Differences between amorphous indium oxide thin films

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Abstract A series of ~60 nm thick indium oxide thin-films, all amorphous as determined by x-ray diffraction, were found to have physical and electrical properties that depended on the temperature of deposition. The carrier mobility and film conductivity decreased with decreasing deposition temperature; the best electrical properties of high mobility and conductivity were observed at a deposition temperature just below the temperature at which crystalline films formed. The density of the film also decreased with deposition temperature from 7.2 g/cm³ at +50 °C to 5.3 g/cm³ at −100 °C.

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1. Introduction

Transparent conducting oxides (TCOs) have an established record as important materials for photovoltaic devices and optoelectronic applications [1–3]. Transparent oxide semiconductors (TOSs), are currently being explored as thin film transistor (TFT) materials, an enabling technology for the next generation of computing, communication and identification devices [2,4]. Initially, the technological application of TCOs and TOSs employed these materials in their crystalline form. There is, however, an increasing shift towards the use of these materials in their amorphous form. In 2010 an estimated 30–40% of all flat panel displays employed an amorphous TCO material [5].

Amorphous TCOs and TOSs (a-TCOs and a-TOSs) have several advantages over their crystalline counterparts. In general, amorphous materials are deposited at lower temperatures [6] which tends to simplify the deposition process and expands the number of substrates the material can be deposited on, such as plastics. Amorphous materials, because they lack grain boundaries and are isotropic, tend to etch more uniformly [7–9], have lower surface roughness [10,11], and can be deposited uniformly over large areas [8,12]. Some amorphous materials can also be less prone to fracture, hence more pliable, lending themselves to the possibility of flexible electronics [8,13]. These advantages are realized without a significant loss to the seminal properties of conductivity and transparency for optimized amorphous materials [14].

The electrical and optical properties of crystalline TCOs and TOSs (c-TCOs and c-TOSs) are strongly influenced by the oxygen content of the film [15]; the same is true for a-TCOs and a-TOSs [16]. For c-TCOs and c-TOSs their properties are also affected by factors related to the crystal structure such as grain size [17] and crystallographic direction [18]. For a-TCOs and a-TOSs it is tempting to...
assume a single structure and, therefore, that processing induced changes to the material’s performance are due to factors other than a change in structure; that for a given material system all amorphous materials would have the same “non-structure”. This, however, does not appear to be the case. There are both theoretical and experimental indications that differences exist between amorphous materials of the same material system beyond those caused by differences in oxygen content.

Although pure indium oxide is rarely used in technological applications it is the progenitor of many TCO and TOS systems. Tin, zinc, gallium, as well as other elements, are added to indium oxide to produce technologically useful materials [8,19,20]. Pure indium oxide (IO), however, has an advantage over doped systems as it removes the ambiguity introduced by dopants in comparing experimental studies. Experimentally, the mobility of amorphous IO (a-IO) ranges from $10 \text{cm}^2/\text{V}\cdot\text{s}$ to $51 \text{cm}^2/\text{V}\cdot\text{s}$ [21,22]. Although differences in carrier concentration, and hence density of ionized donor centers, can effect mobility [23], the carrier concentrations reported with the above cited mobilities were $2 \times 10^{20} \text{cm}^{-3}$ and $4 \times 10^{20} \text{cm}^{-3}$, respectively. The carrier concentrations are in the range where ionized donor centers are expected to dominate scattering [24], but with the trend opposite to that expected if the change in mobility were an effect of ionized donor centers. A second difference between the two amorphous materials must exist to explain this range in carrier mobility [25]. In a theoretical study, Rosen et al. [26], varied the cooling time used in molecular dynamics liquid-quench simulations of a-IO. They found that the resulting structures increased in energy (decreased in stability) as the quench time was decreased. They also reported a decrease in both oxygen-indium and indium-indium coordination as quench time decreased (with the exception of the simulation for an instantaneous quench). Although not monotonically increasing as quench time decreased, there was also a general trend towards a larger pseudo lattice constant, $a$, with decreasing quench time, hence a less-dense structure.

