Co-doped p-type ZnO:Al-N Thin Films Grown by RF-Magnetron Sputtering at Room Temperature

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This study reports the structural properties of zinc oxide thin films co-doped with aluminum and nitrogen (ZnO:Al-N) grown by RF magnetron sputtering from an AZO (ZnO with 2 wt% Al2O3) target under nitrogen (N2) atmosphere at room temperature (RT). Nitrogen partial pressures of 0.00, 0.10, 0.25 and 1.00 mTorr were used. The film thickness was around 270 nm. Ultraviolet-Vis-NIR transmittance (T) spectra of the films revealed T values of 80 to 85% in the 400 to 700 nm wavelength range. XRD results indicated that the films had a hexagonal wurtzite structure and were preferentially oriented in the (002) plane. Analyses by EDS indicated that the N atoms tend to be incorporated into the ZnO matrix at the expense of oxygen atoms. The ideal [N]/[Al] was obtained at a N2 partial pressure of 0.25 mTorr, producing a p-type film. For a [N]/[Al] of 1.53, the film also exhibited p-type conduction with an electrical resistivity of 31.92 Ω cm, mobility of 18.65 cm2/V s and carrier density of 1.22 x 1019 cm–3. The low carrier density is attributed to the energetically favorable formation of inactive nitrogen phases instead of acceptor-receiver-acceptor complexes, even at the ideal [N]/[Al].

Keywords: zinc oxide, p-type doping, co-doping, ZnO:Al-N, room temperature.

1. Introduction

Zinc oxide (ZnO) is biodegradable, non-toxic, and composed of elements abundant in the Earth’s crust (Zn – 132 ppm in the Earth’s crust, O – 49.4%), making it important for large-scale applications. Indeed, ZnO is widely used industrially as an additive for rubber, paints, cosmetics and medicines, amongst others. In addition, since it is a semiconductor with a wide direct bandgap of 3.3 eV and high binding energy excitons (60 meV), it is a strong candidate to the energetically favorable formation of inactive nitrogen phases instead of acceptor-receiver-acceptor complexes, even at the ideal [N]/[Al].

As confirmed by electrical measurements, ZnO is an intrinsic n-type semiconductor. Following the success of GaN as a blue light emitter, however, efforts have been remade to obtain p-type doped ZnO, which would permit the fabrication of LEDs, for example. The following strategies have been used to produce p-type doping of ZnO: (i) group VA element atoms substitute oxygen atoms; (ii) group IA element atoms substitute Zn atoms; (iii) co-doping with donors and acceptors.

In the case of group VA elements, nitrogen is most adequate considering the atomic radius and valence energy of the 2p states, which are closer to those of oxygen in comparison with other elements whose difference in radius is greater than 50%. Some theoretical studies, however, suggest that nitrogen is a deep acceptor with a high ionization energy (1.3 eV), producing a reduced concentration of holes. Moreover, Yan et al. predicted that the N atom acts in place of O as an acceptor, but N acts as a donor. Already the theoretical study by Lee et al. indicated that the mechanism of compensation of N acceptors is energetically favorable in the ZnO matrix. This implies that even at low doping levels, the N acceptors are compensated by oxygen vacancies. Based on this reasoning, we conclude that the effects of self-compensation and the low solubility of acceptors in the ZnO matrix are the prime factors responsible for the instability observed experimentally in p-type ZnO films, which convert to n-type upon ageing.

To obtain a greater level of incorporation of N into the crystalline structure of ZnO, Yamamoto suggested a co-doping of elements that donate charge, acting as an activator of the acceptor element. More specifically, Yamamoto and Katayama-Yoshida suggested that codoping of ZnO:N with Al or Ga produces acceptor-energetically favorable donor-acceptor complexes, leading to a reduction in the Madelung energy of delocalized nitrogen atoms and increasing the density of acceptor sites. Thus, the ideal concentration relation between acceptor and donor atoms would be 2:1 to obtain p-type ZnO.

