



Determination of nitrogen-related defects in N-implanted ZnO films by dynamic cathodoluminescence

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Abstract

Visible bands arising from N-related defects are investigated by dynamic cathodoluminescence (CL) and Gaussian deconvolution. The intensity of the red band increases while that of the ultraviolet (UV) band decreases. The intensity of the yellow band also decreases but only slightly as a function of the electron bombardment cycle. The CL behavior of N-doped ZnO after post-annealing in N₂ at high temperature reveals that the N-related defects cannot be easily compensated. The results also confirm the assignment of the N-related defects and are in agreement with the theoretical prediction about Zn–N bonding. Our data provide some clues to the mechanism of the conversion of ZnO into *p*-type by nitrogen doping.

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1. Introduction

Zinc oxide (ZnO) possesses many interesting properties [1] which have attracted much interest for its potential application. Reliable fabrication

of both high-quality *p*-type and *n*-type ZnO films is a prerequisite for their commercial applications in optoelectronic devices [2–5]. So far, fabrication of *n*-type ZnO is relatively straightforward [6] but the same cannot be said about *p*-type ZnO because of the asymmetric doping limitation [2] that can be attributed to certain native point defects [6–8] such as O vacancies, Zn interstitials, or hydrogen. Another reason for the difficulty to perform *p*-type doping in ZnO is the low N-solubility and

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metastable Zn–N bonding [3]. A possible solution is the use of co-doping or an efficient nitrogen source, but the mechanism is not well understood.

First-principle calculations on N-doped ZnO suggest an overtime “invalidation” behavior of the *p*-type dopant according to the local bonding environment [3]. However, there has been no direct evidence on the conversion. It is due to the difficulty in fabricating *p*-type ZnO itself and the existence of unidentified defects in the materials regardless of the crystal structure. Cathodoluminescence (CL) is a useful method to investigate defects in compounds such as ZnO and GaN by measuring the spatial distribution with emission wavelength and intensity [9,10].

Using plasma immersion ion implantation and deposition (PIII&D), ZnO thin films were previously produced and doped with nitrogen [11,12]. However, no *p*-type ZnO was formed using N₂ as the plasma source and it is believed to be due to defects and low solubility of N in the materials. Further investigation of the CL spectra showed unstable N–on–O substitution (Zn–N bonding) [12]. In this work, we study the origin of the problem by studying the visible band responsible for the N-related defects using dynamic CL and Gaussian deconvolution. The CL behavior of the N-implanted ZnO after post-annealing in N₂ ambient at high temperature reveals that the N-related defects cannot be easily compensated. Our exploration provides some clues about the possible path to form *p*-type ZnO via N implantation.

2. Experimental

The substrates were *p*-type (100) 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^{-5} Torr [13–15]. A mixture of gases was bled into the vacuum chamber at various flow ratios [flow rate (O₂:N₂, sccm):20:10 (lightly N-doped); 5:15 (heavily N-doped); working pressure: $\sim 1.0 \times 10^{-3}$ Torr] 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. After nitrogen PIII, the samples were analyzed in a scanning electron microscope (SEM) equipped with an Oxford Instrument Mono CL system at room temperature [9].

3. Results and discussion

In the heavily N-doped ZnO film, the intensity of the ultraviolet (UV) band decreases and that of the visible band increases as a function of electron bombardment time in CL, as shown in Fig. 1. Based on the CL behavior and X-ray photoelectron spectroscopy analysis (not shown here), the existence of unstable Zn–N bonds agrees well with the first-principle calculations [3,12]. It is well known that the visible bands in CL of ZnO originate from several defects that are quite complex [9]. Since there exist visible bands for normal defects in ZnO and their CL intensities generally decrease with electron bombardment [9,12], it can be deduced that the visible band in our heavily N-doped ZnO film should include two kinds of emission centers: normal defects in ZnO and abnormal

