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Optical Reflectance of Pure and Doped Tin Oxide: From Thin Films to Poly-Crystalline Silicon/Thin Film Device

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Abstract**—**Films of pure tin oxide SnO_2 and in presence of antimony atoms (SnO_2-Sb) deposited onto glass substrates have shown a sufficiently high energy gap to be transparent in the visible region, a high electrical mobility and a carrier concentration which displays a good electrical conductivity [1]. In this work, the effects of polycrystalline silicon substrate on the optical properties of pure and Sb doped tin oxide is investigated.

We used the APCVD (atmospheric pressure chemical vapour deposition) technique, which is a low-cost and simple technique, under nitrogen ambient, for growing this material. A series of SnO_2 and SnO_2-Sb have been deposited onto polycrystalline silicon substrates with different contents of antimony atoms at the same conditions of deposition (substrate temperature, flow oxygen, duration and nitrogen atmosphere of the reactor). The effect of the substrate in terms of morphology and nonlinear optical properties, mainly the reflectance, was studied. The reflectance intensity of the device, compared to the reflectance of tin oxide films deposited directly on glass substrate, is clearly reduced on the overall wavelength range. It is obvious that the roughness of the poly-c silicon plays an important role by improving the reflectance and hence the optical parameters.

A clear shift in the minimum of the reflectance upon doping level is observed. This minimum corresponds to strong free carrier absorption, resulting in different plasma frequency. This effect is followed by an increase in the reflectance depending of the antimony doping. Applying the extended Drude theory to the combining optical and electrical obtained results these effects are discussed.

Keywords**—**Doping, oxide, reflectance.

I. INTRODUCTION

TRANSPARENT conductive oxide (TCO) films have found a wide range of applications in electric equipments and coatings where transparency is required. This material constitutes an important commercial use in the manufacture of antifrost windshields (nesa glass) and in the manufacture of thin film resistor. As reported [1], [2] tin containing oxides are promising anode materials for secondary lithium ion battery.

TCO films are extensively used in a variety of optoelectronic devices, such as in flat-panel displays and solar cells [3]. For these applications, it is desired a combination of good transparency in the visible spectral range with low electrical resistivity. Several studies [4], [5] show that tin dioxide SnO_2 in presence of antimony (Sb) dopant displays low resistivity, remaining transparent in wavelength that includes the visible region. In this work, antimony tin oxide thin films (ATO) were obtained by atmospheric pressure chemical vapour deposition (APCVD) under nitrogen ambient. A series of pure SnO_2 and antimony doped tin oxide SnO_2:Sb have been deposited on glass and polycrystalline silicon substrates with different contents of antimony atoms. The investigation concerns the influence of the substrate on the reflectance.

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II. EXPERIMENTAL PROCEDURE

The pure and doped tin oxide films were synthesised onto glass and polycrystalline silicon substrates by APCVD technique. Before deposition, polycrystalline silicon (poly-silicon) substrates were successively cleaned by hot trichloroethylene, acetone, diluted HF at 10% and finely rinsed with distilled water. The substrates were then dried under nitrogen gas flow. For preparation of ATO films, a gas phase mixture of: ($2H_2O$, $SnCl_2$), an amount of $SbCl_3$ and O_2 was used as a precursor. The films were deposited at the same time on microscope glass slides (1.0 × 2.5 cm) and poly-si substrates. The substrate temperature, varying between 350 and 440°C, was monitored with a K-type thermocouple. Deposited time was maintained at 10 min and carrier oxygen gas (O_2) with a flow rate of 2 $l.min^{-1}$ was used. In previous work on tin oxide [4], the antimony Sb dopant ratio was varied between 0% and 4%. Interesting variations on electrical properties as resistivity and optical properties as reflectance-transmittance were significant only in the range of 0.7% to 1.6%. So in this work we will present results only in the later range. Results will be presented only for some selected samples of each substrate.

The film thicknesses were determined by ellipsometry. Optical reflectance-transmittance spectra for the as deposited films were recorded using an UV-VIS-NIR spectrophotometer (CARY 500 DE VARIAN spectrophotometer) as a function of wavelength ranging from 350 to 2500nm. The surface morphologies of the films were examined by scanning electron microscopy (SEM) Philips at 10 kV. From SEM observations given by Fig. 1, we note that the average grain size is comparable to the film thickness which is less than 200nm.

