Sol gel deposition of pure and antimony doped tin dioxide thin films by non alkoxide precursors

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Abstract

Pure and antimony doped tin oxide films have been deposited by the alcoholic sol gel method using non alkoxide precursor SnCl2·2H2O as host and SbCl3 as the dopant precursor. Using the dip coating method, thin films of thickness up to 300 nm have been uniformly deposited on corning 7059, KBr and Silicon substrates. The influence of various parameters such as viscosity and pH of the sol; pulling speed and sintering temperature on thickness of the coatings and their microstructure have been investigated. Pure as deposited films have a visible transmission of (83%) but very high resistivity (7.1 × 10−2 Ω-m). Doping and annealing treatments bring it down to about 5 × 10−6 Ω-m. It has been possible to obtain antimony doped tin oxide films having a sheet resistance of 5 Ω/□ and a visible transmission of 80% after annealing treatment by hydrogen plasma.

Keywords: Deposition process; Electrical properties and measurements; Optical properties; Tin oxide

1. Introduction

Tin dioxide is an n-type, wide band gap semiconductor, transparent to visible light. Its electrical properties depend critically on its stoichiometry, on the nature and amount of dopants and on its microstructure. Stoichiometric and near stoichiometric tin oxide is highly resistive and chemically very stable. It has been widely used in gas sensing applications [1]. Tin oxide can be made to be a conductor without affecting its visible transmission (hence the name transparent conductor) by making it nonstoichiometric or by adding suitable dopants [2,3]. The conductivity of pure nonstoichiometric SnO2 is determined by oxygen vacancies whose concentration is usually difficult to control. Doping tin oxide to introduce electron degeneracy is therefore the preferred method. It is known that the addition of group III elements decreases conductivity and group V elements increases conductivity if they are added in specified quantities [4]. Common dopants generally used for increasing n-type conductivity of SnO2 are Sb and F, although Mo has also been used [5]. Transparent, conducting, thin SnO2 films have found widespread applications. Various aspects of transparent conducting thin films are discussed in excellent reviews on the subject [2,6,7].

A variety of techniques have been used to deposit antimony doped tin oxide (SnO2:Sb) thin films. These include spray pyrolysis [8–12], ultrasonic spray pyrolysis [13], chemical vapor deposition [14], activated reactive evaporation [15], sputtering [16–18], and sol gel [19–25] methods. Sol gel deposition has attracted considerable attention in recent years because it is an economical and energy saving method to deposit high quality films on large areas and axially symmetric objects such as rods and pipes [26]. It has the potential to precisely control the microstructure of deposited films [24]. Sols for thin film deposition can either be prepared from alkoxide precursors or from non alkoxide precursors such as chlorides, acetates, nitrates and carbonates [27]. Alkoxide precursors offer high quality films. The microstructures of these films can be precisely controlled but alkoxides are quite expensive and difficult to handle [28]. Inorganic precursors are comparatively cheap and can be handled conveniently but achieving the required composition and quality of the films formed depends critically on the processing conditions. Inorganic sol gel deposition can be carried out via an aqueous sol gel route [19] or an alcoholic sol gel route [23]. The aqueous sol gel method has mainly been used for fine particle preparation [29], though there is a report on the deposition of SnO2 films, having an average visible transmittance of 75% and electrical resistivity of 10−4 Ω-m, using the aqueous sol gel method [19]. Using zirconium and titanium alkoxide [(Zr(OC8H18)4) and (Ti(OC4H9)4)] as doping precursors and SnCl2 as a host...
precursor, Zr and Ti doped SnO₂ films have also been deposited [23]. An anomalous behavior of electrical conductivity for 3% Ti doped SnO₂ films for temperatures greater than 60 °C was reported [23]. SnO₂:Sb films have also been deposited using inorganic salts (SnCl₂, SbCl₃) as starting precursors but alkoxides were prepared from the precursors before the sol was prepared [20,25].

