CONF-890468--9

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DE89 014665

STUDY OF THE MICROSTRUCTURE OF SILVER FILMS DEPOSITED BY ION ASSISTED DEPOSITION ONTO ALUMINUM OXIDE SUBSTRATES

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To be presented at the International Conference on Metallurgical Coatings
San Diego CA
April 17-21, 1989

Study of the Microstructure of Silver Films Deposited by Ion-Assisted Deposition onto Aluminum Oxide Substrates

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ABSTRACT

Ion-assisted deposition (IAD) can be used to modify the microstructure, density, or other properties of thin films. To understand the effects of ion bombardment on film growth, we studied the film morphology and hardness of evaporated Ag films that had been bombarded by Ar ions during deposition. Cross sections of deposited films were examined by scanning electron microscopy, and film hardness was measured with a diamond indenter.

Substantial increases in film porosity and surface roughness were seen in the 1000-eV Ar-ion-bombarded specimens, compared to vapor-deposited specimens or to specimens bombarded with 300 or 150-eV ions. The IAD films generally had hardness values greater than that of evaporated films. Low hardness values were obtained for a porous 1000-eV IAD film; these are attributed to the presence of compressible pores. No Ar was detected in the films.

INTRODUCTION

Ion-beam techniques are increasingly being studied as a means of improving the tribological performance of thin films. Ion-beam mixing [1,2], ion implantation [3,4] and ion-assisted deposition (IAD) [5] of selected elements have been shown to produce substantially increased wear resistance, lower friction, or both during sliding contact.

In IAD, a thin film is deposited from a vapor or by sputtering while the substrate is bombarded with energetic ions. IAD-deposited Ag films have been studied by a number of workers, and large effects on film texture [6] and nucleation [7] have been found. Low-energy bombardment can modify the film stress of metal [8] or compound [9] films or can produce diamondlike carbon coatings [10], or superior-quality optical coatings [11].

Ion "assisted" modifications may be important for the use of thin metal films in tribological applications. The possibility of using heat-resistant ceramic materials in aerospace bearings and advanced heat engines has evoked considerable interest, but effective lubrication, especially under boundary-lubrication conditions, remains a challenge. Films of solid lubricants, such as soft metals or thin oxides, can provide significant increases in sliding-wear resistance when applied to the ceramic surfaces [2,12]. We have found that thin IAD Ag coatings applied to Al_2O_3 substrates greatly reduce sliding friction and wear [13].

In order to understand the effects of ion bombardment on growing films, a study was made of the effect of deposition parameters on various properties of Ag films.

EXPERIMENT

Depositions were performed in a vacuum chamber equipped with an electron-beam evaporation source. The chamber base pressure was in the low 10^{-5} Pa range, and during deposition the pressure was ~$5x10^{-3}$ Pa. A beam of energetic Ar ions was generated by a commercial hot-cathode, 3-cm-diameter ion source. The ion current density was measured with a calorimeter and the beam was neutralized to reduce substrate charging effects. The Ag evaporation rate was varied in order to attain different ion/atom arrival ratios. The angles of incidence of the vapor and the bombarding ions were 45° and ~125°, respectively, with respect to the plane of the substrate. Commercially obtained Al_2O_3 coupons were ground to a smooth surface with grinding papers and finished with 3-μm diamond paste. Specimens were cleaned with alcohol and acetone and then sputter-cleaned in the vacuum chamber before starting IAD.

After deposition on substrates at ambient temperature, the substrates were fractured in liquid nitrogen and inspected with a scanning electron microscope (SEM). The film hardness was measured with an in situ SEM ultra-microhardness measuring instrument using a Vickers diamond stylus. At least five indentations were measured on each specimen. Indentation depths were typically 0.5 μm and an applied load of 0.5 g was used.

RESULTS

Figure 1 is an micrograph of a film deposited by physical-vapor deposition (PVD). The film appears to have a slightly columnar structure and adhesion of the film to the substrate is poor. The angle of the columns is due to the incline of the substrate relative to the vapor source.

