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Characteristics of alumina films formed by the annealed aluminum films at high temperatures in air

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Abstract. Al films (about 40 nm) were prepared on quartz substrates by thermal evaporation technique, and subsequently annealed in air for 1h at temperature ranging from 600 to 1300°C. The characteristics of the annealed films were investigated in this paper. The measurement results of XRD and Raman show that crystalline phase transformations of the annealed films will convert from γ, γ and α, up to α-Al_2O_3 with the increasing of the annealing temperature at 600 °C, 1200 °C, to 1300°C. AFM and transmission spectra reveal the effects of phase transformations on their morphology and optical properties.

Introduction

Alumina exists in several crystallographic polymorphs [1], and its films are used in wide range of applications including microelectronics and catalysis, as well as diffusion and thermal barrier and wear resistant coatings [2]. The stable α-Al_2O_3 is more preferred than other forms of Al_2O_3 because of its excellent mechanical, chemical properties and thermal stability. Generally α-Al_2O_3 is deposited by Chemical Vapor Deposition (CVD) techniques at high substrate temperatures of 1000°C [3]. It is difficult to maintain high substrate temperatures during deposition and also deteriorates chamber vacuum. Lot of effort has recently been devoted in finding techniques to deposit crystalline alumina films at lower temperatures [4-6]. One method that has attracted attention for crystallization of amorphous films is thermal annealing after the deposition of amorphous alumina [7].

In previous investigations, it is found that amorphous alumina will convert to γ-Al_2O_3 at 300-900°C [6,8,9].In a preceding study author discovery the Al film prepared by thermal evaporation will convert to γ-Al_2O_3 annealing in air for 1h at 600°C. It is, therefore, quite probable that α-Al_2O_3 is obtained by the Al films annealed in air. In this study, Al films, 40 nm in thickness, prepared by thermal evaporation are annealed in air for 1h from 600 °C, till the films convert to α-Al_2O_3. The effects of annealing in air on structure, morphology and optical properties of the films are studied.

Experimental details

The samples were obtained by the Al films annealed in air for 1h at temperature ranging from 600 to 1300°C. The Al films were prepared on quartz substrates by thermal evaporation using Al (99.99% purity) strips. Electric current for evaporation was 70 to 75 ampere and deposition pressure was 5.0×10^{-3} Pa. The deposition rate and thickness (about 40nm) were measured with a quartz crystal micro balance. The crystal structure of the samples was examined by X-ray diffraction

(XRD) and Raman spectra (RS). XRD study was carried out on an X-ray diffraction meter (RIGAKU D/MAX2500) with high-intensity Cu K_{α} radiation (λ=1.5418 Å). Raman spectra were taken in the backscattering geometry at room temperature using a RENISHAW 2000 system. An argon ion laser(514.5 nm)was employed as the excitation source. The surface morphology of the samples was examined by atomic force microscopy (AFM) (CSPM 4000). The transmittance were measured in the 200<λ<800 nm wavelength range by use of a double beam spectrophotometer (UV—2450).

Results and discussion.

2.1 The crystal structure.

The as-deposited Al film was amorphous. The films were oxidized to Al_2O_3 when annealing temperature is higher than above 600 °C. The phase converted from γ, γ and α, up to α with the increasing of the annealing temperature at 600 °C, 1200 °C, to 1300 °C. Fig.1 shows the phase transformations. For the film annealed at 600°C, γ-Al_2O_3 phases could be observed in Fig.1(a(1)) with Fd3m (Fcc) structure having lattice parameters a=7.90 Å[10], and there only existed γ-Al_2O_3 phase because of no peak RS in Fig.1(b(1))[12]. When the annealing temperature increased to 1200°C, γ and α-Al_2O_3 phases exhibited clearly in Fig.1(a(2)), the two RS peaks of α-Al_2O_3 were observed at 415, and 430 cm^{-1}[13],but there were some other peaks unknown (marked with # in Fig. 1(b(2))) which was a result of coexistence of γ and α-Al_2O_3 phases in XRD. Pure α-Al_2O_3 phases appeared in the film annealed at 1300 °C(Fig.1(a(3))), and almost all the diffraction peaks were identified as belonging to α-Al_2O_3 with $R\bar{3}c$ (RH)structure having lattice parameters a=4.76Å and c=12.99Å[11]. In RS results Fig.1(b(3)), 437 and 483 cm^{-1} belonged to α-Al_2O_3[13], 600, 792and 1049 cm^{-1} were attributed to the surface carbonate species and other oxygen species adsorbed on the film.

