Materials Science in Semiconductor Processing 88 (2018) 45–50

Contents lists available at ScienceDirect

Materials Science in Semiconductor Processing

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

Degenerate and non-degenerate In_2O_3 thin films by pulsed electron beam deposition

M. Nistor[a,*], F. Gherendi[a], J. Perrière[b,c]

[a] National Institute for Lasers, Plasma and Radiation Physics (NILPRP), L22 P.O. Box. MG-36, 77125 Bucharest-Magurele, Romania
[b] Sorbonne Universités, UPMC Univ Paris 06, UMR 7588, INSP, 4 Place Jussieu, F-75005 Paris, France
[c] CNRS, UMR 7588, INSP, 4 Place Jussieu, F-75005 Paris, France

ARTICLE INFO

Keywords:
Thin films
Indium oxide
Electrical transport
Quantum corrections
Optical properties
Pulsed electron beam deposition

ABSTRACT

Pulsed electron beam deposition (PED) was used to grow indium oxide thin films on c-cut sapphire single crystalline substrates between room temperature and 500 °C under oxygen gas. A slight difference in oxygen pressure during the PED growth (from 2×10^{-2} to 1.3×10^{-2} mbar) has strong effects on the electrical and optical film properties. The indium oxide thin films grown in these conditions changed from a non-degenerate semiconducting behaviour (at 2×10^{-2} mbar) to a degenerate semiconductor one (at 1.3×10^{-2} mbar), with a metal-insulator transition at 149 K. This crossover from strong to weak localization, evidenced in the temperature dependent resistivity curves, may be due to the effects of a structural disorder in such films. The direct optical band gap was estimated from transmission spectra taking into account non-degenerate/degenerate behaviour.

1. Introduction

Indium oxide, undoped or doped, shows unique electrical (high conductivity) and optical (high transmittance to visible light and high infrared reflectance) properties, that make this material one of the main transparent conducting oxide used in a wide variety of applications. As a matter of fact thin films of this material are currently used in solar cells, thin film transistors, flat panel displays, sensors, etc. [1–5]. Consequently, a large number of studies were devoted to the growth of indium oxide thin films by the main deposition methods, i.e. molecular beam epitaxy [1,5], evaporation [6], sputtering [7], atomic layer deposition [8], and pulsed laser deposition (PLD) [9].

More recently, pulsed-electron beam deposition (PED) has been used to grow oxide thin films and nanocomposite oxide films [10,11]. In its principle, the PED method is similar to PLD since a pulsed electron beam is used instead of a laser beam to ablate a target material with comparable power densities ($\sim 10^8$ W cm^{-2}) for the growth of thin films on substrates [10–16]. In particular, In_2O_3 films were grown by this method, showing electrical and optical properties similar to those of films grown by PLD [2,17–19]. Epitaxial In_2O_3 films were also obtained on c-cut sapphire substrate and $LaAlO_3$ [20]. The physical properties of such PED grown indium oxide films are very sensitive to the oxygen pressure during the growth, i.e. to the presence of oxygen vacancies which may act as electron donors [18].

Our aim in this work was to focus on the correlation between the electrical and optical properties of indium oxide films, and the oxygen pressure during the growth of the films, since this parameter usually plays a major role on the oxide film properties [12–15]. According to the fact that in PED the electron beam can only be obtained in a restrictive range of pressure (around 10^{-2} mbar) [10,16], the films were grown at two distinct oxygen pressures: 2 10^{-2} and 1.3 10^{-2} mbar, which are noted in what follows as high pressure HP (2 10^{-2}) and low pressure LP (1.3 10^{-2}). These films were grown at room temperature (RT) and 500 °C on c-cut sapphire single crystal substrates. Despite the slight oxygen pressure difference, the films properties were drastically different. Actually, the In_2O_3 films grown in these conditions, change from a non-degenerate semiconducting behaviour (at HP), to a degenerate semiconductor (at LP), showing a metal-insulator transition in the temperature dependent resistivity curves. Such effects are related to (i) a drastic change in the carrier density and mobility in the films, and (ii) to differences in the structural disorder of the films according to the growth conditions. The first point is directly related to the oxygen pressure during the growth, while the second one is due to the change in the electron beam characteristics associated with the different oxygen pressures used in this work.

