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Effects of post-deposition annealing on the chemical composition, microstructure, optical and mechanical properties of Y_2O_3 film

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ABSTRACT

Reactive magnetron sputtering is an ideal technique to deposit Y_2O_3 films, but the existence and transformation of the physisorbed oxygen (O_δ) caused by this method were reported to have a strong impact on the films itself. In this paper, not only the Y_2O_3 films but powders were prepared, then the films were annealed at different temperatures (260, 350, 500, and 650 °C) according to the thermal analysis of powders. The results showed that O_δ can be transferred as desorption when the temperature increases to 260 °C, and such transformation further changes the chemical composition and the valences of O and Y elements. The post-deposited annealing can also affect the grain morphology instead of crystalline phase. The as-deposited Y_2O_3 films and the films annealed at higher temperature all have a cubic polycrystal with $I = 100$ for the (222) reflection. However, the typical *orange-peel* characteristics and columnar structures were only found in the Y_2O_3 films below 350 °C annealing. The mentioned changes including composition and grain morphology comprehensively affect the refractive index and nano-mechanical properties of Y_2O_3 films. This paper will provide a precise annealing temperature to obtain Y_2O_3 films with low physisorbed oxygen and stable micro-structure.

1. Introduction

Yttrium oxide (Y_2O_3) has been intensively studied as particle, powder, film, or bulk in civilian and military applications [1–8]. Specifically, Y_2O_3 films have become one of the most promising materials that are widely used as optical layers, e.g., as optical waveguides [9,10], antireflective layers [11], or components of high-quality metal-oxide-semiconductor-based devices [12,13]. These films present high thermal stability (2325 °C for cubic-bixbyite structure), high refractive index (~2.0), large optical band gap (~5.5 eV), broad transparency range (from near-UV to IR), and low emissivity [14,15].

Y_2O_3 films can be prepared in several ways, including pulsed laser [16,17], chemical vapor depositions [18], molecular beam epitaxy [19], sol–gel method [20,21], ion beam sputtering technique [22], and magnetron sputtering [23,24]. Reactive magnetron sputtering is a significant physical vapor deposition technique compared with other methods because of the dense film it produces, and its low deposition temperature below 200 °C and high deposition rate more than 150 nm/h [25]. Generally, reactive magnetron sputtering can be divided into three modes according to oxygen gas flow rate: metallic, compound, and poisoned. To keep a stable sputtering and a high deposition rate, sputtering mode in this work was situated between metallic mode and compound mode by controlling the oxygen gas flow rate as 3 sccm. The mode we chose can avoid the oxides on target surface, but it also tends to make yttrium's sputtering yield higher than the oxygen's supply to form the nonstoichiometric and reduced films [26–28]. Increase in temperature during deposition stage allows the films to suppress the physisorbed oxygen (O_δ), to approach the stoichiometry and to promote the formation of Y—O bond, according to Lei et al. [2,14].

Oxygen, as one of the two reactants, the existence through constant adsorption and the transformation through annealing will have an important impact on the films [29]. O_δ is also closely related to the phase transformation of Y_2O_3 films, which changes from C-cubic to B-monoclinic below 400 °C with increasing substrate temperature [15,30]. Nevertheless, the state of O_δ during heating and the mechanism of oxygen in the transformation without ion bombardment remain unclear. Post-deposition annealing is a more simple and effective method than substrate heating, because ion bombardment and substance supplement are absent during annealing. Although post-deposition annealing does not obviously change the crystalline phase, the deficiency in O_δ and the elevated temperature influence the optical and mechanical properties of Y_2O_3 films by changing the films' composition

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Table 1
Sputtering parameters for Y_2O_3 powders and films.

Parameters	Units	
Ar (99.995%) flow	sccm	30
O_2 (99.99%) flow	sccm	3
Chamber pressure	Pa	2
Power	W	150
Substrate-to-target distance	mm	15
Duration	h	4

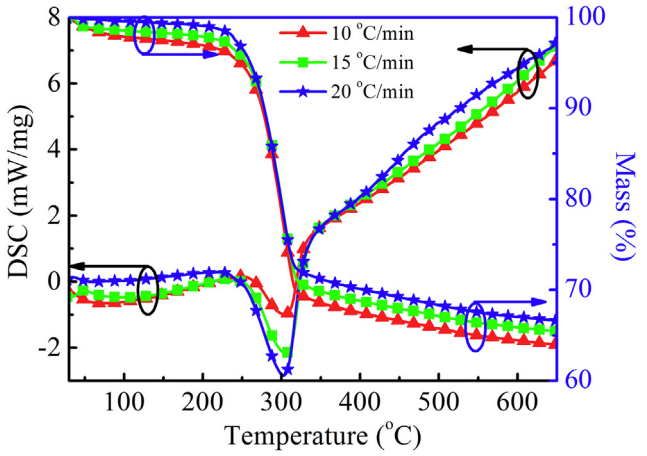

Fig. 1. DSC/TG curves of heat flow/mass versus temperature for Y_2O_3 powders with heating rates of 10, 15, and 20 °C/min.

