LOW-ENERGY DEPOSITION OF HIGH-STRENGTH Al(O) ALLOYS FROM AN ECR PLASMA

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ABSTRACT

Low-energy deposition of Al(O) alloys from an electron cyclotron resonance (ECR) plasma offers a scalable method for the synthesis of thick, high-strength Al layers. This work compares alloy layers formed by an ECR-O\textsubscript{2} plasma in conjunction with Al evaporation to O-implanted Al (ion energies 25-200 keV); and it examines the effects of volume fraction of Al\textsubscript{2}O\textsubscript{3} phase and deposition temperature on the yield stress of the material. TEM showed the Al(O) alloys contain a dense dispersion of small $\gamma$-Al\textsubscript{2}O\textsubscript{3} precipitates (-1 nm) in a fine-grain (10-100 nm) fcc Al matrix when deposited at a temperature of $-100^\circ$C, similar to the microstructure for gigapascal-strength O-implanted Al. Nanoindentation gave hardnesses for ECR films from 1.1 to 3.2 GPa, and finite-element modeling gave yield stresses up to $1.3 \pm 0.2$ GPa with an elastic modulus of 66 GPa $\pm$ 6 GPa (similar to pure bulk Al). The yield stress of a polycrystalline pure Al layer was only 0.19$\pm$0.02 GPa, which was increased to 0.87$\pm$0.15 GPa by implantation with 5 at.% O.

INTRODUCTION

The formation of thick, high-strength aluminum alloys is important for providing strong wear-resistant coatings in low-weight material components and possibly for surface coatings on Al interconnects. Previously \cite{1}, the surface (up to 0.5 $\mu$m) of bulk Al disks was shown to be strengthened by a dense dispersion of 1-3 nm sized particles which were created through 25-200 keV O ion implantation. These alloys contained disordered $\gamma$-Al\textsubscript{2}O\textsubscript{3} precipitates which were coherent with the fcc Al matrix. This work has been extended to compare O-implanted layers to Al(O) alloy layers formed using an O\textsubscript{2} electron cyclotron resonance (ECR) plasma in conjunction with electron beam evaporation of Al. Our first paper on this topic \cite{2} examined the hardness of an ECR Al\textsubscript{0.8}O\textsubscript{0.2} layer deposited on both an Al disk and a Si substrate. This paper reports on the work in progress to form these materials and determine their microstructure and mechanical properties as a function of deposition conditions. Specifically, finite element (FE) modeling is performed using the computer code ABAQUS/Explicit \cite{3} in order to extract the yield stress ($\sigma_{ys}$) and the modulus of elasticity ($E$) from the hardness data. Also, the variation in $\sigma_{ys}$ with increasing volume fraction of the Al\textsubscript{2}O\textsubscript{3} phase and increasing deposition temperature are examined.

The introduction of hard particles into a metal matrix can strengthen the material through several mechanisms which inhibit dislocation motion: dislocations restricted to bowing around particles, work hardening from pile-up of dislocation loops around the particles, and an increase in yield stress due to coherency strain. In addition, the metal matrix may also exhibit an increase in $\sigma_{ys}$ as a result of grain-size strengthening. The effectiveness of dispersion strengthening depends on the particle spacing, the particle size, and the strength of the particle to resist cutting by dislocations. Orowan \cite{4} first described the process of dislocation bowing in terms of the stress $\tau$ required to extrude a dislocation between hard spherical particles of diameter $\delta$ and spaced a distance $L$ apart: $\tau = 2Gb/L$, where G is the shear modulus of the matrix (25.5 GPa for Al) and $b$ is the Burger's vector (0.286 nm for Al). This relationship shows that the $\sigma_{ys}$ ($=2\tau$) increases as $L$ decreases, and for a constant volume fraction (f) of uniformly dispersed particles, a decrease in $L$ corresponds to a decrease in $\delta$ with an increase in the particle density. In general, the different dispersion strengthening mechanisms can be modeled such that the $\sigma_{ys} \sim f^{1/3}$, where $n$ and $m$ can vary depending on the dominant mechanism for strengthening. The volume fraction is calculated from the composition and $\delta$ can be determined from microscopy. For dislocation bowing, $n=\frac{1}{3}$ and $m=1$; and for work hardening, $\sigma_{ys}$ increases with $n=1$ to 1.5 \cite{5,6} and $m=0$. The incremental increase in yield stress due to coherency strain can be modeled such that $n=\frac{1}{2}$ and $m=-\frac{1}{2}$ \cite{1}, or $n=1$ and $m=0$ \cite{7}.
For thermally driven grain growth $D_{\text{max}}=D/f$, where $D$ is the average grain size, and thus for grain-size strengthening ($\sigma_{\text{ys}}=D^{\alpha}$) $n=\frac{1}{2}$ and $m=\frac{1}{2}$.

