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# Effect of thermal treatment on points defects of Al-N codoped ZnO films

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## ABSTRACT

The effect of annealing temperature on the structural properties of Al-N codoped ZnO films were studied by X-ray diffraction, photoluminescence and Raman spectroscopy. ZnO films were deposited by sputtering technique on silicon substrates at 20 ºC, Al-concentration was kept constant and N-flow was changed to 6, 12 and 15 sccm. A thermal treatment was performed by annealing the sample during 30 minutes at 300, 400, 500, 600 and 700 °C. Before annealing, Raman spectra shows two vibration modes located at 275 and 580 cm-1 associated to the nitrogen incorporation and the presence of point defects. Both Raman intensities of modes I275 and I580 decreases when the nitrogen flow increases from 6 to 12 and 15 sccm, which is originated by a decreasing interstitial defects density. The improving of the crystal quality was confirmed by x-ray diffraction and room temperature photoluminescence measurements. After annealing, in the Raman spectra it was observed that I275 increases as the temperature increase, reaches a maximum intensity between 500 and 600 °C, and decreases for higher temperatures. X-ray diffraction measurements show that after annealing the compressive stress decrease progressively as the annealing temperature increase. This study suggests that 275 Raman mode could be used to estimate the optimal thermal treatment in order to achieve p-doping ZnO.

**Keywords:** Zinc oxide, codoping, annealing, Raman spectroscopy, XRD.

## 1. INTRODUCTION

Zinc oxide (ZnO) is a semiconductor with special interest because it has a wide band gap (3.36 eV at 300K) and large exciton binding energy (60 meV), which can be widely used in the manufacture of optoelectronic devices such light-emitting diodes, laser diodes, photo-detectors, transparent electrodes, gas sensors and solar cells. One of the big challenges is to control the p-type doping due to its high activation energy and the low solubility of acceptor dopants. Another feature of ZnO not favorable to the p-type doping is the presence of native defects such as interstitial and vacancies acting as an n-type doping, generating a phenomenon known as self-compensation [1-3]. Nitrogen is the doping elements frequently used in order to replace the oxygen atoms and consequently increases the hole concentration. However, another factor limiting the production of high levels of p-type doping is the low solubility of nitrogen originated by a weak bond N-Zn, which is easily broken at high growth temperatures (300 - 600 ºC). Codoping is an alternative method that has been proposed, using acceptors and reactive donors simultaneously in order to achieve p-type ZnO [4]. In several studies were used elements such as P [5, 6], In [7,8], Be [9], Ag [10] and Al [11-19] in addition to nitrogen atoms, in order to increase incorporation of N into the ZnO crystalline lattice. Other important factors that help to p-doping are the growth temperature and the post-annealing process. Chen *et al.* [8] studied In-N codoped ZnO films grown on different substrates and they found that 540 ºC is the optimal temperature; may be, this is the explanation why Zeng *et al.* [11] got p-conductivity in Al-N codoped ZnO films sputtered at

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500 °C and Shinho *et al.* [12] observed n-conductivity in Al-N codoped ZnO sputtered at 300 °C. Other studies used thermal annealing in order to ensure the nitrogen incorporation in oxygen sites ($N_O$) and to achieve p-type doping [3, 7, 10, 13-17]. Li *et al.* [10] found that p-doping is gotten with post-annealing at 615 ºC during 25 minutes on Ag-N doped ZnO films. With the Al-N codoping system: Liu *et al.* [13] developed p-type films with post-annealing during 30 min at temperatures between 575 and 600 ºC. Kumar *et al.* [14] observed p-type at temperatures higher that 400 °C, they remark that 600 °C is the best. Yang *et al.* [16] studied sol-gel codoped ZnO films and they found optimized p-type conduction at 550 °C.

In this paper, we study the influence of annealing temperature on the structural properties of Al-N co-doped ZnO films grown on Si (100) at 20 ºC by X-ray diffraction, photoluminescence and Raman microscopy in order to get a best understanding of both the intrinsic defects and NO density behavior during the annealing process.

