

## Nanotribological properties of ALD-processed bilayer TiO<sub>2</sub>/ZnO films



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### ABSTRACT

TiO<sub>2</sub>/ZnO films grown by atomic layer deposition (ALD) demonstrated nanotribological behaviors using scratch testing. TEM profiles obtained an amorphous structure TiO<sub>2</sub> and nanocrystalline structure ZnO, whereas the sample has significant interface between the TiO<sub>2</sub>/ZnO films. The experimental results show the relative XRD peak intensities are mainly contributed by a wurtzite oxide ZnO structure and no signal from the amorphous TiO<sub>2</sub>.

With respect to tribology, increased friction causes plastic deformation between the TiO<sub>2</sub> and ZnO films, in addition to delamination and particle loosening. The plastic deformation caused by adhesion and/or cohesion failure is reflected in the nanoscratch traces. The pile-up events at a loading penetration of 30 nm were measured at 21.8 μN for RT, 22.4 μN for 300 °C, and 36 μN for 400 °C. In comparison to the other conditions, the TiO<sub>2</sub>/ZnO films annealed at 400 °C exhibited higher scratch resistance and friction with large debris, indicating the wear volume is reduced with increased annealing temperature and loading.

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### 1. Introduction

Atomic layer deposition (ALD) is regularly selected to produce extremely thin coatings because of its remarkable self-limiting nature and low growth temperature. Many semiconductor materials, such as TiO<sub>2</sub>, ZnO, SnO, and Al<sub>2</sub>O<sub>3</sub>, can be produced by ALD [1–3]. Example materials of TiO<sub>2</sub> and ZnO are based on the following binary CVD reactions and their corresponding reaction enthalpies [4,5]. ZnO is a metal oxide with the property of optical transparency that can be used for applications in optical semiconductor devices or thin-film transistors [6,7]. These material properties have been thoroughly investigated with respect to numerous processing parameters and conditions [8]. Additionally, the selective deposition of TiO<sub>2</sub> by ALD has been reported using polymer masking layers [9,10]. Similarly, the optical properties of these biological replicas have been reported as functions of TiO<sub>2</sub> ALD thickness. [11] Both materials are commonly used because they possess similar band gaps, although the electron mobility of ZnO is higher than that of TiO<sub>2</sub> [12–14].

Novel films have also been studied using ALD for the evaluation of their optical properties. In comparison to single-crystal bulk materials, the deformation properties of thin films processed by ALD are strongly correlated with geometrical dimensions and material defect structures [15]. Thus, the investigation of nanotribological behaviors including the adhesion/cohesion mechanisms of ALD-processed thin films with post-annealing treatments is intriguing. Tribological behaviors are evaluated based on the sliding wear characteristics that are also important for reliability [16–18].

The friction coefficient and volume loss are generally measured from both lubricated and unlubricated conditions at different sliding speeds and distances [19,20]. Related experiments have been conducted using this analytical approach, which exhibits some advantages, such as the free selection of materials, ease in altering the design, and convenient initial facilities [21–23]. Similarly, ALD coating layers can be estimated using the artificial lateral force of scratching to extend the tribological problem for reliability issues. Even now, the research using this approach for the analysis of scratch resistance and adhesion/cohesion failure mechanisms of TiO<sub>2</sub>/ZnO films grown by ALD remains far from conclusive.

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The present paper reports a systematic experimental study on the effect of annealing TiO<sub>2</sub>/ZnO films with respect to reliability. Our main goal in this study was to investigate the tribological and microstructural behaviors of the films. The qualities of the resulting films, in terms of the nanoscratch induced deformation, were examined.

## 2. Experimental details

TiO<sub>2</sub>/ZnO films were deposited on Si (100) substrates using an ALD system operated with the flow-rate interruption method. The wafer was transferred into an ALD reactor in which diethylzinc and water were used as precursors under a processing temperature of 200 °C, and the deposition rate was controlled at 0.2 Å/cycle for ZnO film deposition [6]. The deposition depth ZnO thin film is 30 nm. Subsequently, each ZnO/Si sample was delivered to another chamber for TiO<sub>2</sub> deposition using TiCl<sub>4</sub>/H<sub>2</sub>O precursors with a stable flow rate of 0.7 Å/cycles at 200 °C. Since the ALD-processed films showed only a small thickness variation, the thickness of the stacked film could be easily controlled [24]. After that, a bilayer sample of 10 nm TiO<sub>2</sub> and 30 nm ZnO on a Si substrate was obtained so-called as-deposited condition (RT). Finally, these samples were annealed at temperatures of 300 °C and 400 °C for 1 h in ambient nitrogen with a heating rate of 20 °C/s.

