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Ultra-thin aluminum oxide as a thermal oxidation barrier on metal films

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Abstract

We have investigated the role of aluminum oxide films as barriers to thermal oxidation of Co, Ni, Fe, $Ni_{80}Fe_{20}$, Mn, Ta, Cu and Cr in air. The oxidation of the film is monitored by measuring the electrical resistance following a brief anneal in air. We find that 0.3 and 1 nm Al protect the underlying metal film against thermal oxidation in air at temperatures of a few hundred degrees above the temperature at which the unprotected metal oxidizes. These results suggest that magnetic tunnel junction samples could be annealed in air after the oxidation of Al. The expected benefits of the annealing in air would include the oxidation of any remaining metallic Al, a more uniform Al_2O_3 thickness, and a sharper metal/Al_2O_3 interface.

Keywords: Thermal oxidation; Protective barrier; Ultra-thin metal films

1. Introduction

Magnetic tunnel junctions (MTJs) are a subject of much interest [1–4]. In the best MTJs the tunnel junction is made by exposing an Al film to O_2, a process referred as natural oxidation [5–8]. An important fabrication issue is the quality of the Al_2O_3 barrier. To date all experimental work appears to have used Al oxidation at room temperature. Since annealing often smoothes the surface of a film and makes its thickness more uniform, we sought to determine the maximum temperature to which the films could be annealed without oxidation of the underlying metal (here Co, Ni, Fe or $Ni_{80}Fe_{20}$). Although Mn, Ta, Cu and Cr are unrelated to MTJs, they were included in this study because there is surprisingly little data in the literature on the extent to which thin layers of Al_2O_3 act as a barrier to thermal oxidation of these metals. We also investigated the oxidation of an Al film.

2. Experimental

Si(1 0 0) wafers with a 350 nm thermal oxide at the surface were cleaved into 1×1.5 cm^2 rectangular pieces, cleaned ultrasonically in detergent solution, rinsed in distilled water, blown dry, and installed in the deposition chamber. After using ion milling to remove ≈2 nm of the surface to remove any contamination, metal films were deposited at room temperature by dc-magnetron sputtering. The base pressure of the system was approximately 3×10^{-8} Pa (2×10^{-10} Torr) and 0.3 Pa (2×10^{-3} Torr) Ar was used for sputtering. The thicknesses of the metal films were determined with a quartz crystal microbalance and calibrated to an accuracy of ±3% by using Low Angel X-ray Reflectometry.

Because some metals tend to agglomerate on the SiO_2 surface, 1 nm Ta was first deposited as a seed layer to promote better adhesion of the metal films. Next a 10-nm metal film (Co, Ni, Fe, $Ni_{80}Fe_{20}$, Mn, Ta, Cu or Cr) was deposited on the Ta. These samples were used as substrates for the deposition of 0.3 and 1 nm Al layers. In addition, a separate sample with 11 nm Al (on the Ta seed layer) was investigated for comparison. The study of metal oxidation by the measurement of resistance change is a well-established technique [9–13]. In our work, 4-wire resistance measurements were performed at room temperature after annealing the samples in air. The ohmmeter had a NIST traceable calibration with a quoted accuracy of ±1%. The samples were placed in an oven with a digital temperature control