Figures 2-4 are SEM micrographs of 1000-eV IAD films. For specimen 2 (Figure 2), the ion/atom arrival ratio was 0.43. A portion of this substrate was masked from the ion beam during deposition and the film thickness was 2 μm. Thus considerable sputtering occurred during deposition because the film thickness on the bombarded portion is very thin (0.25-μm). For an intermediate ion/atom arrival ratio of 0.16 (specimen 3, Figure 3), large gaps between the columns can be seen. Specimens 2 and 3 have rough external surfaces. Lowering the ion/atom arrival ratio to 0.03 produced a film with good density and a smooth external surface (Figure 4).

Figure 5 is a micrograph of a 300-eV IAD film. The ion/atom arrival ratio was 0.04. No evidence of columnar structure can be seen. The appearance of a 300-eV IAD film deposited with a different ion/atom arrival ratio (0.12) was similar.

Figures 6 is a micrograph of a 150-eV IAD film. The ion/atom arrival ratio was 0.5. In this specimen, little structure can be seen. The small black spots seen in the figure may be pores in the film. 150-eV IAD films deposited with ion/atom arrival ratios of 0.1 and 0.04 were similar.

Figure 7 shows the effect of sputter-etching a PVD Ag film. The film was sputter-etched with $4.6x10^{22}$ Ar ions/m^2 at 1000-eV (the same total dose as specimen 2). Considerable surface roughening is seen.

Ultra-microhardness measurements were made on all films except that of Figure 2, which was too thin for accurate measurements, and the average values are reported in Table I. Values of E_n, which is defined as the energy delivered by the ions per arriving vapor atom, are also tabulated.

DISCUSSION

Figures 2 and 3 show that 1000-eV ion bombardment causes substantial film porosity and surface roughening. The films have much less integrity than other IAD films or films deposited with no ion bombardment. It has been suggested that during deposition, collisions of energetic ions with near-surface atoms push the atoms into interstitial sites, leaving depleted zones near the surface, which are subsequently filled by arriving vapor [14]. A molecular-dynamics simulation by Müller showed that low-energy ions ($E < 100$ eV) were effective for increasing the packing density of evaporated Ni films [15]. Müller found that the collision of energetic ions with atoms on the porous (on a nm scale) surface effectively densified the surface by dislodging and compacting atoms and aggregates of atoms into the surface. The 1000-eV bombardment seems instead to have created gaps between the columns in the film. This may in part be because higher-energy ions produce cascade damage deeper into the specimen where refilling of the depleted zones by the arriving vapor may be inhibited. Netterfield and coworkers found that the optimum energy for optical-film densification was ~150 eV [11].

As shown in Figure 7, Ag films are strongly textured by sputter-etching. The surface topography produced is on a scale much larger than that observed in Figures 2 or 3. Ion bombardment, however, alters the nucleation kinetics during the start of film growth [16], and a combination of shadowing and higher sputtering rates at 1000 eV during deposition might be responsible for the rough surfaces and columnar microstructure seen in Figures 2 and 3.

Injected Ar may be also be playing a part in the formation of voided areas, but Ar was not detected in any IAD film using wavelength-dispersive x-ray spectrometry.

As shown in Table I, IAD specimens 4-9 had hardness values greater than that of evaporated films. Huang and coworkers studied IAD Ag films with x-ray methods and found that ion bombardment produced large numbers of dislocations [6]. Hardness increases would thus be expected. The substantial hardness decrease observed for specimen 3 can be attributed to the presence of compressible pores in the film, and the film on specimen 2 was too thin

No clear trend can be seen in the hardness values for different ion/atom arrival ratios or E_n. It is thought that substantial dislocation generation may have occurred in all the IAD films studied. Huang and coworkers reported that dislocation densities increased substantially in their Ag films for even the smallest ion doses reported (E_n=20 eV/Ag atom).

It is evident that considerable variation in film microstructure and hardness occurs for different ion energies. The amount of kinetic energy delivered per arriving vapor atom, E_n, is often used in the literature as a means of characterizing ion bombardment. Because the resulting film morphology depends critically on ion energy, studies of bombardment effects should include the effects of ion energy, as well as the ion/atom arrival ratio.

CONCLUSION

The microstructure and hardness of IAD Ag films as a function of ion energy and ion/atom arrival ratio were studied in this work. The film porosity and surface roughness was large in some 1000-eV Ar ion bombarded specimens. This latter effect is attributed to the effects of film sputtering and shadowing. IAD films in almost all cases had hardness values greater than that of evaporated films. Low hardness values obtained for a 1000-eV IAD film are thought to be due to the presence of compressible pores in the film. No Ar was detected in the IAD films.

