Surface & Coatings Technology 229 (2013) 186–190

Contents lists available at SciVerse ScienceDirect

Surface & Coatings Technology

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

Influence of pulsed bias on TiO_2 thin films prepared on silicon by arc ion plating: Experimental and simulation study

Min Zhang [a,*], Lei Liu [b], Xiaoxu Yang [a], Feifei Xu [a], Chengsen Liu [a], Faquan Gong [c], Mengke Li [a]

[a] School of Physics and Electronic Technology, Liaoning Normal University, Dalian 116029 China
[b] Department of Physics, University of Science & Technology Liaoning, Anshan 114051, China
[c] Key Laboratory of Chemical Laser, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China

A R T I C L E   I N F O

Available online 30 May 2012

Keywords:
Pulsed bias
Arc ion plating
Pulsed plasma
Titanium dioxide films
Sheath dynamics

A B S T R A C T

Dielectric TiO_2 thin films were fabricated on p-(100) Si substrates by arc ion plating (AIP). The effects of pulsed negative bias on phase structure and growth of TiO_2 films were investigated by applying a pulsed bias ranging from 0 V to −900 V on the substrates. Phase, microstructure, and growth morphology of TiO_2 films prepared at different bias voltages were evaluated with GIXRD and AFM. The results show that pulsed bias exerts an obvious influence on phase structure and growth morphology. High substrate bias facilitates the formation of rutile phase and a (220) preferred orientation is observed in TiO_2 films obtained at −900 V. AFM images show that pulsed substrate bias exerts a strong influence on the growth of TiO_2 films. As for the TiO_2 films obtained at 0 V, surface islands are tiny, the density of islands is high and RMS roughness is about 1.1 nm. While for the TiO_2 films at −900 V, surface islands are large, the island density is relative low and RMS roughness is around 3.8 nm, three times larger than the case of 0 V. To explain the phenomena observed in this study, pulsed plasma sheath model was used to simulate the ion sheath dynamics. The time evolutions within a pulsed period of the potential distribution and ion density distribution in the sheath were evaluated. By analyzing experimental and simulated results, it can be concluded that film growth and property relate close to ion density and energy in the sheath, which is dominantly governed by negative substrate bias.

1. Introduction

TiO_2 thin films are recently gaining interests due to their unique physical and chemical properties. Rutile TiO_2 thin film has good chemical stability and high refractive index, which is suitable as an optical coating and protective layer on lenses and optical fibers [1]. Anatase TiO_2 film is a preferred photocatalytic material since it can decompose and remove pollutants from its surface [2]. Amorphous titania film has a further advantage of having no grain boundary which is the main mechanism for electrical breakdown, chemical corrosion, or optical scattering [3]. Thus it exhibits higher dielectric constant and substantial chemical stability. It can be widely used in devices for energy conversion and storage, i.e. high power capacitor and new types of batteries [4–7].

Whatever kind the titania is, it is an insulated film with high dielectric constants. Two problems exist in the synthesis of dielectric TiO_2 films by plasma-based PVD process, including arc ion plating and magnetic sputtering. The first one is that micro-arc breakdown always occurs in the experimental process due to poor conductivity of dielectric TiO_2 films. It is caused by positive charge accumulation on the film surface, and it gets more severe when a DC substrate negative bias is applied. This phenomenon always causes a breakdown of the deposition process, resulting in low production efficiency [8], and even worse, it electronically penetrates the growing film, leading to poor film quality [9].

The second one is that a reversed local electric field, which is opposite to the substrate bias electric field, is generated by positive charges accumulated on the substrate surface. Hence the bias is counteracted and cannot efficiently enhance deposited species energy and consequently improve film properties [10,11].

According to our previous study [12–16], pulsed bias arc ion plating, applying a pulsed substrate bias, inherits the advantages of arc ion plating, such as high ionized degree, high deposition rate and strong bonging strength, etc. More importantly, a pulsed bias brings new features in this conventional PVD technique, such as reduced droplets, dense films and low-temperature deposition. Therefore it would be interesting to see the effect of a pulsed negative bias on film deposition and resultant structures and properties.

Mändl et al. [17] investigated the effect of pulsed bias on phase and growth morphology of TiO_x films, but the involved mechanism was not shown in their work. In our previous study, glass substrates were chosen to investigate the effect of pulsed bias on growth and property of TiO_2 films, and the involved mechanism was qualitatively discussed on the basis of pulsed plasma model proposed by Dai and Wang [18–20]. The quantitative simulation was not further shown.

---

* Corresponding author. Tel.: +86 411 84379508; fax: +86 411 84379185.
E-mail address: m.zhang@live.com (M. Zhang).

0257-8972/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
doi:10.1016/j.surfcoat.2012.05.083

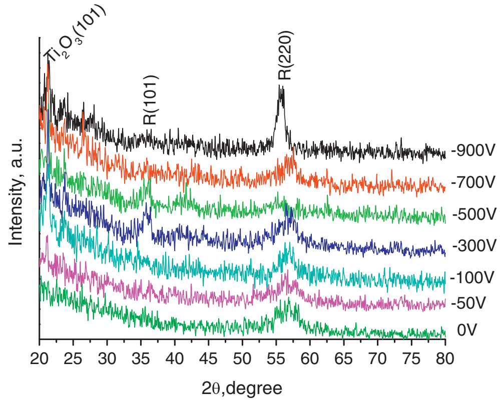

Fig. 1. GIXRD patterns of TiO_2 films prepared at different bias voltages.

