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Epitaxial undoped indium oxide thin films: Structural and physical properties

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ABSTRACT

Indium oxide thin films were grown by the pulsed electron beam deposition method on c-cut sapphire substrates at 10^{-2} mbar oxygen pressure and temperature up to 500 °C. Such conditions lead to the formation of dense, smooth and stoichiometric In_2O_3 films, with the cubic bixbyite structure. Epitaxial thin films were obtained at substrate temperatures as low as 200 °C. Pole figure measurements indicate the existence of (111) oriented In_2O_3 crystallites with different in-plane symmetry, i.e. three-fold and six-fold symmetry. The origin of this effect may be related to the specificities of the growth method which can induce a large disorder in the oxygen network of In_2O_3 , leading then to a six-fold symmetry in the (111) plane of the bixbyite structure. This temperature resistivity behaviour shows metallic conductivity at room temperature and a metal–semiconductor transition at low temperature for In_2O_3 films grown at 200 °C, while the classical semiconductor behaviour was observed for the films grown at 400 and 500 °C. A maximum mobility of $24.7 \text{ cm}^2/\text{Vs}$ was measured at 200 °C, and then it falls off with improving the crystalline quality of films. The optical transparency is high ($> 80\%$) in a spectral range from 500 nm to 900 nm.

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1. Introduction

Indium oxide (In_2O_3) is a transparent conducting oxide which presents a high conductivity (free carriers up to 10^{17} – 10^{19} cm^{-3} range) without intentional doping [1], the origin of which is still under debate [2]. Moreover, undoped In_2O_3 thin films exhibit conductivities with 4–5 orders of magnitude higher than that of the bulk [3], and recently explained by the presence of surface donors instead of bulk defects. When doped with typically 9 at% tin oxide, indium-tin oxide (ITO) is one of the most popular transparent conducting electrode used in thin-film photovoltaics, flat-panel display devices, due to the highest transparency for visible light ($> 85\%$ at wavelengths from 340 to 780 nm) combined with the lowest electrical resistivity ($7.7 \times 10^{-5} \Omega \text{ cm}$) [4]. The recent trend towards higher quality and tailoring transparent conducting electrodes to constraints of specific electronic and solar cell technologies demands the continuous optimisation of In_2O_3 thin film properties and processing conditions [1,2].

The formation of In_2O_3 thin films has been studied by various methods such as molecular organic chemical vapour deposition [5–8], plasma assisted molecular beam epitaxy [9,10], sputtering [11], atomic layer deposition [12] or pulsed laser deposition [13]. The epitaxial growth of In_2O_3 on Y-stabilized ZrO_2 , c-cut sapphire,

InAs or MgO single crystal substrates has been already reported [4,5,13]. Whatever the growth methods, the epitaxial film formation was generally carried out at relatively high substrate temperature, i.e. $T > 500$ °C. However, the crystallisation of In_2O_3 can occur at temperatures as low as 150 °C, following previous reports [14] and studies on indium based oxide materials have indicated that optimum materials properties are obtained for substrate temperature in the 200–400 °C range [15,16]. Low growth temperatures are typically required for transparent conducting layers to avoid the degradation of the solar cell junctions. The possibility to obtain In_2O_3 films with good structural characteristics, low electrical resistivity (about $10^{-4} \Omega \text{ cm}$) and high optical transparency ($> 85\%$) on c-cut substrates in the 200–400 °C range, would open the way to new applications in thin film photovoltaics.

Our first aim in this work was thus to study the growth and properties of indium oxide films in a relatively low temperature domain ($T \leq 500$ °C), i.e. to determine the nature of the crystalline phase, its texture and eventual epitaxial relationships with single crystal substrate, and to correlate these structural characteristics with the optical and electrical properties of the films. Pulsed-electron beam deposition method (PED) which was already used to grow high quality ITO films [17] has been used for the growth of the indium oxide films. Epitaxial In_2O_3 films were thus grown on c-cut sapphire substrates in the 200–500 °C range, with various epitaxial relationships. The physical (optical and electrical) properties of these films were not related to the crystalline quality of the films, but certainly to the oxygen composition.

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2. Experimental

The In_2O_3 thin films were grown by pulsed electron beam deposition method (PED) in the experimental setup previously described [17]. The following parameters were used: an external capacitor of 16 nF, a high voltage of 14 kV, repetition rate 1–2 Hz, 100 ns full width at half maximum (FWHM) pulse width of the electron beam, fluence of about 2 J/cm^2 and an oxygen pressure of 2×10^{-2} mbar. Films with about 50–300 nm in thickness were grown on c-cut single crystal sapphire substrates under controlled substrate temperature in the room temperature to 500°C range. After deposition the films were cooled down at the oxygen pressure used for the growth, or at atmospheric oxygen pressure.

The structural characterizations were carried out by X-ray diffraction (XRD) analyses using a four circle diffractometer (Philips Xpert MRD) with the $\text{Cu K}\alpha$ radiation ($\lambda=0.154 \text{ nm}$) from the PIMM–Arts et Metiers ParisTech in Paris. The nature of the crystalline phases, their axes parameters and their eventual crystallographic textures were investigated in the symmetric Bragg–Brentano geometry. The in-plane epitaxial relationships between the film and the single crystal substrate were studied by asymmetric X-ray diffraction through pole figures measurements.

The resistivity of the In_2O_3 films was measured as a function of temperature from room temperature to liquid helium, by the classical four probe method, with *ex-situ* deposited gold electrodes and wire-bonded contacts. The resistivity and the nature, concentration and mobility of the carriers were determined with a MMR Hall measurement system (in the van der Pauw geometry) at room temperature under a magnetic field of 0.3 T. The transmittance of the films was measured with a spectrophotometer Cary 100 in the wavelength range 190–900 nm.