ACKNOWLEDGEMENT

This work was supported by the U.S. Department of Energy, Energy Conversion and Utilization Technologies Division, under Contract W-31-109-Eng-38.

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Table I. IAD parameters and hardness of film specimens.

Specimen no.	Ion energy (eV)	Arrival ratio (ion/Ag atom)	E_n (eV/Ag atom)	Hardness (kg/mm^2)
1 (PVD)	--	--	--	102
2	1000	0.43	430	*
3	1000	0.16	160	74
4	1000	0.03	30	120
5	300	0.12	36	135
6	300	0.04	12	118
7	150	0.50	75	119
8	150	0.10	15	135
9	150	0.04	6	128

* Accurate hardness measurements are not available.

FIGURE CAPTIONS

1. Micrograph of vapor deposited Ag film, edge and top view.
2. Micrograph of IAD Ag film, 1000-eV ion energy, ion/atom arrival ratio = 0.43, edge and top view.
3. Micrograph of IAD Ag film, 1000-eV ion energy, ion/atom arrival ratio = 0.16, edge and top view.
4. Micrograph of IAD Ag film, 1000-eV ion energy, ion/atom arrival ratio = 0.03, edge and top view.
5. Micrograph of IAD Ag film, 300-eV ion energy, ion/atom arrival ratio = 0.04, edge and top view.
6. Micrograph of IAD Ag film, 150-eV ion energy, ion/atom arrival ratio = 0.5, edge view.
7. Micrograph of PVD Ag film that was sputter-etched with $4.6x10^{22}$ ions/m^2, 1000-eV ion energy, top view.

