EFFECT OF THE ANNEALING TREATMENT ON THE ELECTRICAL AND STRUCTURAL PROPERTIES OF ZnO THIN FILMS

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Abstract—The effect of post treatments (atmosphere and annealing temperature) on the performances of zinc oxide thin films (intrinsic and doped with In and Al) prepared by spray pyrolysis have been studied, with the aim to determine the more adequate conditions to improve the properties of the films. The results show that the annealing temperature leads to substantial changes in the structural and electrical characteristics of ZnO thin films. The most significative improvements were obtained after annealing at 400°C in forming gas, during 2 hours. The ZnO:In film after heat treatment was the one that exhibited the lowest resistivity (\(\rho = 5.8 \times 10^{-1}\ \Omega \text{cm}\)) associated to a high transmittance (T = 86%).

1. INTRODUCTION

Zinc oxide (ZnO) is a degenerate n-type semiconductor. It’s n-type electrical conductivity is due to deviations from the stoichiometry resulting from oxygen vacancies and interstitial zinc, giving rise to a shallow donor level just below the conduction band (Hartnagel et al., 1995). However the electrical behaviour of ZnO thin films could be improved by replacing Zn\(^{2+}\) atoms by elements with higher valence such as In\(^{3+}\), Al\(^{3+}\) and Ga\(^{3+}\) (Kohiki et al., 1994). Besides that it is also observed an improvement on the stability of the films.

Due to its high conductivity and high transmittance in the visible part of the radiation spectra, ZnO thin films are widely used as transparent conductor in optoelectronic devices such as: solar cells (Major et al. 1988 and Belghit et al. 1991), among other applications.

In the last years, several techniques have been developed to prepare ZnO thin films, like thermal evaporation, chemical vapour deposition (CVD) Dutta et al. (1993), spray pyrolysis (Tiburcio-Silver et al. 1991) and magnetron sputtering (Inaki et al. 1995). Independent of the deposition technique used the properties of the films especially the structural and electrical ones, could be improved by proper post-deposition treatments under suitable conditions (temperature and atmosphere) (Nunes et al. 1998).

In this paper, we studied the effect of the annealing conditions on the properties of ZnO thin films (intrinsic and doped) deposited by spray pyrolysis, with the aim to improve the films properties.

2. EXPERIMENTAL DETAILS

The films were deposited by spray pyrolysis on borosilicate glass substrates. The solution used was 0.1 M zinc acetate diluted in methanol. For doping Al\(\text{Cl}_3\cdot H_2\text{O}\) and In\(\text{Cl}_3\) (1at%) was added to the main solution. The solution was sprayed onto a substrate held at 400°C, using as carrier gas nitrogen at a flow rate of 12 l/min. After deposition, the films were annealed at temperatures between 200°C and 500°C during 2 hours in three different atmospheres: vacuum, forming gas (95% N\(\text{\textsubscript{2}}\)+5% H\(\text{\textsubscript{2}}\)) and air.

The structural properties of the films were studied using X-ray spectroscopy on a Rigaku diffractometer having a rotating Cu cathode. The film thickness was measured by a Sloan Dektak 3d profilometer. The optical properties were obtained using a Shimadzu double-beam spectrophotometer equipped with an integrating sphere in the wavelength range from 0.3\(\mu\text{m}\) to 2.5\(\mu\text{m}\). All measurements were performed having the air as reference. The electrical resistivity (\(\rho\)) and Hall coefficient of the films at room temperature were measured by Van der Pauw’s technique using a BioRad HL5500 system.

3. RESULTS

3.1 Effect of the annealing atmosphere

To study the effect of the annealing atmosphere on the properties of ZnO thin films, the films were annealed at 200°C in air, vacuum and forming gas for 2 hours. The X-ray diffraction spectra of ZnO thin films reveal the existence of a single phase with a hexagonal wurzite structure of bulk ZnO.

From the X-ray spectra obtained for the ZnO and ZnO:In thin films it is clear that the intensity of the X-ray peaks increase with the annealing treatment which means that this treatment leads to an improvement in the crystallinity of the films. However the highest changes were observed in films annealed in forming gas. These results could be related with the decrease on the defect density due to the oxygen chemical desorption mechanism at grain boundaries that is more significative when the annealing is performed in a reduction atmosphere.

Figure 2 shows the variation of \(\rho\) with the annealing atmosphere for the different ZnO thin films studied. The results show that lowest values of \(\rho\) occur for films annealed in forming gas. The more significative changes were observed for intrinsic films.
Figure 1 - X-ray diffractograms of ZnO (a) and ZnO:In (b) annealing at 200ºC during 2 hours at three different atmospheres.

Figure 2 - Variation of the resistivity with the annealing atmosphere.

This behaviour could be explained by the enhancement in the mobility and carrier concentration, as it was observed (see figure 3). The increase in the mobility is in conformity with the improvement of the films crystallinity. Besides that, the increase of ρ (related to the increase of the free carrier concentration) is also due to the desorption of O₂ on the grain boundaries, leading to annihilation of oxygen acceptor states at the grain boundaries, which act as trap for electrons (Major et al. 1984). This desorption mechanism is more effective when the annealing process takes place in a reduced atmosphere, such as forming gas.

Figure 3 - Effect of the annealing atmosphere on the mobility and carrier concentration.

