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Highly Conductive, Transparent Films of Sputtered $In_{2-x}Sn_xO_{3-y}$

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ABSTRACT

Highly conductive, transparent films of $In_{2-x}Sn_xO_{3-y}$ have been deposited by d-c diode sputtering with Ar, O_2, N_2, Xe, and O_2-Ar mixtures. Sputtering targets with different In_2O_3/SnO_2 ratios were utilized and the best results were obtained with pure Ar or Xe gas and targets containing 9-13 mole per cent (m/o) SnO_2. The lowest film resistivity achieved was 1.77×10^{-4} ohm-cm, but routine films had resistivity values of about 3×10^{-4} ohm-cm. The use of a very low sputtering gas throughput (10^{-2}-10^{-1} Torr liter/sec) was found to be necessary to develop films with a slight oxygen deficiency. Targets differing in density (porosity) differ in their susceptibility to reduction so that sputtering conditions depend on target density. The films have excellent adherence and will tolerate cleaning, heating, polishing, and bonding without failure. They may be etched in heated acids with standard photoresist techniques used to define electrode geometry. Exposure of the films to temperatures of 500°C in air will cause an approximate factor of 3 increase in resistance at room temperature. Sputtered films with sheet resistance of 1.6 ohms/square, 73% light transmission, and 14% reflection at 500 nm have been obtained. Suitable antireflection coated films of 5-7 ohms/square possessing over 97% light transmission appear feasible.

We wish to describe deposition techniques for and film properties of $In_{2-x}Sn_xO_{3-y}$ (ITO), a substitutional alloy oxide system with oxygen vacancies. Because of their low visible light attenuation, high electrical conductivity, stability, and good adherence sputter deposited films of ITO are expected to find wide application in electrooptic device technology.

Transparent, conductive films have generally been obtained by vapor deposition of thin metal films or by use of vapor reacted films of Sb-doped SnO_2 (1). Recently, characteristics of films of In_2O_3 (2, 3), Sn incorporated in In_2O_3 (4, 5), SnO_2 (3, 6), and Sb incorporated in SnO_2 (7), deposited by sputtering have been described.

In the sputtered pure oxides the reported resistivity at room temperature is approximately 10^{-2} ohm-cm after vacuum or other reducing, annealing treatment. Unless severe reduction has taken place, the oxide films display a high light transmission in the visible. Incorporation of donors such as Sb in SnO_2 and Sn in In_2O_3 yields higher conductivity without the optical absorption caused by excessive reduction. Vossen (5) has recently reported the deposition of films of ITO by rf sputtering using targets of 20 m/o SnO_2:In_2O_3. Resistivity values of 6.25×10^{-4} ohm-cm and optical properties similar to those reported here were obtained.

The films described here have been utilized in display devices such as ferroelectric ceramic light valves (8), liquid crystal light valves (9), and electrooptic polarization switches (10).

Sputtering Procedure

Some attempts were made to deposit In_2O_3 films by d-c diode, reactive sputtering of In and In-Sn alloys with mixtures of Ar-O_2. However, these films were deposited at very low rates with excessive substrate heating and the films had to be reduced by subsequent heat-treatment in nitrogen. Much more satisfactory films were achieved directly by d-c sputtering from In_2O_3 and In_2O_3-SnO_2, hot-pressed ceramic targets.[1] Three target sizes were utilized, 4.45 cm, 12.7 cm, and 22.8 cm diameters with most of the films described here sputtered from the 12.7 cm targets. A potential difference of 4-5 kV was used with an approximate current density of 1 mA/cm² for the small targets and 0.5 mA/cm² for the large targets. The target-to-substrate spacing varied from 5 to 7.5 cm. A thermocouple gauge was used to indicate chamber pressure and 20×10^{-3} Torr was the average pressure indicated during film deposition. Both the target and substrate holder were water-cooled. The substrates were borosilicate glass slides, Corning 7059 glass slides or vitreous silica slides. No attempt was made to thermally lock the substrates to the water-cooled holder.

The best films of ITO are obtained with a controlled throughput of gas. A 4 in. oil diffusion pump equipped with a liquid nitrogen trap was used to pump on the chamber, an 18 in. glass cylinder of either 20 or 50 liter volume. Most of the films to be discussed here were deposited without liquid N_2 in the trap since early in the investigation film properties did not appear to be dependent on cooling the trap. The chamber was equipped with an aluminum shutter that was placed between the target and substrate during pumpdown and predeposition sputtering. Initially, the chamber was pumped to 10^{-6} Torr and then the pumping system was throttled to maintain the admitted sputtering gas at approximately 20×10^{-3} Torr. This usually corresponded to a very low gas throughput

Key words: transparent electrode indium-tin oxide, sputtered sheet conductors.

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[1] Targets were obtained from two sources: (i) Haselden Company, San Jose, California (this company supplied the In_2O_3 target and the high density 9 m/o SnO_2:In_2O_3 targets), and (ii) Materials Research Corporation, Orangeburg, New York (this company supplied all other targets).

rate of $\sim 10^{-2}$ Torr liter/sec but many films were deposited at throughput rates of $\sim 10^{-1}$ Torr liter/sec.

