

# Recent Development of Low Temperature Plasma Enhanced CVD of Transparent Conducting Oxide in Photovoltaic Applications

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**ABSTRACT:** Transparent conducting oxide (TCO) is one of the key components in photovoltaic and display applications. One candidate to replace indium tin oxide as TCO material is tin oxide. It is stable at high temperature, economical to produce and more benign compared to other TCO materials. The bulk resistivity of tin oxide films deposited with conventional methods (PECVD, spray pyrolysis, atmospheric pressure CVD) reaches as low as  $5 \times 10^{-4}$  Ohm-cm. However, the deposition temperature is typically above 350°C which limits temperature sensitive processes such as quantum dots based solar cells or large area plastic substrates. We developed a novel PECVD system to deposit tin oxide at lower temperature (below 130°C) while achieving good conductivity. Our tin oxide films have bulk resistivity of  $2.18 \times 10^{-3}$  Ohm-cm at 130°C which is lower than conventionally deposited films at the same process temperature. Furthermore, the linear PECVD source used in this process is scalable to several meter-wide web substrates with film uniformity better than 3%. The deposition rate is typically 200-300 nm-meter/minute. In the present work, we will discuss the PECVD source used in the process, electrical property (carrier concentration and mobility), optical property and microstructure of the deposited tin oxide based TCO.

Keywords: TCO Transparent Conducting Oxides, tin oxide, PECVD

## 1 INTRODUCTION

Transparent conducting oxide (TCO) thin films have been widely used in many applications; from high efficiency residential windows to high tech devices such as display and photovoltaic cells. Indium tin oxide (ITO) has the best electrical and optical properties of all the commercially available TCO materials. However, indium exists as by-product of mining other metal which has caused its price to increase more than eight times in the last 5 years. Furthermore, ITO is typically deposited by sputtering, which typically have less than 40% efficiency. As a result, a lot of effort has been directed to develop more economical alternative TCO materials such as zinc oxide and tin oxide.

Tin oxide is one of the suitable candidates due to its high conductivity and stability at high temperature. Tin oxide has been produced by various techniques such as spray pyrolysis [1-2], reactive RF and DC sputtering [3-4], chemical vapor deposition (CVD) [5-10]. The typical tin oxide film has a resistivity,  $\rho$ , between  $3 \times 10^{-4}$  –  $1.4 \times 10^{-2}$  Ohm-cm with carrier concentration,  $n$ , of  $\sim 3.9 \times 10^{19}$  cm<sup>-3</sup> and electron mobility,  $\mu$ , of 14 – 40 cm<sup>2</sup> V<sup>-1</sup>s<sup>-1</sup> with deposition temperature or post deposition annealing between 350°C and 570°C. Tin oxide deposition at temperature below 350°C, typically results in degraded electrical and optical properties of the films, hence, reduced device performance.

Conductivity in undoped tin oxide comes from oxygen vacancies, which donate two free electrons into the conduction band to conduct current. Fluorine dopant is typically used because the ionic size of oxygen (O<sup>2-</sup>) is closely matched by fluorine ion (F<sup>-</sup>) (0.133 nm to 0.132 nm). The bond energy of the Sn-F and Sn-O are also comparable (26 kJ/mol and 31 kJ/mol). Fluorine ions have half the charge of oxygen ion which reduce the Coulomb forces that bind the lattice together. Thus, the lattice is undisturbed when oxygen ions are substituted with fluorine ions [1]. Substrate temperature during deposition influences fluorine doping efficiency which is defined as the amount of electrically active fluorine in the films. The doping efficiency of thin films deposited at

450 °C are seven times (7x) lower than those deposited at 600 °C.

Our goal is to develop a thin film process based on an innovative Plasma Enhance Chemical Vapor Deposition (PECVD) source to produce high performance TCO films economically at low temperature to replace ITO. Tin oxide (SnO<sub>2</sub>) is selected because of its economical cost and environmental stability.

