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Study on reactive sputtering of yttrium oxide: Process and thin film properties

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ABSTRACT

This paper investigates the influence of deposition conditions on the properties of yttrium oxide thin films. The paper focuses on the texture, optical and mechanical properties. With this objective, a series of yttrium oxide thin films with different thicknesses were deposited by direct current (DC) unbalanced reactive magnetron sputtering at high and low pumping speed. By changing the oxygen flow, depositions were performed in the three characteristic deposition modes for reactive magnetron sputtering, i.e., metallic, transition and poisoned mode. By using an oxygen flow directed to the substrate, full oxidation of the samples, as shown by X-ray photoelectron spectroscopy (XPS), in the three modes is obtained. Crystallographic characterization by X-ray diffraction (XRD) shows that films crystallize in the cubic phase with a strong (222) out-of-plane orientation at low oxygen flow. As the oxygen flow increases a mixture of cubic and monoclinic phase is obtained. In poisoned mode, the films consist of the cubic phase with preferred (420) orientation. Scanning electron microscopy (SEM) cross sections show, with increasing oxygen flow, a loss of the columnar structure. As the oxygen flow rates increase through the metallic, transition, and the poisoned mode, the grain size becomes gradually smaller. An overview diagram of all experimental results uncovers that the textural changes are closely linked to the oxygen partial pressure rather than the oxygen flow. The optical properties of films were investigated by spectroscopic ellipsometry (SE). The films with a columnar structure demonstrate superior hardness and modulus as well as the high plasticity.

1. Introduction

Yttrium oxide, a rare-earth oxide, has attracted considerable attention over the past several years due to its variably crystallographic characteristics and unique properties, which makes it an important technological material. Briefly, owing to high chemical and thermal stability (melting point is up to ~2349 °C) [1,2], and its mechanical properties (high strength and fracture toughness) [3], yttrium oxide films and particles have been used in thermal or reaction barrier coatings [4] and oxide dispersion strengthened steels [5,6]. Particularly, due to the excellent optical and electric properties, including a wide transmittance range, high refractive index (~2), low absorption, large band gap (~5.4 eV), and high permittivity (~14–18) accompanied with a lattice match with Si and GaAs (for the cubic phase) and graphene (for the hexagonal phase), yttrium oxide thin films become one of the most interesting materials widely used in optical waveguides [7–9], and as an antireflective layer [10], or as a high efficiency phosphor by doping with other rare-earth elements [11,12], as well as one component of high-quality metal-oxide-semiconductor (MOS) based devices [13–18].

Structurally, yttrium oxide has several polymorphic phases, such as A-hexagonal (P32m), B-monoclinic (C2/m), C-cubic (Ia3), H-hexagonal ($P6_3/mmc$), and X-fluorite (Fm3m) [19,20]. At ambient pressure and room temperature, the C-cubic phase is the most stable phase, which transforms to H-hexagonal phase at about 2600 K or to B-monoclinic phase at ~10 GPa [17,21]. As the material properties are structurally dependent, it is important to control the thin film deposition conditions which influence the structure. Compared to other methods, DC reactive magnetron sputtering is an important physical vapor deposition technique in engineering and scientific fields due to its inherent advantages, which include low temperature deposition with ion assistance, high deposition rate, good film quality [22], and its scalability. However, the addition of the reactive gas (such as oxygen or nitrogen) increases its complexity. Indeed, in DC reactive magnetron sputtering a hysteresis of the deposition parameters as a function of the oxygen flow is often reported. The transition from the high deposition rate regime (metallic mode) to the low deposition rate regime (poisoned mode) often occurs

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abruptly resulting in process instability close to the transition points between both modes [23].

Although there have been many reports about thin film deposition of yttrium oxide by a large number of methods, including molecular beam deposition [17,24], electron beam evaporation deposition [25], pulsed laser deposition [26,27], radio frequency sputtering [7,28], chemical vapor deposition [2,29], there are few reports systematically covering the controllable growth of yttrium oxide films by DC reactive magnetron sputtering [30]. The latter research paper still leaves an interesting gap to be investigated, especially, on understanding and controlling the growth of yttrium oxide films within the three different modes from metallic mode, transition zone to poisoned mode. This is a crucial issue to build the relationship of process–structure-properties.

Based on the above background, in this paper, a series of yttrium films with three different thicknesses were deposited by DC reactive magnetron sputtering on glass and silicon substrates using local oxygen supply. In order to obtain stable process in the transition zone, a higher pumping speed was employed to remove the hysteresis loop [23,31]. Influence of different oxygen flow rates on the target state, oxygen pressure, deposition rate, film structure and the optical and mechanical properties was systematically investigated.

