Electrical and optical properties of Sb:SnO$_2$ thin films obtained by the sol–gel method

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Abstract

Transparent conducting thin films of antimony-doped tin oxide have been deposited by the sol–gel dip-coating (SGDC) method. Electrical properties are analyzed, and resistivity, Hall mobility, type and number of carriers measured as a function of the antimony doping.

Optical properties are investigated through the spectral transmision and reflection of the layers. The nature of the forbidden band and the width of the gap are determined.

Optical and electrical properties are compared with results obtaned on Sb:SnO$_2$ thin films elaborated by other methods such as chemical vapour deposition, sputtering and pyrolysis, and specific properties of the SGDC material are outlined. © 1997 Elsevier Science S.A.

Keywords: Electrical properties and measurements, Optical properties, Tin oxide

1. Introduction

Transparent conducting thin films are raising up increasing interest due to their large range of applications such as in photovoltaic cells, liquid crystal displays, photodetectors, etc [1–3]. Semiconductor oxides in general, and undoped or doped tin oxide in particular, are studied and commonly used materials for these devices. Requirements on the properties of the films as well as economical reasons depend on the type of applications considered, and lead then to the choice o specific elaboration techniques. In the case of SnO$_2$ layers used as transparent conducting electrodes, a compromise between a low resistivity and a high transmittance of light mostly in the visible range, is the main goal to reach. Furthermore the deposition process must not perturb the device intrinsic properties, and a low temperature procedure often appears very positive.

For SnO$_2$ several deposition methods exist, such as evaporation, sputtering, pyrolysis, chemical vapour deposition or sol–gel dip-coating (SGDC). We have explored this last soft technique which presents many advantages, and we have shown in previous work [4–7] that the SGDC route leads to very high-quality SnO$_2$ thin films. In our last paper [6], we mainly focused on the introduction of antimony doping atms in the SnO$_2$ matrix, on the way the dopant is incorpoited

and on the determination of the doping level into the elaborated films. In the present study, we investigate the influence of antimony doping on the electrical and optical properties of SGDC Sb:SnO$_2$ layers.

2. Experimental procedure

Details on the elaboration procedure of Sb:SnO$_2$ thin films by SGDC has already been given in previous papers [5,6], and we only recall here the main features. The SnO$_2$ solution was obtained by dissolving 8.37 g of SnCl$_2$2H$_2$O in 100 ml of absolute ethanol. The antimony solution was simultaneously prepared from a given amount of SbCl$_3$ dissolved in 20 ml of absolute ethanol. Both mixtures were separately stirred and heated in a closed vessel. Then the vessels were opened, and the solutions again stirred and heated until the solvents were completely evaporated. We finally obtained two powders that were mixed in 50 ml of absolute ethanol. The doped mixture was finally stirred and heated at 50 °C for 2 h.

The substrates used were plates of Pyrex, cleaned, dried and then coated up. They were dipped into the doped solution and withdrawn at a constant speed of 80 mm min^{-1}. The pulling phase was performed at room temperature. All layers were first dried in air for 40 min at 150 °C and then heated for 30 min at 500 °C (in a constant flow of pure and dry oxygen) for densification. These values have been found

to optimize the quality of the films [4] especially the morphology which plays a major role in optical and electrical properties.

Three coating thicknesses have been considered for each antimony doping level: single layers (noted 1C), obtained in one run on the substrate, have measured thicknesses around 100 nm, and the three- (3C) and five-step (5C) multilayers are respectively 300 and 500 nm thick. In the vertical pulling apparatus used, the material is deposited on both sides of the substrate and this point must be taken into account for the determination of transmittance properties.

In this paper the term "doping" refers to the antimony content measured directly into the films as the ratio Sn/(Sn + Sb): this actual doping of the layers as been found systematically lower than expected from the solution composition [6].

