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HIGH PERFORMANCE TRANSPARENT CONDUCTING FILMS OF CADMIUM INDATE

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HIGH PERFORMANCE TRANSPARENT CONDUCTING FILMS OF CADMIUM INDATE PREPARED BY RF SPUTTERING

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ABSTRACT

We are examining various spinel-structured thin films (e.g., Cd_2SnO_4, Zn_2SnO_4) to develop higher-quality transparent conducting oxides (TCO) than more conventional materials such as indium tin oxide. Here, we report on cadmium indate ($CdIn_2O_4$, CIO), which is another member of this family.

Thin films of CIO were deposited by radio-frequency (RF) magnetron sputtering, from an oxide target, onto borosilicate glass substrates. The variables included the substrate temperature, sputtering gas composition, and pressure. Film properties were measured before and after heat treatment. Characterization involved Hall effect measurements, optical and infrared spectrophotometry, X-ray diffraction, and atomic-force microscopy.

Film resistivities as low as $2.3 \times 10^{-4}\ \Omega$ cm were achieved for a film thickness of 0.55 μm. The transmittance was 90% in the visible region of the spectrum, without correction for substrate losses and without an anti-reflection coating. The plasma resonance occurred at longer wavelengths than for other materials and this, with a bandgap of approximately 3.1 eV, presents a wide window for optical transmittance. The highest mobility was 54 $cm^2\ V^{-1}\ s^{-1}$ and the highest carrier concentration was $7.5 \times 10^{20}\ cm^{-3}$.

INTRODUCTION

Transparent conducting oxides (TCOs) are an essential component of several important applications. These include photovoltaic panels, flat-panel displays, "smart" windows based on electrochromic phenomena, and heat-reflecting windows. In addition, there are smaller applications, including the coating of light-emitting diodes, the properties of which are greatly improved by the use of a TCO coating.

In each of these cases, there is a trend towards larger area devices, that is beginning to place excessive demands on the traditional TCOs such as tin oxide, indium tin oxide, and zinc oxide. As is very well known, the essential properties required of TCOs are high electrical conductance and a high optical transmittance. It can readily be demonstrated from elementary electromagnetic theory [1] that these are somewhat exclusive requirements, because the free electrons needed for a high conductance also lead to optical absorbance. However, traditional TCOs have demonstrated adequate properties until the recent introduction of larger-area devices (display panels are expected to be more than 8 square feet in area, and photovoltaic panels of this area are already being manufactured). Larger areas cause excessive parasitic losses, unless the series resistance introduced by the TCO can be reduced below the values typically achieved with traditional TCOs.

The minimum resistivity achieved in production for the traditional TCOs is about $5 \times 10^{-4}\ \Omega$ cm, and the sheet resistance is typically 10-20 Ω per square. To reduce the sheet resistance below this range, it is vital to reduce the resistivity: increasing the thickness is not viable because of problems of excessive optical absorption and the possibility of mechanical problems during processing. There appears to be little prospect of achieving lower resistivities with the materials mentioned above. Many papers have reported efforts to do so over the last forty years; however, no significant fundamental progress has been made towards reducing resistivity and absorbance.

The essential requirement for progress is the development of novel materials with well-understood properties. At the National Renewable Energy Laboratory (NREL), we have been performing both fundamental and applied research into ternary oxide structures, mainly based on the spinel structure. Among these, we have already reported on cadmium stannate (Cd_2SnO_4) [1], and we are presently developing other materials in the family. Even though the prerequisites of an industrially acceptable TCO include non-toxicity and plentiful elements, we are also interested in gaining a fundamental understanding of the new family of materials, in general, which is why

$CdIn_2O_4$ is included in our study. In addition, there are other applications are less cost-sensitive, and the same demanding criteria do not apply [2].

Cadmium indate, which conflicts with both of the above requirements, has been reported as having promising properties [3, 4]. Despite its toxicity and In content, it may have significant value in certain solar cells, that already contain a significant amount of Cd because of its excellent transmittance in the visible portion of the spectrum. In any event, it is also likely to reveal additional fundamental information, which may lead to a better understanding of the family of materials as a whole. In turn, this could lead to the desired practical result: namely, an improved, industrially acceptable, TCO.

SUMMARY OF MODELLING RESULTS

We have previously discussed the modelling of TCO films in detail [1], and only a summary of the approach and key results will be given here. The optical properties of materials can, to a first approximation, be described by the Lorentz oscillator model. This is a second-order differential equation in which there is a damping term (giving rise to absorption by the free electrons) and a restoring force (giving rise to a natural frequency of oscillation). The equation also contains the concentration of free electrons. Usually, one assumes that the restoring force is too small to be relevant, and a solution of the differential equation is obtained that involves only the damping term. The damping term is simply related to the mobility (strictly, the ac mobility) of the electrons. The solution gives the displacement of the electron as a function of time, which leads to its velocity and ac conductivity.

Maxwell's equation, relates the complex permittivity to the ac conductivity, and hence, to the electron concentration and mobility. The optical constants (the refractive index and the extinction coefficient) can then be obained from the complex permittivity. The reflectance and transmittance can then be calculated for a film of arbitrary thickness on an a substrate with known optical constants, using Fresnel's equations. Hence, electrically measurable quantities (the electron concentration and mobility) may be related to optically measurable quantities (the reflectance and transmittance). All the modelling data assume an effective mass of 0.1 times the free-electron mass, a high-frequency permittivity of 8, and a film thickness of 0.5 µm.

