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Characterization and Investigation of the Tribological Properties of Sol–Gel Zirconia Thin Films

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Sol–gel zirconia thin films were prepared by dip coating in an ethanol solution of zirconium oxychloride. The zirconia films consisted of a completely tetragonal phase and exhibited nanoscale uniformity. They displayed excellent antiwear and friction-reduction performance in sliding against steel. The friction coefficient (0.13–0.15) and the wear life over 5000 sliding cycles were recorded for the films at a sliding speed of 90 mm/min and a load of 0.5 N. The film was characterized by slight scuffing and abrasion at low loads and sliding speeds.

I. Introduction

During the last decade, rapidly increasing interest has been directed toward thin-film materials, particularly wear-resistant coatings.[1] Of these materials, zirconia (ZrO_2) thin films have been focused on as a potential wear-resistant coating in harsh environments, because of its promising physical and chemical properties, such as high mechanical strength, high-temperature resistance, corrosion resistance, low friction coefficient, and long wear life.[2–5] ZrO_2 thin films have been prepared using numerous coating techniques, including physical vapor deposition,[6] sputtering,[7] spraying,[8] plasma-assisted deposition,[3,5] and sol–gel deposition.[2,4,9–12] Of these methods, sol–gel deposition has attracted much interest, because (i) it involves a simple process, (ii) excellent control of the stoichiometry can be maintained, (iii) homogeneous films with a large area can be formed at relatively low cost, and (iv) it has flexible deposition parameters.[11] However, not much work has been conducted in regard to the tribological properties of sol–gel thin films,[13,14] especially those of sol–gel ZrO_2 thin films.

Organo-zirconium compounds, such as zirconium alkoxides, zirconium alkanoates, and zirconium acetylacetonate, have been widely used as the starting materials for the deposition of sol–gel ZrO_2 films.[4,9–11] These organo-zirconium compounds generally are expensive and sensitive to moisture.[2] Thus, inorganic zirconium salts have been recommended as a popular source of zirconium for the preparation of a very stable precursor solution in an ambient atmosphere.

In the present paper, the preparation of ZrO_2 thin films, using zirconium oxychloride octahydrate ($ZrOCl_2 \cdot 8H_2O$) as the starting material and anhydrous ethanol as the solvent, is reported. The morphology, microstructure, and tribological properties of the films have been investigated.

II. Experimental Procedure

Single-crystal silicon (Si(100)) and glass sheets were used as the substrates. The substrates were immersed in piranha solution (3:7 volume fraction of 30% hydrogen peroxide (H_2O_2) and 98% sulfuric acid (H_2SO_4)), heated to a temperature of 70°C for 15 min, and rinsed with distilled water and ethanol. The precursor sol was a mixture of 0.02 mol of $ZrOCl_2 \cdot 8H_2O$ and 100 mL of anhydrous ethanol, and the sol was aged at 30°C for 72 h. The sol–gel films were deposited onto the substrates by dip coating in air at a relative humidity (RH) of 45%–55% and speed of 42.4 cm/min. The films were dried at 50°C for 15 min, then sintered to 550°C at a rate of 10°C/min and held there for 30 min. The above-described procedures were repeated for the preparation of multilayer films. The thickness of the monolayer ZrO_2 film was ~50 nm, as measured by ellipsometry (Model L116-E, Gaertner Scientific Corp., Chicago, IL).

The thermal behavior of the dried gel was investigated via thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) in flowing nitrogen at a scanning rate of 10°C/min (Model 7 Series system, Perkin–Elmer, Norwalk, CT). The surface morphology of the films was observed via atomic force microscopy (AFM) (Model SPM-9500, Shimadzu Corp., Japan). The chemical states in the films were identified via multifunctional X-ray photoelectron spectroscopy (XPS) (Model PHI-5702 Physical Electronics Division, Eden Prairie, MN), using a pass energy of 29.4 eV and an excitation source of Mg$K\alpha$ radiation (h_ν = 1253.6 eV). The binding energy of contaminated carbon (C 1*s*, 284.6 eV) was used as the reference. The microstructure of the film and the morphologies of the worn surfaces were analyzed via X-ray diffractometry (XRD) (Model D/max-RB, Rigaku, Tokyo, Japan), using Cu$K\alpha$ radiation, and scanning electron microscopy (SEM) (Model EPMA-810Q, JEOL, Tokyo, Japan).