Experimentally, studies have used different nitrogen sources and codopants such as Ga16, B17, P18, Ag19,20, In11 and Al22. For the co-doping with Al using magnetron sputtering, Cho23 deposited ZnO:Al-N films at 300°C, varying the N2 flow rate. Reductions in the carrier density and electronic mobility were observed when the N2 flow rate...
was increased. As a consequence, the electrical resistivity increased from 1.2 x 10⁻⁴ Ω cm to 0.13 Ω cm for 30% of N₂ in the N₂⁺Ar mixture. Chou et al²⁴. used N₂O as a reactive gas and the deposition temperature was held at 500 °C. In this case, p-type conduction was observed with a carrier density of 2.5 x 10¹⁷ cm⁻³ and electrical resistivity of 2.6 Ω cm for a p_{N₂O}/(p_{N₂O} + p_Ar) value of 20%. Raising the partial pressure of N₂O, however, changed the electrical conduction to n-type.

Zeng et al²⁵ employed Zn-Al targets containing different concentrations of Al (0 at.%, 0.08 at.%, 0.4 at.%, 1 at.% and 4 at.%). The N₂O pressure was fixed at 3 Pa and the deposition temperature was 500 °C. As a result, films with different types of conduction (p-type and n-type) were obtained, the best result being 28.3 Ω cm at a carrier concentration of 2.52 x 10¹⁵ cm⁻³.

Hence, depending on the concentrations of Al and N, p-type or n-type doping may be produced. In none of these studies, however, were the electrical properties of the ZnO:Al-N films correlated with the ratio [N]/[Al]. Therefore, in this work the correlation between [N]/[Al] in ZnO:Al-N films and their structural and electrical properties were investigated. For this, thin films were synthesized by RF magnetron sputtering using N₂ as the reactive gas and a ZnO:Al₂O₃ (2 wt.%) target. Specifically, the partial pressure of N₂ was varied to obtain films with the ideal ratio of 2:1. At this proportion, the formation energy of the co-doping N-Al-N system is smaller than that of N mono-doping, facilitating the increase in the number of holes²⁶. In addition, the Fermi level shifts to positions closer to the top of the valence band, allowing a more stable p-type ZnO film to be obtained²⁷.

2. Experimental Methods

Glass substrates were used as substrates for the depositions. Each substrate was cleaned for 480 s in each of distilled water, acetone and isopropanol in an ultrasonic bath. Film deposition was by RF magnetron Sputtering using a 3 inch diameter ceramic AZO (ZnO with 2 wt.% of Al₂O₃) target in an Ar and N₂ atmosphere. The partial pressure of Ar was held at 1.00 mTorr, and the partial pressure of N₂ was varied (0.00, 0.10, 0.25, and 1.00 mTorr). An applied power of 60 W was used for 30 min. per deposition. The target-substrate separation was 3 cm and the substrate holder was neither intentionally heated nor polarized.

Film thicknesses, measured using a DEKTAK 150 profilometer, were ~ 270 nm. An Energy-Dispersive X-ray Spectrometer (EDS) attached to a JSM-6010LA Scanning Electron Microscope was used to estimate film chemical composition. Film structural properties were investigated with a Panalytical X'Pert Powder Diffractometer at grazing incidence (2θ). The line width of a He-Cd laser.

Figure 1a presents X-ray diffractograms of the ZnO:Al and ZnO:Al-N samples described in Table 1. For comparison, a diffractogram of bulk ZnO produced by sintering is also shown. All the diffractograms show peaks related to the (002) and (103) planes. This implies the growth of polycrystals with a wurtzite structure with the c-axis preferentially aligned perpendicular to the substrate. At a N₂ pressure of 1.00 mTorr, however, other diffraction peaks such as (100), (101), (102), (110), (200), (112) and (201) are observed, which are in agreement with crystallographic data (JCPDS 79-208). This indicates that with an excess of N₂, there is a structural change in the ZnO matrix, at least an increase in the random spatial orientation of the polycrystals. Moreover, no other peaks which belong to AlN, Zn₃N₂ or Al₂O₃ were detected even though the [N]/[Al] ratio is as high as 4:1.

