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TECHNIQUE FOR SPUTTERING CONDUCTIVE

In_2O_3 - SnO_2 TRANSPARENT FILMS

Jay B. Snelling

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Technique for Sputtering Conductive $\text{In}_2\text{O}_3 - \text{SnO}_2$ Transparent Films*

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ABSTRACT

The technique and apparatus used for sputtering $\text{In}_2\text{O}_3 - \text{SnO}_2$ (ITO) films are discussed. Films typically exhibiting bulk resistivities in the range of $2 - 4 \times 10^{-4} \Omega\text{.cm}$ and sheet resistivities as low as $0.5 \Omega/\text{square}$ have been obtained. The visible light transmission of the films is very high and adherence to a variety of optically polished substrates is excellent. Sputtered ITO films do not require postdeposition annealing or vacuum reduction treatment.

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Introduction

Highly conductive $\text{In}_2\text{O}_3 - \text{SnO}_2$ (ITO) transparent film electrodes have proven useful for a variety of device applications.^[1-12] Ferroelectric electro-optic PLZT ceramic devices, liquid crystal devices, transparent substrate heaters, and photovoltaic solar cells all require electrodes with the temperature stability, adherence, electrical conductivity and transparency provided by ITO films. Reported methods for depositing ITO films include evaporation, chemical spraying, sputtering (DC and RF), and reactive sputtering techniques.^[13-18] This report describes an updated version of a previously reported procedure and apparatus for DC sputtering films from In_2O_3 targets doped with 9 mole % SnO_2 .^[13] The sputtering apparatus described can be used for RF as well as DC sputtering applications.^[12]

Since comprehensive studies of the electrical and optical properties of DC sputtered ITO exist in the literature,^[10,14] they will not be expounded upon in this report. However, the specific procedure and apparatus for sputtering high quality ITO films which do not require post-deposition anneals or vacuum reduction, as well as general observations on sputtering this material, will be presented in considerable detail. Visible light transmission of the ITO films without anti-reflection coatings typically falls between 80 and 90%, depending on sputtering parameters and film thickness. Sheet resistivities of $0.5 \Omega/\text{square}$ have been obtained. Vigorous scrubbing, mechanical polishing, or ultra-sonic cleaning with most solvents does not affect film adherence, electrical or optical properties.

System Description

The belljar chamber layout for sputtering ITO films is shown in detail in Figure 1. The sputtering target is attached to a water-cooled backing plate, and the sample to be coated is placed on a substrate heater. The belljar is evacuated, back filled with argon gas, and 4.5 KV is applied to the target to ionize the gas mixture in the chamber. A sputtering rate of approximately 1 $\mu\text{m}/\text{hour}$ is achieved with a plasma power of 1000 watts. A detailed description of the sputtering equipment and procedure follows.

Equipment

Depositing high conductivity transparent ITO films depends greatly on the composition and pressing parameters of the sputtering target. For optimum results, the In_2O_3 should be doped with approximately 9 mole % SnO_2 . Dense targets should be specified as they require less pre-oxidation treatment before sputtering than porous targets.¹⁴ Films sputtered from dense targets scatter less light and have higher conductivity than films deposited from porous targets. A point to point resistance check across the diameter of a 12.7 cm dense In_2O_3 - 9 mole % SnO_2 target should indicate approximately 0.2 ohms. Target color varies somewhat depending on the manufacturer but generally ITO targets are light gray or light green in appearance. Manufacturers include the Materials Research Corp. (Route 303, Orangeburg, New York) and the Haselden Company (Box 1436, San Jose, California).

The entire target fixture, shown in Fig. 1, is machined from aluminum and is designed for use with a 12.7 cm diameter target. Water tight sealing between the top cover and the target backing plate is accomplished by a 1/8 inch diameter viton "O" ring.

The necessary mechanical, thermal, and electrical bonding between the backing plate and the target is provided by #3025 silver epoxy manufactured by Allied Products Corporation. The entire target assembly is electrically isolated from the belljar top plate by a Teflon ring. Vacuum sealing between the target assembly, Teflon ring, and belljar top plate is accomplished by two 1/8 inch diameter viton "O" rings. DC power is provided by a Bendix SDC-100 sputtering supply. The stainless steel shutter, located directly above the substrate heater, is controlled by a rotary feedthrough.

