



Site location of Al-dopant in ZnO lattice by exploiting the structural and optical characterisation of ZnO:Al thin films



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ABSTRACT

The zinc oxide thin films, highly transparent, doped aluminium were prepared on glass substrates by the reactive chemical spray method. The incorporation nature of Al atoms in the ZnO lattice was determined by X-ray diffraction and optical analyses. Indeed, for low doping $\leq 2\%$, the results of X-ray spectra analysis show a simultaneous reduction of lattice parameters (a and c), this variation, which follows VEGARD'S law, tends to indicate a substitution of Zn by Al. By against for doping $> 2\%$ the increase in the lattice parameters thus the grain sizes, in accordance with the VEGARD'S law can be explained by occupation of the interstitial sites by Al atoms. Beyond 4%, the material tends to get disorderly and the crystallites orientation is random. The studied optical properties show that the variation of the optical gap follows a law of the $x^{3/2}$ form for $x < 3\%$ (x is the aluminium atom fraction incorporated in the ZnO lattice). The granular structure is fairly visible and some local growths are disrupted. The crystallite size at low enlargement is coherent with the XRD results.

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Introduction

The zinc oxides (ZnO) have received considerable attention in recent years in the optical and electronic industries regarding its optical, electronic and acoustic properties. Like a conducting transparent films, ZnO is the most suitable material and more used because of its (i) large band gap (3.2 eV) [1], (ii) ease in doping (iii) chemical stability in hydrogen plasma [2], (iv) thermal stability when doped with III group elements [3], and (v) abundance in nature and nontoxicity. However the electrical properties change of ZnO films from a near-insulator state to semi-metal state can be controlled by thermal annealing in hydrogen plasma [2] or by an appropriate doping process, either by cationic [4–6] or anion [7–9] substitution.

Zinc oxide is a technologically important material. Different deposition techniques have been reported for preparing this material: by sputtering [10], pulsed laser deposition (PLD) [11], CVD [12] and the spray pyrolysis [13]. This last technique can be distinguished from the others due to its rapidity, simplicity, low cost and efficiency.

The electrical conductivity of ZnO thin films can be increased by cationic substitution in the trivalent position of atoms. On the other hand, the impurities incorporation in substitutional sites

affects the optical and structural properties [5,14]. It's for this reason, our work is not only devoted to the preparation and characterisation of the undoped and aluminium doped ZnO thin films but also aims to contribute to deepening the understanding of the Al atom incorporation in the zinc oxide lattice.

Details experimental

The preparation of undoped and aluminium doped ZnO thin films by spray pyrolysis has already been described [15]. The chemical spray pyrolysis method has been recently used intensively for the preparation different types of thin films, especially oxides of many metals and semiconductors.

With the help of compressed air at 2 bars, solutions of starting materials were sprayed at flow rate of 10 ml/min on heated glass substrate held at constant temperature 375 ± 5 °C to get the films. The aqueous solution of zinc nitrate (0.1 M) was used for preparing pure ZnO films, while for the film doped with aluminium, aqueous solutions of zinc and aluminium nitrates (0.1 M) were mixed in the desired proportion(s) (1–5 at% Al with respect to Zn) prior to its use as the spraying solution.

The optical transmittance properties were measured by a UV–vis–NIR scanning spectrophotometer, the structural characteristics by X-ray diffraction (XRD) analysis and the surface morphology was examined by the Scanning Electron Microscope (SEM).

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Results and discussion

Structural properties

The X-ray diffraction spectra for undoped and aluminium doped ZnO thin films prepared at 375 °C are shown in Fig. 1. The spectra indicate that the films are of polycrystalline nature. The undoped ZnO films show a strong peak for the crystallographic plane [002]. Therefore the crystallites are highly oriented with their *c*-axis perpendicular to the substrate plane. This result is in agreement with those reported for ZnO thin films prepared by this technique and also by other process [16–19]. On the other hand, to define the effect of doping atoms on the crystalline structure, we compare the X-ray diffraction spectra of pure and Al doped ZnO (Fig. 2), the analysis of this figure shows that the increase in Al/Zn atomic ratio does not affect the preferential growth of the films (crystalline Symmetry), the relative position of peaks is preserved, the same peaks of pure ZnO appear for Al doped ZnO. However, it's noticed that there is a reduction in the intensities of the peaks and especially that of the (002) plans, of [002] direction, and absence of the additional peaks in the doped ZnO spectra. We can conclude the absence of any free aluminium oxide (in particular Al_2O_3).

