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Atomic layer deposition of highly conductive indium oxide using a liquid precursor and water oxidant

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Abstract

Atomic layer deposition (ALD) of In_2O_3 films was investigated using a novel liquid precursor, [3-(dimethylamino)propyl] dimethyl indium (DADI). Typical ALD growth was observed at a substrate temperature of 275 °C, with relatively high growth rates of 0.6 Å/cycle. The In_2O_3 layer exhibits low resistivity ($9.2 \times 10^{-5}\ \Omega$ cm) with relatively high optical transparency ($>80\%$ between 420 and 700 nm). The carrier concentration is approximately one or two orders of magnitude higher than those reported in the literature. The origin of such electrical properties is investigated with respect to the microstructure and chemical properties of the In_2O_3 film.

Keywords: Atomic layer deposition; Transparent conducting oxide; Thin films; Indium oxide

1. Introduction

Nowadays, considerable efforts are underway in the development of next generation see-through electronics such as transparent thin-film transistors (TFTs) and organic light-emitting diodes (OLEDs) [1,2]. Especially, transparent oxide semiconductors such as In–Ga–Zn–O (IGZO) and related materials have been intensively studied for TFT applications [3]. In addition, transparent conducting oxides (TCO) are also becoming the electrodes of choice to realize fully transparent devices. Transparent electrodes require high optical transmittance ($>80\%$) in the visible region of the electromagnetic spectrum and low resistivity of the order of $\sim 10^{-4}\ \Omega$ cm [4].

Indium oxide (In_2O_3) is a promising candidate TCO material that has been constantly studied by several research groups [2,3,5]. In_2O_3 films can be grown using a variety of methods such as pulsed laser deposition (PLD) [6], sputtering [7,8], chemical vapor deposition (CVD) [9,10], and atomic layer deposition (ALD) [11,12]. State of the art displays are anticipated to require large area uniformity and low temperature processes, especially for the fabrication of mechanically flexible displays on polymer substrates. In that regard, atomic layer deposition (ALD) is a versatile film growth technique that can meet the above requirements [13,14].

ALD growth of In_2O_3 has been formerly investigated using various precursors. However, most precursors used in previous reports either result in high resistivity films or necessitate high deposition temperatures, often exhibiting relatively low growth rates. The use of $InCl_3$ precursor required excessively high deposition temperatures (~ 500 °C), resulting in low growth rate (<0.3 Å/cycle) [15,16]. Also, $In(acac)_3$ [17] and Trimethyl In [18,19] precursors resulted in low growth rates (<0.4 Å/cycle) and high resistivity ($3 \times 10^{-2}\ \Omega$ cm) films. When InCp is used as the precursor, relatively high growth rates may be achieved (1.3 Å/cycle) [20–22], however strong oxidants such as ozone are needed in order to obtain oxide films, otherwise H_2O and O_2 must be injected simultaneously to stimulate the precursor oxidation. In addition, high resistivity values ($\sim 1.6 \times 10^{-2}\ \Omega$ cm) were

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observed in In_2O_3 grown with InCp and ozone, due to the removal of an intrinsic donor [20].

All of the above precursors exist in a solid state at room temperature, which may not be appropriate for use in commercial CVD and ALD instruments. As an alternative, liquid In precursors are anticipated to be more advantageous for practical growth of indium oxides, especially to deposit low resistivity films at moderate temperatures with high growth rates. In this study, we report on the microstructure, electrical and optical properties of In_2O_3 films prepared using a liquid precursor; [3-(dimethylamino)propyl]dimethyl indium (DADI). The deposited In_2O_3 films exhibit relatively high growth rates at temperatures above 250 °C and low resistivity ($9.2 \times 10^{-5}\ \Omega$ cm) with high optical transmittance.

2. Experimental procedures

A homemade ALD system was employed for the deposition of 40 nm-thick In_2O_3 films on Si wafers at a substrate temperature of 275 °C. DADI was used as the metal precursor and water vapor without bubbling was used as the reactant. N_2 was used as the carrier gas, of which the inlets are separated on the side of the chamber. The N_2 flow rate was controlled by a mass flow controller (20 sccm to purge the DADI bubbler). The precursor canister was maintained at room temperature due to the precursor's high vapor pressure. A typical ALD growth sequence for the In_2O_3 layers is composed of exposure to DADI for 1 s, N_2 purging for 10 s, and exposure to H_2O for 1 s. The precursor dose was controlled by controlling the precursor dose time. To characterize the precursor, thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed. The thicknesses and band gap widths of the deposited films were measured by spectroscopy ellipsometry (SE). The electrical resistivity, carrier concentration and Hall mobility were investigated by means of a Hall-effect measurement system. The microstructure was studied by X-ray diffraction and transmission electron microscopy (TEM). Also, the chemical composition and binding structure of In_2O_3 were investigated by X-ray photoelectron spectroscopy (XPS). The optical transmittance was observed by ultraviolet-visible spectroscopy (UV–vis).