Electrical properties were obtained measuring the resistance per square $R_\square$ of the layers, the resistivity ρ of the material being calculated after precise thickness measurements (by means of a Tencor Alphastep profilometer). The four-probe and van der Pauw methods are used, and the Hall mobility, the type and number of carriers also determined.

The transmission and reflection coefficients in the 0.2–3 μm region are measured with a 2200–2300 Varian spectrophotometer. From transmission measurements we can deduce the nature and the width of the gap.

3. Electrical properties

3.1. Resistivity

From the measured $R_\square$ and the thicknesses given by the profilometer, we can calculate the resistivity for 5C samples as a function of the antimony doping level. Undoped SGDC SnO$_2$ thin films present a rather high resistivity above 1 Ω cm. This is linked to the fact, already noticed in our previous papers [5,6], that almost no deviation from stoichiometry exists for undoped (and also for Sb-doped) SnO$_2$ thin films elaborated by the sol–gel technique. We must then underline this difference in behaviour with undoped SnO$_2$ thin films (elaborated by other coating techniques) which present a low initial resistivity attributed to the presence of oxygen vacancies [8,9].

In our case, the evolution of the resistivity as a function of the doping (Fig. 1) is a decrease over several decades as the doping increases, with a minimum of ρ around 4.5×10^{-3} Ω cm for a doping value Sb/(Sn + Sb) around 10% [5]. Then the resistivity seems to increase much more slowly than for Sb:SnO$_2$ elaborated by other methods [10–20]. For a doping of 21%, the resistivity is still 5×10^{-3} Ω cm. Kojima et al. [10] have found for Sb:SnO$_2$ thin films with the same thickness elaborated by spray pyrolysis a minimum of 9×10^{-4} Ω cm for a doping of 3.8%, and for a doping of 20% a resistivity of 10^{-1} Ω cm. The scattering of data points below the 5% doping is due to the uncertainties in the doping evaluation at
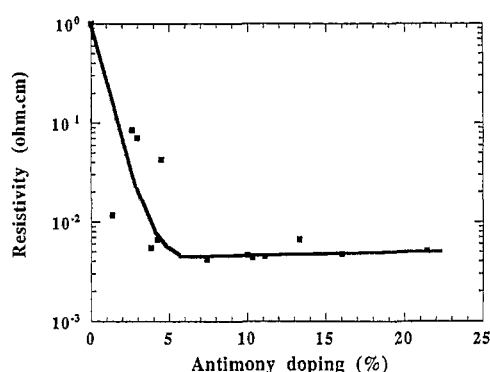

Fig. 1. Resistivity of SGDC Sb:SnO$_2$ thin films as a function of the doping level (the thickness of the films is about 500 nm).

low levels [6] and to a dispersion in resistivity for these samples.

In order to try to understand this resistivity behaviour, we have previously mentioned and evidenced [5,6], as other authors [10,14,21], the possible competition existing between the two oxidation states of antimony, [Sb^{5+}] and [Sb^{3+}], when the Sb content increases. For the low doping levels, [Sb^{5+}] is dominant and leads to the observed decrease in resistivity. When the Sb content continues to increase, the [Sb^{3+}] component appears and its percentage is more and more important. For a given value, a phenomenon of compensation between the two conduction types (n-type doping for [Sb^{5+}] and p-type doping for [Sb^{3+}]) should occur leading to an important rise in resistivity. If such an observation is reported in the literature [10–13], the observed evolution on our samples is quite different: the [Sb^{3+}] component is found to overcome the [Sb^{5+}] in the range of doping 10% to 20% (large range due to the large uncertainties in the XPS decomposition procedure). So in our experiments no increase in resistivity is observed in conjunction with the antimony state of charge evolution.

We must also emphasize at this point the fact that for all quoted authors, the Sb concentration given in the corresponding papers is the one expected from the starting solution composition and not the actual doping obtained from measurements on the layers. A comparison is then made more difficult.

