

Chemical states of nitrogen in ZnO studied by near-edge X-ray absorption fine structure and core-level photoemission spectroscopies

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Abstract

Interaction of low-energy nitrogen ions with ZnO surface has been studied by photoemission spectroscopy (PES) around N 1s core-level and near-edge X-ray absorption fine structure (NEXAFS) around N K-edge. Nitrogen can break Zn–O bonds at the surface and form N–O, Zn–N or Zn–N–O bonds, characterised by specific chemical shifts in PES or absorption peaks in NEXAFS. A distinctive signal from molecular nitrogen has also been observed in ion-bombarded samples in both NEXAFS and PES.

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Zinc oxide (ZnO) is potentially an ideal material for the new generation of blue and ultraviolet light-emitting devices due to its direct band-gap of 3.37 eV and a large exciton binding energy of 60 meV at room temperature [1]. To fully realise this potential of ZnO, it is essential to fabricate a good quality and stable n- and p-type material [2]. However, like most wide band-gap semiconductors, as-grown ZnO is naturally n-type and it is quite difficult to dope it p-type [3].

Nitrogen, a well known p-type dopant in several II–VI materials, has long been considered as the most promising dopant for p-type ZnO [4]. However, a strong compensa-

tion mechanism for N-acceptors in ZnO, most probably by the native donor defects or N-related defects, such as molecular nitrogen on oxygen site, (N₂)_O [5], prevents successful fabrication of stable p-ZnO using a pure nitrogen source.

Recently, it has been demonstrated that p-type doping can be produced by cluster-doping approach using few dopant species that apparently increases the solubility of N in ZnO and stabilises N-atoms on appropriate oxygen sites [6,7]. In addition, the importance of the chemical potential of molecules from different dopant gases used during growth of ZnO has been recognised, as only molecules, such as NO or NO₂, that supply single nitrogen atoms have been shown to produce desirable acceptor-like defects in ZnO [7,8].

On the other hand, controllable electrical doping of ZnO with nitrogen can be achieved by ion implantation [9,10]. Indeed, it has been shown recently that nitrogen-implanted

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ZnO films deposited on Si substrate represent good candidates for a stable and reproducible p-type material [11].

Doping by ion implantation introduces a number of lattice defects that often produce undesirable effects on the properties of the material. While there are many studies on ion-beam-produced lattice defects in ZnO [9,12], little attention has been paid to the reaction of implanted nitrogen with host atoms and the formation of different N-related defect states.

In this Letter we report on the characterisation of nitrogen states introduced into ZnO by low-energy N_2^+ bombardment. We have employed both core-level photoemission spectroscopy (PES) and near-edge X-ray absorption fine structure (NEXAFS) spectroscopy, using synchrotron radiation, to identify these states.

The ZnO samples used in this study were grown by plasma assisted molecular beam epitaxy on *a*-plane sapphire substrates. The samples were ~ 700 nm thick, with a nominal carrier concentration of $\sim 3 \times 10^{17} \text{ cm}^{-3}$ at room temperature and RMS roughness of 0.42 nm.

All measurements were performed in a UHV chamber attached to the 2B1 beam line of the Pohang Light Source, equipped with a hemispherical electron analyser (Gamma-data SES 100) for photoemission measurements and a low-energy ion-gun for sample bombardment with low-energy ions at normal incidence. The surfaces of the as-grown ZnO samples were first cleaned in situ by low-energy argon bombardment, to remove surface contamination (C and O, as confirmed by synchrotron-based XPS), and then bombarded with N_2^+ ions of different energies within the 0.3–2 keV range.

Photoemission was taken around the N 1s core-level, while NEXAFS spectra were recorded in the total electron yield (TEY) mode around the N K-edge. The photon energy scale was calibrated against the Au $4f_{7/2}$ peak at 84 eV from a clean gold film in electrical contact with the ZnO samples. The photon impact angle used for all NEXAFS measurements was 25° , measured from the normal to the sample surface.

