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Crystal Orientation and Morphology on the Tribological and Corrosive Properties of Silver Thin Films

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Abstract

Silver is known to possess method such characteristics as low shear strength, good transfer-film forming tendency and good corrosion resistance. Silver thin films were prepared by e-beam ion plating. They are deposited on various deposition conditions such as argon gas pressures and bias voltages etc.. After the silver films were prepared, the properties in them were examined by gas pressure and bias voltage of substrate. The structure of deposited film was analyzed by X-ray diffraction technique. The morphology of the top surface of films was observed by scanning electron microscope (SEM). Silver films were investigated by not only the tribological properties but also corrosion properties as a function of deposition condition by friction coefficient tester at vacuum ambient and potentio-stat in 0.5M Na_2S solution respectively. After anodic polarization being carried out, the morphology of corroded film was observed by SEM. Tribological and corrosion properties of silver thin films prepared by e-beam ion plating are discussed and compared in this paper.

Keywords : Silver film, ion plating, Solid lubricant, Tribology, Corrosion

1. Introduction

Mechanical materials are requested to possess various properties such as tribology, high hardness and corrosion resistance in parallel with gradual industrial progression. In order to get these properties, many kinds of material surface modification methods have been applied to the surface modification

methods have been applied to the surface of bulk materials. Tribology and corrosion resistance are very important functional characteristics of materials in various industrial fields.

Tribology of solid lubricant, especially, played an important role in the fields of tribology such as space-age transportation system, semiconductor industry in vacuum ambient, advanced heat engine and atomic energy requiring extremely low temperature.

Silver is known to have low shear strength, good transfer forming tendency and corrosion resistance, high electrical and thermal conductibility. In addition, silver films has little to produce wear particle and outgas than any other material for working at vacuum ambient for solid lubricant. However, silver films are easy to occur at ambient where S^- and Cl^- ions exist. If silver thin films corroded, they would lose their characteristics.

In this paper, the silver thin films prepared by e-beam ion plating method were investigated how gas pressure and substrate bias influence on their crystal orientation and morphology by XRD and SEM. They were also studied friction coefficient at vacuum ambient for physical properties and anodic polarization curves for electrochemical properties in relation with crystal orientation.

2. Experimental

The substrate used stainless 440C of martensite. All of the specimens were polished to 0.013m. After they were polished, they were chemically cleaned trichloroethylene 20min., acetone and alcohol 10min, respectively. And then they were inserted into the vacuum chamber and sufficiently vacuumed in chamber at 3×10^{-6}torr. Ion bombardment cleaning carried out by supplied argon gas and induced -700V of substrate bias during 20min for removal of surface contamination.

The structure of deposited silver film was analyzed the range of 2 from 30 to 70 by XRD. The surface morphology observed by FE SEM. The tribology test was carried out ball-on-disc tester under vacuum ambient (< 8×10^{-6}torr) with load of 77g. We measured the anodic polarization of silver film in 0.5M Na_2S solution in order to investigate corrosion behavior of film about S^- ions.

3. Results and discussion

Figure 1 is showed the relative value of XRD pattern under deposited at 1.7×10^{-4}torr and 1.7×10^{-5}torr of argon gas pressure. The films prepared at 1.7×10^{-4}torr are shown the (111) preferred orientation regardless of the substrate bias. On the other hand, the (200) preferred orientation appeared the films prepared under 1.7×10^{-5}torr at all the substrate bias voltages. With increasing the bias voltage in 1.71×0^{-4}torr, the relative intensity of (200) plane showed a tendency of slight increase. On

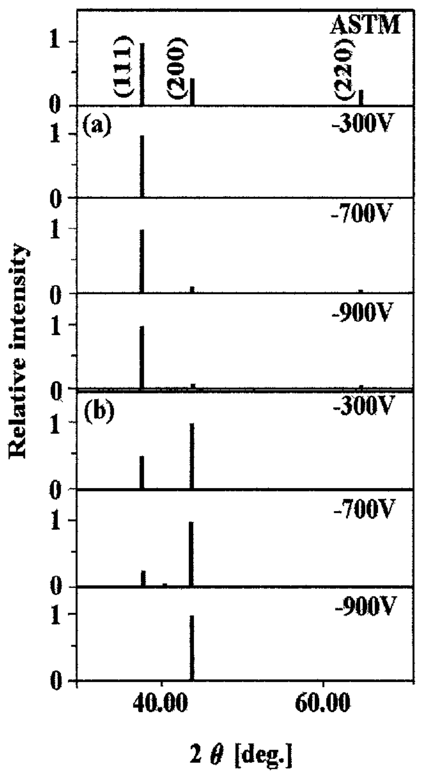

Fig. 1 X-ray diffraction patterns of silver films by relative intensity prepared at 1.7 10^{-4}torr (a) and 1.7 10^{-5}torr (b).

the contrary, the relative intensity of (111) plane on films prepared at 1.7×10^{-5}torr shows a tendency to decrease with increasing the substrate bias. We were considered that the preferred orientation is influenced on the bombard energy of evaporated particles and ions at substrate for deposition.

