Materials Science and Engineering B 174 (2010) 46–49

Contents lists available at ScienceDirect

Materials Science and Engineering B

journal homepage: www.elsevier.com/locate/mseb

Fluorine doped zinc oxide thin films deposited by chemical spray, starting from zinc pentanedionate and hydrofluoric acid: Effect of the aging time of the solution

R.R. Biswal[a,b], S. Velumani[b], B.J. Babu[b], A. Maldonado[b], S. Tirado-Guerra[c], L. Castañeda[d], M. de la L. Olvera[b,*]

[a] Amity Institute of Nanotechnology, Amity University, Sector-125, Super Express Highway, Noida 201301, India
[b] Departamento de Ingeniería Eléctrica, Centro de Investigación y de Estudios Avanzados del Instituto Politécnico Nacional, CINVESTAV-IPN, SEES, Apartado Postal 14740, México, D.F., 07000, Mexico
[c] Escuela Superior de Física y Matemáticas, Instituto Politécnico Nacional, IPN, Apartado Postal 75-544, México, D.F., 07300, Mexico
[d] Instituto de Física, Universidad Autónoma de Puebla, Apartado Postal J-48, Puebla 72570, Mexico

ARTICLE INFO

Article history:
Received 7 September 2009
Received in revised form
19 December 2009
Accepted 4 March 2010

Keywords:
Zinc oxide
Thin films
TCO

ABSTRACT

Fluorine doped zinc oxide thin films, ZnO:F, were deposited on sodocalcic glass substrates, starting from zinc pentanedionate and hydrofluoric acid, by the chemical spray technique. The effect of the aging time of the starting solution on the electrical, structural, morphological and optical characteristics of the ZnO thin films was studied. Uniform, adherent, and mirror-like films were deposited at different days. A high electrical resistivity, was found in the films deposited the first day. However, a decrease in the resistivity, until a minimum, in the order of 3×10^{-2} Ω cm was reached for films deposited after the starting solution was aged for twelve days. The films fit well with the hexagonal, wurtzite-type ZnO structure, with a (0 0 2) preferential growth. Variation in the grain size was observed as a consequence of the aging of the solution. An average crystallite size varied between 17.3 and 22.8 nm due to aging effect, and some variations in surface morphology were encountered. All the films are highly transparent in the near UV–vis range, with an average transmittance oscillating between 83% and 90%.

1. Introduction

Semiconductor oxide films have received considerable attention due to their suitable optical and electrical properties. Some of them can be considered as good candidates for transparent conductive films if doped with suitable impurities. Pure zinc oxide is an intrinsic semiconductor with high electrical resistivity and a direct band gap of about 3.3 eV [1]. Zinc oxide thin films are very interesting materials due to the fact that a high transmittance and low resistivity can occur simultaneously [2]. In addition ZnO thin films show a high chemical stability when they are exposed at a reducing atmosphere, such as in the case of hydrogen plasma of moderate energy [3]. Other interesting characteristic is that, it can be done p-type, for developing highly efficient ZnO based optoelectronic devices [4]. These characteristics make ZnO thin films attractive as a transparent electrode in thin film solar cells based on silicon [5].

ZnO thin films with controlled properties can be obtained by physical [6] and chemical techniques [7]. In the case of the chemical techniques, some problems are encountered when highly conductive films are required, due to the fact that non-intentional impurities and a high density of defects are introduced during the growth process, which in turn increase resistivity. Although the applications of ZnO thin films are reduced by these facts, there are many applications where the films deposited by chemical techniques are still competitive by the low cost and easy deposition on large areas [8].

In this respect, chemical spray technique is a versatile technique for the deposition of ZnO thin films that meets the requirements of low resistivity and high transmittance [9]. As a matter of fact, ZnO thin films doped with Group III elements, mainly In, Al and Ga, with low resistivity and high transmittance have been reported by this technique, and a vast knowledge of the technique has been obtained [10,11]. In this way, the role of solution composition (molar concentration, solvents, precursors), substrate temperature, and post deposition annealing treatments on the physical characteristics of the films are now well established.

