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Synthesis, structuring and characterization of rare earth oxide thin films: Modeling of the effects of stress and defects on the phase stability

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ABSTRACT

This work studies the effects of the deposition parameters on the microstructure and the related residual stress in a rare earth oxide thin film. This study is focused on the yttrium sesquioxide (Y_2O_3) thin films deposited on Si (100) substrates using the ion beam sputtering technique. This technique allows the control of the microstructure and the related residual stress in the thin films by monitoring the energy of the argon beam used in the deposition process. Measurements of the stresses within the oxide layer were performed by the X-ray diffraction-$\sin^2\Psi$ method. The results show that the classic model of a pure biaxial in-plane model of stress, generally proposed in thin films, is not satisfying. A model that includes a hydrostatic stress due to the crystalline defects generated during the deposition process and a biaxial stress called a fixation stress, gives a good agreement with the experimental results. This modeling of the residual stress, based on nanometer-scale inclusions (point, extended defects) inducing a hydrostatic stress field, leads to a quantitative analysis of the nature and the concentration of the defects. This work shows results that establish a relationship between residual stress, defects and non-equilibrium phase stabilization during growth.

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1. Introduction

The rare earth oxides, RE_2O_3, exhibit several polymorphic structures: A-hexagonal (P32m), B-monoclinic (C2/m), C-cubic (Ia_3), H-hexagonal (P63/mmc) and X-fluorite (Fm3m). Phase transitions can be observed when the rare earth oxides are submitted to extreme temperatures, pressures or irradiations [1–3]. This work is focused on the yttrium sesquioxide (Y_2O_3), which has the fluorite-related structure cubic-C (bixbyite, Ia_3–Th_7). This oxide exhibits interesting physical properties making the material an appropriate choice for wave-guide applications (refractive index near $n = 2$), and photonic applications because of its ability to act as a host material for rare earth atoms. Y_2O_3 doped with Yb^{3+}, Tm^{3+}, and Er^{3+} exhibits a bright white up-conversion luminescence [4]. Generally in thin films, due to the growth conditions, the microstructure (defects, residual stress) deviates from the microstructure in the bulk materials.

This work is focused on the control of the Y_2O_3 thin film microstructure produced by the ion beam sputtering technique (IBS) that promotes low irradiation during the deposition process and then produces defects in the growing thin film. It is the atomic peening effect. These defects create strains and residual stresses that modify the stability of the structure and the physical properties of the material. Therefore it is interesting to control the microstructure of the thin film by modifying the deposition conditions and to be able to measure the related effect on the residual stress.

2. Experiments

Y_2O_3 thin films were grown on Si (100) substrates by the IBS deposition technique. Argon beams with different energies (600, 800, 1000 and 1200 eV) sputter an Y_2O_3 sintered stoichiometric target [5]. Thicknesses of 100 nm were realized at 700 °C. In this latter case post-annealing treatments were performed at 300, 700, 900 and 1000 °C in air.

The atomic concentration of each species has been determined by Rutherford backscattering spectrometry. The stoichiometry of the samples is $Y_2O_{2.7}$. The nuclear reaction analysis sensitive to light atoms confirms the oxygen content around $430 \cdot 10^{15}$ at/cm^2. All the samples have the same concentration of entrapped argon that is close to 2 at.%. Furthermore it is worth noting that the argon concentration remains unchanged after the different thermal annealing treatments that strongly modify the stress state of the thin film, indicating that argon is not involved in the residual stress evolution.

Microstructures of the Y_2O_3 thin films were analyzed by X-ray diffraction (XRD) and high-resolution transmission electron microscopy (HRTEM). XRD studies using the Bragg–Brentano geometry were performed with a 4-circle Seifert diffractometer using the Cu Kα radiation. HRTEM investigations were performed using a

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JEOL 3010 high-resolution electron microscope operated at 300 kV.

The stress measurements were realized by the XRD-$\sin^2\Psi$ method [6] that is the measurement of the lattice parameter in different crystallographic directions Ψ with respect to the normal of the surface of the sample. It is a long-range order in the (111) growth direction that is monitored. Assuming a linear relationship between the lattice parameter and $\sin^2\Psi$ and knowing the elastic constants, an in-plane biaxial stress can be obtained from the slope of the lattice parameter versus the $\sin^2\Psi$ straight lines. The elastic constants used in the calculations of the stresses are shown in Table 1.

3. Experimental results

3.1. Modification of the deposition process

All the samples deposited by IBS are textured along the (111) crystallographic direction of the cubic-C structure (Ia_3). The Y_2O_3 thin film deposited by IBS at 1200 eV exhibits a mixture of a highly defective (fluorite-like) structure and a quasi-perfect cubic-C structure that gives an asymmetric (222) X-ray profile [7,8] (Fig. 1). It is possible to strongly modify this microstructure by monitoring the energy of the argon beam used in the sputtering deposition process. Fig. 1-a shows the different (222) Bragg peaks obtained when the energy of the argon beam varies from 600 to 1200 eV. Obviously the lower this energy is, the better the crystalline quality of the thin films seems to be. It is worth noting that this quality also depends on the sputtering rate due to the ion species used in this deposition process. It is the case when xenon ions are used that give a quasi-perfect crystalline quality (not shown here). Generally annealing at different temperatures improves the crystalline quality of the as-deposited thin films, as it is shown in Fig. 1-b.

