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Thermal properties of thin Al_2O_3 films and their barrier layer effect on thermo-optic properties of TiO_2 films grown by atomic layer deposition

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ABSTRACT

We investigate the evaporation of water molecules from the surface of high index, amorphous thin TiO_2 films of various thicknesses t_t, grown by atomic layer deposition (ALD). The desorption of water molecules is impeded by depositing thin ALD-Al_2O_3 barrier layers of various thicknesses on the TiO_2 thin films. Growing ALD-Al_2O_3 diffusion barrier layers with different thicknesses t_a allows us to evaluate the water vapor evaporation rate in terms of the change in the thermo–optic coefficient (TOC) of TiO_2 films over a wide spectral range $380 \leq \lambda \leq 1800$ nm. An average reduction of 33% in TOC is found at a barrier layer thickness of ~36 nm. Furthermore, the temperature dependent index (dn/dT) and density ($d\rho/dT$) of the ALD-Al_2O_3 films of various thicknesses t_a are also presented. The Cauchy model is applied to all the ellipsometric measurement data to retrieve the optical constants, and subsequent modeling by the Lorentz–Lorenz relation provides the material density of Al_2O_3 films. The room temperature values of the thermal coefficients for an ALD-Al_2O_3 film of thickness $t_a \approx 60$ nm at wavelength $\lambda = 640$ nm are found to be $dn/dT = 4.66 \times 10^{-5}$°$C^{-1}$ and $d\rho/dT = 4.66 \times 10^{-4}$g $cm^{-3}C^{-1}$.

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1. Introduction

Titanium dioxide films are extensively used in optical thin film devices owing to their high refractive index, high transmission in the visible and infrared spectral regions, as well as high chemical and thermal stability [1]. Due to these highly attributed characteristics, TiO_2 thin films are suitable materials for applications such as antireflection coatings, multilayer optical coatings, optoelectronic devices, and resonant waveguide filters [2–5]. Most often TiO_2 films are hydrophilic and adsorb water molecules at the active nucleation sites of OH groups in bridging positions due to residual O-vacancies on the surface [6]. The strong adsorption of water molecules results in a change of the effective refractive index of thin TiO_2 films due to a change in the optical path length [7]. This in turn can cause a change in the other thermo–optic properties under environmental effects [8]. The thermo–optic coefficient TOC, (dn/dT) of TiO_2 films inherently depends on the deposition technique being employed [9–11]. The refractive index of the TiO_2 films decreases when increasing the temperature, which has been described as the negative TOC of TiO_2 films due to the evaporation of the hydrogenated species (H_2O, OH etc.) from the near surface region [9]. The evaporation of water molecules from the surface of TiO_2 films makes its use limited in optoelectronic devices due to e.g., the corrosion of the cathode [12]. Similarly, the high variations of the refractive index in a hot environment or in relatively high humidity causes a spectral instability in the central resonance peak of guided mode resonance and passband filter applications [3,8]. The evaporation of hydrogenated species from the surface of TiO_2 films could be minimized by coating inorganic gas diffusion barrier layers to enable the stable operation of such optical devices.

Regarding these diffusion barrier layers, most of the previous work focuses on the high water vapor evaporation rates through polymers, since it explains the behavior of polymer materials that exhibit negative TOC [13]. The water vapor transmission rates have been reduced by depositing inorganic diffusion barrier layers by atomic layer deposition (ALD), typically Al_2O_3 as a single-layer or multilayer stacks on the polymer [12,14] and Si [15] substrates. Several researchers have reported the performance of single-layer Al_2O_3 films as barrier layers to control the water vapor transmission rate on the polymer substrates [16,17]. In one study, the permeability of water molecules was controlled by a deposition of Al_2O_3 followed by the growth of a SiO_2 layer [14]. Similarly, the ALD-Al_2O_3 layers have been employed for surface passivation of III–V compound semiconductors to minimize the electrical leakage current density [18]. In the case of TiO_2 films the impermeable behavior of Al_2O_3 films appears in terms of sealing effects on the TiO_2 films or improved nucleation of Al_2O_3 on porous TiO_2 surfaces due to these defective sites. The measured permeation of H_2O molecules through single-layer inorganic Al_2O_3 films is attributed to the film defects caused by the