The sputtering gases used were O_2, N_2, Ar, Xe, and gas mixtures such as Ar-O_2, and O_2-N_2. No purification of the gases was attempted. Generally, the best film properties were obtained with pure Ar or pure Xe, however, the cost of using Xe may outweigh its advantage of higher deposition rate than Ar. Details of the influence of the sputtering gas will be considered in the discussion of film properties.

Initially in the investigation only porous targets were used and a target conditioning procedure was followed when pure inert gases were to be used to deposit test films. The procedure consisted of sputtering with a gas mixture of 80% O_2 and 20% Ar for as long as 1.5 hr, subsequently, sputtering could be carried out using Ar or Xe. After such an oxidizing treatment the porous target could be operated for more than 6 hr of accumulated sputtering time with pure Ar at low throughput rates with no apparent film deterioration. Prolonged sputtering in a pure inert gas resulted in films with a dark appearance showing that excessive reduction had occurred. With Ar or Xe the porous target would slowly acquire a dark appearance which was ascribed to a reduction of the surface. The darkening disappeared after sputtering with the O_2-Ar mixture.

Later in the investigation deposition procedures were modified so that porous targets could be used, without the O_2-Ar preoxidation. The procedure consisted of sputtering with Ar only and to begin film deposition on the substrates after only 4-10 min of sputtering with the shutter between target and substrate. Without the O_2-Ar oxidation apparently sufficient O_2 was adsorbed from the laboratory atmosphere when the system was open, to permit film deposition for 30 min.

The dense targets were used in a similar manner with pure Ar except that predeposition sputtering with the shutter in place was of 3-5 min duration and actual single deposition times could exceed 2 hr duration.

Deposition rates of ~ 1 μm/hr were routinely obtained with Ar. The highest rates (2.5 μm/hr) were obtained with Xe and the lowest rates (~ 0.5 μm/hr) with O_2 and the O_2-N_2 mixtures.

Physical Properties of the Films

Film structure.—The structure of bulk In_2O_3 is bcc (11). X-ray diffraction by the ITO films deposited during this investigation revealed a similar structure. A strong fiber texture was also detected with the [111] direction normal to the substrate. This preferred alignment of the [111] direction has been reported for pure In_2O_3 films (3) deposited by sputtering. However, Vossen (5) has reported a [100] direction normal to the substrate for ITO. The different orientation may be due to differences in deposition parameters such as substrate temperature.

The preferred orientation of these films may be better appreciated by studying the scanning electron micrographs made of two representative samples. In Fig. 1, a film approximately 2 μm thick deposited by sputtering with an Ar-O_2 mixture is shown at two magnifications, the apparent viewing angle is 45°. The lower magnification shows a uniform crystallite size for the sputtered layer but considerable surface roughness. At higher magnification, the projections appear as high as 0.5 μm and are about 0.3 μm wide. It should be noted that a film such as described here will scatter light and can supply enough friction that the film side of the substrate plate can be discerned by light rubbing with a finger.

A film approximately 1.3 μm thick deposited by sputtering with Ar is shown in Fig. 2 at the same magnifications as in Fig. 1. In the micrograph obtained at the lower magnification a uniform crystallite size is also observed for this film. At higher magnification, however, the crystallites of this film appeared to project only as high as 0.25 μm and are about 0.15 μm wide. The two films depicted in Fig. 1 and 2 also differed strongly in their light scattering properties with the film of Fig. 1 scattering more. In the visible region of the spectrum these films behave as dielectrics, and the increased light scattering is related to crystallite size and the height of projection.

Where necessary, adequate polishing has been effected by the use of either 0.05 or 0.3 μm grain size alumina and a soft cloth. To remove all scratches produced by the alumina grit the films have then been polished with a combination chemical-mechanical polish.[2] Films polished with this two-step process have appeared smooth when viewed in a scanning electron microscope.

One general observation should be noted: smaller crystallites with lower projections are obtained if higher power is used in the plasma (*e.g.*, 0.7 mA or greater per cm^2 of target at 5 kV). The ITO films described here have been deposited on thermally stable substrates which tolerate high plasma powers. However, more delicate substrates such as single-crystal, single-domain $BaTiO_3$ and thin ferroelectric ceramic plates have also been used. Slower deposition on these substrates results in slightly larger ITO crystallites with some increase in light scattering evident, especially when porous targets are used.