## 2 EXPERIMENTAL SETUP

Our tin oxide thin film PECVD process is performed at pressures between  $3 \times 10^{-5}$  –  $1.5 \times 10^{-4}$  torr using a dual Plasma Beam Source™ (PBS™) connected with mid-frequency AC source (Figure 1). Advantages of the PBS™ compared to conventional plasma sources include dense plasma, scalability to over several meters wide with excellent uniformity (within 3%) and controlled ion bombardment to improve film properties at low temperature [11]. The PBS™ feature is available with floating substrate configuration, which is used in current work (Figure 1), thus, is suitable for large area coating.

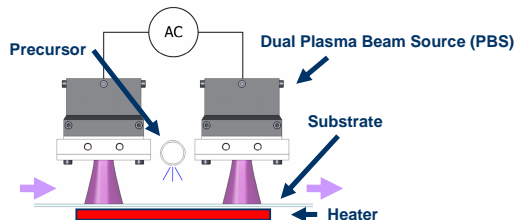
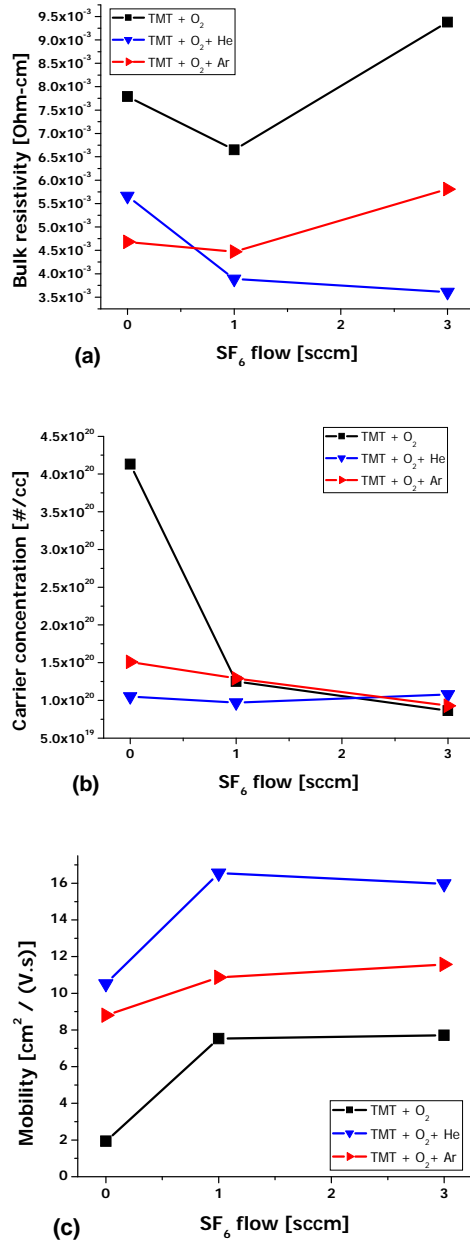


Figure 1. Experimental setup using Dual Beam PBS™

Tetramethyltin (TMT) precursor is used as tin source while fluorine dopant is dissociated from SF<sub>6</sub>. Inert gas, such as helium and argon, is added to the gas mixture to increase chemical dissociation and control ion bombardment. Substrate temperature during deposition is set between 130-315°C.

The electrical properties of deposited films are analyzed using Ecopia HMS 3000 Hall Measurement System and Jandel model RM3 four point probe. Optical transmission and reflection are measured with a Perkin-Elmer Lambda 800 spectrometer and analyzed using Optilayer thin film analysis software. Secondary ion mass spectroscopy analysis was performed using a CAMECA IMS-4f to characterize elemental depth profile of the deposited films. Crystallinity of tin oxide films is also characterized using PANalytical X-Ray Diffraction with Cu K $\alpha$  radiation at 3° incident angle.

