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Effect of compressive stress on stability of N-doped p-type ZnO

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Nitrogen-doped p-type zinc oxide (p-ZnO:N) thin films were fabricated on a-/c-plane sapphire (a-/c-Al_2O_3) by plasma-assisted molecular beam epitaxy. Hall-effect measurements show that the p-type ZnO:N on c-Al_2O_3 degenerated into n-type after a preservation time; however, the one grown on a-Al_2O_3 showed good stability. The conversion of conductivity in the one grown on c-Al_2O_3 ascribed to the faster disappearance of N_O and the growing $N_{2(O)}$, which is demonstrated by x-ray photoelectron spectroscopy (XPS). Compressive stress, caused by lattice misfit, was revealed by Raman spectra and optical absorption spectra, and it was regarded as the root of the instability in ZnO:N. © *2011 American Institute of Physics*. [doi:10.1063/1.3631677]

Over the past decade, intensive attention has been drawn by ZnO for its potential application in short wavelength optoelectronic devices. Nevertheless, almost entire applications in these fields base on the realizing stable and reproducible p-type ZnO. Up to now, nitrogen (N) has been considered to be one of the effective dopants for p-ZnO since electroluminescence has been realized in ZnO homojunction based on N doping.[1–4] However, some severe problems are concerned all through the development of p-ZnO:N, such as low reproducibility and poor stability.[5–8] Although much effort has been devoted, acknowledged method for fabricating stable p-type ZnO:N is still not obtained.

It is well known that residual stresses, including tensile stress and compressive stress, influence the formation of defects in thin films, such as doped impurities. They always exist inevitably in epitaxial films due to lattice mismatch as well as thermal mismatch induced by the difference in the thermal expansion coefficients between the substrate and the film. To minish the above influences, matched substrates are expected for fabricating p-ZnO, but bulk ZnO and $ScAlMgO_4$ cost too much to be widely used. Given these conditions, researches on the effects of lattice mismatch or thermal mismatch on the properties of ZnO:N are necessary.

In this paper, the biaxial compressive stress caused by lattice mismatch between (a-/c-Al_2O_3) and ZnO:N was observed in the ZnO:N films. The influence on the electric properties was studied. The detrimental effect on the stability of p-type ZnO was also demonstrated. The results presented in this paper may provide a clue to obtaining reliable and stable N-doped p-type ZnO.

ZnO:N films were deposited on a-/c-Al_2O_3 at 450 °C for 2 h. 6n-purity Zn metal was used as the zinc source. Radio frequency ionized nitric oxide (NO) (5N) and nitrogen gas (N_2) were employed as dopant and oxygen source. The detailed growth regimes are listed in Table I. The gases were introduced into the growth chamber through each mass flow controller, and the chamber pressure was 2×10^{-5} mbar. For convenience, two groups of samples were labeled as A1-A5 for ZnO:N films on a-Al_2O_3 and C1-C5 for ZnO:N films on c-Al_2O_3, respectively. Chemical bonding states of the films were analyzed by x-ray photoelectron spectroscopy (XPS). Raman backscattering spectra were obtained at room temperature using the 488 nm line of an Ar^+ laser.

The electrical properties of the films were obtained by van der Pauw method using a Hall analyzer (Lakeshore 7707). The results are summarized in Table I. As seen, the p-type conduction was obtained with NO and N_2 both at the flux of 0.6 SCCM, but they (samples A4 and C4) presented poor electrical properties. This probably originates from the self-compensation by intrinsic donors (such as Zn interstitial, Oxygen vacancy) in the nonstoichiometric films demonstrated by EDS (not shown here). However, when the NO flux decreased to 0.4 SCCM with increasing N_2 flux to

TABLE I. Electrical properties of (a) ZnO:N/a-Al_2O_3 and (b) ZnO:N/c-Al_2O_3 grown under different regimes, where p/n denotes an uncertain conduction type.

