DC Reactive Sputtering Of Transparent Conducting Indium Tin Oxide

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Abstract -- A DC reactive sputtering process for thin transparent conducting films of indium tin oxide was developed at RIT for a variety of uses. Thin films were sputtered in a CVC-601 batch sputterer from a 200mm indium-tin target in an argon/oxygen ambient onto 3-inch silicon wafers and 2x3-inch glass slides. An experiment utilizing a central composite design with variables of oxygen flow, argon flow, and DC power was performed.

As-sputtered films exhibited characteristics of either high resistivity and high transmittance due to an abundance of oxygen in the film, or low resistivity and low transmittance due to an oxygen deficiency in the film. Process repeatability was poor. Films with a variety of characteristics were annealed on a hotplate in an air ambient. Low resistivity, low transmittance films tended to increase transmittance during the anneal, coupled with a further decrease in resistivity. The sputtering process with anneal yielded films of resistivity $1.75*10^{-3}$ Ω-cm, average transmission of 76.0 percent over the visible spectrum (400-700 nm), background corrected for a glass substrate, for a thickness of 2000 Å, index of refraction near 2.13, and a deposition rate greater than 150 Å/min.

I. INTRODUCTION

Thin films of indium tin oxide (ITO), also known as tin-doped indium, exhibit a high degree of conductivity while also providing high transmission for electromagnetic radiation in the visible spectrum. The combination of these two properties make ITO a valuable material for optoelectronic device fabrication such as transparent electrodes for display technologies, electrostatic discharge layers, solar cells, heat mirrors, de-icing elements, transparent gates for electronic imagers, and electrochromic devices.[1]

ITO is gaining popularity over other conducting transparent materials such as tin oxide, indium oxide, zinc oxide, cadmium oxide and cadmium tin oxide due to its lower resistivity and better etchability in both dry and wet etch processes.[2] The film conducts due to its non-stoichiometric nature. Tin in the indium oxide acts as a cationic dopant, substituting for the cation indium and releasing free carriers, which are also donated by oxygen vacancies in the film. These carriers provide the film's conductive properties.[3] ITO can be readily etched in a variety of wet chemicals, including dilute HF or HI, as well as dry plasma processes using HI or CH_4.

Deposition techniques for ITO include DC and RF sputtering, evaporation, chemical vapor deposition, and a number of high temperature deposition techniques involving spray or dip processing. Sputtering was chosen for this investigation due to the ability to carefully control the stoichiometry of the film by controlling film deposition rate combined with the amount of oxygen in the sputter chamber.

II. EXPERIMENTAL

Films were deposited using a CVC-601 batch sputterer with a 200mm indium-tin (90/10%) magnetron target onto 2x3-inch glass slides and 3-inch silicon wafers. Base pressure was less than $2*10^{-6}$ Torr. Target-to-substrate distance was 6 cm. Figures 1 and 2 illustrate the experimental setup.