The simulations used to generate the model amorphous-structures, used by Rosin and others, typically involve heating the crystalline form of the material to high temperature to randomize the atomic arrangement followed by a rapid-quench to freeze the atomic arrangement in place. Materials grown by pulsed laser deposition (PLD) undergo just such a process. A small spot on a polycrystalline target made of the material to be deposited is rapidly heated by a laser pulse to ablation (2000–3000 K) and then the plume of ablated material rapidly cooled at the substrate. In the study by Rosin, the rate of quenching had an effect on the resulting structure. The analogous variable in a PLD experiment would be the substrate temperature. For 60 nm thick films grown by PLD, indium oxide is x-ray diffraction amorphous up to a deposition temperature of +50 °C. In this study we look at the physical and electrical differences in x-ray diffraction amorphous indium oxide (henceforth simply referred to as a-IO) as a function of deposition temperature for films deposited between −100 °C and +50 °C. Films grown at +75 °C (the temperature at which evidence of crystallinity is first observed) and +400 °C (a completely crystalline film) are also included for comparison.

2. Materials and methods

2.1. Film growth

Indium oxide thin-films, ~60 nm thick, were grown by pulsed-laser deposition (PLD) from a dense hot-pressed indium oxide target (25 mm diameter). PLD was accomplished with a 248 nm KrF excimer laser with a 25 ns pulse duration and operated at 2 Hz. The 200 mJ/pulse beam was focused onto a 1 mm × 2 mm spot size. The target was rotated at 5-rpm about its axis to prevent localized heating. The target-substrate separation was fixed at 10 cm. The films were grown on fused-silica substrates in an O2 ambient of 8 mTorr. The substrates were attached to the substrate holder with silver paint. For films grown above room temperature a resistively heated substrate-holder was used; for films grown below room temperature a liquid nitrogen cooled substrate-holder was used.

2.2. Film analysis

Sheet resistance ($R_s/\Omega\cdot\text{cm}^2$), carrier type, area carrier-concentration ($n_d/1\text{cm}^2$), and carrier mobility ($\mu_d/\text{cm}^2\cdot\text{V}\cdot\text{s}$) were measured with an Ecopia 3000 Hall measurement system on samples in the van der Pauw geometry. Carrier density ($n$; /cm$^3$) and resistivity ($\rho/\Omega\cdot\text{cm}$) were calculated by dividing the area carrier-concentration and sheet resistance, respectively, by the film thickness. Film thickness ($d$/nm) was measured using a spectral reflectometer (Filmetrics F20) and were shown to range from 50 to 65 nm. X-ray reflectivity (XRR) was performed using an 18 kW Rigaku ATX-G diffractometer. CuK$\alpha$ radiation ($\lambda=1.54\ \text{Å}$) was conditioned by a parabolic multi-layer mirror and collimated to produce a 0.1 mm (vertical) by 5 mm (horizontal) beam with incident flux of $\sim2 \times 10^7$ photons/s. The XRR data was fitted to a two-layer model (film and interfacial layer) calculated by applying Abeles matrix method used in the Motofit package [27] to obtain the thickness, electron density (convertible to mass density given the film composition), and interfacial roughness of each layer. Grazing incidence x-ray diffraction (GIXRD) was performed with the same instrument at a beam incident angle of 0.46°. Film composition was measured by x-ray Photon Spectroscopy (XPS) using a Thermo Scientific ESCALAB 250Xi using a Al K$\alpha$ source and a take-off angle of 90°. An argon ion source was used to clean carbon from the surface prior to analysis. The flood gun was used on all analysis although it was only needed on the more insulating samples to maintain charge neutrality.

3. Results and discussion

3.1. Effect of deposition temperature on crystallinity

For many thin-film material systems, the transition between amorphous and crystalline can be accomplished by changing the temperature of deposition; the crystalline phase being favored by higher deposition temperatures [28]. Such is the case for IO deposited on fused quartz by PLD. Fig. 1 is the GIXRD spectra of IO films ~60 nm thick. Films grown at temperatures of +50 °C and below are all x-ray diffraction amorphous. The first sign of crystallinity is observed at +75 °C where the c-IO/a-IO ratio, as determined by the area of the crystalline XRD peaks and the area of the “amorphous hump”, is 69/4; a crystalline film deposited at 400 °C is included for comparison. The GIXRD spectra for the crystalline film is typical of that observed for polycrystalline bixbyite In$_2$O$_3$; the lattice constant, as determined from the locations of the peaks indexed in Fig. 1, is 10.09 Å; slightly less than the value of 10.12 Å frequently quoted for bulk In$_2$O$_3$ [29].