Friction and wear tests were conducted on a dynamic-static tribometer (Model DF-PM, Kyowa Kagaku Corp., Ltd., Tokyo, Japan) in a one-way reciprocating configuration and at a sliding distance of 10 mm. A steel ball 3 mm in diameter (SAE52100 steel, H_{Rc} 59–61, with the following mass composition: carbon, 0.95%–1.05%; chromium, 1.30%–1.65%; silicon, 0.15%–0.35%; manganese, 0.20%–0.40%; phosphorus, <0.027%; sulfur, <0.020%; nickel, <0.30%; copper, <0.25%; and the balance was iron) was used as the counterpart. All the tests were conducted at room temperature and RH = 50%.

III. Results and Discussion

(1) Characterization of Sol–Gel Zirconia Films

Figure 1 shows the TGA and DSC curves for ZrO_2 gel powders. The weight loss of 40% from 25°C to 500°C is attributed to evaporation of the residual organic solvents and decomposition of the organo-zirconium compounds that had formed via hydrolysis and condensation during the preparation of the precursor sol. No

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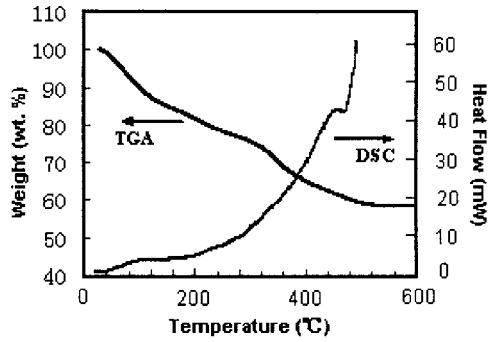

Fig. 1. TGA and DSC curves for ZrO_2 gel powders.

thermal weight loss was observed at >500°C. The weak exothermic peak at ~480°C in the DSC curve corresponds to crystallization of the gel powders.

AFM observation of the film morphology indicated that the film was compact and uniform, with a root-mean-square roughness of <0.3 nm. The film was crack-free and consisted of nanoscale crystallites. Thus, $ZrOCl_2 \cdot 8H_2O$ was determined to be an excellent zirconium source in the sol–gel preparation of the ZrO_2 films.

The XPS spectra of Zr 3*d* and O 1*s* in ZrO_2 films that had been sintered at 550°C are given in Fig. 2. The binding energy of Zr 3*d* at 182.22 eV is identified as the crystallized ZrO_2 phase.[12] The O 1*s* spectrum consists of two branches: the stronger peak at 530.25 eV corresponds to ZrO_2, and the smaller shoulder at 530.25 eV is attributed to SiO_x.[9] The SiO_x interlayer behaves as a buffer; therefore, the adhesion of the ZrO_2 films on a silicon wafer would be greatly improved.

Figure 3 shows the XRD pattern of the multilayer ZrO_2 film. The ZrO_2 films that were deposited on the glass substrates have a well-developed crystalline structure after sintering at 550°C. The peaks at $2\theta = 30.25°$, 35.11°, 50.65°, 60.17°, and 63.10° are respectively assigned to the (111), (200), (220), (131), and (222) lattice planes of the tetragonal ZrO_2 phase. This finding conforms to that which has been reported previously: ZrO_2 films ~450 nm thick sustain a metastable tetragonal structure at low temperature because of the crystallite size effect.[15]

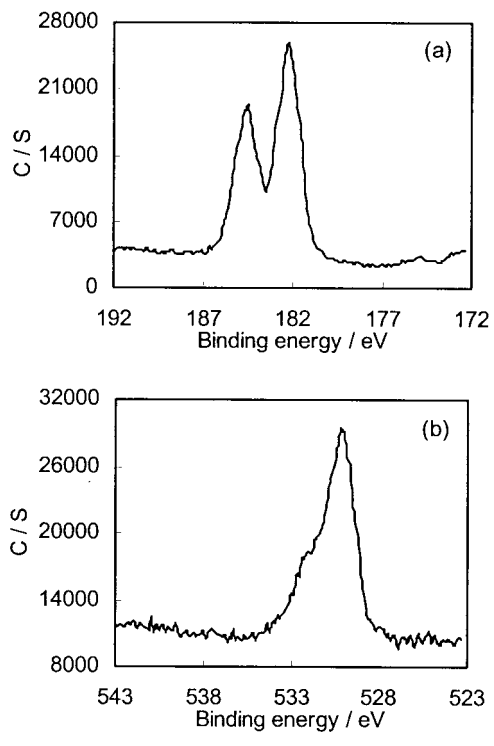

Fig. 2. XPS spectra of (a) Zr 3*d* and (b) O 1*s* in zirconia films.