Figure 1 shows the shift of the plasma edge to shorter wavelengths as the carrier concentration is increased. The mobility is assumed to remain constant at 100 $cm^2 V^{-1} s^{-1}$. This is certainly not a reasonable expectation for the higher carrier concentrations, but it has been obtained for cadmium stannate at lower concentrations [5]. Note that the curves also steepen as the concentration is increased. This is because the parameter actually controlling the optical properties is the conductivity, rather than either the concentration or the mobility alone.

Figure 2 shows the free-carrier absorbance for the film described in Figure 1. The absorbance is obtained from conservation of energy (i.e., $A = 1 - R - T$), and it is very large for higher carrier concentrations, even though the mobility is maintained at 100 $cm^2 V^{-1} s^{-1}$. The height of the absorbance peak increases with carrier concentration simply because there are more oscillators to absorb energy at the resonance condition. The absorbance peak narrows with increasing carrier concentration because the conductivity increases, and this factor controls the selectivity of the filter and the long-wave reflectance.

In Figure 3, the reflectance is modelled with the mobility being treated parametrically and the carrier concentration being kept constant at 10^{20} cm^{-3}. Although the curves steepen with increasing mobility, and the long-wave reflectance increases significantly, the plasma wavelength is not influenced much.

The absorbance is shown modelled in Figure 4, again with the carrier concentration being kept constant at 10^{20} cm^{-3}, and the mobility being treated parametrically. In both figures 3 and 4, the upper limits of the mobility are unrealistically large. Such a high electron concentration would inevitably preclude mobilities of this magnitude. Nevertheless, the model makes the interesting point that the peak height and width both decrease with increasing mobility. If it is necessary to adjust the position of the plasma edge, then this must be done through the carrier concentration; the mobility having only a second order effect on the plasma wavelength.

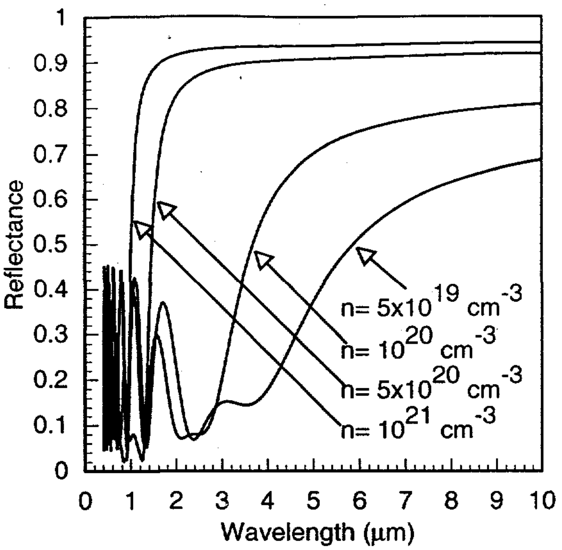

Figure 1: Variation of the reflectance of a film of 0.5 μm thickness, on a glass substrate, with wavelength. The mobility was taken as 100 $cm^2 V^{-1} s^{-1}$, and the carrier concentration was treated parametrically.

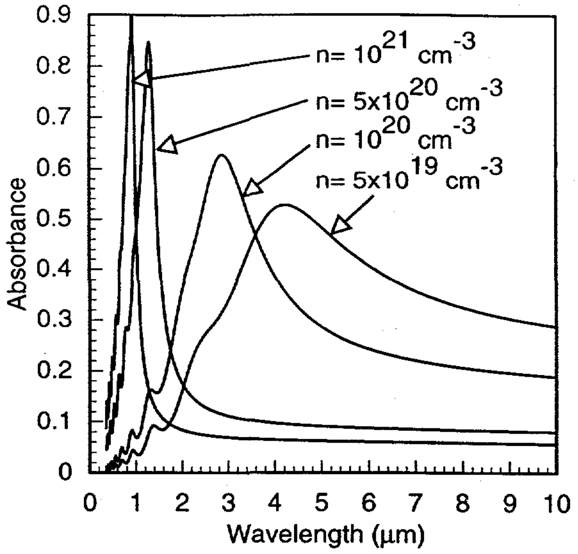

Figure 2: Variation of the absorbance of a film of 0.5 μm thickness, on a glass substrate, with wavelength. The mobility was taken as 100 $cm^2 V^{-1} s^{-1}$, and the carrier concentration was treated parametrically.

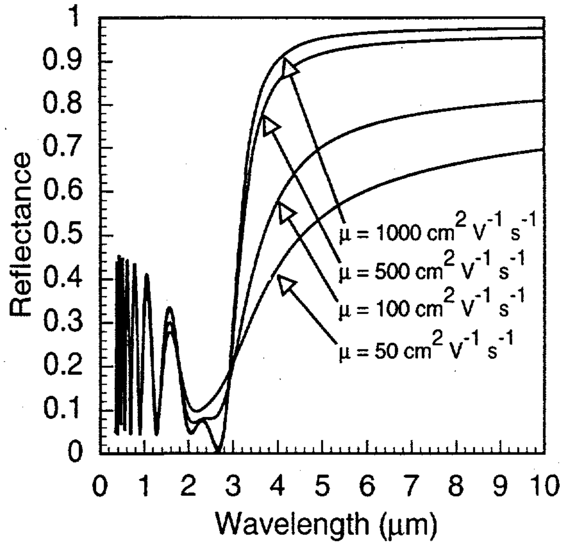

Figure 3: Variation of the reflectance of a film of 0.5 μm thickness, on a glass substrate, with wavelength. The carrier concentration was taken as 10^{20} cm^{-3}, and the mobility was treated parametrically.

