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Epitaxial growth of gallium oxide films on c-cut sapphire substrate

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ABSTRACT

The nature of the crystalline phase present in gallium oxide films grown by pulsed-laser deposition on c-cut sapphire substrate has been studied. Amorphous, polycrystalline or epitaxial gallium oxide films can be obtained depending upon the oxygen pressure during the growth in the 400–500 °C temperature range. Detailed pole figure measurements on epitaxial films demonstrate that the monoclinic β-Ga_2O_3 phase grows epitaxially on c-cut sapphire substrates at $T = 500$ °C under a 10^{-5} mbar oxygen pressure. Two distinct textures were evidenced, i.e., the $(\bar{2}01)$ and (101) planes of the monoclinic β-Ga_2O_3 phase being parallel to the c-cut sapphire substrates. The corresponding epitaxial relationships were determined and interpreted in the frame of the domain matching epitaxy. The differences in the two textures were correlated to the various atomic configurations in the $(\bar{2}01)$ and (101) planes of the monoclinic β-Ga_2O_3 phase.

1. Introduction

Gallium oxide is a wide band gap (4.9 eV) material, whose physical properties can lead to applications in various domains [1–6]. As a result, the growth of Ga_2O_3 thin films has been studied by the main chemical and physical deposition methods [7–14]. The structural characteristics and physical properties of these gallium oxide films are very sensitive to the growth conditions [15], so that the films can be either electrically insulating or conductive, opaque or transparent, and crystalline or amorphous [11,12]. Moreover, the importance of oxygen composition was evidenced [16], through a chemically driven insulator to metal transition in highly deficient gallium oxide ($Ga_2O_{2.44}$) films. These results were explained by the formation of a sub-stoichiometric and conducting phase mixed with a stoichiometric Ga_2O_3 insulating phase [16]. For larger oxygen deficiencies ($Ga_2O_{2.3}$), the oxide was found to be not stable, and a phase separation occurs leading to the synthesis of Ga nanoparticles in a stoichiometric Ga_2O_3 matrix [11,12], i.e., formation of nanocomposite oxide films. Resistivity measurements of such nanocomposite films evidence the melting and the freezing of the Ga clusters, and their superconducting transition [11,12]. Such an influence of the oxygen deficiency on the nature and properties of oxide films has also been evidenced in other oxide compounds [17–20], by the formation of nanocomposite oxide films via the phase separation.

The structural characteristics of these oxygen deficient Ga oxide films have not been precisely presented [11,16]. The aim of this paper is thus to report on the structural characteristics (nature of phase, film textures and epitaxial relationships with the substrate) of Ga oxide films formed on c-cut sapphire substrates. Bulk Ga_2O_3 has been reported to crystallize in five different structures, i.e., the α, β, δ, γ and ε phases, but the β-Ga_2O_3 monoclinic phase ($a = 1.223$ nm, $b = 0.304$ nm, $c = 0.580$ nm and $\beta = 103.70°$) is the most stable whereas the all other polymorphs are not stable and transform into the β phase at sufficiently high temperature. In the case of thin film on c-cut sapphire substrates, the β monoclinic phase has been generally observed [7,9,10,14], but the presence of the hexagonal α phase has been also reported [21]. Some works have shown that the crystalline structure of doped or not Ga oxide films could not be identified with the β monoclinic phase [22–24]. Indeed the X-ray diffraction diagrams could be due to the not clearly known ε phase [22]. Moreover, it was suggested that this ε phase could be described with an orthorhombic structure [24]. The precise axes parameters and stability domain of this possible orthorhombic ($a = 0.512$ nm, $b = 0.879$ nm, $c = 0.941$ nm) ε phase were further studied and calculated [25]. In this paper we present results dealing with the nature (monoclinic or orthorhombic) of the crystalline phases present in Ga oxide films formed by pulsed-laser deposition (PLD), on c-cut sapphire substrates. Depending upon the conditions, amorphous polycrystalline or epitaxial films have

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been obtained. This paper emphasizes the case of epitaxial growth of the monoclinic β-Ga_2O_3 phase, whose precise texture and in plane epitaxial relationships with the substrate have been determined and described in the frame of the domain matching epitaxy [26,27].