3. Results and discussion

Fig. 1(a) and (b) shows the weight variation of the DADI precursor monitored during TGA and the heat flow into it during DSC measurement. Fig. 1(a) shows a rapid mass reduction near 70 °C, which is most likely to take place by vaporization. Another observation is the low amount of nonvolatile residue ($< 3\%$). Fig. 1(b) shows that the heat flow remains almost constant with temperature, above 50 °C, and a sharp drop occurs near 350 °C. The latter is anticipated to occur by the decomposition of the DADI precursor. Fig. 2(a) and (b) shows the growth rates of In_2O_3 deposited by ALD as functions of DADI dose and growth temperatures. The growth rate increases rapidly with increasing dose and saturates at ~0.6 Å/cycle above a dose of 3×10^{-7} mol/cm^2 at 275 °C.

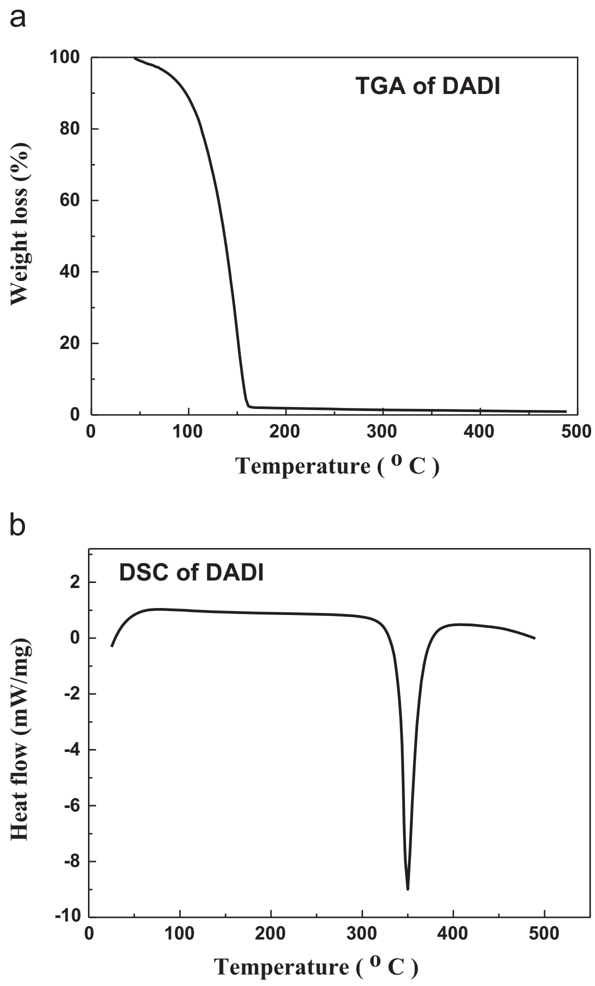

Fig. 1. (a) Thermal gravimetric analysis (TGA) and (b) differential scanning calorimetry (DSC) results of the DADI precursor.

The precursor dose was estimated using the ideal gas equation, $PV=nRT$. Here, n is the number of moles of the precursor gas injected, P the vapor pressure of the precursor, V the volume of the canister, R the gas constant, and T the temperature of the canister. After calculating the number of moles of injected precursor and dividing it by the chamber surface area, the precursor dose was obtained in mol/cm^2 [23,24]. The saturation of the growth rate indicates that typical ALD mode is achieved by self-limited adsorption of DADI on the substrate. Thus, a precursor dose of 3×10^{-7} mol/cm^2 is used in the ensuing experiments. The growth rates of In_2O_3 ALD at various substrate temperatures (T_s) from T_s=150 to 250 °C, are shown in Fig. 2(b). Below 225 °C, no growth occurs, indicating that sufficiently high thermal energy must be provided to induce the surface chemical reactions between the DADI precursor and H_2O. However, above this temperature, the growth rate increases rapidly, up to 0.6 Å/cycle at 275 °C. The decomposition temperature of the precursor is estimated to be approximately 350 °C as deduced from Fig. 1 (b). Therefore in the results shown in this work, the increase in growth rate is not a result of direct thermal decomposition of the precursor molecules. It is more likely that the oxidation