Estimation of optical parameters in tin oxide thin films by UV exposure for photonic applications

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During the present work of investigations, tin oxide films of ~800 nm thickness are grown on glass substrates by using thermal deposition technique. Refractive Index, absorption co-efficient and band gap of the thin film samples are determined. The films were exposed with short UV radiations and results of thickness measurement are compared with stylus profiler for both as-deposited and UV exposed thin films. Surface morphology of thinfilms was found to be improved on UV exposure. The Nonlinear index of refraction (n_2) is estimated by Miller Rule and it is observed that after short UV exposure, Nonlinear refractive index changes from 9.4287×10^{-12} cm^2/W to 1.1720×10^{-11} cm^2/W. The third order nonlinear susceptibility ($\chi^{(3)}$) is measured using semi-empirical formula and found to change slightly from 1.3637×10^{-12} esu to 1.5643×10^{-12} esu after UV exposure of the films.

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1. Introduction

The change in structural and optical properties of transition metal oxides like TiO2 and ZnO is very well known and studied widely for sensing applications such as smoke sensors, humidity sensors, gas sensors etc. due to its semiconductor as well as environmental durability, best reproducibility, lower thermal stress as well as widely tuneable refractive index properties. E. Comini et al (2001) has studied SnO_2 thin films by UV light activation for sensing applications [1, 2].

Also, studies by various researchers [3,4] reveals that there is a change in physical parameters with external stimuli such as thickness, linear absorption constant (α), Optical Band gap (E_g) and extinction coefficient (k), phase of material as well as nonlinear optical properties like non-linear Index of refraction (n_2) and third order nonlinear susceptibility ($\chi^{(3)}$). When semiconductor materials are studied as gas sensors then one deals with polycrystalline materials which have grains with different orientations. In such type of materials oxygen ion sorption may take place resulting to double potential barrier at each grain boundary and this photo excitation may affect transport mechanism across the grain boundaries. The possible mechanism may be understood to be due to following reasons i) Increasing the probability of tunnelling through inter green barriers by decreasing the depletion layer within adjacent grains, ii) Increasing the density of free carrier throughout the material, iii) Decreasing the inter green barrier height by changing the inter green State charge [1]. When there is a radiation illumination, there is change in occupancy of defects by electrons and holes that changes the concentration of absorption centres of each given type and capacity of absorption on the surface of the semiconductor.

However, a film having crystalline or amorphous nature depends upon the method of preparation [5] hence their structural properties as well as their physical properties are affected by the deposition method. Deposition is the technological aspect and its environmental aspect also alters synthesis results.

Neumann et al. [6] have examined atomic distribution in amorphous semiconductor films, deposited by electron beam evaporation method. It is worthy to note that amorphous films of tin oxide have less scattering than that of crystalline thin films. This unique property makes them to use as anti-reflection coating in IR range where high transparency of film is required [7].

It is not necessary that after the irradiation there is any chemical composition change but it may lead to some defects in structure of material, it may increase or decrease the disorder in the semiconductor material. The radiation induced disorder gradually relaxes itself after the illumination has been turned off and it is noteworthy that the higher the temperature the greater the relaxation rate.

The change in thickness plays very important role in photonic devices and therefore the accurate measurement of thickness is of great interest. An appropriate technique used to measure thickness may use transmittance, absorbance or reflectance phenomena. For some high end application one needed *in-situ* measurement of thickness that should be controlled as well. A few methods for monitoring the film thickness during the coating process are available, but in most of the cases, measurements are done after the process of deposition. There are a number of ways to measure the thickness of films of semiconductor materials but when the films are of micron range then one

observes a wave like pattern due to interaction of measuring beam reflected from different interfaces that appear in transmittance and reflectance spectrum which becomes the sources of error while we calculate optical parameters particularly refractive index. So this can be avoided using Swanepoel method [8], which simulates the wavelike pattern in transmittance spectrum and it is best to use because of the fact that it doesn't require reflectance of sample which might be influenced by surface roughness of thin films and hence may cause error in calculations.

In the present work, amorphous SnO_2 Thin films have been prepared by thermal evaporation technique. Optical energy gap is calculated using both transmission and absorption spectra. Further the film thicknesses and optical constants are estimated by applying envelope method to the transmission spectra of these films to verify and validate the data received through *in- situ* thickness monitoring [5]. Determination of nonlinear optical parameters requires complex optical equipment and techniques which might not available in every laboratory hence nonlinear optical parameters has been derived from semi-empirical relations at long wavelength limit.