The crystallinity of the TiO<sub>2</sub>/ZnO films was analyzed by X-ray diffraction (PANalytical X'Pert Pro (MRD), with Cu K $\alpha$  ( $\lambda = 0.154$  nm) radiation for  $2\theta$  from 20° to 60° at a scan speed of 2°min<sup>-1</sup> and a grazing angle of 0.5° under 30 kV and 30 mA. The XRD results were compared to the Joint Committee on the Powder Diffraction Standard Card (JPCDS). A Dimension 3100 scanning probe microscope (SPM, Veeco di-Innova) was utilized with both standard and advanced SPM imaging modes to measure the surface characteristics of the ALD TiO<sub>2</sub>/ZnO films. The nanotribological properties of the TiO<sub>2</sub>/ZnO films were determined with scanning probe microscopy (SPM, Hysitron Corporation), which was combined with AFM (Digital Instruments Nanoscope III) into a nanoscratch measurement system. The nanoindentation measurements used a diamond Berkovich indenter tip (tip radius

~50 nm), suggesting plastic deformation can be generated at a very small load. Laterally, the probe-sample interaction extends only across the tip atom or the atoms involved in the interaction; additionally, the SPM was operated at a constant scan speed of 2  $\mu\text{m s}^{-1}$ . For the TiO<sub>2</sub>/ZnO films, the applied load function was ramped depth mode, and penetrations of 30 nm and 150 nm were examined at room temperature. The maximum load was then maintained while forming 10  $\mu\text{m}$  long scratches. Reliability performance measurements randomly sampled nine positions made on each film. Surface profiles before and after scratching were obtained by scanning the tip at a 0.02-mN normal load (i.e., a load sufficiently small that it produced no measurable displacement). After scratching, the wear tracks were imaged using AFM.

## 3. Results and discussion

To understand the effect of temperature on the bilayer TiO<sub>2</sub>/ZnO films on Si substrates, XRD analysis was used to examine the film phase. The XRD patterns in Fig. 1(a) present crystallization peaks at  $2\theta = 31.5^\circ, 34^\circ$  and  $36^\circ$ , which give clear evidence of crystallized ZnO with (100), (002), and (101) crystallographic planes, according to the reference data of JPCDS No. 79-0206 [6]. Fig. 1(b) presents a cross-sectional TEM image of the bilayer TiO<sub>2</sub>/ZnO films on Si substrates that have been subjected to RT. A bilayer sample of 10 nm TiO<sub>2</sub> and 30 nm ZnO on a Si substrate was obtained. Fig. 1(c) shows the high resolution TEM profiles obtained an amorphous structure TiO<sub>2</sub> and nanocrystalline structure ZnO, whereas the sample has significant interface between the TiO<sub>2</sub>/ZnO films. First, it can be seen the as-deposited TiO<sub>2</sub>/ZnO films processed at 200 °C show no TiO<sub>2</sub> peak [25]. To explain the surface morphology of TiO<sub>2</sub>/ZnO film before scratching, AFM measurements were carried out, as shown in Fig. 2(a) and (c). It can be seen the surface roughness ( $R_a$ ) values are 1.8, 1.5 and 1.4 nm for the RT and post-annealed (at 300 and 400 °C) samples, respectively, which exhibit uniform and fine-grained morphology. With increased annealing temperature, the non-stoichiometric surface may create defects or/and nanoparticles [26] as a result of thermally induced crystallization effects

