unintentional hydrogen impurity, and low N solubility [11,14]. Depth-resolved cathodoluminescence (CL) has been used to characterize defects in ZnO films by varying the accelerating voltage [15–17]. The stability of the N-doping effect in ZnO film can be examined employing CL based on collisions between the accelerated electrons and N atoms.

Here, we report the growth of (1 0 0) ZnO film on Si substrate by plasma immersion ion implantation and describe the N-doping effect in doped ZnO films. In heavily N-doped ZnO film, the intensity of the ultraviolet (UV) band decreases and that of the visible band increases as a function of the electron bombardment cycle, i.e time in CL spectra. The binding energy of N revealed by X-ray photoelectron spectroscopy (XPS) is useful to our understanding of the stability of N-doping and *p*-type doping in ZnO.

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The substrates were *p*-type (1 0 0) silicon wafers with a resistivity of 10–30 Ω cm. The base pressure in the vacuum chamber of our plasma immersion ion implanter (PIII) equipped with a cathodic vacuum arc source was about 1 × 10 Torr [6]. Mixed Gases with various ratio [flow rate (O_2: N_2, sccm): 20: 0 (undoped); 20: 10 (lightly N-doped); 5: 15 (heavily N-doped); working pressure: $\sim 1.0 \times 10^{-3}$ Torr] were simultaneously bled into the vacuum chamber and interacted with the drifting zinc plasma thereby producing a dual plasma consisting of both zinc and oxygen (nitrogen) ions. The samples that were biased to −300 V were positioned about 10 cm from the exit of the plasma stream. X-ray diffraction (XRD) was performed using a Siemens D500 diffrac to meter using the Cu Kα line at 1.5406 Å. An Oxford Instrument MonoCL system in a scanning electron microscope (SEM) was used for the CL studies at room temperature. The X-ray photoelectron spectroscopy (XPS) measurement was conducted using a monochromatic Al Kα excitation line 1486.6 eV on a PHI-5700.

The typical XRD patterns acquired from undoped and doped ZnO films deposited on Si substrate are shown in Fig. 1. The two diffraction peaks observed around 31.2 and 64.9° in the undoped ZnO film (Fig. 1(a)) are those of (1 0 0) and (2 0 0) ZnO, where the *c* axis is parallel to the substrate surface. The ZnO films with different nitrogen doping concentrations exhibit the (1 1 0) orientation as shown in Fig. 1(b) and (c), which may be due to the N-doping nucleation energy. The shifts can be explained as the stress and crystalline quality of ZnO film [6].

Fig. 2(a) and (b) show the CL spectra of the undoped and lightly N-doped ZnO films. It is generally agreed that the UV band comes from free excitonic emission [16] while the visible band is related to defects that are generally due to oxygen vacancies [17]. The nonradiative recombination activities in the vicinity of the grain lead to their weak intensities and explain the absence of the UV band in the lightly N-doped sample [16]. However, strong CL intensity (UV: strong; visible: relatively weak) was observed in the heavily N-doped ZnO film including the UV and visible bands (Fig. 3(c)). Furthermore, the CL spectra reveal an interesting phenomenon that the intensity of the UV band dramatically decreases while that of the visible band increases as a function of the accelerated electron (5 kV) bombardment cycles. After about 10 cycles, the changes a weak UV band and strong visible band are observed. In the undoped and lightly N-doped ZnO films (shown in Fig. 2(a) and (b)), no changes can be detected in the CL spectra after electron bombardment (Fig. 2(a) and (b)) even after many cycles (not shown).

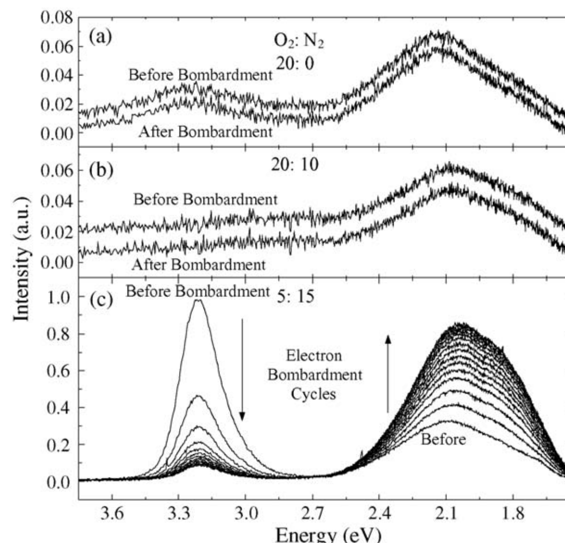

Fig. 2. Cathodoluminescence (CL) spectra of: (a) undoped (O_2:N_2 = 20:0 sccm), (b) lightly N-doped (20:10), and (c) heavily N-doped (5:15) ZnO films on Si substrate before and after electron bombardment.