## 2. MATERIALS AND METHODS

Al-N codoped ZnO films were deposited on silicon (100) substrates by sputtering technique. All Si substrates were ultrasonically cleaned sequentially in acetone, methanol, and then deionized water. All samples were grown using a co-sputtering technique of dual targets: a ceramic ZnO target at RF power of 150 W and a pure Al (purity 99.9%) at DC power of 50 W. During the film deposition substrate temperature and deposition time were kept constant at 20ºC and 17 min, respectively. High purity argon (99.999%) and nitrogen (99.999%) were used as sputtering gases, the flow rate of argon was fixed at 6 sccm, whereas the flow rate of nitrogen was varied at 6, 12 and 15 sccm. The Al-N codoped ZnO films were annealed in air for 30 minutes at temperatures of 300, 400, 500, 600 and 700 °C. The crystallinity of the samples was characterized using X-ray diffraction (XRD, Bruker D8 Advance). Room temperature photoluminescence (PL) was carried out using a He-Cd laser with excitation wavelength 325 and power of 16 mW. Raman microscopy study was performed with a 532 nm laser line of 10 mW as excitation source (DXR model, Thermo Scientific).

## 3. RESULTS AND DISCUSSION

### 3.1 Before annealing

Figure 1 shows XRD patterns of ZnO films before thermal treatment for nitrogen flow rate of 6 (N6), 12 (N12) and 15 sccm (N15). The patterns have a slow mismatch with the reference positions of undoped ZnO films due to the stress originated by the incorporation of both Al and N atoms. In sample N6, seven diffraction peaks corresponding to the (100), (002) (101) (102), (110), (103) and (112) planes are observed, the first three with major intensity. For samples N12 and N15, ZnO films exhibit (002) preferential orientation with the c-axis perpendicular to the substrate. As increase of N content, the full width at half maximum (FWHM) of the (002) peak decreases clearly, indicating the improving crystallinity due to incorporation of N atoms.

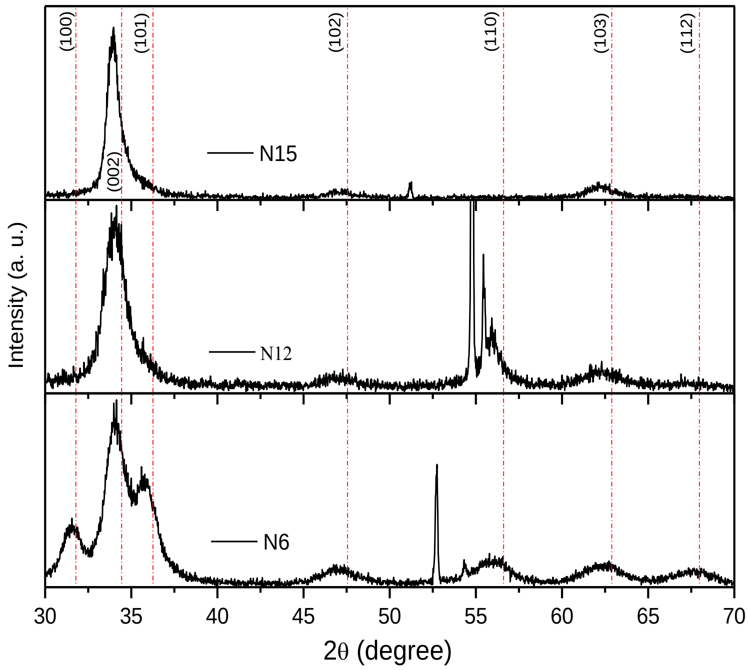


**Figure 1.** XRD patterns of ZnO films as-groth with flow rate nitrogen of 6 (N6), 12 (N12) and 15 sccm (N15) before thermal treatment. Red lines indicate location peak for undoped ZnO films.

Figure 2 shows PL spectra of samples N6, N12 and N15, where is evident a broad band between 1.7 and 3.1 eV that could be originated by interstitial defects ($Zn_i$, $O_i$, $N_i$ and $Al_i$). We cannot see the band to band transition near to 3.36 eV, suggesting a poor crystal quality. On samples where the N content increase (N12 and N15), the signal associated to interstitial defects is diminished, the bandgap transition is possible to see clearly and the signal associated to oxygen vacancies (1.62 eV) is observable too.

In order to estimate the nitrogen incorporation to the oxygen sites ($N_O$), Raman measurements were made. Figure 3 displays the Raman spectra of N6, N12 and N15 samples, where we can see two vibration modes located at 275 and 580 $cm^{-1}$ originated by the Al-N codoped ZnO films and two more by the Si substrate. There is an old controversy about the accurate origin of 275 Raman mode, but it has been frequently related to the NO concentration and to the presence of point defects ($Zn_i$ specifically) [20-24]. Raman intensities of both modes, I275 and I580, decreases when the nitrogen flow increases from 6 to 12 and 15 sccm. Other authors suggesting that the increase of nitrogen flow mitigates the formation of interstitial defects [23]. In this work, we can see good agreement between XRD, PL and Raman measurements: the interstitial defects decrease as the N flow increase in samples grown at 20ºC.

