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Indium tin oxide thin films crystallized at a low temperature using a nanocluster deposition technique

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The crystallized nanoclusters embedded in indium tin oxide films grown at ~60 °C without substrate heating and the triangular granular microstructure of these films deposited at 180 °C, support the potential of low-temperature nanocluster deposition. The structural, electrical and optical properties of such films were investigated at temperatures of less than 260 °C. Films approximately 85 ± 5 nm thick exhibited the lowest resistivity (2.1×10^{-3} Ω cm) and a transparency greater than 80%.

Keywords: Nanocluster deposition; Indium tin oxide; Transparent conductive oxides; Low temperatures

Transparent conductive oxide (TCO) materials are becoming increasingly important in several applications, including large flat-panel displays (FPDs), solar cells, and low-emissivity and electrochromic windows. In this regard, indium tin oxide (ITO) thin films have been extensively investigated and are widely used in optoelectronic industries as TCOs for FPDs or solar cell devices, etc. [1,2]. Reported values for the resistivity of ITO thin films obtained using various deposition methods range between 6.8 and 3×10^{-4} Ω cm with transparency greater than 85% in the visible range [3–11]. However, most of the previously reported ITO films were fabricated at temperatures above 300 °C to crystallize the thin films. However, high-temperature processing may cause serious deterioration in the performance of ITO thin-film-based devices [12]; thus, investigation of ITO thin films crystallized at low temperatures (⩽250 °C) is essential.

In this regard, metal–organic chemical vapor deposition (MOCVD) is not suitable for deposition of ITO thin films crystallized at low temperatures [8–11]. However, MOCVD has various advantages and is the most prominent emergent versatile technique for film deposition, because precursors adsorbed to substrates decompose at high temperatures. A new method, which has been termed nanocluster deposition (NCD), for low-temperature (~50 °C) deposition of crystallized Bi_3NbO_7 (BNO) high-*k* dielectric oxide thin films, has been introduced by Jeon et al. [13]. The NCD technique has shown great potential for deposition of TCO films crystallized on glass or flexible polymer substrates at temperatures below 200 °C, suggesting that in situ crystallization of ITO films at low temperatures (i.e. below 200 °C) is indeed possible. In this paper, ITO thin films crystallized using NCD at temperatures below 250 °C were grown, and their electrical and optical properties were investigated as a function of growth temperature. To grow ITO thin films using the NCD technique, the precursors must decompose at low temperatures. Trimethyl indium (TMIn, i.e. $(CH_3)_3In$)) or triethyl indium (TEIn) are frequently used as precursors during indium oxide/ITO thin-film deposition. Brien et al. [14] reported that TMIn with *N*,*N*-dimethyldodecylamine (DMDA) is one of the best precursors, and might successfully be applied to the deposition of indium oxide and/or ITO films. On the other hand, tetramethyl tin (TMT, i.e. Sn $(CH_3)_4$)) is one of the most widely used precursors for deposition of tin oxide-related materials by MOCVD.

In the present study, ITO thin films were deposited on a glass substrate at temperatures ranging from 180 to 260 °C using NCD. TMIn with an amine solution (1:1) and TMT were the source materials, and H_2O (water vapor maintained at 60 °C) and Ar were the reaction and carrier gases, respectively. The bubbler temperatures of the indium and tin sources were maintained at 30 and 50 °C, respectively. The argon flow rates for the indium and tin sources were maintained at 200 and 50 standard cc min^{-1} (sccm), respectively. Indium and tin vapors were removed by the Ar and water vapors, and directly entered the chamber. The principle of the

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NCD process, which is fundamentally different from that of conventional CVD, has been described in detail in our previous work [13]. The key factor in the use of NCD for growth of thin-films of oxide is a showerhead maintained at a high temperature. A schematic diagram of the NCD apparatus is shown in detail in Figure 1. Figure 1b shows the NCD process, which occurred at the showerhead as a result of using the bubbler in the deposition system (see Fig. 1a). The vapors of indium, tin and oxygen arrived at the showerhead, which was located 3 cm from the substrate in the growth chamber. The temperature of the showerhead was kept high for sequential decomposition of the precursors, reaction with reaction gases, and formation of ITO nanoclusters at the showerhead. During this process, the showerhead temperature and working pressure should be appropriately controlled to prevent gas-phase reactions. The showerhead temperature was constantly maintained at 325 °C, to facilitate reaction between oxygen and indium and tin vapors. Oxygen enters the chamber and then forms crystalline nanoclusters at the showerhead maintained at high temperature. The crystallized nanoclusters were directly deposited on a glass substrate maintained at a low temperature, in a manner similar to physical vapor deposition. The deposition pressure was maintained at 7.3×10^2 Pa for all deposited films, the thickness of which was approximately 85 ± 5 nm for the various deposition temperatures. The structural properties of the ITO films were studied with X-ray diffraction (XRD, Rigaku D/MAX-RC) using Cu K_α radiation and a Ni filter. The microstructure and the surface roughness of the films were investigated by scanning electron microscopy (SEM, Topcon DS-130C) and atomic force microscopy (AFM, Auto Probe CP), respectively. The thickness of the films deposited on glass substrates was determined from the SEM cross-sectional images. Electrical properties of ITO thin films were obtained by Hall measurement (HMS 3000) using the Van de Pauw method, which was performed at room temperature and at an applied magnetic field of 0.51 T on sample sizes of approximately 10–15 mm. Sheet resistance of the samples was measured using the four-point probe technique. Optical properties were measured with an HP 8453 UV–Vis spectrophotometer.