Further, from the comparison of the spectra, we observed a light shift of the Al doped ZnO peaks in comparison with those of pure ZnO. The Fig. 2 shows well this shift of the peaks, for all the directions of Al doped ZnO in comparison with those of pure ZnO, the displacement takes place towards the great values of 2θ . This shift is proportional to the aluminium concentration in the ZnO films. From the concentration 2%, the shift towards the great values of 2θ stops and the material has tendency to amorphisation (disorder). This concentration seems to represent a particular value of the doping ZnO by aluminium. Indeed, a variation of lattice parameters involves a variation in θ , we can say that this shift of the peaks influences the lattice parameters of the structure and lattice size. The variation of the ZnO lattice size suggests that the aluminium atom can take two channels to incorporate either (i) in substitutional site instead of zinc atom or (ii) in interstice between zinc and oxygen atoms. In order to determine the nature of the aluminium atom site in the ZnO lattice in substitutional or interstitial configuration, a determination of the lattice parameters (*a*, *c*) and grain sizes in function of Al concentration in ZnO films were performed.

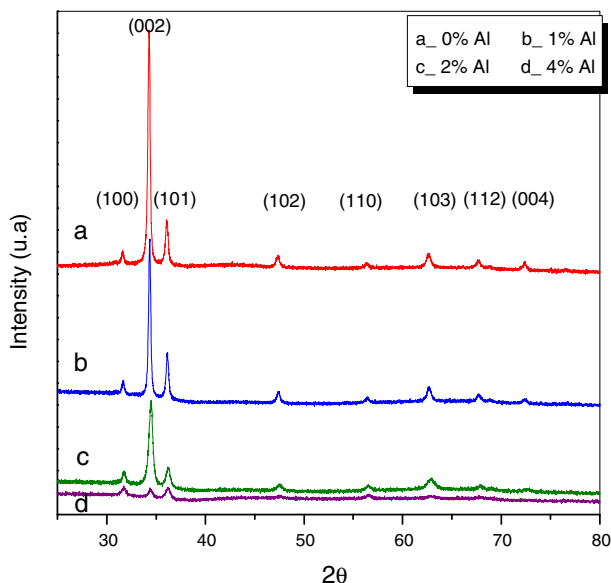


Fig. 1. Diffraction spectra of ZnO films for different Al concentrations.

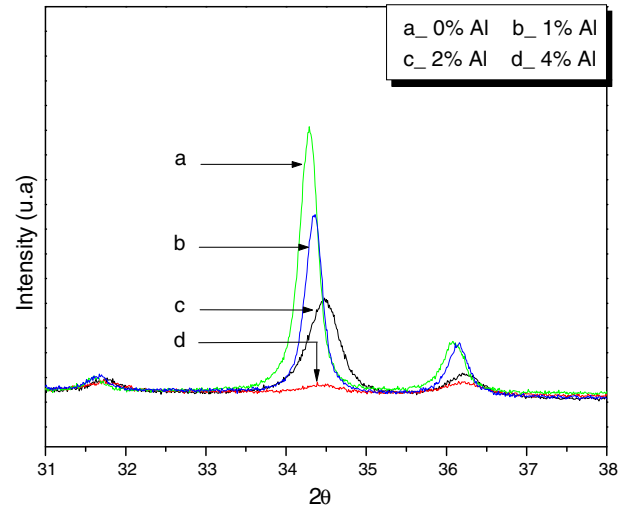


Fig. 2. Presentation of shifting peak in diffraction spectra RX.

