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Permeation behavior of deuterium implanted in electro- and sputter-deposited copper coatings on aluminum alloy substrates

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Abstract

Permeation behavior of deuterium in copper coatings (~6 μm thickness) deposited on Al-6061 substrates by the electro- and the sputter-deposition methods is compared. The electroplated coating contained copper and aluminum phases, and exhibited microcracks that were distributed uniformly all over the surface. The sputtered coating contained Cu_9Al_4 and $CuAl_2$ phases in addition to copper and aluminum, and was fairly dense. Both the coatings contained oxygen at the free surface and at the coating–substrate interface. Deuterium was implanted in both the coatings under identical conditions and the deuterium profiles were subsequently measured using secondary ion mass spectrometry (SIMS). In case of the electroplated coating, the implanted deuterium diffused into the sample without any interference and reached the oxygen-rich interface where it was trapped by the aluminum oxide. On the contrary, in case of the sputtered coating, the diffusing deuterium was trapped continuously before reaching the oxygen-rich coating–substrate interface. The results are discussed. © 2001 Published by Elsevier Science B.V.

1. Introduction

In the proposed accelerator-based method of tritium production, high-energy protons produce spallation neutrons upon impacting a heavy metal target. These neutrons are captured by ^{3}He gas contained inside Al-6061 tubes to produce tritium via the $^3\text{He}(n, p)^3\text{H}$ nuclear reaction [1–5]. Tritium ions are produced with an energy of about 192 keV which is large enough for 10–15% of the tritium ions to be recoil injected into the tube wall [2–5]. Retention and permeation of the implanted tritium in and through the tube is a source of concern [2–5] and there is a need to minimize both the retention and the permeation of tritium in and through the tube wall. This can be accomplished by maximizing the release of tritium from the inside surface of the Al-6061 tube back into the ^{3}He gas stream. Coatings of metals like copper on the inside surface of the Al-6061 tube can help mitigate the problem because of the higher recombination coefficient of atomic tritium on the surface of copper as compared to aluminum [6]. Investigations have already indicated the benefits of using a copper coating on the surface of Al-6061 [2,4]. The microstructure of the copper coating should play an important role in mitigating the tritium retention/permeation problem. The objective of this paper is to compare the permeation behavior of deuterium that was energetically implanted in copper coatings of radically different microstructures. These coatings were deposited on Al-6061 substrates by: (a) electroplating and (b) sputtering. Deuterium was used instead of tritium in order to avoid tritium's radioactivity.

2. Experimental

The Al-6061 substrates used were $25 \times 25 \times 0.82$ mm^3 in size. Prior to deposition, the substrates were ground

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and polished to a mirror finish. For electroplated coatings, the substrates were dipped in sulfuric acid (15 vol.%) at 353 K for 4 min, rinsed with deionized water, dipped in zincating immersion bath at room temperature for 25 s, and double rinsed with deionized water. This was followed by copper strike, first at 260 A/m^2 for 2 min and then at 130 A/m^2 for 4 min, both at 323 K. Strike was followed by plating in a cyanide bath at 320 A/m^2 and 323 K for 8 min. The anode was electrolytic grade copper. For sputtered coatings, a radio frequency (RF) magnetron system was used with a 99.999% pure copper target. Before deposition the substrates were dipped in 15 vol.% sulfuric acid at 353 K for 5 s, rinsed with deionized water, dipped in 50 vol.% nitric acid at 298 K for 5 s and finally rinsed with deionzed water. Sputtering was carried out under the following conditions: RF power = 250 W, reflected power = 4 W, argon gas flow rate = 10 sccm, base pressure $\leqslant 6 \times 10^{-4}$ Pa, deposition pressure = 0.25 Pa, substrate temperature = 473 K, substrate–target distance = 60 mm, substrate bias = −60 V and deposition time = 35 min. Other details are provided elsewhere [3].

