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Controllable phase formation and physical properties of yttrium oxide films governed by substrate heating and bias voltage

Pei Lei[a], Bing Dai[a], Jiaqi Zhu[a,*], Xiaoting Chen[b], Gang Liu[c], Yuankun Zhu[d], Jiecai Han[a]

[a]Center for Composite Materials, Harbin Institute of Technology, P. O. Box 3010, Yikuang Street 2, Harbin 150080, PR China
[b]Key Laboratory for Liquid-Solid Structural Evolution and Processing of Materials (Ministry of Education), School of Materials Science and Engineering, Shandong University, Jingshi Road 17923, Jinan 250061, PR China
[c]Center for High Pressure Science and Technology Advanced Research, Shanghai 201203, PR China
[d]School of Materials Science and Engineering, University of Shanghai for Science & Technology, Shanghai 200093, PR China

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Abstract

In order to understand the growth behavior of yttrium oxide films driven by thermodynamics and kinetics, two fundamental growth parameters, substrate heating and biasing, were investigated to control film structure and properties comprehensively. We observed two distinct areas, normal deposition area (area 1) and abnormal deposition area (etching area, area 2) at different substrate bias voltages regardless of the substrate temperature. X-ray diffraction (XRD) results show that heating promotes cubic phase formation, whereas ion bombardment induces monoclinic phase growth. Atomic force microscopy (AFM) measurements exhibit that the ions slightly enlarge the surface islands in area 1, whereas they flatten and smoothen the surface in area 2. X-ray photoelectron spectroscopy (XPS) results demonstrate that high temperature suppresses the physisorbed oxygen, and the ion bombardment favorably selects oxygen etching in area 1, causing excess oxygen vacancies. This selectivity almost disappears in area 2. Furthermore, the refractive index and band gap can be enhanced by both substrate temperature and bias voltage. The surface wettability of films can be modulated by the surface chemical composition.

Keywords: C. Optical properties; Y_2O_3 film; Magnetron sputtering; Structure; Wettability

1. Introduction

Yttrium oxide, both a rare-earth oxide and a transition oxide, is a theoretically interesting and technologically useful material. Numerous studies have reported that yttrium oxide films can be used in a wide variety of scientific and engineering applications due to their natural properties. They include high crystallographic stability (up to 2325 °C) [1,2], superior mechanical strength [3], high permittivity (~14–18) [4,5], high refractive index (~2) [6,7], wide band gap (~5.8 eV) [8], low lattice mismatch with silicon (cubic phase) [9] and graphene (hexagonal phase) [10], well-known host matrix for rare-earth ions [11,12], and a component of several complex materials [13,14].

Similar to other rare-earth oxides, yttrium oxide has several crystallographic structures [2]. Among these crystal structures, cubic one is the most stable phase in atmospheric temperature and pressure, while other phases need much harsher conditions, i.e. high temperature and high pressure [15]. Thus, compared with other phases, cubic yttrium oxide can be easily obtained under common conditions.

Up to now, yttrium oxide films have been prepared by various methods, including molecular beam epitaxy (MBE) [16,17], pulsed laser deposition (PLD) [8,18], sputtering [7,19,20], electron beam deposition [21] etc. Most reports synthesized the cubic phase, while just a few papers reported the successful formation of other phases of yttrium oxide films. Taking monoclinic phase as an example, monoclinic yttrium oxide can be only obtained by certain conditions. Studies have shown that monoclinic yttrium oxide films have been prepared

*Corresponding author. Tel./fax: +86 451 86417970.
E-mail address: zhujq@hit.edu.cn (J. Zhu).

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by Chang et al. by MBE [16], by Lacroix through ion beam deposition [20] and by Gaboriaud with ion irradiation [22]. Similar results have also been observed for erbium oxide [23,24]. Indeed, monoclinic phase is a thermodynamically metastable phase, whose formation deviates from equilibrium. Recently, understanding and controlling the formation of cubic and/or monoclinic phases of yttrium oxide film have been the critical issues for its research and application.