On the other hand, the anionic doping of ZnO thin films deposited by chemical spray, has not attracted attention due to the fact that F incorporation into the host lattice is deficient and hence films with a high resistivity are obtained. It was not until our group accidentally discovered the role of the solution aging that successful fluorine doped ZnO thin films were reported [12]. The role of the solution aging on the transport properties of ZnO:F thin

* Corresponding author. Tel.: +52 55 5747 3784; fax: +52 55 5061 3978.
E-mail address: molvera@cinvestav.mx (M. de la L. Olvera).

0921-5107/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.mseb.2010.03.013

films and interesting photoluminescent characteristics have been reported by other authors [13,14].

Among the key variables involved in the deposition of ZnO thin films by the chemical spray technique, the kind of precursor dissolved into the starting solution is one that has been well established [15]. In this case, zinc pentanedionate can be a very interesting alternative for deposition of fluorine doped ZnO thin films by chemical spray. Contrary to zinc acetate, the molecular chain at which Zn is bonded is longer. Hence, the Zn pentanedionate has to be dissolved in a mix containing a great amount of acetic acid, a situation more complicated than in the case of Zn acetate, affecting the properties of the materials. In this work the effect of the solution aging on the electrical, structural, morphological, and optical characteristics of ZnO:F thin films deposited by chemical spray, starting from Zn pentanedionate and HF is reported. These precursors are for first time considered for studying the aging effect.

2. Experimental

Fluorine doped ZnO thin films were deposited from a 0.2 M starting solution of zinc pentanedionate (Alfa) dissolved in a mix of de-ionized water, acetic acid, and methanol (3:1:6 volume proportion). Hydrofluoric acid diluted at 10% in volume in de-ionized water was used as doping source. The relative atomic concentration of F with respect to Zn, [F]/[Zn], was taken as reference for doping. In this case, the [F]/[Zn] value in the starting solution under consideration in our work was 20 at.%. This value was selected based on our previous work [12]. In fact, we have noticed that optimum properties of ZnO:F thin films deposited by chemical spray are obtained around this value. Sodalime glass plates, with a 2 cm × 1 cm area, were used as substrates, after a standard cleaning procedure. The films were deposited at a constant temperature of 475 °C. Nitrogen was used as carrier gas with a flow of 8 l/min. A solution constant flow rate of 10 ml/min was used in all the cases. Films deposition was carried out from the precursor solution, starting from the fresh solution to a solution aged for twelve days (fresh, 2, 4, 6, 8, and 12 days).

The sheet resistance of the ZnO:F thin films was measured by the four-point probe technique, taking into consideration the corresponding geometric corrections. The film thickness of the films was measured; after a step was manufactured using a 10% diluted solution of chloride acid, with a KLA Tencor P15 profilometer. The thickness magnitudes were around 550 nm in all the samples. The films structure was obtained by means of X-ray diffraction, using a PANalytical X-ray diffractometer by the θ–2θ technique based on Cu-Kα radiation (λ = 1.5405 Å). Surface morphology was observed directly by scanning electron microscopy (SEM) in a XL FEG/SFEG/SIRION. The optical transmittance at normal incidence was measured with a double-beam spectrophotometer (UV-2401PC from Shimadzu) in the UV–vis region (300–1000 nm).

3. Results and discussion

3.1. Electrical properties

Fig. 1 shows the effect of the aging time of the starting solution on the electrical resistivity of ZnO:F thin films. A high resistivity was found in samples deposited from a fresh solution. As the aging time of the solution increases, the resistivity of the films decreases, reaching a saturation value, in the order of 3×10^{-2} Ω cm (see Table 1). As has been reported early, this result is because in films deposited from aged starting solutions, the F atoms are incorporated effectively into the ZnO lattice, where it is believed they are located in oxygen sites [12]. In respect of the improved F incorporation into the film with the aging time of the starting solution, it

