# Plasma-enhanced Chemical Vapor Deposition of Tin Oxide Thin Films

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**Abstract:** We are developing a novel manufacturing process using plasma-enhanced chemical vapor deposition (PECVD) for the synthesis of transparent conducting oxide (TCO) thin films like tin oxide. In order to develop PECVD as a reliable manufacturing technology we plan to employ *in-situ* metrology coupled with nonlinear feedback control. Gas composition and film properties will be monitored in real time using optical emission spectroscopy (OES) and laser reflectometry, respectively. Control designs will be developed through nonlinear system identification and semi-global empirical modeling. In this paper we discuss our approach and report on our preliminary experimental results for tin oxide deposition and OES analysis.

**Introduction:** TCO materials possess the unusual ability to both transmit visible light and to conduct electricity. This basic electronic material finds widespread commercial use as transparent electrodes in flat panel displays and solar cell modules. Additional applications of this unique material include protective coatings, low-emissivity window glass, and gas detection sensors [1]. In this research, we will develop plasma-enhanced chemical vapor deposition (PECVD) as an alternative manufacturing approach for low temperature TCO synthesis.

PECVD offers several potential advantages over current processing technologies. Foremost is the opportunity to reduce deposition temperatures to below 250 °C. Achievement of this goal will create opportunities for device fabrication on lightweight, flexible polymer substrates. Second, reactant species may be introduced into the low-pressure PECVD reactor by direct liquid injection. This attribute offers many benefits including improved control, enhanced safety, and waste minimization. We plan to use this technique to investigate the synthesis of new TCO materials. Recently it has been reported that certain ternary and non-stochiometric oxides have shown promising optical and electronic properties. Through *in-situ* monitoring and control we will be able to deposit films with unique properties. PECVD is also

compatible with current integrated circuit manufacturing processes.

Along with the advantages of PECVD is the realization that it is a highly complex system. In order to develop PECVD as a reliable manufacturing technology we plan to employ *in-situ* metrology coupled with nonlinear feedback control. Gas composition and film properties will be monitored in real time using optical emission spectroscopy and laser reflectometry, respectively. Control designs will be developed through nonlinear system identification and semi-global empirical modeling. A critical element of model development will rely on *ex-situ* evaluation of material properties. Full electrical, optical and microstructural characterization of the deposited films will be performed using the extensive analytical tools that are available to us through our membership in CSM's Center for Solar and Electronic Materials.

**Experimental:** The reactor for this work is partially shown in Figure 1. It is a custom-made, stainless steel thin film deposition system. Currently, the system is configured as a PECVD system. In addition to mechanical pumps, the system has a turbomolecular pump which attain a base pressure of $10^{-7}$ torr. The plasma is generated using a 300 Watt 13.6 MHz RF power supply and match network, with a 4" diameter deposition area. The reactor was provided through an agreement with our partners, Green Development, and was recently installed in the PI's laboratory. There is an extensive gas-handling manifold, electronic mass flow controllers, pressure, and substrate temperature control. Previously this unit was employed for the deposition of high quality amorphous silicon films for photovoltaic applications [2].

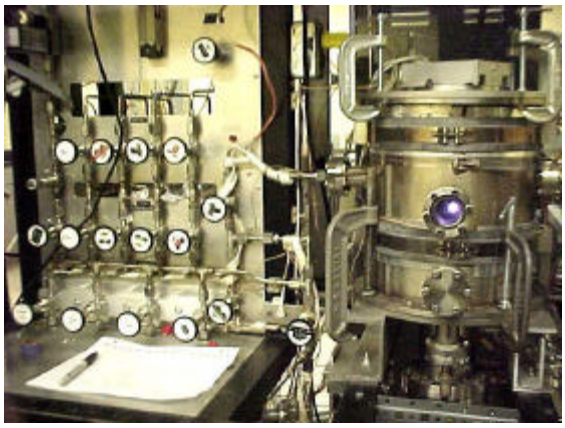

**Figure 1:** Picture of the PECVD reactor employed in these studies.

The reactor is equipped with a fiberoptic-based spectrometer (Ocean Optics) for OES studies. In the near future we plan to modify the reactor to allow optical access to the substrate and permit *in-situ* reflectometry studies of the growing films.

Our initial studies have focused on the synthesis of tin oxide, $SnO_2$, a widely used TCO. Tin tetrachloride ($SnCl_4$) and oxygen diluted in argon are used as source gases. We have extensive experience with tin oxide deposited by traditional thermal CVD [3], and expect that comparisons with PECVD material will be enlightening. Table I provides a summary of the experimental variables and ranges that have been studied to date.

**Table I**: Typical experimental parameters.

| ***Variable*** | ***Range*** |
|---|---|
| Power [W] | 25-150 |
| Pressure [mtorr] | 100-300 |
| Total Flowrate [sccm] | 10-50 |
| Substrate Temperature [$^o$C] | 150-300 |
| $O_2$:$SnCl_4$ Ratio | 1 - 5 |

Deposited films have been characterized by a number of techniques including variable angle spectroscopic ellipsometry (VASE), UV-VIS-IR transparency, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), 4-point probe (sheet resistivity), and atomic force microscopy (AFM).

