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Fabrication of transparent conducting amorphous Zn–Sn–In–O thin films by direct current magnetron sputtering

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Abstract

Amorphous ZnO–SnO_2–In_2O_3 films were grown by direct current magnetron sputtering from vacuum hot pressed ceramic oxide targets of Zn:In:Sn cation ratios 1:2:1 and 1:2:1.5 onto glass substrates. X-ray diffraction analysis showed that the microstructure remained amorphous during annealing at 200 °C for up to 5 hours. By monitoring the electrical resistivity, oxygen content and substrate temperature were optimized during deposition. The optimal films were characterized by Hall Effect, work function and optical spectroscopy measurements. Films of 1:2:1 composition showed the lowest resistivity (7.6×10^{-4} Ω-cm), when deposited onto substrates preheated to 300 °C. Transmissivity of all films exceeded 80% in the visible spectral region. The energy gap was 3.52–3.74 eV, and the work function ranged 5.08–5.22 eV, suitable for cathode applications in organic light emitting diodes. Overall, the film characteristics were comparable or superior to those of amorphous tin-doped indium oxide and zinc-doped indium oxide films and may serve as viable, lower-cost alternatives.

Keywords: Transparent conducting oxide; Indium tin oxide; Amorphous semiconductor; physical vapor deposition; Photoelectron spectroscopy; Work function; Optical properties; Hall Effect

1. Introduction

Transparent conductive oxide (TCO) thin films enable a wide variety of applications that require optical access in the visible region through the electrode materials. In the flat panel display (FPD) industry, films of two In-rich compositions are predominantly used-indium oxide doped with tin (ITO; In_2O_3–10 wt.% SnO_2) and, increasingly, doped with zinc (IZO; In_2O_3–10 wt.% ZnO) to stabilize the amorphous microstructure of room temperature, as deposited films. Such films show metal-like electrical resistivity, $1–2\times10^{-4}$ Ω-cm and $3–6\times10^{-4}$ Ω-cm respectively, and transmissivity of 80–90% of visible light. Despite a slightly higher resistivity, *a*-IZO films are more attractive for FPD applications that require a faster, isotropic wet etch rate, enabling the transfer of finer line-width patterns.

The high cost and relative scarcity of indium encourages the development of lower-cost alternatives to *a*-ITO and *a*-IZO, motivating extensive investigation for candidate replacement TCO materials such as ZnO [1]. However, the performance of indium-based TCO materials and their well established processing parameters and wide processing window, combined with an excellent chemical and physical stability in the thin film form, suggests that adoption of new materials may meet resistance. In particular, materials that preserve the processing and service performance of amorphous IZO are of great interest. One possibility is the use of ternary oxides of ZnO–In_2O_3–SnO_2 (ZITO) system, which retains the highly stable amorphous structure of *a*–IZO but displaces as much indium oxide as possible by incorporation of ZnO and SnO_2.

In the crystalline state, ZnO has a very low solid solubility in In_2O_3 (<1 wt.%) due to the requirement that divalent zinc assumes a tetrahedral coordination with oxygen while trivalent In requires six-fold oxygen coordination. In the amorphous state, the coordination polyhedra would be preserved, but much higher concentrations of ZnO in In_2O_3 have been reported [2]. It appears that the presence of the ZnO stabilizes the amorphous structure, by inhibiting the ability of the indium octahedra to

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relax and rotate into the complex bixbyite structure of the thermodynamically stable crystalline phase. When the material did recrystallize at high temperatures (*i.e.*, at 500 °C annealed in air), it formed a complex, interleaved, layered structure of alternating layers of InO_6 and ZnO_4 polyhedral units [3]. ITO, by contrast, begins to crystallize at significant rates at temperatures as low as 120 °C [4].

Previous work on ZITO systems has focused on targets in which co-substitution of SnO_2 and ZnO in In_2O_3 was demonstrated to increase the bulk solid solubility of both components up to ~20 wt.% for each [5]. Thin films sputtered directly from such targets tended to have poor crystallinity in the as-deposited state, attributable to structural frustration while attempting to accommodate the preferred tetrahedral coordination of Zn^{2+} together with the octahedral coordination of In^{3+} and of Sn^{4+}. Such films offer an enormous technological advantage—a highly isotropic wet-etch uniformity would enable higher resolution lithographic patterning.

When sputtering a multi-cation-containing target, control over the film composition produced has been limited. In particular, different oxidation potentials among the cations could give rise to films with a stoichiometry differing from that of the target [6], while surface adsorption-limiting kinetics could also enable the formation of metastable phases. To compare amorphous films of different composition, the ratio of the relative amounts of different cation species was used. Accordingly, electrical and optical properties have been reported to be tunable via the film composition, when prepared by pulsed laser deposition [6] and radio frequency magnetron sputtering [7]. The best reported values for resistivity ranged from $3–8\times10^{-4}$ Ω-cm, from ~2.9–3.65 eV for the absorption edge and a work function of ~4.9 eV. Films closer to thermodynamic equilibrium conditions were also produced by metal organic chemical vapor deposition, and their optical properties offered an even wider window of visible light transmission than ITO [8].