For Sb:SnO$_2$ thin films elaborated by other techniques we note a high increase in resistivity for the highest doping levels, often associated with an intense bluish coloration or even a darkening (not observed in SGDC). We think that this difference in behaviour could find its origin in the large number of oxygen vacancies existing in such materials, and also in their interaction with the two antimony states of charge.

A study in temperature of $R_\square$ obtained with the four-probe method has been realized from 293 K to 423 K. We find that in this range the resistivity is not sensitive to the temperature. Confirmation has been obtained by the van der Pauw method on square samples (1 cm^2) on which indium–gallium alloy contacts were deposited on each corner. These results show
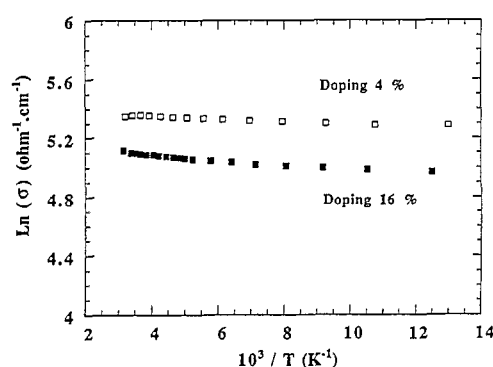
Fig. 2 Electrical conductivity of SGDC Sb.SnO$_2$ layers as a function of temperature for two doping levels, 4 and 16%.

Table 1
Hall mobility, type and number of carriers as a function of the level of antimony doping in the SGDC SnO$_2$ thin films.

Antimony doping (%)	Hall mobility (cm^2 V^{-1} s^{-1})	Type of carrier	Number of carriers (cm^{-3})
4	2–3	n	(4.2–6.2) × 10^{20}
10	2–5	n	(3 1–7 8) × 10^{20}
16	2–3	n	(3 5–5.2) × 10^{20}
24	0.1		2 3 × 10^{20}

that the SGDC Sb:SnO$_2$ is a degenerated material where the donor level merges into the conduction band.

Another study has been conducted in a much lower temperature range from 80 to 293 K. We note an evolution of the conductivity which is extremely low, although measurable. The corresponding activation energy has been determined for two different doping levels (Fig. 2): 1.3 meV for 16% and 0.7 meV for 4%. This confirms the hypothesis that the Sb:SnO$_2$ elaborated by the sol–gel method is a degenerated material. Maddalena et al. [22] have obtained for undoped SnO$_2$ realized by the sol–gel technique a much higher activation energy of 0.22 eV, but in this case no information was given on the stoichiometry and the conductivity had probably a different origin probably related to oxygen vacancies.

3.2. Hall mobility

The Hall mobility μ_H of carriers in SGDC Sb:SnO$_2$ layers has been analyzed in the 80–293 K temperature range. Measurements at low temperature are very stable, and we observe no evolution of μ_H when the temperature increases. Since it is rather difficult to obtain accurate measurements, only ranges of order are given in Table 1. Up to a Sb doping of 16%, μ_H is found between 2 and 5 cm^2 V^{-1} s^{-1}, and for the highest dopings (24%), μ_H decreases to 0.1 cm^2 V^{-1} s^{-1}. A similar behaviour is noticed by Kim et al. [12] for Sb:SnO$_2$ thin films elaborated by chemical vapour deposition (CVD).

The type of carriers could also be determined for Sb dopings between 4 and 16%: the carriers are, without any doubt, electrons (n-type), but for the highest doping (24%) we could not determine with certitude the type of carriers. We can then notice that the proposed compensation phenomenon between [Sb^{3+}] and [Sb^{5+}] species leading to a change in the conduction type (n-type for low doping level to p-type for higher dopings) and expected to occur between 10 and 20% is not verified experimentally in the SGDC case.

The number of carriers n can be deduced from $n = 1/(\rho e \mu)$ with $\mu = r\mu_H$ where r is a coefficient function of the resistivity ρ. With the hypothesis that μ is identical to μ_H ($r \cong 1$), the values found are reported in Table 1. The number of carriers varies between 2×10^{20} and 8×10^{20} cm^{-3}.

