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# Characterization and tribological investigation of $Al_2O_3$ and modified $Al_2O_3$ sol-gel films

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### Abstract

Thin films of  $Al_2O_3$  and modified  $Al_2O_3$  were prepared on a glass substrate by a dip-coating process from specially formulated aqueous sols. The tribological properties of the as-prepared thin films sliding against an  $Si_3N_4$  ball were evaluated on a one-way reciprocating friction and wear tester. The worn surface morphologies and chemical compositions of the films were examined by means of atomic force microscopy (AFM), scanning electron microscopy (SEM), and X-ray photoelectron spectroscopy (XPS), respectively. Thermogravimetric analysis (TGA) and differential scanning calorimetric analysis (DSC) of dried sols were performed to explore the thermal events occurring during the annealing process of the sol-gel  $Al_2O_3$  films. The wear mechanisms of the films are discussed based on SEM observation of the worn surface morphologies. As the results, modified sol-gel Al<sub>2</sub>O<sub>3</sub> films are of higher wear resistance than the unmodified one. Meanwhile, the wear life of the modified films is correlated to the additive amount in the starting aqueous sol. In other words, the higher the additive amount in the starting aqueous gel, the longer the wear life of the sol-gel  $Al_2O_3$  film. SEM observation of the morphologies of worn film surfaces indicates that wear of glass is characteristic of brittle fracture and severe abrasion. Wear of unmodified Al<sub>2</sub>O<sub>3</sub> film is dominated by microfracture and abrasion, while that of modified films by plastic deformation and/or microcracking. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: A. Thin films; A. Oxides; B. Sol-gel chemistry; D. Mechanical properties; D. Surface properties

# 1. Introduction

There have been many investigations of oxide films derived from the sol-gel method because of several advantages, such as low processing temperature, homogeneity, the

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possibility of coating on substrates with large areas, and low cost. Sol-gel oxide films have found wide applications as functional materials in optical, microelectronics, and photoelectronics industries, and for the purpose of protection as well [1-4]. It is known that the tribological or mechanical properties of the films coated on the substrate will influence their function, lifetime, and productivity [5]. Therefore the physical and mechanical properties of the films have been largely focused on [6,7]. At the same time, the triblogical investigations of ceramic films used as microdevice materials are drawing much attention of both tribologists and scientists engaged in material science [8]. Unfortunately, less is available about the tribological properties of sol-gel films. Liu and co-workers found that sol-gel TiO<sub>2</sub> thin films had very good plasticity even at room temperature as well as good bonding ability with the microscopic slide, which sets the prerequisite for the film to show excellent friction reduction and wear resistant ability [9]. However, many basic problems, such as the relationship among the process, structure, and the tribological properties of the film is still obscure.

Aluminum oxide thin films are widely used in many mechanical, optical, and microelectronic applications because of the excellent properties such as chemical inertness, good mechanical strength, and high hardness [10,11], transparency, high abrasive and corrosion resistance, as well as insulating and optical property [12,13]. Usually, aluminum oxide film is prepared by techniques such as chemical vapor deposition [14] and physical vapor deposition [15]. However, it is difficult to prepare large, strong, and homogeneous film by these methods.

In this work we report on the fabrication, tribological behavior of  $Al_2O_3$ , modified  $Al_2O_3$ thin films prepared by sol-gel, and dip-coating methods from inorganic salt. The relationship among the process, structure, and the tribological properties of the sol-gel films is discussed as well.