In Fig. 1 we show normalised photoemission spectra from the N 1s core-level taken by 650 eV photons from surfaces bombarded with 0.3 keV and 2 keV N_2^+ for 30 min. The N 1s emission spectra (full circles in Fig. 1) were fitted numerically with mixed Gaussian–Laurentian functions [13] with peak energies (see Table 1) of 396.4 eV (curve A), 397.8 eV (curve B), 399.5 eV (curve C) and 403 eV (curve D). An additional curve at 406.0 eV (curve E) was used to achieve the best fit for the emission spectrum from the surface bombarded with 0.3 keV ions.

The third spectrum in Fig. 1 represents the N 1s emission from the sample bombarded with 2 keV N_2^+ and then annealed in situ for 1 h at $\sim 400^\circ\text{C}$. Upon annealing, the N 1s emission is greatly reduced (note the magnification factor of 100 for this spectrum in Fig. 1) due to the loss of nitrogen from the surface at elevated temperatures. Further, the lower binding energy component A almost completely disappears after annealing, indicating that the

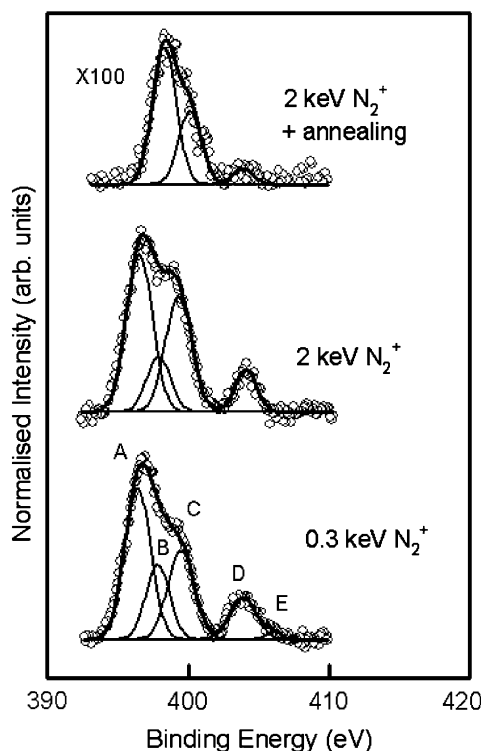


Fig. 1. N 1s core-level photoemission spectra (full circles) obtained from ZnO surfaces bombarded with 0.3 and 2 keV N_2^+ ions for 30 min and after annealing at 400°C for 1 h. Solid lines are numerical fits of experimental curves.

Table 1
The position and assignment of fitting curves for the N 1s emission spectra of ion-bombarded ZnO

Photoemission peaks	Peak position (eV)	Assignment
A	396.4	Zn–N bonds (N _O)
B	397.8	N–H bonds
C	399.5	N–N bonds
D	403.9	NO ₂
E	406.0	N ₂ O

N-related bonds associated with emission A, B and C have quite different stability. Finally, the intensity of component D and the relative ratio, D/B, is also greatly reduced upon annealing.

To further investigate the nature of the nitride phases formed on nitrogen-bombarded ZnO surfaces, we have undertaken NEXAFS measurements around the N K-edge on all bombarded and annealed samples. In Fig. 2 we plot typical NEXAFS spectra, recorded in the TEY mode around the nitrogen K-edge, from the same ZnO surfaces as in Fig. 1. All NEXAFS spectra were deconvoluted into several Gaussians to simulate different resonant electron transitions from the N 1s initial state to the final N-related states of p-symmetry [14] and to determine the peak posi-