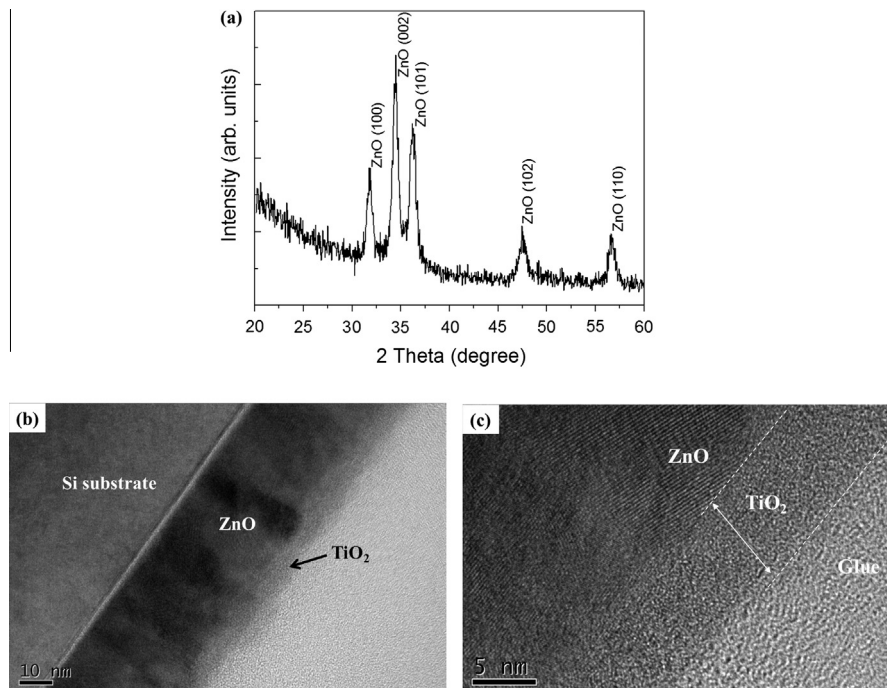


Fig. 1. (a) An XRD pattern of the TiO<sub>2</sub>/ZnO films with and without annealing. (b) and (c) TEM profiles obtained a significant interface between of the TiO<sub>2</sub>/ZnO films.

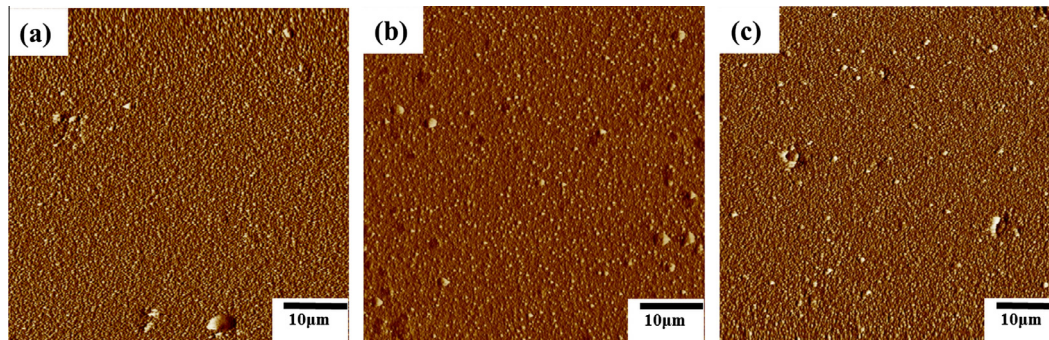


Fig. 2. The surface morphologies of the  $\text{TiO}_2/\text{ZnO}$  films at (a) RT, (b) 300 °C and (c) 400 °C before scratching.

[27]. However, the generation of defect areas should significantly lower the mobility of transport carriers through the bulk [28].

