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ADHESION AND WEAR BEHAVIOR OF NANOSTRUCTURED TITANIUM OXIDE THIN FILMS

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ABSTRACT

This study aims to investigate structural, mechanical and tribological properties of titanium oxide films deposited on glass substrates by radio frequency (RF) magnetron sputtering. All the as-grown titania films possess the anatase structure having a grain size of about 44 nm irrespective of the variation of substrate temperatures. AFM images show a nodular morphology with an increase of surface roughness. From micro-scratch tests, the optical micrographs of the scratch tracks show that the complete delamination of TiO_2 films deposited at higher temperatures appear at a higher value of adhesion critical loads. The highest adhesion critical load between titanium oxide films and glass was found to be 2.24 N for the film prepared at 300 °C. It represents an enhanced adhesion strength for films deposited at higher temperatures. Scratch hardness was also found to increase from 5.5 to 8.4 GPa with increasing substrate temperature. From micro-wear test, it is found that the wear resistance of TiO_2 films deposited at higher substrate temperatures exhibits higher wear resistance.

Keywords: Structural properties, Adhesion strength, Scratch hardness, Tribological properties.

1. Introduction

TiO_2 is one of the most widely studied ceramic materials used as films. These films are frequently employed for many optical devices in optics industry (Pulker, 1999), dye-sensitized solar cells (Sung and Kim, 2007), heat mirrors (Okada et al., 2006) and environmental applications (Fujishima et al., 2000) for their remarkable optical, photocatalytic and hydrophilic properties. TiO_2 films also possess noble antibacterial, disinfection, antifogging and self-cleaning properties (Sun et al., 2008). Now-a-days, TiO_2 films have a wide range of applications on glass substrates such as heat mirror films on building and automotive glasses, self-cleaning glass, air cleaning lamp, wiperless windshield etc. For these applications, thin TiO_2 films with nanometer thickness are mostly employed. As they are exposed to adverse environments, scratch and wear resistance play a significant role for their mechanical stability and durability. A variety of conventional deposition methods have been used to prepare TiO_2 films, such as electron-beam evaporation (Habibi et al., 2007), ion-beam assisted deposition (Yang et al., 2008), DC or RF magnetron sputtering (Okada et al., 2006; Sung and Kim, 2007), sol-gel methods (Wang et al. 2002), chemical vapor deposition (Sun et al., 2008) and plasma enhanced chemical vapor deposition (Yang and Wolden, 2006) etc. Sputter deposition technique is popular to produce adherent and uniform film over wide areas with better stoichiometric control. A number of studies on the deposition of TiO_2 films by sputtering appear in the literature recently (Okada et al., 2006; Sung and Kim, 2007; Karuppasamy and Subrahmanyam, 2007; Ye et al., 2007; Zhang et al., 2007). Most of the studies investigated structural, morphological and optical properties of TiO_2 films. Few reports are available in the literature on the adhesion properties, wear and scratch resistance of TiO_2 films (Chen et al., 2006; Chung et al., 2009; Jaworski et al., 2008; Kuo and Tzeng, 2002; Lackner et al., 2004; Leng et al., 2003). These studies attempted to evaluate adhesion strength and/ or wear resistance of TiO_2 films deposited mostly on metal substrates prepared by a variety of deposition techniques other than magnetron sputtering. Few reports are found to study tribological behavior of TiO_2 films deposited on metallic substrates using ball-on-plate or pin-on-disk tests (Chung et al., 2009; Lackner et al., 2004; Leng et al., 2003). These studies evaluated mechanical or/and tribological properties for titania films with micron-scale film thicknesses using micro and macro-scale measurements. However, majority of the transparent functional titanium oxide films on glass substrate have thickness in the nanometer range. Evaluation of mechanical properties of such films requires measurement technique with control capability at the nanometer level. Kuo and Tzeng (2002) reported adhesion strength of TiO_2 films with a nano-scale thickness of 240 nm deposited on silicon substrates using RF magnetron sputtering. In that work, a conventional scratch testing machine with an indenter tip radius of 200 μm was employed to evaluate adhesion critical load of nano-scale films.

