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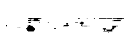

DEPOSITION OF ADHERENT Ag-Ti DUPLEX FILMS ON CERAMICS

IN A MULTIPLE-CATHODE SPUTTER DEPOSITION SYSTEM

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SUMMARY

The Adhesion of Ag films deposited on oxide ceramics can be increased by first depositing intermediate films of active metals such as Ti. Such duplex coatings can be fabricated in a widely-used 3-target sputter deposition system. It is shown here that the beneficial effect of the intermediate Ti film can be defeated by commonly used in-situ target and substrate sputter-cleaning procedures which result in Ag under the Ti. Auger electron spectroscopy and wear testing of the coatings are used to develop a cleaning strategy resulting in an adherent film system.

INTRODUCTION

Active metals such as Ti and Cr have a history of use as intermediate coatings for joining noble metals to oxide ceramics. These active metals react with the oxides to form a strong bond yet maintain a metallic nature at their free surface to promote adhesion to metals which will not otherwise bond to the ceramic. One such system uses a thin Ti coating to bond Ag to Al_2O_3 (ref. 1). This allows Ag, which otherwise does not adhere well to Al_2O_3, to function as a solid film lubricant. Friction and wear testing of Al_2O_3 pins on this duplex coating system has shown increased wear life and a reduction in friction coefficient when compared to samples without the Ti interlayer.

These films were deposited by cathodic sputtering, a form of physical vapor deposition (PVD). During the course of their development it was discovered that some of the techniques commonly used within PVD to enhance the adhesion and purity of films could, when done improperly, actually degrade the performance of the duplex coating. At this point a brief explanation of these techniques is in order. (For a more thorough discussion see, e.g., ref. 2.) In cathodic sputtering, atoms of the coating material are ejected (sputtered) from the cathode (target) as a result of positive ion bombardment. The ejected atoms then condense on nearby surfaces to form a film. Backsputter etching is the reversal of this process so that the substrate is bombarded by ions. This is done as a pre-deposition step which allows the removal of surface contamination and oxides and can result in a cleaner substrate surface thereby promoting better adhesion of subsequently deposited films. Target cleaning is the process of operating the cathode at or near deposition conditions for a period to remove surface contamination, oxides, and possible cross contamination from other targets in a multi-target system. This is also done as a pre-deposition step with other targets masked and the substrates masked, removed from the chamber or rotated away from the target, depending on the system.

It will be shown here that pre-deposition substrate backsputter etching and target cleaning, when not done properly, can result in the wrong material being deposited initially onto the substrate. It will also be shown that these unintentional deposits can lead to premature lubricating film failure. Procedures will then be outlined to minimize these effects.

This study consists of three parts. The first is to operate the PVD system in the target cleaning mode with Si substrates as witnesses at different positions in the deposition chamber. The second is to

operate in the backsputter etch (substrate cleaning) mode with Si substrates on different underlying supports. After removal from the PVD system the Si substrates are then examined by Auger electron spectroscopy (AES). Third, to illustrate the effects, friction and wear tests are conducted on duplex Ag-Ti coatings deposited onto Al_2O_3 disks which were first subjected to selected pre-deposition treatments.

EXPERIMENTAL

AES analysis was done on a PHI-545 Scanning Auger Microprobe at 3 keV, ~15 μm spot size and 1 μA beam current. The substrates were optically polished Si wafers which were ultrasonically cleaned in acetone and ethanol before the treatments outlined below.

The depositions were made, separate from the AES analysis, in a Materials Research Corporation Model 8667 r.f./d.c., Magnetron sputtering system. Shown schematically in figure 1, it is a batch process machine with a rotatable table and three target stations spaced 90° apart on a 41 cm diameter. Each target station has a movable shutter. In the r.f. mode power can be directed through any combination of table and targets for simultaneous sputtering with or without substrate bias. Power can also be directed through the substrate table alone for substrate etching. Target to substrate vertical spacing for this study was 8 cm.

For the target cleaning part of this study, Si substrates were positioned at 0, 90, and 180° relative to the target position while operating the target at 1.1 Pa Ar, 500 W. r.f. for 5 min with the shutter open. Targets used were Ag, Al, and Ti. During this, and subsequent procedures, targets not in actual use were kept shuttered.