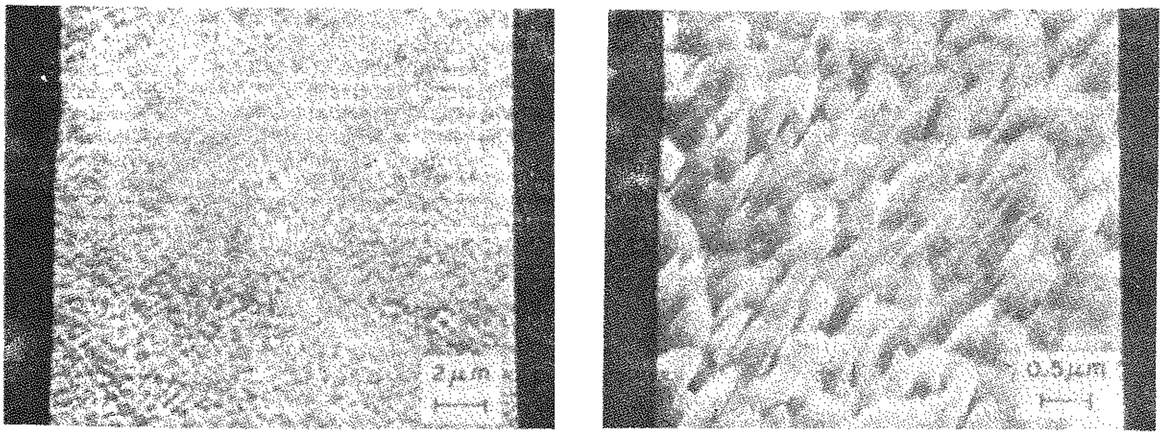

Fig. 1. Scanning electron micrographs of an $In_{2-x}Sn_xO_{3-y}$ film sputtered from an In_2O_3-9 m/o SnO_2 target with an Ar-O_2 gas mixture. The apparent viewing angle is 45°.

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[2] Syton HT-30, Monsanto Company, St. Louis, Missouri.

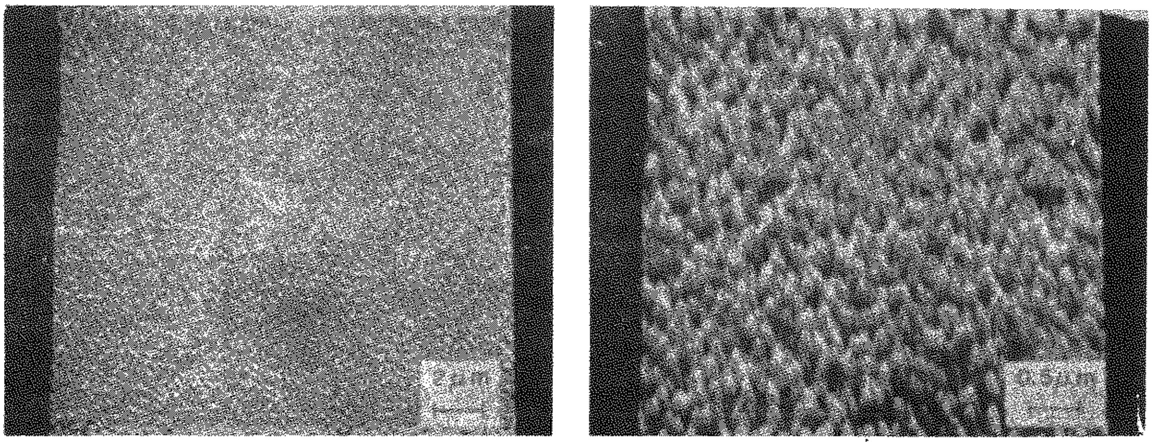

Fig. 2. Scanning electron micrographs of an $In_{2-x}Sn_xO_{3-y}$ film sputtered with Ar only from an In_2O_3-9 m/o SnO_2 target.

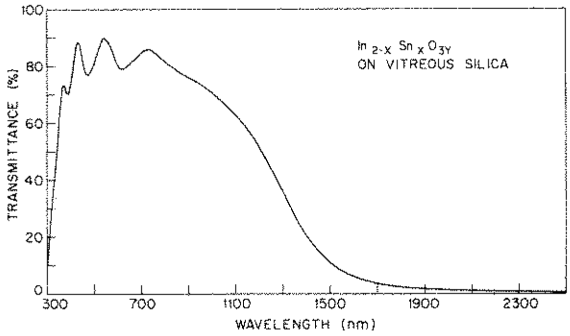

Fig. 3. Transmission characteristics from 300 to 2500 nm of an $In_{2-x}Sn_xO_{3-y}$ film on vitreous silica sputtered from an In_2O_3-9 m/o SnO_2 target.

Optical properties.—Films of ITO sputtered with Ar are highly transparent in the visible as may be seen in the plot of per cent transmission *vs.* wavelength shown in Fig. 3. The data plotted in Fig. 3 were obtained from a 0.5 μm thick film sputterd with Ar from an In_2O_3-9 m/o SnO_2 target. A vitreous silica substrate 0.5 mm thick was used. The structure of this film is similar to that depicted in Fig. 2. The reflection data for this film obtained at an angle of incidence of 14°, are shown for a similar spectral range in Fig. 4. Both the transmission and reflection data are accurate to within 1% and show channel spectrum fringes. Assuming negligible light absorption the reflectance maxima occurring near 480 and 620 nm yield refractive index values of 2.03 and 1.95, respectively, which are in good agreement with the index values measured by Müller (2) for pure In_2O_3 films. Transmission fringes have been used to obtain the values of film thickness, d, shown in Table I. Fringes near 500 nm in wavelength have been used with a refractive index of 2.0. From the data presented in Fig. 3 and 4, it is evident that the light absorbed or scattered by the ITO film is about 2% of the incident near 500 nm and that the major cause of transmission loss is reflection. It is clear that suitable antireflection coatings and substrates would permit in excess of 97% of the light to be transmitted within a given spectral region near 500 nm wavelength for such ITO films. The film described here has a sheet resistance of approximately 7 ohms/square. Films with similar optical characteristics have been deposited with even lower sheet resistances (approximately 5 ohms/square).

