Plasmonic nanostructures of SnO₂:Sb thin film under gamma radiation response

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This paper is a part of a natural dye solar cell project. Conductive transparent oxide (CTO) films have been deposited onto preheated glass substrates using a spray pyrolysis technique. The optical, electrical, structural properties as well as thermal annealing and gamma radiation response were studied. The average optical energy gap of doped films for direct allowed and direct forbidden transitions were found to be 3.92 and 3.68 eV, respectively. The plasmon frequency and plasmon energy after doping were found to be $3.48 \times 10^{14} \text{ s}^{-1}$ and 0.23 eV. The negative absorbance of the doped film was observed in UV-Vis range after applying both thermal annealing and γ -dose irradiation with 22 kGy. The negative refractive index of the doped film in UV range (220 – 300 nm) is promising for optical applications. The electron mobility μ_e reached a maximum of $27.4 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ for Sb concentration of 10 %. The corresponding resistivity ρ , and sheet resistance R_s reached their minimum values of $1.1 \times 10^{-3} \text{ } \Omega \cdot \text{cm}$ and $35 \text{ } \Omega \cdot \text{sq}^{-1}$, respectively. The dopant concentration has been increased from 4.13×10^{19} to $2.1 \times 10^{20} \text{ cm}^{-3}$. The doped film was found to exhibit three diffraction peaks associated with (2 2 2), (2 0 0), and (2 1 1) reflection planes, of which the peak of (2 2 2) of Sb₂O₃ and the peak of (2 0 0) were very close.

Keywords: CTO; doping; optical properties; electrical properties; structure; radiation

1. Introduction

Plasmons are collective electronic excitations that are coupled strongly with external fields such as light or fast propagating charges. In metals, their excitation gives rise to charge oscillations which can be localized either in the interior of the metal or at its surface. The conductive transparent oxides (CTOs) are employed as transparent electrodes in flat-panel displays, light-emitting diodes, electrochromic windows, and solar cells [1–4]. Photovoltaic applications have been reviewed by Scott [5] and Fortunato [6] where CTOs were employed as front electrodes in solar cells. For organic conductors, the band alignment at the CTO interface is expected to depend directly on CTO work function [7, 8]. The plasmonic properties of nanoparticles have attracted much attention in the past decade. Localized surface plasmon resonances in metal nanoparticles are utilized for chemical sensing [9], cancer treatment [10], bio-sensors [11]

and to increase solar cell performance [12]. Two-dimensional (2D) plasmons are found at metal surfaces and thin films [13], in graphene [14–17] and other atomically thin 2D materials such as metallic transition metal dichalcogenides [18]. Surface plasmon resonance can be found at the surface of most materials. The family of metals (e.g. the noble metals Ag and Au which in addition are little reactive) with a wavelength-dependent dispersion of the dielectric function, prone to provide resonance conditions in IR and visible spectral domains, has been most often investigated up-to-now. Recently, Al has also been considered because of its potential applications in the UV domain [19]. The wide-band gap semiconductors, SnO₂ and doped SnO₂ are known to have a wide range of technological applications and now they seem to be more attractive for their luminescence properties [20–22]. Antimony doped tin oxide (SnO₂:Sb) thin films are deposited by various methods, viz. sputtering [23], chemical vapor deposition [24], DC glow discharge [25], dip coating [26], sol-gel [27] and spray pyrolysis [28–30]. Localized surface plasmon resonance is, at its

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core, a damped harmonic oscillator whose resonance conditions are determined by the geometry of particle, the dielectric constant of metal, and the local environment [31]. Plasmonic nanostructures improve solar energy conversion efficiency via the following mechanisms: (a) enhancing the light absorption in the semiconductor by photonic enhancement through increasing the optical path length and concentrating the incident field [12] (b) directly transferring the plasmonic energy from metal to semiconductor to induce the charge separation in the semiconductor by direct electron transfer [32, 33] or by plasmon induced resonant energy transfer [34].