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deposition technique being employed or by the substrate imperfections [19]. The deposition process plays a significant role on the effective nature of the inorganic gas diffusion barrier layers. The water vapor transmission rate through a barrier layer of Al_2O_3 deposited by electron beam evaporation on polyethylene naphthalate substrate is ~500 times larger than that of the Al_2O_3 barrier films coated by ALD [20]. Atomic layer deposition is a technique that can produce uniform, dense, conformal, and nearly pinhole free [21] thin Al_2O_3 films on the TiO_2 films as gas diffusion barrier layers. ALD is a unique thin film deposition technique, in which the substrate surface is saturated by the sequential use of self-terminating gas–solid reactions of supplied precursor vapors [22]. Due to the saturative nature of the reaction steps, thin film growth proceeds in cycles with a tight control on composition at atomic scale, a uniform thickness and coverage of corrugated surface profiles over large areas [23]. One ALD reaction cycle contains four steps or two half-reactions: (i) A self-terminating reaction of the first precursor, (ii) purging or evacuation to remove the non-reacted species and reaction by-products, (iii) a self-terminating reaction of the second precursor or another treatment to activate the surface again for the reaction of the first precursor, and (iv) purging or evacuation to make the surface ready for step (i) [9,24–26].

In this paper we report on the perspective of using the ALD-Al_2O_3 diffusion barrier layers in a slightly different way to investigate the evaporation of water vapors, qualitatively and quantitatively, from the near surface region of optical grade thin TiO_2 dielectric films in terms of the rate of change of refractive index with temperature. The idea is to enunciate the surface porosity model speculated in our recent publication (see Ref. [9] and Fig. 1) as being responsible for the change in the refractive index of TiO_2 films. The TOC of TiO_2 films is studied after ALD coating of Al_2O_3 barrier layers with fixed and variable thicknesses. Furthermore, a study of the TOC of Al_2O_3 films fabricated by ALD process is presented herein. To this end, three different sets of samples are fabricated by ALD. In the first set the Al_2O_3 barrier layers of constant thickness t_a ~ 6 nm and TiO_2 films of different thicknesses t_t ~ 60–500 nm are considered, all fabricated by the ALD technique. In the second set TiO_2 films of constant thickness t_t ~ 60 nm are coated with Al_2O_3 barrier layers of different thicknesses t_a ~ 6–36 nm. In the third set we consider only Al_2O_3 films with thicknesses t_a ~ 60–500 nm to explicitly study their TOCs. The paper is organized as follows: first the experimental details of the fabrication and characterization of the samples are described in Section 2. In Section 3, the modeling of the ellipsometric measurement results of the TOC of ALD-Al_2O_3 films is presented. The experimental results relating to the effects of Al_2O_3 diffusion barrier layers of fixed and variable thicknesses on the TOCs of TiO_2 films and the TOC of Al_2O_3 films are discussed in Section 4. Finally, the conclusions are presented in Section 5.

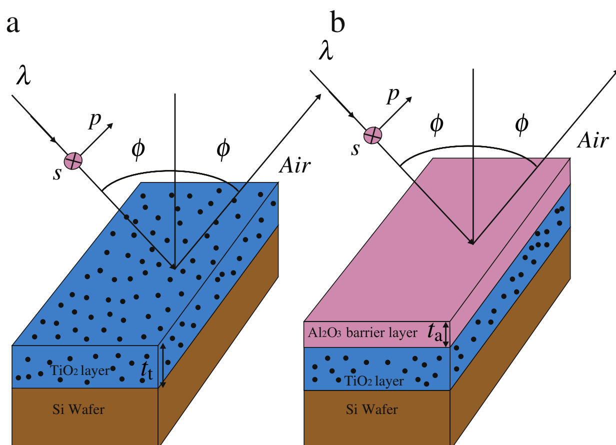

Fig. 1. (a) Porosity model on the near surface region of a TiO_2 film. (b) Model for a TiO_2 film coated by an Al_2O_3 barrier layer.