Our objective in this work was to prepare pure and antimony doped SnO₂ films by the alcoholic sol gel method using non alkoxide precursors. We have used inorganic precursors both as host and dopant material. Even though many sol gel deposition methods such as dip, spin, spray, electrophoresis, thermophoresis, sedimentation and ultrasonic spray [30] are now available, we have deposited the films by the popular and convenient dip coating method. The films have been characterized for their electrical and optical properties under various annealing treatments. The results of these studies are presented in this article.

2. Experimental

The deposition of pure and antimony doped tin oxide films was done in four stages; sol preparation, formation of the liquid film, drying and sintering. The processing stages are outlined in Fig. 1.

Sol preparation and stability of the sol are important for getting a reproducible final product. Reagent grade SnCl₂ 2H₂O (BDH) and SbCl₃ (E-Merk) were used as the starting materials. 3 × 10⁻³ tool each of SnCl₂ and of SbCl₃ were refluxed in 100 ml of ethanol separately at around 80 °C for 3–5 h and then mixed in desired proportions to get the doped sol. It is essential to coat the samples only in a constant viscosity and pH regimes for reproducible film properties. We controlled the pH of as prepared solution (so that stable precipitates do not form) by varying the quantity of solute added and also by the addition of HCl. The sols were then aged in an atmosphere controlled at 60RH for periods ranging from 20 to 25 h to get sols of desired viscosity. It may be pointed out that doping levels referred to in the text correspond to mol% of antimony in the sol. The concentration of antimony in the sintered films is likely to be different from that in the sol.

Precleaned corning 7059 glass and freshly prepared KBr pellets were drawn from the sol with varying speeds ranging from 5 to 45 cm min⁻¹. The liquid films so obtained on the substrates were kept in a controlled atmosphere of 76 RH (NaCl saturated solution) for 15 min, dried at 100 °C for about 20 min and finally sintered at 450 °C for 10 min (sintering temperature was decided from IR results discussed below). Films thus formed had a typical thickness of around 800 Å. To get films of higher thickness, the sequence of dipping in sol, keeping in constant RH controlled atmosphere and drying was performed a number of times. The sintering was, however, done only after the final dipping step. The film thickness was measured using a surface profiler [Taly Step-Taylor-Hobson, UK] with an accuracy of 20 Å.

As prepared films were annealed in either vacuum, argon or oxygen atmospheres. Vacuum annealing was carried out at 350 °C for 20 min in a vacuum ≈ 10⁻⁴ Pa. For argon and oxygen annealing, the vacuum chamber was initially evacuated to about 10⁻⁴ Pa and then flushed with the respective gas. The pressure of the oxygen/argon was maintained around 13 Pa and the annealing carried out at 350 °C for 20 min. Some of the as deposited films were exposed to a low pressure (0.13 Pa) hydrogen plasma for 20 min in a plasma enhanced chemical vapor deposition system (Anelva PECVD 301 Japan), maintaining the film temperature at 150 °C during the treatment.

In order to decide the appropriate sintering temperature, liquid films were deposited on freshly prepared identical KBr pellets and heated to different temperatures (40, 150, 350, 450 and 500 °C) and then gradually cooled to room temperature. Infrared spectra of these samples were taken in the transmission mode using IR spectrometer [Perkin Elmer 683]. The core level spectra of the films was recorded using an ESCA system [PHI 1800] to confirm the composition of the films. The structural changes during sintering and the ultimate evolved structure was examined by Rigaku X-ray diffractometer [Giegerflux D/Max-RB-Ru 200B] in glancing angle [GAXRD] mode using Cu Kα radiation. The surface morphology of the films was examined with a scanning electron microscope [Philips SEM-525M]. Reflectivity (R) and transmissivity (T) as a function of wavelength was measured for a single film after removing the film from the other side of corning 7059 glass substrates, using an UV-Visible-NearIR double beam spectrometer [Hitachi - 330]. The refractive index (n) and extinction coefficient (k) of both as-deposited and annealed films in the range 0.5–5.5 eV were then calculated using expression derived by Tomin [31].

