Applied Surface Science 285P (2013) 713–720

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Investigation on thermal stability of Ta_2O_5, TiO_2 and Al_2O_3 coatings for application at high temperature

Peng Shang[a,b,*], Shengming Xiong[a], Linghui Li[a], Dong Tian[a], Wanjun Ai[a]

[a] Institute of Optics and Electronics, Chinese Academy of Sciences, Chengdu 610209, China
[b] Graduate School of the Chinese Academy of Sciences, Beijing 100039, China

ARTICLE INFO

Article history:
Received 29 April 2013
Received in revised form 22 August 2013
Accepted 24 August 2013
Available online 31 August 2013

Keywords:
Thermal stability
$TiO_2/Ta_2O_5/Al_2O_3$
Coating
Mismatch

ABSTRACT

In this paper, tantalum pentoxide (Ta_2O_5), titanium dioxide (TiO_2) and aluminum oxide (Al_2O_3) coatings are deposited on silicon substrates by ion beam sputtering (IBS). The influences of the thermal exposure at high temperature in air on the surface morphology, roughness, and the structure were investigated. The results indicate that the chemical composition of the as-deposited TiO_2 and Ta_2O_5 coatings are apparently close to the stoichiometry ratios and both of them are amorphous structures. The peaks corresponding to anatase TiO_2 appear at 400 °C while the anatase-to-rutile transformation is not observed after 800 °C and 1000 °C bake. Ta_2O_5 coating crystallizes at 800 °C and 1000 °C to form the hexagonal structure and orthorhombic structure, respectively. TiO_2 and Al_2O_3 single layers all develop catastrophic damage at 400 °C in the form of noted spallation or blisters, whereas there is no visible damage for the Ta_2O_5 coating even at 1000 °C. To understand possible damage mechanisms, the thermal stress distributions through the thickness of Ta_2O_5 and TiO_2 coatings and the influence of the microstructure transformation are discussed. Finally, some possible approaches to improve the thermal stability are also proposed.

1. 1 Introduction

Because of the development of optical coatings which are deployed in more extreme environment, the stability of coating subjected to different thermal loading becomes an issue of crucial importance [1,2]. So thermal robustness must be taken into account when designing the coating requiring long term temperature stability up to 1000 °C [3]. TiO_2 and Ta_2O_5 are the most commonly used high refractive index materials in the multilayer dielectric mirror due to their high transmittance, low optical loss and low self-emission at high temperature [4,5]. In addition, they also possess excellent chemical and thermal stability, and favorable mechanical properties which are of advantage to be used as protective coatings [5–7]. So more recently, TiO_2 and Ta_2O_5 coatings have received significant attention and have been applied to a wide range of scientific and technological applications [1,7–13]. Many techniques have been explored to deposit the Ta_2O_5 and TiO_2 coatings such as chemical vapor deposition (CVD), RF magnetron sputtering, ion beam assisted deposition and the sol–gel method [1,2,14–20]. Some literatures [19,21] reveal that Ta_2O_5 and TiO_2 coatings deposited by ion-beam sputtering possess good properties such as high refractive index, low absorption, less defects and typically amorphous microstructure. As the temperature increases, the first phase transition occurs at the temperature between 600 °C and 800 °C for Ta_2O_5 and ~300 °C for TiO_2. And another phase transition can be observed at ~1000 °C for Ta_2O_5 and ~1100 °C for TiO_2 [22–24]. These behaviors have a great influence on the stability of structure and applications.

However, the thermal stability of the coatings deposited by IBS is seldom reported although this deposition method can provide the higher density coatings using hard and durable optical materials [3]. In this paper, single TiO_2, Ta_2O_5 and Al_2O_3 layers are deposited on silicon substrates ($\phi\,30 \times 3$ mm) by ion beam sputtering (IBS). The influences of thermal exposure at high temperature on the coating composition, microstructure, surface morphologies and the root mean square values of roughness (RMS) are characterized systematically. The thermal robustness of Ta_2O_5, TiO_2 and Al_2O_3 coatings are conducted by experiments. To understand possible damage mechanisms, the thermal stress distributions through the thickness of Ta_2O_5 and TiO_2 coatings and the influence of the microstructure transformation are discussed. Finally, some possible approaches to improve the thermal stability are also proposed.

2. Experimental

2.1. Fabrication

The single TiO_2, Ta_2O_5 and Al_2O_3 layers were deposited on silicon substrates using Veeco Ion Tech SPECTOR system. They are fabricated in an IBSD-1000 coater, equipped with a 160 mm ion

---

* Corresponding author. Tel.: +86 028 85101036; fax: +86 028 85101036.
E-mail address: shangpeng163@163.com (P. Shang).

0169-4332/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.apsusc.2013.08.115

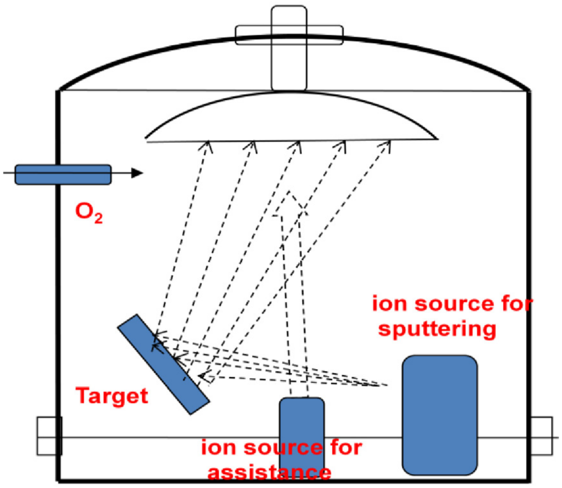

Fig. 1. Schematic diagram of the ion beam sputtering deposition system IBSD-1000.