We note that the mobility decreases for the highest doping levels while the number of carriers remains relatively constant (change over less than a decade). We can consider the classical semiconductor theory with the effective mobility μ depending on two mechanisms: $1/\mu = 1/\mu_i + 1/\mu_L$ where μ_i is the mobility related to ionized sites and μ_L the mobility related to phonons. The mobility μ_i should remain constant with doping since the concentration of carriers is almost constant. This leads consequently to the decrease of μ_L when the doping level increases. In another paper [6] we have observed that the crystallite size decreases as the doping level increases and this could explain the decrease of the effective measured mobility for the highest dopings.

4. Optical properties

4.1. Determination of the gap

The fundamental absorption which corresponds to electron excitation from the valence band to the conduction band can be used to determine the nature and value of the optical band gap. Depending on the characteristics of the material, theoretical developments lead to different laws for the absorption coefficient α as a function of the photon energy $h\nu$. For all investigated samples, although polycrystalline, the $\alpha(h\nu)$ curves correspond to the case of a crystalline material with direct allowed transitions (direct gap) according to the following relation: $\alpha(h\nu) = A^*(h\nu - E_g)^{1/2}$ where A^* is a constant depending on the material.

Then a plot of the square of the optical density (OD) ($= \log(100/T)$ as a function of $h\nu$ (Fig. 3) gives the gap width for samples with various doping levels. Curves are limited at high photon energies by the absorption of the substrate. The values found for the gap are around 3.85 eV with an uncertainty of ± 0.2 eV due to apparatus and calculation. We find this value whatever the sample thickness (1C or 5C) and whatever the Sb content. For undoped SnO$_2$, the optical gap is found equal to 4 ± 0.2 eV. However it is rather difficult to attribute this difference between Sb-doped SnO$_2$ and undoped SnO$_2$ to a decrease of the optical gap due to the presence of doping states into the forbidden band since we have seen in the previous paragraph that the Sb:SnO$_2$ material seems to be degenerated even at very low temperatures. Uncertainties
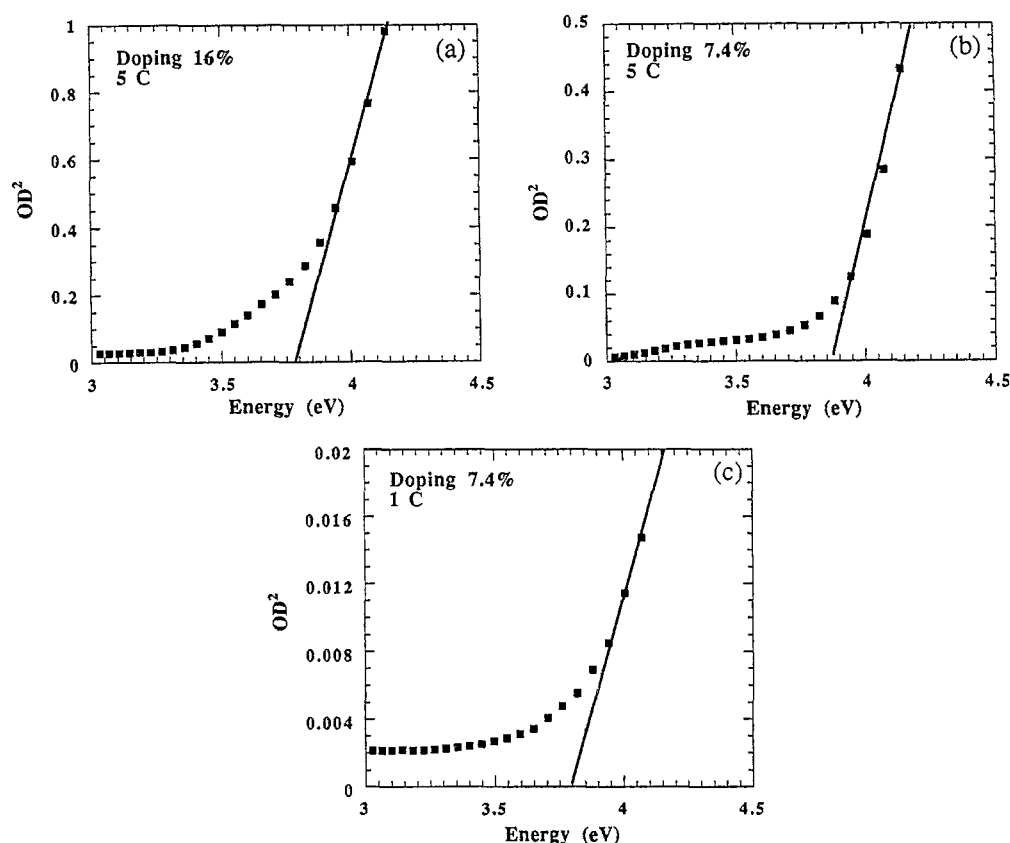
Fig. 3. Determination of the direct forbidden band: (a) 5C sample with a 16% doping level; (b) 5C sample with a 7.4% doping level; (c) 1C sample with a 7.4% doping level.