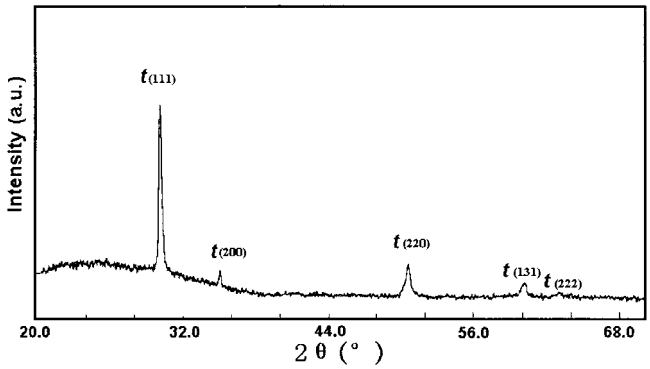

Fig. 3. XRD pattern of ZrO_2 films deposited on glass substrate.

(2) Friction and Wear Behavior

Figure 4 shows the tribological properties of the monolayer ZrO_2 films on silicon substrates sliding against the steel. ZrO_2 films display excellent antiwear and friction-reduction performance under a low load of 0.5 N (see Fig. 4(a)). Up to 5000 sliding cycles, the friction coefficient stabilizes at ~0.14, and no wear track is visible on the surface of the film in this case. An increase in load causes a considerable increase in the friction coefficient at extended sliding cycles. In particular, the friction coefficient increases sharply after ~800 sliding cycles as the load increases to 3 N. Moreover, as shown in Fig. 4(b), the friction coefficient increases as the sliding speed increases at a fixed load of 3 N. In other words, the film is more liable to fail at larger sliding

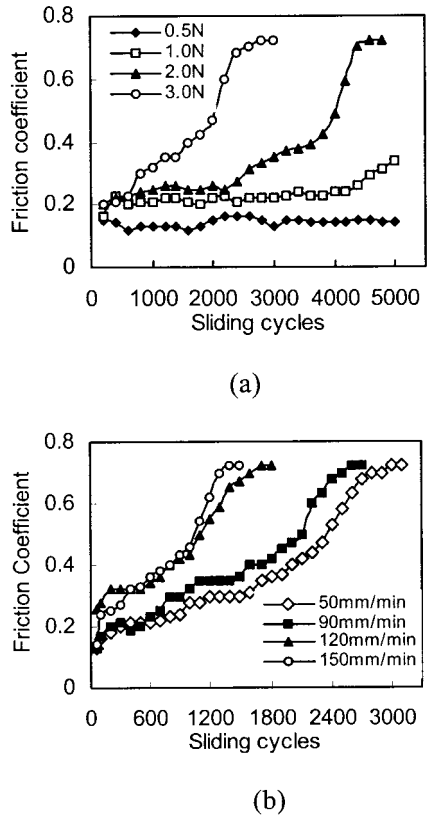

Fig. 4. Friction coefficients, as a function of the number of sliding cycles, at (a) a sliding speed of 90 mm/min and various loads and (b) an applied load of 3.0 N and various sliding speeds.