3.2. Measurements of the residual stress

Fig. 1 shows that it is possible to strongly modify the microstructure of a thin film either by modifying the deposition parameters or by annealing the as-deposited sample. As a consequence, each microstructure exhibits a different strain/stress state that can be characterized. From a given azimuthal angle Φ and different angles Ψ the measurement of the strain is realized from the relationship:

$$\varepsilon_{\Phi,\psi}^{hkl} = \frac{a_{\Phi,\Psi}^{hkl} - a_{ref}}{a_{ref}} \tag{1}$$

where a_{ref} is a reference lattice parameter in the absence of stress equal to a_O for a bulk material.

The measurements of the stresses corresponding to the thin films that are shown in Fig. 1 are depicted in Fig. 2.

Assuming a linear relationship between the lattice parameter a_ψ^{111} and $\sin^2\Psi$, it is possible to determine the evolution of the stress as a function of the deposition parameters or the annealing temperatures. When the stress has a pure in-plane biaxial character, the relationship between the lattice parameter and $\sin^2\Psi$ for a (111) direction of growth is given by:

$$a_\Psi^{111} = a_{ref}\left[1 + \left(2s_{11} + \frac{2}{3}J + \frac{S_{44}}{2}\sin^2\Psi\right)\sigma_{//}\right] \tag{2}$$

Table 1
Elastic constants obtained from Brillouin spectrometry used in the calculations of the stress in the Y_2O_3 thin films.

C_{11}/GPa	C_{12}/GPa	C_{44}/GPa	S_{11}/TPa^{-1}	S_{12}/TPa^{-1}	S_{44}/TPa^{-1}
223.70	112.40	74.60	6.73	−2.25	13.40

where s_{ij} are the elastic compliances of Y_2O_3 and J the anisotropic factor

For the sake of clarity, with yttrium oxide being a cubic almost isotropic oxide, this equation can be given by the following relationship that introduces the Poisson coefficient υ and the Young modulus E:

$$a_\psi^{111} = a_{ref}\left[1 + \left(\frac{1+\upsilon}{E}\sin^2\psi - \frac{2\upsilon}{E}\right)\sigma_{//}\right]. \tag{3}$$

The intersections of the straight lines that are obtained from the different experiments indicate the angle where the lattice parameter is stress-free. Therefore, the corresponding value of $\sin^2\Psi$ can be calculated. By using the elastic constants of Y_2O_3 (Table 1), this value is $\sin^2\Psi = 0.44$. Obviously it is not the case in our experiments as shown in Fig. 3 where $\sin^2\Psi = 1$ and 0.74. Therefore the description of the stress state in terms of an in-plane-biaxial stress field is not satisfying and should be improved by considering a triaxial stress field that is more coherent with a hydrostatic component of the stress due to the insertion of point or extended defects in the thin films during the deposition process.

A triaxial stress field model that takes into account the insertion of point defects created into the thin films is used [9]. Details and development of this analysis that is given elsewhere [10–12] introduce a hydrostatic and a so-called biaxial fixation stress component which are linearly linked: $\sigma_{hyd} = -\beta\sigma_{fix}$. This β parameter characterizes the size effect of the defects introduced in the thin film during the growth or the annealing process.

This triaxial stress field is compatible with the mechanical equilibrium that requires a normal stress component null at the surface of the film. The relationship at a free surface $\sigma_{ij} \cdot n_j = 0$ is verified. The hydrostatic stress in the matrix is balanced by the opposite stress experienced by the defects. During the growth, the film is free to contract or expand along the growth direction. The thin film is wholly characterized by a biaxial fixation stress.

The hydrostatic stress creates a hydrostatic strain

$$\varepsilon_{hyd} = \frac{a_{def} - a_0}{a_0} \tag{4}$$

where a_0 is the lattice parameter stress free and free of defects ($a_0 = 1.0604$ nm). a_{def} is the lattice parameter of the dilated thin film. This hydrostatic stress can be easily deduced from the Eshelby's model [13] and gives:

$$a_{def} = a_0\left[1 + \frac{1-2\nu}{E}\sigma_{hyd}\right]. \tag{5}$$

When the dilated sample is fixed on the substrate, the corresponding strain is:

$$\varepsilon_\psi = \frac{a_\psi - a_{def}}{a_{def}} = \frac{1+\nu}{E}\sigma_{fix}\sin^2\psi - \frac{2\nu}{E}\sigma_{fix}. \tag{6}$$

When a_{def} of Eq. (5) is introduced in Eq. (6), the relationship that gives a_ψ^{111} as a function of a_0 that includes both the hydrostatic and the fixation stresses, is:

$$a_\Psi^{111} = a_0\left[1 + \frac{1+\upsilon}{E}\sigma_{fix}\sin^2\psi - \frac{2\upsilon}{E}\sigma_{fix} + \frac{1-2\upsilon}{E}\sigma_{hyd}\right]. \tag{7}$$

In this model, two limiting cases are considered; large misfits and small misfits that give two different values of β that allow the knowledge of σ_{fix} and σ_{hyd}. This parameter can be calculated from the intersections of the straight lines in the plots of Fig. 2. From the values of β it is possible to have a good idea of the misfit and then of the crystallographic defects that are responsible of the stress.

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