Naturally, the microstructure and properties of as-deposited films can be governed by a competition process between thermodynamics and kinetics [25], which directly links to the heating and ion bombardment. These two approaches can influence the film growth processes through different ways and accordingly determine the final structures and properties. Although numerous studies have been conducted to understand the growth and properties of yttrium oxide films, the controllable phase formation and properties of yttrium oxide films under the combined substrate temperature and bias voltage are still not clear. Furthermore, it requires large work to explore the growth phase diagram and the desirable properties of yttrium oxide films under the favorable conditions for further application.

In this paper, based on above background, several groups of yttrium oxide films were prepared by magnetron sputtering under the designed conditions. The controllable growth behavior of yttrium oxide films under different substrate temperatures and bias voltages was investigated. Furthermore, the evolution of deposition rate, microstructure, optical and wettable properties was studied and discussed.

2. Experimental details

2.1. Film growth

A series of yttrium oxide films were grown on p-type silicon wafers (1×1 cm^2) by radio frequency magnetron sputtering. Metal yttrium target with the purity of 99.999% was used as the target. Argon (99.995% purity) and oxygen gas (99.995% purity) were employed as background and reactive gas respectively. The distance between the substrate and target was 70 mm. Before the deposition, the substrates were cleaned with alcohol and acetone in an ultrasonic bath for around 30 min. During deposition, three groups of samples were prepared under three different substrate temperatures (25 °C (RT), 200 °C and 600 °C). For each group, the substrate bias voltage varied from 0 V to |−320 V|. For all samples, sputtering power of 130 W and work pressure of 1.0 Pa were employed. The deposition time was two hours for all the samples to study the microstructure, morphology, chemical composition, optical constant and wettability properties. Another special group of about 500 nm yttrium oxide films was deposited on the quartz substrate for UV transmittance and optical band gap.

2.2. Film characterization

The crystalline structure of the films was determined by glancing incident X-ray diffraction (GIXRD, Philips X'pert) with Cu Kα source (40 kV, 30 mA). The surface composition was detected by X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 250) using a monochromatized Al Kα source with a step size of 0.1 eV. No argon sputtering for XPS measurement was to avoid the surface damage by ions interaction and to keep the initial fingerprint. The binding energy of the XPS spectra was calibrated using the C1s binding energy (~284.6 eV) of adventitious carbon. Atomic force microscope (AFM, Bruker dimension icon) was used to measure the surface morphology in contact mode at atmospheric temperature and pressure. Spectroscopic Ellipsometer (SE) was employed to investigate the optical properties in the range of 380–800 nm at the incident angle of 70°. The ultraviolet–visible spectrophotometer was used to measure the transmittance spectra of films on quartz in the range of 190–1000 nm. As for the evaluation of film wettability, the contact angles on yttrium oxide surface were measured by using a dataphysics OCA20 with a 4 μl water and glycol.

3. Results and discussion

3.1. Film deposition rate

The deposition thickness under different growth conditions was measured by SE; the results are shown in Fig. 1. It is clear that there are two obvious areas, the large thickness (~130 nm) in area 1, and the small thickness (below 30 nm) in area 2. In this work, heating seems to play a small role in film deposition thickness, whereas ion bombardment induced by substrate bias voltage gives a great contribution to the reduced thickness. The film surface suffers from slight ion bombardment in area 1, which has small influence on thickness. Whereas, when the negative voltage increases up to |−240 V|, ions with high energy bombard the surface. In this case, the etching effect becomes dominant, removing surface adatoms and resulting in the smaller thickness compared with that in area 1. Etching plays a great role in area 2, which is consistent with the extended structure model proposed by Anders [26].

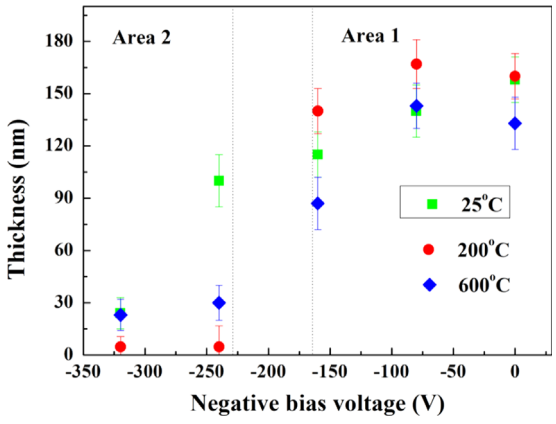

Fig. 1. The deposition thickness of films under different bias voltages and temperatures for 2 h.