# 2. Experimental

## 2.1. Sample preparation

Crystal aluminum chloride (99.99%), ammonia, glacial acetic acid, and organic additive polyethylene glycol (brand name P400, abridged as PEG, MW = 400) were commercially obtained and used without further purification as the raw materials for preparation of the aqueous sol. The organic additive P400 was used as a kind of binder to improve the toughness of the sol-gel ceramic film. In the preparation of the aqueous sol, excessive amount of ammonia solution (5 M) was first dropped to an aqueous aluminum chloride solution (0.13 M) at room temperature until a pH value of 9 was reached. The resultant hydrated precipitation was then filtered and washed with distilled water and ethanol, respectively. Finally, the cleaned hydrated precipitation was aged for 48 h and peptized with glacial acetic acid for 0.5 h at room temperature under stirring to obtain the target translucent, homogeneous, and stable sols. The final pH value of the aqueous sols (coded as A1, A2, and A3) for preparation of modified ceramic coatings were prepared in the same way as above, except that the modifier P400 was formulated in the starting solution at a volume fraction of 0.2, 0.4, and 0.6%, respectively. The target aqueous sols were aged for 24 h and then served for preparation of the sol-gel Al<sub>2</sub>O<sub>3</sub> films.

The glass substrate was first cleaned with ethanol-potassium hydroxide solution in an

ultrasonic bath for 20 min, then washed with distilled water and dried at ambient conditions. Sol-gel  $Al_2O_3$  films were prepared on the glass substrate by means of a dip-coating process. This was realized by drawing and pulling of the substrate in the aqueous sols at a speed of 38 cm/min, accompanied by drying of the dipped substrate at room temperature for 15 min and annealing at 500°C for 20 min in an oven. The target sol-gel  $Al_2O_3$  films were finally obtained by cooling of the sintered glass substrate to ambient temperature in the oven.

# 2.2. Experimental apparatus and measurements

The composition and structure of the films were characterized by means of TGA, DSC, XPS, and AFM. DSC and TGA analyses were performed in nitrogen on a Perkin-Elmer DSC-7 and TGA-7 system. The programmed heating rate was 10°C/min. The samples used for thermal analysis were obtained by evaporation of the precursor solutions at room temperature for 72 h. XPS analysis was conducted on a PHI-5702 XPS/AES system, using Mg-K $\alpha$  radiation operating at 250 W and a pass energy of 29.35 eV. The binding energy of C<sub>1s</sub> (284.6 eV) was used as the reference. XPS depth profiling was performed with Ar<sup>+</sup> ion gun bombardment. The structure of the films was examined with an SPM-9500 atomic force microscope, while the morphologies of the worn surfaces of the films observed with a JSM-5600LV scanning electron microscope.

The tribological properties of the glass and coated glass sliding against a stationary ball (diameter 3 mm, made of  $Si_3N_4$ ) were evaluated on a Kyowa DF·PM model one-way reciprocating friction tester at ambient conditions (RH: 40–44%). The sliding velocity and stroke are 9 cm/min and 7 mm, respectively. The normal force is selected as 3, 2, and 1 N, in anticipation that the sol-gel  $Al_2O_3$  films would experience failure above a normal force of 3 N because of the excessive Hertzian contact stress. The physical and mechanical properties of the counterpart  $Si_3N_4$  ball are shown in Table 1. The coefficient of friction and sliding passes were recorded automatically. A relatively low friction coefficient was recorded at the early stage of sliding. It rose sharply to a higher stable value after sliding for a certain passes. It is usually recognized that the film fails at this point. Therefore, the corresponding sliding pass numbers were recorded as the wear life of the film. Three replicate tests were carried out for each specimen, and the average friction coefficients and wear lives of the three replicate tests were cited in this article. The relative error for the replicate tests was no more than 5%. Prior to the friction and wear test, all the samples were cleaned in an ultrasonic bath with ethanol and acetone for 10 min and then dried in hot air.

# 3. Results and discussion

#### 3.1. Characterization of film precursor

Fig. 1a shows the DSC diagram of precursor A (without P400 as additive) and A3 (with P400 additive at a volume fraction 0.6%). It is seen that precursor A shows two endothermic peaks, while precursor A3 shows three endothermic peaks. A peak appears around 90°C for both A and A3, indicating that the two precursors experience the same process at this



Fig. 1. DSC and TGA diagrams of the Al<sub>2</sub>O<sub>3</sub> film precursor (A and A3).