An optical emission spectrometer (Ocean Optics, SD2000) has been purchased, installed and is operational. This is one of the primary *in-situ* diagnostics that will be employed to investigate and control the process.

**Preliminary Results:** Deposition studies are being pursued rigorously using statistically designed experiments. The goal is to develop quantitative models that relate responses such as growth rate, transparency, resistivity, etc. to the processing variables listed in Table I. Those studies are in progress and a quantitative analysis is not available. However, here we present selected results from these ongoing investigations.

Films are deposited on 2" x 2" glass substrates. Substrates are mounted on the grounded electrode which is independently heated to the desired deposition temperature. Film thickness and uniformity are evaluated by primarily by VASE, with complimentary measurements provided by profilometry. High growth rates (200 - 400 Å/min) have been obtained at substrate temperatures as low as 150 C. In addition the films consistently show good uniformity (~10%) at the conditions examined.

XPS characterization confirms that the films are indeed tin oxide, and also slightly deficient in oxygen as deposited. Typical deposition times are 10 minutes, resulting in film thickness between of 200 - 400 nm. The transparency of the films is excellent as shown in Figure 2. The films are nearly 100% transparent in the visible and IR regime, and highly absorbed at $\lambda < 300$ nm. The interference fringes in the visible are characteristic of the film thickness. We intend to take advantage of this feature to obtain *in-situ* growth rate measurements through laser interferometry. Atomic force microscopy reveals that the films have a small grain, polycrystalline morphology. The AFM image shown in Figure 3 has a RMS roughness of ~ 2 nm.

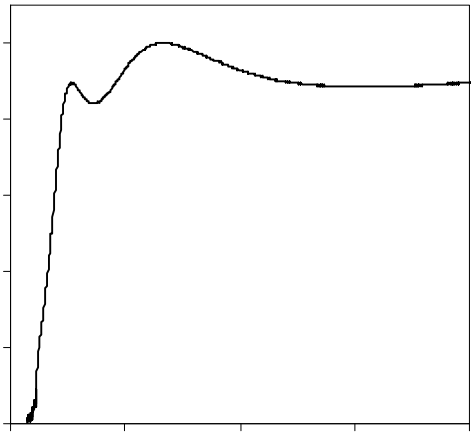

**Figure 2:** Optical transparency of two films with different thickness.

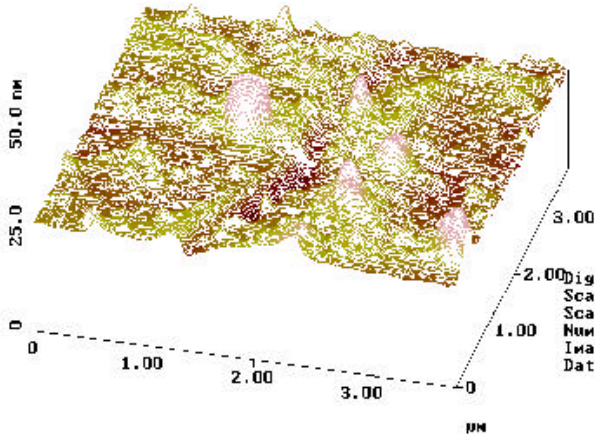


**Figure 3:** AFM image of a PECVD-deposited $SnO_2$ film. The RMS roughness of this film is only 2 nm.

Figure 4 shows two spectra obtained from OES. The spectrometer has a range of 250-1200 nm, however only a subsection of the spectra is displayed in Fig. 4 to illustrate the utility of OES. The solid line is taken from an Ar/O2 plasma while the dashed line is from an Ar/O2/SnCl4 plasma used to deposit films. Most of the features overlap, however there are a number of spectral features that are unique to the second composition. It is believed that these features result from chemical species that are intermediates in the tin oxide PECVD process. We are currently in the process of identifying these peaks an assessing their usefulness as signals for process monitoring and control. Our approach to this is through principle component analysis, which is described in more detail below.

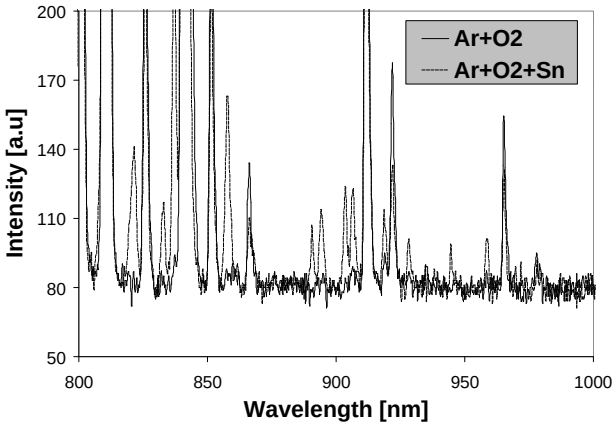


**Figure 4:** OES spectra of an Ar/O2 plasma and an Ar/O2/SnCl4 plasma.

**Principal Components Analysis:** Our immediate goal is to relate the gross behavior of the emission spectra to plasma conditions. Quantitative measurements of fluorine and oxygen concentrations are available through actinometry, however emission spectra of the film precursors have not yet been well established. We are using the statistical analysis of principal component analysis (PCA) in order to establish correlation between inputs, outputs, and emission spectra. PCA has previously been used with emission data for fault diagnostics in [4], but our current emphasis is on building an understanding of the correlation between the observed spectra and process conditions. This is one step towards and eventual goal of building a more complicated nonlinear model.