Previous work [9] on ion implanted Al found that $\sigma_{\text{ys}}$ increased from 1.4 to 2.9 GPa as the composition varied from 5 to 20 at.% O. Also, the sample with 20 at.% O retained a strength of 1.2 GPa after annealing at 550°C, in which $\delta$ increased by a factor of 2 to 5. While implantation serves as a good technique for improving the tribological properties of an Al surface, ECR plasma deposition offers the possibility to combine the benefits attained from implantation with the ability to deposit thick layers ($\geq 1 \, \mu m$).

**EXPERIMENT**

Both ECR-deposited and O-ion implanted samples were prepared on Si substrates for ultra-low load indentation evaluation. A horizontally positioned ECR plasma source was used in conjunction with a downstream electron-beam evaporation source for depositing hard Al(O) layers. Microwaves (2.45 GHz) were injected into the ECR chamber to excite the O$_2$ with 80 Watts of power. Two electromagnets establish the resonance region at 875 Gauss in the upstream chamber. The ECR-system base pressure was 0.5-1×10$^{-8}$ Torr and the operating pressure was 2-3×10$^{-5}$ Torr for O$_2$ gas flow rates of 0.7-1.0 sccm. The samples were electrically isolated relative to ground, yielding an O$_2^+$ ion energy ≈24 eV as determined from Langmuir probe measurements near the sample. The composition and phase of the films were measured as a function of Al deposition rate, O$_2$ flow rate, and ion energy for growth temperatures from 35°C to 400°C. Al evaporation rates were measured using a quartz crystal monitor and films were grown at 1.0-2.5 nm/sec. ECR Al(O) films were deposited with thicknesses ranging from 610 nm to 1.24 μm. In order to compare ECR films to O-implanted Al, 650 nm thick Al films were deposited from the electron beam evaporation source onto Si substrates and then implanted to concentrations of 5 at.% and 20 at.% O. Multiple O$^+$ energies from 25 keV to 300 keV were used and their fluences were adjusted to produce uniform composition-depth profiles up to $\approx$600 nm deep. The composition of the layers was obtained using Rutherford Backscattering spectrometry (RBS), and the phase and microstructure were characterized for films deposited on SiO$_2$-coated transmission electron microscope (TEM) grids.

Nanoindentation results gave load versus displacement-depth response curves using the methods described in references [10]. The layers were indented on a Nano Instruments Nano Indenter II® in 10 different areas which were separated 15 μm apart. For each indentation area, a load was applied to the indenter and the diamond tip was inserted at a constant rate, while recording the load as a function of penetration depth for up to three different depths. At each nominal depth (50, 100, and 200 nm) the load was held constant for 15 sec. and then the indenter was retracted to measure the load-depth response for unloading. In general, for a thin film on a substrate the nanoindentation measurements are strongly affected by the properties of the substrate, particularly when the indentation depth is a substantial fraction of the layer thickness. Therefore, computational simulations of the nanoindentation process were done to determine $\sigma_{\text{ys}}$ and $E$ of the Al(O) layer using the Explicit version of the FE code ABAQUS [3]. A detailed description of this modeling approach is given in reference [11]. The density, Poisson's ratio ($v$), and a stress-strain curve including $E$ and $\sigma_{\text{ys}}$, were input for the diamond tip and each material in the sample. For each sample, a series of simulations were performed to determine the best fit to the load-depth curve while varying $E$ and $\sigma_{\text{ys}}$ for the Al(O) layer. The slope of the unloading portion of the curve is sensitive to $E$ [10], while the overall indentation response is sensitive to both $E$ and $\sigma_{\text{ys}}$. Using this method, simulation of nanoindentation in single-crystal Al gave $\sigma_{\text{ys}}=0.041$ GPa, equal to published values.

**RESULTS AND DISCUSSION**

Alloy layers with compositions ranging from 9 at.% O to 27 at.% O were deposited using the ECR plasma, and thin specimens (150-190 nm thick) were made for TEM investigations under the same
conditions as those used for nanoindentation testing. The bright-field (BF) TEM image in Fig. 1a is typical for Al(0) samples deposited near 100°C. This sample, grown at 127°C and containing 26 at% O, has a polycrystalline Al microstructure with small grains 12-80 nm in size. The typical grain size of a pure Al film deposited from this evaporator is an order of magnitude larger than that for these films containing oxygen. The polycrystalline diffraction pattern for this film (not shown) is dominated by sharp rings corresponding to fcc Al. A dark-field (DF) image is shown in Fig. 1b, in which much of the field of view is covered with small, brightly illuminated spots approximately 1-2 nm in size. These small spots are made visible in the DF image because most of the Al grains, which are an order of magnitude larger in size, are out of the Bragg condition for the portion of the diffraction ring chosen for imaging. Therefore, most of the Al grains appear black or poorly illuminated, with only a few (~10) of the larger Al grains being near the Bragg condition and appearing brightly illuminated. In our previous work with O-ion implanted Al disks [see 9], similar 1-2 nm size particles were identified as γ-Al2O3 precipitates coherently aligned with the Al matrix. In that study, the large Al grains (~100 μm) could be oriented to give single crystal Al diffraction patterns and then diffraction from the nm-sized particles appeared as diffuse reflections around sharp reflections from the fcc Al matrix. The fcc γ-phase has a spinel structure in which the lattice constant for the O²⁻ sublattice is only 2.5% less