### 3 RESULTS AND DISCUSSION



**Figure 2:** Effect of fluorine dopant on electrical properties of tin oxide films deposited at 130°C; (a) bulk resistivity; (b) carrier concentration; (c) electron mobility

Figure 2 shows the effect of fluorine flow on tin oxide electrical properties. The gases flow other than SF<sub>6</sub> (TMT, O<sub>2</sub>, inert gas) are fixed while the SF<sub>6</sub> flow varies between 0 to 3 sccm. Substrate temperature during deposition is fixed to 130°C. Fluorine addition, as shown in Figure 2a, does not always decrease films bulk resistivity. As bulk resistivity is directly proportional to product of carrier concentration and electron mobility, Hall measurement system measures carrier concentration and electron mobility. Both carrier concentration and electron mobility measurement provide further insight on how fluorine addition influences tin oxide electrical properties at 130°C substrate temperature.

Figure 2b reveals that fluorine addition decreases carrier concentration in all experimental conditions except the one with helium addition. The decrease in electron concentration is most likely caused by fluorine occupying oxygen vacancies in the structure and reduces free electrons [1]. The carrier concentration in the deposition with helium addition has insignificant increase with addition of 3 sccm SF<sub>6</sub> flow (from 1.05x10<sup>20</sup> /cc to 1.08x10<sup>20</sup> /cc). In this case, fluorine atoms have most likely occupied interstitial sites of Sn-O structures and became electrically inactive [1].

Electron mobility, however, increases with fluorine addition, as illustrated in Figure 2c. This phenomenon is also observed in depositions with different gas ratio (TMT, oxygen and inert gas ratio). Fluorine addition occupies oxygen vacancies and induces preferential growth along [2 0 0], which induces more crystallization [1].

Table I summarizes electrical properties of tin oxide developed using dual PBS<sup>TM</sup> PECVD sources. Bulk resistivity of the tin oxide films depends on substrate temperature during deposition. Tin oxide films deposited at 315°C, 225°C and 130°C have bulk resistivity of 6.82x10<sup>-4</sup> Ohm-cm, 8.64x10<sup>-4</sup> Ohm-cm and 2.18x10<sup>-3</sup> Ohm-cm; respectively.

| Temperature                       | 130°C                  | 225°C                  | 315°C                  |
|-----------------------------------|------------------------|------------------------|------------------------|
| Bulk Resistivity [Ohm-cm]         | 2.18x10 <sup>-3</sup>  | 8.64x10 <sup>-4</sup>  | 6.82x10 <sup>-4</sup>  |
| Carrier Concentration [#/cc]      | -2.74x10 <sup>20</sup> | -3.36x10 <sup>20</sup> | -3.02x10 <sup>20</sup> |
| Mobility [cm <sup>2</sup> /(V.s)] | 10.96                  | 20.96                  | 30.28                  |

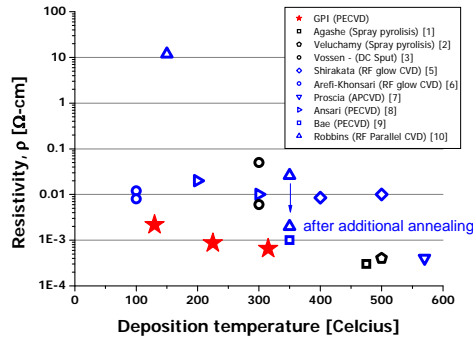
**Table I:** Summary of electrical properties of tin oxide deposited with dual PBS<sup>TM</sup> at different substrates temperature. Negative value of carrier concentration denotes n-type conductor.

Hall measurement shows bulk resistivity decreases with increasing substrate temperature mainly correspond to an electron mobility increase, from 10.96 to 30.28 cm<sup>2</sup>/(V.s) while the carrier concentration has slight increase, from 2.74x10<sup>20</sup> /cm<sup>3</sup> to 3.02x10<sup>20</sup> /cm<sup>3</sup>.

Deposition rate of tin oxide in current work only reaches up to 77 nm-m/minute due to power supply output constraint. Faster deposition rate is possible with

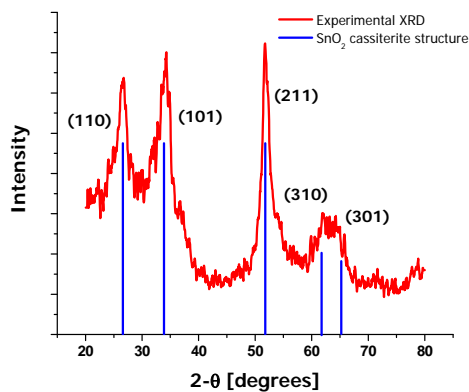
higher power output. Typical optimum deposition rate of PBS<sup>TM</sup> reaches between 200-300 nm-m/min [13].