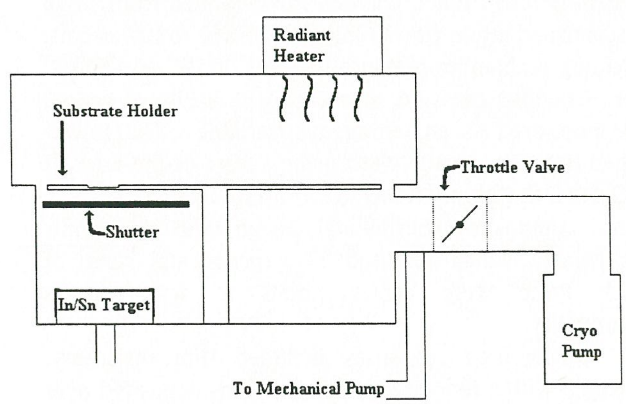

Figure 1: CVC-601 Schematic, Side View

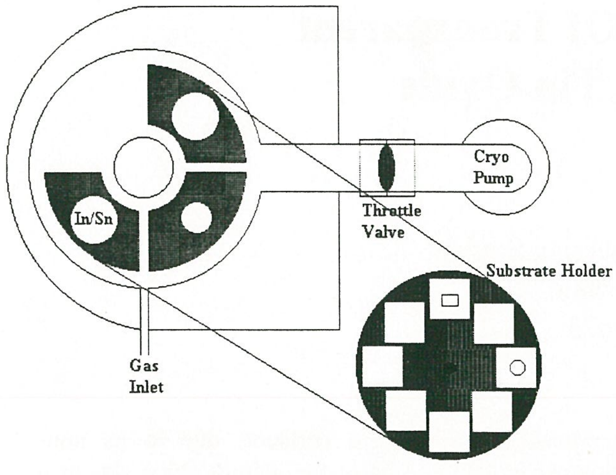

Figure 2: CVC-601 Schematic, Top View

Films were sputtered in an oxygen/argon ambient. Samples were not rotated throughout the chamber, but were held stationary over the target. Chamber pressure could not be controlled directly, so gas flows were varied, keeping the throttle valve in the fully closed position during sputtering. Prior to each experimental run, the target was cleaned by pre-sputtering in a pure argon ambient at a power of 300W for a minimum of five minutes, continuing until the resulting potential and current stabilized. Target cleaning was followed by a pre-sputter using the gas flows and power the current experiment called for in order to condition the target. This step continued a minimum of five minutes, also continuing until the resulting potential and current stabilized.

An initial screening experiment was run to determine a process window for further optimization. Gas flow settings for argon and oxygen were varied to provide a window encompassing both transparent, insulating, oxygen-rich films and opaque, conducting, oxygen-deficient films. Oxygen flows ranged from 11 to 17 sccms and argon flows ranged from 240 to 280 sccms, providing a chamber pressure between $1*10^{-3}$ and $5*10^{-3}$ Torr. Chamber pressure, measured with a Piranhi gauge, was monitored as an extraneous variable. DC Power ranged from 200 to 300 watts using a state-of-the-art ENI RPG-50 DC Plasma Generator. From these settings a central composite experimental design with star points was created which required 17 experimental runs, of which three were center points to test process repeatability.

Measured responses included film resistivity, measured with a four-point probe on films deposited over glass slides. Refractive index was obtained from ellipsometric measurements of ITO films on bare silicon. Film thickness was measured by ellipsometry along with fringe interference counting. Transmission was measured at g-line by irradiating a photoradiometer from a GCA g-line (436 nm) stepper with a plain glass slide and the ITO-coated glass slide and comparing the detected irradiance. Spectral plots were obtained from a Perkin-Elmer UV/VIS Lambda 11 Spectrometer, background corrected for air.

Following characterization of as-sputtered films, selected films were annealed on a hot plate in air at 250 °C for 10 minutes. The films were then re-measured to provide post-anneal characteristics.

III. RESULTS AND DISCUSSION

The original designed experiment showed poor repeatability from run to run as well as low statistical correlation. This is attributed largely to variations in chamber conditions given the same experimental parameters. For a constant gas flow rate of 240 sccms argon and 11 sccms oxygen, pressure readings varied from 3.6 mTorr to 7 mTorr, a 51 percent variation in a parameter critical to the process. Possible explanations for this variation include using the mass flow controls near their maximum and minimum flow specifications leading to inaccurate gas flows, vacuum leaks, mass flow controller failure, Piranhi gauge failure, or throttle valve variations.

Several general trends in film performance were evident with adequate statistical significance, however. Figures 3 and 4 show how films of low oxygen content tended to display metallic properties of low resistivity and low optical transmittance, much like the alloyed target from which they were sputtered, while films of high oxygen content tended to display glass-like properties, exhibiting high optical transmittance and high electrical resistivity.