In this work, dielectric TiO_2 films are deposited on p-(100) Si substrates by pulsed bias arc ion plating. Bias voltage, with frequency 20 kHz and duty cycle 40%, is altered from 0 to −900 V to investigate the effect on film growth, phase and microstructure. Dynamic simulation of pulsed plasma sheath is preformed as well to interpret the experimental results obtained herein.

2. Experimental

TiO_2 thin films were deposited by the arc ion plating system as described in detail elsewhere [13,14]. The system incorporated a cylindrical deposition chamber, which was fabricated of stainless steel with a size of Φ800 mm × 1000 mm. Two 99.9% pure titanium targets were mounted at the end of linear ducts which were connected to the vertical chamber. Both ducts consisted of a two-step magnetic coil. The first-step coil was to steady the burning arc and the second-step was to constrain the plasma and efficiently remove macroparticles. P-(100) Si substrates were ultrasonically cleaned in acetone, ethyl ethanol and deionized water sequentially for 15 min. Then they were blown dry and put on holders. Both Ti cathodes were operated at an arc current of 80 A to obtain the plasma. The base pressure was 4×10^{-3} Pa. Prior to the deposition, glow discharge cleaning was carried out for 10 min with a pulsed bias −900 V × 20 kHz × 40% (voltage, frequency, and duty cycle) in ambient Ar at 2.0 Pa. Then a mixture of oxygen and argon was introduced into the chamber. The working pressure was fixed at 0.5 Pa. The films were grown on p-(100) Si substrates at room temperature and without any additional heating. A thermocouple is used to monitor the deposition temperature and the highest deposition temperature detected in this work is lower than 200 °C. A pulsed negative bias was applied on the substrate, the frequency and duty cycle was

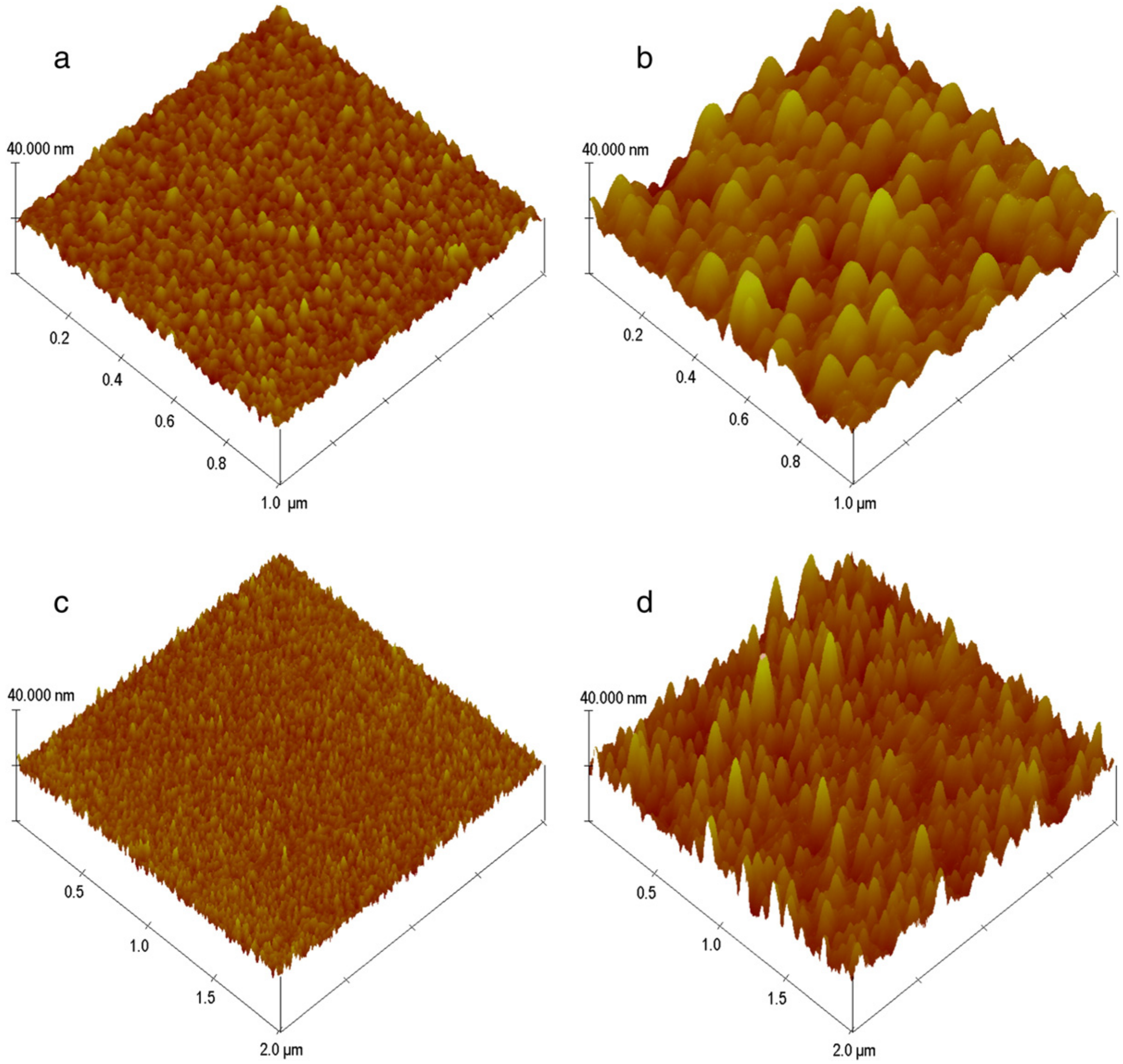

Fig. 2. AFM images of TiO_2 films obtained at 0 V (a, c) and −900 V (b, d).