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Growth characteristics and properties of indium oxide and indium-doped zinc oxide by atomic layer deposition

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ABSTRACT

We investigated the growth of indium oxide (In_2O_3) and indium-doped zinc oxide (In-doped ZnO, IZO) thin films synthesized using thermal atomic layer deposition with dimethylamino-dimethylindium as the precursor, while varying the In_2O_3/ZnO ratio. The IZO films were deposited using the supercycle method, and the doping concentration of these films was controlled by changing the In_2O_3/ZnO cycle ratio. The microstructural properties and chemical compositions of the films were analyzed using X-ray diffraction analysis and X-ray photoelectron spectroscopy. Further, the electrical properties of the IZO films, including their carrier concentration, mobility, and resistivity, were investigated through Hall measurements. The lowest resistivity (6.15×10^{-2} Ω·cm) was exhibited by the IZO film. The highest carrier concentration and mobility exhibited by the IZO films grown at 300 °C were 4.4×10^{18} cm^{-3} and 28.7 $cm^2/V \cdot s$, respectively.

1. Introduction

Indium oxide (In_2O_3), which has a wide band gap, is being researched extensively for use as a transparent conducting oxide (TCO), owing to its low resistivity, good chemical stability, and high transparency in the visible-light region [1,2]. Given these attractive properties, In_2O_3 is employed in many applications, including in electro-opto devices such as flat panel devices [3], photovoltaic devices [4], heat-reflecting mirrors [5], and sensors of oxidizing gases [6,7]. Further, of the many TCOs being studied as alternatives to indium tin oxide, indium-doped zinc oxide (In-doped ZnO, IZO) is particularly attractive because it is cheaper and has good electrical and optical properties and high structural stability at high temperatures [8–10]. IZO thin films can be deposited by many methods, including radio frequency (RF) sputtering [8], pulsed laser deposition [11,12], spraying [9,13] and chemical vapor deposition (CVD) [10]. Atomic layer deposition (ALD), which is a modified CVD technique, is an effective method for depositing thin films with large-area uniformity and high conformality, as it involves the surface saturation of the chemicals used; this is a unique advantage of ALD [14,15]. Furthermore, in case of doped material, the dopant concentration can be controlled readily by changing the ratio of the ALD cycles [16].

In most previous studies, In_2O_3 thin films had been deposited using precursors such as cyclopentadienyl indium( ) (InCp), tri-methyl-indium (TMIn), or indium chloride ($InCl_3$) [2,17–20]. In this study, we deposited In_2O_3 films by thermal ALD (Th-ALD) using dimethylamino-dimethylindium (DMLDMIn) as the precursor and deionized (DI) water as the reactant. Further, we deposited IZO films using the supercycle method with the aim of using them as TCO films. The supercycle method involved the sequential deposition of the two types of films [16]. The microstructural properties and chemical compositions of the films were analyzed. In addition, the electrical properties of the films, such as their resistivities, carrier concentrations, and mobilities, were measured to determine their conductivities.

2. Experimental details

A commercial Th-ALD system was employed for depositing the In_2O_3 and IZO films. DMLDMIn and diethylzinc were used as the metal-organic precursors for the In_2O_3 and ZnO films respectively, and DI water was used as the reactant. Ar gas was used for purging and as the carrier gas for the precursor; a mass flow controller was used to control its flow rate (10 sccm for bubbling and 20 sccm for purging). The growth temperature (T_s) was fixed at 300 °C for all the In_2O_3 and IZO films unless mentioned otherwise. The IZO thin films were deposited by supercycling, which involved varying the number (n) of the ZnO ALD cycles between 99, 49, 9, and 1 for every In_2O_3 ALD cycle; the thus-synthesized IZO films are labeled SP_{99}, SP_{49}, SP_9, and SP_1, respectively. The films were grown on Si (100) wafers. All the substrates were cleaned sequentially in acetone, isopropyl alcohol, and DI water. The thicknesses of the grown film were measured by spectroscopic ellipsometry (Elli-SE-F, Ellipsotech). The microstructural properties and chemical compositions were determined by X-ray diffraction (XRD) (D/Max-2500H, Rigaku; in the 20°–70° 2θ range with 0.02° step, monochromatic

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source (4 bounce Ge 022 channel), 3 kW X-ray tube with Cu target, room temperature) and X-ray photoelectron spectroscopy (XPS) (220i-XL, Escalab; Mg Kα/Al Kα 1253.6 eV twin X-ray source with power of 15 kV, 300 W, base pressure of 4.8×10^{-9} mbar, sputter cleaned surface with 3 kV Ar ion gun) analysis. The binding energy scale of the XPS data was calibrated using C 1 s peak (285 eV) with the software application, XI-SDP Viewer 13. The carrier concentrations, mobilities, and resistivities of the films were measured using a Van der Pauw-style Hall measurement system (HMS-3000, Ecopia) at room temperature; the measurements were performed on an area of 2×2 cm^2 on 20 nm-thick films.