Figures 2 shows the SEM photographs of the top surface morphology. The crystal grain size is slightly small and uniform, while the film was prepared at 1.7×10^{-4}torr than 1.7×10^{-5}torr. It is deduced an influence on argon gas adsorption to the substrate. One nucleus is coalesced on the substrate adjacent to other nucleus. However, this coalescence is inhibited with adsorbing argon gas. Therefore, the nucleation is occurred faster than the nucleus growth on the substrate.

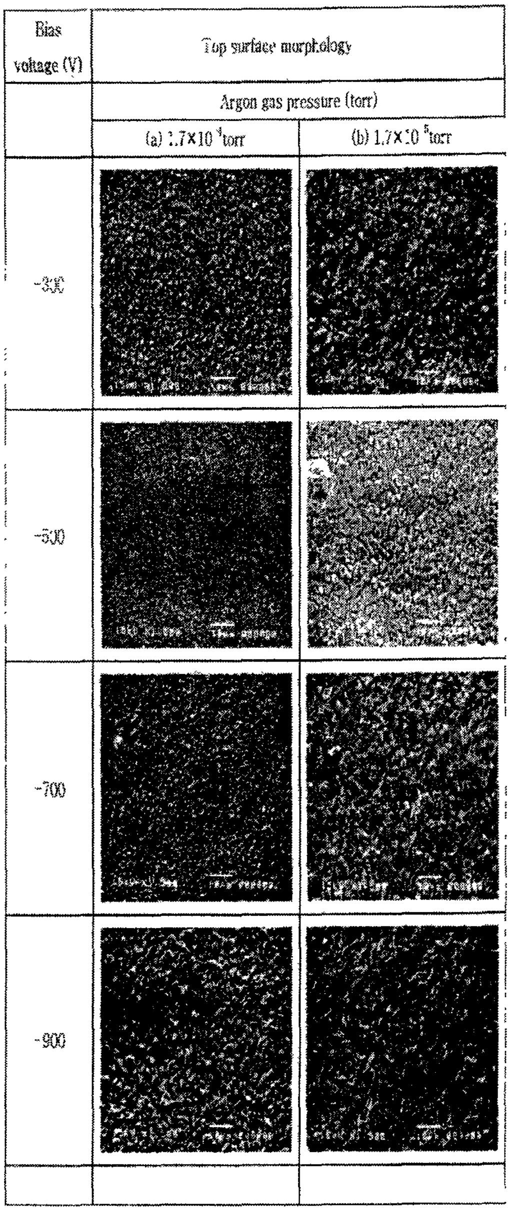

Fig. 2 SEM photograph of surface morphology for silver films.

Figure 3 shows the change of friction coefficient for films prepared at 1.7×10^{-4}torr and 1.7×10^{-5}torr. From the figure 3(a), the value of the friction coefficient is low and stable on the start of the test. Friction coefficient is shown lower value on films prepared at -900V and -700V of substrate

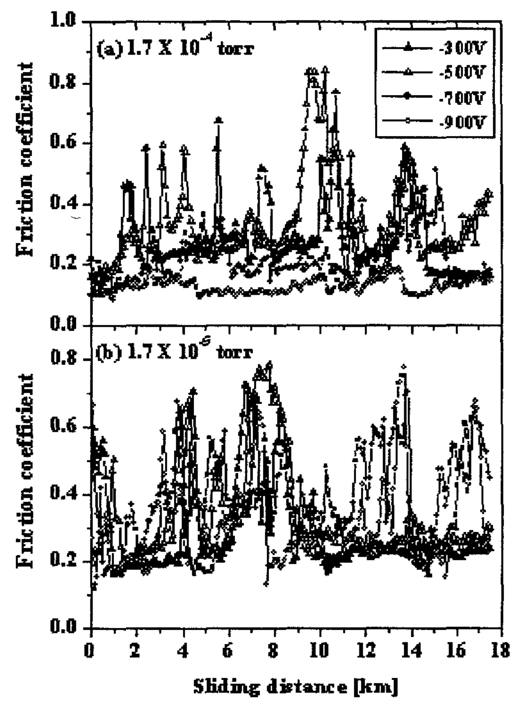

Fig. 3 Variation of friction coefficient with sliding distance for silver films deposited at 1.7×10^{-4}torr (a) and 1.7×10^{-5}torr (b).

bias. Especially, the friction coefficient was lowest and most stable while the film prepared at -900V substrate bias. On the other hand, the friction coefficient of films, which prepared in 1.7×10^{-5}torr, was showed high and unstable on the whole as shown in figure 3(b). Nevertheless, the change of friction coefficient was reduced with decreasing the substrate bias. Within films prepared at 1.7×10^{-5}torr, the lower value of friction coefficient shows the film prepared at -300V of substrate bias.

