Ag-N dual acceptor doped p-type ZnO thin films by DC reactive magnetron co-sputtering

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ZnO thin films were deposited by dual acceptor co-doping using nitrogen and silver via DC reactive magnetron co-sputtering. As precursor material were used a Zn and an Ag metallic targets with a purity of 99.99%. X-ray energy dispersive spectroscopy (EDX) confirmed the presence of Ag and N in ZnO:Ag,N films. The electrical properties were explored by Hall Effect measurement and showed a low hole concentration for the as-deposited ZnO:Ag,N film. However, after annealing treatment, the films remained p-type and the electrical properties were improved significantly. The best electrical properties showed a low resistivity of $8.56 \times 10^{-3} \, \Omega \cdot cm$, Hall mobility of 23 $cm^2/Vs$ and a very high hole concentration of $3.17 \times 10^{19} \, cm^{-3}$.

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1. Introduction

II-VI semiconductor materials have been of great interest due to their properties for optoelectronic devices. In this group, ZnO is widely used in electronic and photonic materials, and it has a great potential for applications in information technology, biotechnology, short wavelength semiconductors and nanoscale science and engineering [1–4]. However, to develop the ZnO based on optical devices, the principal difficulty has been the fabrication of high quality and electrical stability p-type ZnO thin films due to the low solubility of the acceptor dopants, deep acceptor level, and the compensation effect between the acceptor dopants and the native donors in ZnO [5–7].

Recently, a dual-doping method using two acceptor agents namely Li-N [8–10] or As-N [11] was proposed to prepare p-type ZnO. In this line, the dual-doping method has demonstrated to be the best channel to overcome the difficulties in achieving p-type ZnO thin films and theoretical researches have suggested that Ag and N are the better candidates for producing p-type ZnO considering the strain effects and energy levels of substitutional Ag-Zn and N-O acceptors [12,13]. In the experimental context, publications focused to the fabrication of p-type ZnO:Ag,N thin films with good electrical properties have been reported using ultrasonic spray pyrolysis technique [14–18], ion beam assisted deposition [19] and sol-gel method [20]. However, until this moment, there are not reported studies on ZnO:Ag,N thin films by co-sputtering process in the literature.

In the present paper, the deposition of p-type ZnO:Ag,N by DC reactive magnetron co-sputtering method is reported. Additionally, the influence of dual doping on the structural and electrical properties of samples are presented.

2. Experimental details

Ag-N dual acceptor doping ZnO thin films were deposited on GaAs (100) substrates by DC reactive magnetron co-sputtering using zinc (99.99%) and silver (99.99%) metallic targets as precursors. For this purpose, the deposition chamber was evacuated to a base pressure of $3.5 \times 10^{-6} \, Torr$ and the room temperature depositions were performed at a pressure of $6 \times 10^{-3} \, Torr$, employing a power densities of 4 and 1.5 W/cm² on zinc and silver targets respectively, in presence of a reactive atmosphere of argon (99.99%), oxygen (99.99%) and nitrogen (99.99%). The gas flux
ratio $N_2$(sccm)/$O_2$(sccm)/$Ar$(sccm) was set at: 0/2.5/5 for the ZnO films and 15/2.5/5 for the ZnO:N and ZnO:AgN films. During the growth process, the shutter for the silver target was opened intermittently, 10 s closed and one second open for the deposition. After the growth, the samples were annealed at 300 °C and 400 °C for 1 h in a nitrogen atmosphere with heating rates of 10 °C/min and cooled rate of 5 °C/min. The films were characterized in an Energy Dispersive Spectrometer INCA X-sight Oxford Inst. Model 7558, using an accelerating voltage of 18 kV. The crystalline structure of the ZnO:Ag,N thin films was studied in a Siemens D-5000 Diffractometer using the CuKα line (λ = 0.1541 nm). The X-ray diffraction patterns were obtained in a grazing angle mode at 1.5°. The electrical resistivity, mobility, and carrier concentration were measured in an Ecopia HMS-3000 Hall Effect Measurement System, using the Van der Pauw method with a current of 2 μA, magnet flux density of 0.55 T and thickness of 142, 125 and 110 nm for the ZnO, ZnO:N and ZnO:Ag,N films respectively.