As the ionic radius of aluminium (0.53 Å) is lower than that of zinc (0.60 Å), it is predicted by VEGARD's law [20,21] that if the incorporation process takes place by substitution, the addition of aluminium should shrink the lattice appreciably. On the other side, if the incorporation occurs in the interstitial sites between the zinc and oxygen atoms, however, this effect should expand the lattice. The results, given in Fig. 3, show that the lattice parameters *a* and *c* decrease with the increase in the aluminium concentration up to the value 2%, beyond this value, these parameters increase with the addition of aluminium in the initial solution. We can interpret this phenomenon as follows: (i) in the interval (0–2%), there is a narrowing of ZnO lattice in the two principal directions (*a*, *c*), in accordance with the VEGARD's law, this in consequence of a substitution of the zinc atom by the aluminium atom in the ZnO lattice. (ii) Beyond the value 2%, the increase in the lattice parameters thus the grain sizes (Fig. 4), in accordance with the VEGARD's law can be explained by occupation of the interstitial sites by Al atoms. Therefore beyond 2%, a saturation of substitutional sites takes place and this leads to another mode of Al incorporation, which seems to privilege the interstitial sites and which ends by leading (beyond 4%) to an amorphization. However, according to the relative values of diffraction intensities for the various rays, indicates that the excessive addition of aluminium (beyond 4%) leads to the crystallite disorientation which tends to

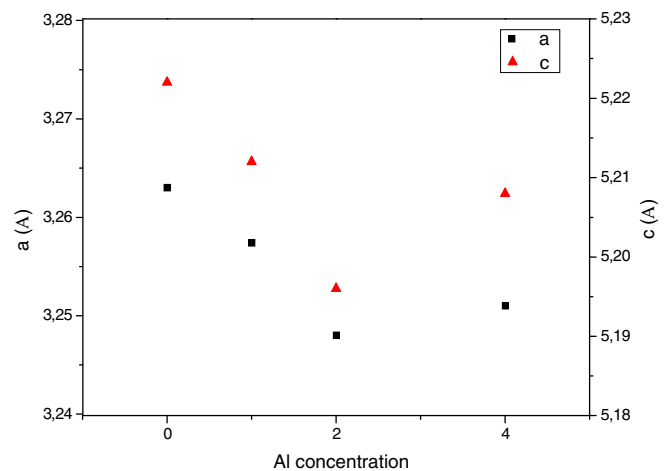


Fig. 3. Lattice parameters variation as a function of the Al concentration.

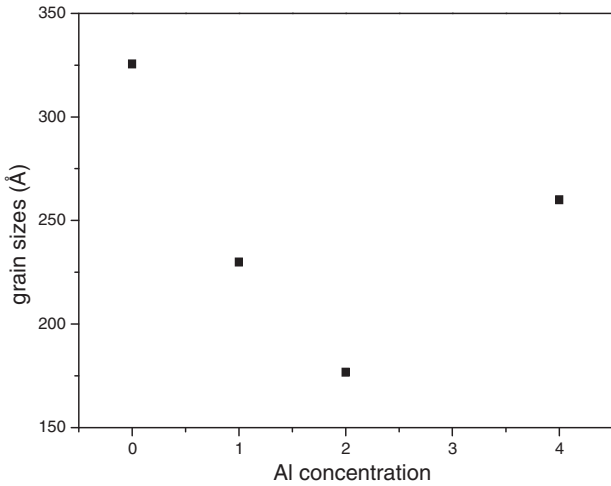


Fig. 4. Grain size variation as a function of Al concentrations.

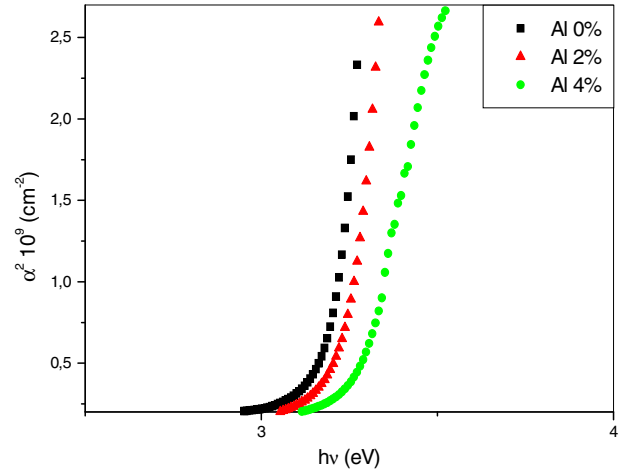


Fig. 6. Absorption coefficient square for different Al concentrations.

an amorphization of material. Therefore our analysis on this phenomenon is that the excessive introduction of aluminium into the interstitial sites will generate a great number of defects from where a distortion of the crystal structure of material.