### 3.2 After annealing

Figure 4 shows the XRD patterns of sample growth with 12 sccm nitrogen flow after the annealing process at temperatures between 300 and 700 ºC. As we can see, the (002) peak shifts to high angles (residual stress decrease) and the FWHM decrease as the temperature increase. Patterns of N6 and N15 samples presented similar behavior (not showed here). The XRD patterns behavior is clear evidence that the crystal quality has improved after annealing treatment, this suggests that interstitial defects concentration decreases as the temperature increase.

Figure 5 shows the Raman spectrum of N12 samples after annealing, where we can see that both I275 and I580 modes increases as the temperature increases, reaches a maximum around 500 °C and decreases at higher temperatures. Considering that interstitial defects are decreasing, the I275 behavior is generated mostly by the $N_O$ concentration. At high temperatures, this signal is diminishing because more. oxygen vacancies are generated, which play like n-type doping. The Raman behavior is in good agreement with other reports where has reported that optimal temperature is between 500 and 600 ºC [13,16].

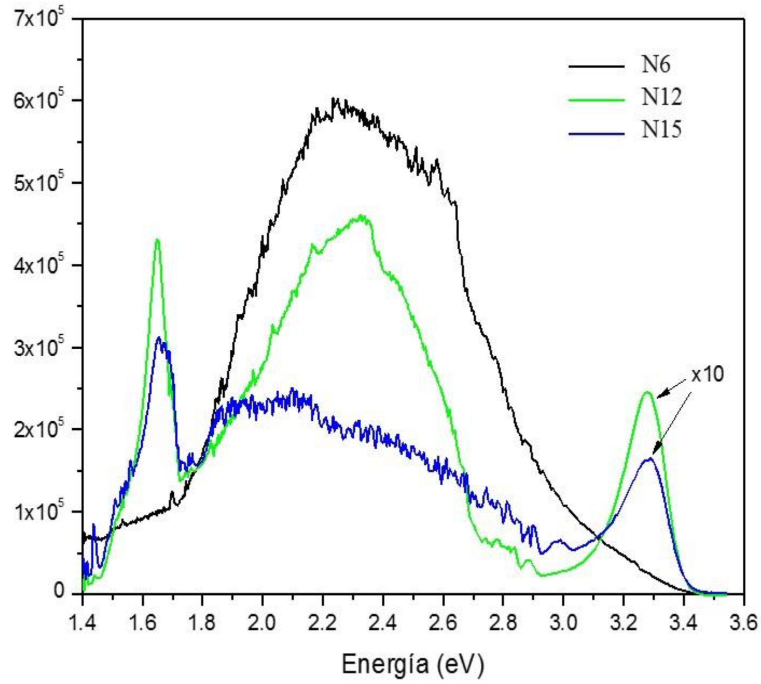


**Figure 2:** Room temperature photoluminescence of Al-N codoped ZnO with 6, 12 and 15 sccm nitrogen flow. The N12 and N15 spectra were magnified by 10.

