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ORIGINAL PAPER

Tribological properties of multilayer nanostructure TiO_2 thin film doped by SiO_2

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Abstract Multilayer of TiO_2 and TiO_2:SiO_2 thin films were grown on a glass substrate by sol–gel processes, followed by high temperature treatment at 500 °C. The fine grained TiO_2 films controlled by SiO_2 dopant showed very good wear resistance and endurance life. Energy dispersive X-ray spectroscopy was used to indicate the elements in the films. X-ray diffraction analyses indicated that TiO_2 and TiO_2:SiO_2 film contain only anatase phase. The morphologies of the original and worn surfaces of the samples were analyzed by means of scanning tunneling microscope and scanning electron microscopy. The tribological properties of TiO_2 and TiO_2:SiO_2 thin films sliding against AISI52100 steel pin were evaluated on a pin on disk friction and wear tester. The results showed that 25-layer TiO_2:SiO_2 films are superior in reducing friction and resisting wear compared with the glass substrate.

Keywords Sol–gel · Nanostructure · Thin films · TiO_2 · SiO_2 · Tribological properties

1 Introduction

TiO_2 Sol–gel ceramic films are of interest for researchers due to their excellent tribological and mechanical properties [1–9]. The application of this technique has been focused on purification and tribological properties that are important in the application of environmental protection fields such as nature, life space and wear resistance [7, 9–19]. Recently, Physical and mechanical properties of the TiO_2 as a functional film have been largely focused on [17, 20–27]. Both tribologists and scientists engaged in material science are drawing much attention of the tribological investigations on ceramic films because of their usage as micro-device materials [5, 18, 28]. Although, there still remain considerable challenges in reducing wear as well as improving adhesion on various substrates; however these materials have shown good tribological properties [4, 5, 21]. Lower wear rate of fine grained ceramics in comparison with those of coarse-grained was shown with numerous studies in both sliding [5, 18, 27]. Addition of La_2O_3, CeO_2, CuO, Fe_2O_3, SiO_2, or other oxides into anatase TiO_2 can improve the thermal stability and prevent the growth of titania grains [4, 27, 29]. Presence of some dopants could increase the adhesion and mechanical stability of thin film on substrates, which are a key issue in device reliability [5, 27, 29]. Several techniques such as: physical vapor deposition, chemical vapor deposition, pulsed laser deposition, magnetron sputtering, and electro deposition are used to produce TiO_2 thin films [2, 3, 5]. However, due to the complexity of the experimental set up and high cost of production, applications of these techniques are limited to the production of small scale films [3, 5, 18]. The sol–gel technique is regarded as a cost effective method for the production of TiO_2 films and involves simple processing steps [16, 17, 19]. The sol–gel process is a wet chemical method based on the hydrolysis/polycondensation of metal precursors, which leads to a large variety of oxide materials [3, 19].

In this paper, TiO_2 and TiO_2:SiO_2 thin films were deposited on glass substrate via the sol–gel method. The tribological properties of the films were investigated. The

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friction coefficient and wear life of the thin films were discussed in details. Number of layer was changed as 5, 10, 15, 20 and 25 layer for analyzing wear resistance of the films. In fact we have made a comparison between tribological properties of multi-layer TiO_2 and TiO_2:SiO_2 thin films.

2 Experimental

2.1 TiO_2 and TiO_2:SiO_2 film preparation

Tetraisopropoxy titanium (TTIP, Merck), tetraethylorthosilicate (TEOS, Merck), ethanol, hydrochloric acid, and acetylacetone (ACAC, Merck) are used for synthesis of TiO_2 and TiO_2:SiO_2 solutions [2–4]. For the synthesis of the starting solution, TTIP (9 ml) was dissolved in ethanol solution (143 ml) that contained hydrochloric acid (0.5 ml) and water. Then TEOS (1 ml) was added to the solution. Afterwards, ACAC (2 ml) was added in order to stabilize TiO_2 and the solution mixed magnetically for 2.5 h [2, 3, 8]. Finally, the sols were aged in a sealed beaker for 24 h [8]. For preparation of pure TiO2 sol above procedure was repeated without addition of TEOS.