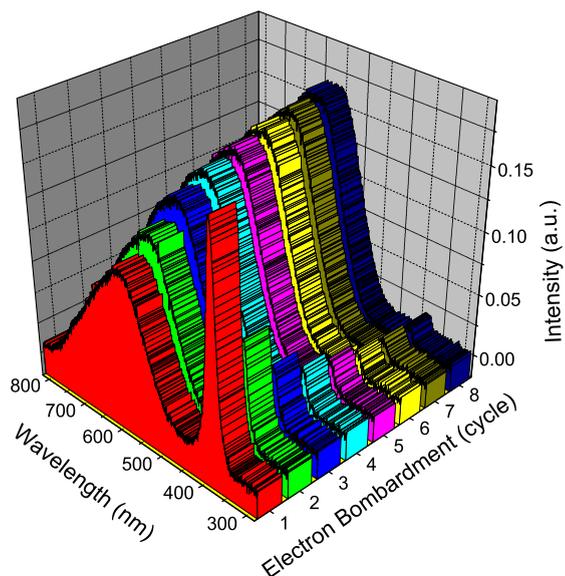


Fig. 1. Cathodoluminescence spectra acquired from heavily N-doped (5:15) ZnO films on Si substrate as a function of electron bombardment cycle.

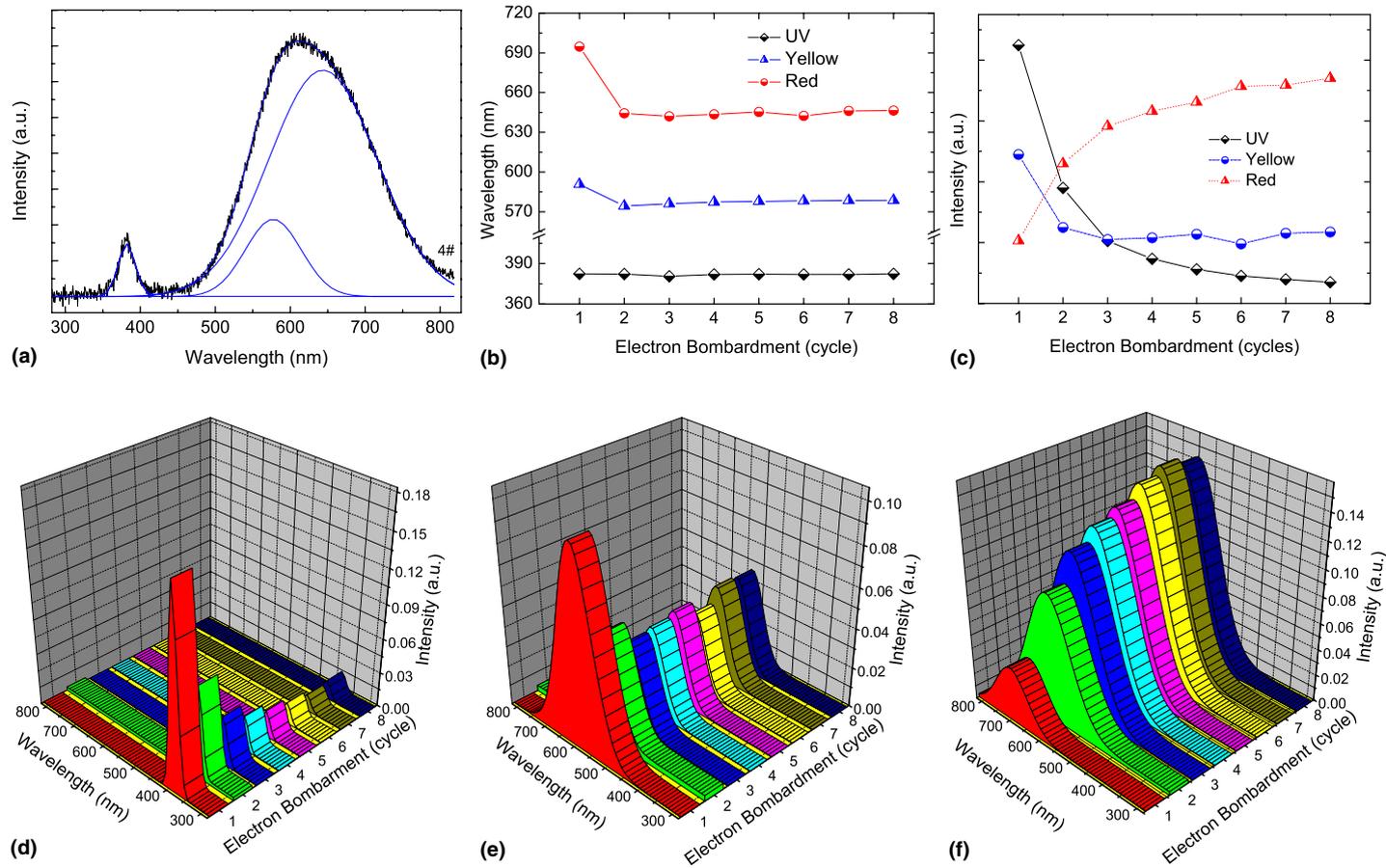


Fig. 2. (a) Cathodoluminescence spectrum of heavily N-doped (5:15) ZnO films on Si substrate at cycle 4 of electron bombardments; (b) peak shifts; (c) intensities of ultraviolet, yellow, and red bands as a function of electron bombardment cycle; Cathodoluminescence spectra of (d) ultraviolet, (e) yellow, and (f) red bands after Gaussian deconvolution as a function of electron bombardment cycle.

center for the unexpected CL characteristic (increase in the visible range). The visible part of CL spectra are deconvoluted and shown in Fig. 2(a). Two bands, yellow (~ 570 nm) and red (~ 640 nm), can be observed at cycle #4 of electron bombardment. In Fig. 2(b), each visible band shows very little shifts except that at first cycle. We believe that it is due to surface defects such as V-shaped defects [16], thermal annealing effects due to electron bombardment which can weaken or enhance some normal defects, or impurities [17], and more work is being conducted in our laboratory to further investigate this issue.

As shown in Fig. 2(c), (d), and (e), the intensities of the ultraviolet (UV) and yellow bands diminish as function of the electron bombardment cycle, while that of the red band increases. The change of the yellow band [Fig. 2(e)] is consistent with previous results and our CL spectra acquired from the undoped ZnO