are too high to state that there is a modification of the optical gap after doping.

The above values correspond to those given in the literature by different authors (values varying between 3.6 and 4.1 eV depending on the elaboration methods [23–27]).

4.2. Transmission and reflection studies

We have determined the transmission coefficient T and the reflection coefficient R of the Sb:SnO$_2$ layers. These two quantities have been measured on a Varian 2200–2300 spectrophotometer working in UV, visible and near-IR (185–3150 nm).
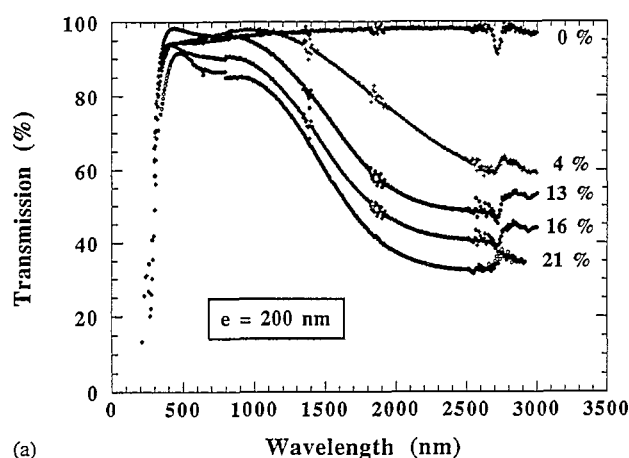
4.2.1. Transmission

In transmission analysis the intensity detected corresponds to the intensity of the beam having passed through the first coating of Sb:SnO$_2$ on one side of the Pyrex substrate, the substrate itself and then the second Sb:SnO$_2$ coating on the other side. To determine the transmission corresponding to the films, a Pyrex reference is used.

Highly doped samples elaborated by the sol–gel technique present a bluish coloration. This coloration is also observed, but in a more intense way, on Sb:SnO$_2$ films elaborated by other techniques [10,14,18,19,21,28], and with a blackening in some cases [10,21,28]. Kojima et al. [10] attributes this

blackening to a charge transfer between the two oxidation states of antimony, Sb^{3+} and Sb^{5+}. For other authors [21,28], this charge transfer between [Sb^{5+}] and [Sb^{3+}] should generate only the bluish coloration, and the blackening would result from the formation of a new Sb–O phase at high doping levels.

In SGDC Sb:SnO$_2$ thin films the antimony is in the [Sb^{5+}] state at low doping levels, then, as seen above, the [Sb^{3+}]/ [Sb^{5+}] ratio increases with higher doping levels and could explain the bluish coloration observed. However no oxide other than SnO$_2$ could be detected in these films [6]. We must note also that for these high doping levels the large concentration of free carriers shifts the plasmon edge to wavelengths located into the visible range sufficiently to induce the bluish coloration observed (Fig. 4(a) and 4(b)).