Dip coating method was used for preparation of TiO_2 and TiO_2:SiO_2 thin films. The glass slides were dipped in the aged solutions at a drawing speed of 70 cm $min^{-1}$and then obtained films were dried at room temperature for 15 min and in final step those thin films were heated at 500 °C for calcinations for 4 h. The double and multi-layer films are obtained by repeating the above procedures properly.

2.2 Film characterization

X-ray diffraction using Cu Kα ($\lambda = 1.5406$ Å) radiation in the region of $2\theta = 20°–75°$ was used to indicating grain size and crystallinity of the TiO_2 films. In addition, the grain or crystalline size (L) was estimated by Scherrer's formula as following [3]:

$$L = \frac{k\lambda}{\beta \cos\theta}$$

where L is the crystallite size of pure TiO_2, k is a constant value (= 0.94), λ is the wavelength of X-ray (CuKα = 1.54065 Å), β is the true half-peak width, and h is the half diffraction angle (in term of degree) of the centroid of the peak.

The surface morphology of the films was studied using a scanning electron microscope (SEM, Leo 1450 VP, Zeies, Germany) and scanning tunneling microscope (STM). Energy dispersive X-ray spectroscopy (EDS, 7353, Axford, England) was used for elements analysis.

2.3 Tribological properties test

A pin on disk friction and wear testerwas used for attaining thetribological properties of the films at a sliding velocity of 100 mm min^{-1}. TheAISI52100 steel pin counter-part (diameter 5 mm) was fixed and the applied normal force was 3 N. The chemical composition of the AISI52100 pin is shown in Table 1. The friction coefficient of the thin films was recorded as a function of distance that pin passes on the films. Prior to the friction and wear tests, all the samples were cleaned in an ultrasonic bath with acetone for 2 min.

3 Results and discussion

3.1 Characterization of the film

The film composition was evaluated by EDS analysis. Figure 1 shows the EDS pattern of TiO_2 and TiO_2:SiO_2 films. Main peaks of Ti, Si, O and also small amounts of Na, Ca, Mg is observed in EDS results. Na, Ca and Mg are existing in glass substrate. Therefore; X-ray can diffuse into the film thickness and these elements would be detected. According to Fig. 1 the peak of Si is more vigorous in comparison with other elements. This can be attributed to presence of Si in SiO_2 form which is major composition of glass substrate. Moreover, presence of SiO_2 can cleavage the Ti–O–Ti and change it to Ti–O–Si. Therefore this phenomenon can shift the Si binding energy to higher value [13, 14]. The attendant of oxygen in EDS results is possibly related to the formation of TiO_2 and SiO_2 in the films, but oxygen could diffuse during the calcinations from the air to the thin films.

Figure 2 shows XRD patterns of thin film at 500 °C. There are several major peaks at $2\theta = 25.45$, 48.225, 62.9 for TiO_2 films and 25.8, 48.25, 62.915 for TiO_2:SiO_2 thin films, respectively, which are attributed to a TiO_2 structure,

Table 1 Chemical compositions of AISI-52100 steel pin

Composition (wt%)									
	Fe	C	Si	Mn	P	S	Ni	Cu	Cr
AISI52100	Balance	1.03	0.22	0.31	0.01	0.01	0.07	0.06	1.39

