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Phase separation in oxygen deficient gallium oxide films grown by pulsed-laser deposition

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ABSTRACT

The oxygen pressure and the substrate temperature during pulsed-laser deposition play a major role on the nature and properties of gallium oxide films. At moderate substrate temperature (673 K) and under high vacuum (10^{-7} mbar) a nanocomposite film composed of Ga metallic clusters embedded in a stoichiometric Ga_2O_3 matrix may be obtained without postdeposition annealing. The growth of such films is due to a phase separation of largely oxygen deficient metastable gallium oxide films Ga_2O_x ($x = 2.3$) into the most stable phases (Ga and Ga_2O_3) and occurs for particular growth conditions. The composition and the surface morphology of films as well as their electrical behaviour are interpreted according to the effects of the parameters governing this phase separation (oxygen deficiency and temperature). It is suggested that the initial step in the disproportionation reaction is the formation of stoichiometric Ga_2O_3 nanocrystallites in the metastable sub-oxide Ga_2O_x phase. The crystallization of such nanosize particles is governed by the local distribution of oxygen and gallium species impinging the substrate during the growth and allowing nucleation centre with the Ga_2O_3 composition.

1. Introduction

Ga_2O_3 is considered as potentially interesting deep UV transparent oxide semiconductor [1]. The bulk material also exhibits original luminescence [2–4] and magnetic [5] properties due to intrinsic defects. In the prospect of integrating this material into devices several studies were interested in the modulation of the electrical and optical properties when switching to thin films. In the general case, the oxygen stoichiometry in oxide films plays so far a major role not only on their structural and physical properties [6–10], but also on their nature, i.e. homogeneous or heterogeneous [11,12]. Indeed, recent studies have shown that a large oxygen deficiency in Ga oxide films can lead to a nanocomposite system presenting an insulator to metal transition and constituted with the crystalline β-Ga_2O_3 phase and an amorphous gallium sub-oxide ($Ga_2O_{2.4-\alpha}$) [13]. This phase separation driven by solid state reactions can be therefore written as follows:

$$Ga_2O_x \rightarrow \alpha/3Ga_2O_3 + Ga_{2-2\alpha/3}O_{x-\alpha} \quad (1)$$

in which the oxygen deficient metastable Ga_2O_x oxide evolves towards the more stable phases, i.e. stoichiometric Ga_2O_3 oxide, which grows at the expense of the remaining suboxide which becomes more and more oxygen deficient and conducting [13]. Moreover, a complete phase separation at increasing oxygen deficiency (Ga_2O_x with $x < 2.3$) was further observed [14], resulting in the formation of metallic Ga clusters embedded in a stoichiometric Ga_2O_3 matrix, via the following reaction:

$$Ga_2O_x \rightarrow x/3Ga_2O_3 + (2 - 2x/3)Ga \quad (2)$$

In this case, the films present very specific transport properties [14]. Indeed, resistivity measurements as a function of temperature evidence the superconducting transition in the Ga clusters, as well as their melting and freezing temperatures through corresponding changes in the film resistivity [14]. More generally, the phase separation could occur in other oxide compounds presenting metastable sub-oxide phases, as it has been recently reported for highly substoichiometric indium tin oxide films [15,16] grown by pulsed-electron beam deposition [17,18]. In the same way, phenomena observed in indium zinc oxide (IZO), Al doped IZO or Ga doped indium oxide could be due to a phase separation in oxygen deficient materials [19–21].

In this work, our aim was to study the effects of the two main parameters governing the phase separation, i.e. the oxygen deficiency and the substrate temperature, in the particular case of gallium oxide films. Pulsed-laser deposition (PLD), which allows the control of oxygen incorporation, was used to grow the Ga oxide films. The major highlight of this paper is that the formation of Ga metallic clusters in a stoichiometric matrix can be obtained *in situ* at

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moderate substrate temperatures (673 K) without postdeposition annealing.

2. Experimental

The gallium oxide films were grown by the PLD method [22] onto c-cut sapphire substrates or thermally oxidized Si oxide films on (0 0 l) Si wafers, using a frequency quadrupled Nd:YAG laser (λ = 266 nm), in the set-up previously described [23]. The film growth occurred under vacuum (10^{-7} mbar) and substrate temperature in the room temperature (RT) to 773 K range. An *in situ* post deposition annealing at 673 K was made on films grown under vacuum (10^{-7} mbar) at room temperature.

The thickness, composition and in-depth distribution of chemical elements were measured by Rutherford backscattering spectrometry (RBS) using the 2.5 MeV Van de Graaff accelerator of the SAFIR IBA laboratory, University of Pierre and Marie Curie. The relative accuracy of oxygen in films was close to 4%. The surface morphology of the films was investigated by scanning electron microscopy (SEM – Zeiss Supra40-GREMI facilities). The SEM images were obtained with a low beam voltage of 2 kV at normal incidence and the secondary electrons were collected with an in-lens detector. X-ray diffraction diagrams (XRD) were recorded on a Philips XPert system operating in the Bragg–Brentano geometry (CuKα wavelength). The electrical resistivity of films was determined as a function of temperature via four-point (probe) measurements with gold contacts.