Both the electroplated and the sputtered copper coatings were implanted with deuterium (D) in an ion accelerator [2]. For this purpose 7 mm diameter discs were punched out from the samples. All implantations were carried out under the following conditions: substrate temperature = 350 K, chamber pressure $\leqslant 6 \times 10^{-4}$ Pa, D^+ flux = 1.1×10^{17} m^{-2} s^{-1} and D^+ fluence = 3×10^{21} m^{-2}. Implantations were carried out either under monoenergetic (40 keV) or multienergetic (starting at 40 keV and switching to 120 keV) conditions. In either case the total fluence was 3×10^{21} D^+ m^{-2}, and in the case of the multienergetic implant, equal fluences were used at the two ion energies.

Copper, aluminum, oxygen and deuterium depth profiles were measured using negative secondary ion mass spectrometry (SIMS). Sputtering was accomplished by a Cs^+ primary ion beam under the following conditions: primary beam voltage = 10 kV, sample bias = −4.5 kV, primary beam current = 30 nA, primary beam incidence angle = 24.5°, penetration depth = 10.3 nm and beam diameter = 50 μm. Base pressure was less than 9.3×10^{-8} Pa. The primary ion beam was rastered over an area of 200 × 200 μm^2, while the negative secondary ions were analyzed from only the central 30 μm in order to eliminate spurious ions from the crater edges. Sputtering rates were determined by measurements of the sputtered crater depths using the Dektak^{3}ST surface profilometer with a 2.5 μm diameter stylus, and dividing the measured crater depths with the total sputtering times. There was a 5-day lag time between deuterium implantation and SIMS measurements. During this lag time, samples were stored at room temperature.

3. Results and discussion

From the sample weight gain during deposition, deposition area, coating density (assuming coatings to be pure copper) and deposition time considerations, electroplated and sputtered coating thicknesses were estimated to be 6.1 and 6.3 μm, respectively. Scanning electron microscope (SEM) images of the surfaces of the electroplated and the sputtered coatings are presented in Fig. 1. Both types of coatings appear to have roughly the same grain size (0.5 − 2.0 μm) and degree of porosity. However, the electroplated coating contains microcracks that were distributed uniformly all over the surface. X-ray diffraction (XRD) patterns of the electroplated and the sputtered copper coatings are shown in Fig. 2. The electroplated coating indicates the presence of single-phase copper. Signals from aluminum are also present. The diffraction pattern of the sputtered coating indicates the presence of Cu_9Al_4 and $CuAl_2$ phases in addition to copper and aluminum. Since this coating was deposited at a substrate temperature of 473 K, Al diffused from the substrate surface towards the coating surface (as the coating thickened) resulting in precipitation of the aluminide phases. It is assumed that the aluminide precipitates are uniformly distributed in the copper matrix. SEM images and XRD spectra of the

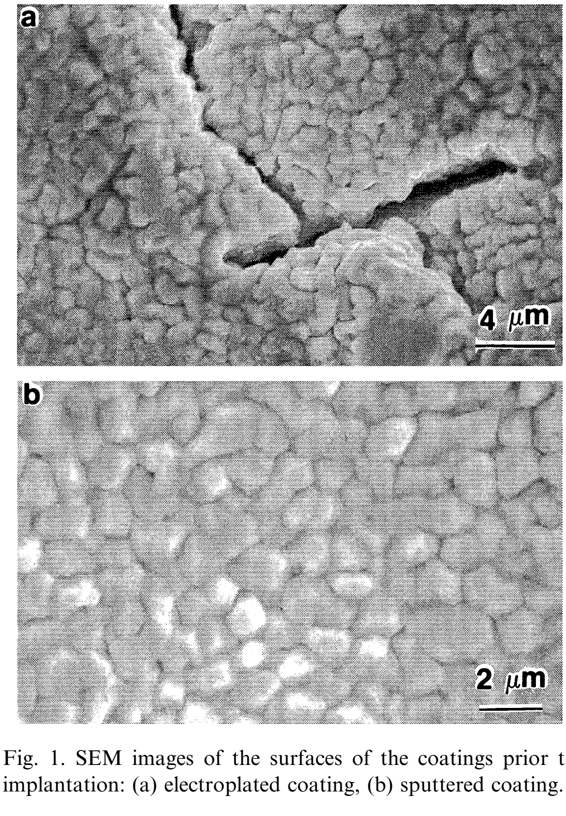

Fig. 1. SEM images of the surfaces of the coatings prior to implantation: (a) electroplated coating, (b) sputtered coating.