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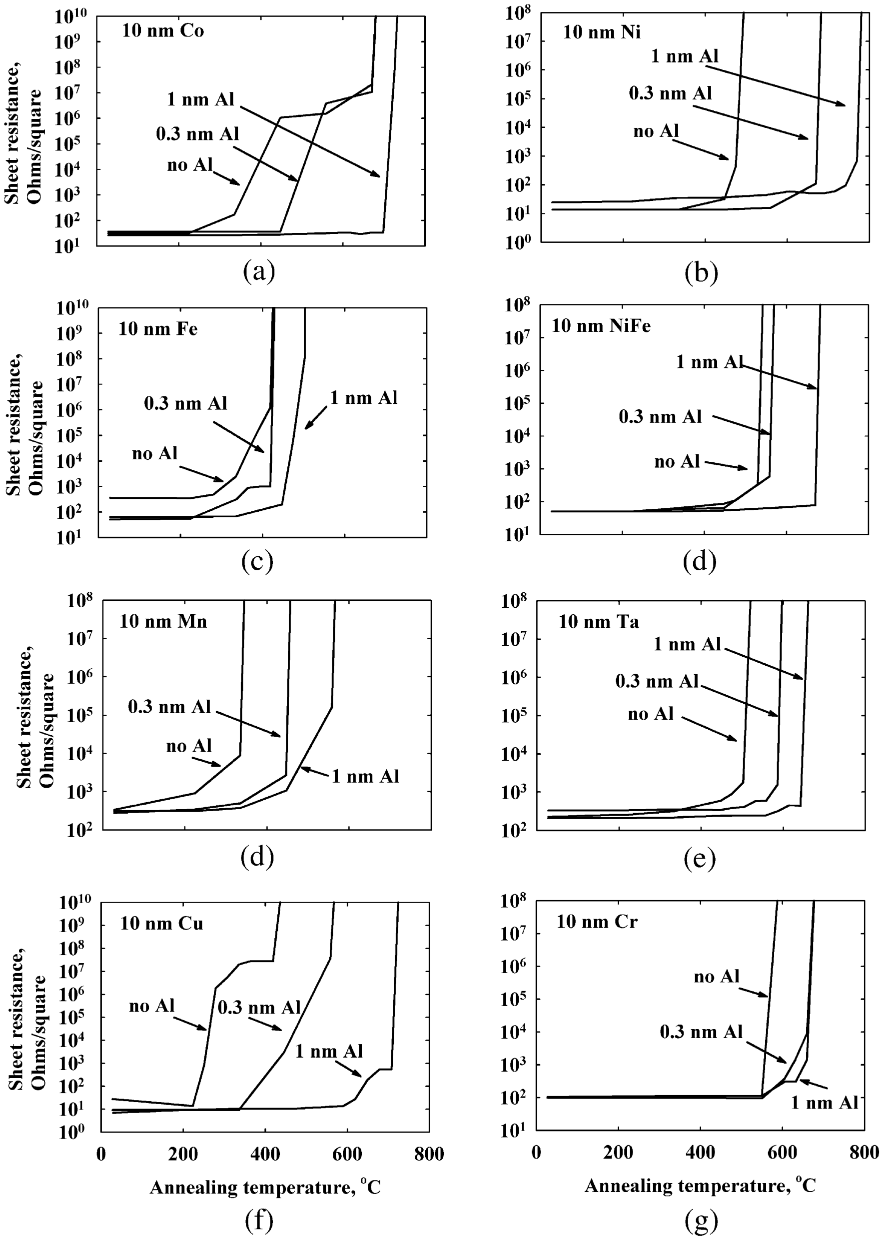

Fig. 1. The room temperature sheet resistance of metal films with Al protection layers of different thickness following annealing for 30 s at the indicated temperatures.

calibrated to $\pm$10 °C for approximately 1 min, which allowed them to reach the reported temperatures after approximately 30 s, and then were cooled by quenching in water.

3. Results and discussion

The measured sheet resistances versus annealing temperature are presented in Figs. 1 and 2. With increasing temperature, some samples showed slight decreases in resistance, probably due to the annealing out of defects. All samples were heated to successively higher temperatures until the resistance exceeded the 20 MΩ limit of the ohmmeter.

The largest effects of the Al protective layer were found for Co in Fig. 1a and Ni in Fig. 1b. The onset of appreciable oxidation is increased by $\approx$300 °C for 1 nm Al. The smallest effect is found for Fe, a 100 °C temperature change, in Fig. 1c. Permalloy (Ni$_{80}$Fe$_{20}$) is an intermediate case, in Fig. 1d. The Co, Fe and permalloy cases are of the most interest for MTJ studies. The implication of these results is that a naturally oxidized MTJ tunnel barrier can be annealed to temperatures of approximately 400 °C for Fe, 650 °C for

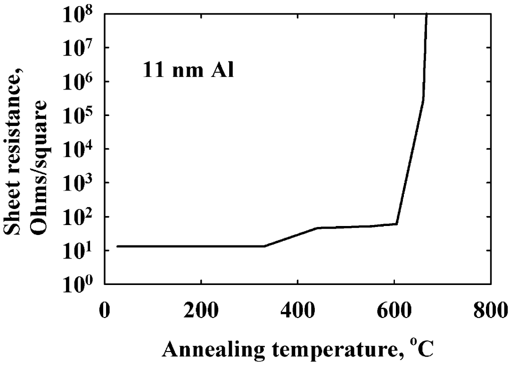

Fig. 2. The room temperature sheet resistance of an Al film following annealing for 30 s at the indicated temperatures.

$Ni_{80}Fe_{20}$, 600 °C for Co, and 700 °C for Ni without significant oxidation of the underlying magnetic metals. Perhaps the most surprising result of the study is that a mere 1 nm Al (which becomes 1.3 nm Al_2O_3 in air) can protect Co and Ni films from oxidation in air at temperatures of over 600 and 700 °C, respectively. This result was most unexpected and suggested that smoothing of the Al_2O_3 film by annealing might be possible. A recent study showed that 2.4 nm Al_2O_3 on Si(0 0 1) can withstand over 900 °C before serious degradation, which provides additional evidence for the thermal stability of Al_2O_3 films [14].

