Journal of Nuclear Materials 455 (2014) 189–193

Contents lists available at ScienceDirect

Journal of Nuclear Materials

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

Phase structure and surface morphology evolution of Al–Ti–O films irradiated by electron beam

J.J. Yang *, F.M. Miao, H.L. Zhu, X.Y. Shu, B. Huang, J. Tang, J.L. Liao, Y.Y. Yang, N. Liu

Key Laboratory of Radiation Physics and Technology of Ministry of Education, Institute of Nuclear Science and Technology, Sichuan University, Chengdu 610064, China

ARTICLE INFO

Article history:
Available online 14 June 2014

ABSTRACT

Al–Ti–O films were prepared on Si substrates by reactive magnetron sputtering technology. Then the as-deposited and annealed films were treated by electron beam irradiation. The phase structure and surface morphology of the films were investigated by scanning electron microscopy and atomic force microscopy. Especially, height–height correlation function measurement was introduced to quantitatively characterize the film surface evolution. The results show that both electron irradiation and annealing induce well-crystallization of as-deposited films, while the irradiation leads to the phase change of annealed films. In contrast to those of as-deposited films, the surface morphologies of annealed films exhibits roughening characteristic and steep local surface slope due to the formation of new phases and the preferred grain growth. The electron irradiation can result in a rougher surface due to the irradiation-induced structural damage.

1. Introduction

In international thermonuclear experimental reactor (ITER), one of the essential issues in design of test blanket module (TBM) is the permeation of hydrogen isotopes through the structural materials into the secondary circuit [1]. The use of thin film as tritium permeation barrier (TPB) is an effective solution to solve this problem. Among them, Al_2O_3-based film has been regarded as a promising candidate of TPB due to its excellent tritium permeation resistance, irradiation resistance, and compatibility with Li–Pb [2,3]. However, Al_2O_3 is a polymorphous material with several metastable phases and only one stable rhombohedral Al_2O_3 phase. High deposition temperature of about 1000 °C is usually necessary to prepare the thermally stable Al_2O_3 films [4]. This situation strongly limits the application of Al_2O_3 as TPB due to the fact the high temperature treatment deteriorates the mechanical properties of structural components. Thus, numerous efforts have been devoted to the development of deposition process or method which allows the crystallization temperature of stable Al_2O_3 phase to be decreased.

The addition of selected elements into Al_2O_3 films seems to be a potential approach for decreasing the crystallization temperature of Al_2O_3 films. Recently, Musil et al. [5] studied the effect of Ti addition into Al_2O_3 films on their structure, mechanical properties, and thermal stability. They demonstrated that the well-crystallization Al–Ti–O films can be yielded at low deposition temperature (⩽500 °C) by regulating the Ti content in the films. Meanwhile, a moderate addition of Ti can enhance the film hardness and oxidation resistance. In addition, several researchers also studied the preparation, microstructure, and optical properties of Al–Ti–O films [6–8]. However, referring to the application of Al–Ti–O film as TPB, there are few studies on the irradiation response of film microstructure and properties.

The objective in this study is thus to make a fundamental study on the effect of electron beam irradiation on phase structure and surface morphology of Al–Ti–O films. Especially, the height–height correlation function is first introduced to quantitatively characterize the irradiation-induced surface evolution. Further, the microscopic mechanisms for the evolution of phase structure and surface morphology induced by electron irradiation are discussed in detail.