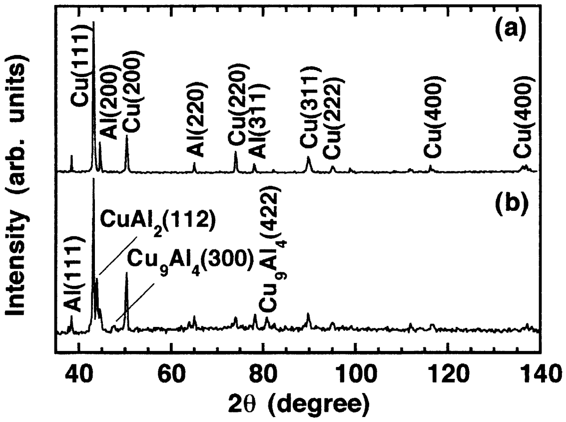

Fig. 2. XRD patterns of the coatings prior to implantation: (a) electroplated coating, (b) sputtered coating. Radiation is Cu Kα.

samples taken after the deuterium implantation did not exhibit any change.

SIMS spectra of Cu, Al and O in the electroplated and the sputtered coatings prior to D^+ implantation are presented in Fig. 3. In the case of the electroplated coating, the coating–substrate interface is relatively sharp as seen by the rapid fall and rise of Cu and Al signals, respectively. On the other hand a rather diffuse coating–substrate interface was observed in the sputtered coating. In both coatings, the fraction of Al increases with increasing depth below the coating surface indicating an Al gradient within the coatings. In both coatings, the O signals are high at the surface (surface adsorbed oxygen and/or oxide) but decrease rapidly before peaking again at some depth below the surface. In case of the electroplated coating, the O signal peaks at a depth where the Cu signal begins to decrease rapidly and the Al signal reaches saturation. This position perhaps marks the substrate surface. In case of the sputtered coating, the O signal peaks at a depth where the Cu signal begins to decrease rapidly but the Al signal has not yet reached saturation. This position marks a location in the coating but close to the substrate surface. Obviously in both the coatings, oxygen is present at or near the interface, most likely in the form of aluminum oxide.

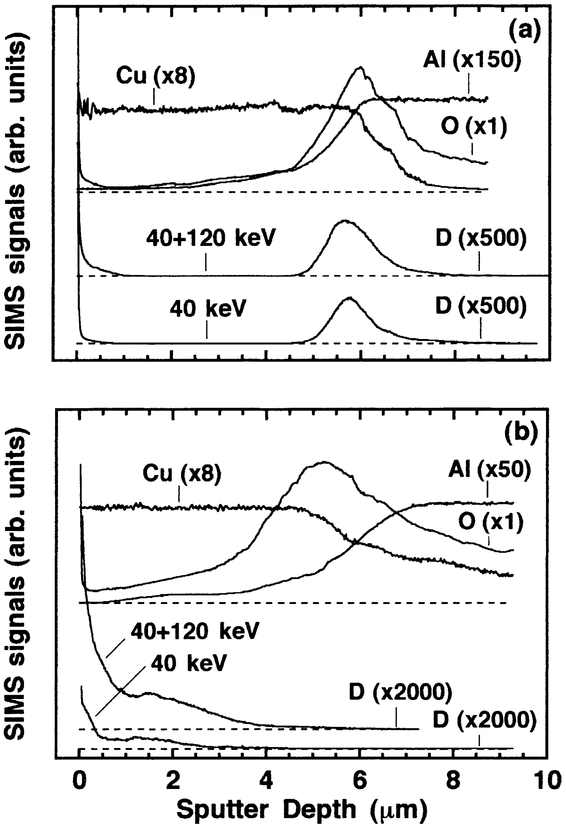

Fig. 3. SIMS spectra of O, Al and Cu in the coatings prior to implantation and of deuterium (D) after implantation at the two ion energies: (a) electroplated coatings, (b) sputtered coatings. Spectra are displaced vertically for clarity. Dashed lines indicate zero counts/s levels for each ion. Cu, Al and D signals are enhanced for better viewing. Multiplication factors used for enhancement are shown.

