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Abstract: During the first six months, undoped, tin-doped and boron-doped indium oxide film samples (on fused silica substrates) have been prepared by spray pyrolysis. Evaluations have been made with various pieces of apparatus, some of which is undergoing development. This includes: electrical conductivity and Hall mobility measurements, optical transmission versus wavelength measurements, Brewster angle measurements at 633 nm. wavelength, and X-ray diffraction measurements. Mobilities for undoped and tin-doped samples are usually approximately $10 \text{ cm}^2 \text{ V}^{-1} \text{ sec}^{-1}$; the lattice constants for these same samples are slightly less than 10.1 Å; the optical absorption edge for the as-deposited samples is approximately 3.5 eV; and the refractive index at 633 nm. is approximately 2.0-2.1. For the few samples that have been prepared with boron doping, the lattice constant appears to decrease (and long range order disappears for heavy boron concentrations); the absorption edge moves to higher energies; and the refractive index (at 633 nm.) decreases. Two classical dielectric models have been invoked to explain the refractive index decrease; one model assumes an admixing of refractive indices of the component oxides, and the other model uses a modified additivity of the electronic polarizabilities of the component ions. The latter model yields predictions for the refractive index as a function of boron concentration which is in better agreement with experiment than that predicted by the former model. Consequently, it is tentatively suggested that boron is disordering the lattice while substituting for indium.

Introduction - The major goal of this research project is to determine the feasibility of predictably modifying the wavelength dependence of the optical constants of films of indium oxide by composition/structure changes, so that such films could be more practically employed for solar energy applications. In particular, for photothermal applications it is desirable to use such films either as combination infrared reflectors/solar spectrum antireflection coatings or possibly as selective absorbers. Also, for photovoltaic applications, it is desirable to use such films as combination solar spectrum antireflection/high dc electrical conductivity electrodes. For either application, photothermal or photovoltaic, a relatively low value of refractive index (n_{Solar}) at least at one film surface, (if the index is graded in the thickness direction), would be useful for achieving solar spectrum antireflection properties. Further, if the second film surface is in contact with either a selective absorber (e.g., silicon) or with a photovoltaic cell semiconductor, a relatively high refractive index for the indium oxide film at this second surface would be required; i.e., it would be valuable to achieve a graded index. Therefore, we are seeking to determine the extent to which n_{Solar} of indium oxide films can be raised or lowered by appropriate composition/structure changes. In addition, we seek to determine the extent to which the infrared and dc electrical conductivities are modified as n_{Solar} is altered.

For the first six months, the major focus has been to attempt to lower n_{Solar} by doping, with particular emphasis on doping with boron; and at the same time to improve upon the fabrication and evaluation techniques.

Description of First Six Months Efforts

Fabrication Apparatus:

1. Single Temperature Zone Spray Pyrolysis - except for minor repairs, our original hot-plate based system, with a compressed gas spray gun has been steadily used for the majority of sample fabrications, including that of doped samples, (in the temperature range: $400^{\circ}\text{C} \leq T \leq 650^{\circ}\text{C}$).
2. Two-Temperature Zone Spray Pyrolysis - A system consisting of an open quartz tube, placed in a two-temperature zones apparatus, has been assembled and tested. It has been used to fabricate a few samples, but the results have not been as satisfactory as with the hot-plate based system.
3. Sputtering - dc reactive sputtering of 2 samples was attempted in a conventional 6" oil diffusion pumped vacuum system (CVC-18). We are considering the purchase of used rf sputtering parts that would be compatible with the CVC-18 vacuum system.

Annealing - An electrically heated carbon hot stage has been fabricated for annealing in a second vacuum chamber into which forming gas can be introduced. Several anneals have been performed satisfactorily [and the usual increase in free charge carrier concentration has been observed in tin-doped oxide films - (ITO), as evidenced by a sharp decrease in transmission in the near infrared, (indicating that the plasma edge has moved to higher photon energies), and an increase in the electrical conductivity]. The annealing efforts are being delayed until we have more complete evaluations on most of the samples.