The achievement of the lowest possible resistivity is of practical significance in that it provides some freedom in selecting the film thickness while still maintaining satisfactorily low sheet resistance. For example, thin films have very broad interference transmission maxima and the use of low resistivity films permits useful sheet resistance to be obtained with maximum transmission (~90%) over a band of wavelengths.

A potentially useful characteristic of these sputtered films is their high reflectivity in the infrared. Transmission data obtained through film and substrate and reflection data are shown out to 15 μm in Fig. 5. The sample used for these measurements was the same as that used for obtaining the data of Fig. 3 and 4. For comparison the reflection data obtained for the vitreous silica substrate are also included in Fig. 5. The transmission is essentially zero over the entire infrared spectrum scanned. The infrared mirror properties are evident in the reflection data from the film surface since none of the characteristics of underlying vitreous silica reflection was detected.

Carrier concentration can be related by a simple theory to the wavelength corresponding to minimum reflectivity which occurs before the onset of constant high reflectivity at longer wavelengths (12). Calcula-

Table I.

Nominal target composition	Sputtering gas, conditions	R (ohm/square)	d (μm)	% T (at 500 nm)	ρ (10^{-4} ohm-cm)	Figure of merit (% T/R)
In_2O_3	Ar	26.8	0.500	77	13.4	2.87
In_2O_3 + 9 m/o SnO_2	O_2	285.0	0.262	81	74.5	0.284
In_2O_3 + 9 m/o SnO_2	O_2 (then reduced in N_2 at 300°C)	8.14	0.755	87	6.15	10.7
In_2O_3 + 9 m/o SnO_2	O_2/Ar (10/90)	12.2	1.02	83	12.5	6.80
In_2O_3 + 9 m/o SnO_2	N_2	69.4	0.223	86	15.5	1.24
In_2O_3 + 9 m/o SnO_2	Ar	3.23	0.840	70	2.72	21.7
In_2O_3 + 9 m/o SnO_2	Xe	3.21	0.770	79	2.47	24.6
In_2O_3 + 9 m/o SnO_2	Ar ($T > 500$°C substrate)	3.10	0.573	83	1.77	26.8
SnO_2	Ar	9×10^4	0.335	78	$3.02 \times 10^{+4}$	8.68×10^{-4}
SnO_2 + 7 m/o Sb_2O_3	Ar	550.0	0.990	64	540.0	0.116

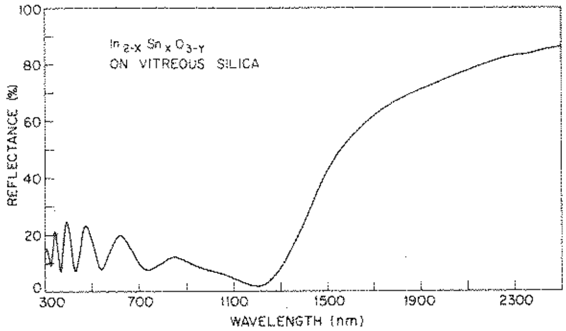

Fig. 4. Reflection characteristics from 300 to 2500 nm of an ITO film on vitreous silica sputtered from an In_2O_3-9 m/o SnO_2 target. The angle of incidence is 14°.

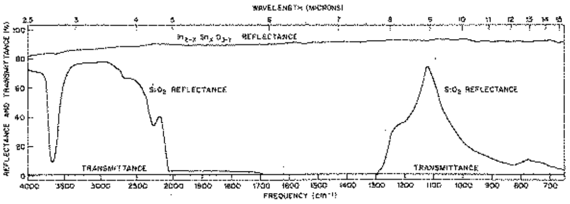

Fig. 5. Transmission and reflection for wavelengths from 2.5 to 15 μm of an ITO film on vitreous silica sputtered from an In_2O_3-9 m/o SnO_2 target. For comparison, a trace of the vitreous silica reflectance is also shown. The reflectance data were obtained at an angle of incidence of 14°.

tions based on the wavelength for this minimum reflectivity of an ITO film have yielded a carrier concentration that agreed well with a value based on Hall measurements. Since not all the ITO films of this investigation have been measured for both reflectance and transmittance, the transmission at 1.5 μm was chosen arbitrarily as a rough indication of carrier concentration. For empirical purposes of film evaluation, a roughly linear relation over a limited range of film resistivity and transmission at $\lambda = 1.5\ \mu m$ was found; 10% transmission for $\rho = 3.5 \times 10^{-4}$ ohm-cm and 77% transmission for $\rho = 13 \times 10^{-4}$ ohm-cm. The ITO films compared were sputter deposited from a single 9 m/o SnO_2:In_2O_3 target.

It was found that films deposited using gas mixtures, such as O_2-N_2, O_2-Ar, or O_2-N_2-Ar, scattered light much more than films deposited using a single gas. This scattering could be observed even in films less than 1 μm thick by placing the coated substrate plate edge-on in an intense light beam. The path of the light beam was clearly revealed by scattering. The scattering is related to the larger more protrudant crystallites formed more readily at the lower film deposition rates obtained with the gas mixtures.