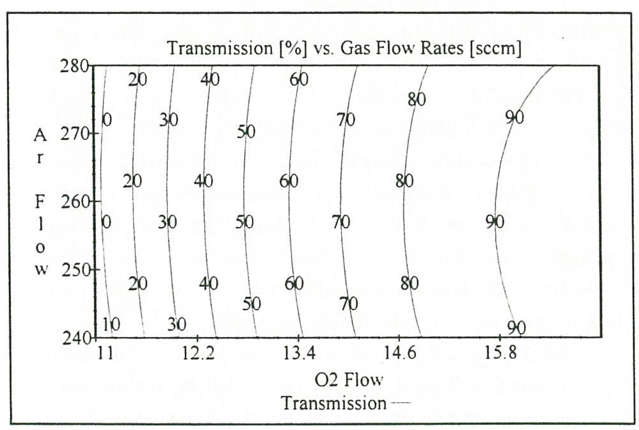

Figure 3: Transmission as a Function of Gas Flows

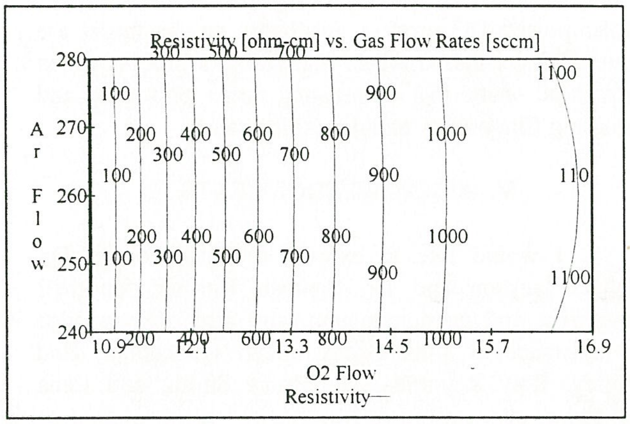

Figure 4: Resistivity as a Function of Gas Flows

The measured responses index of refraction and deposition rate each showed a slight correlation with gas flow rates at a DC power setting of 300W, depicted in figures 5 and 6. Statistical significance of these responses at other power settings for these variables was minimal.

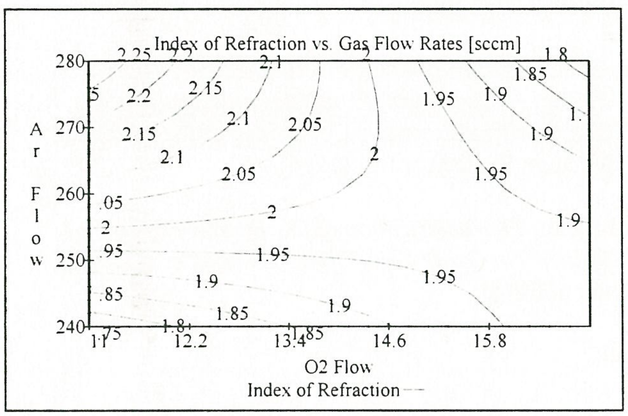

Figure 5: Index of Refraction as a Function of Gas Flows at 300W DC Power

As expected, index of refraction tends to vary over the selected process window between 1.9 and 2.1, typical values for index of refraction measurements for ITO films. Deposition rate tends to increase as oxygen flow decreases, indicating that at higher oxygen flows a dielectric layer of oxygen-rich indium tin oxide is forming a capacitive layer over the indium/tin target, reducing the sputtering rate. Lower oxygen flows tend to produce more conductive films and therefore a higher deposition rate is realized. A trend toward higher deposition rates with a lower argon flow is also visible and may be attributed to a higher sputter pressure causing increased scattering of the deposited material due to an increase in collisions.[4]

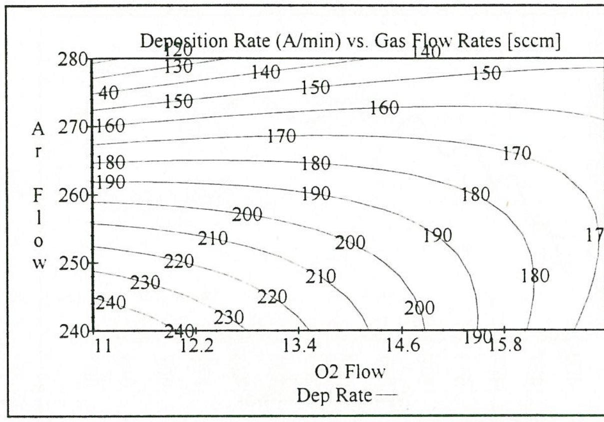

Figure 6: Deposition Rate as a Function of Gas Flows at 300W DC Power

Annealing of the oxygen-rich glass films in air showed no significant effects on either transmission or resistivity. Annealing of the oxygen-deficient metallic films showed a profound shift upward in the transmission characteristics of the films over the visible wavelengths as shown in Figures 7 and 8 combined with a further decrease in resistivity. The increase in transmission is partially attributed to further incorporation of oxygen into the film combined with an increase in film crystallinity. The increase in conductivity is attributed to an increase in carrier mobility, also a result of improved crystallization.[5]

