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Local chemical states and thermal stabilities of nitrogen dopants in ZnO film studied by temperature-dependent x-ray photoelectron spectroscopy

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Local chemical states and thermal stabilities of N dopants in ZnO:N film are investigated by temperature-dependent x-ray photoelectron spectroscopy. Different types of N local states are detected, including N_2 molecules occupying O sites $[(N_2)_O]$, –NO species, substitutional N atoms in O- and N-rich local environments (α- and β-N_O). Compared to the β-N_O, the α-N_O shows a better thermal stability up to 723 K. However, the transformation from α-N_O acceptor to undesirable $(N_2)_O$ donor occurs above 743 K. The variation of N local states also affects Zn and O binding energies. Photoluminescence studies indicate the shallow acceptor nature of α-N_O. © *2009 American Institute of Physics*. [doi:10.1063/1.3259644]

With a wide band gap of 3.37 eV and a large exciton binding energy of 60 meV, ZnO is currently attracting great interests for its potential applications in short-wavelength optoelectronic devices. The greatest challenge for practical device applications, however, remains the fabrication of stable and high quality p-type ZnO, due to its asymmetric doping limitation. Nitrogen (N) is considered as one of the most promising p-type dopants. Though the homojunction light-emitting diodes based on p-type N-doped ZnO (p-ZnO:N) have been demonstrated by several groups,[1–4] their high performance is difficult to achieve, due to strong self-compensation effect, low solubility of N acceptors, and high defect densities in p-ZnO:N. On the other hand, the p-type conduction of ZnO:N films suffers from the problem of instability. For example, our group has observed that the ZnO:N film undergoes a classic-mixed conductivity transition from p type to n type when it is irradiated by 2.72 eV photons.[5] Generally, the changes in local structures of N dopants and complex defects play an important role in the instability of p-ZnO:N.

To solve the difficulty of p-type N doping, it is fundamentally important to study the local chemical states of N dopants in ZnO:N films, and their thermal stability. X-ray photoelectron spectroscopy (XPS) is a sensitive technique to probe the chemical states of compounds. The XPS studies have indicated the presence of various complicated N local states in ZnO:N films, such as substitutional N atoms and N_2 molecules on O sites [N_O and $(N_2)_O$], N–O, N–H, C–N complexes, etc. Their binding energies cover a wide range from ~395 to 410 eV. However, the assignment of N_O related XPS peak is still somewhat controversial. More importantly, few reports are available on their thermal stabilities, which is crucial for the high-temperature operations of ZnO based optoelectronic devices. In this work, we have studied the local chemical states and the thermal stabilities of N dopants in ZnO:N films by *in situ* temperature-dependent XPS in the range of 297–823 K. Four different types of N local states were observed, and their evolutions depend strongly on the heating temperatures.

The ZnO:N film was epitaxially grown on c-plane sapphire by plasma-assisted molecular beam epitaxy (MBE). NO plasma was employed as N-doping source, and the substrate temperature is 698 K. The detailed growth process was described in our previous report.[6] XPS measurements were performed in the temperature range of 297–823 K, using a VG ESCALAB MK-II system with an Al $K\alpha$ (1486.6 eV) radiation source. Prior to XPS measurements, the sample surface was cleaned by Ar^+ ion bombardment, which significantly enhanced the N 1s signals. The binding energy scale was calibrated using the C 1s line at 284.6 eV. The photoluminescence (PL) spectra of ZnO:N films were collected with a Jobin-Yvon HR800 micro-Raman spectrometer. A 325 nm line of a He–Cd laser was used as the excitation source.

Figure 1 shows the N 1s core-level XPS spectra of the ZnO:N film measured in the temperature range of 297–643 K (a) and 723–823 K (b), respectively. Three peaks around 396, 398, and 400 eV were detected at room temperature. Table I lists the N 1s binding energies and their possible assignments reported in some literatures. The ~400 eV peak is believed to originate from -NO species due to the introduction of NO plasma during film growth. However, the origins of ~396 and ~398 eV peaks are controversial. Both are ascribed to the N_O acceptor by different researchers. In fact, the inconsistent assignments can be understood if we consider the differences in local environments of the N_O. Figure 2(a) displays a local lattice structure in ZnO:N. The central N_O atom is bonded to four Zn atoms, and both N and O atoms are randomly distributed on other anion sites. Two extreme situations are that most of them are occupied by N

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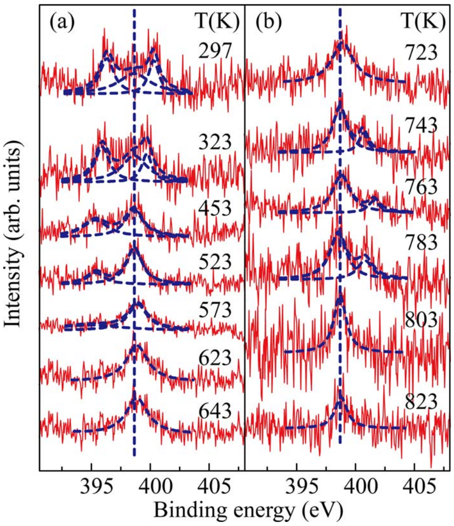

FIG. 1. (Color online) N 1s core-level XPS spectra of ZnO:N film in the temperature range of (a) 297–643 K and (b) 723–823 K. The dash lines show the fitted peaks by Lorentz functions.