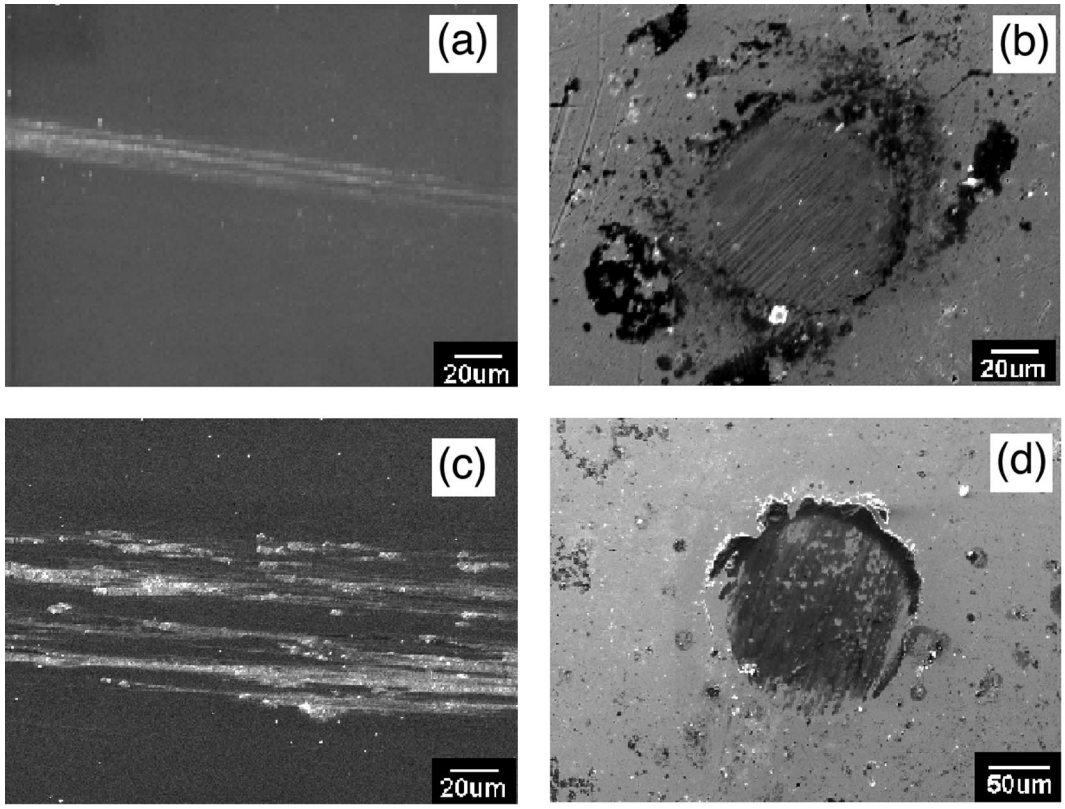

Fig. 5. SEM micrographs of the worn surfaces of ZrO_2 film and the counterpart steel ball at various testing conditions ((a) ZrO_2 film and (b) steel ball at sliding speed 90 mm/min and load 1.0 N for 5000 sliding cycles; (c) ZrO_2 film and (d) steel ball at sliding speed 120 mm/min and load 3.0 N for 700 sliding cycles).

velocities and loads. Thus, it can be concluded that sol–gel ZrO_2 film on a silicon substrate is unsuitable for high-speed and high-load applications.

SEM micrographs of the worn surfaces of the ZrO_2 films and the corresponding counterface are shown in Fig. 5. At low sliding speed and load, the worn surface of the ZrO_2 film (see Fig. 5(a)) is characterized by slight scuffing and is crack free. Very little fine debris at the edges of the wear track is observed in this case. The wear scar on the corresponding surface of the steel ball is relatively glossy and characterized by slight abrasion (see Fig. 5(b)). Thus, the film is characterized by scuffing and slight abrasion at low sliding speed and load. Contrary to the above-mentioned conditions, the worn surface of ZrO_2 film at high speed and load shows signs of severe plastic deformation, with visible rough grooves that are attributed to abrasive wear (see Fig. 5(c)). Some large wear particles appear on the wear track, which act as abrasives to accelerate wear of the film. The wear scar of the counterpart is characterized by severe adhesion (see Fig. 5(d)). Thus, the ZrO_2 thin films are characterized by severe plastic deformation, adhesion, and abrasion under a high load and sliding speed.

IV. Conclusions

Nanoscale sol–gel ZrO_2 films on Si(100) and glass substrates have been prepared by dip coating in an ethanol solution of zirconium oxychloride ($ZrOCl_2$). $ZrOCl_2$ is a suitable zirconium source in the sol–gel preparation of ZrO_2 films. The ZrO_2 films consist of a completely tetragonal phase and exhibit nanoscale uniformity. They display excellent antiwear and friction-reduction performance in sliding against steel. The friction coefficient stabilizes at ~0.13–0.15 at a sliding speed of 90 mm/min and loads of 0.5 N, and the wear life is over 5000 sliding cycles. Observation via scanning electron microscopy indicates that the ZrO_2 film is characterized by slight scuffing and abrasion under a low load and sliding speed, whereas severe plastic deformation, adhesion, and abrasion are observed under a high load and sliding speed.

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