3. Results and discussions

3.1. Structural properties

EDX analysis confirmed the presence of Zn, O, Ag and N in the respective films; the un-doped ZnO film is nearly to the ideal atomic percentages of a stoichiometric sample; a consequence of the dopants incorporated to the film, the percentage of zinc is reduced from its initial value, while the oxygen percentage remained practically constant. The behavior of the dopants (Ag,N) as effect of annealing temperature as showed in Fig. 1. As incremented the annealing temperature, the amount of oxygen in the films increased while the percentage of nitrogen decreased, inversely proportional to the amount of oxygen incorporated. In addition, the atomic percentages of zinc and silver in the films remains constants.

Fig. 2 shows the XRD spectra for the different films in a range of 2θ=20°–50°. As it is seen in this figure, the number of peaks, their position, Full Width at Half Maximum (FWHM), and relative intensity are changed dramatically with the dopant incorporation and the annealing process. The pattern for the un-doped ZnO film (Fig. 2(a)) presented three peaks at 34.48°, 36.38° and 47.59°, that corresponded to the diffraction planes (002), (101) and (102) respectively of wurtzite structure of hexagonal ZnO [1]. The incorporation of nitrogen in the film, causes a reduction of the (002) line intensity and the rise of diffraction lines corresponding to (100) and (101) crystal planes; additionally, a wide peak centered near to 37°, could be associated with the presence of Zn3N2 [21]. Moreover, the dual doped caused that the as-deposited ZnO:Ag,N film become amorphous as showed in Fig. 2(c). With annealing treatment at 300 °C the crystalline phase content in the ZnO:Ag,N films are slightly increased as it is shown in Fig. 2(d). Finally, the XRD pattern of the film annealed at 400 °C (Fig. 2(e)) showed three well defined peaks associated to the (100), (002) and (101) planes of the initial wurzite structure. Although the hexagonal wurzite structure was recovered, the intensity in the diffraction peaks of the annealed samples are lower than the un-doped ZnO sample, indicating that the volume fraction of the crystalline phase is low and probably a considerable fraction of the film still amorphous.

The measured FWHM and calculated crystallite diameter $D$, interplanar distance $d$ and average lattice constants $a$ and $c$ are

![Fig. 1. Atomic percentages for the different species present in the ZnO:Ag,N films as a function of the annealing temperature.](image1)

![Fig. 2. XRD diffractogram of ZnO, ZnO:N and ZnO:Ag,N films.](image2)
showed in Table 1. The crystallite diameter was obtained using the Scherrer formula [22] and the lattice parameters were calculated using the relation for the hexagonal plane spacing equation [16].

\[ d_{hkl} = \frac{\lambda}{B \cos \theta} \]

where \( d \) was obtained from the Bragg law \( d_{hkl} = \frac{\lambda}{2 \sin \theta_{hkl}} \) and \( h, k \) and \( l \) are the Miller indexes.

Additionally, it is well known that the annealing temperature provided energy to film atoms to enhance mobility allowing the atoms diffuse into the material to achieve the minimum energy sites that result in the reduction of defects in the ZnO:Ag,N films and improve the crystallization process. In this context, the XRD patterns from Fig. 2(c), d and d showed a markedly evolution as effect of the increases in annealing treatment, taking a count the raise in intensity and the reduction of the FWHM in the (002) peak as seen in Table 1, and is clearly that the crystalline quality of ZnO:Ag,N films improved as the annealing temperature increases. Moreover, as effect of annealing treatment and the associated crystallization process, part of the silver and nitrogen presented in the film were inserted in the substitutional sites of the structure, giving as a result that the diffraction angle \( \theta \) of the (002) peak is shifted to lower values, from 34.48° (for the ZnO film) until 34.24° (for the ZnO:Ag,N annealed at 400 °C film), as a result of compressive stress generated in the cell of the crystal lattice.

### 3.2. Electrical properties

The typical conduction mechanism of ZnO films is mainly dominated by the electrons produced from the donor sites associated with oxygen vacancies and zinc interstitials, and like is typical for undoped ZnO films, the n-type conduction is presented with resistivity of 4.46 × 10^{-2} Ωcm, mobility of 2.08 cm²/Vs, and electron density of 6.73 × 10¹⁹ cm⁻³. In the same way, the ZnO:N sample manifested n-type conductivity, and the effect of the nitrogen was a decrease on the electron density giving a value of 1.41 × 10¹⁵ cm⁻³ and relatively high resistivity of 79.0 Ωcm. Although one might think that the ZnO:N films could display p-type conductivity, it is well known that conductivity of as-grown ZnO doped with N is n-type, because N can preferentially be incorporated as N₂ molecules which are donors [23], in addition, ZnO:N was prepared under O-poor condition to incorporate N at O sites. However, the O-poor condition also enriches the formation of other sites. Finally, for Ag and N doping, there are several mechanism that result in the formation of acceptors, the most relevant are the substitutional, this is when the Ag ion occupies the Zn site while N ion is on the O site forming AgZn and NO acceptors, and the formation of AgZn-NO pairs and/or NO–AgZn–NO triangles, which can create impurity bands above the valence-band maximum of ZnO due to the p–d interaction between accepters and hence offer improved incorporation and activation of acceptors [26].