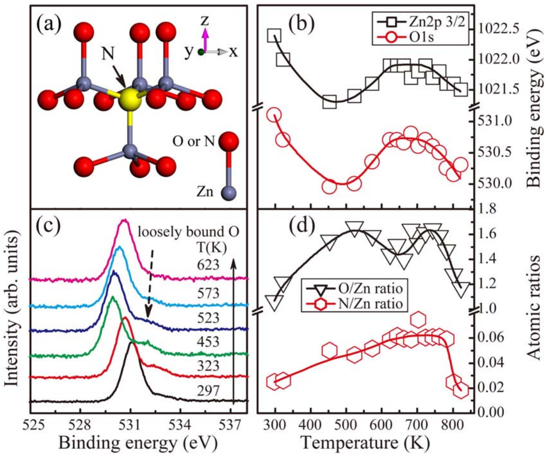

FIG. 2. (Color online) (a) A local atomic configuration in ZnO:N lattice; (b) Zn $2p_{3/2}$ and O 1s binding energies as a function of temperature in the range from 297 to 823 K (see Ref. 21); (c) O 1s core-level XPS spectra in the temperature range of 297–623 K; (d) the atomic ratios of O/Zn and N/Zn as a function of temperature in the range from 297 to 823 K.

or O atoms, which correspond to the N- or O-rich local environment, respectively. The difference in local environments can cause the shift of the N_O binding energy. Because the O^{2-} ions have stronger attraction to electrons from the Zn cores than the N^{3-} ions, the electron screening effect of the N_O located in O-rich environment is weaker than that in N-rich environment. Thus, the N 1s has a larger binding energy in the former than in the later. Based on the above discussion, we tentatively assign the peaks at ~398 and ~396 eV to the N_O in O- and N-rich local environments (α- and β-N_O), respectively. In fact, the 396 eV peak is usually observed in heavily N-doped ZnO,[7–11] and its position is very close to the binding energy of N–Zn bond in Zn_3N_2 (395.8 eV).[12] These reported results further support our assignments. Moreover, theoretical and experimental studies have indicated a high probability of introducing hydrogen impurities into ZnO:N films during growth. The N_O acceptors can be passivated by forming neutral N–H complexes. Some researchers have used Raman and infrared spectra to judge their presence, where a signal around 3100 cm^{-1} is thought to arise from N–H vibrations.[18–20] However, this characteristic signal is absent in our Raman studies (not shown here), suggesting that the hydrogen concentration may be very low, and even negligible in our MBE-grown ZnO:N films. Thus, the N–H component is not considered in our XPS studies.

The α- and β-N_O exhibit different thermal stabilities. As shown in Fig. 1, the ~396 eV peak loses its intensity rapidly with increasing temperatures, and disappears at 573 K. The poor stability of the β-N_O may be associated with its unstable Zn_3N_2-like microstructure. Similar observation has also been reported in Ref. 8. In contrast, the ~398 eV peak dominates all the XPS spectra measured at 453–823 K. When the temperature reaches to 743 K, a new XPS peak appears at about 402 eV, which is usually attributed to the $(N_2)_O$ molecules. The appearance of this peak implies that a part of α-N_O acceptors start to transform into the undesirable $(N_2)_O$ donors, due to the thermal diffusion of α-N_O. That is, the α-N_O is stable up to 723 K. This temperature is close to the optimized growth temperature (698 K) of the ZnO:N film. The relatively good thermal stability of the α-N_O acceptor is beneficial for high-temperature applications of p-ZnO:N films.

