Thermochimica Acta 572 (2013) 85–93

Contents lists available at ScienceDirect

Thermochimica Acta

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

Non-isothermal kinetics of phase transformations in magnetron sputtered alumina films with metastable structure

Š. Zuzjaková*, P. Zeman, Š. Kos

Department of Physics and NTIS – European Centre of Excellence, University of West Bohemia, Univerzitní, 8, 306 14 Plzeň, Czech Republic

ARTICLE INFO

Article history:
Received 12 July 2013
Received in revised form 6 September 2013
Accepted 11 September 2013
Available online 30 September 2013

Keywords:
Alumina films
Phase transformations
Non-isothermal kinetics
Kinetic triplet
Differential scanning calorimetry

ABSTRACT

The paper reports on non-isothermal kinetics of transformation processes in magnetron sputtered alumina thin films with an amorphous and γ-phase structure leading ultimately to the formation of the thermodynamically stable α-Al_2O_3 phase. Phase transformation sequences in the alumina films were investigated using differential scanning calorimetry (DSC) at four different heating rates (10, 20, 30, 40 °C/min). Three isoconversional methods (Kissinger–Akahira–Sunose (KAS), Flynn–Wall–Ozawa (FWO) and Friedman (FR) method) as well as the invariant kinetic parameters (IKP) method were used to determine the activation energies for transformation processes. Moreover, the pre-exponential factors were determined using the IKP method. The kinetic models of the transformation processes were determined using the Málek method. It was found that the as-deposited structure of alumina films affects kinetics of the transformation processes. The film with the amorphous as-deposited structure heated at 40 °C/min transforms to the crystalline γ phase at a temperature of ~930 °C ($E_{a,\mathrm{IKP}} = 463 \pm 10$ kJ/mol) and subsequently to the crystalline α phase at a temperature of ~1200 °C ($E_{a,\mathrm{IKP}} = 589 \pm 10$ kJ/mol). The film with the crystalline γ-phase structure heated at 40 °C/min is thermally stable up to ~1100 °C and transforms to the crystalline α phase ($E_{a,\mathrm{IKP}} = 511 \pm 16$ kJ/mol) at a temperature of ~1195 °C. The empirical two-parameter Šesták–Berggren kinetic model was found to be the most adequate one to describe all transformation processes in magnetron sputtered alumina films.

1. Introduction

Alumina (Al_2O_3), the only solid oxide of aluminium, and alumina based materials are widely used for widespread applications, where high thermal stability, high hardness and wear resistance are demanded. Alumina occurs in several metastable (χ, κ, η, γ, δ, θ) phases and only one thermodynamically stable α phase [1,2].

Transparent and wear-resistant alumina thin-film materials with the α-phase structure can be prepared by CVD (chemical vapour deposition) and PVD (physical vapour deposition). A drawback of CVD processes is a high deposition temperature (~1000 °C), which limits the choice of heat sensitive substrates [3,4]. On the other hand, special PVD processes, such as high power impulse magnetron sputtering [5] or AC inverted cylindrical magnetron sputtering [6], allow to prepare alumina films with a predominant α-phase structure at lower temperatures ($\leq$650 °C).

In most cases, magnetron sputtering produces alumina films at temperatures lower than 600 °C, which results, however, in a metastable structure of the films [7–9]. Post-deposition annealing of the metastable films leads to succesive phase transformations and finally to a formation of the α phase. The number of metastable phases occurring during annealing and the temperature range of their presence depend on an as-deposited structure and deposition conditions [10,11]. In our previous work [7], where the thermal stability of alumina thin films with the γ-phase as-deposited structure has been investigated, we found that the γ phase is stable up to 1000 °C and starts to transform to the α phase at a temperature of ~1050 °C. The γ-to-α transformation is, however, accompanied by cracking of the film due to a difference in mass densities of the two phases ($\rho_\gamma = 3.65\ \mathrm{g/cm^3}$, $\rho_\alpha = 3.99\ \mathrm{g/cm^3}$ [1]). Hence, understanding the kinetics of individual transformation processes in magnetron sputtered alumina thin films is crucial for the control of their thermal stability.