2. Experimental details

Ternary Al–Ti–O films were deposited on single-crystalline Si substrates by reactive magnetron sputtering technology. The deposition was performed by simultaneously sputtering Al (99.99% purity) and Ti targets (99.99% purity) in an Ar + O_2 mixture gas (base pressure is 5×10^{-5} Pa). The Ar flow rate was 200 sccm and the O_2 flow rate was 30 sccm. The sputtering gas pressure was controlled at 0.6 Pa by a throttle valve. The sputtering power of Al and Ti were 300 W and 100 W, respectively. The deposition rate is about 20 nm/min. A series of Al–Ti–O films with different thicknesses (200 nm–1 μm) were obtained by varying sputtering

* Corresponding author. Tel.: +86 02885412613.
E-mail address: jjyang@scu.edu.cn (J.J. Yang).

http://dx.doi.org/10.1016/j.jnucmat.2014.06.006
0022-3115/

time. After film deposition, some samples were annealed in vacuum ambient (3×10^{-5} Pa) at 700 °C for 30 min. Then the as-deposited and annealed films with the deposition time of 30 min were irradiated by the high-energy electron accelerator at Key Laboratory of Radiation Physics and Technology of Ministry of Education, Sichuan University, China. The irradiation processes were carried out in ambient atmosphere at room temperature with the electron beam energy of 1.5 MeV and the beam current of 8 μA. The irradiation fluence changed from 2.4×10^{14} e/cm^2 to 2.4×10^{15} e/cm^2 by varying the irradiation time from 5 min to 50 min.

Film chemical composition was analyzed using energy dispersive spectroscopy (EDS) attached to scanning electron microscope (SEM). Within experimental uncertainty, all films almost have the same element composition: 20–22 at.% Al, 10–12 at.% Ti, 66–70 at.% O. Film phase structure was investigated by X-ray diffraction (XRD) operating in θ–2θ mode with monochromatic Cu Kα radiation (λ = 0.15406 nm). Film surface morphology was characterized by atomic force microscope (AFM, Si_3N_4 tip) with tapping mode under atmospheric conditions. The AFM provided height data with a resolution of 512 × 512 pixels. A planar background was subtracted from the data to compensate for the tilt of sample relative to the scanning plane. The results were checked for reproducibility by imaging several regions of the same sample and varying scanning area.

3. Results and discussion

3.1. Phase structure

Fig. 1 shows typical XRD spectra of Al–Ti–O films. For as-deposited films, only two weak diffraction peaks corresponding

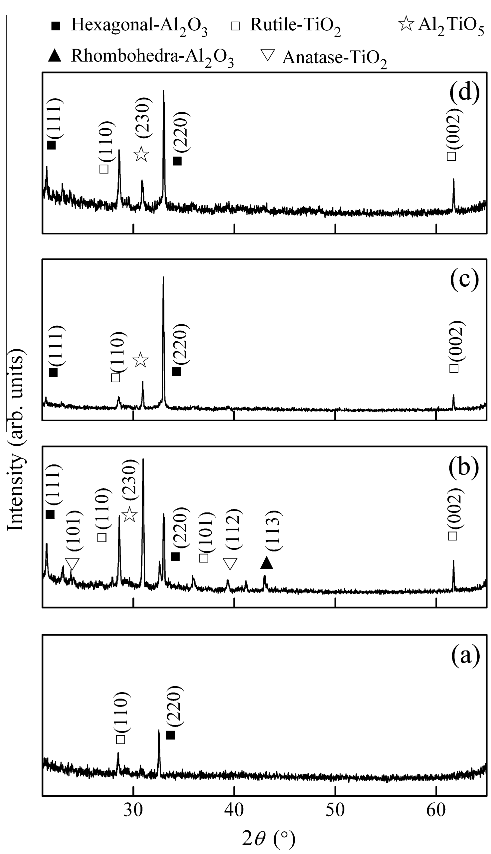

Fig. 1. Typical XRD patterns of (a) as-deposited and (b) annealed Al–Ti–O films, and (c) as-deposited and (d) annealed Al–Ti–O films irradiated by electron beam.