The rationale for using PCA is the following: It is desired to fit a response surface that predicts inputs or outputs given the observed emission spectra. The problem as stated is generally ill posed, as the number of spectral lines is much larger than our experiments. To overcome this problem the dimension of the emission data is reduced by finding the principal components – a basis of spectral lines which best explains the data. Let the vector $\mathbf{s}_i = [s_{i1} \quad s_{i2} \quad \cdots \quad s_{im}]'$ be the collection of $m$ OES spectra for operating point $i$. We seek the $n$ principle components $\mathbf{\ddot{o}}_j$, with $n<m$, such that

$$\mathbf{s}_i = a_{i1}\mathbf{\ddot{o}}_1 + a_{in}\mathbf{\ddot{o}}_n + \cdots + a_{in}\mathbf{\ddot{o}}_n + e$$

for some coefficients $a_{ij}$ and error $e$. By selecting $\mathbf{\ddot{o}}_j$ to be the eigenvectors of the sample covariance of $\mathbf{s}_i$ with the largest associated eigenvalues, we have the required expansion with several nice properties, including orthogonal $\mathbf{\ddot{o}}_j$, and other statistical properties [5]. Because $\mathbf{\ddot{o}}_j$ are orthogonal, the values of $a_{ij}$ for a particular operating point can be found via $a_{ij} = \mathbf{s}_i'\mathbf{\ddot{o}}_j$ The response surface can then be generated using the coefficients $a_{ij}$. Let the vector $\mathbf{p}_i = [p_{i1} \quad p_{i2} \quad \cdots \quad p_{im}]'$ contain the values at each operating point of the variable that it is desired to predict, such as forward power or deposition rate. Let **A** be a matrix of OES coefficients

$$\mathbf{A} = \begin{bmatrix} a_{11} & \cdots & a_{1n} \\ \vdots & \ddots & \vdots \\ a_{n1} & \cdots & a_{nn} \end{bmatrix}.$$

A linear predictive model can be found by solving the least squares problem

$$\min_{\hat{\mathbf{e}}} \left\| \mathbf{p}_i - \mathbf{A}\hat{\mathbf{e}} \right\|$$

Given a new operating point and emission spectra **s**, the predicted value of variable *p* is then

$$\hat{p} = \mathbf{s}' \begin{bmatrix} \ddot{\mathbf{o}}_1 & \ddot{\mathbf{o}}_2 & \cdots & \ddot{\mathbf{o}}_n \end{bmatrix} \hat{\mathbf{e}}.$$

Alternatively, we can look at the term $f = \begin{bmatrix} \ddot{\mathbf{o}}_1 & \ddot{\mathbf{o}}_2 & \cdots & \ddot{\mathbf{o}}_n \end{bmatrix} \hat{\mathbf{e}}$ as containing information about the correlation between spectral lines and the variable of interest, with large values of elements of *f*. indicating high correlation with the relevant spectral line.

Preliminary analysis has shown that most inputs can be predicted well over a small operating range, especially power, and flow. We are currently attempting to correlate film properties with the OES data to locate emission spectra that are characteristic of film precursors, but results are not yet available. One stumbling block is the large amount of time it takes to compete a complete design of experiments. The future installation of *in-situ* reflectometry sensors will also allow us to do many experiments with small perturbations that will conform with the linear assumptions implicit in the PCA analysis.

**Future Directions:** In this section we outline the major directions that the research will follow in the coming year. First, the plasma chamber component of the reactor is being redesigned and will be rebuilt to address several issues. Foremost is the goal to create additional optical access, which will enable both for laser interferometry measurements of the growing film and spatially resolved OES. In the redesign we are also looking at changes that will lead to improved uniformity and better control of substrate bias/ion energy.

A number of materials issues remain to be addressed. High growth rates and optical transparency have been established, critical concerns include improving the degree of crystallinity and the electrical properties. Additional areas include deposition on flexible substrates and expanding to other TCO materials.

Work will clearly continue using the PCA approach to dissect the OES measurements. A similar approach will be used to address the interpretation of laser reflectometry. Ultimately we will combine measurements of material properties, OES spectra, and laser interferometry to develop process models that will enhance the further development of TCO PECVD.

**Conclusions:** We have described are experimental system and analytical approach to PECVD of TCO films. Promising results include demonstration of high rate, low temperature deposition of smooth, transparent films. An optical emission spectrometer has been purchased, installed and is being employed to investigate the process. Work is underway using statistical analysis techniques (PCA, DOE) to develop quantitative models that relate processing conditions, diagnostic measures, and film properties.

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