Several authors have reported studies on the kinetics of phase transformations in alumina and alumina based bulk materials. The apparent activation energies for the γ-to-α transformation determined using isothermal kinetics were reported in the range of 200–620 kJ/mol [12–15]. Non-isothermal kinetic analyses of the same transformation yielded the values in the range of 450–600 kJ/mol [16–19]. A direct comparison of the apparent activation energies is an issue because of a difference in investigation methods, experimental conditions and initial materials used for the alumina production.

Although much information about the transformation processes in alumina bulk materials can be found in the literature, a comprehensive kinetic analysis of the transformation processes in alumina

---

* Corresponding author. Tel.: +420 377632265.
E-mail address: sazuz@kfy.zcu.cz (Š. Zuzjaková).

0040-6031/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.tca.2013.09.019

thin-film materials is still missing. The aim of this article is to analyze alumina thin films with different as-deposited metastable structures from a kinetical point of view and to find the activation energies, pre-exponential factors and kinetic models (kinetic triplets) for the mathematical description of all transformation processes during post-deposition annealing.

2. Methodology

2.1. Experimental details

Alumina thin films with different structures were prepared by reactive dc pulsed magnetron sputtering in an Ar + O_2 mixture using a dual magnetron system equipped with two Al targets (99.5% purity). For more technical details concerning the deposition system, see our previous paper [7]. The films were deposited in the oxide mode of sputtering onto substrates held at a floating potential at the following constant deposition parameters: the substrate-to-target distance $d_{s-t} = 110$ mm, the oxygen partial pressure $p_{O_2} = 0.2$ Pa and the total pressure $p_T = 1.5$ Pa. The substrate temperature and discharge power were selected as the important parameters determining the final as-deposited structure of the films. Heating of the substrate up to 500 °C and the discharge power of 1.2 kW resulted in a crystalline γ-phase structure. On the contrary, holding the substrate at room temperature and a low discharge power of 0.6 kW resulted in the deposition of a film with an amorphous structure.

The phase transformations in the alumina films were investigated by differential scanning calorimetry (DSC) using a Setaram Labsys DSC 1600 system. The calorimeter was calibrated by melting of Al, Ag and Ni standards with purity of 99.998 ± 0.001. The DSC analysis was carried out in synthetic atmospheric air flowing with a rate of 1 l/h under non-isothermal linear regimes in the temperature range from room temperature up to 1300 °C. The heating rates were 10, 20, 30 and 40 °C/min.

To obtain a sufficient DSC signal and to exclude an influence of a substrate, approximately 4 μm thick films were deposited onto aluminium foils (50 mm × 50 mm × 0.1 mm), which were subsequently chemically removed using hydrochloric acid with a concentration of 19%. After filtering, washing in water and drying, freestanding film fragments were mechanically ground in an agate mortar to provide a fine powder. A mass of approximately 4 mg of the powder was charged into a 100 μl alumina crucible covered with a lid and used for each DSC measurement. An identical uncharged crucible was used as a reference. Each run was immediately followed by a second run under the same conditions to serve as a baseline.

X-ray diffraction (XRD) measurements of as-deposited and annealed films after their cooling down to room temperature were carried out on a PANalytical XíPert PRO diffractometer working in the Bragg–Brentano configuration using Cu Kα radiation ($\lambda = 0.154187$ nm). The data were collected using an ultrafast detector X'Celerator in the 2θ range of 15–95° with a scanning step size of 0.02° and a counting time of 50 s per step.

2.2. Kinetic analysis

The experimental results of the non-isothermal differential scanning calorimetry can be used to calculate kinetic parameters for the mathematical description of the process investigated.

