Applied Surface Science 307 (2014) 455–460

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Effects of substrate and ambient gas on epitaxial growth indium oxide thin films

M. Nistor[a], W. Seiler[b], C. Hebert[c,d], E. Matei[e], J. Perrière[c,d,*]

[a] National Institute for Lasers, Plasma and Radiation Physics (NILPRP), Atomistilor Str. 109, L22 P.O. Box. MG-36, 077125 Bucharest-Magurele, Romania
[b] PIMM, UMR CNRS 8006 Arts et Métiers ParisTech, 151 Boulevard de l'Hopital, 75013 Paris, France
[c] Sorbonne Universités, UPMC Univ Paris 06, UMR 7588, INSP, F-75005 Paris, France
[d] CNRS, UMR 7588, INSP, F-75005 Paris, France
[e] National Institute of Materials Physics (NIMP), Atomistilor Str. 105 bis, P.O. Box MG-7, 077125 Magurele-Ilfov, Romania

ARTICLE INFO

Article history:
Received 20 December 2013
Received in revised form 20 March 2014
Accepted 7 April 2014
Available online 18 April 2014

Keywords:
Indium oxide
Thin films
Epitaxial growth
Nanocomposites
Pulsed electron beam deposition (PED)

ABSTRACT

Indium oxide thin films were grown by pulsed electron beam deposition method at 500 °C on c-cut sapphire and (0 0 1) oriented $LaAlO_3$ single crystal substrates in oxygen or argon gas. The effects of ambient gas and substrate symmetry on the growth of indium oxide thin films were studied. Stoichiometric In_2O_3 films are formed in oxygen, while oxygen deficient $In_2O_{2.5}$ films are grown in argon, with In metallic nanoclusters embedded in a In_2O_3 matrix (nanocomposite films). In both cases, epitaxial In_2O_3 films having the bixbyite phase were grown with various orientation relationships, depending upon the substrate symmetry and gas ambient (oxygen or argon). Domain matching epitaxy was used to describe the precise in-plane epitaxial film–substrate relationships. The differences in film texture were correlated to the differences in growth conditions, while the differences in the film properties were correlated to the film oxygen composition.

1. Introduction

Owing to its specific optical (high transparency in the visible domain) and electrical (high conductivity) properties, indium oxide (In_2O_3) is used in a lot of applications in thin film form [1–4]. However, transport properties of this oxide are still a matter of discussion [5–8], and therefore the growth of In_2O_3 epitaxial thin films has been studied to determine their intrinsic physical properties [9–11]. The ideal substrate for the epitaxial growth of In_2O_3 thin films is cubic Y-stabilized ZrO_2 (YSZ) due to the small mismatch (1.7%) between the In_2O_3 bixbyite and the YSZ fluorite [11]. Such epitaxial In_2O_3 films on YSZ present interesting transport properties [12,13] with electron mobility as high as 226 $cm^2/V\,s$ [12]. Epitaxial In_2O_3 thin films were also obtained on c-cut sapphire substrate [10] despite the higher film–substrate mismatch, but the electron mobility was lower than that for the films grown on YSZ [9]. All these results were obtained on (1 1 1) oriented In_2O_3 films. From both applied and fundamental aspects, it is important to understand the pertinent factors affecting the structural characteristics and physical properties in epitaxial In_2O_3 films.

In this paper, we report thus on the study of the growth of In oxide films formed on different substrates and under different gas ambient (oxygen and argon). Two single crystal substrates were used: c-cut sapphire and (0 0 1) oriented cubic $LaAlO_3$. For the latter substrate, epitaxial indium oxide thin films were not reported yet. According to the differences in substrates symmetry, different film textures and microstructures are expected. Moreover, as the precise oxygen composition influences the nature, structure and properties of oxide films [14–16], the effect of oxygen deficiency in indium oxide films was also checked in this work. Pulsed electron beam deposition (PED) was used to grow such films since it allows the control of the oxygen incorporation in the films [15]. Epitaxial indium oxide films were thus obtained with texture and epitaxial relationships depending upon the substrate symmetry and growth conditions. These structural differences are related to the differences in the indium and oxygen fluxes reaching the surface of the growing film, while physical properties are mainly depending on the oxygen composition of the films.