The substrate heater assembly consists of two stainless steel heater plate clamps, a 0.635 cm thick by 15 cm square quartz plate electroded on one side with a conductive ITO film, four ceramic standoffs, and four stainless steel heater supports. Gold wires are placed between the ITO coated heater plate and the plate clamps to insure excellent electrical contact between the two. Quartz plate heater shields are used during deposition to prevent excessive ITO buildup on the top side of the heater assembly. Power for the heater is supplied by a variac-controlled 60 Hz isolation transformer. Using an isolation transformer for the heater drive permits the substrate to be DC biased or floated with respect to ground. When in operation, the transformer output voltage is applied between the two heater plate clamps causing current flow through the ITO film electrode. The heater assembly and sample substrate are brought to the desired temperature by controlling the ITO heater film current. Using an ITO film for the heater current carrier allows transparent substrates to be visually monitored from below as well as above while the deposition is taking place. ITO film heaters

have been operated for hundreds of hours in the 200°C to 450°C range without failure. Heater temperatures are monitored by a thermocouple wedged into a small hole located in the bottom center of the heater plate. Heat sensitive substrates require cooling during the sputtering process. Circulating water through a substrate holder consisting of a target backing plate assembly mounted in an upside down position inside the chamber provide substrate cooling when needed.

Stainless steel gas inlet tubes are located near the plasma area. When sputtering, gas flow is directed over the substrate via the aluminum throughput guide which has a gas exit channel located opposite the gas inlet tube in the chamber. Pirani and thermocouple gauges monitor chamber pressure and a thermocouple gauge in the foreline as well as an ion gauge above the diffusion pump provide readings under the gate valve. Use of brass, zinc, silicon grease, and other potential contaminants are avoided in the sputtering chamber.

Figure 2 illustrates the gas flow for the system. Two gas supplies are used, typically argon and oxygen. Oxygen is used for pre-oxidizing the target before sputtering with argon. Matheson Gas Products valves select which gas bottle supplies the system and Granville Phillips leak valves control the chamber gas flow rate. By simultaneously adjusting the two leak valves, a controlled mixture of oxygen and argon can be obtained. Both bottle regulators are set at 15 psi. The CVC manual gate valve is used to control chamber pressure during the sputtering run. All gas tubing is 1/4 inch diameter 316 stainless steel. A 2500 liter/second CVC diffusion pump charged with Dow Corning 705 silicon pump fluid is used.

Procedure

Although sputtering parameters vary somewhat with changes in targets and substrate composition, a general procedure for sputtering ITO is outlined in this section. Some of the more common problems associated with sputtering ITO as well as a summary of observations covering the sputtering technique will be covered in a later section of this report.

Figure 3 illustrates the procedure and sputtering parameters followed for depositing ITO on most ceramic, glass, or quartz substrates. Samples to be coated are scrubbed with a tooth brush in a solution of Joy dishwashing detergent and tap water. After scrubbing, samples are rinsed with tap water and immediately flushed in methyl alcohol then blown dry with filtered air. When PLZT ceramics are to be included in the run, they are annealed in air at 600°C for 20 minutes after cleaning with alcohol.

Samples are placed on the substrate heater and the unused heater area is covered with glass slides. The slides provide deposition monitor samples as well as prevent unnecessary ITO buildup on the heater shields. During the system pumpdown, the target water and substrate heater (if used) are turned on so both temperatures will stabilize before sputtering. Target cooling water temperature is typically 10°C. The power required to maintain a given substrate temperature drops as the run progresses because of the heat generated by the plasma. For most depositions, the heat generated by the sputtering plasma is sufficient to generate film resistivities in the $2 \text{ to } 4 \times 10^{-4} \Omega\text{cm}$ range. Substrate temperatures will stabilize at 450°C with a 1000 watt plasma and a 6.5 cm target to substrate

spacing. The use of additional substrate heat is, therefore, required only when the ultimate in film conductivity is needed.