For the backsputter etching part of this study, the Si substrates were placed on 15 cm square Al backing plates which had first been coated with approximately 0.5 μm of Ag, Al, Ti, or C. Etch conditions were 2.7 Pa Ar, 500 W. r.f. for 5 min.

The substrates used in the friction and wear testing were polycrystalline Al_2O_3 pins and disks. These, and the pin-on-disk friction and wear testing apparatus and procedures, are described elsewhere (refs. 1 and 3). Essentially, 2.54 cm radius pins were slid against the disks for 60 min at 1 m/s and 0.5 kg in room temperature air. Three runs were made on each disk, each with a new pin. The friction coefficient was continuously monitored during the run. At the end pin and disk wear were measured.

Two different combinations of pre-deposition treatment and deposition were tested for friction and wear. These were designed to give the optimum condition (for this PVD system) and one of a number of possible nonoptimum conditions.

Optimum conditions:

(1) Presputter etch on a Ti backing plate
(2) Ti target clean, substrate at 180°
(3) Ti deposition (25 nm)
(4) Ag target clean, substrate at 180°
(5) Ag deposition (1.5 μm)

Nonoptimum conditions:

(1) Presputter etch on a Ti backing plate
(2) Ag target clean, substrate at 90°
(3) Ti target clean, substrate at 180°
(4) Ti deposition (25 nm)
(5) Ag target reactivation, <2 min, substrate at 180°
(6) Ag deposition (1.5 μm)

Procedures for substrate solvent cleaning prior to introduction into the sputter chamber and conditions for presputter etch and target cleaning were the same as those given for the Si substrates.

RESULTS

AES Analysis of Pre-deposition Treatments

For the AES analysis part of this study a number of materials were sputtered in the target cleaning mode or used as underlying support to the Si substrates while backsputter etching, as outlined in the experimental section. Only the Ag results will be shown here. All of the other materials used gave similar AES results consistent with their respective sputter rates and Auger sensitivities.

The AES surveys are shown in figure 2. Survey (a) is from a solvent-cleaned Si wafer, taken as a reference. It shows O, carbonaceous C present as an adventitious surface layer, and Si. The Si peak is split. The low energy portion is indicative of oxide Si. The high energy portion is indicative of metallic Si. This is consistent with the sub-stoichiometric nature of the native oxide present on Si (ref. 4). This dual chemical nature of the Si peak is common to all of the spectra taken.

Survey (b) is from a Si wafer that had been positioned 180° from the Ag target while that target underwent sputter-cleaning. It shows O, C, and Si as above. There is relatively less Si present than in the reference spectra. Ag appears in this spectra. Also, small amounts of S and Cl are present.

Survey (c) is from a Si wafer that had been positioned 90° from the Ag target while that target underwent sputter-cleaning. It shows the same elements that are present in the 180° sample, in different proportion. Ag dominates this spectrum. Carbon is present but is difficult to separate from the Ag MNN peaks at 260 and 266 eV.

Survey (d) is from a Si wafer backsputter etched on a Ag coated backing plate. It is virtually indistinguishable from survey (c) in Si, Ag, and O. It does contain less S, Cl, and C than survey (c).

Friction and Wear Testing

The pin wear data shows a significant difference between the two specimens. The specimen coated under optimum conditions displayed about 20 times less pin wear ($1.1\times10^{-6} \pm 5\times10^{-8}$ cm^3) than the specimen coated under the nonoptimal conditions ($2.2\times10^{-5} \pm 1\times10^{-5}$ cm^3). The friction coefficient (0.4) was the same in both cases. Disk wear, all in the Ag film, was also measurably the same in both cases.