ZnO films with various orientations i.e. (1 0 0). (1 1 0). and (0 0 1) have been produced by our method. but there is no similar CL feature. Orientation effect should be ruled out. Based previous results [16] reported and the fact that there were no changes of CL in our undoped and lightly N-doped ZnO film after electron bombardment, we deduce that the changes in the CL in heavily N-doped ZnO film originate from nitrogen-related defects. Since the changes in the CL spectra in the lightly N-doped ZnO film are not similar, we suspect that nitrogen occupy different positions in the ZnO crystal lattice in the lightly and heavily N-doped ZnO films [11,12]. Hence, the binding energies of Zn, O, and N in the three samples were checked by XPS.

Fig. 3(a) displays the XPS spectra corresponding to $Zn2p_{3/2}$ around 1020.8 eV indicating that the positions in three samples are about the same (±0.05 eV). The XPS spectra of O1s are shown in Fig. 3(b) and some difference can be observed between the undoped and N-doped ZnO films (including lightly and heavily doping). The shift of the main peak is related to N-doping, whereas the new shoulder in the XPS spectrum for the N-doped samples may come from nitrates [18]. The N1s region in Fig. 3(c) about N-doped samples shows an obvious shift. For simplicity, there are two basic possible bonds of nitrogen in ZnO: O–N and Zn–N, which can be understood as N replacements of Zn and O, respectively [11]. In Maki's work [19], the peaks around 398 eV attributed to Zn–N bond were observed in the N-doped ZnO single crystal. The peak at 400 eV was suggested as the chemical states of neutrally

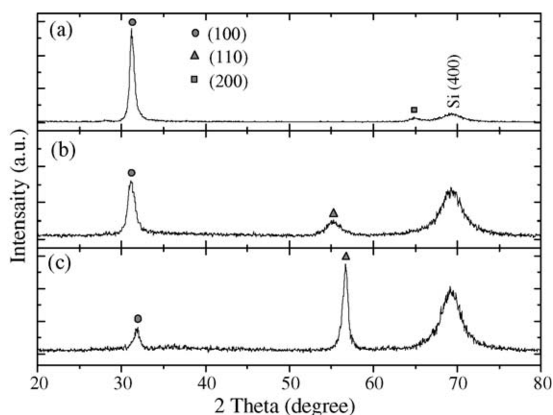

Fig. 1. X-ray diffraction patterns of: (a) undoped (O_2:N_2 = 20:0), (b) lightly N-doped (20:10), and (c) heavily N-doped (5:15) ZnO films on Si substrate produced by PIII.