Although modulated by interference effects, the transmission coefficient T decreases slowly with increasing thicknesses and doping levels (Fig. 4(a) and 4(b)). At a wavelength of 500 nm (Fig. 5) and for a thickness around 200 nm (1C) T varies between 85 and 95% in the visible range, for 3C layers between 80 and 90% and for 5C between 65 and 80%. If we compare these transmission values in the visible range for SGDC Sb:SnO$_2$ films to those indicated in the literature for the same material obtained by other techniques [10,11,13,14,19,21,29,30], we note that they are rather high even for larger thicknesses and higher doping

(a)
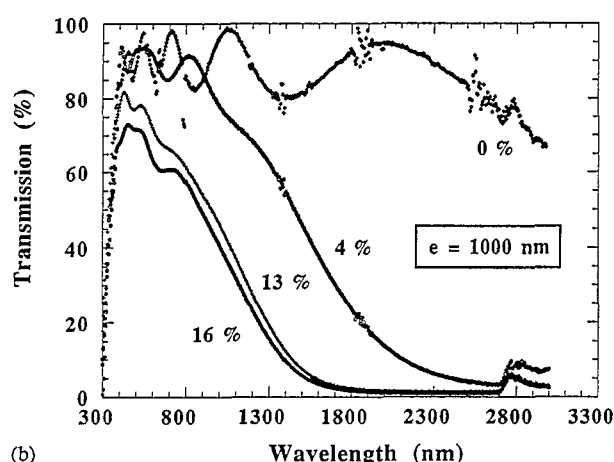
(b)

Fig. 4. Transmission spectra of SGDC Sb:SnO₂ layers with different doping levels· (a) 1C sample, 100 nm on each side of the substrate; (b) 5C sample, 500 nm on each side of the substrate.
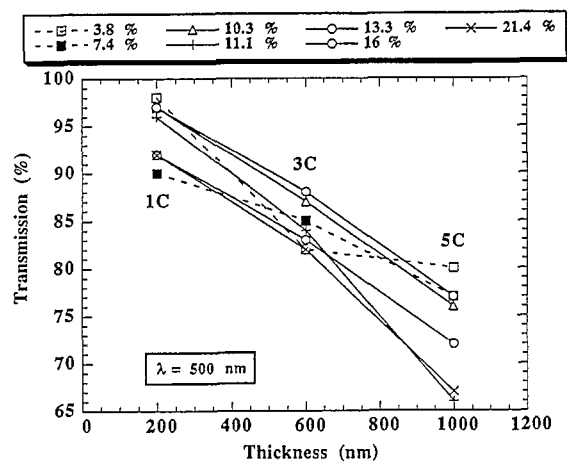

Fig. 5. Transmission of SGDC Sb:SnO₂ layers at a given wavelength of 500 nm as a function of the total crossed thickness (both sides) and for various doping levels.

levels. This point is certainly to be related to the quite good quality (morphology) of Sb:SnO₂ thin films elaborated by the sol–gel technique [4].

In order to try to observe the influence of free carriers on the optical transmission, we have compared the spectra
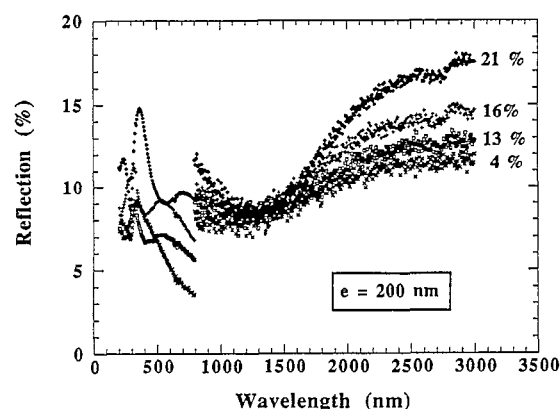

Fig. 6. Reflection spectra of SGDC Sb·SnO2 layers with different doping levels for a 1C sample (100 nm thick).

recorded at 14 K to those obtained at an ambient temperature. No difference could be detected and this behaviour emphasizes the fact that Sb:SnO₂ elaborated by the sol–gel technique is a degenerated semiconductor. In this case, the Fermi energy lies into the conduction band and the carrier concentration is independent of the temperature [31].