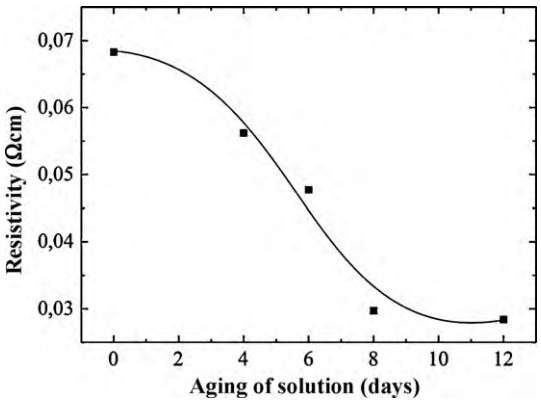

Fig. 1. Resistivity variation of ZnO:F thin films as a function of the aging time of the starting solution.

is supposed that, chemical complex formed by chains that strongly bind F and In ions are gradually formed in the solution. In this case, when solution is atomized on the hot substrate, the volatilization of F occurs at lower rate, as compared with fresh solutions, increasing the F incorporation into the lattice. This in turn, decreases the corresponding electrical resistivity, as consequence of the effective carrier concentration increasing.

It is noteworthy to mention that the minimum resistivity value of the ZnO:F thin films, reached from a twelve-day aged solution, is still high as compared with those doped with In, where values in the order of 3×10^{-3} Ω cm are easily obtained, even when the films are deposited on sodalime glass substrates [11]. The effect of long-term aging of the solution is still in progress.

3.2. Structural properties

Fig. 2 shows the X-ray diffraction spectra of films deposited at 475 °C from solutions aged at different times, namely 0, 4, 6, 8, and 12 days. All the films were polycrystalline and the spectra fit well with the hexagonal wurtzite-type ZnO. In all the cases the (0 0 2) preferential growth was observed, irrespective of the aging time.

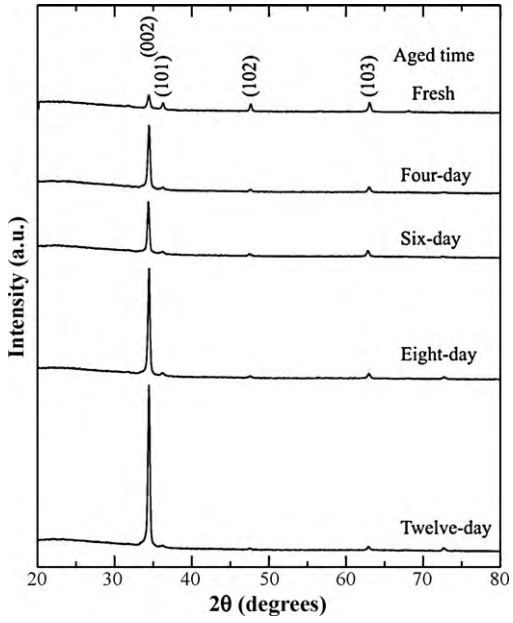

Fig. 2. X-ray diffraction spectra of ZnO:F thin films deposited at 475 °C and from a starting solution aged for: (a) fresh, (b) four-day, (c) six-day, (d) eight-day, and (e) twelve-day.

Table 1
Physical characteristics of the ZnO:F thin films.

Temperature	Aging of solution	Average optical transmittance (%)	Resistivity (Ω cm)	Crystallite size (nm)	Grain size (nm)
475 °C	Fresh	83.13	0.0683	17.3	180
	4 days	91.04	0.0566	20.7	125
	6 days	92.69	0.0476	21.1	–
	8 days	89.87	0.0297	21.7	–
	12 days	91.89	0.0283	22.8	–

This characteristic may be due to the fact that F has an adverse effect on all the planes but (0 0 2), hindering the growth, as has been showed by Smith and Rodriguez-Clemente [16]. The orientation of the films on the amorphous substrates was reported by Bauer [17], according to which there are two possible orientations, both of which result from the nucleation at the film/substrate interface. The initial orientation favors a nucleus to develop a free energy configuration. The final growth orientation results from survival of nuclei having an energetically unstable plane parallel to the substrate surface among randomly oriented nuclei because of their different growth rates. This means that, the growth orientation is developed into one crystallographic direction of the lowest surface energy. Then, the grains turn larger as the film grows with lower surface energy density.