1.1. Gamma radiation effect

Gamma ray transport in solid matrix involves multiple gamma quanta and secondary electrons interactions with host material valence and core atomic electrons as well with atomic nuclei, leading to modifications of the crystal structure by the formation of some amount of point defects, like ionizations, color centers and atom displacements from crystalline sites. These defects modify the irradiated target microscopic and macroscopic properties in a specific way, which is usually referred as gamma radiation damage. Energy deposition spatial distribution can be calculated by means of Monte Carlo assisted gamma quanta transport codes, like EGS-4 [35, 36] or MCNP [37].

2. Experimental

2.1. Undoped SnO₂ film

Spray pyrolysis is a physical deposition technique where the endothermic thermal decomposition is taking place at a hot surface of a substrate to give the final product. The nanostructured films have been prepared from crystalline hydrate of tin tetrachloride (SnCl₄·5H₂O) in the amount of 5 g by its dissolution in 5 mL pure methanol. The substrate temperature was in the range of 400 – 500 °C.

2.2. Doped SnO₂:Sb film

The most commonly used dopant for increasing n-type conductivity of tin dioxide is antimony. The

solution process begins by mixing metal chloride precursors with methanol. Tin (IV) chloride hydrate (SnCl₄·5H₂O, Sigma Aldrich 98 %) and antimony (III) oxide (Sb₂O₃, Sigma Aldrich, 99 %) were dissolved separately. To achieve Sb doping, antimony trioxide (Sb₂O₃) was dissolved in concentrated hydrochloric (HCl) acid. Coating solution was prepared by adding 5 g tin chloride powder into 5 mL methanol and 0.1 g antimony trioxide powder into 1 mL HCL for controlling the dopant concentration. Then, the two solutions were mixed under stirring for 4 h followed by filtration. Dilution was used during the coating to control the bluish color and resistance with increasing of methanol volume up to 55 mL. The substrate temperature was adjusted in the range of 400 – 500 °C. In order to make high quality CTO thin films, the multiple spraying coating was introduced. Each time, every layer was coated and sintered inside a furnace at ~500 °C. In this multiple spraying coating process, subsequent spraying coatings filled porosities left from the previous solvent drying process. By changing the number of the spraying coating processes, different thicknesses of high quality CTO thin films were prepared. The quality of these films depended on various process parameters such as air pressure, distance between the nozzle and substrate, spray time, annealing temperature and the ratio of the solution. Microscopic glass slides were used as substrates. An increase in the spray time caused thermal shock of the substrate due to excessive cooling. The spray time was maintained at ~3 s and heat interval in furnace at ~2 min. The optimum distance between the nozzle and substrate was kept at ~25 cm and at normal direction. After deposition, the films were allowed to cool at room temperature.

2.3. Measurement of film thickness

The thickness of layers used as a transparent electrode in optoelectronic devices is a critical parameter. On one hand, a layer must be thick enough to minimize ohmic losses ($R \propto d_{\text{film}}^{-1}$). The ratio of absorbed light increases exponentially with d_{film} according to the Lambert-Beer law as in equation 1:

$$I(d) = I_0 \cdot e^{-\alpha_{\text{opt}} d_{\text{film}}} \quad (1)$$

where d_{film} is the distance travelled through the medium, and α_{opt} is the absorption coefficient, a frequency dependent material constant. Layer thickness values found in actual applications of optical coatings often are a few hundred nm. As this length scale is of the same order of magnitude as wavelengths in the visible spectrum, interference effects have to be considered in optical characterization of such systems. These effects result in a modulation of experimental transmittance (T_{opt}) and reflectance (R_{opt}) values as a function of wavelength. In its essence, the mechanism can be described as follows: light passing through the air/film/substrate/air system used in an actual measurement is subjected to Fresnel reflection. Photons can be reflected at internal interfaces several times before leaving the system on the same side they entered it (detected as reflected), or on the other end (detected as transmitted). If the path a photon traverses before it is 'coupled out' of the system is of the order of its coherence length, constructive or destructive interference of photons travelling either way will result. This will modulate the measured transmittance and reflectance spectra with an oscillating function.