3.2. Effect of deposition temperature on density

Although the films deposited between −100 °C and +50 °C are all diffraction amorphous, both their physical and electrical properties
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are dependent on deposition temperature. For a given material such as indium oxide, mass density has a linear relation to electron density provided stoichiometry is fixed. Hence, x-ray reflectivity (XRR), a technique sensitive to the electron density profile of the thin films is used to characterize mass density. The reflected photons are collected under the Kαα condition, which keeps the momentum transfer, \( Q = 4\pi \sin(2\Theta/2)\lambda \), normal to the surface of the film. Therefore, the reflectivity can be expressed as a function of momentum transfer. The XRR data is fitted to a two-layer model (film and interfacial layer with RMS roughness) calculated by applying Abeles matrix method used in the Motofit package [27] to obtain the thickness and electron density of each layer, as well as interfacial roughness between each layer. Fig. 2 is a typical XRR spectrum and best-fit result performed over a \( Q \) range of 0.08–0.4 Å\(^{-1}\).

The electron density of the films, as measured by XRR, decreases from a value of 1.89 Å\(^{-3}\) at +50 °C, the same as for bulk c-IO, to 1.42 Å\(^{-3}\) at −100 °C, a difference of 30%, Fig. 3. There are two possible origins for the change in density; a change in structure or a change in composition. XPS was used to compare the composition of the films; all the films had the same In/O ratio within ±5% with no observable trend with respect to deposition temperature. The right hand axis of fig. 3 is the mass density assuming a stoichiometry of In\(_2\)O\(_3\); again this is a difference of 30% between +50 °C (7.17 g/cm\(^3\)) and −100 °C (5.37 g/cm\(^3\)). This difference is large but comparable to that observed in other systems such as quartz where α-quartz [30] has a density of 2.65 g/cm\(^3\) and fused quartz [31] a density of 2.20 g/cm\(^3\), a difference of 19%.

### 3.3. Effect of deposition temperature on electrical (Hall) properties

The electrical properties of the films, as measured by Hall apparatus, are also dependent on deposition temperature. The carrier concentration, \( n \), decreases with decreasing deposition temperature between +50 °C and −50 °C a difference of 32%, Fig. 4a; the film deposited at −100 °C was too resistive to measure. Care was taken to insure the oxygen partial pressure during deposition was kept constant between deposition temperatures as this can have a profound effect on carrier concentration. Any variation in oxygen partial pressure would be due to the precision of the pressure sensor and random. A portion of the decrease in carrier concentration can reasonably be attributed to the lessening of film density with decreasing deposition temperature; between +50 °C and −50 °C the film density decreased from 7.17 g/cm\(^3\) to 6.27 g/cm\(^3\), a difference of 12%. To account for the additional decrease in carrier concentration two logical possibilities are: fewer carriers are generated (per unit mass) or traps that remove carriers are introduced as the deposition temperature is decreased. If fewer carriers are generated there should be fewer ionized oxygen vacancies and, at the high carrier concentrations present, the carrier mobility should increase with decreasing deposition temperature (carrier concentration) [14]. If carrier traps are generated then not only would the ionized oxygen vacancies scatter electrons but the charged carrier traps would also scatter electrons and the mobility should decrease with decreasing deposition temperature. This point will be revisited below in the discussion of carrier mobility. There is no sudden change in carrier concentration with the advent of crystallinity at +75 °C. For the highly crystalline film, there is a large decrease in carrier concentration: Highly crystalline IO frequently has low carrier concentration, hence the common practice of doping with tin to form ITO.

The carrier mobility, \( \mu_\text{tr} \), decreases with decreasing temperature over the entire measurable amorphous range of +50 °C to −50 °C, Fig. 4b. As discussed above, this indicates the introduction of a scattering center in addition to the ones produced by ionized oxygen vacancies. Although this result supports to possibility of charged carrier traps, it is not possible to conclude the decrease in mobility is due to charged carrier traps; the decrease in mobility can also be due to structural imperfections that scatter the
what would be expected given impurity centers on mobility can be calculated from the expression:

\[ \mu = \frac{24\pi^3 (e\phi_E)^2 \frac{h^3 n}{[e^3 m^* g(x)Z^2 n_i]} \right] \]

where

\[ g(x) = \ln(1 + 4/x) - 1/(1 + x/4) \]

with

\[ x = \left( \frac{4e^2 m^*}{[4\pi(x\phi_E)]h^2(3x^2)^{1/3}n^{1/3}} \right) \]