* Corresponding author.
E-mail addresses: mnistor@infim.ro (M. Nistor), floring@infim.ro (F. Gherendi), jacques.perriere@insp.jussieu.fr (J. Perrière).

https://doi.org/10.1016/j.mssp.2018.07.024
Received 26 March 2018; Received in revised form 11 July 2018; Accepted 16 July 2018

2. Experimental set-up

In_2O_3 thin films were grown by (PED) using the home-made set-up presented in previous works [10,16,17]. An In_2O_3 ceramic target (Kurt J. Lesker Company, 99.99% pure) was ablated by the pulsed electron beam under two oxygen pressures 2 10^{-2} mbar (HP), and 1.3 10^{-2} mbar (LP) respectively. The following PED parameters were used: an external capacitor of 16 nF, a high voltage of 14 kV, repetition rate 1 Hz, 100 ns full width at half maximum (FWHM) pulse width of the electron beam, fluence of about 2 J/cm^2 and HP and LP oxygen pressures, respectively. The difference in oxygen pressure will induce some modifications in the electron beam characteristics which could have noticeable effects on the films growth [10,16].

Films about 200–600 nm thick were grown on c-cut sapphire substrates (Crystek, both side polished 10 × 10 × 0.5 mm) at RT and 500 °C. Following deposition, the samples were allowed to cool down at the oxygen pressure used for the growth. The film thickness and composition were obtained by Rutherford backscattering spectrometry (RBS) using the 2.5 MeV He^+ ion beam of the Van de Graaff accelerator of the SAFIR IBA Laboratory (University Pierre and Marie Curie). The structural characterizations were carried out by X-ray diffraction (XRD) analyses in the θ-2θ Bragg geometry using a Philips Xpert MRD with the Cu Kα radiation (λ = 0.154 nm). X-ray photoelectron spectroscopy (XPS) measurements were performed *ex-situ* within the ESCALAB Xi + spectrometer at NILPRP using the monochromated Al-Kα x-ray source (1486.6 eV). Survey spectra were measured with 100 eV pass energy and 0.1 eV energy step size, and O 1s and In 3d core levels spectra were measured with 20 eV pass energy and 0.1 eV energy step size. To remove surface contamination and preserve the film chemistry, each film was etched for 60 s by a 2 keV Ar^+ ion beam.

The resistivity, mobility and carrier density of films were measured in the van der Pauw geometry with a MMR Inc. Hall H-50 measurement system at RT under a magnetic field of 0.3 T. Ohmic point-like contacts with conductive silver epoxy were made in the four corners of the films with wire-bonded contacts. The current-voltage measurements of these contacts showed ohmic behaviour for each film investigated. Temperature dependent resistivity curves of the In_2O_3 films were measured by the classical four-probe method from room temperature to liquid helium. The transparency of the films was determined using a spectrophotometer Cary 5000 in the wavelength range 190–2500 nm.

3. Results

Whatever the growth conditions (substrate temperature and pressure), RBS measurements showed that indium oxide films does not contain impurities which could play the role of donors for n-type conductivity. Moreover, these films present a uniform in-depth composition, without any interdiffusion with the substrate as shown in Fig. 1, which represents a typical RBS spectrum obtained for a film grown at 500 °C and 1.3 10^{-2} mbar. The square symbols represent the experimental data, while the In_2O_3 composition is determined via the simulation of the spectrum with the RUMP software [21], the fit being shown in the figures by the solid line. For both pressures, a stoichiometric In_2O_3 composition was deduced from the RBS spectra. However, owing to the accuracy of RBS for light elements determination (4%), we cannot exclude a small oxygen composition difference between the films grown under LP and HP. Finally, the main difference observed between films grown under different conditions was the deposition rate, which was two times higher at LP than HP as indicated in Table 1. This difference is clearly related to the change in the electron beam characteristics due to the difference in pressure.