Sample	NO Flux (sccm)	N_2 Flux (sccm)	Resistivity (Ω cm)	Hall Mobility ($cm^2 V^{-1} s^{-1}$)	Carrier Concentration (cm^{-3})	Carrier Type
(a)						
A1	1.2	0	1.16	2.16	2.56×10^{18}	n
A2	1.0	0.25	0.28	4.34	5.37×10^{18}	n
A3	0.8	0.4	6.23	1.76	5.71×10^{17}	n
A4	0.6	0.6	1260	0.26	1.87×10^{16}	P
A5	0.4	0.8	11800	2.62	2.11×10^{14}	p/n
(b)						
C1	1.2	0	8.23	0.19	9.74×10^{18}	n
C2	1.0	0.25	1.41	0.94	4.68×10^{18}	n
C3	0.8	0.4	18.95	0.33	9.84×10^{17}	n
C4	0.6	0.6	6280	0.27	3.86×10^{15}	p
C5	0.4	0.8	85400	0.83	9.07×10^{13}	p/n

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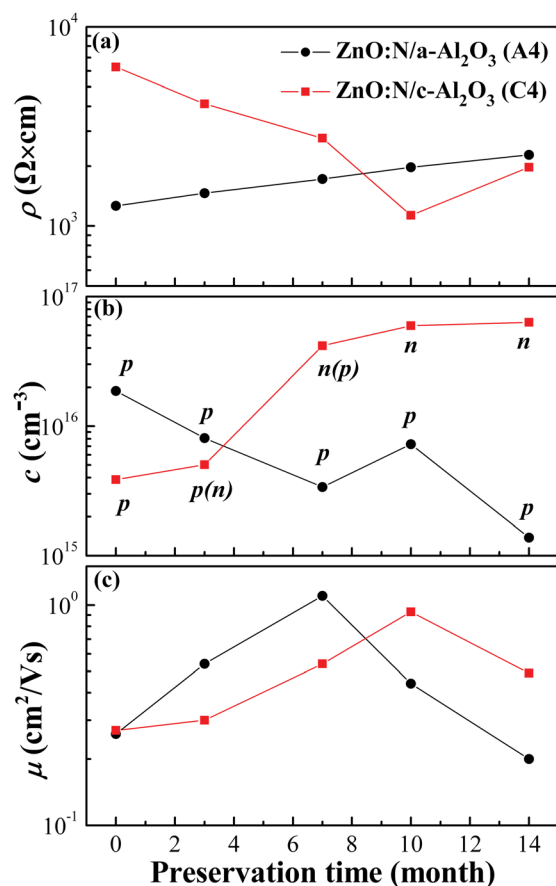b) Electronic mail: yaobin196226@yahoo.com.cn.

FIG. 1. (Color online) The electrical properties of samples A4 and C4 (a) resistivities; (b) Carrier concentrations and (c) Carrier mobilities as a function of the preservation period; the $n(p)$ or $p(n)$ marked in (b) means the measurement gives indefinite sign of Hall coefficient (R_H).

0.8 SCCM, the samples began to show semi-insulating characters and gave the indefinite type of conductivity.

After measurements, the samples were stored in an electronic dry cabinet at constant room temperature. With time elapsing, A4 and C4 displayed different behaviors on the electrical properties, as shown in Figure 1. Unlike the stable conductivity of A4, the conduction of C4 converted from p-type to n-type.

As well known, molecule adsorption, such as H_2O and O_2, can influence the charge distribution on semiconductor surface and then the electrical properties, especially for ZnO, a gas sensor material. But this possibility has been excluded because of the unaltered electrical properties, obtained by repeated measurements after samples being dried by an electric blower for 5 min. Therefore, the conversion of the conduction type and the carrier density rising more than one order of magnitude in sample C4 may derive from the inner changes.

In order to understand the evolutions in solubility and chemical state of N in samples A4 and C4, XPS measurements were carried out again 14 months later, which were compared with the ones performed before preservation. All the N_{1s} XPS spectra are illustrated in Figs. 2(a)–2(d). Prior to the XPS measurement, both of them were etched by Ar^+ ion for 60 s.