Hence, in order to predict the durability of nanometric titanium oxide films on glass substrate and a coating/substrate system of great practical interest, it is important to have adequate data on their mechanical properties. Investigations dealing with the mechanical properties of titanium oxide at the nanometer level are scarce in the literature. In the present work, nano-TiO_2 thin films have been deposited on glass substrates by RF reactive magnetron sputtering at a constant sputtering pressure of 3 Pa. The main objective of this study is to evaluate mechanical properties such as scratch adhesion and wear resistance for TiO_2 thin films deposited on glass substrates by NanoTest platform having a depth and load resolution better than 0.2 nm and 1 mN, respectively. The effects of substrate temperatures on the mechanical properties have also been evaluated.

2. EXPERIMENTAL DETAILS

Anatase TiO_2 films were prepared on microscope glass slides as substrates by radio-frequency (RF) reactive magnetron sputtering of Ti target of 4 N purity. First the target was pre-sputtered in an argon atmosphere in order to remove the oxide layer. Sputter deposition was performed in a mixture of 46 sccm of Ar (99.999%) and 10 sccm of O_2 (99.999%) atmosphere supplied as working and reactive gases, respectively, through an independent mass-flow controller. The sputtering chamber was evacuated down to5 $\times 10^{-4}$ Pa by the turbo-molecular pump and the working pressure was kept at about 3 Pa. During deposition, the RF power was maintained at 250 W and the substrates were kept at room temperature, 200 and 300 °C respectively. Prior to deposition, the glass substrates were sequentially cleaned in an ultrasonic bath with acetone and ethanol. Finally, they were rinsed with distilled water and dried.

The crystalline quality of the TiO_2 films were investigated by X-ray diffraction (XRD) measurements (Model-D 5000, Siemens) in θ-2θ geometry using Cu K_α radiations (λ=0.15406 nm). The grain size of the films was calculated by using the Scherrer equation:

$$d = \frac{0.89\lambda}{B\cos\theta} \qquad (1)$$

where d is the grain size, λ the wavelength of X-ray, B the full-width at half-maximum of diffraction peak (FWHM), and θ is the diffraction angle. The thickness of the as-deposited film on unheated substrate was measured by a field emission scanning electron microscope (FESEM). For surface morphology, atomic force microscope (AFM) images were recorded using Nanoscope IIIa scanning probe in a tapping mode. The NanoTest platform by Micro Materials Ltd., UK, was used for the micro-scratch and wear testing. The system has a depth and load resolution better than 0.2 nm and 1 mN, respectively. A 25 μm radius spherical diamond indenter probe (Rockwell sharp diamond) was used for the tests. The micro-scratch test was performed with a constant indenter velocity of 5 μms^{-1}. An initial load of 2 mN was applied during the first 100 μm of the scratch, and the load was then increased to 2500 mN over a distance of 1900 μm at a fixed rate of 7 mNs^{-1}. Optical micrographs for the scratch tracks were captured by an optical microscope OLYMPUS BX61, Japan. The scratch hardness, which is a measure of the resistance of the material to normal penetration, is defined as (Malsbender et al., 2002):

$$SH = \frac{8.N}{\pi.d^2} \qquad (2)$$

where SH is the scratch hardness, N is the applied normal force and d is the corresponding scratch width. In this investigation, scratch hardness of the studied films is measured at three positions on the scratch tracks before the coating failure and the average value was taken into consideration.

The procedure for wear tests involved a set of five topography scan and four wear scan at a constant velocity of 1μms^{-1} along the same surface on the films unidirectionally. In each topography scan including the first scan, the indenter moves at a constant load of 2mN. In each wear scan, an initial load of 2 mN was applied during the first 200 μm, and then a constant load of 500 mN was abruptly applied for the further scan of 800 μm. Each wear scan is followed by a topography scan.

3. RESULTS AND DISCUSSION

In our previous work, the thicknesses measured by optical spectrophotometry for the as-deposited films at room temperature, 200 and 300 °C were found to be 315, 335 and 345 nm respectively (Hasan et al., 2009). A cross-sectional image of the as-deposited TiO_2 films on unheated substrate is shown in Figure 1. It is found that the thickness of the film is approximately 330 nm which is in good agreement with the optical thickness. The cross-sectional view shows that the film possesses granular structure. It also shows dense and compact nature for the as-deposited TiO_2 film prepared at room temperature. It may be mentioned that Eufinger et al. (2007) obtained a columnar structure in their dc magnetron sputtered TiO_2 films at a power of 60 W.