A program employing an algorithm using the Newton–Raphson method was developed and used for this purpose. Electrical
resistivity and Hall effect measurements were carried out on
the samples using van der Pauw configurations.

3. Results and discussion

The quality of the films depends on the sol structure (po-
lymeric or particulate sol) and evaporation and condensation
rates apart from pulling speed, viscosity, surface tension and
contact angle with the substrate [32]. The sol structure
depends on the pH of both the starting solution and the sta-
bilized sol [28]. It was observed that the film deposition took
place only when the pH of the as prepared solution was in
the range 1.8–2. pH values greater than 2 did not form a clear
solution but only stable white precipitates. However, for pH
less than 1.8, a clear solution was obtained but the stabiliza-
tion pH (after refluxing and ageing) fell below 1 and the
liquid films deposited from these sols did not stick to the
substrate. The refluxing and ageing processes decrease the
initial pH value. After refluxing, the measured pH decreased
from the initial value of 1.8–2 to 1.5–1.7 depending on the
dopant concentration. On ageing, the pH changed with time
and stabilized in the range 1.3–1.4. The normalized viscosity
of the sol, measured with respect to ethanol (η =
1.199 \times 10^{-2} \text{ Poise}), was about 1.28 immediately after
refluxing. It increased on ageing and stabilized at a higher
value of about 1.84. These trends of pH and relative viscosity
changes are shown in Fig. 2. Fig. 3 shows the variation of
film thickness as a function of the pulling speed and number
of dippings (at a constant speed of 45 cm min^{-1}) for the
films deposited from a stabilized sol (pH of 1.3–1.4 and
relative viscosity = 1.84). It is clear that an increase in the
number of dips increases the thickness of the deposited film,
however both uniformity and adhesion of films of thickness
greater than 600 nm was found to be rather poor.

IR transmission spectra of liquid films deposited on KBr
substrates were measured after each heat treatment. For a
liquid film heat treated to temperatures = 40 °C, the IR spec-
trum shows an absorption peak corresponding to deformed
water (1600 cm^{-1}) [19] and a broad absorption peak in the
spectral range 700 to 400 cm^{-1}. A literature survey reveals
IR absorption peaks corresponding to SnO_{2}, HCSnCl_{3},
Sn (CH_{3})_{2}Cl, C_{2}H_{5}SnCl_{2}, and C_{6}H_{5}SnO_{2}Sn_{2} in the spectral range
671–505 Cm^{-1} and therefore it is difficult to unambiguously
draw any conclusion from this broad peak. With the increase
in temperature, the intensity of the 1600 cm^{-1} peak decreases
and the peak completely disappears in IR spectra of the films
heated above 200 °C. The broad peak in the spectral range
700–400 Cm^{-1} starts splitting with an increase of tempera-
ture and for the films heated above 400 °C, two humps —
one corresponding to SnO_{2} (665 cm^{-1}) and another to SnO
(540 cm^{-1}) — are clearly discernible. The intensity of the
SnO_{2} peak is maximum for films heated at 450 °C. There is
no appreciable difference in the peak intensity for any further
increase in the processing temperature. We have therefore
processed subsequent films at 450 °C. The IR spectra corre-
sponding to various processing temperatures are shown in
Fig. 4.

The IR spectra of doped films processed at 450 °C still
show the humps corresponding to SnO_{2} (665 cm^{-1}) and
SnO (545 cm^{-1}). However, the peaks are no longer as sharp
as in pure films but become broad and diffused. This may be

![Fig. 2. Variation of pH and viscosity with time during the aging of SnO_{2} sol.](image)

![Fig. 3. Variation of film thickness as a function of i) pulling speed and ii) number of dippings (at constant speed of 45 cm min^{-1}) for the SnO_{2} films processed at 450 °C.](image)

![Fig. 4. IR transmission spectra of SnO_{2} films processed at a) 40 °C; b) 150 °C; c) 350 °C; d) 450 °C and e) 500 °C.](image)
caused by the absorption of Sb$_2$O$_3$ (600 cm$^{-1}$ and 770 cm$^{-1}$) [19].