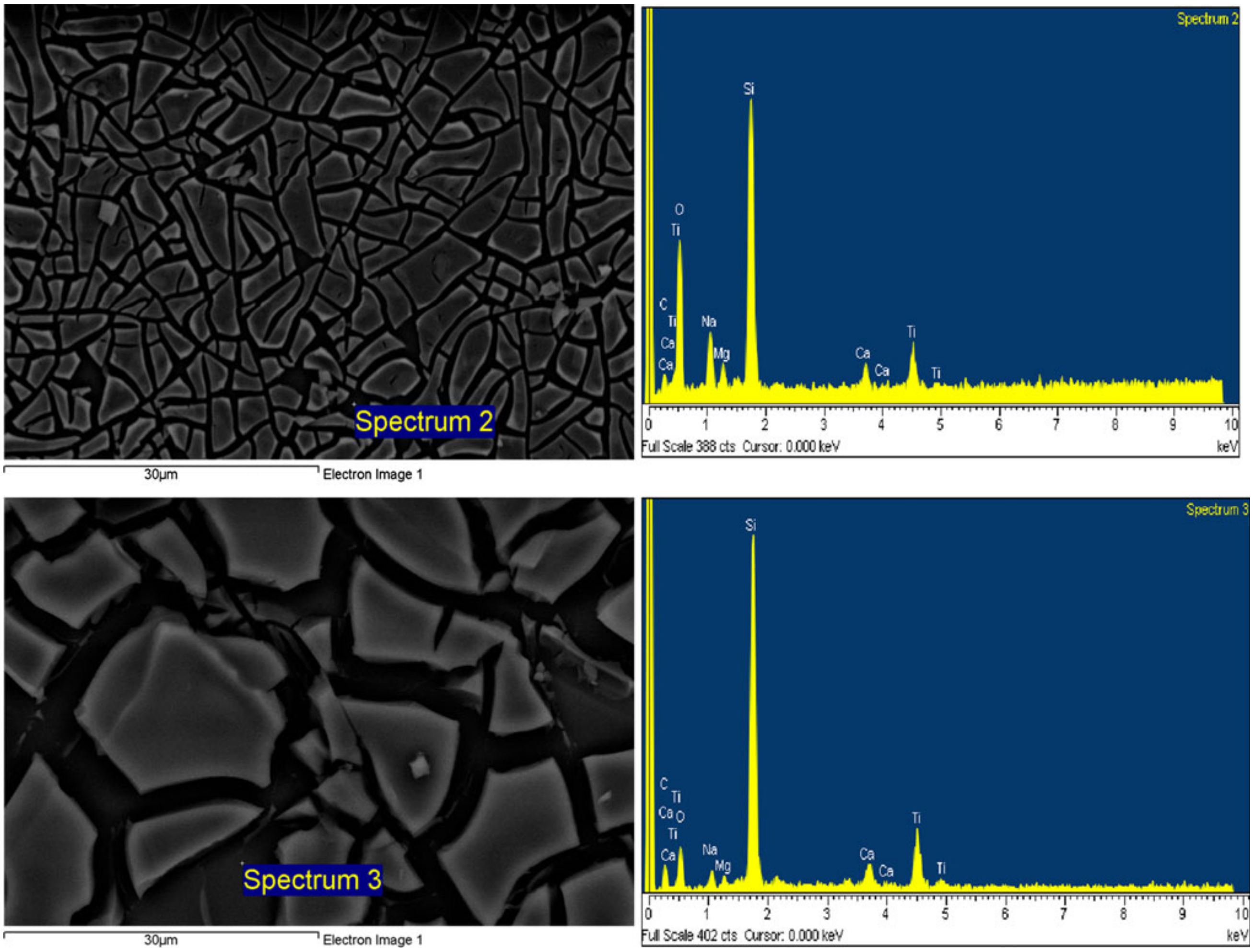


Fig. 1 EDS analyses of the films: Spectrum 2 TiO_2, Spectrum 3 TiO_2:SiO_2

indicating that the major phase of the TiO_2:SiO_2 thin films that was calcined at 500 °C is TiO_2. From XRD line broadening and using the Scherrer equation average grain size of TiO_2, TiO_2:SiO_2 is 33 and 10 nm, respectively. According to these results lower crystallization and grain size of TiO_2 can happen in high content of SiO_2. This strong retarding has been often ascribed to a good chemical homogeneity of the starting gels, i.e., to a high degree of Si–O–Ti bonding, which is believed to be a reason of restricting the growth of grains during heat treatment [16, 17]. Therefore mole percent of SiO_2 should be choosing in optimal percent.