respectively to the (1 1 0) orientation of rutile TiO_2 and the (2 2 0) orientation of hexagonal Al_2O_3 are observed. This suggests that the films could include amorphous or nano-crystallines. Previous studies demonstrated that Al–Ti–O film deposited at room temperature mainly presents amorphous phase due to its low atomic mobility [9]. For annealed films, a well-crystallization pattern of XRD spectrum is found. There are several diffraction peaks corresponding to the orientations of rutile TiO_2 [(1 1 0), (1 0 1), and (0 0 2)], anatase TiO_2 [(1 0 1) and (1 1 2)], hexagonal Al_2O_3 [(1 1 1) and (2 2 0)], rhombohedra Al_2O_3 (1 1 3), as well as orthorhombic Al_2TiO_5 (2 3 0). In contrast to those of as-deposited films, the diffraction peaks of rutile TiO_2 and monoclinic Al_2O_3 are sharper and stronger, implying the annealing-induced grain growth. Meanwhile, several new phases emerge under our annealing temperature of 700 °C. Stable rhombohedra Al_2O_3 is observed, which is often obtained at very high temperature of about 1000 °C [4]; Al_2TiO_5 intermetallic oxide is also found because of the Al/Ti compositional ratio in our case [5]. Obviously, this result shows that the addition of Ti into Al_2O_3 films can result in the decrease of crystallization temperature. After electron irradiation, two distinct evolution behaviors of phase structures for as-deposited and annealed films are observed, respectively. For the former, the irradiation also leads to the sharpening of diffraction peaks, indicating obvious grain growth. For annealed films treated by electron irradiation, the diffraction peaks of anatase TiO_2 and rhombohedra Al_2O_3 disappear, and the Al_2TiO_5 phase reduces. This similar phase transition under electron irradiation impact was also observed in previous studies [10]. It should be noted that, the electron irradiation seems to yield the similar phases for as-deposited and annealed films. Only the diffraction peaks of rutile TiO_2 [(1 1 0), (1 0 1), and (0 0 2)], hexagonal Al_2O_3 [(1 1 1) and (2 2 0)], and orthorhombic Al_2TiO_5 (2 3 0) can be observed in the two cases. This phenomenon shows that the mechanism of electron irradiation induced phase transition could be similar for the as-deposited and annealed films.

To understand this mechanism, two factors should be considered. The first is the temperature rise of the sample due to the heating by electron irradiation. The second is the atom mobility and arrangement related to irradiation-induced damage. The temperature rise due to beam heating for film sample is approximatively estimated by Eq. (1) [11,12]:

$$\Delta T = W_0[1 + 2\ln(R/r_0)]/4\pi l_0 k \ (W_0 = \varepsilon V \rho_0 \pi r_0^2). \tag{1}$$

Here W_0 is the total absorbed power; R is the radius of film sample; r_0 is the radius of irradiated region; l_0 is the film thickness; k is the thermal conductivity; ε is the fraction of energy absorbed, usually 0.01; V is the accelerating voltage; ρ_0 is the current intensity. In our case, R equals to r_0 (=1 cm) due to the fact that the sample surface is irradiated fully, and l_0 is about 600 nm. The k values are 10 W/m^{-1} K^{-1} for Al_2O_3 and 1.8 W/m^{-1} K^{-1} for TiO_2, respectively. According to the film chemical composition (the atomic ratio of Al:Ti ≈ 2:1), the k value of 5.9 is used. For the electron beam with ρ_0 = 800 μA/m^2 and V = 1.5 MV, the temperature rise is about 65 K. Clearly, the effect of irradiation heating on film phase structure could be excluded. On the other hand, the phase structure transition induced by electron irradiation has been studied previously. Chen et al. [10] investigated the electron irradiation induced phase transformations between Al_2O_3 polymorphs. They showed that the transformation of stable α-Al_2O_3 to metastable κ-Al_2O_3 phases arises from the knock-on collision between incident electrons and Al^{3+} cations. Hong et al. [13] investigated the effect of electron irradiation on the texture of tin-doped indium oxide (ITO) films. They suggested that the preferred grain growth occurs with irradiation proceeding. Additional supports can be found in these studies on the electron irradiation induced phase and/or