The X-ray diffractograms of films processed at temperatures up to 200 °C show only a broad peak indicating the amorphous nature of the films. For the processing temperatures beyond 200 °C, sharp peaks appear in the diffraction pattern and the peak intensity increases with increase in processing temperature up to 450 °C. The 'd' values of the films (processed at 450 °C) determined from the XRD are given in Table 1. Comparison with standard 'd' values given in JCPDS (Joint committee for powder diffraction standards) shows that the film structure corresponds to the tetragonal cassiterite structure of SnO$_2$. The diffraction patterns of antimony doped films do not show any appreciable changes from those of pure films. This may be as a result of low concentrations of antimony in the films. The typical diffractograms for SnO$_2$:Sb films drawn from a sol having 5 mol% antimony (hereafter referred as SnO$_2$:Sb (5%)), for processing temperatures of 150, 350, 450 °C are shown in Fig. 5.

Fig. 6 shows the core level spectra of tin and oxygen in SnO$_2$ films deposited on silicon substrates. The spectrum was recorded after sputter cleaning the sample to remove surface contamination. The peak positions in $N(E)$ vs. $E$ spectrum match with the standard binding energies of Sn 3d$_{3/2}$ (493.3 eV), Sn 3d$_{5/2}$ (486.5 eV) and O$_{1s}$ (529.8 eV) in SnO$_2$ [33] confirming that the film is stoichiometric SnO$_2$. This is reflected in the observed high resistivity of pure SnO$_2$ films (discussed later).

All the films processed at 450 °C are smooth and strongly adherent to the substrates. The average rms roughness was roughly about 40 Å. Fig. 7 shows a typical scanning electron micrograph for SnO$_2$: Sb (5%) doped films indicating a fine grained surface.

The optical transmittance and reflectance of pure and doped films deposited on corning 7059 glass substrate before and after post deposition treatments were measured in the wavelength range 0.2–0.8 μm. The average transmittance in the visible region was about 83% for a 0.18 μm thick film. Antimony doping slightly reduces this value. For example a SnO$_2$:Sb (5%) film of the same thickness had an average transmittance of about 80%. Fig. 8 shows the transmission and reflection spectra for pure and antimony doped SnO$_2$:Sb (5%) films.

Different annealing treatments had different effects on the average visible transmission. It decreased by about 10% in vacuum annealed samples and by about 15% for the samples subjected to hydrogen plasma annealing. Oxygen and argon annealed films did not show any noticeable change in the average transmission. The $n$ and $k$ values of the films subjected to different annealing treatments were in the range 1.8–

### Table 1

<table>
<thead>
<tr>
<th>S. No</th>
<th>Miller indices (hkl)</th>
<th>II/I$_0$</th>
<th>Measured 'd' values</th>
<th>Standard 'd' values</th>
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<tr>
<td>1.</td>
<td>110</td>
<td>100</td>
<td>3.36</td>
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<td>2.</td>
<td>101</td>
<td>83</td>
<td>2.649</td>
<td>2.644</td>
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<td>3.</td>
<td>200</td>
<td>23</td>
<td>2.371</td>
<td>2.369</td>
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<td>4.</td>
<td>211</td>
<td>67</td>
<td>1.766</td>
<td>1.735</td>
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<tr>
<td>5.</td>
<td>220</td>
<td>15</td>
<td>1.679</td>
<td>1.675</td>
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</table>

![Fig. 5. X-ray diffractograms of SnO$_2$ films processed at a) 150 °C, b) 350 °C and c) 450 °C temperatures.](image)

![Fig. 6. ESCA core level spectra of tin and oxygen in SnO$_2$ films.](image)