Table 2
Results of DSC/TG tests for Y_2O_3 powders thermal analysis.

Heating rate/ °C·min^{-1}	Sample mass/ mg	Endothermic peak			Mass loss/ %
		T_0/°C	T_m/°C	ΔH_f/J·g	
10	21.8	262.4	326.3	−557.4	23.8
15	20.3	268.8	336.5	−678.5	22.6
20	20.9	259.0	335.8	−696.7	23.7

and microstructure [1,31–33]. Most importantly, investigating the influence of post-deposition annealing on reactively sputtered Y_2O_3 films can provide meaningful insights into the possible application of Y_2O_3 films [34–37].

Y_2O_3 powders and films were prepared by reactive magnetron sputtering in this work. Four annealing temperature points (260, 350, 500, and 650 °C) were defined clearly. The evolution of chemical composition, microstructure, and optical and mechanical properties was investigated and discussed.

2. Experimental details

2.1. Preparation of Y_2O_3 powders and films

Y_2O_3 powders and films were prepared by radio frequency (RF) reactive magnetron sputtering method on aluminum foil substrate (0.5 mm in thickness) and on sapphire substrate (0.5 mm in thickness, (0001)), respectively. The aluminum foils were prepared through pickling-caustic washing treatment. The sapphire substrates were cleaned ultrasonically in alcohol and acetone solution. Subsequently, the foils and the substrates were mounted on the sample holders inside the deposition chamber with a yttrium target (99.99 wt%) in it. The typical key parameters are listed in Table 1 by following the previous research [38]. Prior to the sputtering process the substrates were exposed to Ar^+ etching for 5 min to remove any contaminants on the surface. After deposition, the samples were kept in vacuum chamber without gas' supplement until the substrate temperature dropped to room temperature. Then, the aluminum foil substrate with Y_2O_3 was immersed in an alkali solution to obtain nano-powder after centrifuging, washing and filtering process. Y_2O_3 films with sapphire substrates were then annealed at 260, 350, 500, and 650 °C in static air atmosphere for 2 h with a heating rate of 15 °C/min.

2.2. Characterization of Y_2O_3 powders and films

Differential scanning calorimetry (DSC) experiments were performed on a Netzsch STA 409PC system coupled with alumina crucible. The tests were range from 30 °C to 700 °C in the N_2/O_2 mixed atmosphere. The heating rates selected were 10, 15, and 20 °C/min. X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 250XI) was used a monochromatized Al Kα X-ray source (radiation at 1486.6 eV) with energy step size of 0.100 eV. The binding energy of contaminated carbon (C1s 284.6 eV) was used as the reference. All samples were placed in a vacuum chamber and etched by argon ion for 5 min to remove surface contaminations before XPS testes. Crystal structure was studied by grazing incidence X-ray diffraction (GIXRD, Philips X' Pert) using Cu Kα source (0.154 nm). Incidence angle was kept at ~1.0° and the samples were scanned in a 2θ range of 10–70° with a scan step size of 0.077°. The microstructure was analyzed by scanning electron microscope (SEM, HITACHI S-4800) on the surface and cross-section as well. Spectroscopic ellipsometry (SE, M-2000U) measurements were used to investigate the optical properties of films in the spectral range of 400–1000 nm at an incidence angle of 65° and 75°. The elastic modulus E_{IT} and hardness H_{IT} of the films were evaluated by using Nanoindenter XP with a continuous stiffness measurement mode. Three measurements were made on each sample and the average values were used. The following experimental parameters were chosen: strain rate, 0.05 s^{-1}; allowable drift rate, 0.05 nm/s; and depth limit, 1200 nm.

3. Results and discussion

3.1. Composition and chemical bonding

Previous works showed that O_δ caused obvious compositional change in Y_2O_3 films prepared by reactive magnetron sputtering [2,14,30]. Therefore, differential scanning calorimetry/thermogravimetry is first applied with non-isothermal method to obtain the thermal curves and thermo-kinetic parameters of substances, as shown in Fig. 1 and Table 2.

Experimental results indicate that only a single typical endothermic peak of heat flow and apparent mass reduction are observed below 400 °C. However, endothermic/exothermic peak is not visible above 400 °C. A marked mass decrease by 23% happens in the powders while the endothermic peak appears with the temperature increasing to 260 °C. O_δ is transferred by desorption at the starting temperature of 260 °C during annealing because of its presence in the as-deposited Y_2O_3 powders. The reactive gas (O_2) in the deposition chamber is responsible for O_δ formation. Thus, O_δ can be desorbed or removed from the as-deposited Y_2O_3 by resynthesizing O_2 (gas). This conclusion shows another possible means to transform O_δ besides previous studies [14,39]. Moreover, the energy given by the ion bombardment leads to point defects in the oxygen-deficient state and further stabilizes the