For depositions requiring more than 1 hour of sputtering, a target pre-oxidation treatment is normally necessary to prevent the formation of reduced films that are dark and opaque. Target pre-oxidation is accomplished by flushing the chamber and sputtering in pure oxygen with a S.S. shutter shielding the substrates from the plasma area. Initially the system is pumped down to 5×10^{-6} torr. After pumpdown, the gate valve is partially closed, and oxygen gas is passed through the system. The oxygen variable leak valve and chamber gate valve are adjusted simultaneously to achieve the desired chamber pressure and gas throughput. Chamber pressure oxygen levels vary between 14 and 16 microns and throughput levels typically fall between .01 and .15 torr liters/second. Thermo-couple gage foreline pressure readings can be used as an indication of the system throughput. After the chamber is flushed, parameters are allowed to stabilize for approximately 20 minutes before striking the 800 to 1000 watt plasma. Sputtering in oxygen is continued for 20 to 30 minutes before removing plasma power and turning off the oxygen leak valve. This pre-oxidation of the target will permit sputtering in argon for 4 to 5 hours without severe target or film reduction.

Sputtering on the substrates is normally conducted with pure argon. Using a mixture of oxygen and argon decreases the rate of target reduction but increases film resistivity, lowers the sputtering deposition rate, and increases the light scattered by the deposited films.

The argon leak valve and Hi-Vac gate valve are adjusted for a chamber pressure of approximately 9 microns. After stabilizing the chamber for approximately 2 minutes a plasma, concentrated between the target and shutter, is formed by applying 4.5 KV to the target assembly. Sputtering is continued for 3 minutes before opening the shutter, exposing the 6.5 cm gap that exists between the target and substrate. Plasma power in the 1000 watt range sputters approximately $1\mu\text{m}/\text{hour}$. Care must be taken throughout the run to maintain the plasma shape illustrated in Figure 4. Variations in chamber pressure alter the configuration of the plasma light and dark areas. When the chamber pressure is reduced, the plasma dark area moves closer to the substrate surface. This can alter the stoichiometry of the film, reduce the deposition rate, and cause arcing between the top surface of the substrate and the substrate holder. Chamber pressure is controlled throughout the run by adjusting the Hi-Vac valve.

After removing target power, the argon supply valve is turned off and the substrates allowed to cool for 20 minutes before back-filling the chamber.

General Observations

1. Increasing target density will:
 - a. Reduce target pre-oxidation requirements.
 - b. Reduce rate of target reduction during run thus permitting sputtering runs of longer duration at higher power levels.
 - c. Reduce film resistivity.
 - d. Reduce light scattering of deposited film.
2. Increasing substrate temperature will:

- a. Increase chances of substrate damage.
 - b. Reduce film resistivity.
 - c. Reduce light scattering of deposited film.
3. Increasing chamber throughput will:
- a. Increase deposition rate.
 - b. Increase reduction rate of the target and film.
 - c. Reduce film resistivity.
4. Increasing plasma power will:
- a. Increase chances of discoloring PLZT ceramic substrates.
 - b. Increase deposition rate.
 - c. Increase rate of target reduction.
 - d. Reduce light scattering of deposited films.
 - e. Reduce film resistivity.
5. Increasing chamber pressure will:
- a. Increase rate of target reduction.

Results

Films sputtered from In_2O_3 - 9 Mole % SnO_2 targets exhibit high electrical conductivity and excellent optical transmission, and adhere well to a variety of substrates. Samples for checking resistivity are made by brushing silver paint electrodes 1" apart over an ITO film deposited on a 1" wide substrate. Sheet resistivity in ohms/square is measured in the plane between the silver painted electrodes. Film thickness is measured with a Sloan Dektak. Bulk resistivity is determined by multiplying sheet resistivity in ohms/square times the film thickness in cm. Resistivity values between 2 and $4 \times 10^{-4} \Omega\text{cm}$ are obtained routinely without the use of a substrate heater.