temperature. The second process for A is delayed compared with A3, indicating that the second process is easier to happen for A3. This is supposed to be related to the action of the organic additive, which may act as a crosslinker. In other words, in the presence of the P400 additive, the molecules of sol are easier to crosslink with each other and enhance the formation of  $Al_2O_3$  particles in the subsequent heating process. Fig. 1b shows the TGA diagram of precursor A and A3. In combination with the corresponding DSC analytical results, it is inferred that the weight loss ratio for A and A3 is almost the same during the first



Fig. 2. XPS spectra of typical elements in as-prepared Al<sub>2</sub>O<sub>3</sub> film (A) and modified Al<sub>2</sub>O<sub>3</sub> film (A3).

phase, and then a larger weight loss is observed for A3, which is due to the loss of organic compound or more coordinated water.

#### 3.2. Characterization of the film

XPS is applied to detect the chemical states of some typical elements in as-prepared  $Al_2O_3$ films (films A and A3). Fig. 2 shows the XPS spectra of  $Al_{2p}$  and  $Si_{2p}$  on the surface of A and A3. The binding energy of  $Al_{2p}$  at 74.20eV (Fig. 2a and c) is consistent with that of Al in sapphire  $Al_2O_3$  [16], indicating that target  $Al_2O_3$  film has been successfully obtained in our work. The signal of  $Si_{2p}$  (Fig. 2b) is too weak to be detected, indicating that the surface of film A is covered by  $Al_2O_3$ . The binding energy of  $Si_{2p}$  at 102.5 eV (Fig. 2d) is assigned to the glass substrate [16,17]. Fig. 3a shows the XPS depth profile of as-prepared  $Al_2O_3$  film. It is seen that the intensity of  $Al_{2p}$  decreases gradually and that of  $Si_{2p}$  and  $O_{1s}$  increases with



(a) XPS depth profile of A





Fig. 3. XPS depth profile of as-prepared Al<sub>2</sub>O<sub>3</sub> film (A) and modified Al<sub>2</sub>O<sub>3</sub> film (A3).

sputtering cycle increasing. Accordingly, it is concluded that diffusion took place between the glass substrate and sol-gel  $Al_2O_3$  film during the annealing process. This helps to increase the bonding strength between the film and the substrate and, hence, improve the tribological properties of the film. The peak of  $C_{1s}$  disappears after two cycles of sputtering, illustrating that contaminated carbon exists only in the very outer surface of the film, and the raw materials were completely converted or removed during the heating process. Fig. 3b shows the XPS depth profile of A3 film. Compared with film A, the most significant difference is that the signal of  $C_{1s}$  still exists even after five sputtering cycles, which is identified to the



Fig. 4. AMF images of Al<sub>2</sub>O<sub>3</sub> films and corresponding friction force.

bulk film but not absorbed carbon. We suppose that such carbon originates from the additive that was burned while heating and embedded in the film. This carbon may play a role to modify the film structure. The second difference is that the intensity of  $Al_{2p}$  in A3 keeps stable and high with sputtering cycle extension, which indicates that the addition of P400 helps to generate thicker sol-gel  $Al_2O_3$  film. The third difference is that the intensity of  $Si_{2p}$  in the first three cycles is higher compared with film A, indicating that the diffusion between film A3 and the substrate is stronger. Thus, it can be concluded that P400 additive helps to enhance the diffusion between the sol-gel film and the glass substrate as well.

Fig. 4 shows the AFM images and corresponding friction force pictures of the films. It can be seen that the AFM images of A and A3 are different. Nano-size particles of film A arrange in specific orientation, illustrating that the growth of unmodified  $Al_2O_3$  nanoparticles is accompanied by a preferential orientation. The surface of film A3 is relatively smooth and



Fig. 5. Friction coefficient of different couples as a function of wear passes near to failure.

some "island" distributes in the "marshland", indicating that the addition of P400 has changed the growing process of the film and led to totally different structure. From the images of friction force of films A and A3 (Fig. 4b and d), it can be seen that the friction







force is correlated to the morphology to some extent. Namely, larger friction force is recorded at the bulges of the film surfaces. Moreover, it is interesting to note that smoother film A3 registers larger friction force than relatively rougher film A. This indicates that the friction force of the sol-gel films is not only dependent on the morphological features but also on other factors, especially the superficial and interfacial effects. As a matter of fact, the friction at nanoscale or atomic level is largely dominated by surface forces including van der Waals force, hydrogen bond force, and electrostatic and/or double layer forces [18]. Consequently, the excitation of atomic lattice vibrations (phonons) and electronic excitations contribute largely to the friction force at atomic level [19,20].