2. Experimental

Thin films of tin oxide on glass substrate were synthesized using Thermal evaporation technique. Glass substrate was first washed with soap solution and then rinse properly in water. Then the slides were soaked in Dilute H_2SO_4 and then ultra-sonicated in distilled water for 10 minutes and dried. After that they again sonicated in closed vessel having toluene for 10 minutes. Further these were sonicated in acetone for 5 minutes which is followed by further sonication in ethanol for 5 minutes. Finally, these were ultra-sonicated in isopropyl alcohol and dried to be ready for load in vacuum chamber. Films of thickness 799 nm were deposited using appropriate quantity of SnO_2 in Powder form, sigma Aldrich (Purity 99.999 %) in a Molybdenum boat at vacuum of 4×10^{-6} mbar. A Vacuum of 2×10^{-2} mbar was achieved by first roughing process and then higher vacuum achieved with the help of diffusion pump. To avoid the oil contaminant or moisture higher vacuum was maintained for further three hours and then with liquid nitrogen trap for further one hour before the coating process started. No External heating was provided during deposition process while vacuum during deposition was maintained ~ 4×10^{-5} mbar. The distance between boat and substrate was 20 cm. Chamber was opened after next 24 hours. As- deposited (AsD) Films of SnO_2 were exposed under UV lamp having short UV (UV2H) wavelength ~254 nm for 120 minutes. After that both as-deposited and UV exposed, X-Ray diffractogram of brownish films of SnO_2 has been recorded using Rigaku X-ray Diffractometer (Miniflex-II) to confirm the nature of Films. The absorbance and transmittance has been obtained using UV-VIS-IR Spectrophotometer (Varian Cary-5000) at room temperature in wavelength 350-1800 nm which predicts the IR transparency of these films. Optical band gap of these films is estimated by Tauc's relation [9].

$$\alpha h\nu = B(h\nu - E_g)^n \quad (1)$$

Here n can have values ½ and 2 in case of direct and indirect transitions respectively. Here α is linear absorption coefficient, hν is photon energy and B is tailing parameter. Indirect band gap obtained using by extrapolating best fit line intercepting the hν axis in graph between $(\alpha h\nu)^{1/n}$ vs hν.

3. Results and discussion

3.1. XRD analysis

Fig. 1 shows the X-Ray diffractogram for as-deposited Tin Oxide thin film on glass substrate of thickness 799 nm deposited at room temperature. There is no prominent peak in diffractogram instead it has broad hump that indicates amorphous structure of films. Moreover, when films were exposed under UV then there is decrease in the intensity count that indicates the local structural change with increase in amorphous nature. This trend is prominent in higher exposure time of UV radiations.

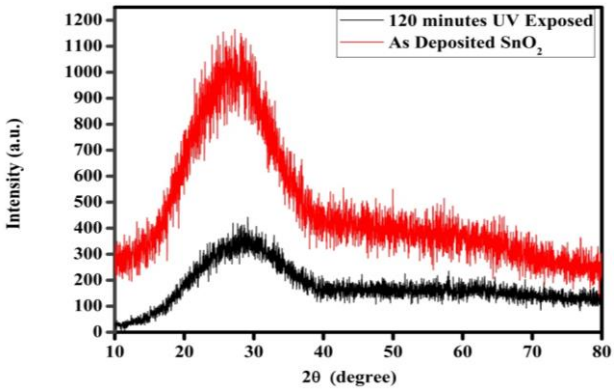

Fig 1. X-ray Diffraction pattern of as deposited SnO_2 thin films (AsD) as well as short UV exposure for 120 minutes (UV2H) *(color online)*

3.2. Morphological analysis

The effect of UV exposure on morphological structure of thermally deposited SnO_2 films was investigated by AFM analysis. The morphological structure in thin films studies has a great importance and for this purpose AFM provides best morphological behaviour of films. For optical application one need films with uniform thickness and should be adhesive enough not to be peel off. The AFM reveals that films deposited have a rough texture P-V value is ~100nm with some exception of ~200nm at some area but it is distributed uniformly throughout the surface. It is mentioned earlier that amorphous nature of tin oxide films gives lesser scattering than the crystalline films. A change in surface morphology observed and it is

concluded that surface morphology can be tuned of films for desired photonic application. It is observed that roughness of films is decreased upon post UV exposure for two hours which shows that after UV exposure of thin films surface become more smooth (shown in Fig. 2 a, b). Hence we can conclude that desired surface profile can be achieved by post deposition external stimuli (UV exposure time). AFM image also shows that films are homogenous in nature.