2. Experiment details

2.1. Sample fabrication

The fabrication of the TiO_2 and Al_2O_3 films on silicon substrates (n-type with phosphorous dopant) of diameter 50.80 mm, thickness 380 ± 25 μm and crystal orientation <100> is accompanied by employing ALD. The fabrication process started by cleaning the silicon wafers with isopropanol, followed by blow drying with dry N_2. Subsequent to substrate cleaning, thin amorphous films of TiO_2 and Al_2O_3 of different thicknesses were grown on the substrates using a Beneq TFS 200–152 ALD reactor. The commonly known precursor materials used for TiO_2 and Al_2O_3 films were $TiCl_4/H_2O$ and $Al(CH_3)_3/H_2O$, respectively. We used a low deposition temperature of 120 °C, with chamber and reactor pressures of 680 Pa and 159 Pa, respectively. Nitrogen (N_2) was used as a carrier gas for all the precursors and as a purging gas after each precursor pulse during an ALD cycle. The chamber and process flows for both the TiO_2 and Al_2O_3 films were 200 sccm (Standard cubic centimeter per minute) and 300 sccm, respectively. The pulse durations of $TiCl_4$ and $Al(CH_3)_3$ were 150 ms followed by a purging pulse for 750 ms. For the H_2O precursor, a pulse duration of 150 ms with a subsequent purging pulse for 1 s was applied. The growth rates of the deposited TiO_2 and Al_2O_3 films were 0.065 and 0.12 nm per cycle, as measured by the Dektak 150 stylus surface profilometer (Veeco Metrology) and by an ellipsometer. After deposition, three different sets of samples were formed: the first set consisted of TiO_2 films of 60, 100, 200, 300, 400, and 500 nm thicknesses followed by an overcoated thin layer of Al_2O_3 of thickness ~6 nm; we call these samples $S_{A(1-6)}$. The second set consisted of TiO_2 films of constant thickness of ~60 nm followed by overcoated layers of Al_2O_3 of thicknesses 6, 12, 18, 24, 30, and 36 nm; we call these samples as $S_{B(1-6)}$. The third set composed of only Al_2O_3 films of thicknesses 60, 100, 200, 300, 400, and 500 nm; we call these samples as $S_{C(1-6)}$.

2.2. Thermo–optical measurements

The wavelength- and temperature-dependent refractive indices $n \equiv n(\lambda,T)$ of the TiO_2 and Al_2O_3 amorphous films were measured by a variable angle spectroscopic ellipsometer (VASE, J. A., manufactured by Woollam Co.). We assume plane-wave illumination on the sample at two different angles of incidence $\phi = 65°$ and $\phi = 75°$, with two orthogonal orientations of linear polarization and a beam spot size of 3 mm as shown in Fig. 1. The illumination wavelength scan covers a spectral range from $\lambda = 380$ nm to 1800 nm with a scan step of 20 nm. The illuminated sample was mounted firmly on a home-made Al heating assembly directly attached to the ellipsometer stage. The surface temperature of the sample was monitored with a Convir ST8811 Handheld Infrared Thermometer (Calex Electronics Ltd.) with an accuracy of ±2°C. Each thermal measurement was performed with a temperature interval of 10 °C from room temperature $T = 20$ °C up to $T = 150$ °C with a temperature increase rate of 0.5 °C/min with an accuracy of ±0.1 °C.

2.3. Structural characterization

The structural characterization of the TiO_2–Al_2O_3 thin amorphous films was performed by a scanning electron microscope (SEM), LEO 1550 Gemini. The samples were sputter coated with a thin ~8 nm conductive Cu layer by a sputter coater K675X. The phase of as deposited TiO_2 thin films on a fused silica substrate was characterized by X-ray diffraction (XRD). In a powder diffraction experiment we used Brueker Advance D8 in Bragg–Brentano geometry, a step-scan

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