3. Results

The oxygen composition in oxide films plays so far a major role not only on their structural and physical properties [18–20], but also on their nature, i.e. homogeneous or heterogeneous [17,21]. Indeed, recent studies have shown that a large oxygen deficiency in indium tin oxide films can lead to the formation of a nanocomposite system with metallic clusters embedded in a stoichiometric matrix [22]. To avoid the formation of such heterogeneous nanocomposite systems, the films were grown by PED under oxygen gas which precludes large oxygen deficiencies. However oxygen vacancies could be present in the films and could play a major role on the electrical conductivity of the In_2O_3 films [23].

In_2O_3 crystallises in two distinct structures, the body-centred cubic bixbyite ($a=1.0118 \text{ nm}$) and the rhombohedral ($a=0.5478 \text{ nm}$ and $c=1.451 \text{ nm}$) structure. In our work, all the PED In_2O_3 films grown at $T \leq 500^\circ\text{C}$ were found to crystallise in the pure bixbyite structure. As a matter of fact, Fig. 1 represents typical diffraction patterns for In_2O_3 films grown on c-cut sapphire between 200 and 500°C . Two peaks located at 30.475° and 35.455° can be observed in the diagrams recorded on the film grown at 200°C . These peaks can be identified with the (222) and (004) family planes of the In_2O_3 bixbyite indicating preferential (111) and (001) textures. For increasing growth temperatures up to 500°C , the (004) peak is no longer observed, the films being highly (111) textured, and the intensity of the (222) peak is an increasing function of the growth temperature.

Considering the surface free energy of formation of the main planes of the In_2O_3 bixbyite phase, the (111) texture is expected since the high atomic density (111) plane of the bixbyite presents a lower surface free energy than the polar (001) plane, as it has been previously discussed [24]. The presence of the (001) texture

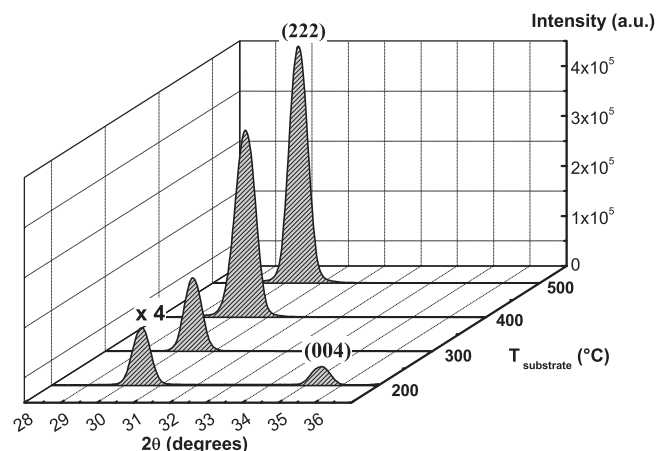


Fig. 1. θ – 2θ X-ray diffraction patterns recorded for In_2O_3 films grown on c-cut sapphire substrates at 200, 300, 400 and 500°C . The intensity of the patterns of the film grown at 200°C is multiplied by a factor of 4.

Table 1

Temperature ($^\circ\text{C}$)	200	300	400	500
(222) peak	30.475°	30.415°	30.385°	30.355°
FWHM peaksize	0.58°	0.57°	0.65°	0.60°
FWHM rocking curve	7.5°	5°	2.3°	1.6°
Crystallite size (nm)	14.2	14.4	12.6	13.7

is *a priori* unexpected from surface energy considerations, but other parameters like the fact that the c-cut sapphire plane is a polar plane and/or possible epitaxy of the (001) oriented In_2O_3 on the c-cut sapphire may play a role (see below).

Table 1 summarises the main insights drawn from these XRD patterns. The 2θ values of the (222) plane were found lower than the bulk value (30.581°), even more and more lower for increasing growth temperature. The corresponding increase in axis parameter could be due to a slight oxygen deficiency and/or the existence of stresses in the grown films. The crystallite size (coherence length) was estimated from the (222) line width using the Debye–Scherrer formulae, and was found roughly constant as a function of the growth temperature. The FWHM of rocking curves are presented in Table 1 and show decreasing values with increasing growth temperature, which means an increase in the crystalline quality of the In_2O_3 films, as it is generally observed.

Despite the high values of the film mosaicity (see Table 1), the possible epitaxy of the films was checked. Pole figures for the (044) planes of In_2O_3 ($2\theta=51.04^\circ$) were recorded on films grown between 200 and 500°C , and are presented in Fig. 2. On these figures three poles located at a declination angle ψ equal to 57.6° are observed (assigned with the * symbol). They represent the poles of the (02–24) planes of the sapphire substrate, which are observed owing to their diffracting angle 2θ (52.56°). Such poles allow us to determine the epitaxial relationships between film and substrate. For the film grown at 200°C , two series of poles are present. Twelve poles are located at a ψ value equal to 45° (assigned with the @ symbol), i.e. the value expected for the (044) poles of the (001) oriented In_2O_3 crystallites. These 12 poles are related to the respective symmetry of the film and substrate (4×3), i.e. four from cubic film and three from the rhombohedral sapphire substrate. In addition, six poles are observed at a ψ value equal to 35.3° (assigned with the # symbol), corresponding to the (111) oriented In_2O_3 crystallites. This figure also shows that three of these six poles due to (111) oriented crystallites are more intense than the others.

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