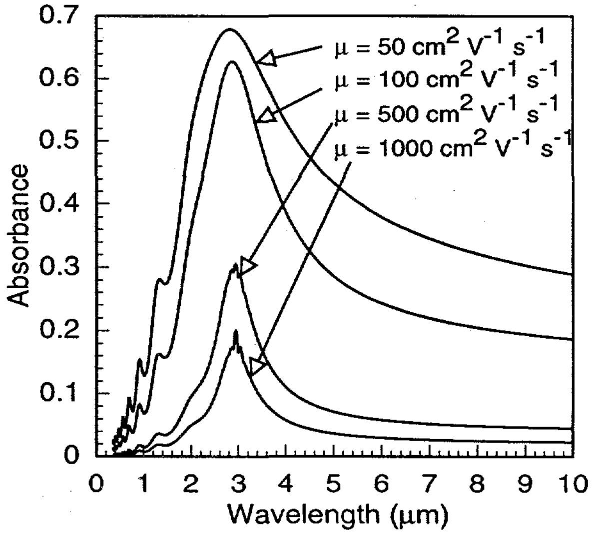

Figure 4: Variation of the absorbance of a film of 0.5 μm thickness, on a glass substrate, with wavelength. The carrier concentration was taken as 10^{20} cm^{-3}, and the mobility was treated parametrically.

The essential features to emerge from this treatment are:

I) The absorbance decreases with mobility but increases with carrier concentration;

ii) There is a transition from a high transmittance to a high reflectance in the near-i.r. region, at a wavelength known as the plasma wavelength (usually about 1-2 μm for a TCO);

iii) The steepness of the transition (important for some applications) increases with the mobility; this also leads to decreasing free-carrier absorbance in this region; and

iv) The long-wave reflectance increases with both mobility and carrier concentration

These results are summarized in Figures 1-4, which are part of a modelling study originally published in reference 1.

Many assumptions are involved in this elementary modelling, amongst which is that the relaxation time of the electrons under the very-high frequency electric field of the electromagnetic radiation is the same as that inferred from electrical measurement of the mobility. It is by no means apparent that this is realistic. We have also assumed that a single-oscillator model is adequate to describe the infra-red optical properties of the materials. More complicated models have been used [6] to account for the optical properties in the visible, but we have restricted our attention to the region in the immediate vicinity of and beyond the plasma wavelength.

We see from this summary that a high electron mobility is essential for optimum films, and it is this quality that attracted us originally to the spinel family of materials. The evidence seems to be that these have higher mobilities than conventional TCOs [5], which has been confirmed by a number of workers for cadmium stannate [1] and, to a lesser extent, for cadmium indate [3]. Possible reasons for this include a smaller effective mass, a longer relaxation time, or a combination of these. We are interested in determining which of these is more important, and then in using the knowledge to help design new, improved TCOs. The relaxation time may be controllable through the deposition parameters, while the effective mass may only be controlled though a careful choice of materials. Therefore, the research is aimed at both of these: optimization of the deposition parameters, and working with a variety of materials that appear to have the potential of having lower effective mass. We are also interested in determining the species responsible for the donor action, since it is almost certain (for these materials) that the usually-postulated oxygen vacancies cannot be the cause. This will be explained in further detail later.

EXPERIMENTAL

The films were deposited by RF sputtering in a CVC SC3000 system, and the targets consisted of equal molar fractions of CdO and In_2O_3. The purity of the powders was 99.5%. The powder mix was pre-reacted and the reacted material was hot-pressed into 2" diameter sputtering targets, supplied by Cerac Inc. The separation between the substrate and the target was maintained at 6 cm, and the r.f. power was 120 watts. This typically resulted in a deposition rate of 1 Å s^{-1}. We note that this rate is much lower than that for Cd_2SnO_4, using the same deposition conditions. The films were deposited in pure argon, pure oxygen, or argon/oxygen mixtures, and the composition of the mixture was controlled using two mass flow controllers, with an accuracy of ±0.1 sccm. The pressure of the sputtering gas was 20 mTorr ±0.1 mTorr. A range of deposition temperatures was used, and annealing (of some samples) was performed in pure argon up to a temperature of 680°C. The substrates were Corning glass 7059 or polished silicon wafers, and were cleaned using standard procedures.

The films were between 3000-6000 Å in thickness and they were characterized by Hall effect measurements, ultravioletvisible spectrophotometry up to 2 μm (using a Cary 2300), Fourier transform infrared spectrophotometry at longer wavelengths, X-ray diffraction using a Rigaku machine with Cu-Ka radiation, and atomic-force microscopy. We note that, in our work on cadmium stannate, we were also able to shed some light on the effect of the deposition and annealing parameters using Mossbauer spectroscopy [1]. This is not applicable to cadmium indate because indium does not have a significant Mossbauer signature.

RESULTS

Figure 5 shows the variation of the carrier concentration and mobility as a function of the gas composition in the sputtering system. The film was deposited at a substrate temperature of 200°C, and no annealing was used. The carrier concentration (and conductivity) peaked at an oxygen:argon flow-rate ratio of 0.3%, i.e., 3 parts per thousand. Note that the vacuum system had been pumped down to a base pressure of about 10^{-7} Torr, so it is reasonable to claim control to this level of accuracy. The carrier concentration is quite significantly influenced by the gas composition although this is not true of the mobility, which changes minimally. The carrier concentration passes through a maximum and the resistivity through a minimum. Hence, we should expect to see this reflected in the optical properties.