Fig. 1. a) Bright field TEM image of ECR Al(26 at.% O) deposited at 127°C without bias, and b) dark-field (DF) image of Al grains (not strongly diffracting) containing a high density of ~1 nm γ-Al2O3 precipitates.

Fig. 2. a) Bright field TEM image of ECR Al0.900.1 deposited at 400°C reveals a rough microstructure, b) dark-field (DF) image shows the density of precipitates is much lower than that found for samples deposited at 100°C, and c) high magnification DF image shows the smallest precipitates are ~4 nm in size.
than that of the fcc Al, and therefore the less intense, diffuse reflections from the small precipitates are obscured by the more intense, superimposed reflections from the Al matrix. The small 1-2 nm sized precipitates could be brightly illuminated in DF when the Al grains were tilted slightly out of the Bragg condition, as was done for the image in Fig. 1b. Although the Al grain size for the ECR samples is much smaller than for the ion-implanted Al disks, the presence of the finely dispersed nm-size particles is much the same. This high density of small precipitates was not present in the electron-beam evaporated, pure Al film. Further, the fact that the grain sizes of the plasma-deposited samples are similar for a given deposition temperature and are an order of magnitude less than the sizes for pure Al demonstrates that the incorporation of the $\gamma$-Al$_2$O$_3$ precipitates hinders the growth of larger grains in the Al(0) alloys.

In order to examine possible changes in microstructure for growth with a displacive ion beam, TEM samples (80-165 nm thick) were grown with the same microwave power, flow rate, and deposition rate as above, but with the addition of a bias from -80 to -300 V. The energetic ions from the biased ECR plasma had little effect on the grain structure of the Al(0) film but did increase the surface roughness slightly from $\approx$ 14 nm to 23 nm. Also, the surface roughness was comparable to the grain size for these films.

In contrast, the surface roughness was increased to over 100 nm and the microstructure changed dramatically when the deposition temperature was increased to $\geq$360°C. The BF-TEM image (Fig. 2a) for a sample grown at 400°C, containing 10 at% O, shows a bimodal microstructure with two distinct grain sizes: 30-100 nm size grains, and $\sim$1 mm size grains. An atomic-force-microscope image of a similar sample grown without a bias at 360°C also showed an irregular surface with hillocks $\sim$1 mm in lateral extent. This roughness is a result of the large grains which are apparently protruding above and around the 30-100 nm size grains. A low magnification DF image in Fig. 2b shows that a few of the 30-100 nm Al grains are brightly illuminated while the large Al grain is weakly illuminated. Brighter areas in the large grain showing patterned features result from weak diffraction contrast due to thickness effects and Moiré fringes due to overlapping grains. Areas away from these patterned features shows a much lower density of isolated, illuminated features and such imaging is like that used to observe oxides in Fig. 1b. The DF image in Fig. 2c (same magnification as Fig. 1b) shows the smallest possible precipitates are $\sim$4 nm in size, much larger and occurring in a much lower number density than for the alloys grown at $\sim$100°C.

The results for four nanoindentation tests on ECR samples deposited on Si, without an applied bias, are shown in Fig. 3: 1) a 610 nm thick ECR Al$_{0.8}$O$_{0.2}$ layer deposited at 100°C (volume fraction, $f=0.22$), 2)
a 1.24 μm thick ECR Al0.91O0.09 layer deposited at 100°C (f=0.09), 3) a 690 nm thick ECR Al0.73O0.27 layer deposited at 400°C (f=0.31), and 4) a 650 nm thick layer of pure Al (f=0). The apparent hardness (H) for these layers was determined from the loading portion of the curves and is defined as the load divided by the effective area of the indenter [10]. The load-depth curves for the samples deposited at low temperature are typical of the results from the nanoindentation measurements; however, greater variability in the indentation response curves was found for the sample deposited at 400°C. A summary of the hardness data for the ECR Al(O) samples and an Al/Si film implanted with O at room temperature (RT) are given in Table I. (A 20 at% O ion-implanted Al layer on Si was also prepared, but this layer showed signs of exfoliation before indentation tests could be performed.) The value of H measured for the Al film on the Si substrate is 2% times greater than H found from Vickers indentation testing of cold-rolled Al, which implies a significant amount of grain-size strengthening occurs in the electron-beam evaporated Al film.