Doped samples have an appearance of bluish coloration due to the addition of doping atoms which was predictable since it was reported by many authors [5], [6].

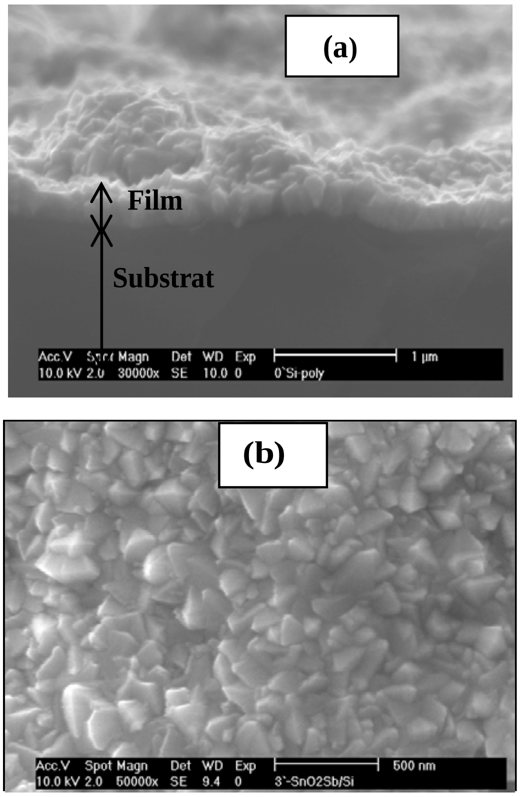

Fig. 1 SEM micrographs of doped (0.92%) SnO2 films deposited on polycrystalline silicon substrate at 443°C; (a) cross section, (b) plane view

III. Results and Discussion

A. Crystallographic Structures

The crystal structures of the films, deposited on poly-silicon substrates were identified by XRD measurements, using an X-Ray diffractometer with a monochromatic Cu Kα radiation. The diffraction data were collected at each 0.015° step width over a 2θ range from 0 to 60°. The dependence of the X-Ray diffraction patterns on the substrate temperature is presented in Fig. 2. The examination of XRD spectra makes it possible to affirm that the obtained layers crystallize in cassiterite type structure. One can see that all the peaks are well defined; this confirms a good crystallisation of tin oxide on poly-silicon substrate with no traces of either SnO or Sn. It is also readily seen that all preferred orientation were further emphasized by increasing the substrate temperature that why we choose the deposition temperature of 443˚C. For ATO films deposited by plasma-enhanced chemical vapour deposition (PECVD) on corning glass, Keun-Soo Kim and al. [7] observed that a gradual decrease in the resistivity occurs on rising the temperature of deposition up to 450˚C and that further raising the deposition temperature above 500˚C resulted in a little increase again of the film resistivity.

B. Optical Properties

Before reflectance measurement on silicon substrate, reflectance and transmittance of pure SnO_2 thin layers deposited on glass substrates at different temperature varying between 375˚C and 443˚C were recorded. From Fig. 3 it is clearly seen that in the visible region, the transmittance is about 90% which gives a very low absorption.

The goal of this paper is to show the evolution of optical reflectance not only versus Sb doping rate but also with respect to the nature of the substrate. Thus, we present some selected reflectance spectra represented in Fig. 4 for the first influence and in Fig. 5 for the second one.

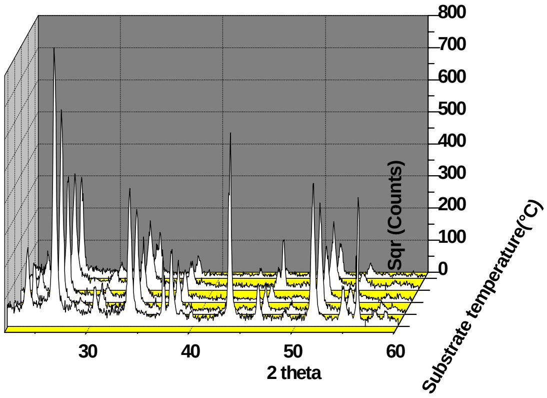

Fig. 2 Variation of XRD patterns of Sb-doped SnO_2 films grown on polycrystalline silicon substrate upon deposition temperature

Fig. 4 shows the optical transmittance and reflectance spectra (Fig. 4-a) associated with the variation of the resistivity (Fig. 4-b) of ATO films deposited on glass substrate as a function of Sb doping. The first remark is that the doping reduced considerably the transmission.