2. Experimental

Ga oxide thin films (in the 50 to 500 nm thickness range) were grown by PLD by focusing a frequency quadrupled Nd:YAG laser ($\lambda = 266$ nm, $\tau = 7$ ns, 5 Hz repetition rate) onto a Ga_2O_3 ceramic target, the experimental set-up being presented elsewhere [28]. Pulses in the 0.5 to 2 J/cm^2, i.e., in the 50 to 200 $\cdot$ 10^6 W/cm^2 power density range, were fired on the target, whose distance to the substrate was equal to 5.5 cm. The film growth on c-cut sapphire substrates was carried out under controlled pressure, between the base pressure ($5 \cdot 10^{-7}$ mbar) up to 0.1 mbar in oxygen pressure. The substrate temperature was regulated in the 300 to 500 °C range. After the deposition, films were allowed to cool to room temperature under the same oxygen pressure used for the growth.

The thickness and composition of the films were determined by Rutherford backscattering spectrometry (RBS), using the 2 MeV Van de Graaff accelerator of the INSP. Such measurements gave composition determination for the Ga cations, with a rather good accuracy, while the oxygen content was only determined with a 4% precision, owing to the low RBS yield on light elements like oxygen.

The crystalline structure of the films was studied by X-ray diffraction analyses (XRD) using the PANalytical Xpert MRD diffractometer at the INSP and at the ENSAM. The nature of the phases was investigated either in the Bragg–Brentano mode or in the grazing incidence geometry, and by asymmetric diffraction, i.e., pole figure measurements [9, 29]. In this last geometry, the epitaxial relationships between gallium oxide films and single crystal substrates were studied and the precise in-plane orientations between film and substrate were determined.

3. Results and interpretations

Previous studies on the PLD process have shown that the oxygen incorporation in oxide films can be controlled by the laser fluence and oxygen pressure P_{O_2} during the growth [17,30–32]. It follows that the pertinent parameter governing the nature, composition and properties of the Ga oxide films is the ratio of the flux of gallium [Ga] and oxygen [O] atoms reaching the surface of the growing film, i.e., the ratio [Ga]/[O] [31].

For high P_{O_2} (10^{-1} mbar), the oxygen flux is largely higher than the Ga flux emitted by the target, and stoichiometric Ga_2O_3 films are grown [11,12]. For decreasing oxygen pressure (down to 10^{-4} mbar), the ratio [Ga]/[O] increases and as a result, the incorporation of oxygen atoms in the films decreases, leading to the formation of oxygen deficient Ga oxide, i.e., Ga_2O_x with $2.5 < x < 3$. On the other hand, the films grown under vacuum ($5 \cdot 10^{-7}$ mbar), are largely oxygen deficient (Ga_2O_x with $x < 2.3$). Between these two extreme cases, an intermediate situation can be observed. Indeed, at 10^{-5} mbar and moderate laser power density, insulating and slightly absorbing $Ga_2O_{2.5}$ films are grown.

In the present work, all the Ga oxide films grown on c-cut sapphire substrates at P_{O_2} higher than 10^{-5} mbar and T < 400 °C were found to be optically transparent, insulating and amorphous [11,12]. Such a behavior has been already reported [23], and it could be the consequence of the disorder introduced by the significant oxygen deficiency and/or to the low substrate temperature, which does not allow the crystallization of the films.