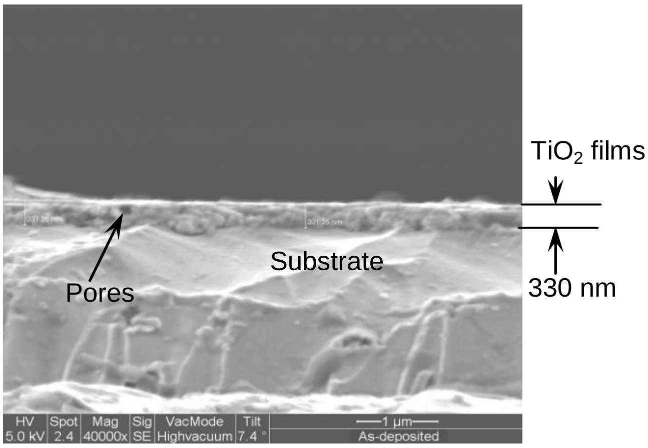

Figure 1. SEM cross-sectional image of the TiO_2 film deposited at room temperature.

A few voids are also found in the cross section (arrow) to exhibit its porous structure. The diffraction patterns of TiO_2 films deposited at different substrate temperatures are shown in Figure 2. From Figure 2, as-deposited TiO_2 film prepared at room temperature is found to be crystalline and possesses anatase structure as it shows few strong peaks of anatase (101), (200) and (211).

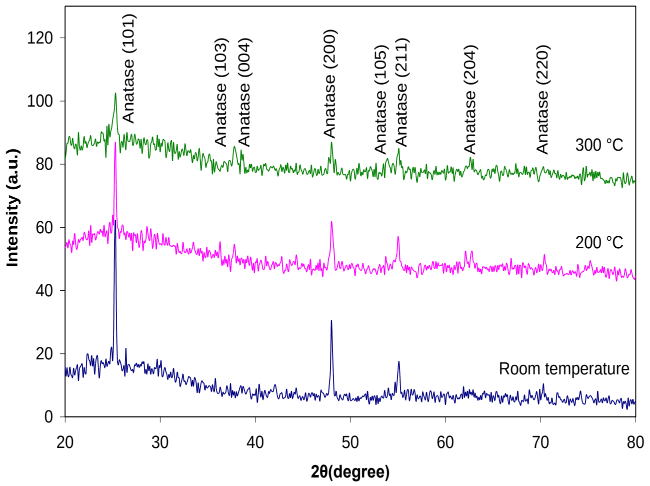

Figure 2. X-ray diffraction patterns of TiO_2 films deposited at room temperature, 200 °C and 300 °C.

Although at a high pressure the depositing species have lower energy, there are suggestions that high density negative oxygen ions are movable at high pressure which impart high energy to the growing film (Karuppasamy and Subrahmanyam, 2007). This may be the reason for the growth of crystalline anatase phase in the present study even at room temperature.

Some additional weak peaks along the anatase planes (103), (004), (105), (204) and (220) appear for the samples of heated substrates. It is also observed that the peak intensities of the anatase planes (101), (200) and (211) decrease significantly with increasing substrate temperature. It may be inferred that crystallinity is found to decrease with increasing substrate temperature. Tomaszewski et al. (2007) reported that sodium ion from glass substrate diffused into their TiO_2 films during annealing treatment which suppressed anatase crystallization. Alkali ion diffusion from glass slides to titania films might also occur in the present study to decrease the crystalliniy. In the present work, the crystallite sizes calculated by Scherrer equation for TiO_2 films prepared at different substrate temperatures are seen to have a grain size of ~44 nm. Substrate temperature does not seem to have any significant effect on the grain size. It is observed that the range of grain size of the deposited films on microscope slides obtained in the present study is close to that obtained by Eufinger et al. (2007).

The surface morphology of TiO_2 films as recorded by AFM in the tapping mode is shown in Figure 3.