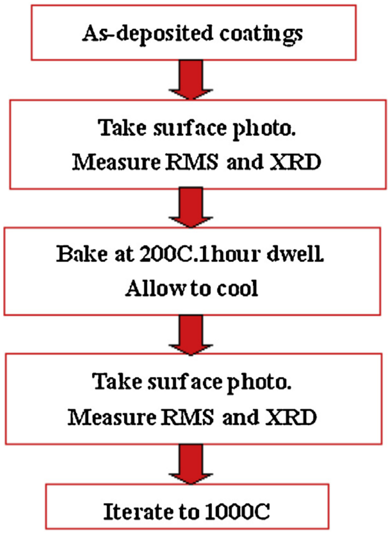

Fig. 2. Flow chart of experimental procedure for bake experiments.

source for sputtering and a 120 mm ion source for assistance (see Fig. 1). High purity (99.999%) argon and oxygen are used as bombarded and reactive gas, respectively. The physical thickness is controlled by deposition time based on the stable deposition rate. The thicknesses of the coatings are all 500 nm in design and the error is about ± 2 nm. All the silicon substrates used in our experiments came from the same batch and had been polished at the same time. Before the substrates were placed in the chamber, they were subjected to a series of chemical cleaning. All samples are deposited with optimized process in our experiments. And the detailed process parameters are outlined in Table 1.

Heat treatment on samples is performed in a furnace with air environment to the desired temperature (200 °C, 400 °C, 600 °C, 800 °C and 1000 °C) for 1 h. They are then rapidly cooled to room temperature in air and the cooling rate is about 50 °C/s. Fig. 2 presents the flow chart of experimental procedure. All samples are carefully packed in a ceramic vessel for avoiding contamination.

2.2. Characterization

The evolution of surface morphology and RMS roughness for Ta_2O_5 and TiO_2 coatings as a result of thermal exposure to different temperatures are investigated by scanning electron microscope (SEM) (or Normarski microscopy) and optical profilometer made by BRUKER, respectively. X-ray photoelectron spectroscopy (XPS) is used to analyze the composition of the as-deposited coatings. The XPS patterns are recorded using Mg Kα radiation at 12 KV and 10 mA. The crystalline structure is characterized by X-ray diffraction (XRD) measurement with Cu Kα as the incident radiation in the $\theta-2\theta$ mode. The crystallite size L of TiO_2 coating is determined using the following formula.

$$L = 0.9\lambda/(\beta\cos\theta) \tag{1}$$

Where λ, β and θ are the wavelength of X-ray (0.1541 nm), the full width of peak at half maximum intensity (FWHM) and the Bragg diffraction angle, respectively.

The average residual stress in the coating is composed of thermal stress and intrinsic stress. The thermal stress originates from the different CTE between the coating and substrate. Combing the analytical model of Tsui and Clyne [25] with the well-known Stoney's equation [26], the thermal stress of the film can be obtained as

$$\sigma_f = \frac{E_{ef}\int_{T}^{T_d}(\alpha_s-\alpha_f)dT}{1+4(E_{ef}/E_{es})(h/H)} \tag{2}$$

where $E_{ef}=E_f/(1-\upsilon_f)$, $E_{es}=E_s/(1-\upsilon_s)$, E_f, E_s, h, H, α_s, α_f, υ_s, υ_f, T_d and T are effective Young's modulus of the film, effective Young's modulus of the substrate, Young's modulus of the film, Young's modulus of the substrate, film thickness, substrate thickness, CTE of the substrate, CTE of the film, Poisson's ratio of the substrate, Poisson's ratio of the film, deposition temperature and the bake temperature, respectively. The physical and mechanical properties of the Ta_2O_5, TiO_2 and silicon materials are given in Table 2. The values are taken from references [33–35]. It is worth noting that the CTEs of TiO_2 and Ta_2O_5 films in this study are taken as an average value over the temperature range between room temperature and high temperature. To analyze the thermal stress in the coating, it is assumed that all the materials are isotropic and linear thermoelastic, have perfect bonding between coating and substrate and plain biaxial stress. Thermal loading is applied by setting the reference temperature as the bake temperature (400 °C) and uniform temperature as the room temperature (20 °C). The thermal stress distributions through the thickness of Ta_2O_5 and TiO_2 coating are evaluated by COMSOL Multiphysics system, respectively.

Table 1
Deposition conditions of single layers by IBSD.

Thin film	Target material	Chamber pressure (torr)	Deposition rate (Å/s)	Flow rate of Ar(O$_2$) (sccm)
TiO_2	Titanium dioxide	4.0×10^{-6}	0.08	–
Ta_2O_5	Tantalum	4.0×10^{-6}	0.15	8(25)
Al_2O_3	Aluminum	4.0×10^{-6}	0.14	8(25)