3. Results

Previous experiments on the oxide growth mechanisms by PLD indicate that the oxygen incorporation in the films depends on the oxygen pressure (PO_2) and/or the laser power density during the ablation process [24–26]. The flux of Ga atoms reaching the surface of films for each laser pulse can be estimated from the deposition rate assuming a sticking coefficient equal to 1. Depending upon the laser fluence (in the 1–2 J cm^{-2}) this flux of atoms was in the 10^{13}–10^{14} atoms per cm^2 per pulse [27]. As a result, oxygen deficient Ga oxide films are easily obtained by PLD [14], and a typical RBS spectrum for a film grown at room temperature and 10^{-7} mbar is presented in Fig. 1a. A $Ga_2O_{2.3}$ composition is determined from this spectrum, and for comparison purpose, the calculated RBS spectrum for a Ga_2O_3 film is also presented. This $Ga_2O_{2.3}$ composition only represents an overall or average composition, and various chemical phases can be present in the films. In addition, SEM analysis (Fig. 1b) shows that dense and smooth films are grown in these conditions. These films are amorphous, optically transparent and electrically insulating, despite the large oxygen deficiency which could induce electrical conductivity, as it has been observed in other oxide compounds [28,29].

It has been already shown that $Ga_2O_{2.4}$ films deposited at 773–873 K under Ar atmosphere then annealed in an inert atmosphere at 663 K display a strong increase of conductivity related to the disproportionation reaction previously reported [13]. To check the possibility to induce the same phase separation into our as-deposited oxygen deficient $Ga_2O_{2.3}$ films grown under vacuum at room temperature, a post deposition annealing was carried out at 673 K under vacuum (10^{-7} mbar) during 2 h. As shown in Fig. 2a (RBS spectrum) and b (SEM image), this leads to smooth films with an overall $Ga_2O_{2.5}$ composition. The effect of the post deposition annealing is just to slightly increase the incorporation of oxygen (may be due to the finite oxygen residual pressure 10^{-7} mbar). After annealing the films still remain amorphous, transparent and insulating, meaning that the simple heating of a dense and highly oxygen deficient Ga_2O_x is not efficient to induce the thermal phase separation leading to the formation of conducting clusters in a stoichiometric matrix.

Very different results are observed for Ga oxide films grown at 10^{-7} mbar at a substrate temperature of 673 K. Indeed, the RBS spectrum presented in Fig. 3a shows an in-depth variation in the oxygen concentration (see the insert) deduced from the use of the RUMP simulation program. A noticeable oxygen enrichment is present in the near surface region of the film, leading to a two-layers-like behaviour with an average $Ga_2O_{2.15}$ composition near the substrate, and a $Ga_2O_{2.75}$ near the surface layer. These formula have to be related to the global amounts of Ga and O atoms and do not correspond to a single Ga–O phase with a gradual in-depth composition in the films. Moreover, the shape of the overall spectrum with large tails on both the rear edge of the Ga contribution and front edge of the Si one indicates a rough surface morphology. This point has been checked by SEM analysis. Fig. 3b represents a SEM image of this film, which shows particles for which the lateral size (in-plane dimension) is in the 50–300 nm. However, the out of plane dimension of particles (in the overall depth of film) cannot be deduced from SEM analyses. These particles do not correspond to the classical micron size droplets often observed on PLD deposited films [30]. These particles are due to phenomena taking place during the film growth at 673 K.

Assuming that these surface particles have a Ga_2O_3 composition and cover a fraction S of the film surface, by comparison with the oxygen profile deduced from the RBS spectrum (Fig. 2a) we can deduce the following relationship:

$$3S + 2.15(1 - S) = 2.75 \text{ and thus } S \approx 70\%$$

The analysis of the SEM image (Fig. 3b) shows that such an estimation of the surface area covered by the particulates appears as a reasonable value, as a careful analysis of the SEM image leads to a similar value of surface coverage by the particles. The Ga oxide films grown in these conditions are formed by a continuous-like underlayer with a high oxygen deficiency (with an average $Ga_2O_{2.15}$ composition), mixed with a random distribution of Ga_2O_3 particles. The comparison of the overall oxygen content in films grown at RT and 673 K indicates that these quantities are almost identical. A difference cannot be evidenced within the measurement accuracy (4%). The substrate temperature during the growth plays only a role on the in-depth oxygen repartition, the oxygen incorporation being independent of the substrate temperature [14].

The films grown in these conditions are optically absorbing, electrically conducting and partly crystalline as indicated by the XRD diagram recorded on a film grown on a c-cut sapphire substrate at 673 K and 10^{-7} mbar. The large increase in intensity towards the lower diffraction angles ($2\theta < 25^\circ$) characterizes either the presence of an important amount of amorphous material in the film, or scattering by heterogeneities. In addition, broad and low intensity peaks, characteristic of a polycrystalline material, are observed in this diagram. These reflection peaks can be identified with the main planes of the Ga_2O_3 structure given in the JCPDS file 41-1103, although their intensities do not fully correspond to those given in this file that may indicate some alignment or texturing effect (Fig. 4).

At this stage, it should be noticed that the oxygen deficiency plays a major role on the physical properties of the films, and recently it has been shown that the substrate itself can also have an effect on the film properties [31]. According to the various substrates used in this study, no measurable differences were observed in the oxygen composition of films depending on the substrate within the RBS accuracy. However, the nature of the substrate plays a role on the crystallization of the films and as a consequence on the film properties. Actually, Fig. 5 shows the variations of the room temperature sheet resistance $R_\square$ of the films grown at 673 K on a