Fig. 3(a) and (b) show typical AFM profiles with varying penetration at 30 nm and 150 nm, respectively. The wear volume increases with time for ALD films fabricated under the RT condition, and it can be observed the total volume was swiped by the indenter, which depended on the projected area of the indenter during application of the scratching test [23,29]. The typical surface morphology with a smooth plane and no fibers is obtained at a ramped loading penetration of 30 nm; additionally, a small amount of debris on the surrounding surface can be observed. Further, the grinding cracks and debris can clearly be found at the last tracking line, which had a penetration of 150 nm. Fig. 3(c) and (d) reveal scratched groove morphologies under a ramped loading test for the sample with a given annealing temperature of 300 °C. However, the use of an appropriate annealing treatment can remove defects, which may have originated from dangling oxide bonds present near the surface or interface, following the ALD process with layer-by-layer deposition. The annealing process also provides enough activation energy for atoms to diffuse into stable atomic sites in the crystal lattice [30]. Thus, the friction surface appears smooth and without debris following the penetration test from 30 to 150 nm. The possible reason for this may be the edge of the friction film becomes tough, improved by the application of an annealing treatment at 300 °C. Fig. 3(e) and (f) reveal scratch groove morphologies in the samples thermally treated at the higher temperature of 400 °C. The smooth tracking line can only be obtained at the light loading penetration of 30 nm; however, a clearly deep track occurred at the penetration of 150 nm, followed by the development of severe debris with particle-gathering morphologies. Thus, we found the occurrence of debris on the edge of the friction film [28,29] depended on the temperature of the annealing treatment. Additionally, it is believed the contact and true volume values increase with the *in-situ* loading force. The related investigations will be discussed in the following content, including a comparison of the data collected for the friction and lateral force curves.

Fig. 4 shows the lateral force as a function of the duration of displacement. It can be observed the applied lateral loading increased with scratching time. In Fig. 4(a), with a loading penetration of 30 nm, the unstable lateral force can be observed with increasing time. However, the samples treated with annealing temperatures of 300 °C and 400 °C exhibit some degree of intermittence under force testing. This appears to be reflected by the fluctuation. The loading condition associated with this event is called the “critical load,” and the uncertainty of the displacement profile is called “pile-up” [31,32]. In Fig. 4(b), unusual lateral force behavior can be observed for the sample at the duration of 18–19 s, due to the film pile-up and the measured critical loads of 21.8, 22.4, 36 μN. In comparison to the loading test results for the other conditions,

i.e., treatment at RT and 300 °C, the fluctuation is lower. According to the combined plastic deformation of ZnO by intra film shear (slip) of partial dislocations along the ZnO {0002}, basal stacking faults via a dislocation glide process contribute to a lowering of friction and wear [33]. Fig. 5(a) was recorded at a loading penetration of 30 nm; the friction traces can clearly be observed for each sample. The absence of the load and unloading segments of the load–displacement curve suggests ten times pressure-induced was involved by nanoscratch traces (Fig. 6). The parallel measurements to ensure reproducibility can be given by SPM modes to measure the reliability performance of the ALD  $\text{TiO}_2/\text{ZnO}$  films. In addition, the penetration distance can be well controlled to contact the  $\text{TiO}_2$  films and not the ZnO films. The plots recorded at the loading conditions of RT, 300 °C, and 400 °C indicate the oscillation trend occurred continuously under the friction force after the setting down step. Consequently, the oscillation trends are similar for each sample, in both the on- and off-load scans at the duration of 19 s. The data recorded at the RT loading condition exhibited more oscillating fluctuations than those recorded at the loading conditions of 300 °C and 400 °C, as can be observed in Fig. 5(b). However, an unusual forcing profile is apparent under RT. Fig. 3 shows an