Figure 3 compares bulk resistivity of tin oxide films shown in Table I with others deposited using other methods published in literature. Similar to our observation, tin oxide films bulk resistivity depends on processing temperature; higher processing temperature typically produces lower resistivity films. In some case, post-deposition annealing is required to improve as-deposited electrical properties [10].



**Figure 3:** Bulk resistivity comparison between tin oxide films deposited with dual PBS<sup>TM</sup> sources and other methods published in literature.

Arefi-Khonsari et al., developed tin oxide with conductivity of 0.01 Ohm-cm at 100°C substrate temperature, which is lower than the trend shown in Figure 3 [6]. They modified the conventional RF (radio frequency) system and biased/grounded the substrates. Therefore, the ion bombardment in this modified RF configuration substitutes for thermal energy to produce tin oxide with good electrical properties. However, this configuration might not be suitable for roll to roll coating or insulator substrates, such as plastic substrates.

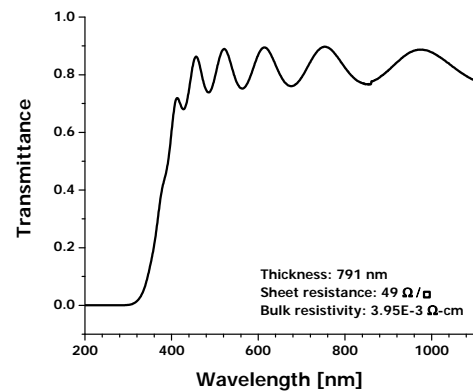


**Figure 4:** XRD diffraction angle of tin oxide. The solid blue lines represent diffraction peak of SnO<sub>2</sub> tetragonal cassiterite structure from ASTM data file

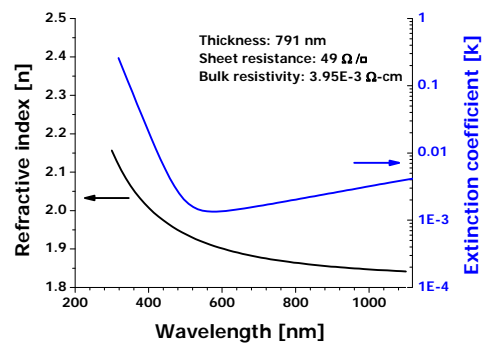
Figure 4 shows diffraction peaks of undoped tin oxide films deposited at 130°C. These diffraction peaks are compared to reference cassiterite structure which has tetragonal form of SnO<sub>2</sub>. The XRD peaks pattern contains no diffraction peak corresponding to SnO

structure, thus confirms the deposited tin oxide structure resembles that of SnO<sub>2</sub> [14-15]. The tin oxide films deposited at 130°C in the current work shows more crystallinity compared to the ones deposited using conventional RF PECVD at same substrate temperature [15]. Dual PBS<sup>TM</sup> sources provide ion bombardment in the range of 30-100 eV with floating substrate configuration. Other PECVD process such as parallel plate configuration, atmospheric pressure PECVD and other conventional PECVD typically do not have controlled ion bombardment. The ion bombardment provides additional energy to compensate for thermal energy at low temperature which results in tin oxide with lower bulk resistivity compared to conventional methods at 130°C.

In addition to ion bombardment, SIMS analysis shows that less than 1% of carbon incorporated into the tin oxide films. Low carbon content in the films proves the excellent dissociation of TMT precursor which consists of four C atoms for every Sn atom, thus, improving electrical properties of deposited films.



**Figure 5:** Optical transmission of tin oxide film deposited at 130°C substrate temperature. Total thickness of the film is 791 nm. Bulk resistivity of the film is  $3.95 \times 10^{-3}$  Ohm-cm.