2. Experimental details

2.1. Thin film deposition

Yttrium oxide thin films were prepared on glass and silicon (100) substrates by DC reactive unbalanced magnetron sputtering. The glass substrates were cleaned by distilled water and methanol in ultrasonic bath for 10 min. The silicon substrate was washed via RCA cleaning procedure. A metallic yttrium target (99.5% purity, 50.8 mm in diameter and 3 mm in thickness, Testbourne Ltd.) was mounted on a magnetron which is oriented perpendicularly to the center of substrate holder in a stainless steel vacuum chamber. The oxygen inlet was positioned close to the substrate in order to obtain fully oxidized films even in metallic mode. The vacuum chamber was evacuated to a base pressure lower than 10^{-4} Pa (10^{-6} mbar) by combination of a turbo-molecular and a rotary pump. The argon pressure was fixed at 0.5 Pa by the combination of a throttle valve and an argon flow controller. In this way, experiments were performed at low (120 L/s, 35 sccm Ar) and high pumping speed (500 L/s, 148 sccm Ar). Experiments were performed at constant current (I = 0.5 A, Hüttinger Elektronik 1500 DC power supply). Before deposition, pre-sputtering was performed for 10 min to clean the target surface. At the same time, the substrate was protected by a shutter. The distance between target and substrate was kept constant at 10 cm. The substrate was neither intentionally heated nor cooled. The films with thickness of about 250, 550 and 1000 nm were obtained by adjusting the deposition time from several minutes in metallic mode up to more than 10 h in poisoned mode.

2.2. Thin film characterization

The film thickness was evaluated by contact profilometry (Taylor–Hobson Talystep) and checked again by cross section SEM images and spectroscopic ellipsometry (SE). The deposition rate can be calculated from the measured thickness and the deposition time. X-ray photoelectron spectroscopy (XPS) was employed to detect the chemical composition on the surface and subsurface of films after ion bombardment (4 keV argon). The XPS spectra were measured using monochromatized Al Kα (1486 eV). For survey measurements a pass energy of 152.55 eV was used, while the O1s and Y3d spectra were measured with a pass energy of 107.8 eV. Crystallographic properties were measured by X-ray diffraction (XRD) using Cu Kα radiation (0.154 nm) in Bragg–Brentano geometry with a LynxEye Silicon Strip detector. The samples were scanned in a 2θ range from 20 to 68° with a step size of 0.04°. The cross-section morphology was studied on gold-coated samples by a FEI Quanta 200 scanning electron microscope using a high voltage of 20 KV. Ellipsometry (J. A. Woollam Spectroscopic Ellipsometer, SE) was used to evaluate the optical properties of films in the spectral range of 250–1690 nm at an incidence angle of 70°. The hardness and elastic modulus of the films were evaluated by Nanoindenter XP with continuous stiffness measurement mode. Four measurements were made on each sample and then the average value was used in this work.

3. Results and discussion

3.1. Selection of the deposition conditions

To select the deposition conditions, a so-called hysteresis experiment is performed by a stepwise increase of the oxygen gas flow rate up to a maximum of 3.0 sccm for the low pumping experiment, and up to 8 sccm for the high pumping speed experiment. After reaching the maximum oxygen flow, the flow rate is stepwise decreased until the initial conditions. Sufficient time is allowed to stabilize the process before the oxygen flow is changed. During the experiment the discharge voltage and total pressure is measured. The latter allows to calculate the oxygen partial pressure by subtraction of the constant argon pressure (0.5 Pa). Fig. 1 summarizes the obtained results.

Fig. 1(a) shows the variation of discharge voltage as oxygen flow rate increases and decreases at pumping speed of 120 L/s. As the supply of oxygen increases from 0 to about 1.7 sccm, the discharge voltage remains at a high value of about 400 V. Above this oxygen flow, the discharge voltage decreases abruptly to around 200 V. When the oxygen flow rate is subsequently decreased, the discharge voltage remains at a low value of about 200 V up to a flow rate of 1.3 sccm. The change in the discharge voltage corresponds to a change of the oxygen partial pressure.

This behavior of both the discharge voltage and oxygen partial pressure is well known during the reactive sputtering from a metallic target. The low oxygen partial pressure regime corresponds with the so-called metallic mode. At high oxygen partial pressure, and low discharge voltage the target is poisoned (an oxide layer covers Y target surface) which can be evaluated from the low deposition rate (see further, Fig. 2). Both modes are separated from each other by the transition region (an oxide layer partially covers target surface). Using only a flow controller, it is impossible to access stable conditions within the transition region. To circumvent the hysteresis phenomenon, several methods have been suggested: nitrogen addition [32], increasing pumping speed [23,31], changing target area [23]. In this work, we obtained a stable process in the transition zone by using a high pumping speed of 500 L/s. Fig. 1(b) and (d) illustrate the behavior of the discharge voltage and oxygen partial pressure at high pumping speed. It is clear that under these conditions the deposition process can be stabilized, allowing to perform depositions at intermediate oxygen partial pressures.

Based on these measurements, 11 deposition conditions were chosen. Five points (A1 to A5) were performed at low pumping speed. Six points (B1 to B6) were selected at high pumping speed (see red markers in Fig. 1).

3.2. Deposition rate

Fig. 2 shows the measured deposition rate at high and low pumping speed. In metallic mode, a deposition rate of approximate 50 nm/min was obtained. The deposition rate abruptly drops to values as low as 1 nm/min in poisoned mode. The low rate in poisoned mode can be understood from the large difference in sputter yield of the Y metal (~0.6) and the oxide (~0.015) [33,34].