Electrical properties.—The properties of a number of representative films are listed in Table I. The resistivity values were obtained from bridge measurements of sheet resistance and thickness values obtained from transmission channel spectra. These results are representative of resistivity values obtained directly from the sputtering process and involve no post-deposition annealing except where specifically indicated. A film approximately 1.5 μm thick deposited by sputtering with Ar and a 9 m/o SnO_2:In_2O_3 target was measured by the van der Pauw technique (13) and the parameters obtained were: resistivity, $\rho = 3 \times 10^{-4}$ ohm-cm; carrier density, $n = 8.6 \times 10^{20}$ cm^{-3}; Hall mobility, $\mu_H = 24$ cm^2/V-sec.

Since the goal is to obtain stable films with the lowest sheet resistance and highest optical transparency, a figure of merit for the films has been obtained by dividing per cent light transmitted at 500 nm (obtained from an average transmission curve drawn through the fringes over the range 450-550 nm) by the sheet resistance of the film. The figure of merit has units of [(per cent transmission)·(square/ohm)]. For brevity, these units will be dropped and the figure of merit will be cited as a number.

Factors Determining Film Characteristics

Target composition.—Incorporation of substitutional Sn into the In_2O_3 crystal structure yields donor centers; consequently, the Sn content of the target influences the resistivity of the sputtered films. Targets were obtained which ranged in composition from In_2O_3 to SnO_2 with a series of the mixed oxides varying from 2 to 23 m/o SnO_2 in In_2O_3.

In order to evaluate the influence of target composition on film properties, a standard procedure was developed for putting a target into service. The target to be tested was first oxidized in Ar-O_2 by sputtering for 30 min. Three distinct sputter depositions were then made using Ar only and resistivity values were obtained from the third deposition. Argon throughout was maintained at approximately 0.01 Torr liter/sec and all other parameters were maintained constant during the series of depositions.

Comparison of the film resistivities on the basis of nominal target composition yielded a discrepancy for films deposited using a target containing 7 m/o SnO_2. As a result, a count ratio of Sn/In obtained from x-ray fluorescence of the actual films was used for a relative Sn content value. Since all films were about 0.4 μm thick it was assumed that this analysis would be valid for a relative comparison. Some of the targets had a speckled appearance and some segregation of the oxides during the target fabrication could have occurred which would cause a discrepancy between the nominal target composition and actual film composition. Incorporation of impurities such as Sb, Pb, Ti, or Bi in a target could also increase the film resistivity (5) and cause some of the scatter in Fig. 6.

A plot of sputter deposited film resistivity *vs.* the x-ray measured Sn/In ratio is shown in Fig. 6 for targets containing from 0 to 23 m/o SnO_2. Small variations in oxygen vacancy content could account for the scatter of the points. Lowest resistivity films occur for Sn/In ratios from 0.18 to 0.28. These low resistivity films were deposited using targets containing 9, 11, and 13 m/o SnO_2. Vossen (5) obtained minimum resistivity from targets containing 20 m/o SnO_2 while the present investigation yielded minimum resistivity in films obtained from targets containing about 10 m/o SnO_2. The discrepancy in optimal target composition may be ascribed to differences in film deposition conditions.

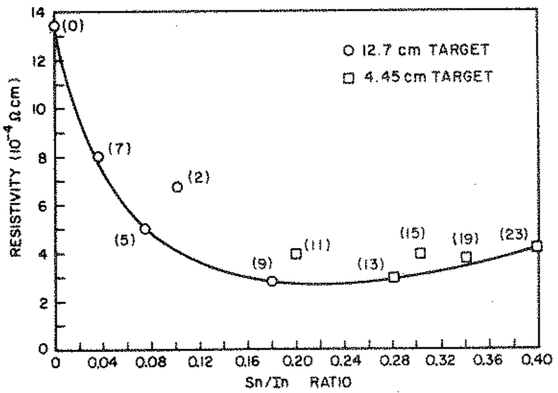

Fig. 6. Resistivity of In_2O_3 films containing varying amounts of SnO_2 plotted as a function of the Sn/In ratio measured by x-ray fluorescence. The numbers in parentheses indicate nominal SnO_2 m/o content of the targets used.

For the films, no significant light absorption was measured and only the reflection loss limited transmission. Not shown in Fig. 6 is the resistivity representative of the SnO_2 target. Under similar sputtering conditions, the SnO_2 target yielded films with ρ values of 0.1 ohm-cm to more than 10 ohm-cm.

One point concerning the data in Fig. 6 should also be made. Note that the effect of adding even an optimal amount of Sn to the In_2O_3 film is only to decrease the resistivity by an approximate factor of 4 from that obtained from a target containing only In_2O_3. The data shown in Table I and Fig. 6 indicate that film resistivity is more sensitive to the oxygen vacancy content than it is to the Sn content. For example, the ITO film deposited by sputtering with O_2 gas and a 9 m/o SnO_2:In_2O_3 target yielded a resistivity more than a factor of 5 greater than that of the film obtained by sputtering Ar and the In_2O_3 target. Further, sputtering with O_2 gas and a 9 m/o SnO_2:In_2O_3 target and then reducing the film in N_2 at 300°C yielded a resistivity only a factor of 2 greater than that obtained for films deposited from the same target using Ar. These results indicate that the same target may yield vastly different resistivities depending on the extent to which oxygen vacancies are incorporated into the deposited films.