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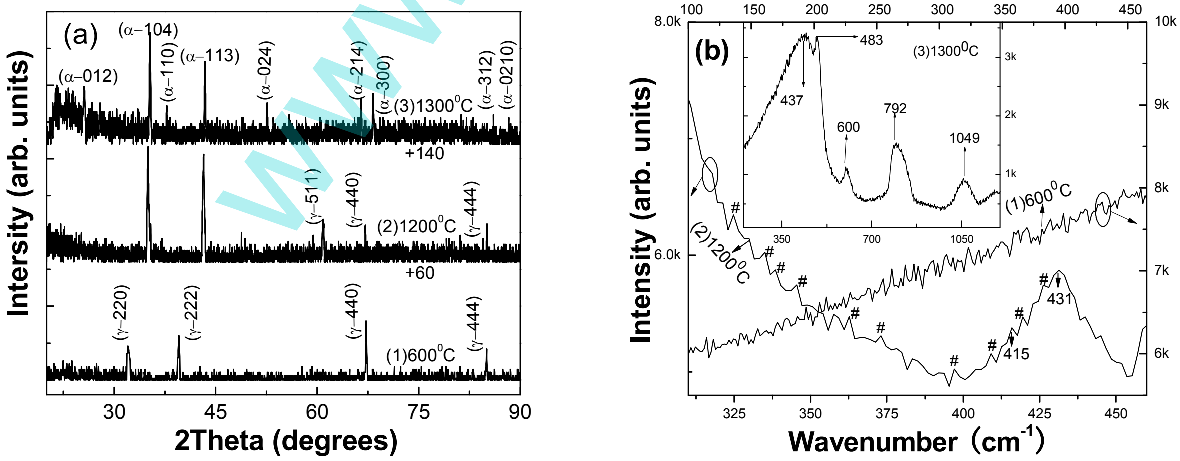

Fig. 1. (a)XRD and (b)RS of the annealed Al films in air for 1h at (1)600,(2)1200 and (3)1300°C.

2.2 The surface morphology and Optical properties.

The surface morphology and transmission spectra of the annealed Al films in air for 1h at 600, 1200 and 1300°C are presented in Fig.2 and 3. As shown in Figs. 2(a), for the film annealed at 600°C, the porous surface morphology indicates clearly γ-Al_2O_3. There are some big grains are visible on the porous surface of the film annealed at 1200°C in Figs. 2(b). The transmission curves of the film annealed at 600 and 1200°C are similar. However, for the film annealed at 1300°C, the surface morphology and transmission are also different from these of the film annealed at 600 and 1200°C. Some pure clubbed clusters are shown in Figs. 2(c) and higher transparency (>85%) from 350 to 900nm wavelength is indicated in Fig. 3. There are no two low transmission peaks (visible at 600 and 1200°C) in 200 to 400nm wavelength region. Due to the limitation of measurement in the short wavelength direction of the spectrometer, the UV absorption edge was not clearly observed (shorter than 190 nm).

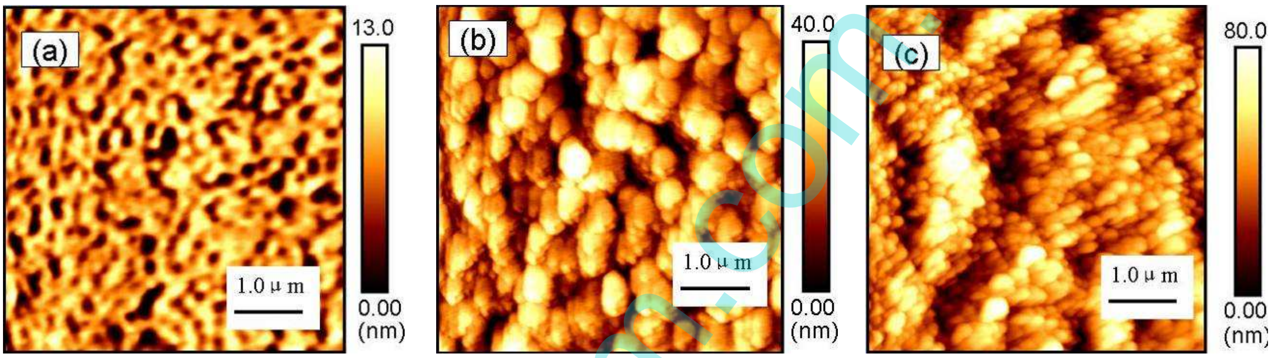

Fig.2. AFM images of the annealed Al films in air for 1h at: (a)600, (b)1200 and (c)1300°C.