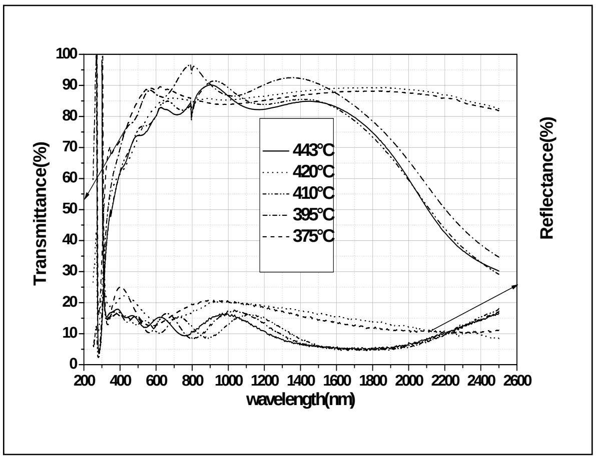

Fig. 3 Transmittance and reflectance spectra of SnO_2 films deposited at different temperatures on glass substrate

The average transmission over visible region of the obtained SnO_2: Sb film is about 50%, value that found much less than for undoped films. This low transmittance is attributed to the excess of doping atoms, which causes surface darkening [8]. The effect of antimony doping with Sb/Sn >0.75% on decreasing considerably the transmittance and continuously in the range of study with darkish blue in color must result from light absorption in the film. It was reported by Elanghovan [5] that when a material contains an element in two different oxidation states or in a mixed oxidation state, it manifests abnormally deep and intense coloration. The reason is that electron transfer between the different oxidation states of the element, namely Sb^{5+} and Sb^{3+} in our case, causes intense light absorption. All spectra exhibit a minimum of reflectance in the NIR domain which reflects a strong absorption. For doping ranging between 0.75% and 0.92% the metallic nature of the films increases and causes a clear decrease in resistivity as shown in Fig. 4-b. From this figure which represents the resistivity variation upon doping level, we can remark a clear correlation between optical and electrical properties. In the visible region, the transmittance *T* increases with the decrease in resistivity until the lowest value of resistivity ($4.8\times10^{-4}\Omega$.cm) then *T* decrease with the increase in resistivity. The lowest resistivity and the highest transmittance correspond to the same sample with 0.92% Sb ratio, which correspond to the optimum doping of our results.

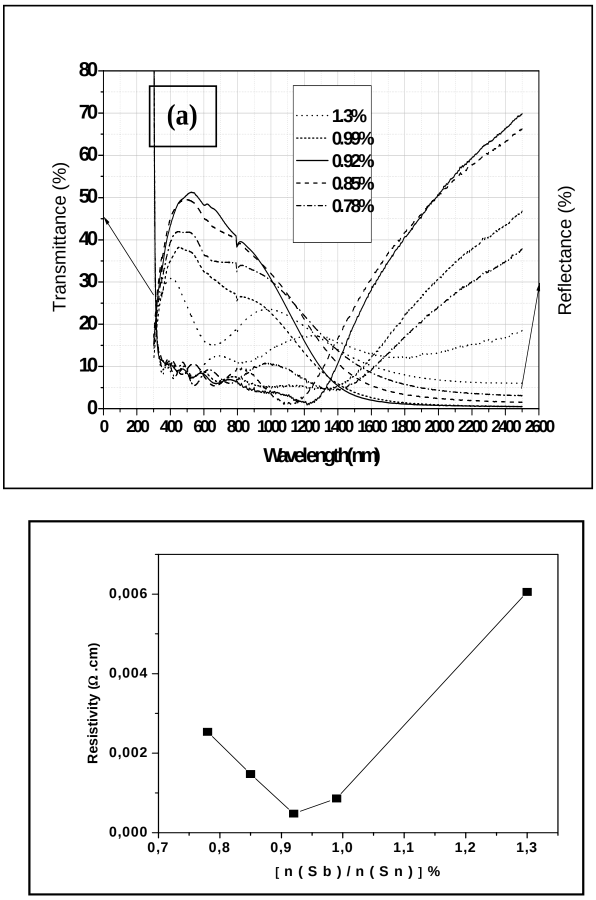

Fig. 4 Transmittance, reflectance a) and resistivity b) upon [n(Sb)/n(Sn)] % concentration respectively, (T_s=443°C, O_2: 2 L/min) showing that the best resistivity correspond to the weakest reflectance