In the present study, the method of transmission spectrum has been used to measure the film thickness and refractive index. The film thickness has to be of the order of wavelength according to the basic expression:

$$2nd = m\lambda \quad (2)$$

where n is the refractive index, d is the film thickness, λ is the wavelength of light and m is the order.

If the refractive indices are obtained at the maxima or minima of the transmission spectrum, the thickness of the film can be deduced. Assuming n_1 and n_2 to be indices of refraction at two adjacent maxima (or minima) at λ_1 and λ_2 , it follows from equation 2 that:

$$d = \frac{\lambda_1 \lambda_2}{2(\lambda_1 n_2 - \lambda_2 n_1)} \quad (3)$$

where λ_1 and λ_2 are the wavelengths of two adjacent maxima (or minima), n_1 and n_2 are corresponding refractive indices,

which could be calculated by the following formulas [38]:

$$n = \sqrt{N + \sqrt{N^2 - n_s^2}} \quad (4)$$

$$N = 2n_s \frac{T_M - T_m}{T_M T_m} + \frac{n_s^2 + 1}{2} \quad (5)$$

where n_s is the refractive index of the substrate ($n_s = 1.5$ for glass), T_M is the maximum transmittance (e.g. 74 % for a thickness of 506 nm) and T_m is the corresponding minimum transmittance (e.g. 73 % for a thickness of 506 nm) for the same wavelength ($\lambda = 370$ nm) while the adjacent one T_M is the maximum transmittance (86 % for a thickness of 506 nm) and T_m is the corresponding minimum transmittance (72 % for a thickness of 506 nm) for the same wavelength ($\lambda = 491$ nm) as shown in Fig. 1. The film thickness has been estimated from the UV-Vis spectra. The optical transmittance spectra of $\text{SnO}_2\text{:Sb}$ films were measured in the wavelength range of 190 nm to 1100 nm by means of the Specord 210 plus UV-Vis spectrophotometer (made in Germany). The electrical parameters were studied by using automatic RCL meter (Philips/Fluke PM6303A) at room temperature. Undoped and doped films were exposed to a Co-60 gamma-radiation source with a dose rate $1.52 \text{ kGy} \cdot \text{h}^{-1}$ at room temperature in National Center for Radiation Research and Technology, Egyptian Atomic Energy Authority. The exposure dose was selected in the range of 0.1 – 22 kGy which is based on the medical/industrial applications. The deposited thin films were examined by X-ray diffraction method using an X-ray diffractometer Shimadzu model XD-DI with $\text{Cu-K}\alpha$ radiation as a target, $\lambda = 1.548 \text{ \AA}$, operated at 400 kV and 30 mA using Bragg-Brentano method. The average crystallite size was estimated from the width of X-ray lines by Scherrer method.

3. Results and discussion

3.1. Undoped and doped films (thickness effects)

Optical transmittance of the sample in the visible regime, $T_{\text{opt,vis}}$, as a function of thickness is

visualized in Fig. 1. Average transmittance is relatively constant inside UV region of 300 to 370 nm for doped film and transmittance value reaches there $\sim 75\%$. The spectra can be seen to change as a function of thickness in the VIS and NIR regime (Fig. 1). The following points summarize these changes from the perspective of a gradually increasing film thickness for doped film: (a) the onset of transmittance is started at the wavelength of 310 nm, (b) transmittance in the VIS-NIR regime is reduced with the thickness increase.

Fig. 1. Transmittance of doped SnO₂:Sb films at different thicknesses.

The addition of HCl made the solution transparent, mostly, due to the breakdown of the intermediate polymer molecules. The transparent solution thus obtained and subsequently diluted by methanol, served as a precursor. At adding methanol up to 55 mL during thin film preparation, which was chosen as optimum condition in this study, blue color of the films slightly faded. It was, however, discussed whether the blue coloration was caused by an absorption process related to a mixed-valence charge transfer [39, 40], which is suspected for the case of Sb-doped TiO₂ [41], or by the shift of the plasma absorption edge into the visible red region due to very high intragrain charge carrier densities [42]. Both explanations are compatible with the findings of present study.

