Vacuum 120 (2015) 155–161

Contents lists available at ScienceDirect

Vacuum

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

Coupled effects of deposition and annealing temperatures on optical, electrical and mechanical properties of titanium oxide thin films

Mark J. Miller, Junlan Wang*

University of Washington, Department of Mechanical Engineering, Stevens Way, Box 352600, Seattle, WA 98195, United States

A R T I C L E I N F O

Article history:
Received 26 June 2015
Received in revised form
8 July 2015
Accepted 9 July 2015
Available online 11 July 2015

Keywords:
TiO_2 thin films
Wear resistance
Nanoindentation
High-resolution XPS
Reactive magnetron sputtering

A B S T R A C T

In this study the influence of deposition temperature and a post-deposition annealing process on the optical, electrical, mechanical, and tribological properties of titanium oxide thin films was investigated. Based on high-resolution XPS, it was observed that the films became more metallic as the deposition temperature was raised from 15 to 450 °C. Moreover, the mechanical and tribological properties of the film deposited at 450 °C were at least 50% greater than for the film deposited at 15 °C. After annealing at 450 °C for 30 min in air, the films all became transparent and insulating. However, the annealing process had mixed effects on the mechanical and tribological properties such that the 15 and 250 °C films softened, but the 450 °C film hardened. This mixed trend is attributed to the different as-deposited film stoichiometries. The results show that the coupled effects of deposition temperature and post-deposition annealing are quite complex and that the mechanical properties of TiO_2 thin films can be controlled independently of their optical and electrical properties. This is important because TiO_2 coatings are often used as the outer-most layers in optical devices.

1. Introduction

Titanium(IV) oxide, also referred to as titania, is an important dielectric material with applications in optics, catalysis, and many other areas [1–7]. The thin film form of TiO_2 is particularly useful due to its high refractive index, photocatalytic functionality, hydrophilicity, and durability [1,2,8,9]. There are numerous approaches for producing TiO_2 thin films which fall into categories comprising chemical vapor deposition (CVD), plating, sol–gel, and physical vapor deposition (PVD) [8,10–12]. One type of PVD, magnetron sputtering, is suitable for producing dense and smooth films with high purity [8]. Stoichiometric TiO_2 targets can be sputtered with an RF-powered plasma, or metallic Ti targets can be reactively-sputtered in a mixed environment of inert gas and O_2 using either RF or DC power [13–15].

Although the primary function of titania films is typically not structural, the mechanical and tribological properties of the material are nevertheless critical for system performance and reliability. This is especially true considering that TiO_2 films are often used as the outer-most layers in optical applications such as anti-reflective coatings [1,16]. The mechanical properties of TiO_2 films deposited on unheated substrates are well known and documented [17–20]. However, fewer studies have been performed on titania films grown at elevated temperatures. One study showed that increasing the deposition temperature from 25 to 300 °C increased the wear resistance of the coatings [9]. Another study reported that the strength of room temperature-deposited TiO_2 films could be increased by annealing them at 300 °C [21]. An earlier paper by Mayo et al. showed that the strength of nanophase titania could be increased by sintering the material at up to 900 °C [22]; however, it should be noted that this is a different form of the material compared to the continuous thin film form of TiO_2. These studies raise the question “What is the interplay and combined effect of both elevated deposition temperature and post-deposition annealing on the mechanical and tribological properties of titanium oxide thin films?” This seemingly simple question is actually non-trivial due to complex mechanisms such as film densification, grain growth, residual stress, non-stoichiometry, and more.

To answer the aforementioned question, titanium oxide thin films were deposited with three different substrate temperatures and subsequently annealed in air. The chemical composition and optical, electrical and mechanical properties of the films were systematically characterized. It was found that the mechanical and tribological properties of the samples improved by 50% or more as

* Corresponding author.
E-mail address: junlan@u.washington.edu (J. Wang).

http://dx.doi.org/10.1016/j.vacuum.2015.07.005
0042-207X/

the deposition temperature was raised from 15 to 450 °C. This was attributed to film densification. The post-deposition annealing process had mixed effects on the mechanical properties, such that the 15 and 250 °C films softened but the 450 °C film hardened. These mixed effects were attributed to stoichiometric differences at the start of the annealing process (the 450 °C film was more metallic), as well as a reduction in the residual stresses in the films. The results show that the combined effects of deposition temperature and post-deposition annealing are quite complex and that the mechanical properties of TiO_2 thin films can be controlled independently of their optical and electrical properties.

2. Experimental procedure

Thin titanium oxide films were deposited on 1 mm thick glass substrates by reactively sputtering a 99.995% pure Ti target (50.8 mm diameter × 6.35 mm thickness) in a mixed Ar + O_2 environment using an Orion 5 UHV magnetron sputtering system (AJA International, Inc.). The films were deposited at substrate temperatures of 15, 250, and 450 °C, respectively, using a PID controller with feedback from a Type K thermocouple. The deposition power was 150 W and the distance between target and substrate was approximately 130 mm. Ar and O_2 flow rates were 20 and 1 sccm, respectively, and absolute deposition pressure was 1.16 Pa. These conditions resulted in a deposition rate of approximately 7.33 nm min^{-1}. Each of the deposition processes was carried out for 75 min, which resulted in a nominal film thickness of 550 nm. The process was controlled carefully since the structure and properties of reactively-sputtered thin films are known to rely strongly on the processing conditions [23–27]. After deposition, samples were annealed in quiescent air at 450 °C for 30 min using a Barnstead Thermolyne 47900 furnace. The 450 °C annealing temperature was chosen based on a series of parametric studies. This temperature was found to be high enough to induce the amorphous-to-crystalline transition of the titanium oxide film, yet still below the melting temperature (700 °C) of the glass substrate.