Four other metals were also investigated primarily out of curiosity. They were Mn, Ta, Cu and Cr, in Fig. 1e–h. In the case of Cu (Fig. 1g), the flat region at around 400 °C for the 'No Al' sample is quite reproducible and seems to reflect a semi-conducting oxide, probably Cu_2O. A similar flat region is found for Co (Fig. 1a). Fig. 2 shows the measured sheet resistance of an Al film as a function of annealing temperature for comparison with the results in Fig. 1. We see that the Al sheet resistance increases rapidly at approximately 600 °C.

In some cases, we can use published data to estimate the temperatures needed to oxidize 10 nm of a metal oxidized in air for a few seconds. Using the standard oxide growth rate expression

$$\Delta M/A = K_p t \tag{1}$$

where ΔM is the change of mass, A is the film area, t is oxidation time, and K_p is the parabolic rate constant which is a function of temperature. Using the K_p value from the references [15–17] for the oxidation of macroscopic Ni films, the temperature needed to oxidize 10 nm Ni in 30 s is estimated to be ~600 °C. For the 'no Al' sample in Fig. 1b, the oxidation temperature is observed to be ~500 °C. It is likely that our samples have a smaller grain size and may thus be more readily oxidized. A neutron reflectometry study showed that for Co the onset of oxidation during annealing in air is around 300 °C, in agreement with our results in Fig. 1a [18].

It is likely that annealing these samples in air promotes a smoother Al_2O_3 film of more uniform thickness and with a sharper metal/Al_2O_3 interface. If so, this approach might be useful in achieving improved MTJs. When there is a large amount of ferromagnetic metal oxidized under Al_2O_3, the electrical measurement shows a noticeable increasing in the resistance. But if there are only several monolayers of oxides formed at the metal/Al_2O_3 interface, the electrical measurements are not sensitive to it. For the MTJs the formation of several monolayers of ferromagnetic oxides at the interface could alter the tunneling properties substantially. In order to detect the minor oxidation at the interface and clarify the results of Fig. 1a and b, X-ray photoelectron spectroscopy (XPS) was used to study the oxidation process. Although the XPS could detect several monolayers oxidation at the interface, in the case of Ni it is possible the formation of one monolayer of NiO could not be ruled out by XPS.

Fig. 3 shows that without an Al overlayer, the Co 2p peaks shifted to larger binding energy after annealing at 300 °C indicating that CoO is formed, as expected. For comparison, the intensity of the oxygen 1s peak is also reported (the O 1s peak width was approximately constant in these data).

For the Co film with 1 nm Al on top, Fig. 4 shows that the Co peaks did not shift to the CoO binding energy until the samples were annealed to 800 °C. This result supports the interpretation of Fig. 1a that the 1 nm thin Al film not only protects the underlying Co from air oxidation, but also increases the onset oxidation temperature of Co by ≈300 °C. At 800 °C, it seems that interdiffusion between Al_2O_3 and CoO took place since the Al peak disappeared. An interesting feature of

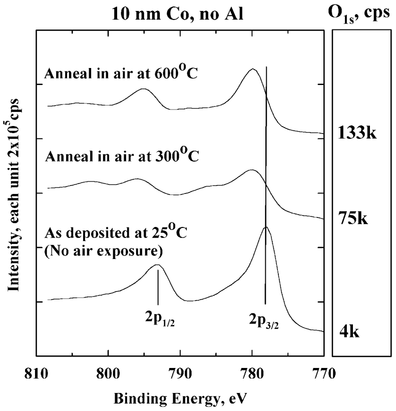

Fig. 3. XPS data on a pure Co film after annealing at different temperatures. Also reported are the corresponding peak intensities for the O 1s core level.

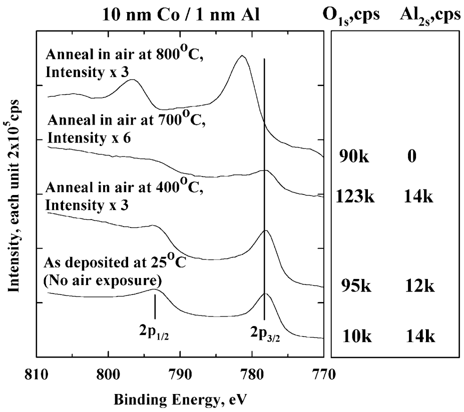

Fig. 4. XPS data on a Co film with an Al protection layer after annealing at different temperatures. Also reported are the corresponding peak intensities for the O 1s and Al 2s core levels.

