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Charge mobility increase in indium-molybdenum oxide thin films by hydrogen doping

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ABSTRACT

The increase of charge mobility in transparent conductive indium molybdenum oxide (IMO) films is correlated with the presence of hydroxyl groups. The introduction of H_2 in the chamber during sputtering deposition compensates the excess charge introduced by cationic Mo doping of indium oxide either by oxygen or hydroxyl interstitials. Films present a linear increase of carrier mobility correlated with H_2 content only after vacuum annealing. This behavior is explained because vacuum annealing favors the removal of oxygen interstitials over that of hydroxyl groups. Since hydroxyl groups offer lower effective charge and smaller lattice distortions than those associated with interstitial oxygen, this compensation mechanism offers the conditions for the observed increase in mobility. Additionally, the short-range order around molybdenum is evaluated by extended X-ray absorption fine structure (EXAFS) spectroscopy, showing that Mo^{4+} is placed at the In site of the indium oxide.

1. Introduction

Transparent conducting materials (TCM) are at the basis of the development of devices in which smart transparent windows are fundamental for the use of flat-panel displays, touch screens, photovoltaic cells or light emitting diodes [1]. Typically, TCM layers are described as thin films with high visible wavelength transparency and low electrical conductivity ($\rho < 10^{-3}\,\Omega\,\text{cm}$). These properties typically require a band gap wider than 3.0 eV and charge carrier densities (N) near $10^{20}\,\text{cm}^{-3}$. Since the electrical conductivity (σ) is proportional to both the carrier concentration (n) and the mobility (μ) through $\sigma = 1/\rho = n\,\mu e$ (where e is the elementary charge), conductivity can be improved either by increasing n or μ. Nevertheless, the increase of n may result in the degradation of transmittance at near infrared (NIR) wavelengths, which restricts possible application, for instance in solar cells devices. For this reason, high mobility transparent conducting oxides (HMTCO) are an attractive matter of current research [2].

Indium tin oxide (ITO) is the most commonly used TCM in electronic devices because of its excellent electrical and optical properties [3]. In terms of mobility, ITO does not present excellent characteristics, though some other doped indium oxides have been reported to have higher carrier mobility values making it possible to combine high NIR transmittance with high conductivity. This is the case of indium titanium oxide (ITiO) [4,5] and particularly indium molybdenum oxide (IMO) for which mobility values up to $250\,\text{cm}^2\,\text{V}^{-1}\,\text{s}^{-1}$ have been reported [6] in pulsed laser deposited films.

In ITO, the lower mobility values as compared to In_2O_3 is explained by the strong hybridization of In s-states (lowest conduction band) with Sn s-states [7] resulting in effective carrier mass increase. Higher mobility in IMO is attainable because the d-states of Mo do not hybridize with the s-states of In [8,9] resulting in charge carriers effective mass similar to that in undoped In_2O_3.

Magnetron sputtering (MS) has been commonly used to prepare IMO films. Typically, films with high mobility are obtained when substrates are heated during deposition. For instance, $\mu = 83\,\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ was reported for films deposited by RF magnetron sputtering at $T_S = 350\,^\circ\text{C}$ from IMO target [10], $\mu = 80\,\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ at $T_S = 290\,^\circ\text{C}$ by reactive environment hollow cathode sputtering from In and Mo metal targets [11],

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$\mu = 50\,\mathrm{cm^2V^{-1}s^{-1}}$ at $T_S = 350\,^\circ\mathrm{C}$ by reactive DC magnetron sputtering from a Mo-embedded In metal target [12], $\mu = 65.3\,\mathrm{cm^2V^{-1}s^{-1}}$ at $T_S = 550\,^\circ\mathrm{C}$ by reactive RF magnetron co-sputtering from In_2O_3 and MoO_3 targets [13] and $\mu = 99\,\mathrm{cm^2V^{-1}s^{-1}}$ at $T_S = 450\,^\circ\mathrm{C}$ (with post-deposition heat treatment) by reactive RF magnetron co-sputtering from ceramic In_2O_3 and metallic Mo targets [14]. Alternatively, films deposited by sputtering without intentional substrate heating have been reported to have lower mobility values ($\mu < 20\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$) [15–17]. In a first step, the presence of Mo^{6+}, detected by X-ray photoemission spectroscopy (XPS), in IMO films deposited at high substrate temperature, was considered to explain the observed increase in mobility [2,6] in contrast with those prepared at room temperature. Nevertheless, a clear correlation between Mo^{4+} content and charge carrier concentration was finally established [18,9].

In the present work, we report on the properties of IMO films deposited on substrates nominally at room temperature, by co-sputtering of In_2O_3 and metallic Mo, with different $Ar/O_2/H_2$ gas mixtures and post-annealing treatments in order to evaluate the compromise between transparency, charge carrier density and mobility. Since the oxidation sate of molybdenum is a determining parameter for electrical properties, the lattice position and oxidation state of Mo in the In_2O_3 lattice has been studied by X-ray absorption spectroscopy in films deposited with Ar and Ar/O_2 mixture sputtering gas.

On the other hand, transparent Sn doped In_2O_3, ITO, films with low electrical resistance have been prepared at low processing temperatures by the addition of hydrogen to the sputtering gas [19–21]. Detected hydroxyls [22] have been reported to contribute to an increase in carrier concentration resulting in low resistivity values without any deterioration in transparency [23]. For this reason, the effect of H_2 addition in the gas mixture during the IMO growth is also investigated.