DISCUSSION

AES Analysis of Pre-deposition Treatments

It is clear from figures 2(c) and (d) that there is significant Ag coverage of the substrate as a result of target cleaning with the substrate at 90° to the target and, also, as a result of backsputter etching with the substrate on the Ag backing plate. Estimating the amount of coverage from AES is difficult because Ag is known to grow on Si by island formation (ref. 5). However, these two spectra show a near-total attenuation of the Si signal. This, combined with the fact that the escape depth for 90 eV electrons is approximately 2 monolayers (ref.6), indicates that the islands have nearly grown together. Reference 7 contains a study using ion scattering spectroscopy and AES on Ag coatings on (111) Si. It shows that there is a small Si signal even at a coverage of 35 equivalent monolayers (EML). This suggests an estimate for the Ag coverage of these two samples of 30 to 40 EML or 8 to 10 equivalent nm. Where one would have expected the backsputter etching to produce a clean substrate surface it actually resulted in the substrate being contaminated with the material that it rested upon. A similar result followed from the substrate positioned at 90° while target cleaning; even though, with the shutters closed, there is no clear line of sight between the target and that position.

Even the substrate positioned at 180° to the target while target cleaning, shown in figure 2(b), has significant Ag contamination. Applying the relationship that Zhu et.al. (ref. 5) found (between the normalized intensity of the Si peak to coverage for Ag coatings of up to 4 equivalent nm) to the Si attenuation in this spectrum produces an estimated Ag coverage of 3 nm (~12 EML).

As a comparison, directly under the target (0°) the measured coverage is 1.15 μm, or approximately 4400 monolayers.

Summarizing, estimated Ag coverage at 0, 90, and 180° during target cleaning is 1.15 μm, 8 to 10 nm and 3 nm, respectively. The respective center-of-target to substrate distances are 8, 30, and 42 cm. Fickian diffusion modeling does not fit this coverage versus distance-from-the-target profile. This is not surprising. There is a strong directional dependence on coverage of substrates directly under the target. This argues that a significant portion of the impinging atoms retain energy (velocity) from the sputtering process. This is not true at the distances, greater than 50 mean free paths, to the other stations. Also, with a mean free path at 1 Pa of ~0.5 cm, elemental transport is in a transition region between viscous flow and free molecular movement. There is no accurate model which encompasses these three regimes.

There are some elements present in the AES spectra that are the result of contamination, specifically, Cl, S, C, and O. The source of the Cl here is unknown. S is commonly found in films deposited in this system. It is residue from MoS_2 that is routinely sputtered in this system in support of research on solid lubricants. C is always present on samples exposed to air, as is the O in the native oxide on the surface of most metals.

Friction and Wear Testing

The difference in pin wear between these two samples shows how important pre-deposition steps can be to coating life. The coating prepared under nonoptimum conditions showed more than an order of magnitude greater wear. This indicates that the Ag lubricant film did not adhere well to the oxide

substrate, in spite of the use of a Ti bond layer. This poor adherence is attributed to the Ag "contamination" from the inappropriate cleaning that unintentionally put Ag first on the Al_2O_3 preventing the Ti from forming the desired bond with the oxide.

Note that having pin wear as the significant difference is consistent with studies done previously (ref. 1). The test period was not long enough to cause complete failure of the films, where other differences might have appeared. So the partner in continuous contact, the pin, should display the greatest effect.

Note, also, that the nonoptimum condition chosen was not the worst possible. That would have had the disks on an Ag covered plate during the presputter etch instead of on Ti. The chosen conditions illustrate that the Ti first deposited in the presputter etch (1 to 2 nm) is not enough to anchor the subsequent films.

Recommendations

The recommended conditions for minimizing interfacial contamination are those outlined under the optimum conditions label in the experimental section. These recommendations come out of this study and out of personal experience with this and other systems; therefore, along with the recommendations, some explanation is in order. Regardless of the nature of the coating, if backsputter etching is used to prepare the substrate for coating then the substrate should be supported by the material that is to be deposited first. An alternative would be to place the substrate on a backing plate that is the same material as the substrate. In either event, the backing plate should be as clean as possible. Target cleaning prior to deposition should be done with the substrate as far as possible from the target, or masked, to minimize pre-deposition contamination. Finally, individual target cleaning should take place immediately before deposition from that target to minimize recontamination of the target or the substrate.