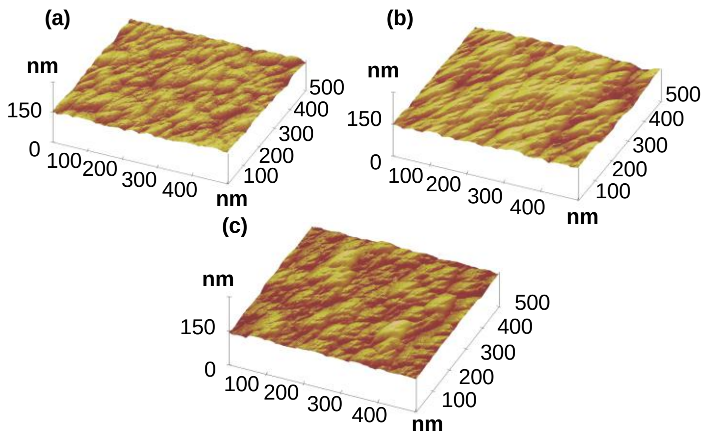

Figure 3. AFM images of TiO_2 films deposited at: (a) Room temperature, (b) 200 °C and (c) 300 °C.

The anatase TiO_2 films are all found to be as compact and dense. AFM images exhibit a nodular morphology. Substrate temperature does not appear to have a significant effect on the morphology of the film. From AFM surface roughness analysis, the root mean square (rms) surface roughness of TiO_2 films deposited at room temperature, 200 °C and 300 °C are found to be 4.75, 5.23 and 6.26 nm, respectively. It indicates an increase of rms roughness with increasing substrate temperature. Hou et al. (2003) observed a lower rms roughness (2.38 nm) for their AC magnetron sputtered TiO_2 films having comparable thickness as in the present study.

The adhesion critical load of the studied TiO_2 films was determined by the micro-scratch tests combined with the observation of the scratch tracks under the optical microscope. Three different micro-scratch tests were performed for each TiO_2 films deposited at different substrate temperatures and all the tests give consistent results. Optical micrographs of the scratch scars on TiO_2 films are shown in Figure 4. It is observed that each scratch track gets wider uniformly with progressively increasing load.

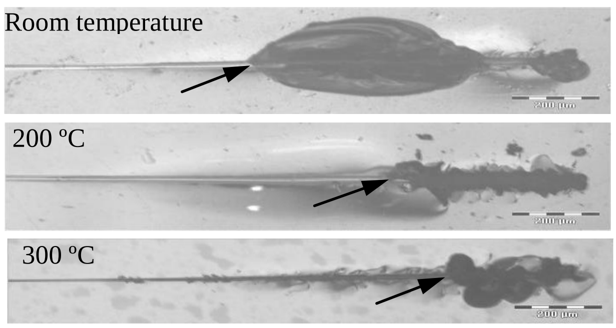

Figure 4. Optical micrographs on TiO_2 films deposited at different substrate temperatures.

At a certain point (shown by arrows) a wide damaged area appears representing a complete delamination of the films which can be defined as the critical load for adhesion. Two types of failure are mainly encountered in scratch tests, namely, cohesive failure of the coating or substrate and interfacial failure of the coating-substrate interface (Malsbender et al., 2002). The cohesive failure of a coating is mainly accompanied by partial conical cracks and some debris at the side of the scratch tracks (Beake and Ranganathan, 2006). The complete delamination of films is due to the interfacial failure at the coating-substrate interface. From Figure 4, it is observed that no cohesive failure mode appears for the film deposited on unheated substrate, but for the films prepared at higher substrate temperatures exhibit an earlier damage with small cracks and some debris. It may be attributed to the higher surface roughness. Higher residual stress resulting from mismatch of coefficients of thermal expansion of the substrate and films deposited at higher temperatures might also contribute to this. The critical loads of TiO_2 films deposited at room temperature, 200 and 300 °C were estimated by the scratch tests and found to be 1.5, 2 and 2.24 N, respectively. It is thus seen that higher substrate temperatures lead to improved adhesion of TiO_2 films on glass substrates. There are suggestions that cohesive bonding in anatase structure and interdiffusion of film/substrate interface can cause enhanced film adhesion (Chung et al., 2009). The increase of adhesion critical load may be due to interdiffusion of atoms in the film/substrate interface and densification of the films at higher substrate temperatures.