Previously [2], a simple estimate ($\sigma_{ys} = H/3$) was used to approximate the yield stress of films from nanoindentation measurements, but now through the use of finite-element (FE) analysis to model the deformation process, $\sigma_{ys}$ and E can be determined accurately. Examples of simulated load-depth curves for the ECR Al(O) alloys are shown as solid lines in Fig. 3, and a summary for the determinations of $\sigma_{ys}$ are given in Table I. As can be seen by comparing the third and fourth columns in Table I, the method of approximating the yield stress from the hardness of these Al(O) layers is good to better than 20%. However, this estimation of $\sigma_{ys}$ for the Al layer on Si differs from the FE determination by nearly 60%.

The yield stress, as shown in this table, is dependent on oxygen concentration and also appears to be strongly dependent upon the preparation temperature. At the low temperatures, $\sigma_{ys}$ increases as f increases, but $\sigma_{ys}$ decreases dramatically for the sample deposited at 400°C even though the oxygen content is increased. For these thin films, substrate effects become evident in a determination of E at very small penetration depths without the use of FE simulations. In contrast to the yield stress, the elastic moduli determined using FE analysis were found to vary little with O content; and within experimental error, the elastic moduli of the ECR Al(O) films was equal to the literature value [12] for bulk Al (68 GPa).

As mentioned above, the electron-beam evaporated Al film on Si exhibits a greater strength than found for large grain, well annealed bulk Al ($\sigma_{ys}=0.041$ GPa). This difference may be due to the small size of the grains in the deposited film. In fact, the Al film shows that at most the small grain size may only account for ~0.15 GPa increase in the strength of the Al over that of well annealed Al. Using the measured grain sizes to estimate the possible strength attained strictly from grain-size strengthening in the Al(O) alloys would only account for 20-40% of the increase in strength of these alloys over that of the Al layer and therefore another mechanism must be acting to give these materials their high strengths.

In order to better understand the mechanism governing the strength of these Al(O) alloys, the values for $\sigma_{ys}$ were plotted as functions of $N/M$ for the values of n and m discussed in the introduction. The best fit to the data was found for $n=1/3$ and $m=1$, and a plot of $\sigma_{ys}$ as a function of $1/M$ is shown in Fig. 4. Remarkably, all the data lie near the straight line shown in Fig. 4, even though the preparation techniques and sample temperatures varied considerably. These values for n and m, therefore, tend to support the direct dislocation-particle interaction mechanism as the dominant strengthening mechanisms to inhibit dislocation mobility; rather than work hardening, particle coherency stress, or grain-size strengthening. Thus, the addition of hard oxide particles during the deposition process or through ion implantation after deposition can serve to effectively retard plastic flow in the samples. This figure also suggests that a
substantial factor for the difference in yield strength between the RT implanted sample and the ECR samples is the deposition temperature, which gives rise to a difference in $\Delta$. Although the ECR films show a lower strength than alloys of the same oxygen concentration formed by ion implantation, the ECR process produces Al(O) alloys with gigapascal strengths (1.3 GPa), which are much higher than found for conventional aluminum alloys and similar or greater in strength to 18%Cr-8%Ni stainless steels. The difference in $\sigma_y$ between the two synthesis techniques (keV ion implantation and low energy ECR plasma deposition) appears to be primarily a result of the difference in precipitate sizes as a function of the preparation temperature. Therefore, future work will concentrate on actively cooling the ECR samples during deposition in order to compare the attainable yield stresses from different preparation techniques at the same temperature.

CONCLUSIONS

The ECR growth of Al(O) alloys offers a complementary technique to ion implantation for the synthesis of thick, high-strength Al layers. The microstructure and yield stress of ECR Al(O) alloys is similar to ion-implanted high strength Al(O), and we conclude that the deposition temperature strongly influences the yield stress such that preparation of samples at lower temperatures may produce higher strength layers. The ECR Al(O) alloys deposited at 100$^\circ$C exhibit strengths (from 0.6 GPa to 1.3 GPa) that are large enough to be of use for hard coating layers on light-weight Al components. Further, the results from the ECR samples are consistent with the previous work [1] on O ion implanted Al disks and suggest that the dominant mechanism governing the strength of the Al(O) layers is direct blocking of dislocation motion. The expected increase in yield stress as a function of the decreasing grain size cannot fully explain these large increases observed for the Al(O) alloys, and the mechanisms of work hardening by dislocation-loop pile-up and coherency strain would give a functional forms of $\Delta/n/\Delta m$ which are inconsistent with either the previous results or the current results. Finally, the Al(O) alloys retain much of the elasticity of the Al metal matrix, which may prove useful for producing toughened ceramic-metal layers.

REFERENCES and ACKNOWLEDGMENTS

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