3. Results and discussion

3.1. Growth characteristics of In_2O_3 film

As this study was a preliminary investigation of the feasibility of growing In_2O_3 films by ALD using DMLDMIn as the precursor, the growth characteristics of the films were investigated in detail. As there are no previous reports on the ALD of In_2O_3 using DMLDMIn, the In_2O_3 films were deposited at different growth temperatures to determine the effects of temperature (Fig. 1(a)). To determine the lowest temperature for growing In_2O_3 using DMLDMIn, the temperature was increased from 200 °C to 400 °C with intervals of 50 °C. No growth was observed until 250 °C; however, In_2O_3 films were deposited at temperatures greater than 300 °C. The growth rate was 0.61 Å/cycle at 300 °C, 0.65 Å/cycle at 350 °C, and 1.1 Å/cycle at 400 °C. The growth rate increased slightly with the increase in the growth temperature because the reaction between precursor and surface species is a thermally activated process [21,22]. Fig. 1(b) and (c) shows the growth rates of In_2O_3 by Th-ALD for different precursor exposure times, reactant exposure times, and Ar flow rates. As can be seen in Fig. 1(b), the growth rate of Th-ALD In_2O_3 increased gradually when the precursor exposure time was increased to more than 3 s. The trend in the case of the reactant was similar. After 3 s of precursor exposure and 2 s of reactant exposure, the growth rate saturated at the maximum value, which was 0.6 Å/cycle. This was because the chemical species did not adhere to the substrate surface sufficiently for other exposure times. This phenomenon is a unique characteristic of ALD and is caused by surface saturation. Further, similar phenomenon have been reported previously too [14,15]. Fig. 1(c) shows the growth rate of the In_2O_3 films as a function of the Ar purge time. After a purge time of 7 s, the growth rate of the In_2O_3 films saturated at 0.6 Å/cycle. The interesting thing is that for a purge time of 6 s or lower, the growth rate of the film was higher (approximately 0.9 Å/cycle) and even more than the saturated growth rate when the precursor and reactant exposure times were varied. This is probably because the precursor and reactant remained on the substrates in small quantities until 6 s. As a result, the growth rates for purge times of less than 6 s were higher than the saturated growth rate (0.6 Å/cycle). This means that during ALD cycling, the films were deposited in the absence of surface saturation. This phenomenon has been reported in several studies [14,15,17]. We also deposited In_2O_3 films using a greater number of deposition cycles to demonstrate that the growth rate during ALD remains constant. Fig. 1(d) shows that the thickness of the Th-ALD In_2O_3 films increased linearly with the number of ALD cycles. These figures demonstrate that high-quality In_2O_3 films were deposited by ALD, given that the growth rate of the films was constant. This, in turn, was owing to the self-limited nature of the surface reaction, which is one of the important characteristics of ALD [17,23] performed using DMLDMIn as the precursor.

3.2. Properties of Th-ALD In_2O_3

The chemical compositions of the In_2O_3 films deposited by Th-ALD were analyzed by XPS; the XPS data are shown in Fig. 2. From these data, the elemental compositions of the In_2O_3 films could be

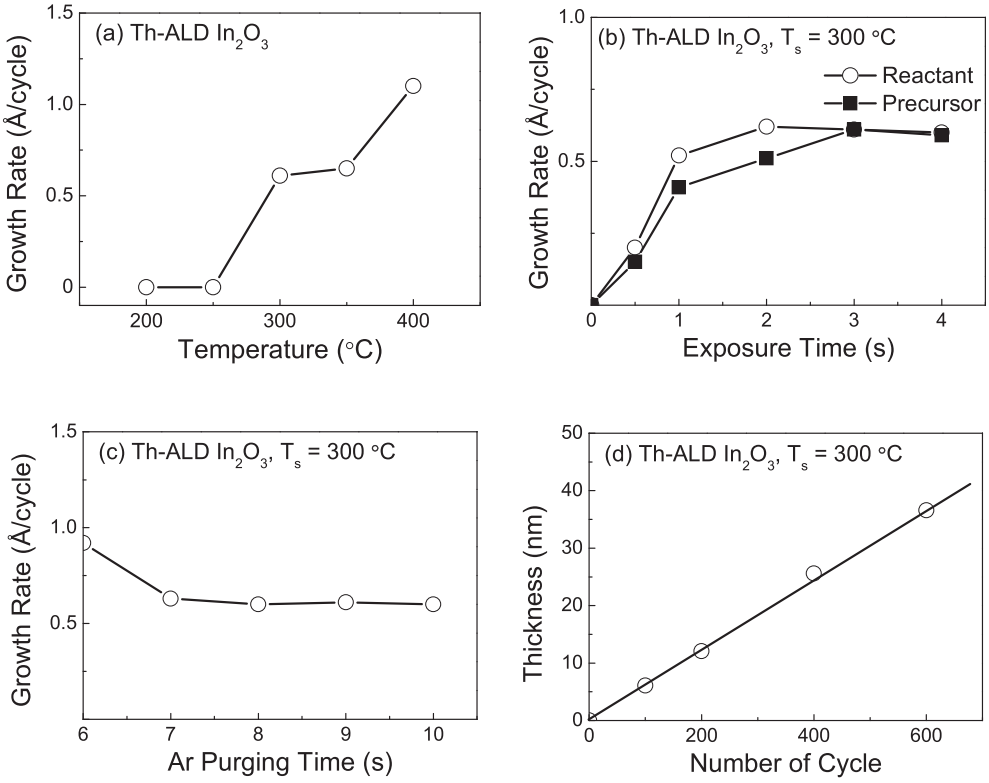

Fig. 1. Growth rate of Th-ALD In_2O_3 films as a function of (a) temperature, (b) precursor and reactant exposure times using a fixed Ar exposure of 7 s; cycle times were x–7–2–7 and 3–7–x–7, respectively, and (c) Ar purging time using a fixed precursor and reactant exposure of 3 s and 2 s, respectively. (d) Thickness of the Th-ALD In_2O_3 films as a function of the number of cycles. The cycle times for In_2O_3 were 3–7–2–7 s.