3.3. Linear optical analysis

In the transmittance plot of SnO_2 Thin films of thickness 810 nm (through quartz crystal thickness monitor) obtained from UV-VIS-NIR Spectroscopy, interference fringes are observed in high transmission region of wavelength (Fig. 3 a-c)

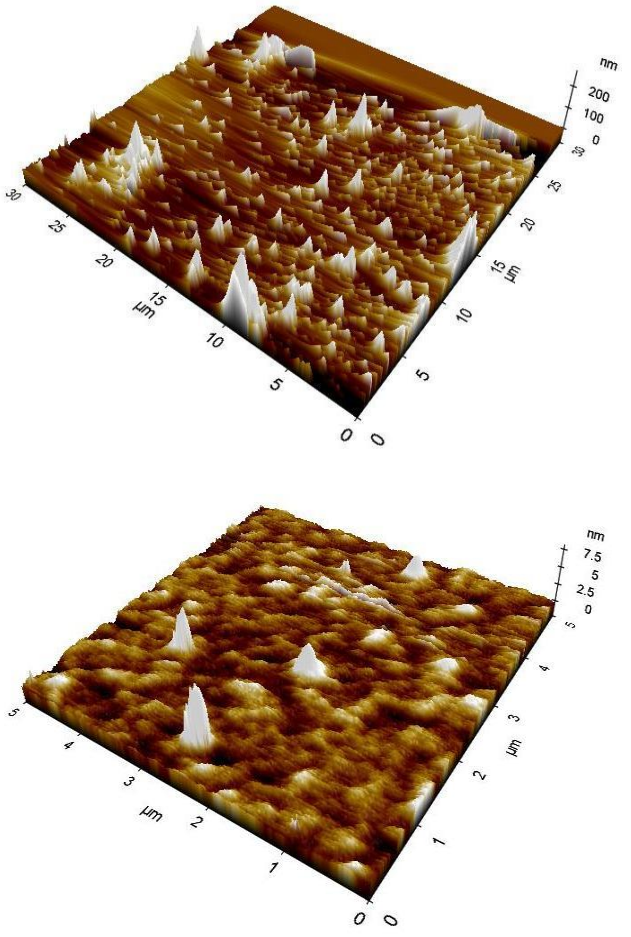

Fig. 2. AFM image of SnO_2 (a) As Deposited Films (AsD) (b) UV exposed for 2 Hours (UV2H) (color online)

The transmittance of thin films is more than 80% in IR region which concludes that as deposited films can be used in IR range applications. After UV exposure there is a shift in transmission towards lower wavelength region i.e. blue shift which is due to local structure modification on the UV exposure. This leads to more smoothness of films with slight change in transmittance spectra. This shows that films become more stable with UV exposure. Before proceeding to thickness measurement we identified three regions of measurement, strong absorption region 350-450 nm, medium absorption from 450-540 nm and weak absorption or high transmission region above 540 nm. The thickness d is calculated from transmittance spectra envelope using Swanepoel envelop technique [8].

It is observed that the transmittance of thin films after UV exposure increases that may be due to elimination of oxygen vacancies after UV exposure.