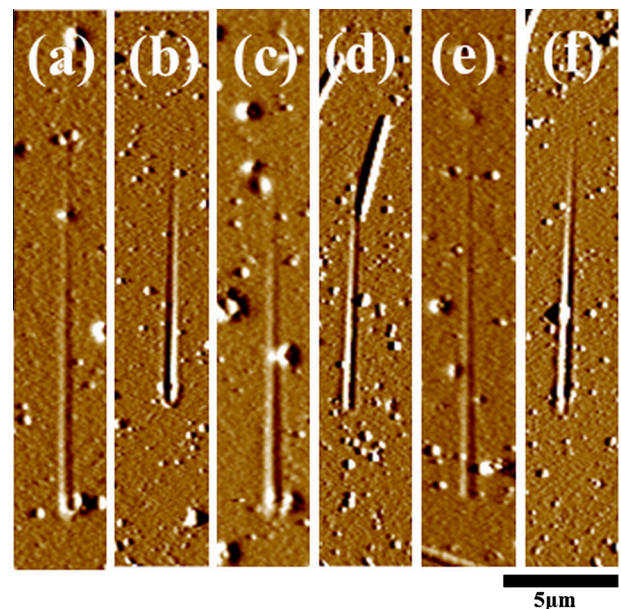
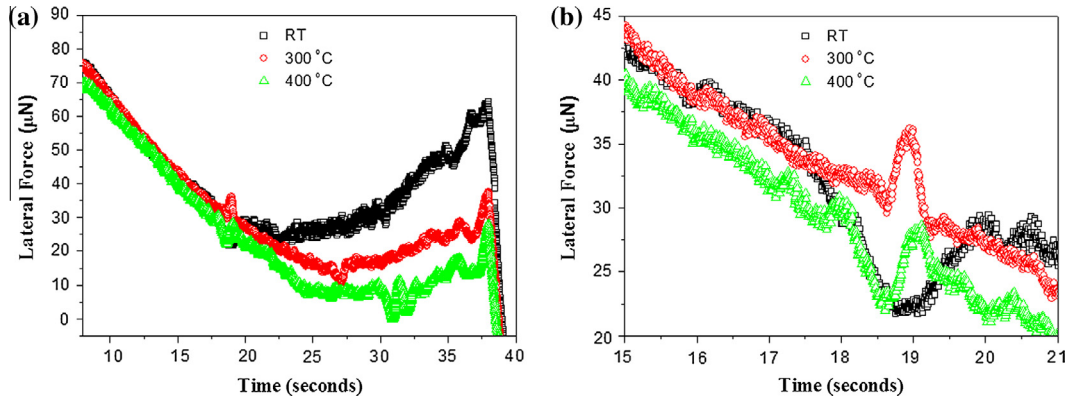


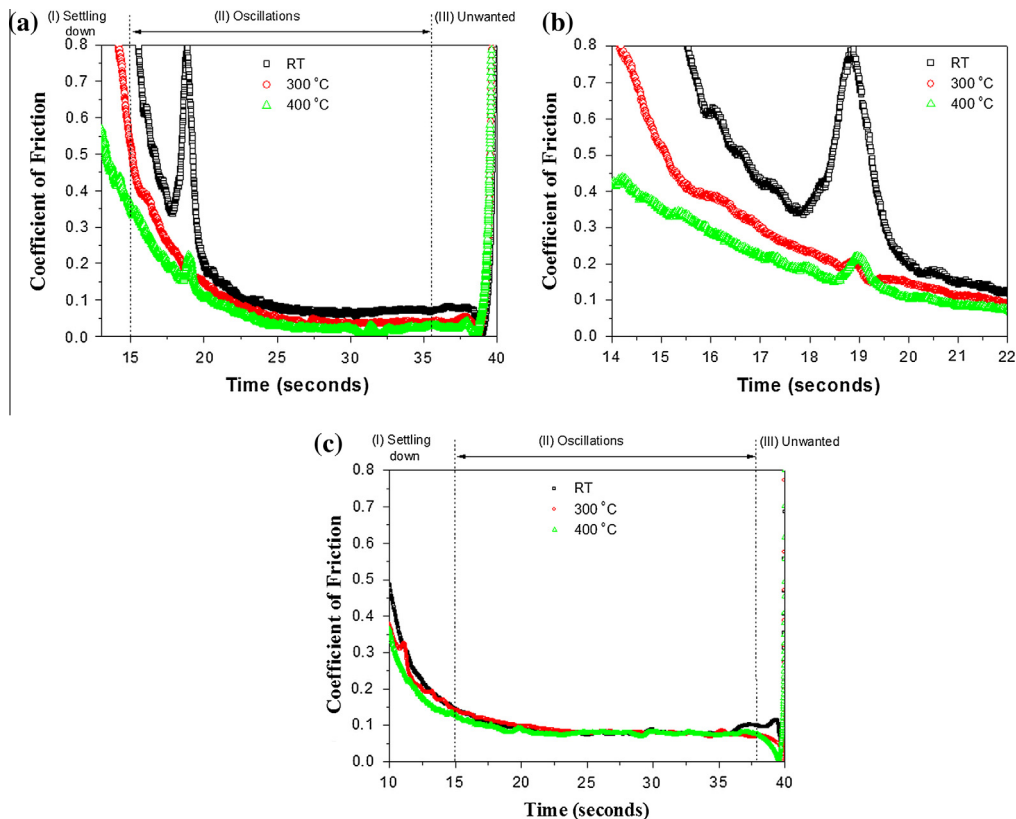
Fig. 3. The surface morphologies of the  $\text{TiO}_2/\text{ZnO}$  films under different annealing conditions after the nanoscratch tests. The RT samples without annealing, subjected to ramped loads of 500–2000 μN, are shown in (a) and (b). The samples treated with the annealing temperature of 300 °C, are shown in (c)–(d), annealing temperature of 400 °C, are shown in (e) and (f), respectively.