Fig. 2a shows θ-2θ XRD patterns of In_2O_3 films grown on c-cut sapphire substrates at RT and 500 °C under HP and LP, respectively. The films grown at 500 °C presents the bixbyite phase with (111) preferential texture, as expected for In_2O_3 films grown on c-cut sapphire substrates [17]. The axis parameter deduced from these patterns shows

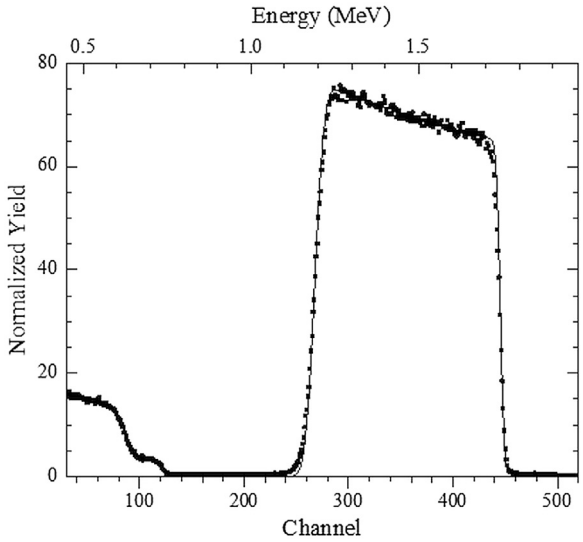

Fig. 1. Typical RBS spectra of the In_2O_3 thin films grown by PED on a single crystal c-cut sapphire substrate at 500 °C (square symbols) at LP 1.3 10^{-2} mbar oxygen (b). The solid line is the simulated spectrum.

that both films formed under LP (1.0162 nm), and HP (1.0179 nm) has a parameter larger than the bulk value (1.0118 nm) of In_2O_3. The evaluation of the crystallite size through the FWHM of the (222) peaks, varies slightly from LP (20 nm) to HP (24.9 nm). At RT the In_2O_3 films are not well crystallized: a very small (222) peak is present, superimposed on background characteristics of an amorphous phase. In Fig. 2a, the intensity of these patterns was multiplied by a factor of 50 for both pressures.

The rocking curves of the (222) reflection peak for the films grown under LP and HP are presented in Fig. 2b. A noticeable difference in the FWHM values is evidenced: the LP film showing a broader (2.44°) distribution of the (222) texture than the HP film (1.72°). A lower crystalline quality is thus present in the LP film. This difference may be due to the higher deposition rate of the LP film which can induce more structural defects during the film growth. This lower crystalline quality of the LP film is confirmed by the φ scan and pole figure measurements recorded on the LP and HP films (Figs. 1, 2 in Supplementary information). The pole figure for the HP film presented 6 well defined poles, characteristics of the epitaxial growth of In_2O_3 on the c-cut sapphire substrate, similar to the previous results [20]. Differently, the pole figure recorded on the LP film does not present very well-defined poles. It follows that only a fraction of the LP film was epitaxially grown, while the main part of the film was only (222) textured, without any in-plane epitaxial relationship with the substrate. This structural analysis leads to the conclusion that the LP film presents a higher density of structural defects by comparison with the HP film. The origin of this difference may be the higher deposition rate of the LP film.

The transport properties of the films were studied and Table 1 summarizes the results of Hall measurements at RT as a function of the growth conditions. In_2O_3 films are n-type and a slight change in the oxygen pressure leads to drastic effects on the film properties. Indeed the film grown under LP presents a resistivity that is 2 orders of magnitude lower than that of the film grown under HP at 500 °C.(Table 1). Both carrier density and mobility are ten times higher in the film grown at the lowest oxygen pressure LP (Table 1). The same trend is observed for In_2O_3 grown at RT but with a 4 orders of magnitude difference compared to the films grown at 500 °C.

Such a drastic difference in physical properties of oxide films grown under slightly different oxygen pressures has been previously observed for Nd-doped ZnO films grown by PED under 1 and 2 10^{-2} mbar oxygen pressure [10]. Actually a large variation in resistivity (five orders of magnitude) has been also observed in sputtered MoO_x films