Figure 3 shows STM image of the TiO_2 and TiO_2:SiO_2 thin films. According to Fig. 3 TiO_2 thin film is thicker than TiO_2:SiO_2 thin film because of higher grain size of TiO_2. Actually in the TiO_2:SiO_2, thin film of SiO_2 would restrain the growing of TiO_2 crystals that discussed above; therefore the thin film of pure TiO_2 has a thicker layer in comparison with TiO_2:SiO_2 film. The surface of TiO_2:SiO_2 films are smothering than TiO_2 films and adhesion of these films is more stable on the glass substrate. So this can be concluded from the results that the films, which contain SiO_2, have much lower friction.

3.2 Tribological properties

In present study, starting sol of TiO_2 and TiO_2:SiO_2 were prepared in constant mol percent of TiO_2 and SiO_2; on other hand, after the evaluation of tribological properties of the films with a pin on disk system, layer number of the thin film was changed. Figure 4 shows the attained friction coefficient of TiO_2 and TiO_2:SiO_2 thin films as a function of distance. For the glass slide the coefficient of friction increases sharply only after several meters, indicating that the glass substrate has a low wear resistance. With exploration in the results, 25-layer TiO_2:SiO_2 film sliding against AISI52100 pin exhibited much lower friction coefficient and longer wear life under low loads. According to Fig. 4b 25-layer thin film of TiO_2:SiO_2 has best wear resistance in compare with other films. Figure 4a, b shows that all of the