Figure 6 shows the optical properties of three films deposited as described for Figure 5, but for three different oxygen:argon ratios. This demonstrates that the position of the plasma edge could be adjusted by changing this ratio: an effect that is simply related to the carrier concentration, as described in the modelling results above. For ratios of 0.21, 0.03, and 0.47%, the plasma wavelengths were 2.21, 1.86, and 2.97 μm, respectively. The carrier concentration peaks at 0.3%, and this corresponds to the shortest plasma wavelength.

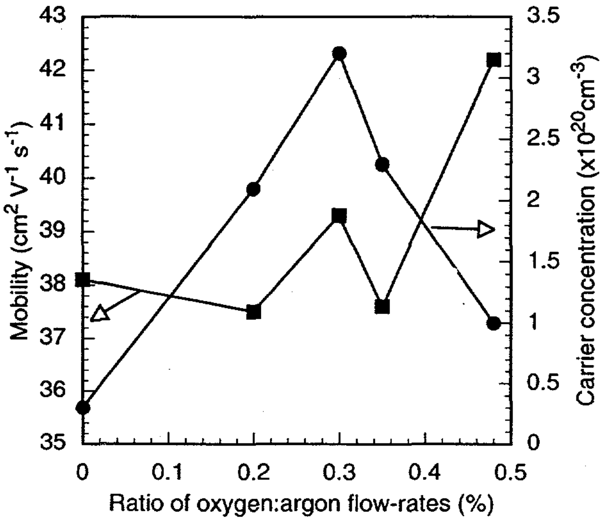

Figure 5: Variation of the mobility and carrier concentration for CIO films deposited at different oxygen: argon flow-rate ratios.

Figure 7 shows the X-ray diffraction spectra of films deposited at various substrate temperatures from room temperature up to 400°C. The atmosphere was a 0.3% mixture of oxygen:argon, established as giving the highest carrier concentration. The films were not annealed after deposition. The key feature is that the only evidence of any crystallinity was the (222) peak of In_2O_3, although amorphous material was presumably also present. The maximum mobility for these films was 45 cm^2 V^{-1} s^{-1} and the minimum resistivity was $4.5x10^{-4}$ Ω cm, both occuring for a substrate temperature of 250°C. Although the resistivity is quite low, significantly superior results have been obtained on more conventional materials systems. It is evident from these data that the spinel phase cannot be formed for films deposited in relatively low partial pressures of oxygen.

The data in Figure 8 are for a film deposited in pure oxygen, at room-temperature and then annealed in pure argon at progressively higher temperatures. This figure shows that these are

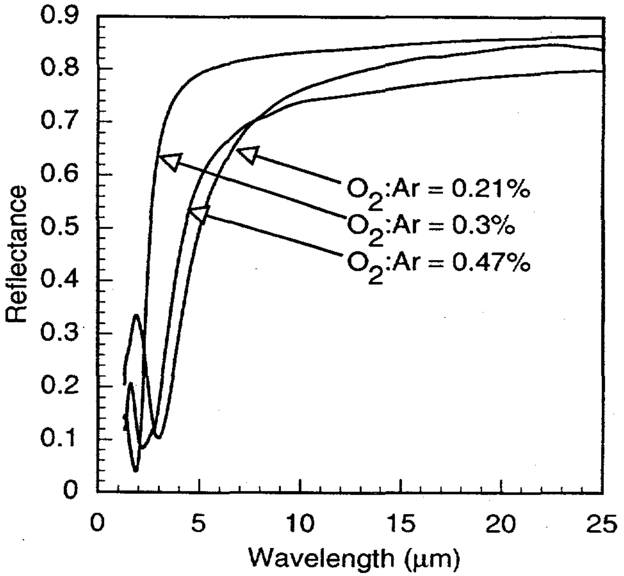

Figure 6: Variation of the specular reflectance of three films deposited at different oxygen:argon flow-rate rate ratios. The substrate was not heated and annealing was not used.

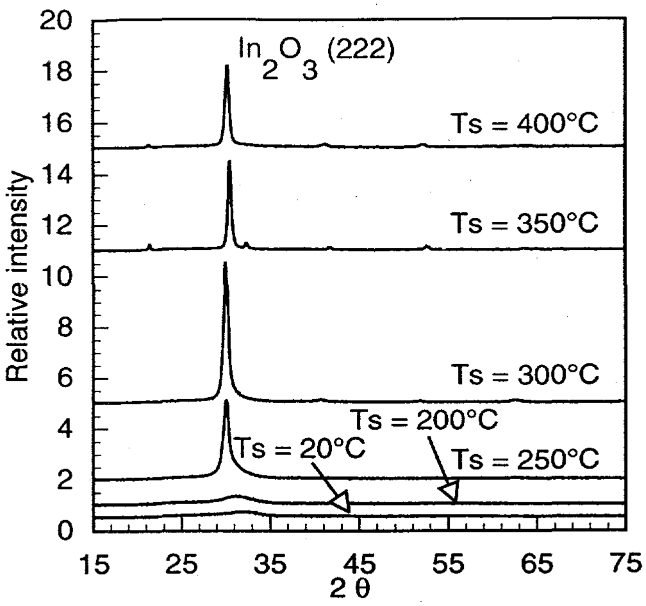

Figure 7: X-ray diffraction spectra of CIO films deposited in a 0.3% oxygen:argon mixture on substrates at various temperatures, and annealed in pure argon.