4.2.2. Reflection

Their reflectivity in the infrared range make transparent conducting oxides good candidates for thermal shields. In the spectrophotometer used for such reflectivity measurements, the beam undergoes two reflections. As a consequence, the reflection coefficient R is obtained from the square root of the measured intensity. We consider as negligible the reflections at the front and rear interfaces with the substrate.

The reflection coefficient R (Fig. 6) is very low in the visible range ($\leq 10\%$) whatever the doping level. The plasmon resonance appears in the near-IR according to the high concentration of the free carriers in the films ($\approx 10^{20} \text{ cm}^{-3}$). The reflection coefficient increases in the IR between 11 and 18% for dopings varying from 4 to 21%.

4.2.3. Factor of merit

By combining electrical conductivity and optical transmission we can define a factor of merit ϕ. It can be expressed through the following relation:

$$\phi = T_{\text{m}} / \rho$$

where T_{m} is the mean transmission in the visible range (400–800 nm) and ρ is the mean resistivity. This factor has been calculated for 5C samples and is found maximum for Sb dopings around 7%. It represents the quality of the SGDC Sb:SnO₂ material as regards to the compromise to found between optical transmission and electrical resistivity.

5. Conclusion

As a main result on electrical properties of Sb:SnO₂ thin films elaborated by the sol–gel dip-coating (SGDC) tech-

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nique, we note that the resistivity behaviour as a function of antimony doping is quite different than that observed for the same material elaborated by other deposition methods. First, SGDC thin films are highly resistive when undoped (very few oxygen vacancies). As the doping level increases to a few percent, the resistivity decreases over several decades, and a minimum of 4.5×10^{-3} Ω cm is observed for a doping level around 10%. When the Sb content continues to increase up to 25%, the resistivity remains almost constant. No further increase in resistivity is recorded. There is no obvious correlation between the resistivity evolution and the state of charge of Sb species. The number of carriers stays relatively constant (some 10^{20} cm^{-3}) whatever the doping level. At high doping levels the Hall mobility decreases strongly from 5 to 0.1 cm^2 V^{-1} s^{-1}.

Concerning optical properties, the polycrystalline Sb:SnO$_2$ elaborated by SGDC is a material with a direct forbidden band and the measured gap is found equal to $3,8 \pm 0,2$ eV. The transmission is rather high in the visible region, ranging between 65 and 80% for a 1000 nm thickness, in spite of the light bluish coloration taken by the SnO$_2$ thin films when they are highly doped with antimony. With regards to the electrical and optical properties, the SGDC Sb:SnO$_2$ material appears as a "different" material in comparison with Sb:SnO$_2$ obtained by other classical elaboration techniques.

Acknowledgements

References

[1] C M. Lampert, *Solar Wind Technol*, 4 (3) (1987) 347–379

[2] C M Lampert, *Solar Energy Mater.*, 6 (1981) 1–41.

[3] J.R. Bellingham, W A. Phillips and C J Adkins, *J. Mater. Science Lett.*, 11 (1992) 263–265.

[4] J.P. Chatelon, C. Terrier, E. Bernstein, R Berjoan and J A. Roger, *Thin Solid Films*, 247 (1994) 162–168.

[5] C Terrier, J.P. Chatelon, R. Berjoan and J A. Roger, *Thin Solid Films*, 263 (1995) 37–41.