Sample Evaluations

1. Optical Constants $[n(\lambda), k(\lambda)]$ from Transmittance $[T(\lambda)]$ Measurements -

Much effort has been devoted to this evaluation technique. A classical oscillators model with adjustable parameters, including film thickness, is used in conjunction with an IBM Share least squares fitting program [1]; and when the model prediction for $T(\lambda)$ is close to $T(\lambda)$ obtained experimentally with a Cary 17 Spectrophotometer, the optical constants, $n(\lambda)$ and $k(\lambda)$, are obtained. This is a technique that was first reported by Verleur [1], and it has been successfully used by subsequent workers, including ourselves. However, we have been having two major difficulties in measuring the optical constants for our indium oxide films:

- a. We have had major problems with our original program, and consequently are reworking it.
- b. Our digital data acquisition system has failed; and in spite of a major trouble-shooting effort, we cannot locate the problem. Therefore, we are currently redesigning the apparatus. In the meantime, we can still record data by hand and punch it into the DECsystem-10 for the computer fit analysis.

2. Optical Constants at Discrete Wavelengths by Ellipsometry - Although we have been constructing an ellipsometer which could be used at a continuum of wavelengths, at various angles of incidence, etc., to expedite measurements, it has been decided to purchase the parts of a commercial unit (Rudolph Research RR 100). This should provide us with a technique for determining the optical constants at a single wavelength with a high degree of precision and confidence.

3. Brewster/Abelès Technique for Measurement of n - we have assembled a crude apparatus for obtaining n at 633 nm. using the Brewster/Abelès technique^[3]. This technique takes advantage of zero reflectivity for p-polarization (TM) when a lossless dielectric is irradiated at the Brewster angle, $\theta_B = \tan^{-1}(n)$. Because of reflection from the substrate (fused silica in our case) the technique employs a comparison reflection measurement between bare substrate and coated substrate; when the two are the same the Brewster angle of the film has been reached. Even with the present crude apparatus, we estimate that we can determine n to ca. ± 0.05 , and it has been used to measure n for several of our boron-doped samples. The system is currently undergoing major redesign, and we anticipate using it for determining k as well. Furthermore, we are computer studying the sensitivity of the apparatus for determining, if not the actual profile, at least whether or not an inhomogeneous refractive index profile exists. The central idea is to compare the reflectivity vs. angle in the vicinity of the Brewster angle with predicted values for uniform and nonuniform profiles [3]. We are also attempting the same computer analysis approach with $T(\lambda)$ data.
4. Waveguide Modes Coupling Technique for Measuring n and Thickness - Two polished ZnSe prisms have been obtained and one is being used to evaluate the technique recently reported by Wei and Westwood [4]. The principle of the technique is that normally a ray entering a side surface of a prism will be totally reflected from the prism's base and exit the other side surface of the prism. However, if an optical waveguide (thin film) is placed close (within a fraction of a wavelength) to the base of the prism, and if the ray is at a waveguide mode angle, the ray will couple to the waveguide and thus be absent from the rays which are otherwise exiting from the prism exit face. Thus, by irradiating the prism waveguide system with a cone of rays, there should be a series of dark lines at the exit of the prism, and by knowing the wavelength, the angles associated with the dark lines, the associated waveguide modes can be uniquely determined from which the refractive index and thickness can be computed. We are presently evaluating the technique.
5. Structure Measurements by X-Ray Diffraction - All our samples (undoped In_2O_3 and tin-doped In_2O_3), with the exception of the heavily boron-doped ones, show approximately the same lattice spacing ($\leq 10.10 \text{ \AA}$), with a predominant (400) peak. All films show the b.c.c. structure, and appear very similar to that reported by Fan et al.[5].

In the case of the heavily B-doped samples, no evidence of crystallinity appears. There is only a strengthening of a broad peak at ca. 22° , strongly suggesting that the boron leads to a destruction of long range order.

6. Composition Analyses - We are attempting to have composition analysis work done by AES, ESCA, etc., at either M.I.T. and/or General Telephone Laboratories. Scheduling difficulties have prevented us from doing this so far, but we do not anticipate any major problems with this effort.
7. Conductance/Mobility Evaluations - DC electrical conductance and Hall mobility have been routinely measured on samples as they are fabricated. Until the thicknesses are known more accurately, the electrical conductivity will not be known accurately. However, the room temperature dc conductivities for ca. 10% tin (atomic %, as estimated from starting solution concentrations), are approximately $10^1 - 10^2 (\Omega\text{cm})^{-1}$ for the annealed samples. For the few samples which have been annealed by heating in the presence of forming gas the conductivity increases by an order of magnitude.