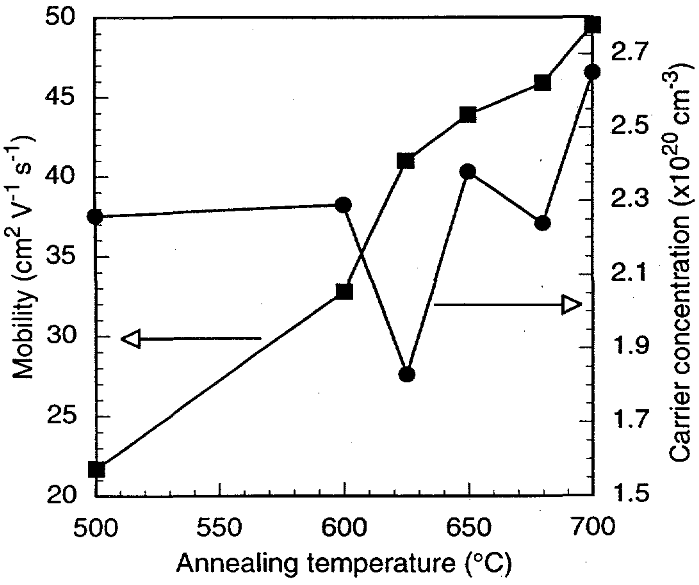

Figure 8: Variation of mobility and carrier concentration with annealing temperature. The films had been deposited in pure oxygen, on an unheated substrate, and then were annealed in pure argon.

superior deposition conditions. The mobility increases from 20 to 50 $cm^2 V^{-1} s^{-1}$, although there is a less pronounced effect on the carrier concentration. The highest mobility for any film deposited in this way was 54 $cm^2 V^{-1} s^{-1}$. Figure 9 shows the X-ray diffraction spectra of CIO films deposited in pure oxygen on substrates at various temperatures. They were not annealed after deposition, and only the (222) peak of In_2O_3 was observed.. Figure 10 illustrates the benefits of post-deposition annealing for films deposited in pure oxygen at several substrate temperatures. Annealing was performed in pure argon at 680°C, after which all the peaks associated with the spinel phase were observed. Hence, we conclude that post-deposition annealing is essential for the formation of the spinel phase.

The data shown in Figure 11 apply to another film deposited in pure oxygen on an unheated substrate, but annealed in CdS/Ar at 680°C, that had previously been shown to have beneficial effects on Cd_2SnO_4 films [1, 4]. The carrier concentration attained a value of nearly $6x10^{20} cm^{-3}$, the highest for any film fabricated being $7.5x10^{20} cm^{-3}$. Even with such a high carrier concentration, the mobility was relatively large, 30 $cm^2 V^{-1} s^{-1}$. The resistivity of this film was $2.3x10^{-4}$ Ω cm, the lowest to our knowledge attained for cadmium indate. The precise nature of the doping by the CdS is unknown, although it is tempting to speculate that it is due to interstitial cadmium. This, however, is an open issue.

Figure 12 shows the effect on the X-ray diffraction spectrum after the CdS/Ar annealing procedure. It is clear that there is extensive crystallization of the film, with all the peaks associated with the spinel phase being present.

This probably accounts for the large increase in mobility. An as-deposited film is also shown, and this is clearly amorphous. This was also suggested in Figure 9. It should also be mentioned that a simulation of the X-ray diffraction spectrum of cadmium indate has been performed. A comparison between the simulation and the actual data shows that we are justified in claiming that the CIO is single-phase spinel after annealing.

This has also been confirmed by reference to the JCPDS file.

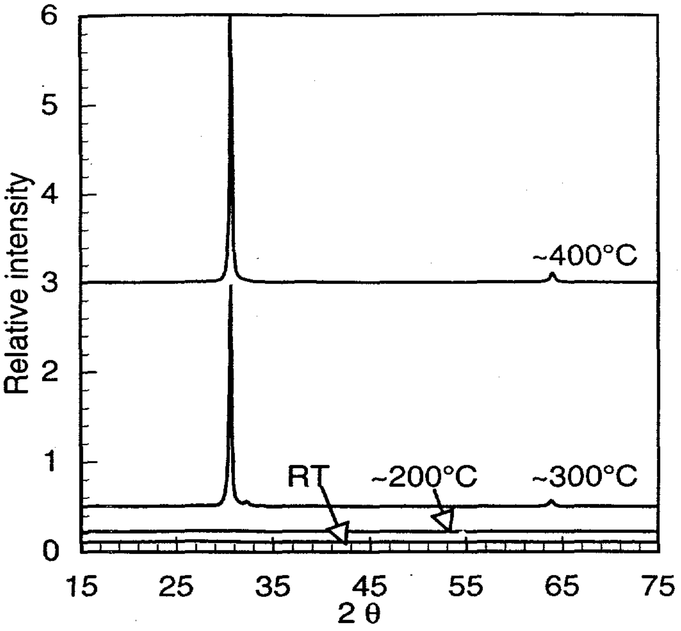

Figure 9: X-ray diffraction of CIO films deposited in pure oxygen on substrates at various temperatures. The films were not annealed.