A number of researchers reported on the adhesion critical load for titanium oxide films. Chen et al. (2006) reported an increase of adhesion critical loads from 1.5 to 19.25 N using a scratch tester with 200 µm tip radius diamond indenter. They investigated sol-gel prepared TiO_2 films (6.7-10 µm thick) on stainless steel at different annealing temperatures, 400 to 600 °C. Kuo and Tzeng (2002) evaluated critical loads for 240 nm thick RF sputtered TiO_2 films on silicon substrates varying substrate temperature from 200 to 500 °C. They estimated the critical load using a diamond indenter of tip radius 200 µm and it was found to be about 7 N without any significant effects of substrate temperatures. In this study, a spherical diamond indenter of tip radius 25 µm was drawn with progressively increasing load during micro-scratch tests. Due to the smaller radius of the indenter tip, a force was applied on a smaller contact area of films. Although a low force was applied, it produces a high contact pressure and severe plastic flow with a very few asperities. This mechanism is most likely responsible for the coating failures at lower values of critical loads in the present investigation. As a result, it can be inferred that the lower values of critical loads obtained in this work may be attributed to the combined effects of film thickness, indenter tip radius, substrate materials and coating-substrate interfaces.

The scratch hardness is a measure of coating cohesion. The values of scratch hardness calculated using equation (2) are found to be 5.5, 6.7 and 8.4 GPa for TiO_2 films prepared at room temperature, 200 and 300 °C respectively. Because of the nano-scale thickness of the films, it is likely that the substrate also contributes to the measurements of both critical load and scratch hardness. It is observed that scratch hardness is found to increase with the increase of substrate temperatures. Joworski et al. (2008) reported a scratch hardness of 3.6 GPa for their anatase titania films where the scratch test were done using a 200 um indenter tip under a higher load of 30 N. In addition, Lackner et al. (2004) reported an increase of surface hardness from 4.25 to 11.16 GPa determined by nanoindentation with the decrease of oxygen flow rate. The scratch hardness values found in the present study is nearly comparable to the surface hardness values found in that study.

In tribological tests, a spherical diamond indenter of radius 25 µm of NanoTest high load head equipment is drawn unidirectionally along the same surface using a load of 500 mN at a sliding speed of 1 µm/sec for a wear track distance of 800 µm. Figure 5 shows the profilometry of four successive wear passes including the as-grown film surface. From the figure, it is observed that upon the application of load, the penetration depth suddenly increases. The penetration becomes progressively deeper as the number of passes on the same weak track increases. Data extracted from Figure 5 is tabulated in Table 1. It is seen that films deposited at higher substrate temperature exhibits lower penetration. Thus higher deposition temperature results in titanium oxide film with improved resistance to penetration.

Table 1 Penetration depth for TiO_2 films deposited at different temperatures during wear test.

Substrate temperature (°C)	Penetration depth (nm)			
	1st Pass	2nd Pass	3rd Pass	4th Pass
25	100	170	200	250
200	80	150	175	210
300	50	120	140	180

This result correlates well with the increase of scratch hardness for higher substrate temperatures as discussed earlier. The wear track width was measured at three different positions along the wear tracks of the studied films. The mean width of the wear tracks of TiO_2 films deposited at different substrate temperatures are given in Table 2. It is observed that the width of the wear track is found to decrease with increasing substrate temperature which is consistent with the penetration data. Thus it can be inferred that wear resistance is found to improve with higher substrate temperatures