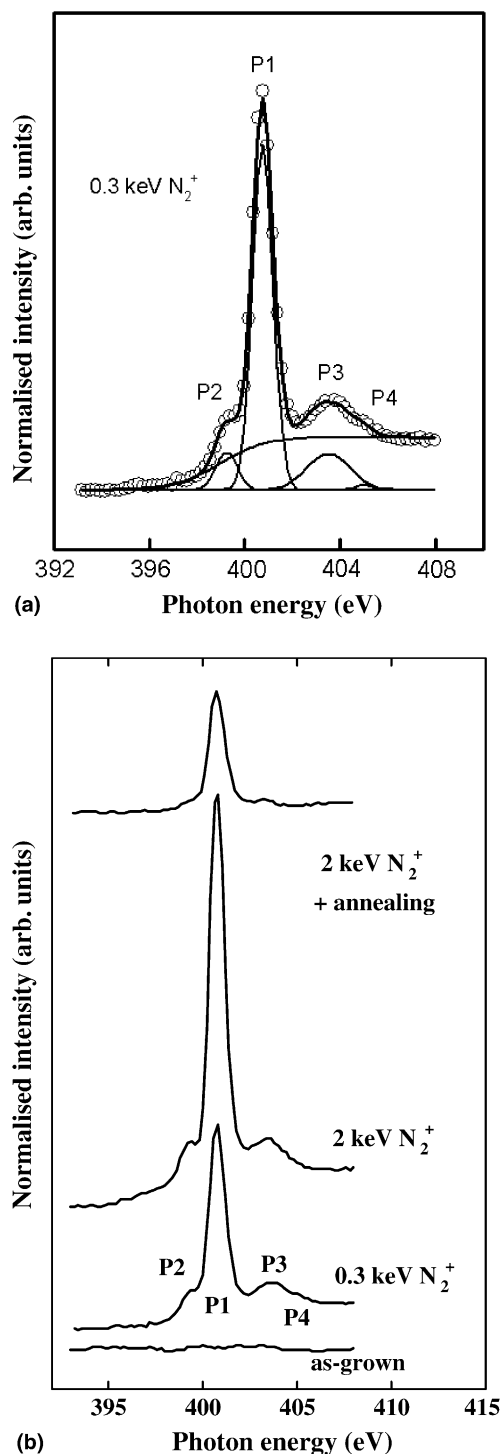


Fig. 2. N K-edge NEXAFS spectra from ZnO surfaces (a) bombarded with 0.3 keV N_2^+ ions (thin solid line is a numerical fit of experimental curve), and (b) from the same samples as in Fig. 1.

tion for these transitions, as show in Fig. 2a for the 0.3 keV bombardment.

We first note that all spectra in Fig. 2 are dominated by a strong resonant peak P1 at 400.7 eV. A similar sharp resonance, close to the position of resonance P1, has been observed previously on many different surfaces, such as CrN

[15], InSb and InAs [16] or GaN [13], irradiated with nitrogen. This resonance has been associated with the characteristic N 1s – π^* transition in molecular nitrogen that is characterised by an intense peak around 400.8 eV [14]. Therefore, we argue that the resonance P1 observed in our measurements is indeed a signature of molecular nitrogen produced in ZnO by nitrogen bombardment. Indeed, our recent high-resolution NEXAFS measurements of P1 in nitrogen-bombarded ZnO [17] have clearly shown the vibrational fine structure of molecular nitrogen.

We further note that the strong N_2 -related resonance may prevent detection of some metal-N-related bonds in NEXAFS measurements around the N K-edge. Namely, NEXAFS of transition metal nitrides, MN (M = Ti, Zr, Cr, Ta, Ni, Cu), consists of several peaks around the N K-edge [18], assigned to the excitation of N 1s electrons to the hybridised molecular orbitals of MN. The features at lower photon energy (399–401 eV), corresponding to the transitions involving hybridized N 2p and M 3d orbitals, may be completely masked by the strong resonance P1 [18].

Extending the above arguments to nitrogen-bombarded ZnO (to our knowledge, there is no NEXAFS data on ZnN or nitrogen-bombarded ZnO in the literature) one can assign the shoulder P2 in Fig. 2 to the transition involving (Zn3d + $N2p\pi$) orbitals [15,18]. The transition involving (Zn3d + $N2p\sigma$) orbitals most likely overlaps with P1 as in the case of other transition metal nitrides [18] and it cannot be resolved from the NEXAFS spectrum in Fig. 2a.