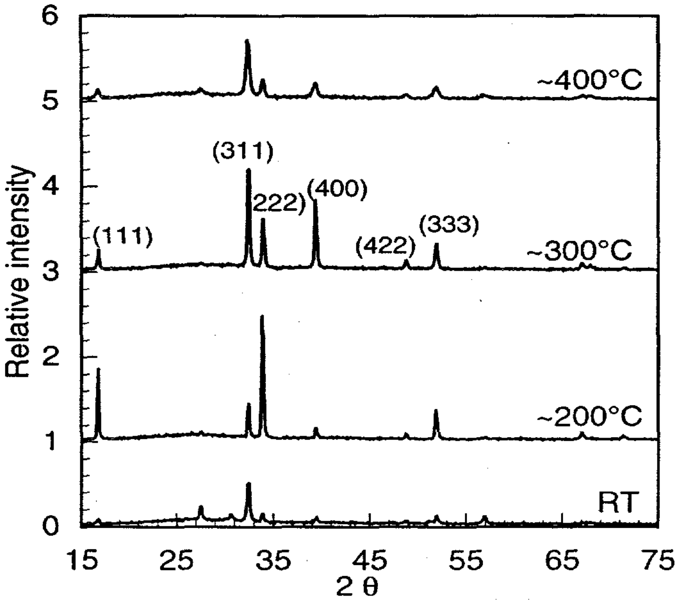

Figure 10: X-ray diffraction of a CIO film deposited in pure oxygen at various substrate temperatures, after annealing in pure argon at 680°C

Figure 13 shows the optical properties of a CIO film deposited and annealed according to the optimal procedures described above. The mobility of this film was 36.5 cm^2 V^{-1} s^{-1} and its carrier concentration was $6.8x10^{20}$ cm^{-3}, giving a resistivity of $2.3x10^{-4}$ Ω cm. The film thickness was approximately 5500 Å, thus giving a sheet resistance of 4.2 Ω per square.

Notice that the free-carrier absorbance is approximately 70% at its peak, i.e., at the plasma wavelength, as predicted by the model described earlier. The plasma wavelength for this film was approximately 1.5 μm, and the film does not cut off in the short-wave region until about 0.4 μm, giving a very wide wavelength range of high transmittance. Absorbance in the visible portion of the spectrum is less than 5% for most of the wavelength range, implying that this material could have significant use for a variety of visible-light applications. It could also be valuable for infra-red reflecting applications, as is illustrated in Figure 14.

This shows that the long-wave specular reflectance is approximately 95%. According to the theory of electromagnetism, the long-wave limit reflectance should only be controlled by the sheet resistance of the reflecting film [7]. Based on a value of 4.2 Ω per square, a reflectance of 95% is expected, again making the point that a simple modelling approach appears adequate to explain the properties of these films.

Figure 15 shows an atomic-force micrograph of a film deposited and annealed under the optimized conditions described in this section. The area examined is 0.5x0.5 μm and, although the surface appears rough, the root-mean-square roughness is only ±25 Å. At this level, there is very little scattered light, which is why the specular properties remain so high. For some applications, a totally specular film is essential, while for others, a high degree of texturing is required. We have not yet attempted to develop texturing techniques.

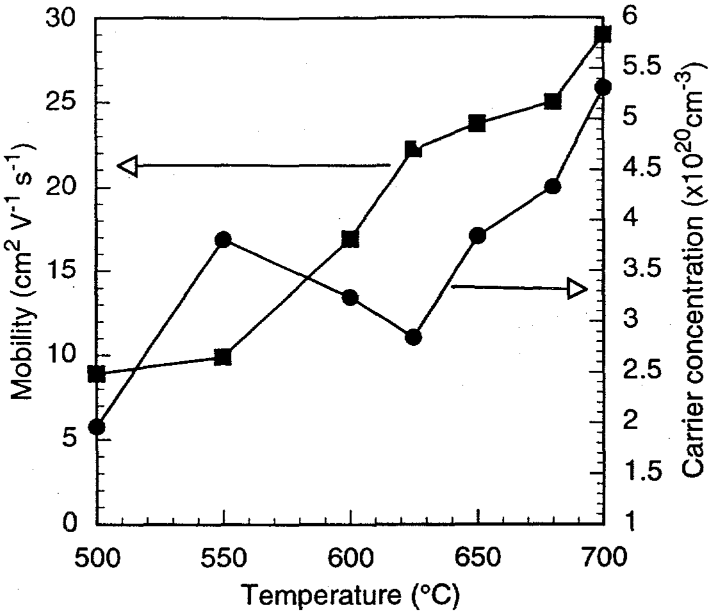

Figure 11: Variation of mobility and carrier concentration with annealing tempertaure. The films were deposited in oxygen on an unheated substrate and annealed in CdS/Ar 680°C