Optical properties

For even the effect of the aluminium incorporation on the optical properties of ZnO thin films we measured optical transmittance for Al doped and undoped ZnO thin films.

All the films (for various doping) are highly transparent in the visible range (Fig. 5). Transmittance reaches 90% for undoped films and 85% for doped films. The decrease in plateau of the transmittance of the doped films relative to undoped can be explained by the texture of the film surface and internal morphological nature of the films during deposition of the material. Indeed, the results of the X-ray diffraction analysis show that the grain sizes decreases when doping increases. This can be the reason of the decrease in transmittance [17].

The use of the optical absorption data allows us to determine if the material has a direct or indirect gap. The curves $(\alpha)^2$ and $(\alpha)^{1/2}$ in function $(h\nu)$ are analysed for all films. A linearity is observed in the first case as shown in Fig. 6. We can conclude that the direct transitions dominate in doped ZnO films and undoped. The optical

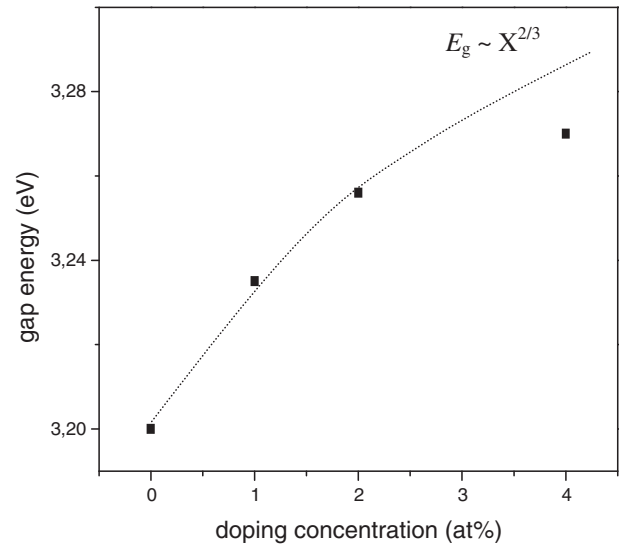


Fig. 7. Gap variation as a function of the doping concentration.

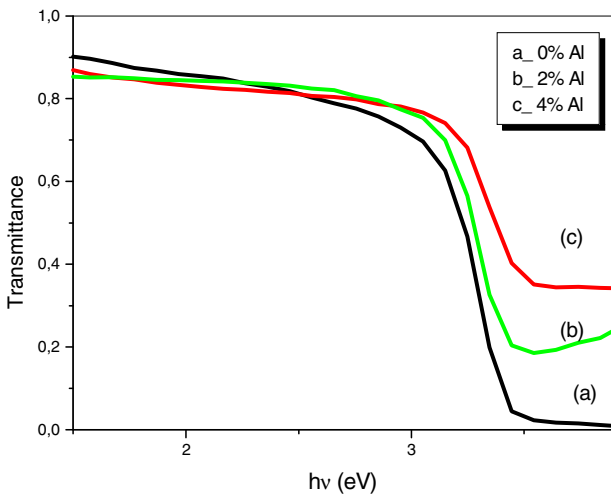


Fig. 5. Transmission spectrum for different Al concentrations.

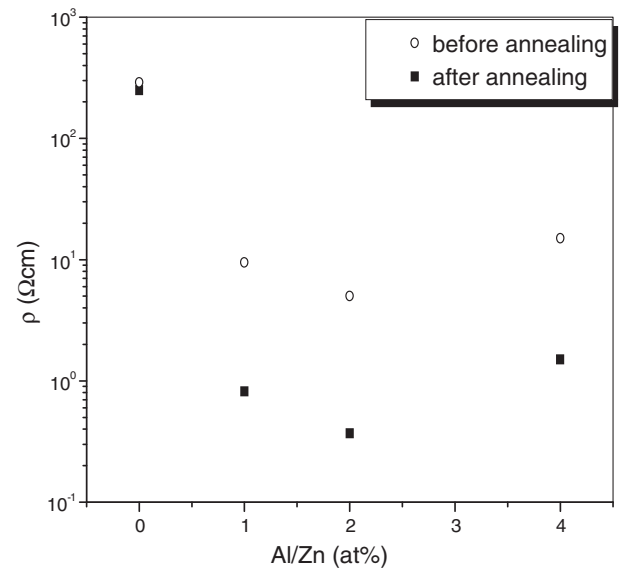


Fig. 8. The evolution of the electrical resistivity as a function of doping concentration before and after the thermal annealing.