For comparison, in addition to the films of SnO_{2-y}, films of $Sn_{1-x}Sb_xO_{2-y}$ were also deposited using the same sputtering parameters as this series of ITO films. The results for two representative films are included in Table I. The Sn-based films show higher resistivity and lower light transmission when deposited by the same methods as the ITO films. As in the case of ITO films, the resistivity of the Sn-based films was primarily dependent on oxygen deficiency. Further oxygen deficiency would have to be incorporated to lower the Sn-based film resistivity to values comparable to those for the In-based films.

Target density.—Most of the sputter deposition of ITO was carried but using targets with 70-80% of solid density. However, two targets with over 90% solid density were acquired and the films deposited with these targets differed from those obtained from the less dense targets. All the targets used in a comparison of films from porous and dense sources were nominal 9 m/o SnO_2:In_2O_3. Generally, less light scattering was observed in ITO films obtained from the dense targets. Also, single long duration sputter depositions resulted in dark (more reduced) films when porous targets were used and much lighter films when dense targets were used.

Porous targets.—A series of films was deposited using a 12.5 cm diameter target. Prior to each deposition the target was conditioned by sputtering with an Ar-O_2 mixture for 10 min. The duration of the film deposition for each test film was 30 min. Only Ar gas was admitted during each deposition period. Power was kept at 275W and spacing fixed at approximately 7 cm. The variable for the deposition series was Ar throughout.

The results of varying the Ar throughput and sputtering from a porous target are shown in Fig. 7-10. In Fig. 7, sheet resistance is plotted *vs.* throughput, and it may be seen that sheet resistance varied by more than a factor of 6 over the series. Film thickness varied by more than a factor of 6 over the series. Film thickness varied by more than a factor of 2 (Fig. 8) with higher rates of deposition occurring at greater throughput of Ar. Resistivity *vs.* throughput is shown in Fig. 9 where an approximate factor of 4 decrease is shown over the range of throughput. From Fig. 9, it may be seen that increasing the throughput of the Ar should yield lower film resistivity. For the sputtering conditions used in this series of depositions such increases of Ar throughput would also yield more light absorption. A figure of merit was calculated for each film but because transmission was limited only by reflection for this series of films, the figure of merit was simply the inverse of the sheet resistance values of Fig. 7.

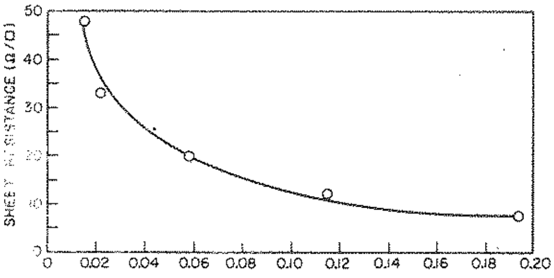

Fig. 7. Sheet resistance obtained after 30 min of sputtering vs. Ar throughput.

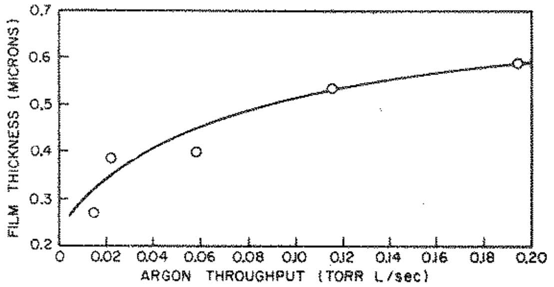

Fig. 8. Film thickness for a 30 min deposition vs. Ar throughput

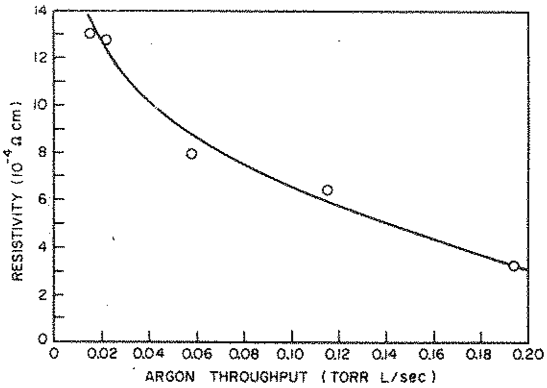

Fig. 9. Film resistivity obtained for a 30 min deposition as a function of Ar throughput.

The results obtained with a porous target and Ar throughput variation can be interpreted in terms of oxygen removal by an increasing flow of Ar through the sputtering chamber. At high throughput, the increased Ar flow may scatter more O_2 from the region between the target and substrate, thus contributing to lower resistivity in the deposited film. Similarly, with more Ar present between the target and substrate, the sputtering is more efficient and the rate of deposition will be increased. In the case of porous targets additional oxygen loss is attributed to poor heat transfer through the target which causes the surface of the porous target to operate at a higher effective temperature than a dense target. Some of these hypotheses have been investigated in experiments with porous and dense targets.