The room temperature dc Hall mobilities are generally in the vicinity of $10 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$. Because of thermal effects; noise arising from contacts, etc., and because of possible grain boundary effects influencing the conductivity and mobility measurements, we have constructed a contactless microwave ($\approx 10 \text{ GHz}$) apparatus for measuring these two parameters. It is undergoing evaluations and calibrations.

8. Refractive Index Reduction by Boron Incorporation - Results and Models:

A. Results - To date this has been our major technical accomplishment. We have achieved significant refractive index reduction by incorporating boron into our starting spray solution. A Proponal solution of BF_3 was added to our normal InCl_3 solution. The resulting solution was spray deposited (in air) on fused silica substrates at approximately 625°C . For a large $[\text{B}]:[\text{In}]$ molar ratio (2.8:1) the refractive index at 633 nm. reduced from $n \approx 2.1$ for undoped In_2O_3 to $n \lesssim 1.7$ for the boron-doped case. The resistivity, however, increased markedly, to a value which was not measured. The absorption edge was determined from optical transmission measurements on a Cary 17. It changed from approximately 3.5 eV for undoped In_2O_3 to approximately 4.6 eV for the boron-doped case. Furthermore, there was a dramatic change in the X-ray diffraction pattern; all evidence of crystallinity disappeared for the $[\text{B}]:[\text{In}]$ ratio of 2.8:1. [e.g., we normally observe a strong (400) diffraction peak; and with modest boron doping (5-10%), (222) and (440) peaks appear; but when $\text{B}:\text{In} \approx 2.8:1$, there were no diffraction peaks, although there was an increase in a background peak in the vicinity of 22° , which we generally associate with the bare fused silica substrate.]

B. Models - Although our results are incomplete, we believe that most likely a B_2O_3 substructure forms which is disordering the In_2O_3 lattice; but we suggest that the boron is frequently locating on or near indium sites. The basis for this view is the comparison of two related classical models for the refractive index. In one model, Model A, we assume an admixing of the In_2O_3 and B_2O_3 . As we shall see that underestimates the amount of boron necessary to achieve the observed refractive index change. The other model, Model B, however, which assumes cation substitution, but also assumes a smaller local electric field at the indium sites than at the oxygen sites, is more successful in predicting the amount of boron required to lower the refractive index from 2.1 to 1.7.

Model A - Model A assumes a mixed phase situation. In particular, we use a modified Lorentz/Lorenz model for the refractive index [cf. reference 6 for a similar recent application of such a model]. This model is described by equation (1):

$$\frac{n^2 - 1}{n^2 + 2} = x \left(\frac{n_1^2 - 1}{n_1^2 + 2} \right) + (1 - x) \left(\frac{n_2^2 - 1}{n_2^2 + 2} \right) \quad (1)$$

where n = refractive index of composite system

n_1 = refractive index of $B_2O_3 \approx 1.46$

n_2 = refractive index of $In_2O_3 \approx 2.1$

x = fractional concentration of B_2O_3

$1 - x$ = fraction concentration of In_2O_3

For $n = 1.7$, this predicts that $x \approx .56$, as compared with the experimental value of .74, (as estimated from our starting solution concentrations; the actual film composition still needs to be determined, which we are presently attempting to have done - by Auger Electron Spectroscopy).

Model B - Model B is based upon the assumption of the additivity of the electron polarizabilities of the constituent ions for each unit cell, or molecule. The model is based on the Lorentz/Lorenz equation (2):

$$\frac{n^2 - 1}{n^2 + 2} = \frac{4\pi}{3} N\alpha, \text{ (cgs units)} \quad (2)$$

where n = refractive index,

N = number of molecules/volume,

and α = electronic polarizability of each molecule.

If there are two or more (e.g., m) different ions per molecule then we write:

$$N\alpha = \sum_{j=1}^m N_j \alpha_j, \quad (3)$$

where N_j = number of type j ions per volume,

and α_j = electronic polarizability of type j ion.