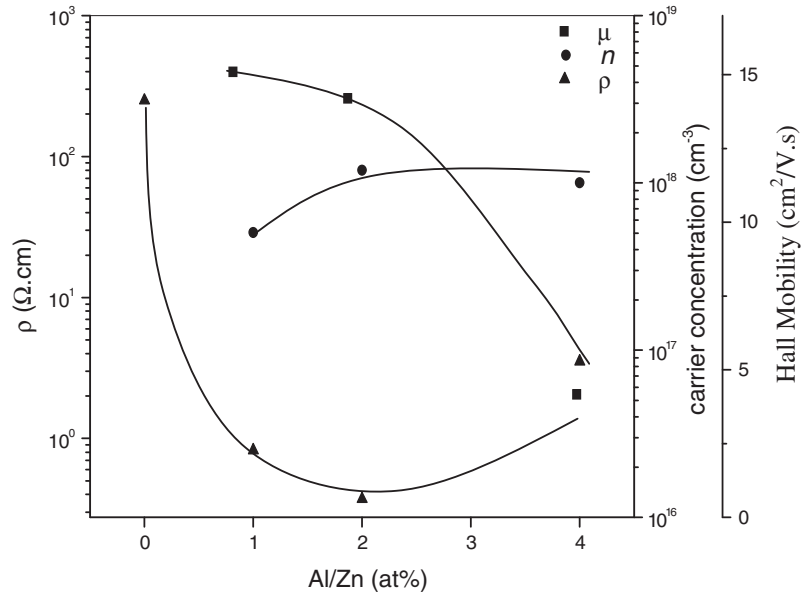


Fig. 9. The Variation of μ , n and ρ with the Al concentration.

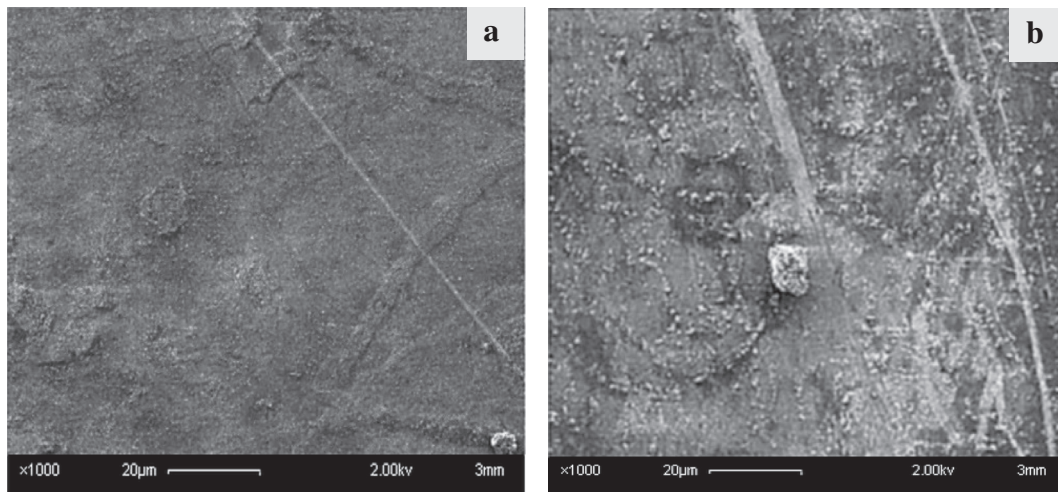


Fig. 10. SEM images for pure ZnO and Al-doped ZnO thin films (a) undoped, (b) doped with 2 at% Al.