A 7059 slide with Au-Cr electrodes defining a clear square in the center of the slide was used to show that continual reduction occurs during deposition. Leads were attached to the metal electrodes and sheet resistance was measured at intervals during the deposition. A 22.5 cm diameter target was used and the throughput of Ar was 0.01 Torr liter/sec. The target was not conditioned by sputtering with Ar-O_2. Predeposition sputtering against a shutter was performed for 10 min. Resistance was measured after approximately 8 min of sputtering. From previous results the deposition rate of the film was assumed to be approximately constant. Resistance of the square film area was measured directly and the product of resistance times elapsed deposition time (Rt) was assumed to be proportional to the bulk resistivity of the film. A plot of Rt *vs.* t is shown in Fig. 10 where a decrease of over 75% in the value of the product occurs for the total deposition period. This is interpreted in terms of continuous outgassing of the target and an increase in the state of reduction of the film as sputtering proceeds. A break in the curve is due to readsorption of air when the system was vented to the atmosphere and operated for 30 sec with the shutter masking the substrate. The film layer deposited after the brief exposure to the atmosphere shows a different rate of change of resistivity as the target outgasses. For sputter depositions of 1 hr with this particular target the films were strongly reduced and darker in appearance than films deposited for the same total time with a brief interruption to introduce oxygen after 20 min of sputtering.

Dense targets.—Two dense targets 12.5 cm in diameter were acquired and similar ITO films were obtained from them.

A series of films was deposited using one of the dense targets. Argon throughput was approximately 0.1 Torr liter/sec and power in the discharge was 275W. Predeposition sputtering was performed for 10 min with the shutter in place, and Ar-O_2 sputtering was not used to condition the target. The films were deposited by continuous sputtering without interruption for readmission of air. From the linear relation of film thickness and deposition time (Fig. 11) the deposition rate appears to be constant. Sheet resistance *vs.* time is plotted in Fig. 12 and figure of merit *vs.* time in Fig. 13. From a plot of ln I/I_o *vs.* thickness, a value for the absorption constant at 500 nm was obtained, $\alpha \sim 10^3$ cm^{-1} (0.4 dB/μm).

The resistivity of these films varied from 4.3×10^{-4} to 2.9×10^{-4} ohm-cm for the shortest and longest sputtering times respectively. This change in resistivity is considerably less than the change in Rt (Fig. 10) displayed by the film obtained from a porous target and is attributed to a lower rate of oxygen loss by the dense target. From the assumption of constant resistivity of 3×10^{-4} ohm-cm and optical absorption of 10^3 cm^{-1}, a maximum figure of merit of 84 should be obtained in a film 7 μm thick from the dense target.

In summary, the differences that are observed between ITO films obtained by sputtering with Ar from dense or porous targets are: (*i*) Dense targets yield a smaller gradient in the state of reduction through the film thickness and hence a smaller gradient in resistivity. (*ii*) Dense targets do not appear to be as sensitive to Ar throughput. (*iii*) Single depositions resulting in thick ITO films without excessive light absorption are more easily performed with dense targets. (*iv*) ITO films obtained from porous targets tend to scatter light more than films obtained from dense targets.

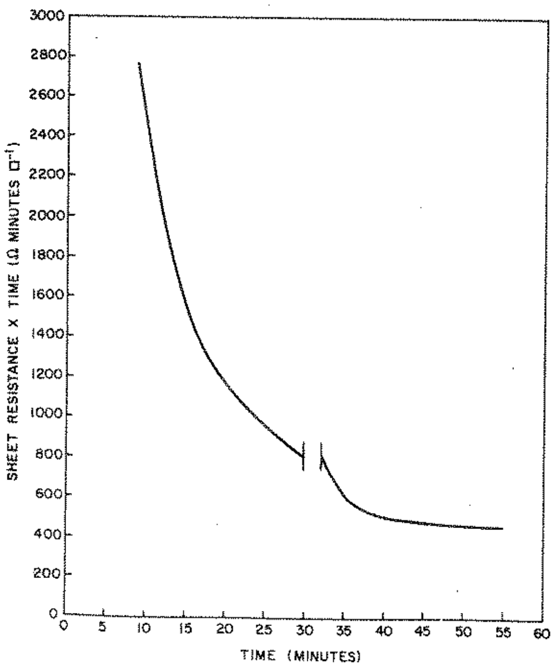

Fig. 10. Product of film sheet resistance times elapsed time *vs.* elapsed time. The break in the curve shows where sputtering was stopped, system vented, and 30 sec was spent sputtering against the shutter.