We were considered that the friction coefficient related with XRD pattern and surface morphology of SEM. We can represent (111) and (200) planes in figure 4. These planes are exposed on the surface of films by preferred orientation. We can consider that the contact area of atoms is probably larger at

(200) plane than (111) plane while the film contacted with ball of ball-on-disc tester. In addition, the (200) plane was easy to adsorb wear debris and kept it long time due to higher surface free energy. It is considered to cause unstable and high friction coefficient value. Also, we observed that the crystal grain size was smaller and more homogenous while the films prepared at 1.7×10^{-4}torr. The friction coefficient is related with contact area (A) and friction force (F) from the equations.

$$F = A\ S$$
$$F = (W/P_f)\ S$$
$$\mu = F / W = S / P_f$$

Where, F, A, S, W, P_f and indicate friction force, real contact area, shear strength, weight, plastic fluidity and friction coefficient, respectively. Here, the contact area would be small when the crystal grain size of film was small and homogenous. It affected low friction coefficient.

A Na_2S solution was dissociated as follow (1) and (2) formulas,

$$NaS^{2-} \leftrightarrow 2Na^{+} + S^{2-} \quad (1)$$

$$H_2O + S^{2-} \leftrightarrow HS^{-} + OH^{-} \quad (2)$$

Also, silver films is led (3) formula by means of anodic polarization,

$$Ag \rightarrow Ag^{+} + e^{-} \quad (3)$$

Figure 5 shows anodic polarization curves in 0.5M Na_2S solution. Anodic reaction showed the activity with increasing current density from the start of anodic polarization. Its Ag^+ ions are dissolved on film surface actively by (3) formula. And then the current density isdecreased sharply. It was that S^- ions produced the corrosion products of Ag_2S

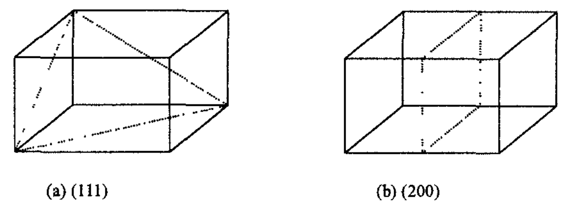

Fig. 4 Lattice plane of cubic.

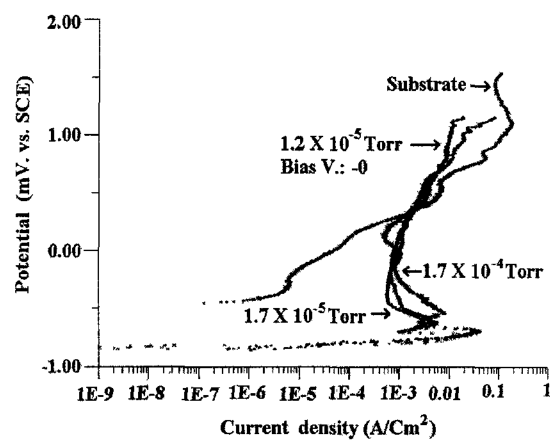

Fig. 5 Anodic polarization curves of silver films prepared at -300V of substrate bias voltages and film of vacuum deposition in 0.5M Na_2S solution.

(acanthite) at some anodic polarization potential due to reaction with Ag^+ ions. The Ag^+ ions were prevented to dissolution by corrosion products of Ag_2S. Therefore, corrosion products of Ag_2S affect the decrease of current density like passive film. It was considered that current density repeated the increase and decrease in passivity area owing to repeating of formation and destruction corrosion products. The (200) plane actively reacted in solution because of the (200) plane was higher surface free energy than (111) plane. The ground boundary increased in unit area while the crystal grain size enlarged. This grain boundary acted like anode in solution. The grain boundary produced dense corrosion products since affected more active than grain.

Therefore, the (200) plane of films prepared at 1.7×10^{-5}torr gave priority to formation of corrosion products. However, the potential was above 0v, their passive current density was increased by destruction of corrosion products layer. These films were difficult keeping the passive film caused by inhomogeneous and irregular of surface morphology.

4. Conclusions

Silver films were prepared by e-beam ion plating. The morphology and crystal orientationdeposition condition. With increasing argon gas pressure, the crystal grain size was slightly of silver films were studied in compliance with
decreased on silver film. It was understood that argon gas affected like inhibitor of nuclei growth on the substrate. The (111) preferred orientation plane was exhibited on film surface prepared at 1.7×10^{-4}torr and (200) preferential orientation was films of 1.7×10^{-5}torr.

The friction coefficient showed most stable and lowest on silver film of prepared at 1.7×10^{-4}torr of argon gas pressure and -900V of substrate bias. It was considered the effect of
morphology and preferential orientation. The corrosion behavior of silver film was influenced corrosion products of Ag_2S.

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