**Fig. 4.** Three typical profiles of the coefficient of friction ( $\mu$ ) as a function of scratch duration for the TiO<sub>2</sub>/ZnO films treated under different annealing conditions of RT, 300, and 400 °C. Ramped loads of (a) 500  $\mu$ N and (b) zoom for (a).

elastic reaction occurs, caused by elastic deformation between the groove and film after high-temperature annealing. This sample was plowed by indenter tips; this result could be expected because the use of a higher annealing temperature increases film crystallization. Hence, the tip can extend the dislocations in addition to the contact asperities, leading to the occurrence of elastic formation on the TiO<sub>2</sub>/ZnO films. It can be seen the lower degrees of adhesion reflect interlinking, and rearrangement tends to result in fluctuations in the values of  $\mu$  at the ZnO film. Following the uncertainty of the initial  $\mu$  profile, pile-up occurred in Fig. 5(b), which was recorded at the annealed conditions of 300 °C and 400 °C. The coefficient of friction profiles are generated as a function of the increased loading penetration of 30 nm. The marked oscillations under the friction force and abrupt oscillations can be observed

at the conditions of RT in comparison to that of 300 °C and 400 °C. We summarized the ploughed and scratched data under critical loads, as measured from the TiO<sub>2</sub>/ZnO films with different penetrations at 150 nm and annealing temperature, presented in Fig. 5(c) for comparison. According to the above experimental results, the annealing temperature affects the nanotribological behaviors, including the plastic deformation between the TiO<sub>2</sub> and ZnO films, delamination and particle loosening. We also confirmed the microstructure of the TiO<sub>2</sub>/ZnO films changed as the annealing temperature was increased from 300 °C to 400 °C, causing changes in the composition of the bilayer structure. The failure mechanism during scratching of the TiO<sub>2</sub>/ZnO films at the respective critical loads is shown in Fig. 5(c). Note, no critical pile-up occurs at RT or for the annealing conditions of 300 °C and 400 °C.



**Fig. 5.** shows the lateral force as a function of the displacement duration. It can be observed the applied lateral loads increase with testing time for the three samples (RT, 300 °C and 400 °C) with ramped loads of (a and b) 500 and (c) 2000  $\mu$ N.

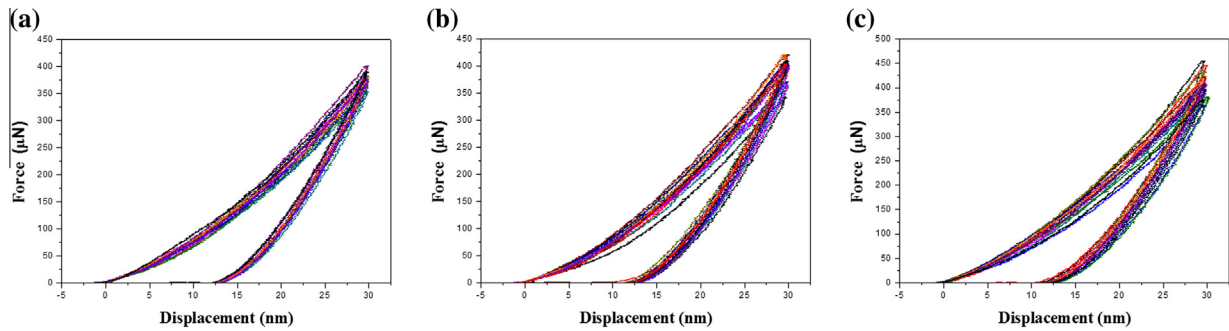


Fig. 6. shows the ten times load and unloading segments of the load–displacement curve by nanoscratch traces.