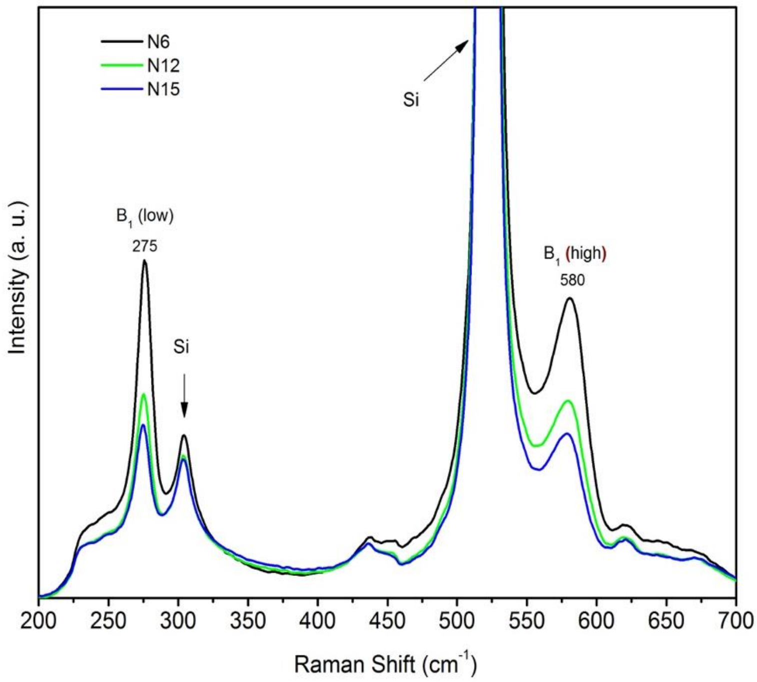


**Figure 3:** Raman spectra of ZnO films codoped with 6 (N7), 12 (N12) and 15 sccm (N15) nitrogen flow.

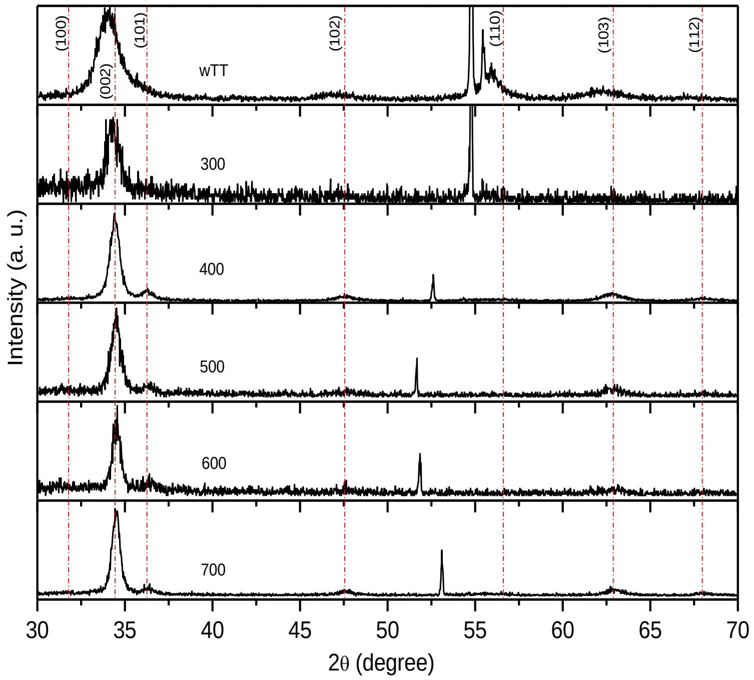


**Figure 4:** XRD patterns of N12 after thermal treatment compared wit the spectra without thermal treatment (wTT).

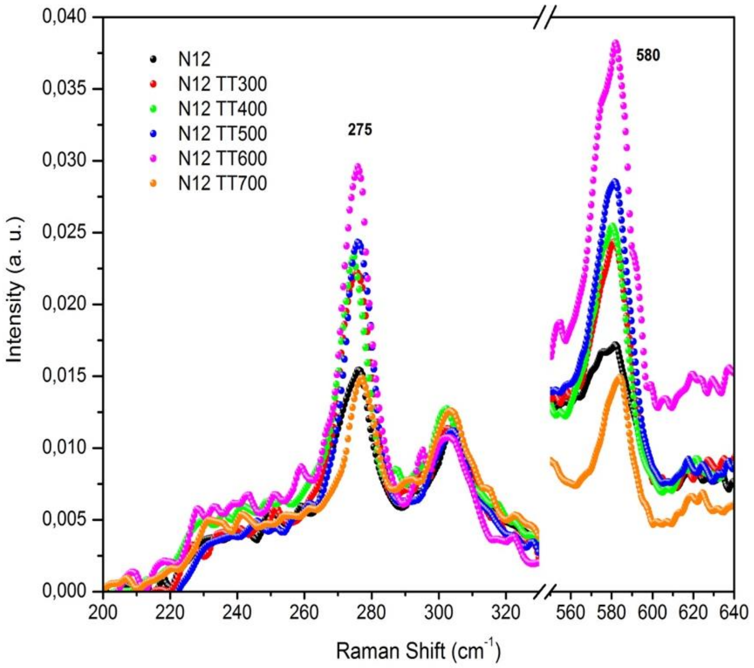


**Figure 5:** Raman spectra of N12 sample after thermal treatment at different temperatures, compared with the spectrum without treatment.

## 4. CONCLUSIONS

In this work, the effect of annealing temperature on the structural properties of Al-N codoped ZnO films have been studied. When the nitrogen content was increased a better crystal quality was observed by XRD, photoluminescence and Raman measurements, originated by the diminishing of the interstitial defects concentration. After annealing, in the Raman spectra it was observed that the Raman mode associated to the complex $Zn_i$-$N_O$ (I275) increases as the temperature increase, reached a maximum intensity between 500 and 600 °C, and decreased for higher temperatures. X-ray diffraction measurements showed that after annealing the compressive stress decrease progressively as the temperature annealing increase. This study suggests that 275

Raman mode could be used to estimate the optimal annealing temperature in order to achieve p-doping ZnO films.

## 5. ACKNOWLEDGMENTS

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