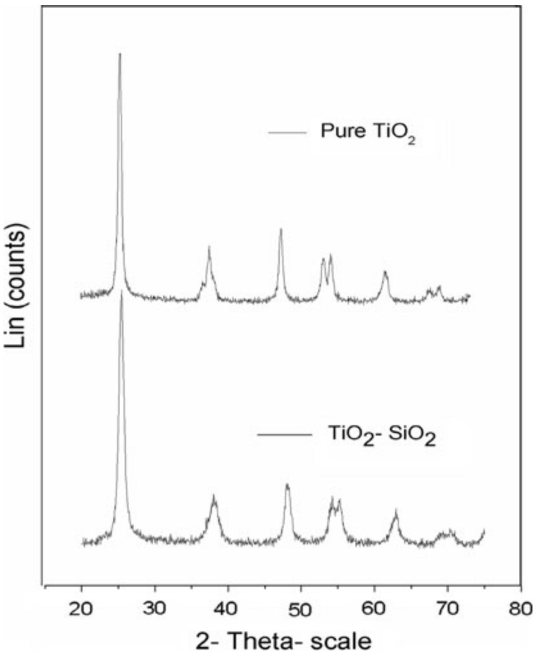


Fig. 2 XRD patterns of the obtained films at 500 °C for 4 h

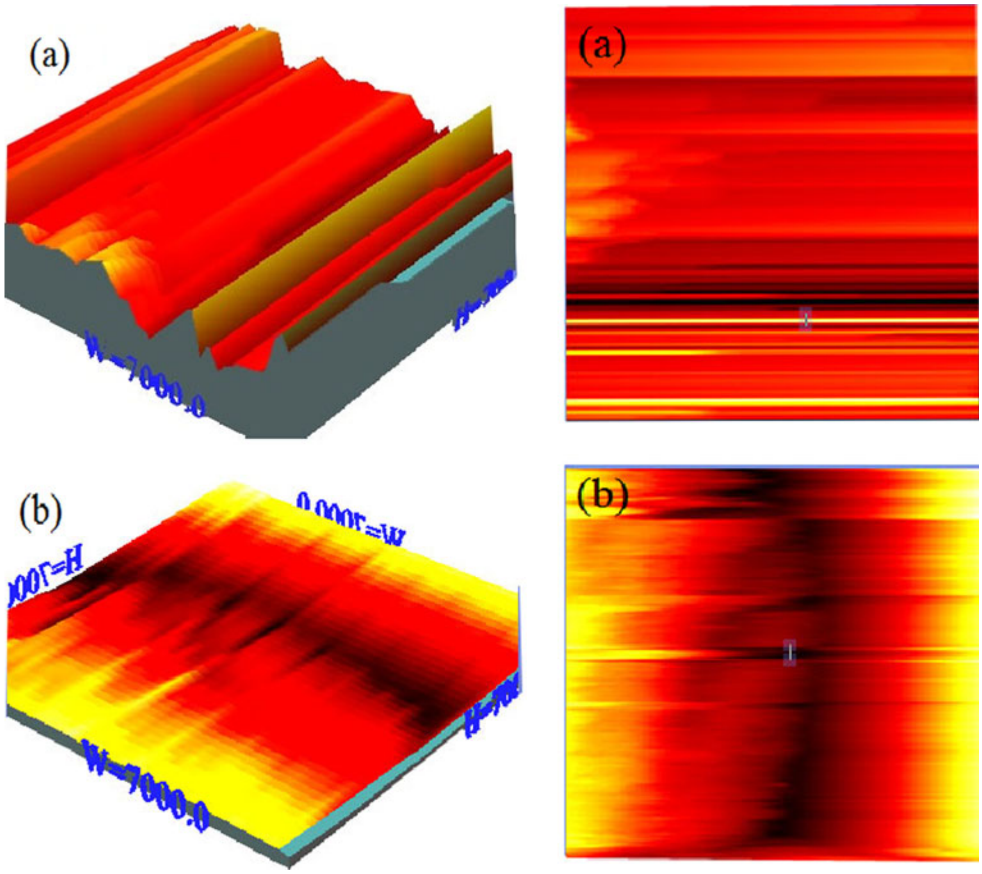
films have good wear resistance until the films don't lose their wear resistance in contact with steel pin but after destruction of the films friction coefficient sharply rising. Additionally, with comparing the Fig. 4a–c it seems that initial friction coefficient of all of the films is similar to glass substrate but when distance is increasing the films with higher layer have lower friction coefficient. Therefore, this can conclude that glass substrate has low wear resistance and changing the number of TiO_2 and TiO_2:SiO_2 layers influence the wear resistance of TiO_2.

Above results indicate that higher layer of the thin films have more wear resistance, therefore for more wear resistant of the TiO_2 coatings in constant mol percent of SiO_2, the number of layer should choose in higher level. More wear resistance of thin films with higher layer can be attributed to constructing of more dense and more homogeny of the films in higher layer.

Result indicates that TiO_2 and TiO_2:SiO_2 thin films register good wear resistance in contact with steel pin. Primacy of TiO_2:SiO_2 films in comparison with other TiO_2 films is attributed to presence of SiO_2 where this compound can improve adhesion of TiO_2 on glass substrate, therefore presence of SiO_2 can improve tribological properties of TiO_2:SiO_2 thin films. This indicates that the sol–gel TiO_2:SiO_2 film on a glass substrate has relatively long wear life and this can reduce the friction between glass and steel.