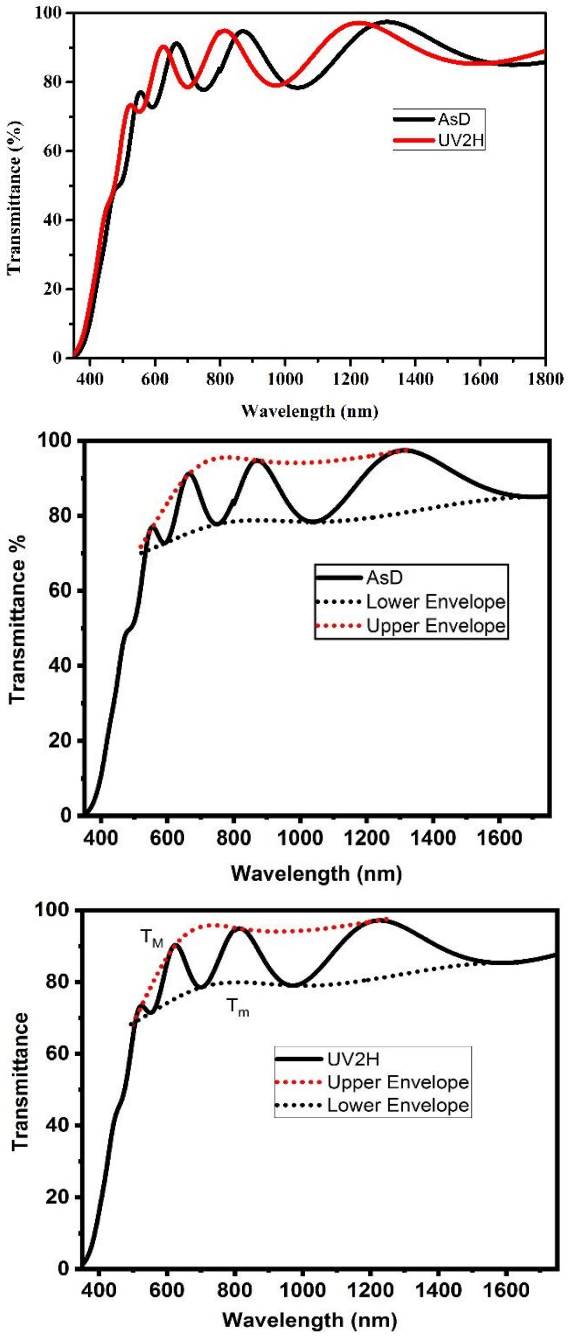

Fig. 3. Envelope of transmission spectra of SnO_2 films (a) both as deposited (AsD) and short UV exposed (UV2H) for 120 min (b) envelope of as deposited films (AsD) (c) envelope of 2 hours UV exposed thin films (UV2H) (color online)

The oxygen in interstitial sites causes increase in band gap which is confirmed by bandgap measurement of thin films. It is well known that the basic cause for Interference fringes in transmission spectrum is

$$2nd = m\lambda$$

where n is refractive index of film, d is thickness of film, and m is an integer for maxima and it has half integer value for minima.

Now to measure thickness, an envelope was created using origin and then Microsoft excel for solving the equations. The refractive index (n) of films is given by [8].

$$n = [N + (N^2 - S^2)^{1/2}]^{1/2} \quad (2)$$

where

$$N = 2s\left(\frac{T_M - T_m}{T_M T_m}\right) + \frac{s^2 + 1}{2} \quad (3)$$

for medium and weak region,

$$N = \left(\frac{2s}{T_m}\right) + \frac{s^2 + 1}{2} \quad (4)$$

for transparent region,

The glass substrate used to deposit the thin films has refractive index of 1.54. Hence thickness is measured using [5]

$$d = \frac{\lambda_1 \lambda_2}{2(\lambda_1 n_1 - \lambda_2 n_2)} \quad (5)$$

The thickness of films was found to be 799 nm that is in the range as measured by quartz crystal thickness monitor during deposition as well as match with measured using profiler (MarSurf LD 260 Y from Mahr GmbH) which is 801 nm. Similarly thickness of thin films after UV exposure becomes 759 nm. This decrease in thickness may be due to increase in packing density after UV exposure of films. The value of n has been selected to be 1/2 (for allowed direct transition band gap) as illustrated in Fig. 4 because it was most probable transition and by using n = 1/2, the graph gave the best line fit [10,11].

Optical band gap (E_g) is obtained from Fig. 3 and using equation-1 that is found to be 3.41 eV and UV exposed films have band gap more than those as-deposited film which is 3.37 eV. Further static refractive index of the films under reference have been estimated using the relation [13,14] (Table 1).

$$n_o^4 E_g = 77$$

Optical band gap (E_g) is obtained from Fig. 3 and using equation-1 that is found to be 3.40 eV and UV exposed films have band gap less than those as-deposited film which is 3.22 eV. Further refractive index of the films under reference have been estimated using the relation [13,14] (Table 1).

$$n_o^4 E_g = 77$$

The increase in refractive index from 2.181 to 2.211 on UV exposure may be due to local structure modification that brings the thin films denser.