SIMS spectra of D in the electroplated and the sputtered coatings after D^+ implantation under mono- and multienergetic conditions are also presented in Fig. 3. In both coatings, D signals are high at the surface but decrease with increasing depth below the surface. Transport of ions in matter (TRIM) simulation code [7] calculations predict the D^+ implantation depth in copper to be 0.31 and 0.78 μm for D^+ ion energy of 40 and 120 keV, respectively. Once implanted, D migrates both toward the free surface and the interface. Upon reaching the free surface, D atoms recombine and desorb from the surface as molecular gas [8]. The high D counts at or near the free surface in both of the coatings indicate a build-up of D in the region due to trapping by the oxide layer (alumina in case of the sputtered coating and perhaps copper oxide in case of the electroplated coating). In the case of the electroplated coating, the D counts decrease rapidly to the background level within a depth of about 1 μm below the coating surface and remain at that level until the interface is reached where the signal peaks again. This indicates that after the coating surface or the near surface region, no trapping states exist until the interface is reached where Al_2O_3 binds the permeating D atoms. The experimental results on the sputtered coatings are quite different. The D counts decrease at a much slower rate and reach the background level after a depth of ~3 (for 40 keV) and ~5 μm (for 40 + 120 keV). Furthermore, the signals never peak again at or near the interface. The slight peaking of D at depths of 1.25–1.50 μm below the surface indicates D trapping in the region. For both types of coatings, the SIMS data clearly shows D to depths that are several times the depth of penetration as calculated by the TRIM code. This indicates significant permeation of deuterium in the coatings from the implant region towards the interface. However, the electroplated coating seems to be much more permeable to D than the sputtered coating. This observation may be attributed to the presence of microcracks in the electroplated coating which allow D to migrate through the cracks and reach the interface without diffusing through Cu or by diffusing through a much smaller distance in Cu. The data clearly indicate the importance of the coating microstructure in controlling the permeation of D.

The benefits of copper coating (on the inside surface of Al-6061 tube) in minimizing the retention and permeation of implanted deuterium by maximizing the release of implanted deuterium from the surface has already been demonstrated [2,4]. In the accelerator production of tritium (APT), both electroplated and sputtered copper coatings (of the microstructure discussed above) will probably release a majority of the implanted tritium, and the part that is not released will diffuse into the coating. In case of the electroplated coating, there will be no interference, and that amount eventually will reach the oxygen-rich interface. For the sputtered coating, the diffusing tritium will be trapped by the Al_2O_3 before it ever has a chance to get to the interface. With this argument, it is difficult to say which is the better material to use for APT-like applications. In case of the electroplated coating, tritium will definitely accumulate more rapidly at the interface. However, for the sputtered coating, eventually the near surface traps will become saturated allowing inward migration of tritium to the interface. In either case, the total retention is likely to remain the same.

4. Conclusions

Permeation behavior of deuterium implanted in electroplated and sputtered copper coatings of very different microstructures but equal thicknesses was examined. While the electroplated coating contained copper and aluminum, along with microcracks that were distributed uniformly all over the surface, the sputtered coating contained Cu_9Al_4 and $CuAl_2$ phases in addition to copper and aluminum, and was fairly dense. Both the coatings had an aluminum gradient and contained oxygen at the free surface and at the coating–substrate interface. In case of the electroplated coating, the implanted deuterium diffused rapidly to the oxygen-rich coating–substrate interface where it was trapped by the aluminum oxide. On the contrary, for the same implantation ion energy and fluence, in case of the sputtered coating, the inward diffusing component of the implanted deuterium was continuously trapped and never reached the oxygen-rich coating–substrate interface. The data clearly indicate the absence and presence of deuterium traps between the coating surface and the coating–substrate interface for the electroplated and the sputtered coatings, respectively. It is suggested that for the sputtered coating, once these deuterium traps become saturated, further deuterium will diffuse freely and reach the interface to accumulate there as observed for the electroplated coating. Coating microstructure is indeed important in controlling the deuterium permeation behavior.

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