In order to determine the effect of the annealing atmosphere on the optical properties of ZnO thin films, we calculate the absorption coefficient (α) from transmittance measurements data, for a wavelength (λ) of 550nm.

The increase observed in α with the annealing treatment is due to the enhancement in the free carrier concentration observed. The highest value occur in the films annealed in forming gas.

Figure 4 - Effect of the annealing atmosphere on the absorption coefficient for λ=550nm.

The widening of the direct band gap (E_{opt}) of the ZnO thin films studied is directly related to the increase in the carrier concentration due to Burstein-Moss shift (Sarkar et al. 1991). That is, E_{opt} shifts to higher energies with the increase in carrier concentration (see figure 5).
Figure 5 - Variation of the $E_{op}$ with the annealing atmosphere.

To assist the selection of the ZnO thin films produced concerning their application on optoelectronic devices it is used the figure of merit ($F_{TC}$) defined as (Gordon et al. 1996):

$$F_{TC} = \frac{1}{\rho \alpha}$$  \hspace{1cm} [1]

The data achieved of $F_{TC}$ for the different films produced are shown in figure 6, as deposited and after annealing treatment in different atmospheres. There we notice that the most significative changes are observed in undoped ZnO films annealed in forming gas.

Figure 6 - Effect of the annealing atmosphere on the figure of merit.

3.2. Effect of the annealing temperature.

The effect of the annealing temperature on the properties of ZnO thin films depend on the atmosphere used. For that reason, we study the annealing in oxidant and reduction atmospheres. All ZnO thin films studied were annealed at temperatures between 200ºC and 500ºC during 2 hours.

3.2.1. Oxidant atmosphere

As the annealing temperature increases it’s possible to observe an increase in the films cristallinity volume as can be taken from the X-ray spectra depicted in figure 7.

Figure 7 - X-ray difractograms of ZnO annealing in air during 2 hours at different temperatures.

The enhancement in the film’s crystallinity leads to an increase in the carriers mobility (see figure 8). However this effect is not enough to improve $\rho$ since it depends on free carriers concentration and on the defects associated to grain boundaries.

In figure 9 its possible to observe an increase in $\rho$ with the annealing temperature. This behaviour could be explained by the oxygen absorption mechanism that occurs when the films were annealed in oxidant atmosphere such as air. This oxygen absorbed in the grain boundary act as traps for the carriers leading to a decrease in the carrier’s concentration (figure 8).

Figure 8 - Effect of the annealing temperature on the mobility and free carrier concentration of ZnO thin films annealed in air.

As show in figure 10 $\alpha$ increases up to an annealing temperature of 200ºC and then decreases. This behaviour could by related with variation of the crystallinity and carrier’s concentration of the ZnO thin films studied.
As expected from the variation of the electro-optical properties of ZnO thin films with the annealing temperature, when an oxidant atmosphere is used, \( F_{TC} \) decreases with the increase of the annealing temperature (see figure 11).

3.2.2. Reduction atmosphere
To study the effect of the annealing temperature in the films annealed in a reductive atmosphere, we used forming gas.

Like for films annealed in an oxidant atmosphere, the film crystallinity increases (figure 12) with the annealing temperature. This effect depends on the temperature used and its independent of the atmosphere used.

3.2.3. Forming gas
As expected from the variation of the electro-optical properties of ZnO thin films with the annealing temperature, when an oxidant atmosphere is used, \( F_{TC} \) decreases with the increase of the annealing temperature (see figure 11).

The electrical properties of ZnO thin films are the most affected by the annealing treatment. The resistivity of the films decreases with the increase of the annealing temperature (see figure 13) due to the enhancement in the mobility and carrier’s concentration (see figure 14). This behaviour could be explained by desorption mechanism of oxygen that occurs in the grain boundaries, which is more pronounced at high temperatures.
Figure 14 - Effect of the annealing temperature on the mobility and free carrier concentration of ZnO thin films annealed in forming gas.

Figure 15 - Variation of the absorption coefficient with the annealing temperature.

To summarise the variation of the electro-optical properties with the annealing temperature, we calculate $F_{TC}$ (figure 16), for films annealed in a reduction atmosphere. Under these conditions we notice that $F_{TC}$ increases more than 2 orders of magnitude for films annealed in forming gas up to, 400°C.

Figure 16 - Effect of the annealing temperature on the figure of merit of ZnO thin films.

4. CONCLUSIONS

From the work performed we conclude that the post-heat treatment under controlled conditions of the ZnO thin films are quite important, in order to improve the final characteristics of the films produced, aiming their applications in optoelectronic devices.

The annealing treatment leads to significative changes on the structural and electrical properties of ZnO films, especially for intrinsic ZnO thin films.

Depending on the annealing atmosphere (reduced or oxidant) it is possible to improve or deteriorate the electro-optical properties of the ZnO films.

From all the annealing treatments performed the ones that lead to most significative improvements on the properties of ZnO thin films was the ones realised in forming gas at 400°C during 2 hours. With this post-heat treatment, it is possible to decrease $\rho$ of the films for more than 3 orders of magnitude. From all films studied the ZnO:In films annealed in forming gas are the most suitable for applications in optoelectronic devices, where it is required a low $\rho$ ($\rho=5.8\times10^{-3}$ $\Omega$cm) and a high transmittance (T=86%).

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