The films grown under vacuum (residual pressure: $5 \cdot 10^{-7}$ mbar) were found to be widely oxygen deficient ($Ga_2O_{2.3}$), optically absorbing in the UV–Visible domain, electrically conducting [11] and polycrystalline. Fig. 1 represents typical diffraction patterns (in the grazing incidence geometry) for a film corresponding to a $Ga_2O_{2.3}$ composition. Numerous broad and low intensity peaks superimposed on a noticeable background are observed in this diagram, indicating that a fraction of the film is in the amorphous state. For comparison purpose, the position and intensity of the diffraction peaks of the monoclinic β-Ga_2O_3 phase (as given in the JCPDS 43-1012 file) are presented in this figure. A rather good agreement is observed between the peak positions and the experimental diagram which would indicate that the β-Ga_2O_3 phase is formed in the film grown under residual pressure. Previously [22] it has been reported that the diffraction diagrams of gallium oxide films could be identified with the diffraction peaks of the ε-Ga_2O_3 phase (JCPDS 11-0342 file). As the angular position of some of the diffraction peaks of this ε phase are very close to those of the β-Ga_2O_3 phase, it is not a priori possible to completely exclude the presence of this phase in the film.

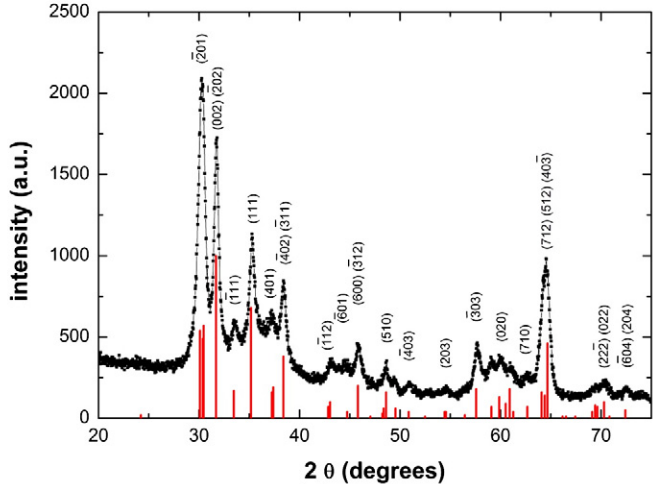

Fig. 1. X-ray diffraction diagram in grazing incidence for a gallium oxide films grown on a c-cut sapphire substrate at 400 °C under $5 \cdot 10^{-7}$ mbar (residual pressure).

In the intermediate oxygen pressure regime (about 10^{-5} mbar), crystalline gallium oxide thin films on sapphire substrates were obtained for temperatures higher than 400 °C. Fig. 2 represents a typical XRD diagram recorded in the Bragg–Brentano geometry, for a film grown at 10^{-5} mbar and 500 °C. Three intense and well defined peaks are observed in this diagram. These three peaks were already reported in the literature for Ga oxide films grown on c-cut sapphire [23,24], and can be attributed to either the $(\bar{2}01)$, $(\bar{4}02)$ and $(\bar{6}03)$ planes of the

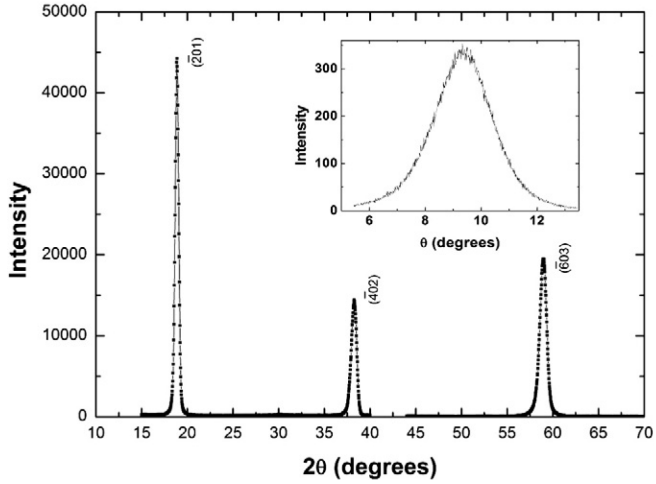

Fig. 2. X-ray diffraction diagram in the Bragg–Brentano geometry for a gallium oxide film grown in a c-cut sapphire substrate at 500 °C under 10^{-5} mbar. The inset shows the rocking curve recorded for the peak at $2\theta = 38.5°$.