In this paper, it will be shown that the role played by H_2 when preparing IMO is in clear contrast with that played in ITO. For films grown at room temperature, the use of H_2 in the sputtering chamber renders low resistivity ITO films while having little impact on mobility, in contrast, IMO films grown under the same conditions show high resistivity values, but a clear correlation between H_2 content and mobility is observed.

2. Experimental

IMO films were deposited at room temperature on fused silica substrates by co-sputtering from two 2 inches targets placed in magnetron sources. One of them is a homemade sintered In_2O_3 disk (from Aldrich powder) operated by RF power (PFG 300RF, Huttinger gmbH) and the other is a 99.95% pure metallic Mo disk from Goodfellow. The sputtering chamber had a typical base pressure of 1×10^{-4} Pa and the load-lock attached chamber was used for introducing the substrate. After pre-sputtering target cleaning, the film deposition process was carried out at a constant pressure of 0.8 Pa with a mixture of Ar, O_2 and H_2 with variable ratio, regulated by three independent mass flow controllers. Three series of samples were prepared: (i) “IMO_Ar” films, deposited with Ar as the sputtering gas, (ii) “IMO_ArOx” films, where a mixture of O_2/Ar was used; we used three different oxygen contents: 7, 10 and 14% (no appreciable difference between them was observed) and (iii) “IMO_ArOxH”, deposited using a $H_2/O_2/Ar$ mixturewith an oxygen content of 14% and a hydrogen content ranging from 0 to 3.6%. Prior to loading them into the deposition chamber, substrates were cleaned successively, in acetone and propanol and dried in a high purity N_2 gas. The thickness of the IMO films was determined by a Veeco Dektak 150 profilometer.

Two types of post-deposition thermal treatments of IMO films were carried out for 2 h at 600 °C using a quartz tubular furnace, either in vacuum at 1×10^{-4} Pa or in a flowing oxygen atmosphere of 2 Pa.

The Mo/In ratio was determined by analyzing the energy dispersive X-ray fluorescence (EDX) with an EDAX Genesis XM2i analyzer coupled to a FEI NanoSEM Nova 230 field emission-scanning electron microscope (FE-SEM).

X-ray absorption spectroscopy (XAS) at the Mo K-edge was measured in the fluorescence yield mode at the BM25-Spline Spanish beamline of the European Synchrotron Radiation Facilities (ESRF).

Extended X-ray absorption fine structure (EXAFS) analysis was performed using the VIPER software [24]. EXAFS oscillations, obtained after removing the atomic background by a cubic spline polynomial fitting and normalizing to the edge jump, let obtaining neighbor distances and coordination numbers by fitting to the well-known expression [25]:

$$\chi(k) = S_0^2 \sum_j \frac{N_j}{k{R_j}^2} e^{(-2k^2\sigma_j^2)} e^{(-2R_j/\lambda(k))} f_j(k) \times \sin(2kR_j + \Phi_j(k)) \qquad (1)$$

Eq. (1) describes the EXAFS oscillations for a Gaussian distribution of N_j atoms at mean distances R_j around the absorbing atom, considering single scattering and plane-wave approximation. ${S_0}^2$ is an intrinsic loss factor, N_j is the average coordination number for the Gaussian distribution of distances centred at the R_j value, σ_j is the Debye-Waller factor and $\Phi_j(k) = 2\delta(k) + \gamma_j(k)$ is the phase shift, being $\delta(k)$ and $\gamma_j(k)$ the central and backscattering atom phase shifts, respectively. $f_j(k)$ is the backscattering amplitude magnitude corresponding to the j^{th}-neighbor atom, and λ is the mean free path of the photoelectron travelling from the absorbing atom to the backscatterer in the j^{th}- shell and the life time of the core hole. The amplitude and phase functions introduced as inputs in the analysis were obtained by the FEFF8 code [26,27].

Transparency was characterized by means of optical transmission spectroscopy, spectra were measured on a Cary-4000 Varian spectrophotometer in the 200–900 nm wavelength range. The signal from the substrate was eliminated by measuring the corresponding bare substrates. The room temperature electrical properties were measured with a Keithley 2400 source-meter and a Keithley 2000 digital voltmeter managed by a home-made computer software to quantify I–V and V–H curves. According to the van der Pauw method [28,29], four silver paint contacts were placed on the IMO films surface corners of squared samples to measure its sheet resistance (R_S) and resistivity (ρ). Hall effect measurements were made by placing the samples in a variable magnetic field provided by a standard electromagnet ($-0.8\,\mathrm{T} < \mathrm{H} < 0.8\,\mathrm{T}$).

3. Results and discussion

3.1. Short range order and oxidation state of Mo in IMO films

The influence of oxygen in the sputtering gas on the oxidation state and on the location of Mo in the lattice has been studied using XAS. For this purpose, Mo K-edge EXAFS and XANES (X-ray absorption near edge structure) spectra were collected from films belonging to two of the series previously described: “IMO_Ar” series, “IMO_ArOx” series (specifically $O_2(10\%)/Ar(90\%)$). Afterwards, the effect of annealing has also been characterized. The “as-deposited” films from the “IMO_Ar” series were subjected to post-deposition O_2-annealing at 600 °C and those from the “IMO_ArOx” series were subjected to vacuum annealing also at 600 °C.

As summarized in Table 1, each series contains several samples with different Mo content (in the range of 1–5 at.%) that were obtained by changing the applied power to the Mo cathode.