To apply Model B to the problem of estimating what dopant, (and in what concentration), should be used to modify n by a desired amount, not only must the electronic polarizabilities be known, but the relative strength of the exciting electromagnetic field at the particular ion site must be known. Furthermore, the model assumes an independence of the constituent ions; e.g., it neglects covalent bonding. This assumption of the additivity of polarizabilities has been questioned by others [7,8,9].

For In_2O_3 we adopt the additivity law, but we argue that the local field, at least in the cation (In) sites, cannot be the Lorentz/Lorenz field. This argument is based on the electrostatic field calculations made by deWit [10]. He found that the local field at 24 of the 32 indium sites (of the In_2O_3 unit cell) was approximately 37% of that at all the 48 oxygen sites; and that at the remaining 8 indium sites the field strength was less than 0.3% of that at the oxygen sites. Thus, on the average, the indium sites see a local field approximately 28% of that found at the oxygen sites. For our model we therefore write:

$$\begin{aligned} \alpha_{\text{In}_2\text{O}_3} &= (0.28) \times 2 \alpha_{\text{In}} + 3 \alpha_{\text{ox}} \\ &= 0.56 \alpha_{\text{In}} + 3 \alpha_{\text{ox}} \end{aligned} \quad (4)$$

where $\alpha_{\text{In}_2\text{O}_3}$ = electronic polarizability of the In_2O_3 molecule,

α_{In} = electronic polarizability of the indium ion,

and α_{ox} = electronic polarizability of the oxygen ion.

The published values for α_{ox} varies from 0.4 to $3.2(\text{\AA})^3$ [11]. Therefore, we have fixed $\alpha_{\text{In}} = 6.5 (\text{\AA})^3$ [9]. Using $n_{\text{In}_2\text{O}_3} = 2.1$, and $N_{\text{In}_2\text{O}_3} = \frac{1}{64.5} (\text{\AA})^{-3}$, (from Avagadro's number; $\rho_{\text{In}_2\text{O}_3} = 7.18 \text{ gm/cm}^3$; and the molecular weight of In_2O_3 , $M_{\text{In}_2\text{O}_3} = 278 \text{ gm/mole}$), we obtain $\alpha_{\text{In}_2\text{O}_3} = 8.16(\text{\AA})^3$. This yields: $\alpha_{\text{ox}} = [\alpha_{\text{In}_2\text{O}_3} - .56 \alpha_{\text{In}}]/3 = 1.5(\text{\AA})^3$ which is within the published range for α_{ox} [$0.4 - 3.2 (\text{\AA})^3$].

By substituting for a fraction, x , of the indium sites, an ion of electronic polarizability, α_D (D = dopant), this model predicts:

$$\left(\frac{3}{4\pi N}\right) \left(\frac{n^2 - 1}{n^2 + 2}\right)_{\text{Doped In}_2\text{O}_3} = 0.56 [x\alpha_D + (1 - x)\alpha_{\text{In}}] + 3\alpha_{\text{ox}} \quad (5)$$

The synthesis problem is to find x , given a desired n . Defining $R \triangleq [(n^2 - 1)/(n^2 + 2)] (3/4 \pi N)$, and solving (5) for x :

$$x = \frac{\alpha_{\text{In}} - (R - 3\alpha_{\text{ox}})/.56}{\alpha_{\text{In}} - \alpha_D} \quad (6)$$

For example, according to equation (6), to achieve $n = 1.7$, (or $R \approx 6.0$), requires, {for $\alpha_D = \alpha_{\text{Boron}} \approx 1.6(\text{\AA})^3$ [12]}, $x \approx 0.78$.

As pointed out above, by using a starting concentration of approximately $[B]/([B] + [\text{In}]) = x = 0.74$, we found that the doped In_2O_3 refractive index, $n \approx 1.7$. Thus we believe that Model B is more appropriate than Model A, or that the boron could be substituting for indium. To better confirm this view we are presently preparing a series of boron-doped samples from solutions with different boron concentrations, varying from 5% to 60%. These samples will be evaluated by measurements of: the absorption edges, the optical constants, X-ray structures, and the compositions, as we have been doing with our present samples of undoped and tin-doped indium oxide films.

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