**Figure 6:** Refractive index and extinction coefficient calculated from optical transmission and reflection spectra of tin oxide film deposited at 130°C substrate temperature. Total thickness of the film is 791 nm, bulk resistivity is  $3.95 \times 10^{-3}$  Ohm-cm.

In addition to conductivity, TCO thin film requires good optical properties to maximize incoming photon flux and increase device efficiency. Figure 5 shows optical transmission from 200-1100 nm of 791 nm-thick SnO<sub>2</sub> film deposited at 130°C and has 3.95x10<sup>-3</sup> Ohm-cm bulk resistivity. The refractive index, n, and extinction coefficient, k, of the films are calculated from both transmission and reflection and shown in Figure 6.

The extinction coefficient of deposited SnO<sub>2</sub> in the wavelength region close to bandgap (314 nm). However, the film has low extinction coefficient between 400-1100 nm (below 0.01) which is excellent for display and solar cell applications.

#### 4 CONCLUSION

We have demonstrated feasibility of depositing high conductivity SnO<sub>2</sub> TCO with high throughput using dual Plasma Beam Source (PBS™) at 130°C substrate temperature. The bulk resistivity of deposited film reaches as low as 2.18x10<sup>-3</sup> Ohm-cm, which is lower than tin oxide films deposited using other PECVD methods at the same processing temperature. Ion bombardment helps compensate for lower thermal energy at 130°C deposition temperature. High precursor dissociation is also necessary to achieve good electrical properties by reducing carbon incorporation into the films. The deposited tin oxide at 130°C shows low extinction coefficient at 400-1100 nm which is excellent for photovoltaic and display applications.

#### 5 REFERENCES

1. C. Agashe, S.S. Major, *J. Mater. Sci.* **31** (1996), 2625.
2. P. Veluchamy, M. Tsuji, T. Nishio, T. Aramoto, H. Higuchi, S. Kumazawa, S. Shibutani, J. Nakajima, T. Arita, H. Ohyama, A. Hanafusa, T. Hibino, K. Omura, *Solar Energy Materials and Solar Cells* **67** (2001), 179.
3. J. L. Vossen, E.S. Poliniak, *Thin Solid Films* **13** (1972), 281.
4. D. Rosenfeld, R. Sanjinés, W.H. Schreiner, F. Lévy, *Sens. Actuators B.* **15-16** (1993), 406.
5. S. Shirakata, A. Yokoyama, S. Isomura, *Jpn. J. Appl. Phys. Part 2.* **35** (1996), L722.
6. F. Arefi-Khonsari, F. Hellegouarc'h, J. Amouroux, *J. Vac. Sci. Technol. A.* **16** (1998), 2240.
7. J. Proscia, R.G. Gordon, *Thin Solid Films* **214** (1992), 175.
8. S.G. Ansari, M.A. Dar, M.S. Dhage, Y.S. Kim, H.S. Kim, Z.A. Ansari, *J. Appl. Phys.* **102** (2007), 073537.
9. J.W. Bae, S.W. Lee, G.Y. Yeom, *J. Electrochem. Soc.* **154**, (2007) D34.
10. J.J. Robbins, R.T. Alexander, M. Bai, Y. Huang, T.L. Vincent, C.A. Wolden, *J. Vac. Sci. Technol. A.* **19** (2001), 2762.
11. J. Madocks, P. Marcus, P. Morse,., *Society of Vacuum Coaters 49<sup>th</sup> Annual Technical Conference Proceedings* (2006), 569.
12. G.J. Exarhos, *Thin Solid Films* **515**, 7025 (2007).
13. J Madocks, P. Morse and M. George, Society of Vacuum Coaters 50th Annual Technical Conference Proceedings (2007).
14. K. Omara, P. Velachamy, M. Tsuji, T. Nishio, M. Murozono, *J. Electrochem Soc.* **146** (1999), 2113.
15. P.Y. Liu, J.F. Chen, W.D. Sun, *Vacuum* **76** (2004), 7.