2. Experimental

The In oxide films were grown on c-cut sapphire, (1 0 0) Si and (0 0 1) $LaAlO_3$ oriented substrates by the PED method in the experimental setup previously described [8–15]. The growth system

* Corresponding author at: Sorbonne Universités, UPMC Univ Paris 06, UMR 7588, INSP, F-75005 Paris, France. Tel.: +33 1 44 27 61 29; fax: +33 1 44 27 39 82.
E-mail address: jacques.perriere@insp.jussieu.fr (J. Perrière).

http://dx.doi.org/10.1016/j.apsusc.2014.04.056
0169-4332/

consists of a pulsed-electron beam source in the channel configuration delivering pulses with 100 ns duration and 2.5 J/cm^2 fluence. Films in the 50–700 nm thickness range were grown at 500 °C. The pulsed-electron beam ablated a high purity In_2O_3 target in pure Ar or O_2 gas at a 2×10^{-2} mbar pressure. After deposition, the films were cooled down at the gas pressure used for the growth.

The thickness and composition of the films were determined by Rutherford backscattering spectrometry (RBS), using the 2.5 MeV Van de Graaff accelerator of the SAFIR IBA Laboratory, University Pierre and Marie Curie. The precise film composition was obtained via the RUMP simulation program [17]. The surface morphology of the films was studied with a Zeiss EVO 50 scanning electron microscope (SEM). The crystalline structure of the films was studied by X-ray diffraction analyses (XRD) using the Philips Xpert diffractometer PIMM—Arts et Metiers ParisTech in Paris. The nature of the crystalline phases was studied by diffraction in the Bragg–Brentano geometry, and by asymmetric diffraction, i.e. pole figure measurements. In this last geometry, the epitaxial relationships between indium oxide films and single crystal substrates were studied and the precise in-plane orientations between film and substrate were determined. The optical transmittance of the films was measured in the UV–visible range by using a Cary 100 spectrophotometer. The nature, resistivity, concentration and mobility of the carriers were determined at room temperature with a MMR technologies Inc. Hall setup in the Van der Paw geometry at 3300 Gauss magnetic field.

3. Results

It has been previously reported that in pulsed-energy beam deposition methods like PED, the stoichiometry of the oxide films is controlled by the partial oxygen pressure during the growth [15,18,19]. Indeed, the flux of oxygen atoms reaching the surface of the growing film depends upon the oxygen partial pressure (PO_2), and as a result the incorporation of oxygen atoms is reduced when PO_2 is decreased. In this work, In oxide films have been grown under either Ar at a pressure (2×10^{-2} mbar) corresponding to a low PO_2 ($<10^{-5}$ mbar), or oxygen at 2×10^{-2} mbar. Hence, the oxygen concentration changed from the ideal In_2O_3 stoichiometry to a large oxygen deficiency $In_2O_{2.5}$, by solely changing the PO_2.

The growth in oxygen leads to dense, smooth and stoichiometric In_2O_3 films as determined by RBS analysis. However, owing to the accuracy of this method for light elements determination (4%), we cannot exclude a small oxygen deficiency in the films which can play a role on their physical properties [20]. A different behaviour was observed for the films grown at 500 °C in argon. Indeed, Fig. 1a represents the recorded RBS spectrum for such a film (square symbols), whose simulation via the RUMP program leads to an overall $In_2O_{2.5}$ composition (continuous line). This overall $In_2O_{2.5}$ composition does not mean that a specific chemical phase is present in the film. In fact, in RBS measurements, the absolute numbers of In and O atoms are determined independently of the nature of chemical phases. This means that $In_2O_{2.5}$ represents an average film composition. Moreover, the RBS spectrum shows that the film presents a rough surface morphology (as deduced from the width of the back edge of In spectrum and leading edge of the silicon substrate), and this conclusion was checked by the SEM analysis (Fig. 1c), which showed the presence of nanostructures (particles) with a size in the 50 to about few hundred nm range, giving a rough surface morphology. For comparison, the RBS spectrum recorded on a film grown at room temperature in argon pressure and its simulation are also presented in Fig. 1a, showing an abrupt back edge of In spectrum and leading edge of the Si substrate which corresponds to a smooth surface morphology, confirmed by the SEM image shown in Fig. 1(b). It can thus be concluded that particles present at the film surface are