control (not shown here). However, the intensities of the UV and red bands change quite unexpectedly and rapidly (Fig. 2(d) and (f)). As our XPS results suggest, it may be due to unstable Zn–N bonds. In Wang's work [3], first-principle calculations on p-type doping of ZnO reveal that doping ZnO by N₂ leads to $\Delta E_b > 0$ for N–Zn₄ (ΔE_b : the excess bond energy). ΔE_b is about 1.15 eV by first-principle calculation which implies unstable Zn–N bonds. After electron bombardment, the nitrogen in Zn–N is released and then N-related defects (possibly vacancy) are formed as indicated by the increase in the intensity of the red band. The intensity of the UV band decreases due to the destruction of the ZnO crystalline structure. Hence, we can assign the UV band to be free exciton, the yellow band to normal defects, and the red band to N-related defects. Our dynamic CL spectra thus provide experimental evidence for unstable N–on–O substitution (Zn–N bonding) and N-related defects in N-doped ZnO.

Our XPS results [12] show that different N bonds exist in lightly and heavily N-doped ZnO films. In order to confirm the assignment of bonding and N-related defects, both samples were annealed in N₂ (99%) ambient at 800 °C for 1 h and subsequently checked by CL measurement. Their CL spectra are shown in Fig. 3. In the lightly N-doped ZnO film, the CL behavior is similar to

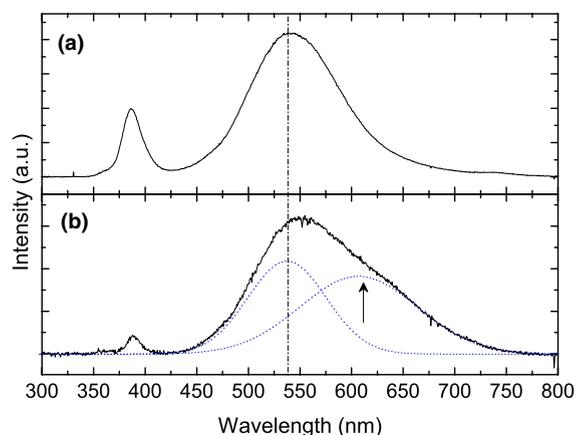


Fig. 3. Cathodoluminescence spectra of (a) lightly and (b) heavily N-doped ZnO films after post-annealing in N₂ ambient at 800 °C for 1 h.