An estimation of the average crystallite size was done by using the well-known Scherrer's formula: $D = 0.9\lambda/(\beta \cos\theta)$, where β is the full width at half maximum intensity (FWHM) in radians of the $(h\,k\,l)$ peak, λ the radiation wavelength (0.15406 nm for Cu-Kα_1), and θ is the Bragg's angle. As the solution was aged, an increase in the crystallite size was obtained. This result confirms the beneficial effect of the aging time on the structural characteristics of the chemically sprayed ZnO:F films. In this respect,

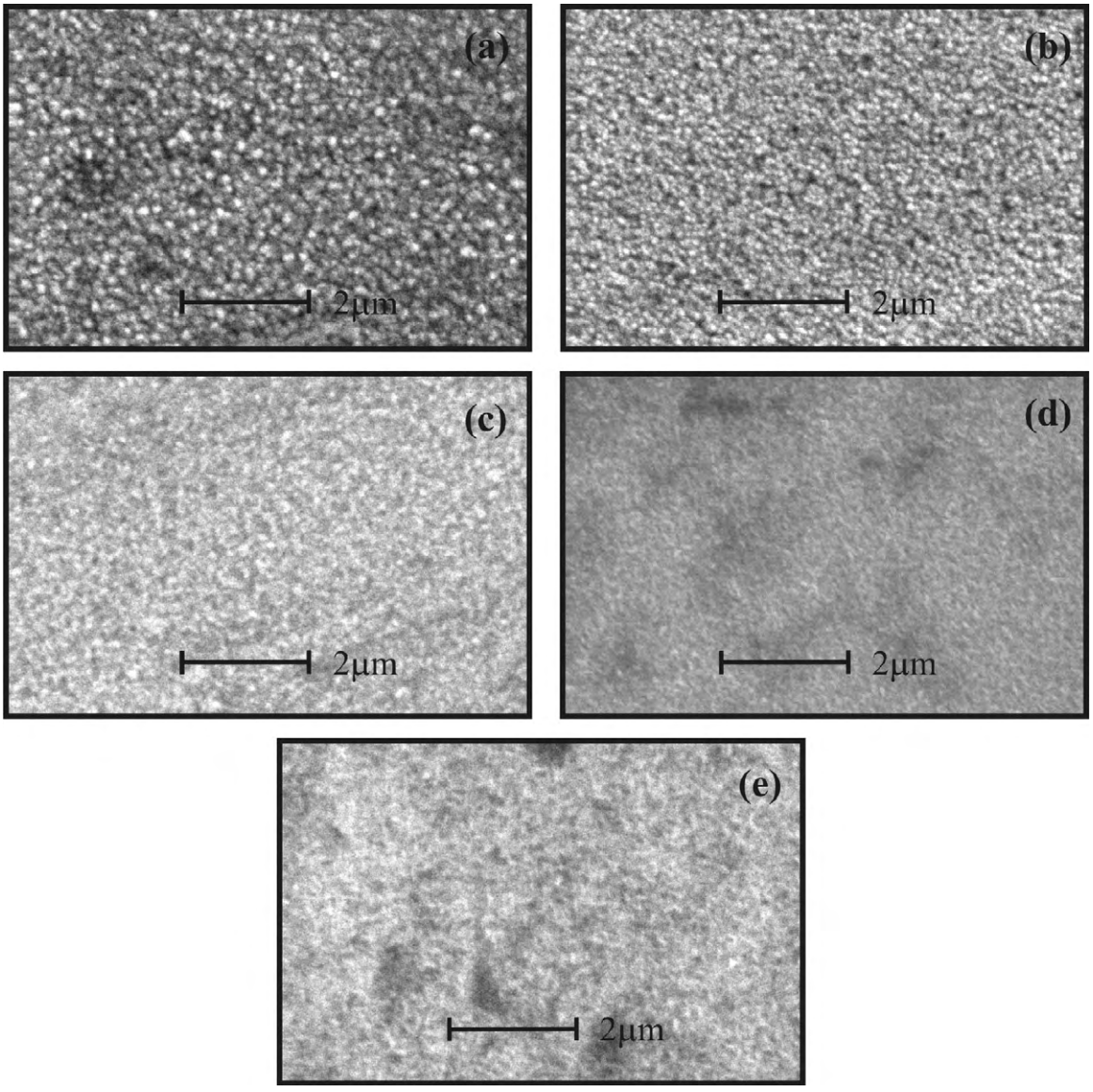

Fig. 3. Scanning electron microscopy of ZnO:F thin films deposited at 475 °C and from a starting solution aged for: (a) fresh, (b) four-day, (c) six-day, (d) eight-day, and (e) twelve-day.

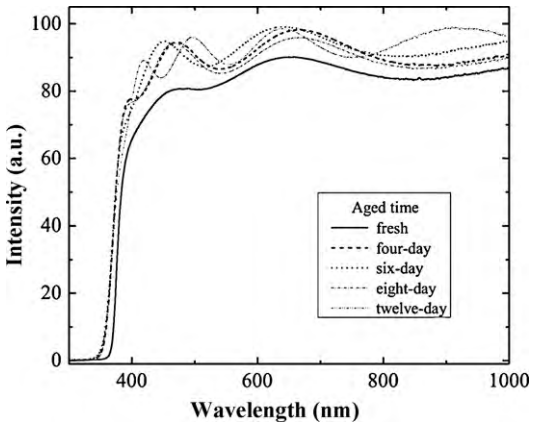

Fig. 4. Optical transmission spectra of ZnO:F thin films deposited at 475 °C from starting solutions with different aging time.

it is well-known that, films with large crystallite is indicative of good quality films, which is very convenient for almost any application requiring good quality films, as is the case of the optoelectronic applications. The calculated crystallite sizes are reported in Table 1.

3.3. Morphology

Fig. 3 shows the surface morphology of ZnO:F thin films deposited at different days. Aging of the solution clearly influences on the corresponding morphology of the samples, as it was expected from the changes in electrical resistivity results. As a matter of fact, for the films deposited from a fresh solution, the surface is rough and formed by round grains, whose average diameter is in the order of 180 nm. In the case of films deposited from a 4-day aged solution, the average size of the grains decreases, at an average value around 125 nm (see Table 1). For films deposited with a solution aged either 6 or 8 days it can be observed a uniform surface, and it is difficult to observe a well-defined grains. Finally, in the case of films deposited from a