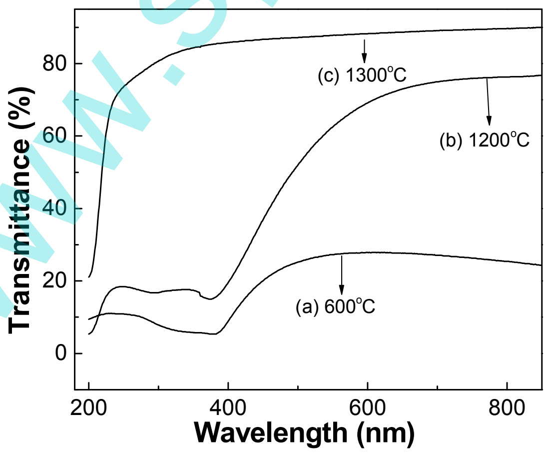

Fig.3. Transmittance of the annealed Al films in air for 1h at: (a) 600, (b)1200 and (c)1300°C.

Conclusion

Alumina films are obtained from the annealed Al films (about 40 nm) prepared on quartz substrates by thermal evaporation in air for 1h at temperature ranging from 600 to 1300°C. The characteristics of the annealed films were investigated by X-ray diffraction, Raman spectra, atomic force microscopy and spectrophotometer. The measurement results of XRD and Raman show that

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crystalline phase transformations of the annealed films will convert from γ, γ and α, up to α-Al_2O_3 with the increasing of the annealing temperature at 600 °C, 1200 °C, to 1300 °C, which reflect on the surface morphology and transmission properties. The porous surface morphology of the annealed films at 600°C indicates clearly the structure γ-Al_2O_3. For the film annealed at 1300°C, some pure clubbed clusters are shown in surface and higher transparency (>85%) from 350 to 900nm wavelength indicated in transmission curves. While transformations of the surface morphology and transmission properties also occurred in the film annealed at 1200°C. Its transmission curve is similar to that of the film annealed at 600°C. In its surface there exist some big grains similar to that of the film annealed at 1300°C.

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References

[1] I. Levin and D. Brandon, ChemInform Abstract: Metastable Alumina Polymorphs: Crystal Structures and Transition Sequences, J. Am. Ceram. Soc. 81 (1998) 1995-1998.

[2] W.H. Gitzen, CERAMIC ABSTRACTS, J. Am. Ceram. Soc. 53 (1970) 295-245.

[3] S. Ruppi, Deposition, microstructure and properties of texture-controlled CVD α-Al2O3 coatings, Int. J. Ref. Met. Hard Mater. 23 (2005) 306-316.

[4] Q. Fu, C.B. Cao and H.S. Zhu, Preparation of alumina films from a new sol–gel route, Thin Solid Films 348 (1999) 99-102

[5] J.M. Schneider, W.D. Sproul and A. Matthews, Reactive ionized magnetron sputtering of crystalline alumina coatings, Surf. Coat. Technol. 98 (1998) 1473-1476.

[6] Ch. Taschner, B. Ljungberg, V. Alfredsson, I. Endler and A. Leonhardt, Deposition of hard crystalline Al2O3 coatings by bipolar pulsed d.c. PACVD, Surf. Coat. Technol. 108-109 (1999) 257-264.

[7] A. Pillonnet, R. Brenier, C. Garapon and J. Mugnier, Influence of annealing temperature on composition and stresses of alumina thin films elaborated by the sol-gel method, Proc. of SPIE. 5249 (2004) 657-660.

[8] A.L. Dragoo and J.J. Diamond, Transitions in Vapor-Deposited Alumina from 300° to 1200°C, J. Am. Ceram. Soc. 50 (1967) 568-574.

[9] R.G. Frieser, Phase Changes in Thin Reactively Sputtered Alumina Films, J. Electrochem. Soc. 113 (1966) 357-360.

[10] JCPDS Card No. 10-0425

[11] JCPDS Card No. 11-0611

[12] A Misra, H.D Bist, M.S Navati, R.K Thareja and J Narayan, Thin film of aluminum oxide through pulsed laser deposition: a micro-Raman study, Mater Sci Eng B. 79 (2001) 49-54.

[13]S. P. S. Porto and R. S. Krishnan, Raman Effect of Corundum, J. Chem. Phys. 47(1967)1009-1012.

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