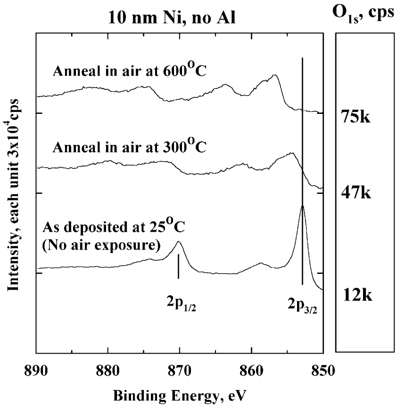

Fig. 5. XPS data on a pure Ni film after annealing at different temperatures. Also reported are the corresponding peak intensities for O 1s core level.

the data is that, after annealing at 700 °C, the Co 2p peaks are quite weak, although they are still at the binding energy for metallic Co. The reason for this is unclear, but may be related to some structural rearrangement due to the softening of the thermal oxide substrate. Thermal oxide is quite similar to glass, and while both are amorphous and thus do not have a melting point, both are quite fluid at 700 °C. It is remarkable the Co does not oxidize and maintains a constant resistance after apparently floating on the liquid thermal oxide during the anneal.

The XPS results in Figs. 5 and 6 for Ni films and the interpretation of them are quite similar to the those of Co, with one clear exception. When Al is deposited on the Ni surface, a strong interfacial reaction occurs leading to the formation of ≈2 nm of NiAl alloy [19]. In this alloy, the Ni 2p peaks are shifted to a binding energy ≈1 eV larger than in pure Ni [20]. What is apparent from Fig. 6 is that, upon initial oxidation of the surface (e.g. Annealing at 300 °C), the Ni 2p peaks shift from the alloy binding energies to the smaller value of the pure metal. The large heat of oxidation of Al provides the thermodynamic driving force for this de-alloying of Al and Ni. The decrease in intensity of the Ni peaks from the as-deposited state following the 300 °C anneal may be attributed to the de-alloying reaction. As deposited, the top 1–2 nm of the sample will roughly be a $Ni_{50}Al_{50}$ [19]. The Ni peak intensity drops as the Al diffuses to the surface to from an overlayer of alloy ≈1.3 nm Al_2O_3. A similar de-alloying reaction very likely occurs in the Co and Fe samples although it is more difficult to observe since there is no corresponding shift of the Co and Fe core-level binding energies and since the extent of alloying is less [19].

In the case of the Co and Ni samples, additional evidence for the de-alloying process comes from the Al 2p and 2s core-level peaks which appear at the binding energy for Al_2O_3 after annealing in air with no detected intensity at the binding energy of metallic Al. Apparently, the de-alloying process runs almost to completion.

As in the case of Co, the Ni peaks remain at the pure-metal binding energy until rapid oxidation finally occurs during the annealing at ≈770 °C. This result is consistent with the constant sheet resistance observed in Fig. 1b until the same temperature is reached. Also, as in the case of Co, there is a decrease in the Ni core-level intensities as the thermal oxide becomes fluid at approximately 600 °C. We do not have an explanation for this intensity decrease and for the absence of any corresponding resistance change.

4. Conclusions

The main conclusions of the work reported here are:

1. Layers of Al as thin as 0.3 and 1 nm provide significant protection against thermal oxidation in air at elevated temperatures for a variety of metals (Co, Ni, Fe, $Ni_{80}Fe_{20}$, Mn, Ta, Cu, and Cr).

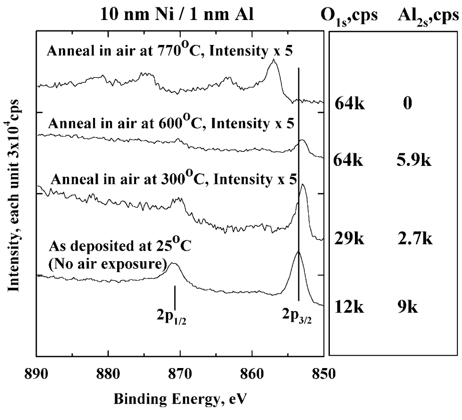

Fig. 6. XPS data on a Ni film with an Al protection layer after annealing at different temperatures. Also reported are the corresponding peak intensities for O 1s and Al 2s core levels.

2. For Co/Al and Ni/Al samples annealing in air promotes a de-alloying process in which the Al intermixed with the Co or Ni upon deposition diffuses to the surface to form an Al_2O_3 layer.

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