SEM images (Fig. 5) are used to investigating the friction and wear mechanisms of the worn surface after

Fig. 3 STM image of the films: **a** TiO_2 **b** TiO_2:SiO_2



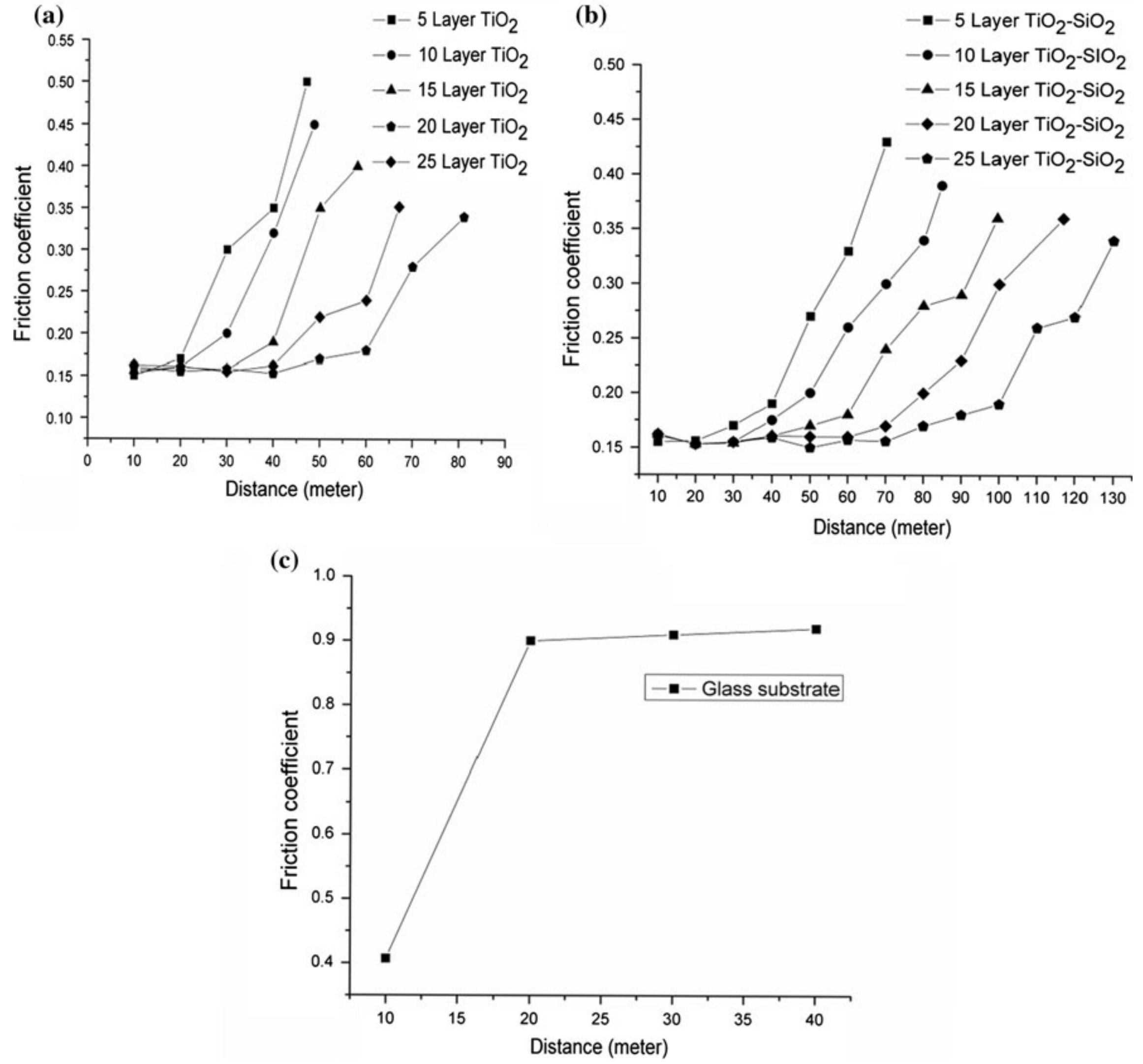


Fig. 4 Friction coefficient of obtained films as a function of distance under 3 N: **a** TiO_2 thin films, **b** TiO_2:SiO_2 thin films, **c** glass substrate