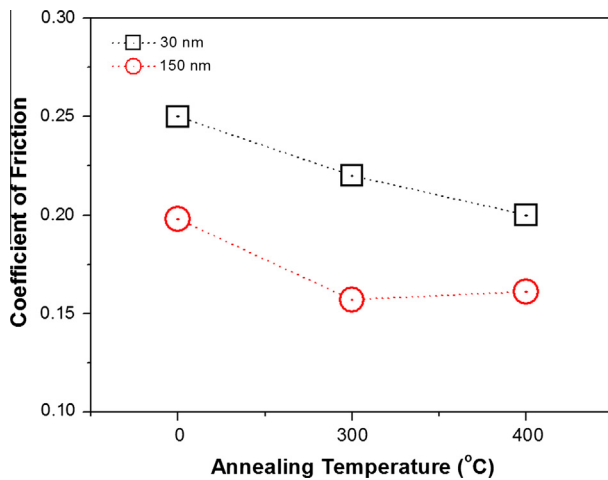


Fig. 7. The distinct critical coefficients of friction as a function of ramped loads of 500 and 2000  $\mu\text{N}$  for  $\text{TiO}_2/\text{ZnO}$  films with processing conditions of RT, 300 °C and 400 °C.

The values of  $\mu$  were recorded from the  $\text{TiO}_2/\text{ZnO}$  films with respect to the annealing temperature; these values of  $\mu$  were determined by averaging the values measured at scratch durations ranging from 15 to 36 s (Fig. 7).

The obtained discordant curves and irregularities appeared in the course of plastic deformation as a result of the adhesion and/or cohesion failure; those transitions were determined from the nanoscratch traces and plastic deformation. However, the profile at the condition of 400 °C is harder than that of RT due to the ploughed effect from the nanoscratch traces.

From this perspective, the friction traces were relatively reproducible but exhibited greater variability for each sample than that of the original surface (Fig. 2). The changes in the scratch groove morphology indicate the improvements in nano-scale wear resistance, as seen in Fig. 3. This figure is an SPM micrograph, recorded at the end of one of the scratch tracks for each sample, where greater contact pressures and greater penetration have led to large areas of the coating being removed from the scratch track (Fig. 4 and 5) as a result of elastic–plastic deformation. When the penetration is increased, the films start to behave differently as a result of the various annealing temperatures (Figs. 6 and 7).

#### 4. Conclusion

We evaluated the film characteristics of ALD-processed bilayer  $\text{TiO}_2/\text{ZnO}$  on Si substrates using XRD, TEM, and SPM techniques. The  $\text{TiO}_2/\text{ZnO}$  films show obvious oscillations under the friction

force in addition to abrupt oscillations and pile-up events at a loading penetration of 30 nm and 21.8  $\mu\text{N}$  for RT, 22.4  $\mu\text{N}$  for 300 °C, and 36  $\mu\text{N}$  for 400 °C. At annealing conditions of 36  $\mu\text{N}$  and 400 °C, the sample exhibits a distinctly higher coefficient of friction with larger debris particles in comparison to that of the RT and 300 °C conditions. A good correlation between the mechanical properties and scratch/wear damage was demonstrated. The higher friction force can be attributed to the intrinsic brittle properties of the ZnO film. Severe plastic ploughing damage, observed at the beginning of wear sliding under a loading penetration of 150 nm, clearly indicates the tip is ploughed across the  $\text{TiO}_2$  layer and then reaches the ZnO material. The nanoindentation technique, combined with scratching and friction, has been applied to ALD-processed  $\text{TiO}_2/\text{ZnO}$  films and used to successfully evaluate the film characteristics for a compressive study. The films displayed significant suppression of the lateral indented deformation, inducing the degree of pile-up. Additionally, the setting down, oscillations, and unwanted material can be explained in terms of the stiffness of the film, which depends on the interatomic distances during the scratch tests.

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