3.2. Optical energy gap (Tauc gap) of doped film

Optical band gaps of semiconductor materials are most often determined from transmittance data. Usually, a Tauc plot is used in order to determine the optical band gap. In this procedure, an absorption coefficient $\alpha_{\text{opt}}(E)$ is calculated from transmittance data. Then, $(\alpha_{\text{opt}} \cdot E)^{1/n}$ is plotted against E , the incident photon energy. The exponent n depends on the type of fundamental optical transition across the band gap and takes the values $1/2$ for direct allowed, $3/2$ for direct forbidden, 2 for indirect allowed and 3 for indirect forbidden transitions. Extrapolating the 'linear onset' of this plot into the baseline should then give an estimate of the optical band gap. The approach has been suggested by Tauc [43] in order to determine an optical band gap in amorphous germanium. The resulting value is sometimes called the Tauc gap. The widely accepted value of the fundamental band gap in tin oxide is 3.6 eV, with the transition being dipole-forbidden [44]. The value has been determined experimentally by two-photon absorption experiments [45, 46], and confirmed by calculations using a many-body perturbation theory approach [47]. Studies on undoped SnO₂ reported a range of 3.6 to 4.1 eV [48], with most studies reporting the values close to 4 eV [49–51]. In this study, undoped SnO₂ film is a degenerate n-type wide band gap semiconductor that has a direct optical band gap of 3.88 eV and 3.96 eV before and after gamma irradiation, respectively [52]. In the suspected presence of SnO phase, i.e. for yellow films, values between 2.5 and 3 eV have been reported [50]. Band gap values most common in literature show an increase by 0.2 – 0.4 eV [53–55], giving optical band gaps of up to 4.4 eV for highly-doped samples [48, 54]. For charge carrier densities in the range $2 \times 10^{20} - 6 \times 10^{20} \text{ cm}^{-3}$, Stjerna et al. [48] and Sanon et al. [51] reported a band gap blue shift $4.1 \rightarrow 4.4$ eV. In the same charge carrier regime, Montero et al. [23] has found $3.7 \rightarrow 4.1$ eV and Feng et al. [56] reported $3.6 \rightarrow 3.8$ eV. The difference in Tauc gaps between the studies is mostly caused by the lack of a reference point. In particular, it is not well defined where

Fig. 2. Tauc plots of undoped and doped films of two thicknesses at room temperature.

to extrapolate the data linearly. The present data is cut off on the y ordinate at 10^{10} (eV/cm) 2 for undoped and doped CTO thin film. Cutoff values are found varying over four orders of magnitude, between 10^9 [49, 51] and 10^{13} (eV/cm) 2 [57]. For nominally undoped tin oxides, Tauc gaps are reported to increase as a function of oxygen flow ratio [58] or substrate temperature [59]. The ambiguity of a Tauc plot is shown in Fig. 2.

To determine Tauc band gap, we divided the linear part and Urbach edge into continuous parts. The average extrapolation values of that parts with different photon energies have been taken, which is represented by Tauc band gap. It is suggested plotting many continuous extrapolation data covering the linear part and Urbach region of undoped (b,d) and doped (a,c) films for direct allowed and direct forbidden transitions.

It is found from the Tauc plots in Fig. 2 that the average optical energy gap of doped SnO $_2$ for direct allowed is 3.92 eV (film thickness 405 nm), 3.92 eV (film thickness 506 nm) and for direct forbidden 3.67 eV (film thickness 405 nm), 3.69 eV (film thickness 506 nm). The presence of the Urbach tail causes absorption at photon energies below the fundamental optical band gap energy, which is why the Tauc plot extrapolation is increasingly shifted to lower values with increasing crystalline disorder [60, 61]. The differences in undoped tin oxide optical band gap values (4.03 eV for direct allowed and 3.75 eV for direct forbidden) have been determined from the Tauc plot, as outlined above. Similar issues have been reported for other oxide semiconductors, such as In $_2$ O $_3$ [61], for which the fundamental band gap value has been debated for the last ten years [62, 63]. The smeared out absorption edge found for oxide semiconductors can be explained as follows: (a) the fundamental band gap transition is either indirect or dipole-forbidden, i.e. the absorption coefficient increases rather slowly [64]; additional direct allowed transitions might be found at slightly higher energies [47, 65] and (b) defect densities in oxide semiconductors are much higher than in classical semiconductors; the Urbach tail density of states is, therefore, comparatively large and further smears out the fundamental absorption edge. By our approach, the Tauc gaps of undoped SnO $_2$ were found 4.03 eV for direct allowed (which is consistent with other study [66]) and 3.75 eV for direct forbidden [51]. In Fig. [3], it is observed that a reduced transmittance started at a wavelength of 860 nm after doping which is related to the plasmon edge. This may be due to the increase in charge carrier density $4.1 \times 10^{19} \rightarrow 2.1 \times 10^{20}$ cm $^{-3}$. The dopant concentration was calculated as:

$$N = \text{mass}(Sb_2O_3) \times (1 \text{ mol/molar mass}(Sb_2O_3)) \times 6.022 \times 10^{23} \text{ cm}^{-3} \quad (6)$$

The plasmon frequency and plasmon energy after doping were found 3.48×10^{14} s $^{-1}$ and 0.23 eV, respectively.

The dopant Sb $^{5+}$ acts as a donor increasing the donor level by 35 meV [67], and hence, the

Fig. 3. Transmittance vs. wavelength for undoped and doped films, ω_p - plasmon frequency, E_p - plasmon energy.

material shows the n-type conductivity. The increased carrier concentration shifts the plasmon edge from 3.2 μm (undoped tin dioxide) to 1.3 μm (tin dioxide doped with antimony) [68]. The plasmon edge shift may occur because the 'electron gas' becomes reflective to radiation. Frequency (ω) is an increasing function of charge carriers. This is a common factor for transparent conductors as exemplified by the case of tin-doped indium oxide and fluorine-doped tin dioxide coatings [69]. Increased carrier concentration in antimony-doped tin dioxide thin film results also in a relatively large band gap broadening [48, 68], which is attributed to the Moss-Burstein effect. In 2009, a Korean research team found a way to greatly improve organic light emitting diode efficiency with the use of plasmon [70]. A group of European researchers led by IMEC started the work to improve solar cell efficiencies and costs through incorporation of metallic nanostructures (using plasmonic effects) that can enhance absorption of light in different types of solar cells: crystalline silicon, high performance III-V, organic, and dye-sensitized [71]. However, for optimal functioning of plasmonic photovoltaic devices, ultrathin transparent conducting oxides are necessary [67]. Full color holograms using plasmonics have been demonstrated [72].

Surface plasmons are those plasmons that are confined to surfaces and that interact strongly with light, which results in polaritons [73]. They

occur at the interface of a material exhibiting positive real part of relative permittivity, i.e. dielectric constant and a material, whose real part of permittivity is negative at a given frequency of light (typically a metal or heavily doped semiconductor). In addition to opposite sign of the real part of permittivity, the magnitude of the real part of the permittivity in the negative permittivity region should be larger than the magnitude of the permittivity in the positive permittivity region, otherwise the light is not bound to the surface (i.e. the surface plasmons does not exist) as shown in the book by Raether [74]. The undoped SnO₂ film with the thickness of 492 nm (Fig. 4a) is found to have a positive part of absorbance, while for the doped SnO₂ film with the thickness of 505 nm (Fig. 4a) a negative part of absorbance in UV range is obtained.

The average refractive index in visible and near infrared range is found 1.93 and 1.67 for undoped and doped SnO₂ film, respectively as in Fig. 4b. The area under the peak in the negative scale for doped SnO₂ film is observed to be greater than the area under the peak of undoped SnO₂ film in positive scale as in Fig. 4b. A negative dielectric constant material is an essential key for creating metamaterials, or artificial negative index materials (NIMs). The NIMs have gained a great attention due to their unique and exotic electromagnetic properties, and can be used for unique optical and microwave applications, including new methods of electromagnetic cloaking and extremely low loss communications. Effective negative dielectric constant and resonance frequency can be controlled by dopant type, temperature, concentration and effective mass of dopant. The negative dielectric constants in UV range (220 – 300 nm) in our results are promising for optical applications.