that of the undoped ZnO film, whereas in the heavily N-doped ZnO film, the CL spectrum in the visible range exhibits a shoulder peak (~ 610 nm) after Gaussian deconvolution that is related to nitrogen. Our results thus indicate that N-related defects cannot be compensated by annealing in N₂ ambient, the phenomenon is consistent with $\Delta E_b > 0$ for N–Zn₄ [3], and the formation of Zn–N bond is difficult by annealing.

4. Conclusion

Visible bands responsible for N-related defects were identified by dynamic CL and Gaussian deconvolution. The intensity change in the red band is completely different from that of the UV and yellow bands during electron bombardment. The CL behavior of N-doped ZnO after post-annealing in N₂ ambient at high temperature reveals that N-related defects cannot be easily compensated thereby confirming the assignment of N-related defects. Our results provide some clues on the possible use of N-doping to produce p-type ZnO.

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References

- [1] B.K. Meyer, H. Alves, D.M. Hofmann, W. Kriegseis, D. Forster, F. Bertram, J. Christen, A. Hoffmann, M. Straburg, M. Dworzak, U. Haboek, A.V. Rodina, *Phys. Stat. Sol. (b)* 241 (2004) 231.
- [2] Y. Yan, S.B. Zhang, *Phys. Rev. Lett.* 86 (2001) 5723.
- [3] L.G. Wang, A. Zunger, *Phys. Rev. Lett.* 90 (2003) 256401.
- [4] E.C. Lee, Y.S. Kim, Y.G. Jin, K.J. Chang, *Phys. Rev. B* 64 (2001) 85120.
- [5] D.C. Look, C. Coskun, B. Clafin, G.C. Farlow, *Physica B* 340–342 (2003) 32.
- [6] D.C. Look, J.W. Hemsky, J.R. Sizelove, *Phys. Rev. Lett.* 82 (1999) 2552.
- [7] S.B. Zhang, S.H. Wei, A. Zunger, *Phys. Rev. B* 63 (2001) 75205.
- [8] C.G. Van de Walle, *Phys. Rev. Lett.* 85 (2000) 1012.
- [9] H.C. Ong, A.S.K. Li, G.T. Du, *Appl. Phys. Lett.* 78 (2001) 2667.
- [10] T. Nobis, E.M. Kaidashev, A. Rahm, M. Lorenz, M. Grundmann, *Phys. Rev. Lett.* 93 (2004) 103903.
- [11] Y.F. Mei, R.K.Y. Fu, G.G. Siu, P.K. Chu, Z.M. Li, C.L. Yang, W.K. Ge, Z.K. Tang, W.Y. Cheung, S.P. Wong, *Materials Science in Semiconductor Processing*, (in press).
- [12] Y.F. Mei, Ricky K.Y. Fu, G.G. Siu, K.W. Wong, Paul K. Chu, C.W. Lai, H.C. Ong, *Appl. Phys. Lett.* (submitted).
- [13] P.K. Chu, S. Qin, C. Chan, N.W. Cheung, L.A. Larson, *Mat. Sci. Engin.: Reports* 17 (6–7) (1996) 207.
- [14] P.K. Chu, B.Y. Tang, Y.C. Cheng, P.K. Ko, *Rev. Sci. Instrum.* 68 (1997) 1866.
- [15] P.K. Chu, B.Y. Tang, L.P. Wang, X.F. Wang, S.Y. Wang, N. Huang, *Rev. Sci. Instrum.* 72 (2001) 1660.
- [16] 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.
- [17] F. Bertram, D. Forster, J. Christen, N. Oleynik, A. Dadgar, A. Krost, *Appl. Phys. Lett.* 85 (2004) 1976.