The thickness of the films was measured using the scanning probe microscopy (SPM) function of a Ubi1 nanomechanical test instrument (Hysitron, Inc.). The chemical compositions of the samples were characterized with high-resolution X-ray photoelectron spectroscopy (XPS) using a Surface Science Instruments S-Probe. Monochromatic Al K_α was used as the radiation source for XPS, and the data was analyzed with CasaXPS 2.3.15. The spectra were corrected by setting the C 1s binding energy at 284.6 eV, which is a standard practice for XPS analysis [28].

Microstructures of the samples were characterized with X-ray diffraction (XRD) using a Bruker D8 Discover with GADDS. Cu K_α was used as the radiation source for XRD, and data was collected from 2θ of 15–70°. Naturally-fractured cross sections of the samples were characterized with a Sirion FEI scanning electron microscope (SEM) in secondary electron detection mode. This technique elucidated the microstructure and also provided a means to verify the thickness of the films. Optical transmittance was obtained with UV–Vis–NIR spectrophotometry using a Varian Cary 5000. The measurement was performed between wavelengths of 250 and 2500 nm. Electrical resistivities of the samples were determined with the 4-point probe technique using a Keithley 2400 SourceMeter and 2182 NanoVoltmeter. Electrical contacts were connected to the films with silver paste. Nanoindentation and nanoscratch characterizations were performed on the films using a Hysitron Ubi1 nanomechanical test instrument. The procedure in this work enabled a systematic study of the influence of synthesis temperature on the composition and microstructure, and optical, electrical, and mechanical properties of reactively-sputtered titanium oxide thin films.

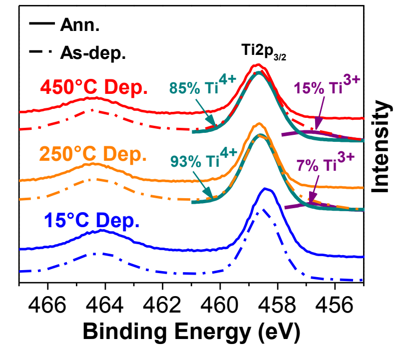

Fig. 1. XPS spectra for as-deposited and annealed TiO_x films.

3. Results and discussion

The compositions of the titanium oxide films were determined with high-res XPS, and the results are shown in Fig. 1. All films are shown to have a TiO_x composition, and x was observed to decrease as the deposition temperature was raised from 15 to 450 °C. This can be seen in Fig. 1 as the percentage of Ti^{3+} increased from 0 to 15% due to the increase in deposition temperature. The stoichiometries of the as-deposited films were approximately TiO_2, $TiO_{1.96}$ and $TiO_{1.92}$, respectively based on the deconvolution of the Ti $2p_{3/2}$ binding energy into Ti^{4+} and Ti^{3+} curves. The reason for the increase in metallic content may have been an increase in sputter rate associated with a decrease in target poisoning. During reactive sputtering, an insulating layer builds up on the surface of the target which results in a decreased sputter rate. This effect is known as target poisoning, and in the current study it appears to have been somewhat offset by the increase in deposition temperature. Following the deposition process, the films were annealed in air and fully oxidized into TiO_2. This can be inferred from Fig. 1 since the percentage of Ti^{3+} of each of the annealed films was 0%.

The XRD results shown in Fig. 2 reveal that the as-deposited films were all amorphous. After annealing the films crystallized into the anatase TiO_2 structure (space group $I4_1/a\ m\ d$; no. 141) [29,30], although the intensity of the XRD peaks was inversely related to the deposition temperature. Additionally, several anatase peaks were observed for the 15 °C-dep/450 °C-ann film that were not observed for the films deposited at 250 and 450 °C. The reason for this inverse relationship may have been the suboxide stoichiometry reported in Fig. 1. The 15 °C film needed energy only to crystallize, whereas the 450 °C film needed energy to both oxidize and crystallize. Thus the 450 °C sample would have required more time to obtain both the stoichiometry and microstructure of the low temperature film.

Naturally-fractured cross sections of the TiO_x films were

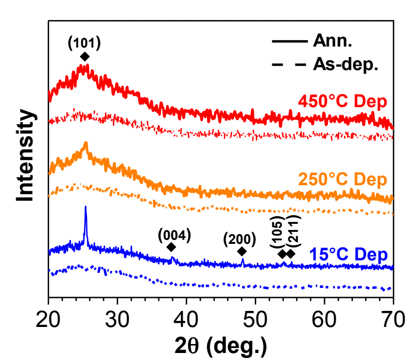

Fig. 2. XRD spectra for as-deposited and annealed TiO_x films.