We should also consider the formation of different N–O bonds in nitrogen bombarded ZnO that may contribute to the NEXAFS structure. Indeed, the positions of resonances P2, P3 and P4 in Fig. 2 are very close to the characteristic absorption peaks of several nitrogen oxides from metal surfaces (see Table 2). For example, the NO_2 molecule exhibits a strong absorption peak at 403.2 eV for the $1s-2b_1$ transition [19], while the N_2O molecule shows a resonance at 404.7 eV for the $1s-3\pi^*$ transition [20]. These energies are close to the position of peaks P3 (403.5 eV) and P4 (404.9 eV), respectively, from Fig. 2. On the other hand, the position of P2 (399.3 eV) in Fig. 2 is close to the absorption energy of NO molecule (399.7 eV for the $1s-2p\pi^*$ transition) [21].

We argue, therefore, that bombardment of ZnO surface with nitrogen ions may produce several different nitrides and oxides, in addition to molecular nitrogen, by breaking Zn–O bonds at the surface and forming Zn–N, O–N or Zn–N–O bonds.

Turning now back to Fig. 1, we first note that peak A has a binding energy very close to that observed for Zn–N bonds in zinc oxynitride films [22] or for chemisorbed nitrogen on different metal surfaces, which lies in the range 396–397 eV [15,23,24]. This similarity indicates the formation of Zn–N bonds at the surface of nitrogen bombarded ZnO that corresponds to nitrogen substitution on the oxygen sublattice (N_O). Further, a double-peak structure of N 1s at energies similar to the position of peaks A and B in

Table 2

Comparison of the energy position of characteristic features of the N K-edge in ion-bombarded ZnO with the characteristic absorption peaks of several N-related molecules from the literature

NEXAFS peaks	Peak position (eV)	Absorption peaks of N-related molecules on metal surfaces			
		N ₂ (1s– π^*) [Ref. [14]]	NO (1s–2p π^*) [Ref. [19]]	NO ₂ (1s–2b1) [Ref. [17]]	N ₂ O (1s–3 π^*) [Ref. [18]]
P1	400.7	400.8			
P2	399.3		399.7		
P3	403.5			403.2	
P4	404.9				404.7

Fig. 1 has been observed previously from surfaces of MOCVD-grown ZnO:N films [24] and surfaces of zinc oxynitride films [22]. The former observation was related to the formation of N–C bonds (MOCVD films may contain a large bulk concentration of C) [24] and the latter to N–H bonds [22], chemically shifted from the dominant Zn–N peak. As the level of carbon is negligible in our MBE-grown samples, the peak B in Fig. 1 may be related to the formation of N–H bonds at the surface.

The position of peak C in Fig. 1 corresponds to the N 1s emission observed previously in several compound materials, such as GaN, and identified as originating from N dangling bonds or N–N bonds [13,25]. The intensity of peak C increases at higher bombardment energy, while, upon annealing, it becomes significantly lower. The same trend is observed for the NEXAFS resonance P1 in Fig. 2b that has been assigned to the N 1s – π^* transition in molecular nitrogen. Therefore, we associate the photoemission peak C with the NEXAFS peak P1 and assigned both peaks to molecular nitrogen formed in ZnO during nitrogen bombardment.

Following further the qualitative similarities between NEXAFS and PES peaks we note that the intensity of NEXAFS peak P3 in Fig. 2, associated with NO₂ molecules, does not change significantly with the bombardment energy, but is strongly reduced upon annealing. The same qualitative behaviour is observed for the PES peak D in Fig. 1. Finally, NEXAFS peak P4, assigned to absorption in N₂O molecule, and PES peak E are clearly visible only from the surface bombarded with 0.3 keV ions. Consequently, we associate peaks D and E to nitrogen oxides, NO₂ and N₂O, respectively. Again, the N 1s peak at similar energy as peak D in Fig. 1 has been observed previously on Cr and Fe surfaces, implanted with nitrogen at different oxygen partial pressures, and associated with the formation of NO₂ molecules [26].

In conclusion, low-energy nitrogen bombardment of ZnO may break Zn–O bonds at the surface and produce nitrogen species of different stabilities, including several nitrogen oxides and/or oxynitrides and molecular nitrogen. The existence of molecular nitrogen in ZnO may have an important implication on the type of conductivity in ZnO. Namely, a possible formation of molecular nitrogen on oxygen sites, (N₂)_O and/or formation of N₂–N_{acceptor}

complexes may greatly compensate nitrogen acceptors and suppress p-type conductivity in ZnO [5].

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