Oxalic acid will etch ITO without damaging the surface of PLZT ceramic substrates. Fine-line ITO pattern definition is achieved by depositing ITO over a substrate coated with a highly defined thin film copper pattern.^[19] The copper pattern shields the substrate where ITO is not required. Removal of the copper/ITO layer is accomplished by immersion in ferric chloride solution. Electrical connection to the films can be made by thermocompression bonding gold wires directly to the ITO films.

Figure 5 illustrates the transparency of a 195 μm thick In_2O_3 -9 m% SnO_2 film deposited over a Fisher brand #12-552 glass slide. Figures 6 and 7 illustrate the light transmittance and reflectance versus wavelengths of the ITO slide pictured in Fig. 5. Anti-reflection coatings of MgF_2 deposited over ITO films will render a substantial increase in visible light transmission.²⁰

Conclusions

A detailed description of the procedure and apparatus for sputtering ITO has been described. The apparatus described has been used for a variety of DC, RF and reactive sputtering applications. ITO films have found application in light valves (both liquid crystal and ferroelectric), substrate heaters, solar cells, PLZT ceramic devices including Ferpac, Cerampic, Fericon, Nuclear Flash-Blindness Goggles, and the photoferroelectric (PFE) device.

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Figure 1. Belljar Chamber Layout

Figure 2. Sputtering Gas Network

RUN NO. 80 DATE 12/14/76 TARGET In₂O₃ - 9 m% SnO₂

Substrates: 4 plain glass slides

Substrate Prep: Washed w/Joy detergent, water rinse, alcohol rinse,
blow dry.

Pre-Pumpdown Target Prep: None

Target to Substrate Distance: 6.5 cm

Time	Procedure
9:50	Rough Down Fill nitrogen trap - turn on target water
10:00	Open Hi-Vac Gate Valve
10:10	Chamber Pressure: 5×10^{-6} torr Open oxygen gas valve, adjust variable leak and gate valve. Allow system to flush and stabilize.
10:30	Apply DC Target Power and Strike Plasma W/Shutter Closed
10:55	Remove Target Power ~ Pre-Oxidation Time = 25 min. Turn off oxygen gas valve. Open argon gas valve, adjust variable leak and gate valve.
10:57	Apply DC Target Power and Strike Plasma W/Shutter Closed
11:00	Open Shutter ~ Adjust Plasma Power
1:00	Close Shutter ~ Total Hours Sputtering <u>2</u> Turn off: DC plasma power - water - pirani and thermo-couple gauge - argon supply.
1:20	Close Hi-Vac Gate Valve and Backfill.

FIGURE 3

At Start of RunAt End of RunTarget Oxidation

Heater Voltage	N/A	
Heater Current	N/A	
Target H ₂ O Temp	10°C	10°C
Chamber Pressure (Oxygen)	15μ	15μ
Foreline Pressure (Oxygen)	20μ	18μ
Oxygen Granville Phillips Leak Valve Setting	118	118
DC Pre-Oxidation Target Volt	2700	2700
DC Pre-Oxidation Target Current	375 ma	375 ma

Deposition

Chamber Pressure (Argon)	9μ	9.8μ
Foreline Pressure (Argon)	32μ	16μ
Argon Granville Phillips Leak Valve Setting	145	145
Gate Valve Handle Position
DC Target Voltage	4500	4500
DC Target Current	225 ma	225 ma
DC Plasma Power	1000 w	1000 w
Temperature on Surface	170°C (After Pre-Oxidation W/Shutter Closed)	450°C

Results

Film Thickness 1.95 μm
ITO Conductivity Test Area 1 square inch
Test Electrodes..... Dupont Conductive Silver Composition
4817.
Sheet Resistivity 1.5 Ω/□
Bulk Resistivity 2.93 x 10⁻⁴ Ω.cm

FIGURE 3 (Continued)

Figure 4. Sputtering Plasma Configuration

Lower slide — clear glass

Upper slide — 2 μ thick In₂O₃—9m% SnO₂ film

Figure 5

Figure 7. Reflectance Versus Wavelength for 1.95 μm thick ITO Film over Glass

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