![Fig. 7. Scanning electron micrograph of SnO$_2$ films.](image)
Table 2

<table>
<thead>
<tr>
<th>Sample</th>
<th>As deposited</th>
<th>Oxygen annealed</th>
<th>Argon annealed</th>
<th>Vacuum annealed</th>
<th>Hydrogen annealed</th>
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<tbody>
<tr>
<td></td>
<td>n</td>
<td>k</td>
<td>$E_g$</td>
<td>n</td>
<td>k</td>
</tr>
<tr>
<td>SnO$_2$</td>
<td>1.82</td>
<td>0.06</td>
<td>3.3</td>
<td>1.96</td>
<td>0.03</td>
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<td>SnO$_2$:Sb2%</td>
<td>1.92</td>
<td>0.04</td>
<td>3.2</td>
<td>2.00</td>
<td>0.03</td>
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<tr>
<td>SnO$_2$:Sb3%</td>
<td>1.97</td>
<td>0.05</td>
<td>3.1</td>
<td>2.11</td>
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<tr>
<td>SnO$_2$:Sb4%</td>
<td>1.86</td>
<td>0.04</td>
<td>3.2</td>
<td>2.00</td>
<td>0.03</td>
</tr>
<tr>
<td>SnO$_2$:Sb5%</td>
<td>1.88</td>
<td>0.04</td>
<td>3.2</td>
<td>1.97</td>
<td>0.02</td>
</tr>
<tr>
<td>SnO$_2$:Sb6%</td>
<td>1.86</td>
<td>0.04</td>
<td>3.3</td>
<td>1.99</td>
<td>0.03</td>
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<tr>
<td>SnO$_2$:Sb7%</td>
<td>1.86</td>
<td>0.04</td>
<td>3.3</td>
<td>1.95</td>
<td>0.04</td>
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<td>SnO$_2$:Sb8%</td>
<td>1.89</td>
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<td>3.4</td>
<td>1.90</td>
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<tr>
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<td>1.92</td>
<td>0.03</td>
<td>3.2</td>
<td>1.98</td>
<td>0.04</td>
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2.03 and 0.02-0.32 respectively except for the vacuum annealed films. The n and k for these films were found to be in the range 1.6-1.9 and 0.02-0.4 respectively. Fig. 9 shows the variation of n and k with wavelength for a SnO$_2$:Sb (5%) films under various treatments.

The absorption coefficient ($\alpha$) was calculated from the relation $\alpha = (4\pi n k)/\lambda$. The optical band gap energy ($E_g$) was then determined from the slope of $(ahv)^{1/2}$ vs. hv graph. The typical plots for SnO$_2$:Sb (5%) films subjected to various annealing treatments are shown in Fig. 10. As deposited films have a band gap of 3.3 eV which changes on annealing. Table 2 gives n, k (at a typical wavelength of 500 nm) and $E_g$ of various samples under different annealing conditions.

Hall effect measurements showed that the films were n-type. The variation of electrical resistivity as a function of the doping concentration for as prepared and annealed samples...
Table 3

The carrier concentration (N), mobility (µ) and resistivity (ρ) of SnO₂:Sb (3,5,7%) films