In this set of equations \( \mu \) is the carrier mobility one would observe if only ionized impurity centers were present, \( \varepsilon_s, \) \( \hbar, \) and \( e \) are the physical constants of the vacuum permittivity, Planck’s constant and the electron charge, \( \varepsilon_s \) is the relative permittivity of indium oxide, \( m^* \) is the effective mass of a conduction electron, \( n \) the carrier density, \( Z \) is the charge of the ionized impurity center and \( n_i \) the density of ionized impurity centers. A relative permittivity of \( \varepsilon_s = 9 \) cited in the literature \([14,32]\) will be used; the reported effective mass ranges between 0.28\( m_e \) and 0.43\( m_e \) \([33–35]\) where \( m_e \) is the free electron mass, in this calculation \( m^* = 0.3m_e \) will be used \([26,28]\); the carrier density, \( n \), is obtained from Hall measurement; the ionized impurity centers will be assumed to be doubly-ionized oxygen vacancies \([21,36,37]\), hence \( Z = 2 \); and that \( n_i \approx n/2 \).

The easiest way to separate out the effect of ionized impurity centers from other sources of scattering is to look at scattering frequency, \( f \), which is simply the inverse of the relaxation time, \( f = 1/\tau \).

Relation times add as an inverse sum,

\[ 1/\tau = \Sigma 1/\tau_i, \]

hence the total scattering frequency is the simple sum of the contributing scattering frequencies,

\[ f = \Sigma f_i \]

The relaxation time is related to mobility by the expression

\[ \mu = e\tau/m^* \]

hence

\[ f = 1/\tau = e/\mu m^* \]

For any film, the total scattering frequency, \( f \), can be determined from the measured Hall mobility, \( \mu_H \), and Eq. (8); the ionized scattering frequency, \( f_p \), can be computed from the measured carrier concentration using Eqs. (1)–(3) and (8). Then the scattering frequency in excess of the ionized impurity scattering, \( f_{EX} \), can be determined using Eq. (6).

\[ f_{EX} = f - f_i \]

In this way the effect deposition temperature has on mobility can be examined independent of changes in carrier concentration in terms of \( f_{EX} \).

The excess collision frequency as a function of deposition temperature is presented in Fig. 5. For a-IO films the excess collision frequency increase as the deposition temperature decreases, again this indicates the introduction of an additional scattering center. It has been proposed that mobility in IO based TCOs is proportional to the portion of edge-sharing InO polyhedral \([38]\); in the absence of edge-sharing polyhedral the scattering frequency increases and mobility decreases. Structural studies of IO by Utosuno et al. \([39]\), reported a lower relative number of edge-sharing to corner-sharing InO polyhedral in a-IO than in c-IO. This would also increase the average In-In bond distance lowering the density of the film. For the films in this study, a decrease in the relative number of edge sharing InO polyhedral with deposition temperature would not only explain the decrease in film density with decreasing deposition temperature but also the increase in excess collision frequency (decrease in mobility). There is also no marked increase in scattering for the electrons. This can be seen in crystalline IO and ITO where films with the same carrier density can have different carrier mobility depending on whether they are single-crystal like or polycrystalline \([13,14]\); the nature of the structural imperfection in the amorphous material, however, may be different than those in the polycrystalline material. The conductivities, \( \sigma \), Fig. 4c, are what would be expected given \( \sigma = ne\mu \).

### 3.4. Effect of deposition temperature on carrier scattering

It is possible to calculate the effect on mobility due solely to ionized impurity centers \([10,22]\) and subsequently separate the effects on mobility of carrier concentration and temperature-induced structural-change from each other. The effect of ionized impurity centers on mobility can be calculated from the expression:

\[ \mu_i = \frac{24\pi^3 (e\phi_E)^2 h^3 n}{[e^3 m^* g(x)Z^2 n_i]} \]

where

\[ g(x) = \ln(1 + 4/x) - 1/(1 + x/4) \]
There are differences in both the physical and electrical properties mechanism [24]. Oxygen impurity centers may not be the dominant scattering center in addition to those produced by ionized oxygen impurities. The analysis, however, is not strictly valid at the low carrier concentration of the sample (3 \times 10^{19} \text{ cm}^{-3}) where ionized oxygen impurity centers may not be the dominant scattering mechanism [24].

4. Conclusions

There are differences in both the physical and electrical properties of a-IO films beyond those that are commonly produced by the variation in oxygen content. One difference that is important to simulation studies is the film density. Our studies show that the film density is dependent on deposition temperature. The resulting differences in physical structure have an effect on the electrical properties of the films. For indium oxide and perhaps many of the indium oxide based systems, the best electrical properties of high mobility and high conductivity are observed for films grown at conditions close to those where crystallinity occurs.

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