To complement the existing literature, we are reporting the deposition of ZITO from ceramic targets using direct current (dc) magnetron sputtering [9]—the manufacturing technique of choice for IZO and ITO in the display industry, due to its large area uniformity. In this paper we present an investigation of the properties of thin films grown by dc magnetron sputtering from two hot-pressed ceramic oxide targets of ZITO, one containing equal amounts of Zn and Sn (1:2:1 cation ratio) and the second being a Sn-rich composition (1:2:1.5 cation ratio). O_2 partial pressure was varied to identify the optimal film deposition conditions [10]. Then, using the optimized deposition conditions, ZITO films were deposited onto glass substrates both at room temperature and pre-heated to 300 °C. To evaluate the performance of ZITO films compared to ITO and IZO, Hall Effect and work function measurement were used to characterize the electrical properties, while the optical properties were characterized by ultraviolet (UV)-visible-near-infrared (IR) spectroscopy.

2. Experimental details

Sputter targets were vacuum hot pressed at 900 °C in Ar from ball-milled ZnO and In_2O_3 powders. To achieve stoichiometric isovalent substitution of In, a target was prepared with a nominal cation ratio of 1:2:1, 10.3 wt.% ZnO and 19.1 wt.% SnO_2. One with excess Sn was prepared with a composition of 9.4 wt.% ZnO_2 and 26.6 wt.% SnO_2, for a cation ratio of 1:2:1.5. Fig. 1 shows the XRD patterns of the target phase compositions, both of which contain a mixture of bixbyite indium oxide, tin oxide, and ternary Zn_2SnO_4 and $In_4Sn_3O_{12}$ phases.

ZITO thin films were deposited onto Corning 0211 glass substrates, with the substrates either unheated or preheated to 300 °C, from each of the two multiphase targets by dc magnetron sputter deposition at a rate of 0.1 nm/s. A total system pressure of 4 Pa and a sputter power of 0.22 W/cm^2 at 280 V were used. The resistivity of the as-deposited material was optimized by adjusting the reactive oxygen content $O_2/(O_2+Ar)$ over a range of 0–10 vol.% in the sputter gas during deposition of a series of 100-nm thick films. A multi-beam optical stress sensor technique [10] was used to calculate $\Delta V/V$ from measured stress-induced structural changes. The optimization results are shown in Fig. 2. For further electrical and optical characterization, a set of films of thickness 43 nm, 93 nm, 138 nm, and 189 nm (±.5 nm) was produced using the optimum conditions for the 1:2:1 ZITO target, *i.e.* with the substrate preheated to 300 °C and a pure (0 vol.% O_2) Ar sputter gas.

Samples for Hall Effect measurements were patterned lithographically using the lift-off technique to obtain the necessary geometry of Hall spiders. The films were annealed at 200 °C in air, during which Hall Effect measurements were performed *in-*

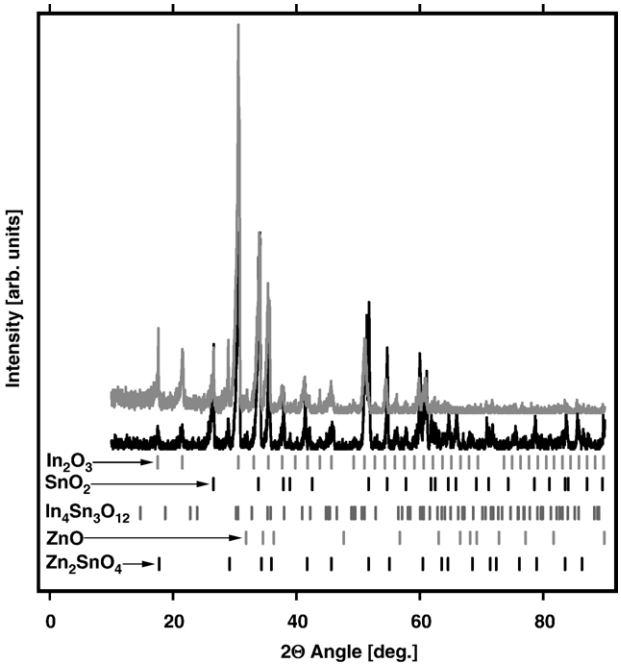

Fig. 1. X-ray diffraction patterns from the two ZITO targets used in this work, of cation ratios 1:2:1 and 1:2:1.5. ZITO 1:2:1 target (solid black line) has a composition of 10.3 wt.% ZnO+19.1 wt.% SnO_2, balanced with In_2O_3, while the ZITO 1:2:1.5 target (dotted gray line) has a composition of 9.4 wt.% ZnO+ 26.2 wt.% SnO_2, balanced with In_2O_3. Both targets contain a mixture phases of as shown in comparison with the standard International Center for Diffraction Data database files for In_2O_3 (note the characteristic {222} peak at ~33°), $ZnSnO_3$, ZnO, $In_4Sn_3O_{12}$, and for SnO_2 [31].