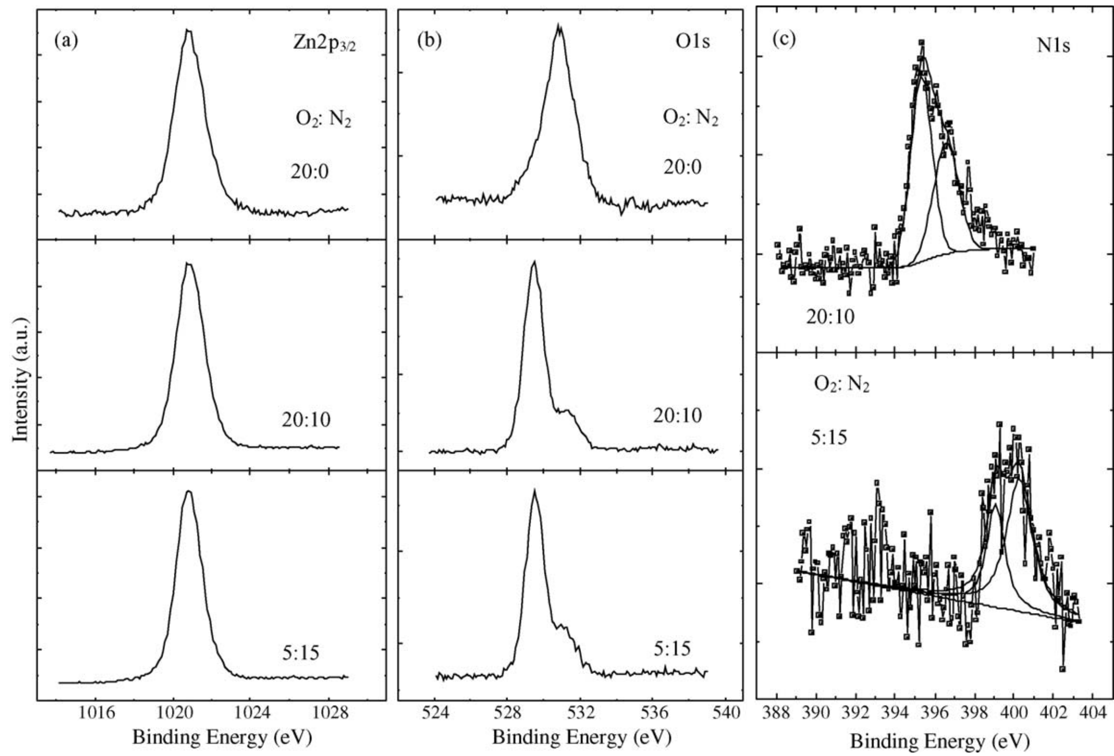

Fig. 3. XPS spectra of: (a) $Zn2p_{3/2}$, and (b) O1s of undoped (O_2:N_2 = 20:0 sccm), lightly N-doped (20:10), and heavily N-doped (5:15) ZnO films on Si substrate; (c) XPS spectra of N1s of lightly N-doped (20:10) and heavily N-doped (5:15) ZnO films on Si substrate.

[7] X.B. Tian, R.K.Y. Fu, P.K. Chu, J. Vac. Sci. Technol. A 20 (2002) 160.
[8] D.T.K. Kwok, T. Zhang, P.K. Chu, M.M.M. Bilek, A. Vizir, I.G. Brown, Appl. Phys. Lett. 78 (2001) 422.
[9] D.C. Look, J.W. Hemsky, J.R. Sizelove, Phys. Rev. Lett. 82 (1999) 2552.
[10] Y. Yan, S.B. Zhang, Phys. Rev. Lett. 86 (2001) 5723.
[11] L.G. Wang, A. Zunger, Phys. Rev. Lett. 90 (2003) 256401.
[12] E.C. Lee, Y.S. Kim, Y.G. Jin, K.J. Chang, Phys. Rev. B 64 (2001) 85120.
[13] D.C. Look, C. Coskun, B. Claflin, G.C. Farlow, Physica B 340–342 (2003) 32.
[14] C.H. Park, S.B. Zhang, S.H. Wei, Phys. Rev. B 66 (2002) 73202.
[15] Y.Z. Yoo, T. Sekiguchi, T. Chikyow, M. Kawasaki, T. Onuma, S.F. Chichibu, J.H. Song, H. Koinuma, Appl. Phys. Lett. 84 (2004) 502.
[16] H.C. Ong, A.S.K. Li, G.T. Du, Appl. Phys. Lett. 78 (2001) 2667.
[17] X.L. Wu, G.G. Siu, C.L. Fu, H.C. Ong, Appl. Phys. Lett. 78 (2001) 2285.
[18] C.D. Wagner, W.M. Riggs, L.E. Davis, J.E. Moulder, G.E. Muilenber, Handbook of X-ray Photoelectron Spectroscopy, Perkin-Elmer Corporation Physical Electronics Division, USA, 1979.
[19] H. Maki, I. Sakaguchi, N. Ohashi, S. Sekiguchi, H. Haneda, J. Tanaka, N. Ichinose, Jpn. J. Appl. Phys. Part I 42 (2003) 75.
[20] I.J. Lee, J.Y. Kim, H.J. Shin, H.K. Kim, J. Appl. Phys. 95 (2004) 5543.
[21] M. Losurdo, D. Giuva, G. Bruno, S. Huang, T.H. Kim, A.S. Brown, J. Cryst. Growth 264 (2004) 139.