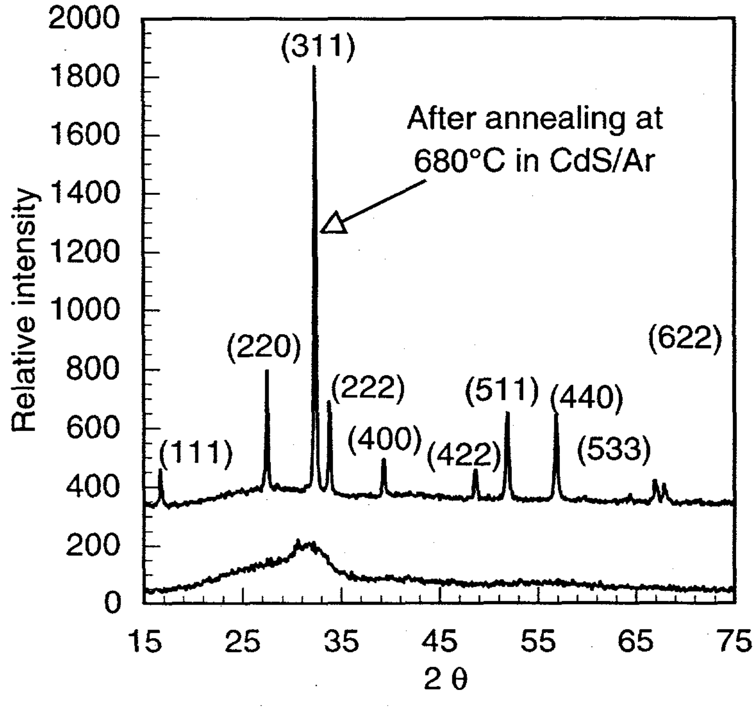

Figure 12: X-ray diffraction of a CIO film deposited in pure oxygen on an unheated substrate and annealed in CdS/Ar at 680°C. Crystallization in CdS/Ar actually occurred at a lower temperature that in Ar alone.

DISCUSSION AND SUMMARY

The modelling work makes a number of interesting, if fairly well-known, points. These are consequences of the Drude theory of electrons in conductors, and the theory of electromagnetism. In particular, it indicates that a high mobility is essential if low-absorbance films are required. If the carrier concentration alone is increased, then the extinction coefficient (and, hence, the absorption coefficient) increases. Consequently, the absorption peak narrows (because of the higher conductivity), but increases in height. On the other hand, if the carrier concentration is kept constant and the mobility is increased, then both the peak height and width decrease. We chose to work on the spinel family because high mobilities had been demonstrated in earlier work by Nozik [5], who suggested that higher mobility was due to a lower effective-mass of conduction electrons, although this remains to be confirmed. This is a somewhat anomalous proposition and Haacke [4] suggested that there may have been additional phases in his films. We have shown that single-phase films can be made by careful choice of deposition conditions, and have also demonstrated high mobilities. This perhaps supports the notion of lower effective-mass, although a longer relaxation time would also account for the superior mobility. Further analysis of the spinel-based materials is needed to establish which of these is responsible.

Films deposited in low partial pressures of oxygen have relatively high mobility after annealing but do not consist of the spinel phase. To produce this, it is essential to deposit the films at room temperature in pure oxygen, and then anneal them at high temperature in an inert atmosphere. Perhaps, the film phase-separates when high-temperature deposition is used. In any event, only indium oxide peaks are observed in the XRD spectra, and the resistivities are not specially low. In addition, the optical absorbance of these films is much larger than that of those made using the optimal procedures.

It appears that some spinel materials form the inverse phase more commonly than the normal spinel phase. Skribljak et al. [8] determined that $CdIn_2O_4$ had the spinel structure (cubic) with a = 9.115 Å. They concluded that it was probably inverse spinel, but noted the difficulty in distinguishing the normal from inverse structure due to the similarity of the Cd^{2+} and In^{3+} scattering factors. More recently, Shannon et al. [9], based on ionic radii considerations, suggested that $CdIn_2O_4$ was probably a normal spinel. Normal spinel would have divalent cadmium on the tetrahedral sites and trivalent indium on the octahedral sites. For the inverse spinel, half of the indium atoms would be located on the tetrahedral sites, while the cadmium atoms plus the other half of the indium atoms would be randomly distributed over the octahedral sites.

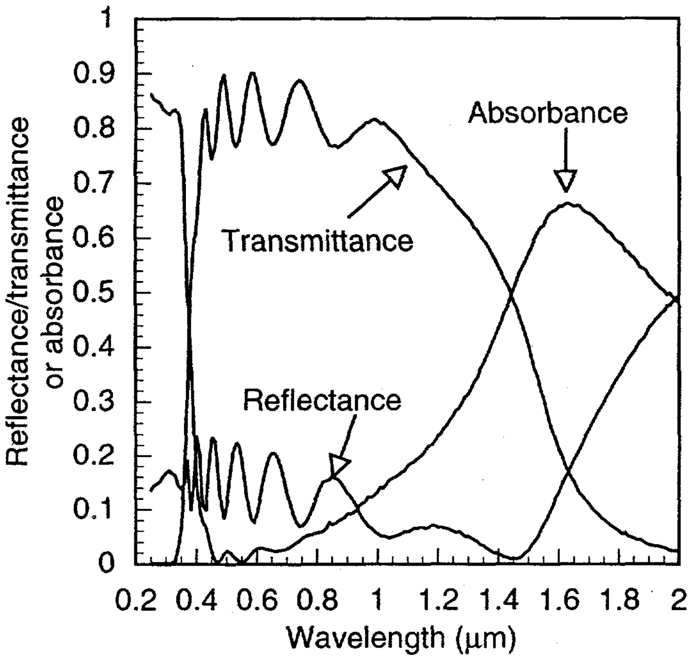

Figure 13: Transmittance, reflectance, and absorbance of a CIO film deposited at room-temperature, in pure oxygen on an unheated substrate, and then annealed in CdS/Ar at 680°C.