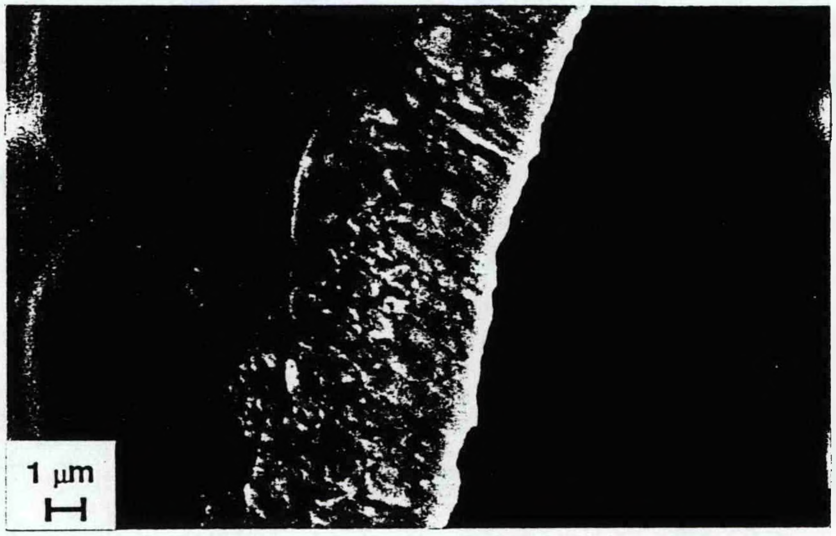

Figure 1

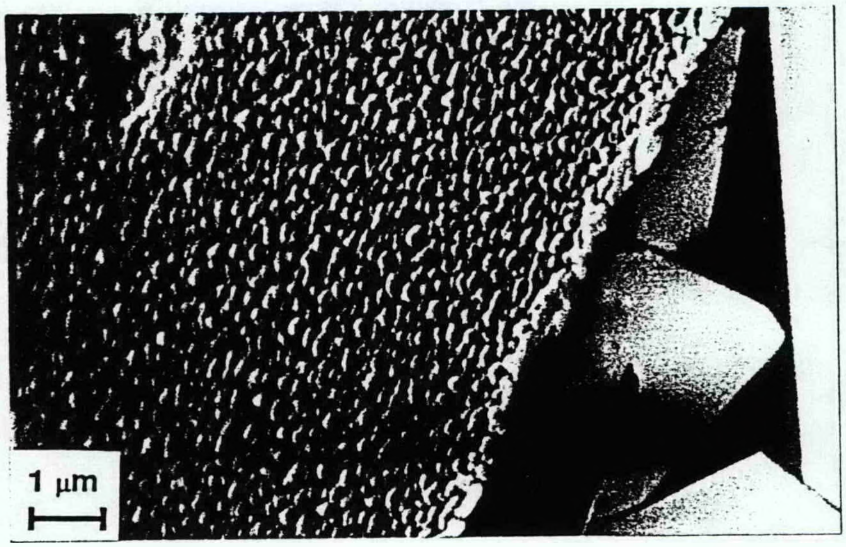

Figure 2

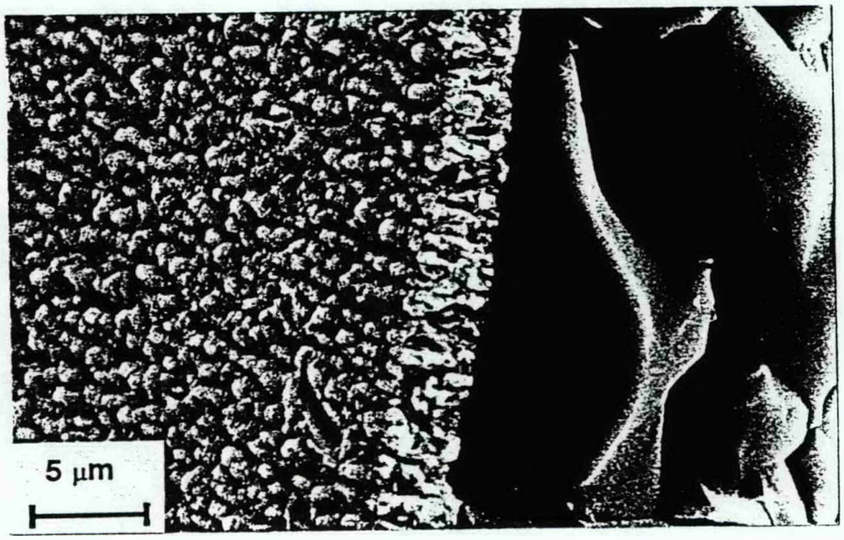

Figure 3

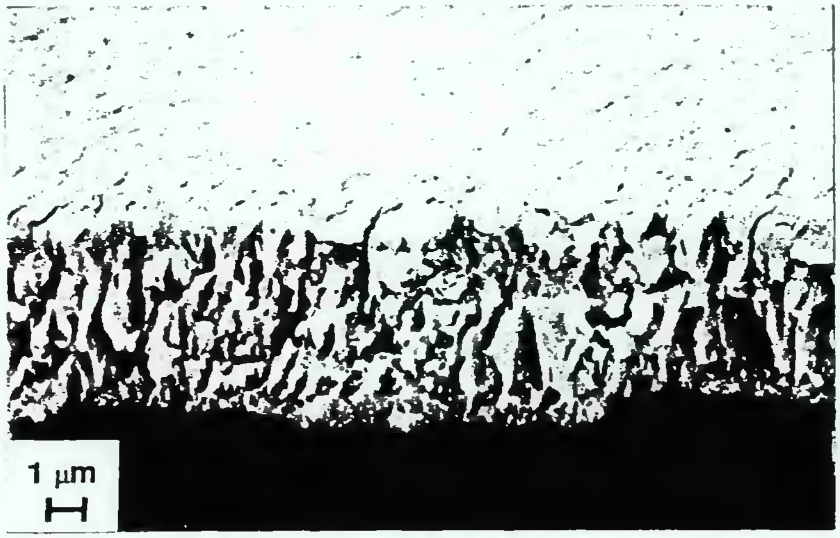