It is obvious that each of the spectra has three N_{1s} peaks, located near the binding energy of 395.5, 399.2, and 404.8 eV,
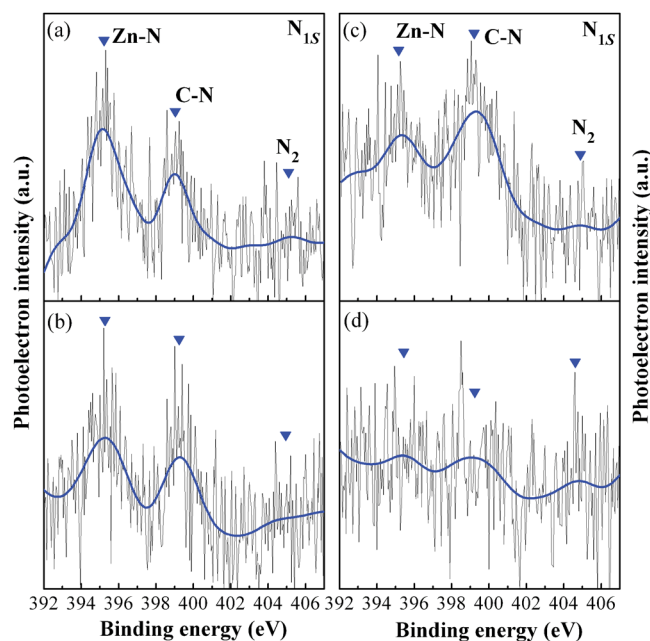

FIG. 2. (Color online) N_{1s} XPS spectra for samples (a) A4; (b) A4 preserved for 14 months; (c) C4 and (d) C4 preserved for 14 months.

correspond to N-Zn,[9,10] C-N bonds,[11] and N-N pair at O site ($N_{2(O)}$),[12] respectively. The content of N_O is calculated to be 0.67 and 0.29 at. % for samples A4 and C4, respectively, as shown in Figs. 2(a) and 2(c). This agrees with that the hole concentration in A4 (1.87×10^{16} cm^{-3}) is larger than that in C4 (3.86×10^{15} cm^{-3}). However, after 14 months, the N_{1s} spectra for C4 showed notable variation compared to sample A4. The amounts of N_O in C4 decreased, but that of $N_{2(O)}$ increased, as indicated by Figs. 2(b) and 2(d). Since $N_{2(O)}$ acts as dual-donor in ZnO:N, the increase of $N_{2(O)}$ will compensate for the remained N_O and cause the inversion of conductivity type of sample C4.

But what caused the evolutions of $N_{2(O)}$ and N_O? It has been demonstrated that p-doping will cause compressive
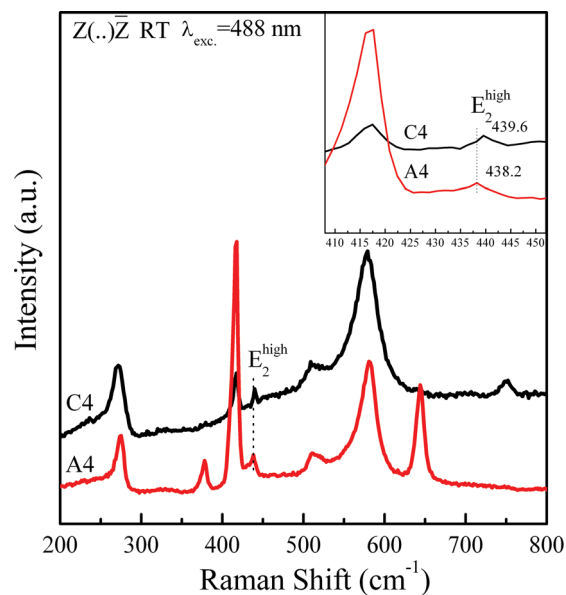