Figure 1b and the Table 2 present the diffraction angles and FWHM of the (002) peak. In addition, the lattice parameters a and c deduced from the positions of the (002) and (103) peaks are shown, together with the crystallite sizes estimated using the Scherrer equation. Comparing the
position of the peaks of the (002) and (103) planes of the ZnO films with those of bulk ZnO, a shift to lesser angles is observed. When only Al is added to the lattice, the peak shifts from 34.42° to 33.86°, implying an expansive stress in the lattice. With the incorporation of nitrogen into the matrix, the peak shows a tendency to shift to greater angles. This causes a compensation effect in the distortion of the crystalline lattice when N:Al proportions are close to 2:1, since other defects like Al and N interstitials tend to increase the lattice parameters. This behavior is supported by the almost constant value of the lattice parameter $a$, except for the sample obtained at 1.00 mTorr, while the lattice parameter $c$ increases from ZnO powder to the ZnO:Al film, decreasing again upon co-doping with N. On the other hand, the films present slightly greater crystallite sizes when the partial pressure of N$_2$ increases.

3.2 Electrical measurements

Table 3 shows the electrical resistivity, mobility, carrier density and conduction type for the ZnO:Al and ZnO:Al-N films. According to the Hall Effect, the ZnO:Al film presented an n-type electrical conductivity, as expected. The films grown in a N$_2$ atmosphere, with a [N]/[Al] close to 2, showed a p-type behavior. There was, however, an increase by up to four orders of magnitude in the electrical resistance compared to the ZnO:Al film, owing mainly to the reduction in carrier density. Finally, the ZnO:Al-N film, grown in excess N$_2$ (partial pressure of 1.00 mTorr) demonstrated n-type behavior and a carrier density of 5.34 x 10$^{15}$ cm$^{-3}$.
the EDS data, the hole and maximum electron density, $n_h$ and $n_e$, may be calculated. For the ZnO:Al film, $([\text{Al}] / ([\text{Al}]+[\text{Zn}]))$ is 3.59%. Consequently, the expected electron density is $1.49 \times 10^{21} \text{ cm}^{-3}$. The carrier density, however, measured by the Hall Effect is $9.72 \times 10^{19} \text{ cm}^{-3}$. These data imply that the ionization efficiency ($n_{\text{Hall}} / n_h$) is only $6.53\%$ (i.e. $6.53\%$ of the Al atoms effectively act as donors of charge in n-type ZnO:Al). A priori, this result may be caused by the compensation mechanism or by the inactivation of Al caused by the formation of inert complexes, such as the homologous phase ZnO/Al$_2$O$_3$. Such formations are strongly dependent on the quantity of O available during deposition.

For the ZnO:Al-N film with $[\text{N}] / [\text{Al}] = 1.53$, considering the N-Al-N complex as an electron receptor, the hole density would be about $1.46 \times 10^{21} \text{ cm}^{-3}$. Supposing a compensation mechanism between substitutional N$_{\text{N}}$ and Al$_{\text{Zn}}$, the hole density would be $1.21 \times 10^{21} \text{ cm}^{-3}$. However, comparing the effective density with the density measured using the Hall Effect, reveals a difference of 5 orders of magnitude ($1.22 \times 10^{16} \text{ cm}^{-3}$) lower than expected. This difference is explicable if not all the Al and N in the ZnO matrix act as donors or acceptors, respectively, as proposed by Yamamoto. Instead of forming acceptor-donor-acceptor complexes, the N$_{\text{N}}$ and Al$_{\text{Zn}}$ substitutional atoms bind between themselves as N$_{\text{N}}$-Al$_{\text{Zn}}$. Another possible mechanism is the formation of secondary structures (such as Zn$_{\text{N}}$N$_{\text{N}}$), which do not act as acceptors. No such structures, however, were apparent in the X-ray diffractograms.

### 3.3 Optical measurements

Figure 3a shows the optical transmittance and reflectance spectra of the samples studied here. Interference fringes and optical transparencies of around 80% in visible range are observed. For wavelengths above 1500 nm, in the spectrum of the ZnO:Al film there is an absorption associated with plasmon oscillations$^{37}$, characteristic of materials with a high carrier density. The value measured for this film was $9.72 \times 10^{19} \text{ cm}^{-3}$. This absorption is not observed in the spectra of the films co-doped with N, confirming the low carrier densities (of about $10^{16} \text{ cm}^{-3}$) observed in the Hall Effect measurements.