[6] C. Terrier, C. Chatelon, R. Berjoan, C. Dubois and J.A. Roger, *J. Sol–gel Sci. Technol.*, accepted JSST 597-96

[7] J.P. Chatelon, C. Terrier and J.A. Roger, *J. Sol–gel Sci. Technol*, accepted JSST 599-96.

[8] Z M. Jarzebski and J.P. Marton, *J. Electrochem Soc.*, 123 (7) (1976) 199C–205C.

[9] A.F. Carroll and L.H. Slack, *J. Electrochem. Soc.*, 123 (12) (1976) 1889–1893

[10] M. Kojima, H. Kato and M. Gatto, *Philos. Mag. B*, 68 (2) (1993) 215–222.

[11] A Tsunashima, H. Yoshimizu, K. Kodana, S. Shimada and T. Matsushita, *J. Mater Sci.*, 21 (1986) 2731–2734.

[12] K.H. Kim, S.W. Lee, D.W. Shin and C G. Park, *J. Am Ceram. Soc.*, 77 (4) (1994) 915–921.

[13] E. Shanti, V. Dutta, A. Banerjee and K.L. Chopra, *J. Appl. Phys.*, 51 (12) (1980) 6243–6251.

[14] I.S. Mulla, H.S. Soni, V.J. Rao and A.P.B. Sinha, *J. Mater Sci.*, 21 (1986) 1280–1288.

[15] S.J.L. Ribeiro, C.U. Santilli, S.H. Pulcinelli, F.L. Fortes and L F.C. De Oliveira, *J. Sol–gel Sci. Technol.*, 2 (1994) 263–267.

[16] Y. Takahashi and Y. Wada, *J. Electrochem. Soc.*, 137 (1) (1990) 267–272.

[17] T N. Blanton and M. Lelental, *Mater. Res. Bull.*, 29 (5) (1994) 537–543.

[18] B. Stjerna, E. Olsson and C.G. Granqvist, *J. Appl. Phys.*, 76 (6) (1994) 3797–3817.

[19] J Kane and H.P. Schweizer, *J. Electrochem. Soc.*, 123 (2) (1976) 270–277.

[20] C.J R. Gonzales-Oliver and I. Kato, *J. Non-Crystalline Solids*, 82 (1986) 400–410.

[21] Y. Nakanishi, Y. Suzuki, T. Nakamura, Y Hatanaka, Y. Fukuda, A. Fujisowa and G. Shimaoka, *Appl. Surf. Sci.*, 48–49 (1991) 55–58.

[22] A. Maddalena, R Dal Maschio, S. Dire and A. Roccanelli, *J. Non-Crystalline Solids*, 121 (1990) 365–369.

[23] Y.S. He, J.C. Campbell, R.C. Murphy, M.F. Arendt and J.S. Swinnea, *J. Mater. Res.*, 8 (12) (1993) 3131–3134.

[24] J.L. Jacquemin, *Thèse de doctorat*, Université de Montpellier, 1974.

[25] J.M. Themlin, R. Sporken, J. Darville, R. Caudano, J.M. Gilles and R.L. Johnson, *Phys. Rev.*, B42 (18) (1990) 11914–11925.

[26] J. Robertson, *J. Phys. C: Solid State Phys.*, 12 (1979) 4767–4776.

[27] T.J. Godin and J.P. Lafemina, *Phys. Rev.*, B47 (11) (1993) 6518–6523.

[28] D.R. Pike, R. Reid and R.J.D. Tilley, *J. Chem Soc. Faraday I*, 76 (1980) 1174–1182.

[29] K H. Kim, S W. Lee, D W. Shin and C.G. Park, *J. Am. Ceram. Soc.*, 77 (4) (1994) 915–921.

[30] B. Stjerna and C.G. Granqvist, *SPIE*, 1727 (1992) 178–193.

[31] K L. Chopra and S.R. Das, *Thin Film Solar Cells*, Plenum Press, New York, 1983.