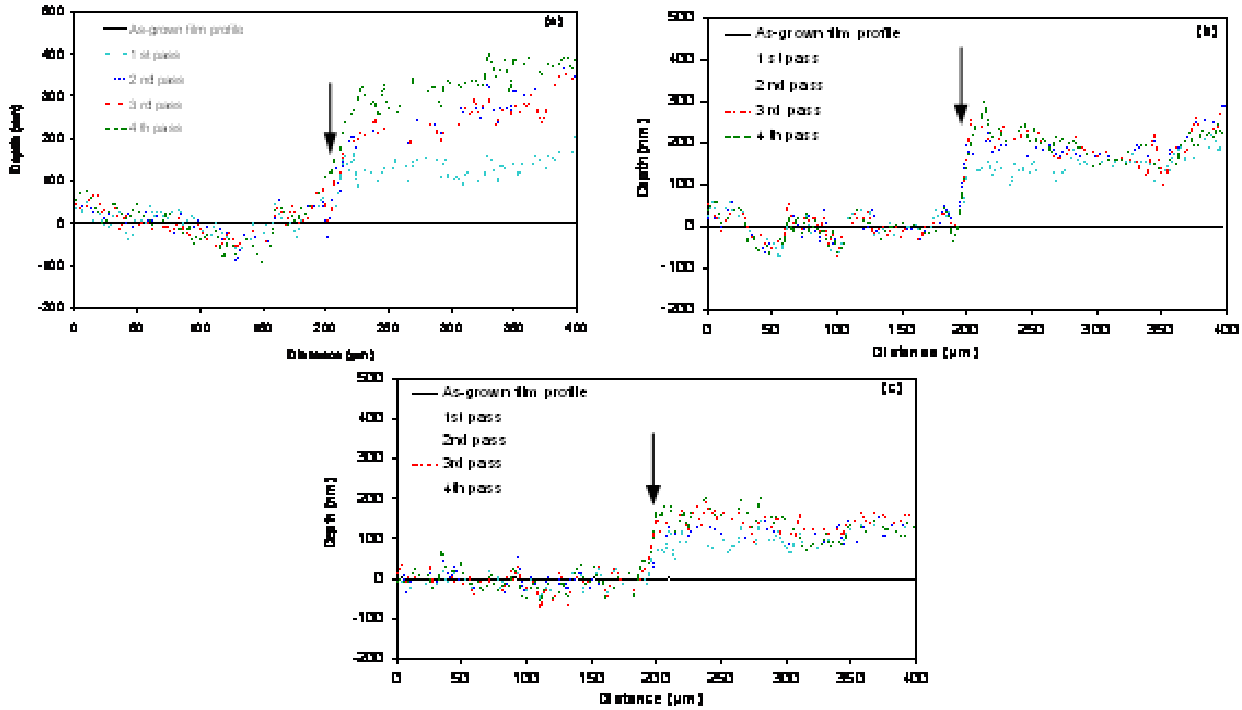

Figure 5. Wear tests for TiO_2 films deposited at (a) room temperature

Table 2 Average wear track width of TiO_2 films deposited at different substrate temperatures.

Sample	Substrate temperature (°C)	Mean wear track width (µm)
1	Room temperature	18.8
2	200 °C	14.2
3	300 °C	9.6

The improvement in the tribological properties may be interpreted as the effects of enhanced adhesion strength and densification at higher substrate temperatures as well. Several reports (Chung et al., 2009; Lackner et al., 2004; Leng et al., 2003) suggested the improvement of wear resistance with the increase of crystallinity, adhesion critical loads and surface hardness in their micro/macro scale wear measurements. In the present work, the enhancement of wear resistance may be attributed to the improvement of critical loads and hardness for films deposited at higher substrate temperatures.

4. CONCLUSIONS

The anatase phase titanium dioxide films with grain size of about 44 nm have been produced by RF reactive sputtering method on unheated and heated glass substrates. AFM images of as-deposited TiO_2 films at different substrate temperatures show a uniform, compact and nodular morphology. The mechanical and tribological properties of TiO_2 films were investigated by micro-scratch and wear tests respectively. The adhesion critical load, scratch hardness and wear resistance are seen to have strong dependence on the substrate temperature. The critical loads of adhesion of TiO_2 films deposited at room temperature, 200 and 300 °C are found to be 1.5, 2 and 2.24 N respectively. The values of scratch hardness are also found to be 5.5, 6.7 and 8.4 GPa for the films prepared at room temperature, 200 and 300 °C respectively. In wear tests, the final penetration is found to decrease for films prepared at higher substrate temperature. Titanium oxide films at higher substrate temperatures show better resistance to penetration. From the optical micrographs of the wear scars, similar trend for the width of wear scars are also observable. The combined decrease of penetration and wear track width results in an enhanced wear resistance for the TiO_2 films deposited at higher temperatures. This improvement of wear properties for the films deposited at higher temperature is likely to be attributed to the improved adhesion critical loads and scratch hardness.

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