The doping mechanisms are also not well-understood and may be related to an inter-play between the normal and the inverse forms. There are additional considerations, however. Films annealed in argon, rather than CdS/Ar, have a higher carrier mobility and the reasons for this are unknown, except to suggest that ionized-impurity scattering is responsible for the reduction in the CdS/Ar case, because of the higher carrier concentration. For cadmium stannate, it has been suggested that there may be a self-doping mechanism whereby group IV-tin atoms occupy group II-cadmium sites, thus acting as double-donors. For cadmium indate, if the equivalent were to occur, lower carrier concentrations would be expected because the anti-site defect would act as a singly ionized donor. This appears to be occur, although this certainly does not confirm the self-doping (anti-site) model. The doping mechanism could also be due to interstitial cadmium although no proof of this exists, of which we are aware. Thus, for both CdS annealing and non-cadmium annealing, there are several questions about the nature of the doping mechanism, which must be answered. We note that, even films deposited in pure oxygen retain quite high carrier concentrations, as-deposited. The usual argument for oxygen vacancies being the source of the carriers does not, therefore, appear satisfactory.

The spinel family is receiving considerable attention because of its apparent ability to provide a novel TCO material with superior properties to the conventional materials. CIO is one of the less-well-investigated members of this family, presumably because it contains both toxic and costly elements, and we have shown it to have considerable promise for various applications requiring either extremely high transmittance in the visible region, or extremely high reflectance in the infrared region. However, there are some applications in which these undesirable properties may not be problematic.

We have also shown that it must be deposited under carefully controlled conditions, to optimize its properties. The single-phase spinel is essential for the best properties and this can only be achieved by depositing the films at room-temperature in pure oxygen, and then annealing them in pure argon, or CdS/Ar, at as high a temperature as possible. This certainly excludes the material as a TCO on temperature-sensitive substrates. This is an early point in our investigation of this material and there are many issues which are not well-understood.

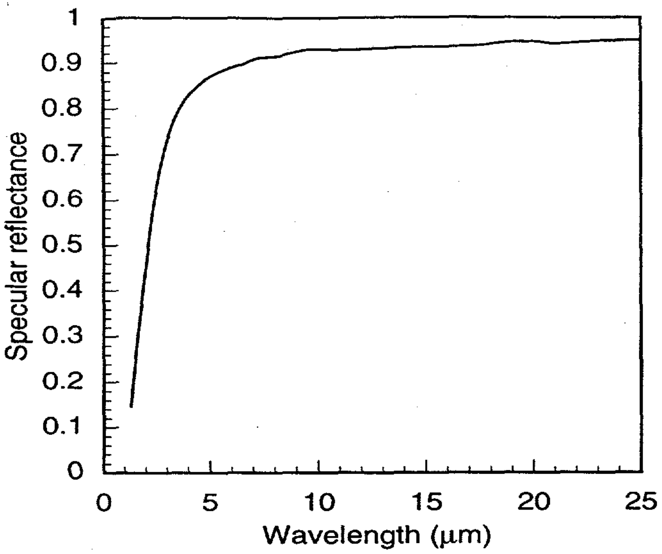

Figure 14: Reflectance of a CIO film deposited in pure oxygen on an unheated substrate, and annealed in CdS/Ar at 680°C.

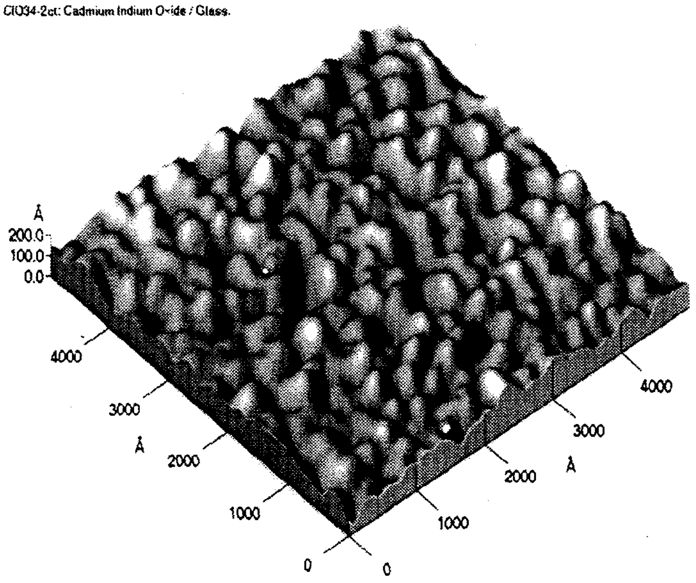

Figure 15: Atomic force micrograph of the surface of a CIO film showing the relative smoothness, on an atomic scale. The film was deposited and annealed under the optimized conditions described above.

We have achieved films with very low absorbance in the visible region of the spectrum (<5%), very high reflectances in the infra-red region (>95%), and sheet resistances as low as 4.2 Ω per square. The plasma edge for the highest carrier concentrations lies at about 1.2 μm and the fundamental absorption edge is at approximately 0.4 μm, again easily adequate for visible light applications. The films may be etched and patterned quite readily in either HCl or HF, which is an advantage over some materials like SnO_2. The films are very smooth even after heat-treatment, which ensures that they reflect and transmit light specularly, rather than diffusely. However, the fact that they can be etched so readily means that they could probably be textured if required. This, however, is usually achieved during growth, by careful choice of deposition parameters.

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