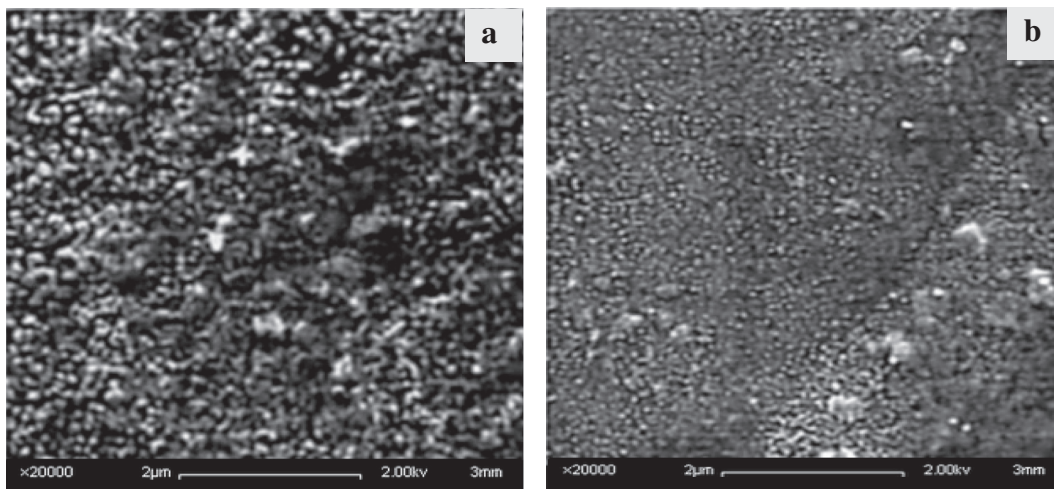


Fig. 11. SEM images for pure ZnO and Al-doped ZnO thin films at a higher enlargement (a) undoped, (b) doped with 2 at% Al.

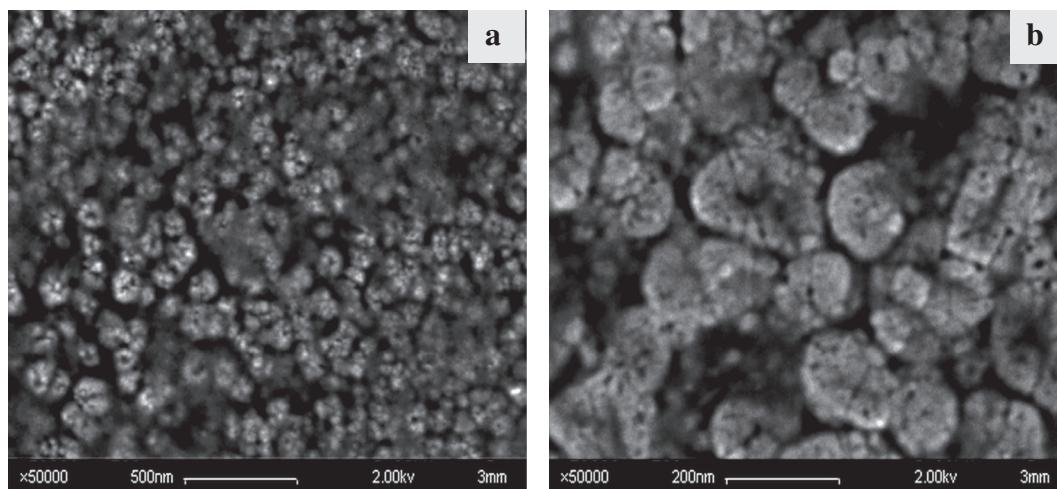


Fig. 12. (a) and (b) SEM image for Al-doped ZnO thin films on larger scale.

gap is determined by the extrapolation of the linear part of the films to the energy axis. The found value of the gap, for the undoped films, is of the order 3.2 eV.

The Fig. 7 also shows that the effect of the doping concentration on the E_g values, it appears clearly that there is increase in the optical gap when the Al concentration increases. This behaviour could be attributed to the way in which the Al atoms were incorporated in the film. If Al is located on the sites of substitution (Al^{3+} instead of Zn^{2+}), then there is an increase in the carrier concentration. According the Fig. 7 we notice that the variation of the measured optical gap, depending on the dopant concentration, is nonlinear and is characterised by a kind of saturation. For the low concentrations <3%, the gap variation follow a law in $E_g \sim \chi^{2/3}$. This shows that for the low concentrations, the aluminium incorporated into ZnO is located on substitutional sites and that this variation follows a law of Burstein–Moss effect [22,23]. Beyond that, there is a discord between the electron concentration and that the dopant atoms. That means that the substitution mechanism does not function anymore and that there is an incorporation channel of Al which does not contribute to the increase of free electrons concentration. These concordant results confirm the conclusions made within the structural study.