twelve-day aged solution, it is possible to observe the formation of small aggregates, from which it is difficult to estimate the respective grain size. From the micrographs one can confirm the existence of an evident effect of the aging time on the surface morphology, however the quantification of this effect is impossible due to the images do not afford the grain size measurement. An interesting fact about these results is that the grain size and the crystallite size show an apparent opposite tendency, which is an odd result.

3.4. Optical properties

In Fig. 4 it is shown the transmittance spectra of the ZnO:F thin films deposited at 475 °C from aged solutions at different days number. The average transmittance estimated in the 400–700 nm interval, is higher than 83%, which is an acceptable value for application as a transparent electrode. From the spectra it can be noticed that the films transmittance shows a slight tendency to increase with the aging time. This is an expected result, since the films quality is improved with the aging time, as was evidenced from both X-ray spectra, and the estimated crystallite size (see Table 1).

The optical band gap was estimated from the linear extrapolation of the square of the absorption coefficient versus photonic energy, by the Manifacier's method for transparent films [18]. The band gap magnitude oscillated around 3.3 eV.

4. Conclusions

Uniform, adherent, mirror-like, and conductive and transparent F-doped ZnO thin films were deposited on sodalime glass substrates by the chemical spray technique starting from Zn pentanedionate and hydrofluoric acid. The maximum transmittance and the lowest electrical resistance were presented in films deposited at 475 °C. As-deposited films showed a high electrical resistivity in the order of $3 \times 10^{-2}\ \Omega$ cm. An average transmission in the UV–vis region oscillating between 83% and 90% was observed in the samples, which is a competitive value with respect to other reported values.