The electrical properties of ZnO:Ag,N thin films were found to vary depending on the annealing conditions. The dependence of \( n \), \( \mu \) and \( \rho \) are presented in Fig. 3 as function of annealing temperature. The as-deposited ZnO:Ag,N films exhibited a very low hole concentration in comparison with the annealed films. After annealing the films remained with p-type conductivity and a gradual increase in hole concentration was observed for the films annealed at 300 °C and 400 °C. The hole concentration significantly increase by six orders of magnitude from 3.44 × 10¹⁰ cm⁻³ (as-deposited film) to 3.17 × 10¹⁶ cm⁻³ (annealed at 400 °C film).

The increment on the carrier concentration with the annealing process is explained taking account that in the process associated with the change in the crystallinity of the samples: when the film crystallize, the Ag and N dopants substitute part of Zn and O, respectively, as showed in XRD patterns. This process leads to formation of new acceptor sites and produce the final increment in the hole carrier density. The hole concentration obtained for this films is really a high concentration for p-type ZnO films, however, similar results had been obtained in p-type InGaN thin films [27,28]. The mobility in highly doped TCOs is affected by scattering centers such as ionized and neutral impurities, grain boundaries, lattice vibrations and dislocations. As the annealing temperature is increased, in this case the dislocations and crystal lattice deformation caused by dopant stress are eliminated, and consequently scattering centers are decreased and carriers mobility are increased as shown in Fig. 3. In addition, while the carrier concentration and mobility are increased with annealing treatments, the resistivity of the sample is decreased and showed the lowest resistivity for the films annealed at 400 °C. The lowest resistivity obtained was 8.56 × 10⁻³ Ωcm with a high mobility of 23 cm²/Vs, and carrier concentration of 3.17 × 10¹⁶ cm⁻³. The p-type conductivity is greatly enhanced in terms of conductivity and carrier concentration by the dual acceptor doping with Ag and N.

### 4. Conclusions

Ag-N dual acceptor doped ZnO thin films had been fabricated by DC reactive magnetron co-sputtering deposition. The structural and electrical properties were investigated for the as-deposited and annealed films. The as-deposited film was amorphous and presented a p-type conductivity, however, after the annealing treatment the crystallization of the films were slightly improved.

### Table 1. Structural parameters of as-deposited and annealed Ag-N dual acceptor doped p-type ZnO films.

<table>
<thead>
<tr>
<th>Film</th>
<th>2θ (degrees)</th>
<th>FWHM (degrees)</th>
<th>D (Å)</th>
<th>d (Å)</th>
<th>a (Å)</th>
<th>c (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO</td>
<td>34.48</td>
<td>0.436</td>
<td>190.83</td>
<td>2.59</td>
<td>–</td>
<td>5.20</td>
</tr>
<tr>
<td>ZnO:N</td>
<td>36.02</td>
<td>1.082</td>
<td>77.23</td>
<td>2.49</td>
<td>3.36</td>
<td>5.19</td>
</tr>
<tr>
<td>ZnO:Ag,N-300</td>
<td>34.37</td>
<td>0.562</td>
<td>148.03</td>
<td>2.60</td>
<td>3.26</td>
<td>5.33</td>
</tr>
<tr>
<td>ZnO:Ag,N-400</td>
<td>34.24</td>
<td>0.543</td>
<td>90.65</td>
<td>2.62</td>
<td>3.33</td>
<td>5.22</td>
</tr>
</tbody>
</table>
and they showed the hexagonal wurzite structure of ZnO; the films remained with p-type conductivity after annealing at 300 and 400 °C and presented an important high hole concentration of \(3.17 \times 10^{19} \text{cm}^{-3}\).

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[26] JCPDS card no 01-088-0618.