An investigation NCD of ITO was performed on Si (0 0 1) substrates for structural analysis without substrate heating. Although the substrates were not heated, the substrate temperature was approximately 60 °C because of heat transfer from the showerhead, which was kept at a high temperature (~325 °C). X-ray photoelectron spectra (XPS) and TEM cross-sectional images of the ITO thin films are shown in Figure 2. The crystallinity of the films grown at 60 °C was not identified by XRD. As shown in the TEM cross-sectional image in Figure 2b, 30 nm thick films were deposited on a Si (0 0 1) substrate and the crystallized nanoclusters with diameters ranging from 10 to 15 nm were embedded in the films. The selected-area diffraction pattern (SADP) in Figure 2c shows that the nanoclusters were clearly crystallized, and the films deposited at 60 °C were identified as an ITO phase based on the XPS spectra of each element (see Fig. 2a). In the films grown at 60 °C, an ITO single phase was identified from the XPS spectra of the films crystallized at 260 °C (data not shown here). Because the growth temperature was too low, complete crystallization of the ITO films did not occur. However, these results clearly indicate that crystallization of ITO films at a low temperature might be possible using NCD technology. The range of growth temperatures used for in situ crystallization of the ITO films was established through investigation of the structural, electrical and optical properties of the films. XRD patterns, microstructure and growth rate as functions of the deposition temperature are shown in Figure 3. As shown in Figure 3a, ITO thin films were polycrystalline even at a substrate temperature of 180 °C. At low temperature, the films were crystallized mostly in the cubic bixbyite structure of indium oxide, thereby showing predominant (2 2 2) peaks with increasing growth temperature. It is interesting to note that, at substrate temperatures greater than 220 °C, the films exhibited additional orientations in the (2 1 1) and (4 4 0) directions, together with some weak peaks along the (4 3 1) and (3 3 2) directions. As shown in Figure 3a, the (2 2 2) diffraction peak remained the dominant peak compared with all other neighboring diffraction peaks, reflecting a change in

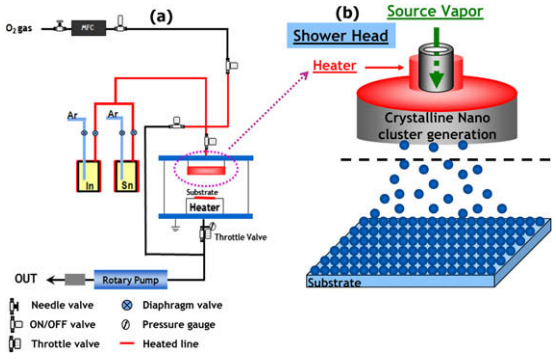

Figure 1. (a) Schematic diagram of the NCD method of ITO film growth, and (b) the detailed NCD process occurring at the showerhead.

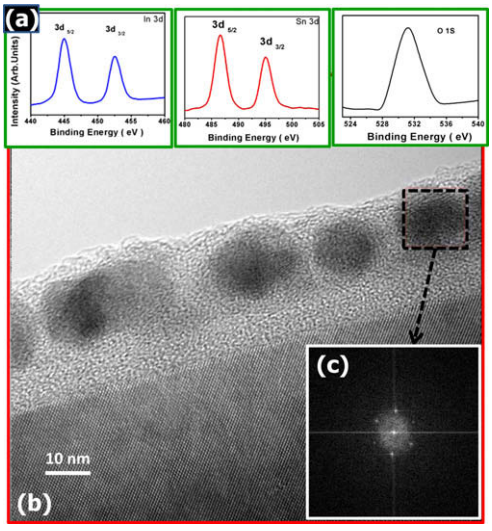

Figure 2. (a) Cross-sectional TEM image of ITO films grown at 60 °C; (b) XPS spectra of each element observed in nanoclusters embedded in the ITO films; (c) SADP of ITO nanoclusters.