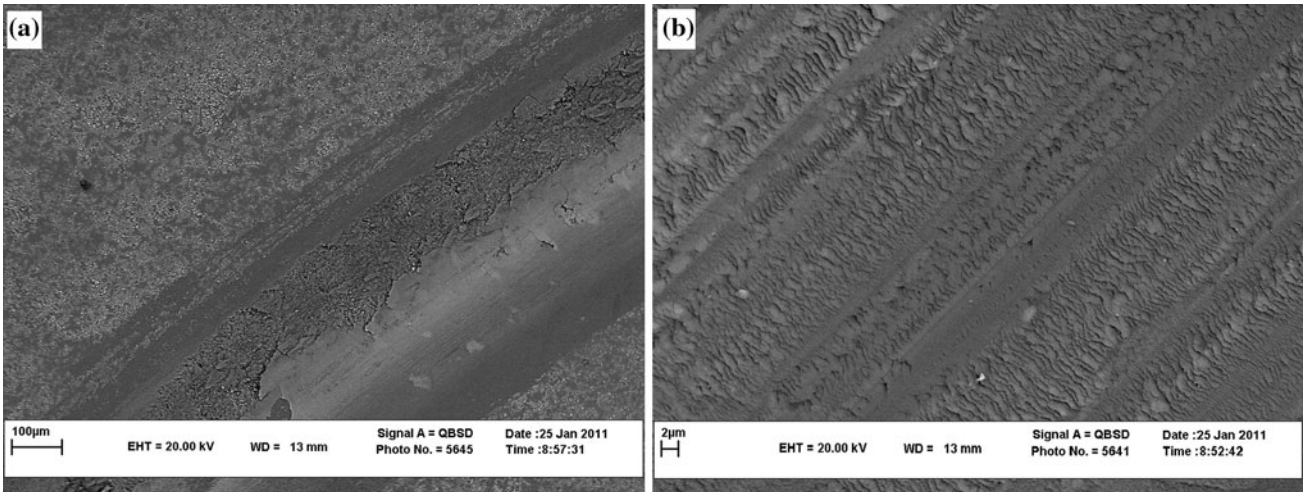


Fig. 5 SEM pictures of worn surfaces of TiO_2 and TiO_2:SiO_2 films sliding against AISI52100 steel pin: **a** TiO_2, **b** TiO_2:SiO_2

destruction sliding against AISI52100 pin. Figure 5 shows the micrographs of the worn surfaces of TiO_2 and TiO_2:SiO_2 film sliding against AISI52100 steel pin. According to SEM micrographs, the surfaces are not very smooth and sever stick happened, which may lead to pull up the coating and reduce the wear resistance of the films. Differently, Fig. 5 shows that the thin films don't lose completely, and their wear resistance is retain after the wear test; so, this indicates that TiO_2 coatings have good wear resistance sliding against the steel pin. Decreasing wear resistance and destruction of the thin film can belong to physical, chemical and mechanical properties of steel pin.

4 Conclusion

TiO_2 and TiO_2:SiO_2 films with high wear resistance were prepared on glass substrate via the sol–gel method. XRD patterns indicate that with higher mole percent of SiO_2, the TiO_2 grain size becomes smaller; therefore TiO_2 with lower crystalline size was more wear resistance. The STM images indicate that TiO_2:SiO_2 film was softer than TiO_2 film. The effects of addition of SiO_2 into TiO_2 film and the subsequent effects on tribological properties were discussed. The cohesion and mechanical stability of thin film on substrates can greatly advance with attendance of SiO_2, which is an important result prompts using this material. According to the results, TiO_2 and TiO_2:SiO_2 thin films cause drastic changes in decreasing friction and resisting wear compared with the glass substrate. The results indicate that higher layer of the films especially 25-layer TiO_2:SiO_2 were more wear resistance, therefore the supreme anti abrasion and friction reduction performance of TiO_2:SiO_2 film in sliding against AISI52100 pin under low load could summaries from the above results.

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