3.2.1. Thermal annealing effect on doped SnO₂:Sb film

It was observed that the transmittance decreased after thermal annealing at 600 °C for 15 min. as shown in Fig. 5. This decrease may be due to small microstructural changes. Two peaks have appeared at the wavelengths of 400 and 555 nm.

(a)

(b)

Fig. 4. a) UV-Vis absorbance spectra of undoped and doped $\text{SnO}_2\text{:Sb}$ films on microscopic glass slide; b) Refractive index vs. wavelength of SnO_2 thin films before and after Sb doping.

The plasmon edge has been shifted from the wavelength 860 nm to 920 nm after thermal annealing.

The plasmon energies of 0.25 eV and 0.21 eV for pre-annealed and post-annealed films, respectively have been calculated. The resistivity of post-annealed film irradiated at γ -dose of 22 kGy has slightly changed; it may be due to small microstructural changes. Pre-annealing of doped film can be applied to help the front electrode of solar cell in light reflecting near infrared over $0.86 \mu\text{m}$ which helps in decreasing the recombination due to the heat initiation. Post-annealing of doped film can be applied as windows in cold countries to permit the diffusion of infrared radiation and reduce the effective cost of heating.

Fig. 5. Transmittance vs. wavelength of doped films before and after thermal annealing.

3.2.2. Gamma irradiation effect on undoped and doped SnO_2 film

The negative absorbance of thermally annealed film in visible and ultraviolet range after γ -dose irradiation has been found at 22 kGy as shown in Fig. 6.

Fig. 6. Absorbance vs. wavelength of doped films after annealing and γ irradiation at 0.0 kGy and 22.0 kGy.

The negative absorbance within the wavelength of 200 – 320 nm for the annealed film at 22 kGy is observed. The reasonable explanation for the negative absorption is a type of emission. The incident light and surrounding environment excite the sample to produce emission, creating a negative absorption or negative absorption emission phenomenon. Negative absorption emission might be

due to the light exciting irradiated samples from the ground states to excited states and then back to ground states, thus producing an emission that results in $A < 0$ (Fig. 4 and Fig. 6) or $T \% > 100 \%$ (Fig. 5). The light source of the spectrophotometer acts on the samples, exciting a larger energy emission, which results in emergent light or emission light energy being higher than the incident light or excitation light energy. It is noticed that the area under the peak in the wavelength range of 220 – 260 nm decreased after γ irradiation. The resistivity of undoped film is seen to decrease exponentially with the increase of gamma dose as in Fig. 7. This decrease is as high as 59 % and 50 % for extreme film thicknesses of 177 nm and 738 nm, respectively. A further decrease is generally found for an increase in film thickness. The resistivity of a film with the thickness of 177 nm has decreased under gamma exposure (up to 22 kGy) from 3.4×10^{-2} to $1.4 \times 10^{-2} \Omega\cdot\text{cm}$. The same behavior of resistivity is observed for a film with a thickness of 738 nm where resistivity decreased from 1.6×10^{-2} to $0.8 \times 10^{-2} \Omega\cdot\text{cm}$.

Fig. 7. Resistivity vs. gamma dose for undoped SnO_2 film.

This finding illustrates the extreme sensitivity of tin oxide material to variations in thickness-stoichiometry. The resistivity of doped film has decreased to $1.1 \times 10^{-3} \Omega\cdot\text{cm}$. These values are consistent with other studies [75, 76].

3.3. X-ray diffraction study of doped $\text{SnO}_2\text{:Sb}$ film

X-ray diffraction pattern of a doped film is shown in Fig. 8. The X-ray diffraction results show that the phase of the deposited Sb oxide is Sb_2O_3 with face-centered cubic structure. The Sb_2O_3 films are found to exhibit three diffraction peaks associated with (2 2 2), (2 0 0), and (2 1 1) reflection planes, of which the peak of the (2 2 2) of Sb_2O_3 and the peak of (2 0 0) are very close. The structural analysis, performed by XRD, indicated that the studied Sb_2O_3 thin films are polycrystalline in nature and have a cubic structure. The lattice parameter of the cubic structure was found to be $a = 11.155 \text{ \AA}$, which is consistent with the standard value (JCPDS 5-0543, $a = 11.152 \text{ \AA}$).