Figure 3b shows the absorption spectra of the ZnO:Al and ZnO:Al-N films calculated from the transmittance and reflection measurements. The optical absorption edge of the ZnO:Al film is at about 3.4 eV. This value is slightly above the observed value (3.3 eV) for undoped ZnO films and is due to filling of the bottom of the conduction band by charge carriers, known as the Burstein-Moss effect$^{38}$. The presence of a step between 2.6 and 3 eV for the ZnO:Al-N samples indicates the creation of localized states within the bandgap for the samples containing N. Localized states are normally related in ZnO films to the presence of defects that present deep excitation levels, such as those of oxygen vacancies. In our case, the localized states may be related to the formation of N$_{\text{N}}$-Al$_{\text{Zn}}$ complexes, which also reduce the carrier density as discussed previously. In Figure 3b, the step increases with the concentration of N incorporated into the ZnO:Al-N films.

Figure 4 shows a photoluminescence (PL) spectra in the 1.5 to 3.7 eV range of ZnO:Al and ZnO:Al-N (1.00 mTorr) films. A spectrum of bulk ZnO, also included, exhibits a peak centered at 3.31 eV, related to transitions between the bottom of the conduction band and the top of the valence band (NBE). The spectra of the ZnO:Al and ZnO:Al-N films show a peak at 3.06 eV and another, wider peak superimposed in 2 to 3 eV range. The first is related to the formation of N$_{\text{N}}$-Al$_{\text{Zn}}$ complexes, which also reduce the carrier density as discussed previously. The presence of a step between 2.6 and 3 eV for the ZnO:Al-N samples indicates the creation of localized states within the bandgap for the samples containing N. Localized states are normally related in ZnO films to the presence of defects that present deep excitation levels, such as those of oxygen vacancies. In our case, the localized states may be related to the formation of N$_{\text{N}}$-Al$_{\text{Zn}}$ complexes, which also reduce the carrier density as discussed previously. In Figure 3b, the step increases with the concentration of N incorporated into the ZnO:Al-N films.

### Table 3: Electrical resistivity, mobility, carrier density and type of conduction obtained by Hall Effect measurements.

| [N]/[Al] | $\rho (\Omega \text{cm})$ | $\mu (\text{cm}^2/\text{Vs})$ | $n (\text{cm}^{-3})$ | Type |
|----------|--------------------------|-----------------------------|------------------------|------|
| 0.00     | 0.00943                  | 6.81                        | $9.72 \times 10^{19}$  | n    |
| 1.53     | 31.92                    | 18.65                       | $1.22 \times 10^{16}$  | p    |
| 2.11     | 116.13                   | 9.27                        | $6.91 \times 10^{15}$  | p    |
| 4.03     | 148.33                   | 11.20                       | $5.34 \times 10^{15}$  | n    |

Figure 2: The carrier density, mobility and electrical resistivity extracted from Hall-probe measurements are depicted with [N]/[Al]. Note that the resistivity increases with increasing [N]/[Al]. The absolute values of the carrier density values are presented.
Films of ZnO:Al-N were obtained using RF magnetron sputtering at different N\(_2\) partial pressures. All of the films exhibited a Wurtzite structure with a preferential orientation along the (002) plane. For a N\(_2\) partial pressure of 1.00 mTorr the film presented a more random orientation of the crystals. From EDS measurements, it was concluded that the N atoms tend to be incorporated into the ZnO matrix by the suppression of oxygen atoms even at low N\(_2\) pressures. The ideal value of [N]/[Al] was obtained at a N\(_2\) partial pressure of 0.25 mTorr, producing a film with p-type conduction. For the partial pressure of 0.10 mTorr (equivalent to a [N]/[Al] of 1.53), the film also exhibited p-type conduction with an electrical resistivity of 31.92 Ω cm, a mobility of 18.65 cm\(^2\)/V s and a carrier density of 1.22 x 10\(^{16}\) cm\(^{-3}\). PL measurements indicate the formation of defects such as N\(_2\)O-Al\(_{12}\) complexes and Zn\(_2\)N\(_3\), since the formation of nitrogen phases is energetically more favorable than the formation of acceptor-donor-acceptor complexes, even at the ideal [N]/[Al].

5. Acknowledgments

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