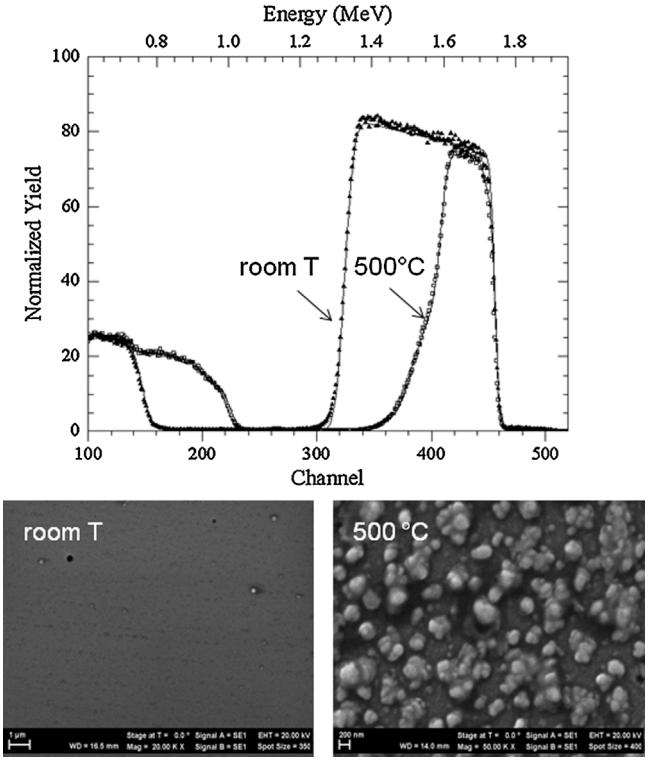

Fig. 1. (a) RBS spectra recorded (square symbols) for In_2O_3 films grown on Si substrates in argon at 500 °C and room temperature, respectively. The solid line corresponds to the simulated spectra; (b) SEM image of the surface morphology of a In_2O_3 film grown at room temperature and (c) SEM image of the surface morphology of a In_2O_3 film grown on Si substrate under argon at 500 °C substrate temperature.

thus certainly related to phenomena taking place at the film surface during the growth at elevated temperature. The driving force for the synthesis of these particles seems to be the temperature as the density and size of the particles were found to be increasing with the temperature. This could be due to the crystallization phenomenon associated with the increase in temperature. However, the temperature is not the sole parameter governing the nanostructure formation. Indeed, during PED film growth in oxygen at 500 °C (i.e. stoichiometric oxide film formation), such nanostructures are not present at the surface of the films. This indicates that the respective fluxes of indium and oxygen species reaching the film surface play a role on the surface nanostructures formation. The interpretation of this fact will be presented in the discussion part of the paper taking into account the X-ray diffraction results.

Under normal conditions, the In_2O_3 stable phase is the cubic bixbyite phase with 1.0118 nm lattice parameter. In_2O_3 is also known with the rhombohedral metastable phase (a = 5.478 Å and c = 14.51 Å), whose growth conditions have been recently studied [24]. In this work, we only observed the formation of the bixbyite In_2O_3 on c-cut sapphire or $LaAlO_3$ single crystal substrates, whatever being the gas during the PED growth.

Figs. 2 and 3 represent the XRD patterns registered on films grown in oxygen and argon on sapphire c-cut (Fig. 2) and $LaAlO_3$ (Fig. 3), respectively. The precise texture of the bixbyite phase depends upon the ambient gas during the growth and substrate. Indeed, in oxygen a (1 1 1) preferential growth is observed on c-cut sapphire (Fig. 2), while the (0 4 4) reflection peak with minor contribution from the (2 2 2) and (0 0 4) planes is observed on $LaAlO_3$ (Fig. 3). The growth in argon leads to the presence of the (2 2 2) and (0 0 4) peaks with similar intensities for the film grown on c-cut sapphire (Fig. 2). The comparison of the intensity ratio of the (0 0 4) and (2 2 2) peaks with the theoretical ratio given by the JCPDS file no. 1312-43-2, leads to the conclusion that about 75% of