Fig. 8. X ray spectrum of the collected Sb / SnO_2 oxide on glass substrate.

The diffraction patterns of the doped samples indicate the tetragonal rutile-type structure, whose unit cell contains six atoms: two tin and four oxygen atoms have an octahedral coordination of Sn^{4+} , Kojima et al. [77] observed, for a heavily Sb doped SnO_2 , the peaks characterizing the SnO_2 phase shift to lower values of 2θ , indicating an increase of the lattice constant. They also noted that the cation/anion concentration ratio is constant and that the SnO_2 crystal structure was retained with a varying Sb/Sn ratio, indicating that Sb is substitutionally incorporated into Sn sites in the SnO_2 lattice. In this case, it is suggested that some of the Sn^{4+} ions in the lattice have been replaced by Sb^{3+} ions.

This is verified by the increase in the lattice constant with the increase of the Sb/Sn ratio, since the ionic radius of Sn^{4+} is larger than that of Sb^{5+} , albeit smaller than that of Sb^{3+} [78, 79]. The crystallites of as-deposited Sb_2O_3 thin films have the mean diameter in the range of 4 – 20 nm, with an average diameter of 7.11 nm, while the mean diameters of annealed film are in the range of 12 – 36 nm, with an average diameter of 17 nm [80–83]. In the present study, the crystallite size of undoped and doped film was calculated as ~ 14 and ~ 31 nm, respectively before both annealing and radiation. The increase in the grain size due to the antimony-doping decreases the grain boundary potential through the film, and also the grain boundary scattering [84]. On the other hand, Sb^{5+} cations on the grain boundaries induce a charged surface site. They produce a significant increase in the surface energy of the material, increasing the content of chemisorbed oxygen on the surface. This increases grain boundary scattering by increasing the grain boundary potential. Other factors assumed to be limiting factors for the conductivity of antimony-doped tin dioxides are precipitation of Sb_2O_5 , and increased disorder [84]. Charge carriers in an external field follow a path of minimum resistance, preferentially traversing large grains in order to avoid grain boundaries [85]. Minimum resistivity achieved in this study for undoped SnO_2 film is comparable to literature results. The lowest resistivity value of undoped film of CTO is $1.2 \times 10^{-2} \Omega\cdot\text{cm}$. By applying antimony as a dopant, the minimum value achieved in this study is $1.1 \times 10^{-3} \Omega\cdot\text{cm}$, which is consistent with previously reported value for sputter-deposited films on an amorphous substrate [66, 86].

4. Conclusions

The optical calculations performed in this work predict the existence of a unique type of plasmon localized on the surface of $\text{SnO}_2\text{:Sb}$ nanofilm. The fundamental properties of this plasmon were investigated in detail. The dopant concentration increased from 4.1×10^{19} to $2.1 \times 10^{20} \text{ cm}^{-3}$. Average optical energy gap of the doped film for direct allowed transition was found 3.92 eV and for

direct forbidden transition – 3.68 eV. The plasmon edge was found at 0.86 μm after doping. The plasmon frequency and plasmon energy were calculated as $3.48 \times 10^{14} \text{ s}^{-1}$ and 0.23 eV, respectively. The negative refractive index of the doped film in UV range (220 – 300 nm) is promising for optical applications. The electron mobility μ_e , reached a maximum of $27.4 \text{ cm}^2\cdot\text{V}^{-1}\cdot\text{s}^{-1}$ for Sb concentration of 10 %. The corresponding resistivity ρ , and sheet resistance R_s reached their minimum values of $1.1 \times 10^{-3} \Omega\cdot\text{cm}$ and $35 \Omega\cdot\text{sq}^{-1}$, respectively. Finally, we proposed that the surface plasmons could be utilized in dye solar cells.

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