<table>
<thead>
<tr>
<th>Samples</th>
<th>Annealing treatments</th>
<th>N (× 10²⁶ m⁻³)</th>
<th>µ (× 10⁻⁴ m² V⁻¹ s⁻¹)</th>
<th>ρ (× 10⁻⁴ Ω m)</th>
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<tr>
<td>SnO₂:Sb3%</td>
<td>As deposited</td>
<td>0.12</td>
<td>2.3</td>
<td>21.70</td>
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<tr>
<td></td>
<td>Oxygen annealed</td>
<td>–</td>
<td>–</td>
<td>1200</td>
</tr>
<tr>
<td></td>
<td>Argon annealed</td>
<td>–</td>
<td>–</td>
<td>224.09</td>
</tr>
<tr>
<td></td>
<td>Vacuum annealed</td>
<td>4.5</td>
<td>8.16</td>
<td>0.17</td>
</tr>
<tr>
<td></td>
<td>Hydrogen annealed</td>
<td>4.8</td>
<td>18</td>
<td>0.0715</td>
</tr>
<tr>
<td>SnO₂:Sb5%</td>
<td>As deposited</td>
<td>1.18</td>
<td>16</td>
<td>0.33</td>
</tr>
<tr>
<td></td>
<td>Oxygen annealed</td>
<td>–</td>
<td>–</td>
<td>700</td>
</tr>
<tr>
<td></td>
<td>Argon annealed</td>
<td>–</td>
<td>–</td>
<td>159</td>
</tr>
<tr>
<td></td>
<td>Vacuum annealed</td>
<td>5.3</td>
<td>20.1</td>
<td>0.07</td>
</tr>
<tr>
<td></td>
<td>Hydrogen annealed</td>
<td>6.15</td>
<td>22.3</td>
<td>0.05</td>
</tr>
<tr>
<td>SnO₂:Sb7%</td>
<td>As deposited</td>
<td>1.32</td>
<td>11</td>
<td>0.426</td>
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<tr>
<td></td>
<td>Oxygen annealed</td>
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<td>–</td>
<td>1332</td>
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<td>Argon annealed</td>
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<tr>
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<td>Vacuum annealed</td>
<td>5.3</td>
<td>12</td>
<td>0.097</td>
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<tr>
<td></td>
<td>Hydrogen annealed</td>
<td>5.36</td>
<td>15</td>
<td>0.078</td>
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</table>

are shown in Fig. 11. The lowest electrical resistivity of 10⁻⁵ Ω·m for as deposited films was achieved with sols of 5 to 6 mol% antimony. Annealing of the films in oxygen and argon atmosphere at 350 °C increased the resistivity to 10⁻² Ω·m. The vacuum annealed samples however showed a decrease in resistivity to about 10⁻⁶ Ω·m. A typical sheet resistance of 0.18 μm vacuum annealed film is 33 Ω/□. The minimum sheet resistance of 5 Ω/□ and visible transmission of 80% were obtained on hydrogen annealing treatment. Table 3 gives the values of the carrier concentration, mobility and resistivity for SnO₂:Sb (3, 5, 7%) films on various annealing treatments. These results can be understood as being because of the change in carrier concentration due to a change in concentration of oxygen vacancies present in as deposited films [34]. From resistivity data, it can be concluded that the hydrogen plasma annealing and vacuum annealing increase oxygen vacancies. However, oxygen and argon annealing decrease oxygen vacancies. Carrier concentration of 5% Sb doped films increased from 1.8 × 10²⁶ to 6.3 × 10²⁶ m⁻³ in vacuum annealed samples and to 6.15 × 10²⁶ m⁻³ for hydrogen plasma annealed samples. The mobility of the same sample also increased from 2.3 to 8.16 cm² V⁻¹ s⁻¹ for vacuum annealed samples and to 18 cm² V⁻¹ s⁻¹ for hydrogen plasma annealed samples. We were not able to measure the Hall mobility for the samples of doping level less than 3% and greater than 7%.

4. Conclusions

SnO₂ and SnO₂:Sb films can be deposited by an economical and energy saving sol gel method using all non alkoxide precursors. The films have electrical and optical properties comparable with SnO₂ films prepared by spray pyrolysis, chemical vapor deposition, activated reactive evaporation and sputtering methods. Pure as deposited films are nearly stoichiometric and have very high resistivity. Doping and subsequent annealing treatment bring down the resistivity to about 10⁻⁶ Ω·m with a visible transmission greater than 80%. Tailoring of the band gap is also possible by annealing treatments. The optical band gap being 3.3 eV for as deposited films, 3.4 eV for oxygen annealed films and 3.1 eV for vacuum and hydrogen annealed films.

References