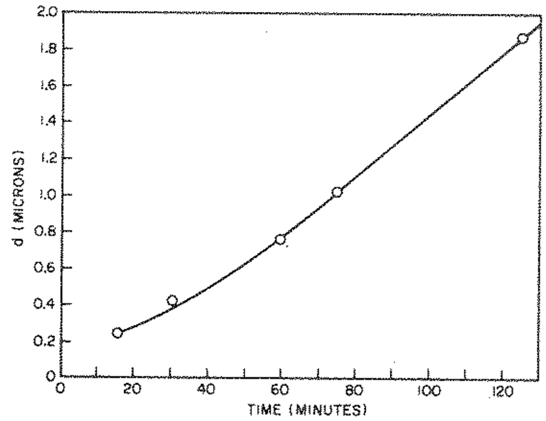

Fig. 11. Film thickness *vs.* sputtering time

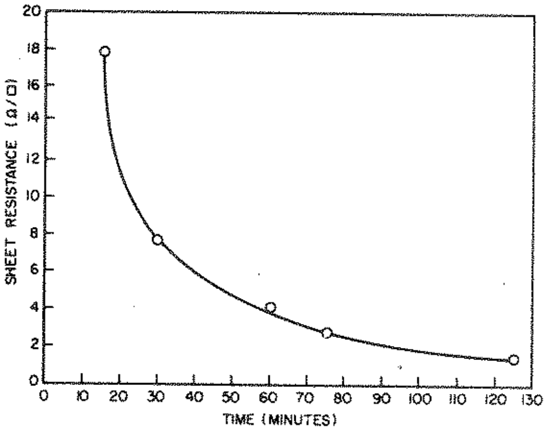

Fig. 12. Film sheet resistance *vs.* sputtering time

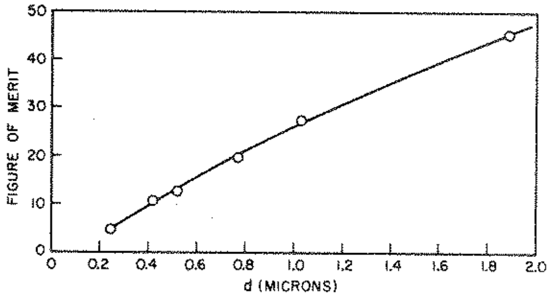

Fig. 13. Figure of merit of films *vs.* sputtering time

The gradient in resistivity through the film thickness may be minimized by increasing the predeposition sputtering with a shutter in place. However, the characteristics of a given target may require that different sputtering procedures be followed than those described for the porous and dense targets of this investigation.

Thermal effects (target and substrate).—Thermal effects are evident at both the substrate and the target. Preliminary results have shown that bonding a substrate to the water-cooled holder increases the film resistivity by more than a factor of 10^2. This higher resistance is attributed to a lower concentration of oxygen vacancies. Generally, the higher the substrate temperature, the lower the film resistivity. An example of a film deposited on a substrate above 500°C is given in Table I. A film resistivity of 1.77×10^{-4} ohm-cm was obtained. Normal substrate temperature was about 420°C during film deposition.

Target surface temperature effects have been varied by operating a porous target at the same power continuously and intermittently with a 50% duty cycle and an on time of 30 sec. The modulation was accomplished by on-off switching the d-c potential applied to the target. For the same total elapsed sputtering times the films deposited continuously had approximately half the resistivity of films deposited with the intermittent plasma. Both target and substrate temperatures are lower in intermittent operation of the plasma, and more oxygen will be retained by the target surface and more will be accepted by the growing film.

Applications

Films of ITO deposited by sputtering from 9 m/o SnO_2:In_2O_3 targets have been used for a variety of applications. The majority of films deposited on 7059 slides have been used as conductive substrates for sputter-deposited CdS films (14), allowing the CdS films to be tested through the ITO layer which acts as an ohmic contact. The ITO-CdS interface has exhibited excellent adherence and CdS films over 20 μm have been deposited without adherence failure. Many films have been deposited on light valve devices, such as the strain-biased ferroelectric ceramic (ferpic) (8), and the ITO has not suffered adherence failure even though strained to more than 10^{-3} in tension. In the same device, a layer of photoconductive CdS is coated with ITO and adherence failures at this surface have occurred only when the surface of the CdS has been contaminated with diffusion pump vapor. Some films have also been utilized in liquid crystal light valve devices. A variety of heater requirements have been satisfied, such as a hot stage for a microscope and a substrate heater for CdS film deposition. The substrate heaters have operated at temperatures as high as 350°C in a sputtering chamber with less than 5% change in the room temperature resistance. Substrate heaters of 3 ohm/square sheet resistance have operated at 250°C for over 300 hr in a sputtering chamber without change or failure. At room temperature, no measurable changes in sheet resistance have occurred in specimens exposed to the laboratory ambient for 2 years.

The ITO films described here would appear to be ideally suited to longitudinal electrooptic devices such as optical polarization switches used in digital light deflector systems. Low optical loss and a low resistivity for high switching speeds and minimal thermally induced refractive index gradients are obvious advantages.

For electrooptic device applications where transparent electrodes of a specific geometry are required, the difficulties associated with sputter-deposition through a mask may be avoided by etching. Various heated acids such as sulfuric, chromic, phosphoric, or mixtures of hydrochloric and acetic acids have been used. A most satisfactory etchant has been oxalic acid in 0.1 molar concentration, which at 50°C, etched ITO films through photoresist defined patterns (15). Pattern definition below 10 μm has been achieved.

Conclusions

Directly usable, highly conductive transparent films of ITO have been deposited by a d-c diode sputtering process. Use of pure Ar or Xe as the sputtering gas yields low resistivity material, but the use of only inert gas requires low throughput rates to avoid excessive reduction of the film and target. Lowest resistivity films have been obtained for In_2O_3 targets containing from 9 to 13 m/o of SnO_2. Target density is important in that more reduced films are obtained from a porous target under a given set of sputtering conditions and conditions must be optimized for an individual target. Generally, high density targets are superior. With suitable antireflection coatings, it is feasible to obtain films with sheet resistances of only a few ohms per square and optical transmission in excess of 95% in regions of the visible spectrum. Due to the excellent adherence and to the desirable optical and electrical properties of the ITO films, application has been found in the strain-biased ferpic, liquid crystal light valves, and as substrates for testing photoconductive films.

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