# 3.3. Friction and wear

Fig. 5 shows the variation of friction coefficient as a function of sliding passes. It can be seen that all the film samples record low initial friction coefficient about 0.1. It rises to a stable and high value at a certain sliding pass, except that film A3 sliding against  $Si_3N_4$  ball registers a gradually decreased friction coefficient at extended sliding pass. All the sol-gel

 $Al_2O_3$  films give considerably increased wear life compared with bare glass substrate, and the longest wear life at load 1 N is recorded with film A3. However, the wear life of all the film samples is short at load 3 N, indicating that the films have low load-carrying capacity. The wear life of the samples under 1 N can be ranked as A3>A2>A1>A. In other words, the higher the additive amount in the aqueous sol, the longer the wear life of the modified sol-gel films. Besides, film A and the modified films show little difference in steady-state friction coefficients, indicating that P400 as additive has little effect on the friction-reduction behavior of the sol-gel Al<sub>2</sub>O<sub>3</sub> films.

To gain more insights into the friction and wear mechanisms of the films, the worn surfaces of the glass slide after 17 passes and of  $Al_2O_3$  thin films sliding against Si<sub>3</sub>N<sub>4</sub> after failure have been observed by SEM. As shown in Fig.6, signs of severe brittle fracture are visible on the worn surface of the glass slide even after 17 passes (Fig. 6a), accompanied by the generation of large wear debris, which accounts for the abrasive wear of the slide and the resultant high friction coefficient. Many microcracks are generated on the worn surface of film A (Fig. 6b); the propagation of these cracks causes microfracture and leads to film failure in a relatively short sliding duration. Contrary to the above, the worn surfaces of films A1 and A3 show signs of slight plastic deformation (Fig. 6c and d), which is beneficial to prevent the generation of microcracks. Besides, no sign of a microcrack is visible on the worn surface of film A3 after sliding against  $Si_3N_4$  at 3 N, while they are observed on the worn surface of film A1 (Fig. 6c). This indicates that P400 additive in the aqueous sol helps to improve the toughness of sol-gel  $Al_2O_3$  film, which affects the spallation of film involving the initiation and propagation of cracks in the film [21]. The above observation conforms well to the friction and wear behaviors of the films. In other words, film A3 of higher roughness shows better wear-resistance than film A1 of lower roughness. Moreover, comparing Fig. 6c with Fig. 6e and Fig. 6d with Fig. 6f, it is seen that film A1 or A3 shows considerably different worn surface morphologies under different loads. Namely, the plastic deformation and/or microcrack on the worn surfaces of films A1 and A3 are effectively abated under relatively low loads (Fig. 6e and f). This agrees well with the extended wear life of the two films at low load as well. In combination with the wear life of the films shown in Fig. 5, it is rational to anticipate that film A3 would be a promising candidate for protection and wear reduction of microdevices in relatively low-load applications.

#### 4. Conclusions

Brittle  $Al_2O_3$  ceramic having a high friction coefficient and severe wear under dry sliding can be made into thin films of a low friction coefficient and long wear life by the sol-gel process. Polyethylene glycol as an additive in the aqueous sol helps to improve the roughness of the target sol-gel  $Al_2O_3$  films, thereby to improve the tribological behavior of the films. Wear of  $Al_2O_3$  film is dominated by microcracking and fracture, that of modified  $Al_2O_3$  films characteristic of plastic deformation and/or microcracking. The plastic deformation is beneficial to retard the propagation of fracture and peeling off of large wear debris; thus, modified  $Al_2O_3$  films show better wear resistance than unmodified  $Al_2O_3$  film.

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