From Fig. 4 the transmittance increases initially with increase in doping concentration and then decreases for higher doping levels which is attributed to scattering and light absorption. While the important optical characteristic of pure TCOs films is their transparency in the wavelengths ranging from 400 to 2500 nm (Fig. 3), the doped TCOs films do not transmit light after 1200nm and their important optical characteristic is a strong absorption in the NIR region (Fig. 4-a). This effect is due to the free-carrier absorption and it is clearly observed as reduced transmission and increased reflection in the near IR region. However, the transmittance and reflectance curves were distinguished by their gradients owing to the Sb-doping concentration. The classical Drude free-electron theory can be used to explain the optical phenomenon near the infrared region. Briefly, the model indicates that the transmittance drop in the near infrared region is associated with the plasma frequency ω_p. At longer wavelengths, reflection occurs because of the plasma edge, and light cannot be transmitted due to a classical phenomenon. The plasma frequency is obtained from the plasma wavelength λ_p which can be obtained from equation (1):

$$\lambda_p = \left(\frac{\varepsilon_1}{\varepsilon_1 - 1}\right)^{1/2} \lambda_0 \qquad (1)$$

where λ_0 is the wavelength at which the reflectance reaches a minimum and ε_1 is the relative electric permittivity determined from the measurement of the refractive index η_1 in the visible region [9], [10].

The plasma frequency ω_p is controlled by the free carrier density n through equation (2):

$$\omega_p = \left(\frac{ne^2}{\varepsilon_0 \varepsilon_1 m^*}\right)^{1/2} \qquad (2)$$

where ε_0 is the permittivity of free space and m^* is the effective mass.

Below the plasma frequency, the films are characterized by a high reflectance, which functions as a screen of the incident electromagnetic wave.

C. Reflectance of SnO_2-Sb/Polycrystalline Silicon

Fig. 5 shows reflectance spectra recorded from SnO_2/polycrystalline Si and SnO_2-Sb/polycrystalline Si devices. Let us remark from Figs. 3, 4-a and 5 that the doped films are more reflective than the pure ones in the entire infrared region. In the case of pure SnO_2 films, we can conclude that the metallic contribution in the dielectric function $\varepsilon_r(\omega)$ tends towards zero contrary to dopes ones. The reflectance spectra for the poly-silicon substrate shown in Fig. 5 expressed a high reflectivity in the NIR region. By the deposition of pure SnO_2 films on polycrystalline silicon substrate we remark a clear decrease in the device reflectance. Antimony doped films deposited on polycrystalline silicon substrate provide best collection of photons which give a better reflectance. The tin oxide layer improves the metallic behavior of the polycrystalline silicon/Sb doped tin oxide structure in the entire range of wavelength.

IV. Conclusion

In the present work, thin films of pure and antimony doped tin oxide thin films are prepared by CVD technique from $SnCl_2$ precursor. The details on the optical properties along with the resistivity values are investigated. The resistivity of the undoped films decreases with initial doping of antimony to attain a minimum value and increases for higher level of doping. The resistivity achieved for the films doped with 0.92 % Sb is the lowest among the earlier reports for these films from $SnCl_2$ precursor.

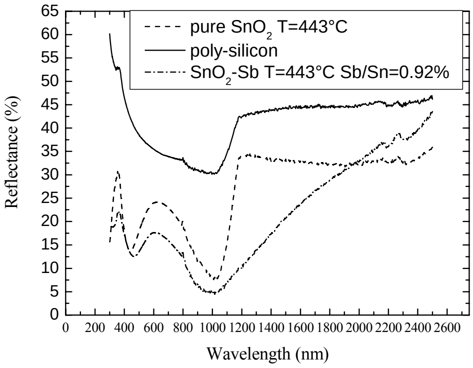

Fig. 5 Comparison between reflectance of undoped and doped tin oxide films deposited on poly-crystalline substrate at the same temperature

The change in the resistivity is explained in terms of different oxidation states of antimony. We study the role of the substrate in the formation of the optical properties of polycrystalline SnO_2 deposited by APCVD. Pure SnO_2 films deposited on polycrystalline silicon substrate show a better reflectance than reflectance of polycrystalline silicon alone and antimony doped films deposited on polycrystalline silicon substrate provide best collection of photons which give a better reflectance.

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