Electrical properties

Fig. 8 shows the evolution of the electrical resistivity of the films as a function of doping concentration before and after the thermal annealing. The resistivity decreases after thermal annealing of 425 °C in air. The chemisorption of acceptor oxygen on the ZnO:Al surface, in the interstices of the film and between grain boundaries forms an electron depletion layer which acts as a surface potential barrier and causes low mobility and carrier concentration [24]. Therefore, we consider that the decrease of the resistivity during the thermal annealing results in a change of carrier concentration and mobility from the movement of Al atoms to Zn lattice sites and the desorption of oxygen from the ZnO:Al surface, interstices and the grain boundaries.

The variation of resistivity ρ , carrier concentration n and mobility μ as a function of Al concentration are shown in Fig. 9. The carrier concentration of the film was found to increase with doping concentration except at higher dopant concentrations, where a tendency towards saturation was observed. Such behaviour was expected as a result of substitutional doping of Al^{3+} at the Zn^{2+} site creating one extra free carrier in the process. As the doping level is increased, more dopant atoms occupy lattice sites of the zinc

atoms, resulting in more charge carriers. However, after a certain level of doping, no more zinc sites that can be occupied by dopant atoms because of the limited solubility of Al in the ZnO crystallites, so the excess aluminium may occupy the interstitial position, also leading to distortion of the crystal structure, as it was shown in the X-ray results. Thus the carrier concentration reaches a maximum when the substitutional doping of the zinc oxide by aluminium at a maximum whereas the mobility will continue to fall as more scattering and grain boundaries barrier effects occur.

Morphological properties

The films fabricated of Al-doped and undoped ZnO perfectly adhere to the glass substrate. A series of images by electron microscopy were obtained to analyse the effect of doping on the films. We give the micrographs at various enlargements.

Fig. 10 gives images of surfaces of the undoped and doped ZnO films for the same enlargements. On Fig. 10a, the corresponding image to undoped films prepared at 650 k, the surface appears too united with a little crystal formations and localised defects. It is observed, however, on the film surface the material trailed of significant dimensions and regular widths. These salient trailed can be due to an inhomogeneous contribution of material during the manufacturing process by chemical spray. On Fig. 10b, the corresponding image of doped films, is observed at this scale crystals of different forms randomly distributed in the surface. The observed crystals often have dimensions of the order of micron. The films also exhibit contrast inhomogeneity which may be due to inhomogeneities in the chemical composition. We encounter sometimes crystals of more significant size the order of 10 μm and which adhere to surface. The analysis of these crystals could not be made and their composition remains unknown. At a higher enlargement, Fig. 11, we realise of the difference in the granules size in surface of the two films. Fig. 11 shows comparatively that the average size of the pure ZnO granules is statically greater than that doped ZnO. This result is confirmed by measurements of X-ray diffraction. The grains at the doped ZnO surface are finer by inspecting a zone or image of the granules is resolved, the presence of surface defects tends to indicate the presence of roughness on the films of doped and undoped ZnO. On some samples for the doped and undoped films, we see fracture lines. These fractures probably result from the difference in thermal expansion coefficients between film and substrate during cooling. On larger scale, Fig. 12a and b, of the doped ZnO surface, the islets with crystallites of forms more or less symmetrical are observed. These islets are

separated by vacant spaces. Each islet or grain is constituted by jointed crystallites. The crystallites form tends to indicate that those grow perpendicular to the substrate surface.

Conclusion

The results of optical, structural and morphological characterisation of ZnO:Al thin films clearly show the effect of Al doping on these films. For structural properties, the pure ZnO films present an intense peak in the direction [002], while for the doped films there's a decrease in peak intensities and especially that of the (002) planes. It was the presence of two incorporation process of aluminium in the ZnO lattice: (a) a substitution of anion Zn^{2+} by Al^{3+} , for concentrations $\leq 2\%$, (b) occupying interstitial sites beyond 2%. For the optical properties, ZnO films have a direct gap $E_g = 3.2$ eV, which varies as a function of doping following to relationship $E_g \propto x^{2/3}$ just for doping concentrations $< 3\%$. Scanning electron microscopic images show that the grain size decreases with increase in doping concentration.

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