The reaction rate of the process at a fixed heating rate can be expressed as:

$$\frac{d\alpha}{dt} = \beta\frac{d\alpha}{dT} = A\exp\left(-\frac{E_a}{RT}\right)f(\alpha) \qquad (1)$$

where α is the dimensionless conversion fraction ranging from 0 to 1 representing the measure of the reaction process, β (°C/min) is the experimental heating rate, A (min^{-1}) is the pre-exponential factor, $f(\alpha)$ is a dimensionless conversion function representing the kinetic model, E_a (kJ/mol) is the apparent activation energy, T (K) is the absolute temperature and R (kJ/mol K) is the universal gas constant. In this form, Eq. (1) provides a basis for differential kinetic methods for the evaluation of the apparent activation energy. In this work, the isoconversional Friedman method based on logarithmic expression of Eq. (1) was used:

$$\ln\left(\beta\frac{d\alpha}{dT}\right) = \ln(Af(\alpha)) - \frac{E_a}{RT_\alpha} \qquad (2)$$

At each given conversion fraction α, the value of E_a is determined from the slope of a plot of $\ln(\beta\, d\alpha/dT)$ versus $1/T_\alpha$.

Integration of Eq. (1) leads to the expression of the integral form of the kinetic model $g(\alpha)$:

$$g(\alpha) \equiv \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta}\int_0^T \exp\left(-\frac{E_a}{RT}\right)dT \qquad (3)$$

This equation lays the foundation for integral kinetic methods. The temperature integral on the right side of Eq. (3) can be expressed in terms of the exponential integral [20]. There is a number of integral isoconversional methods that differ in approximations of the temperature/exponential integral. In this work, the isoconversional Kissinger–Akahira–Sunose (KAS) method [21,22] with the Coats–Redfern approximation [23] and the Flynn–Wall–Ozawa (FWO) method [24,25] with the Doyle approximation [26] of the temperature integral were used.

The KAS method is based on the formula:

$$\ln\left(\frac{\beta}{T_\alpha^2}\right) = \ln\left(\frac{AR}{E_a g(\alpha)}\right) - \frac{E_a}{RT_\alpha} \qquad (4)$$

For each conversion fraction α the plot of $\ln(\beta/{T_\alpha}^2)$ versus $1/T_\alpha$ yields a straight line whose slope is used for the activation energy evaluation.

The FWO method is based on Eq. (5):

$$\log(\beta) = \log\left(\frac{AE_a}{g(\alpha)R}\right) - 2.315 - \frac{0.4567E_a}{RT_\alpha} \qquad (5)$$

For each conversion fraction α the plot of $\log(\beta)$ versus $1/T_\alpha$ yields a straight line whose slope was used for the activation energy evaluation.

If the evaluated activation energy is independent of the conversion fraction, the transformation investigated is simple from the kinetical point of view and can be mathematically described by a unique set of kinetic parameters – activation energy, pre-exponential factor and kinetic model.

To determine the activation energy and pre-exponential factor of the transformation process, the invariant kinetic parameters method (IKP) was used [27]. The IKP method is based on the observation that the same experimental conversion curve ($\alpha = \alpha(T)$) can be described relatively correctly by various kinetic models. The substitution of different kinetic models $f_i(\alpha)$, listed in Table 1, into the integral form of the KAS method (Eq. (4)) leads to:

$$\ln\left(\frac{g_i(\alpha)}{T_\alpha^2}\right) = \ln\left(\frac{AR}{E_a\beta}\right) - \frac{E_a}{RT_\alpha} \qquad (6)$$

where $g_i(\alpha)$ is the corresponding integral form of the kinetic model $f_i(\alpha)$, see Eq. (3).

Fitting this equation with different models to experimental data yields different pairs of the kinetic parameters ($\ln A_i$ and E_i). Although the parameters vary widely with $f_i(\alpha)$ they all show a strong correlation known as a compensation effect:

$$\ln A_i = aE_i + b \qquad (7)$$