FIG. 3. (Color online) Room temperature Raman backscattering spectra of samples A4 and C4.
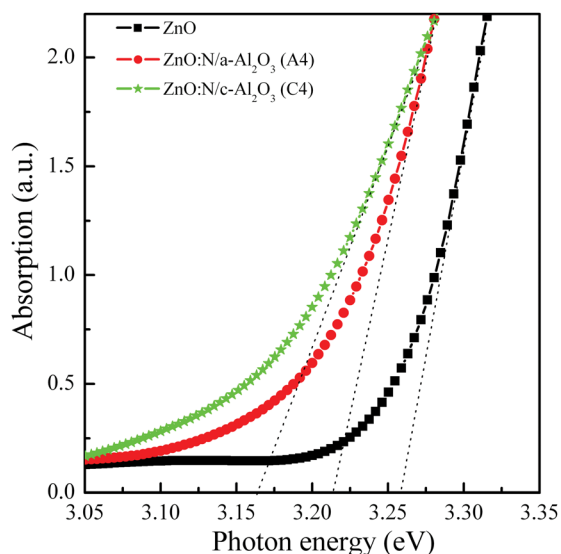
FIG. 4. (Color online) Optical absorption spectra of undoped ZnO film, A4 and C4.

stress in ZnO films, which will elevate the acceptor formation energy. It would suppress the doping level in ZnO.[13] Furthermore, the interstitial oxygen (O_i) is proven to be an unstabilizing factor in ZnO, which would kick out N_O to interstitial site and bond with another interstitial nitrogen atom (N_i) to form $N_{2(O)}$.[14] Is there difference between the strains in C4 and A4 and the compressive stress brings the amount variations of $N_{2(O)}$ and N_O?

To confirm the hypothesis mentioned above, Raman spectra of samples A4 and C4 are measured, as shown in Figure 3. It is well known that the E_2(high) mode at 437 cm^{-1} for ZnO, which was related to the vibration of O atoms indicative of the wurtzite phase formation,[15] can be used to characterize the biaxial stress in ZnO lattice.[16] This peak shifts to 438.2 cm^{-1} for A4 and 439.6 cm^{-1} for C4, as shown in the inset of Fig. 3, meaning larger biaxial compressive stress exists in C4 than in A4. This is also supported by optical absorption spectra shown in Figure 4. The absorption edge of C4 shows larger redshift than A4 compared to stress-free ZnO thin film, indicating that the bandgap of C4 narrows much more significant than A4. According to the relationship between the strain and bandgap in ZnO discussed by Li *et al.*,[17,18] larger compressive stress is deduced to exist in C4 than in A4.

In sample C4, the lattice mismatch between c-Al$_2$O$_3$ and ZnO is −18.4% with 30° in-plane rotation in the relationship of ZnO[2$\bar{1}\bar{1}$0]‖Al$_2$O$_3$[1$\bar{1}$00] and ZnO[1$\bar{1}$00]‖Al$_2$O$_3$[1$\bar{2}$10]. But, the mismatch between a-Al$_2$O$_3$ and ZnO is only −0.038% with the relationship of Al$_2$O$_3$[0001]‖ZnO[11$\bar{2}$0] and −2.4% with the relationship of Al$_2$O$_3$[1$\bar{1}$00]‖ZnO[1$\bar{1}$00], respectively. The "−" denotes that the lattice parameter of substrate is smaller than that of epitaxial layer, meaning in-plane compressive stress in the ZnO films. Sample C4 suffers much larger compressive stress compared to

sample A4, which accelerates the process that N_O is squeezed out of O site to form $N_{2(O)}$ by bonding with another N_O. Reduction of N_O acceptor and formation of new donor $N_{2(O)}$ reverse the conduction type of sample C4 finally.

In summary, the ZnO:N film deposited on c-Al$_2$O$_3$ shows an conversion in the conductivity from p-type to n-type after a preservation period. XPS indicates that both of the reduction of N_O and the augment of $N_{2(O)}$ are responsible for the conversion. The one deposited on a-Al$_2$O$_3$ shows stable acceptor form of N_O and great stability in the electric properties. Biaxial compressive stress in the deposited film caused by large lattice mismatch between ZnO and c-Al$_2$O$_3$ was ascribed to the origin of the instability of the electrical properties. The results enlighten us that reliable and stable nitrogen-doped p-type ZnO film can be fabricated by using substrates with low lattice or thermal mismatch and, thus, may give a direction for the future fabrication of optoelectronic devices based on p-ZnO.

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