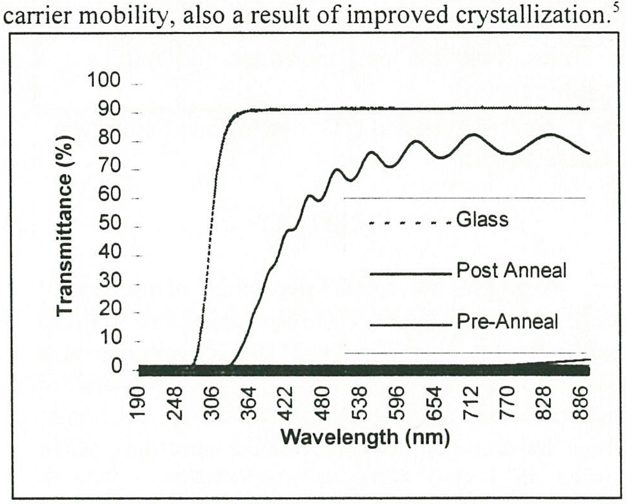

Figure 7: Transmission vs. Wavelength for Selected Films

By sputter depositing films in the oxygen-deficient state and annealing them in air for 10 minutes at 250 °C, thin ITO films of high visible transmittance and low resistivity with an index of refraction near 2.1 and deposition rates of greater than 150 Å/min were repeatably obtained. Typical characteristics for a film deposited as described are presented in table 1.

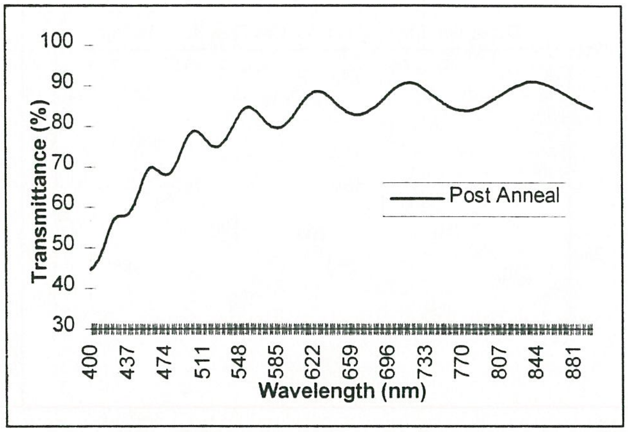

Figure 8: Transmission vs. Wavelength for Annealed ITO Film, Corrected for Glass Substrate

Parameter	Value
Argon flow (sccm)	240
Oxygen flow (sccm)	11
DC Power (W)	300
Anneal temperature (C)	250
Anneal time (min.)	10
Film thickness (Angstroms)	2011
Sheet resistance (ohms/sq)	87
Resistivity (ohm-cm)	0.00175
Index of refraction	2.128
Avg. Trans. [400-700 nm], corrected for glass substrate (%)	76.0

Table 1: Typical Annealed ITO Film Process Parameters and Characteristics

IV. SUMMARY

A process for sputter deposition of transparent conducting thin films of ITO was developed. Films demonstrated resistivity in the $2*10^{-3}$ Ω-cm range at a thickness of approximately 2000 Å with an index of refraction near 2.1 and deposition rates over 150 Å/min. Average transmission over the visible spectrum, when deposited on a glass slide, approached 70%. Due to equipment variability, an anneal step is required for satisfactory film performance.

Further investigation of CVC-601 gas flow and pressure control is recommended, as is optimization of the anneal process. Future work may also include development of an asymmetric bipolar pulsed DC reactive sputtering process utilizing the capabilities of the state-of-the-art ENI RPG-50 DC Plasma Generator currently installed on the CVC-601 equipment. This technology allows for high quality, high rate reactive deposition from metallic targets. Using an asymmetric bipolar pulsed DC process, insulators on the target are sputtered faster than the base material in a process called preferential sputtering, eliminating target poisoning and increasing film quality and deposition rate.[6]

V. ACKNOWLEDGEMENTS

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VI. REFERENCES

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