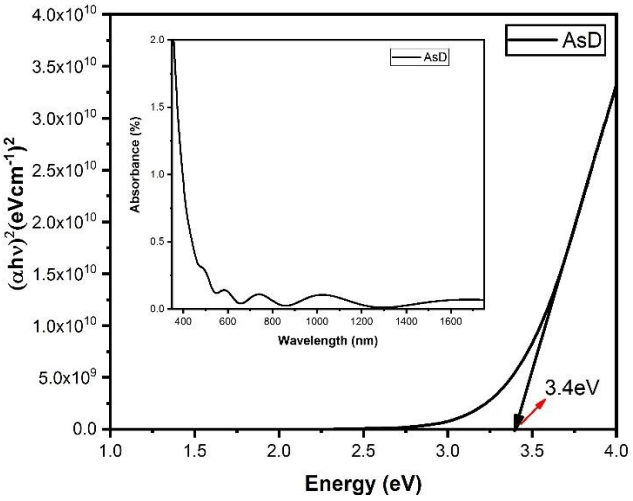

Fig. 4a. Tauc's plot of SnO_2 ~800 nm AsD thin films

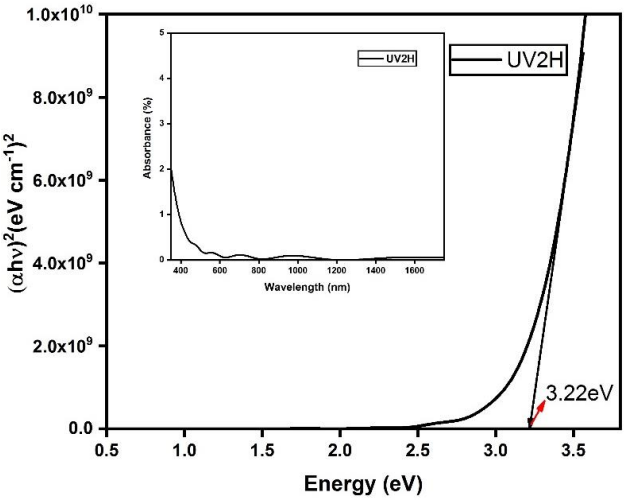

Fig. 4b. Tauc's plot of UV exposed tin oxide (UV2H) thin films

3.4. Nonlinear optical properties

Nonlinear optical response of thin films depends upon polarization of response of material on the intensity of Electromagnetic Radiation falling. Third order nonlinear optical susceptibility of the thin films on glass substrate is calculated using Miller's rule [4].

$$\chi^{(3)}[esu] = A(\chi^{(1)})^4$$

Here A is constant have value 1.7×10^{-10} esu and one can find $\chi^{(1)}$, known as linear susceptibility in long wavelength region using relation

$$\chi^{(1)} = \frac{(n_0^2 - 1)}{4\pi}$$

The value of n_o (static refractive index) for exposed and unexposed films of tin oxide is tabulated in Table 1.

The value of $\chi^{(3)}$ is calculated to be 1.3637×10^{-12} esu and 1.5643×10^{-12} esu for un-exposed and UV exposed films, respectively. The increased value of $\chi^{(3)}$ of UV exposed film is understood to be due to local structural modifications which may lead to enhanced local polarization that results to change in susceptibility. Similarly, the nonlinear Index of refraction is estimated using the relation given by Tichy et. al. [15].

$$n_2 = \frac{B}{E_g^4}$$

where $B = 1.26\times10^{-9}$ [esu $(eV)^4$].

Table 1. Linear and nonlinear optical constants of exposed and unexposed thin films of SnO_2

Parameters	As-deposited SnO_2	UV Exposed SnO_2
$n_o(hv)$	2.181	2.211
Band Gap (eV)	3.40	3.22
n_2 (cm^2/W)	9.4287×10^{-11}	1.1720×10^{-12}
χ^3(esu)	1.3637×10^{-12}	1.5643×10^{-12}

4. Conclusions

Tin Oxide (SnO_2) thin films have been successfully deposited using thermal evaporation over the large surface area and films exhibit good transmittance of more than 80 % in the visible to Infrared spectrum. Thickness of films measured by various techniques viz. *In-situ* using quartz crystal thickness monitor, optical profiler and Swanepoel methods are nearly equal. However, there is decrease in thickness on UV exposure of 2 hours which is 759 nm due to increase in packing density. Also, there is change in Refractive index from 2.181 for as-deposited and 2.211 for UV exposed films. The band gap decreases from 3.40 eV (as-deposited) to 3.22 eV (UV exposed). Nonlinear refractive index changes from 9.4287×10^{-11} cm^2/W (as-deposited) to 1.1720×10^{-12} cm^2/W (UV exposed) and hence third order nonlinear susceptibility changes from 1.3637×10^{-12} esu (as-deposited) to 1.5643×10^{-12} esu (UV exposed).

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