TABLE I. The reported assignments of N 1s peaks

N 1s (eV)	Assignment
~396	N–Zn bond or N_O (Refs. 7–11), polarized triply bounded C–N (Ref. 15), N–O (Ref. 16)
~398	N–Zn bond or N_O (Refs. 2 and 13–17), C–N species (Ref. 7), N–H (Refs. 9 and 10)
~400	C–N species (Refs. 7, 10, and 15), N–H (Refs. 13–15), oxynitride (Ref. 8)
~404	$(N_2)_O$ (Refs. 7, 10, 14, and 15), nitrite (Refs. 2 and 8)

The Zn $2p_{3/2}$ and O 1s binding energies are plotted in Fig. 2(b) as a function of temperature in the range from 297 to 823 K. Both exhibit similar temperature dependence. With increasing temperature, their binding energies show a red-blue-red shift. Such a behavior is thought to be related to the instability of N dopants and the variation of the carrier concentration. As discussed above, as the temperature increases from 297 to 523 K, the unstable β-N_O atoms gradually depart from their lattice sites, leaving large amounts of donor-type anion vacancies. The increase in electron concentration can lead to the enhancement of the electron screening effect. Thus, the Zn and O binding energies decrease. Moreover, we also note in Fig. 2(c) that with increasing temperature, a shoulder peak at ~532.5 eV increases in intensity relative to the O 1s main peak, and disappears above 573 K. This shoulder is usually assigned to the loosely bound oxygen. Its appearance suggests that some oxygen atoms also diffuse out from ZnO lattice, and adsorb on the grain boundaries and the film surface. This process partly contributes to the increase of electron concentration and the decrease of Zn and O binding energies. The out-diffusion of β-N_O and O atoms can also be confirmed by quantitative analysis of surface compositions. As shown in Fig. 2(d), the surface atomic ratios of both N/Zn and O/Zn increase with temperature up to 523 K, indirectly suggesting a decrease in N and O atoms inside the ZnO:N film. It is known that the ionization energy of N

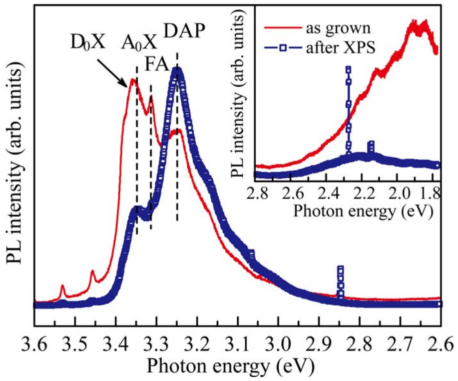

FIG. 3. (Color online) Low-temperature PL spectra of ZnO:N film before and after undergoing temperature-dependent XPS measurements in the energy range of 3.6–2.6 eV. Inset shows the enlarged spectra in the range of 2.8–1.76 eV.

acceptor is 120–200 meV in ZnO.[6] As the temperature is further elevated, more and more N acceptors are ionized, and compensate the native donors. The reduction of electron concentration causes the blueshift of Zn and O binding energies. When the temperature exceeds 723 K, the redshift of binding energies occurs again as a result of the formation of $(N_2)_O$ donors and the removal of α-N_O acceptors. Moreover, the N/Zn atomic ratio decreases rapidly above 783 K, suggesting the escape of N atoms from the film surface. Below this temperature, only the changes of N local structures, as well as the diffusion of N atoms, occur inside the ZnO:N film. This result is consistent with the report by Wang *et al.*[10]

To investigate the effects of N local states on the optical properties of ZnO:N film, we have compared the PL spectra of the film before and after undergoing XPS measurements (see Fig. 3). For as-grown ZnO:N film, the peaks at 3.363, 3.348, 3.313, and 3.250 eV correspond to the neutral donor- and acceptor-bound exciton emissions (D_0X and A_0X), free electron to acceptor (FA), and donor-acceptor pair (DAP) recombinations, respectively.[6] After a high-temperature thermal treatment, the DAP emission is strongly enhanced, and even dominates the whole UV PL band. Considering the fact that only α-N_O is present in high-temperature XPS spectra, we believe that the acceptor state involved in the DAP emission arises from the stable α-N_O, which is a shallow acceptor and favors p-type conduction of the ZnO:N film. On the other hand, the thermal treatment also suppresses the deep-level visible emission as shown in the inset of Fig. 3. We suppose that the thermal quenching of visible emission is related to the removal of β-N_O, which introduces the deep levels in ZnO band gap. However, further work is needed to investigate the electronic structure of β-N_O.

In conclusion, different N local states, as well as their thermal stabilities, have been studied by temperature-dependent XPS measurements. We propose that the XPS peaks at 396 and 398 eV originate from the N_O in N- and O-rich local environments (β- and α-N_O). Compared to β-N_O, the α-N_O, as a shallow acceptor, is more thermally stable up to 723 K. However, thermal treatment above 743 K favors the formation of undesirable $(N_2)_O$ donors. The variation of N local states changes the background carrier concentrations, thus leading to the shift of Zn and O binding energies. The careful studies on the local states of N impurity are helpful for achieving the stable, high-quality p-ZnO:N.

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