Figure 4

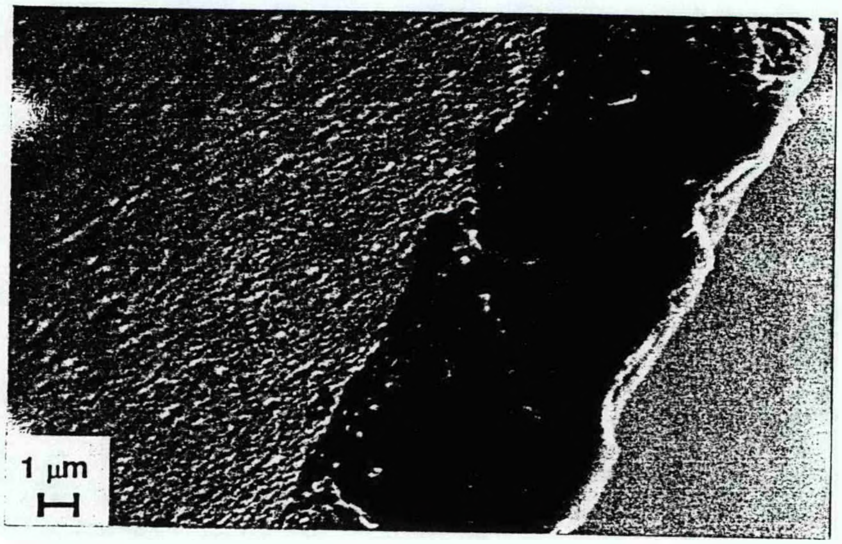

Figure 5

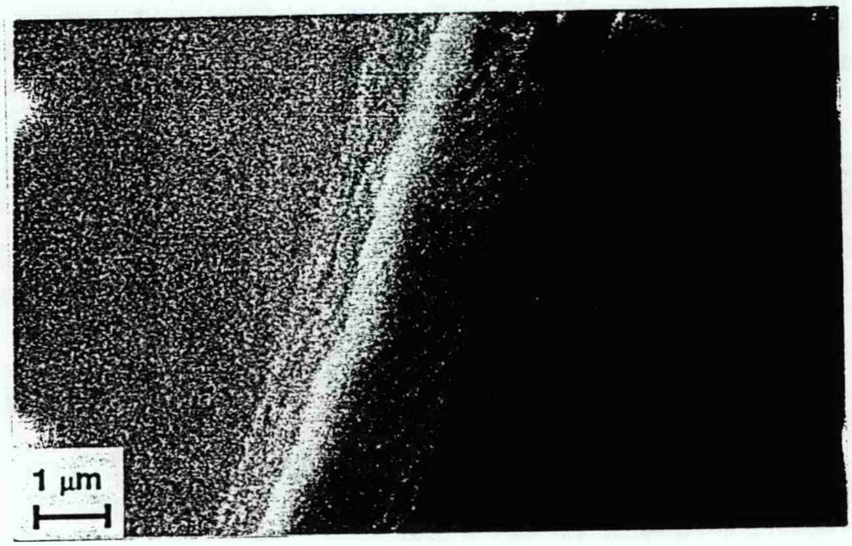

Figure 6

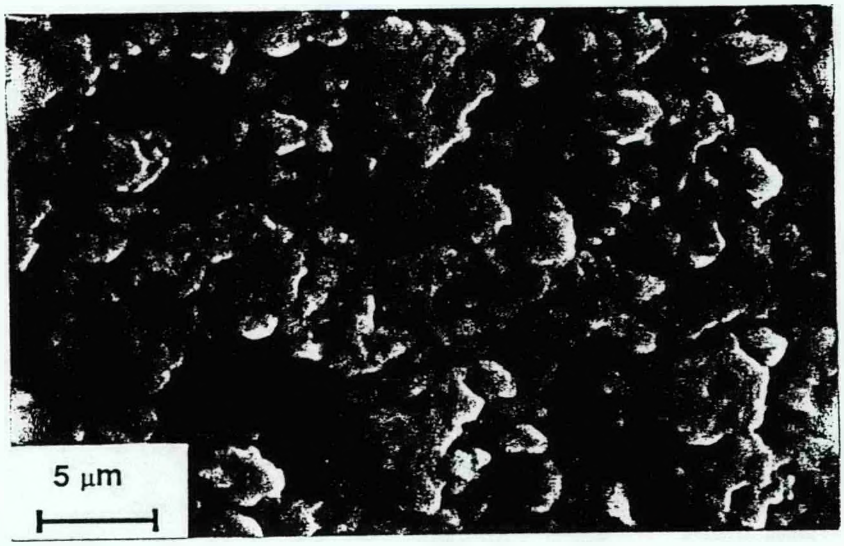

Figure 7