Preferential (0 0 2) growth was observed in all the samples, irrespective of the aging time. A weak contribution of (1 0 1), (1 0 2), and (1 0 3) planes is also observed. From the obtained results it has been shown that zinc pentanedionate and hydrofluoric acid are potentially attractive for the deposition of conductive and transparent ZnO:F thin films by the chemical spray technique. Although the ZnO thin films are highly transparent in the visible region, the electrical characteristics still are far from being satisfactory for manufacturing of transparent electrodes. Hence more detailed investigation on the effect of the deposition variables on the transport characteristics of ZnO:F thin films deposited by chemical spray, are still needed in order to have competitive electrical resistivity values. This work is in due course.

Acknowledgements

The technical assistance of M.A. Luna-Arias, A.G. López-Fabián, and A. Palafox is thanked. The economical support of the CONACyT, through Projects 80689 and 80502, is also acknowledged.

References

[1] O. Madelung (Ed.), Data in Science and Technology: Semiconductors, Other Than Group IV Elements and III–V Compounds, Springer-Verlag, New York, 1992.
[2] C.G. Granqvist, Solar Energy Mater. Solar Cells 91 (2007) 1529.
[3] A. Ortiz, A. Sánchez, C. Falcony, M.H. Farias, G.A. Hirata, L. Cota-Araiza, J. Non-Cryst. Solids 103 (1988) 9.
[4] P. Dai, H. Deng, F.Y. Mao, J.D. Zang, J. Mater. Sci.: Mater. Electron. 19 (2008) 727.
[5] R. Groenen, J. Loffler, P.M. Sommeling, J.L. Linden, E.A.G. Hamers, R.E.I. Schropp, M.C.M. van de Sanden, Thin Solid Films 392 (2001) 226.
[6] Ü. Örgüz, Ya.I. Alivov, C. Liu, A. Teke, M.A. Reshchikov, S. Dogan, V. Avrutin, S.-J. Cho, H. Morkoc, J. Appl. Catal. 98 (2005) 041301.
[7] K.L. Chopra, S. Major, D.K. Pandya, Thin Solid Films 102 (1983) 1.
[8] S.S. Shinde, P.S. Shinde, C.H. Bhosale, K.Y. Rajpure, J. Phys. D: Appl. Phys. 41 (2008) 105.
[9] P.S. Patil, Mater. Chem. Phys. 59 (1999) 185.
[10] A. El Manouni, F.J. Manjón, M. Mollar, B. Marí, R. Gómez, M.C. López, J.R. Ramos-Barrado, Superlattices Microstruct. 39 (2006) 185.
[11] J. Wienke, A.S. Booij, Thin Solid Films 516 (2008) 4508.
[12] M. de la L. Olvera, A. Maldonado, R. Asomoza, O. Solorza, D.R. Acosta, Thin Solid Films 394 (1) (2001).
[13] S.M. Rozati, S. Moradi, S. Golshahi, R. Martins, E. Fortunato, Thin Solid Films 518 (4) (2009) 1279.
[14] P.M. Ratheesh Kumar, C. Sudha Kartha, K.P. Vijayakumar, T. Abe, Y. Kashiwaba, F. Singh, D.K. Avasthi, Semicond. Sci. Technol. 20 (2005) 120.
[15] R. Romero, D. Leinen, E.A. Dalchiele, J.-R. Ramos-Borrado, F. Martin, Thin Solid Films 515 (2006) 1942.
[16] A. Smith, R. Rodriguez-Clemente, Thin Solid Films 345 (1999) 192.
[17] E. Bauer, in: M.H. Francombe, H. Sato (Eds.), Single Crystal Films, Pergamon, London, 1964, pp. 43–67.
[18] J. Hu, R.G. Gordon, Solar Cells 30 (1991) 437.