These recommendations are designed to minimize rather than eliminate interfacial contamination. Backsputter etching will always result in mixing (redeposition) of materials adsorbed on the table. In doing backsputter etching one is in the position of trading existing contamination (at very least the adventitious C and O present as a result of exposure to atmospheric conditions) for that which accrues as a result of the etch. Similarly, when making a decision for or against pre-deposition target cleaning, the choice is between putting down a lessor or greater amount of what is on the surface of the target as the initial deposit. One must decide which effects, if any, are critical.

SUMMARY

It has been shown that significant pre-deposition coverage of substrates can occur as the result of backsputter etching and target cleaning prior to PVD. The thickness of these coatings have been estimated from AES analysis. It has also been shown that these pre-deposition coatings can adversely affect the performance of subsequently deposited duplex coatings. Recommendations have been made to minimize these adverse effects. Those recommendations are:

1. Backsputter etching should be conducted with the substrate on a backing plate of the same material as that to be deposited first or on a substrate-similar material.

2. Target cleaning should take place with the substrate as far as physically possible from the target or masked.

3. Target cleaning should take place immediately before the actual deposition.

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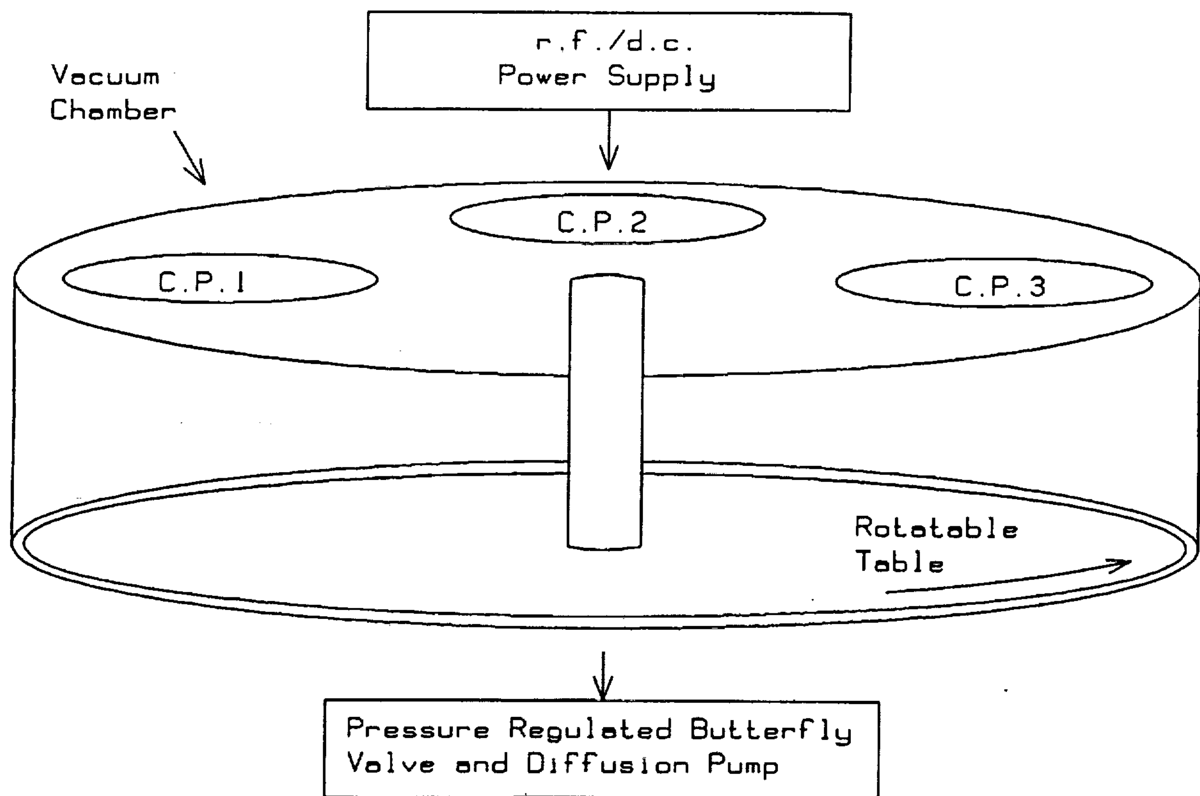
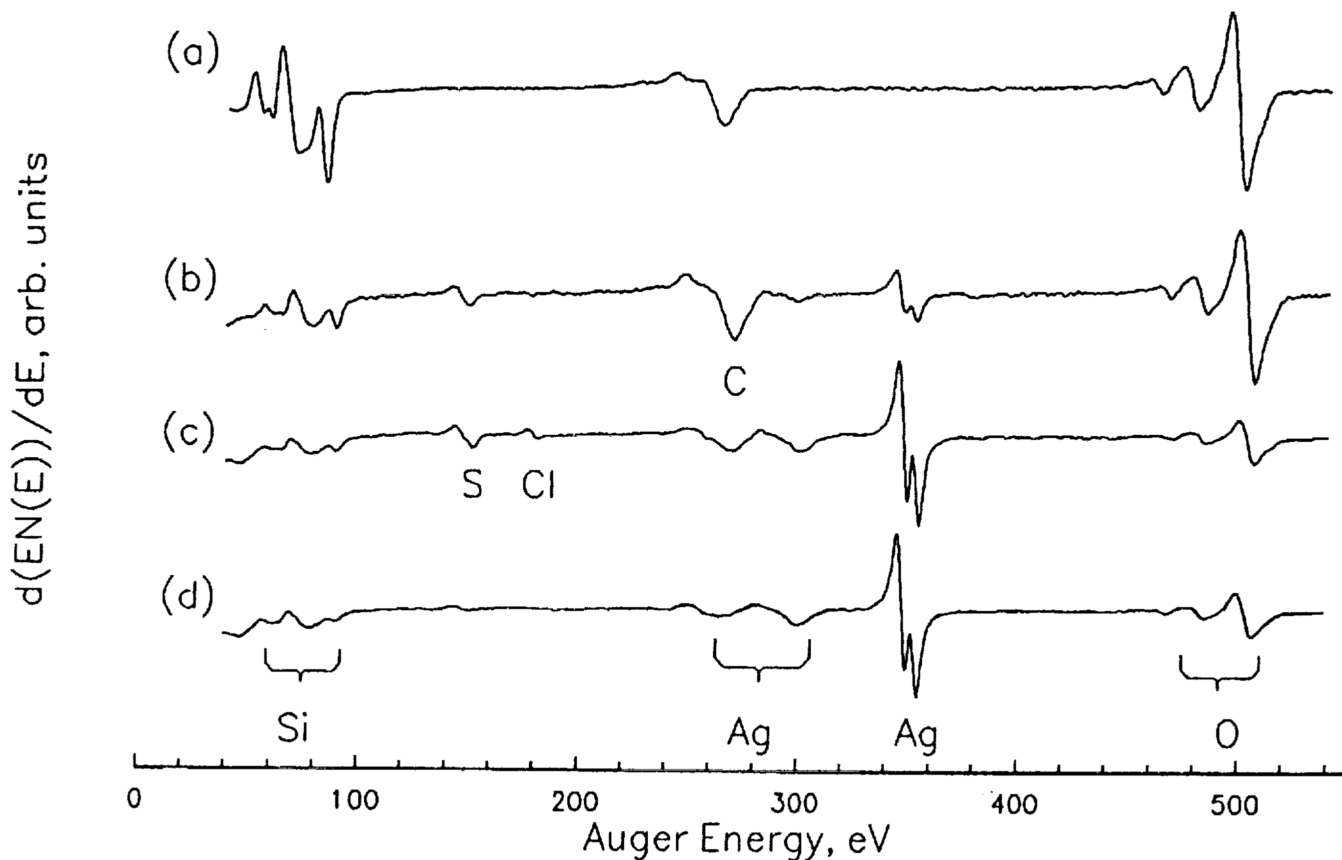


Figure 1.—Schematic of the MRC-8667 physical vapor deposition system. C.P.1, 2 and 3 denote cathode (target) positions.



(a) Si reference, after solvent cleaning.
(b) Si at 180° to Ag target while target cleaning.
(c) Si at 90° to Ag target while target cleaning.
(d) Si on Ag support while backsputter etching.

Figure 2.—Auger Electron Spectroscopy surveys.

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