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Published in:
Journal of Applied Physics

DOI:
10.1063/1.372615

Published: 01/01/2000

Document Version
Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

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Optical and in situ characterization of plasma oxidized Al for magnetic tunnel junctions

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An optical polarization modulation technique was adapted to provide a simple, fast, and flexible method for studying the growth characteristics of thin oxide layers, using $\text{Al}_2\text{O}_3$ as an example. The optical technique allows precise determination of the amount of remaining metallic Al as a function of the initial Al thickness, while scanning a laser spot across the wedge. Optical data suggest that the oxide growth rate for the ultrathin layers may be dependent on the specific microstructure. In situ x-ray photoelectron spectroscopy performed on homogenous samples confirmed the interpretation of the optical results. © 2000 American Institute of Physics.

For fabricating reliable, high TMR (tunnel magnetoresistance) tunnel junctions,1,2 optimization of the plasma oxidation process to ensure minimal unoxidized Al, while preventing oxidation of the underlying electrode, is of critical importance. However, few methods exist3–5 for characterizing the growth of ultrathin oxide layers. An optical polarization modulation technique was adapted to provide a simple, fast, and flexible method for studying the growth characteristics of thin oxide layers, with the potential for in situ process monitoring. To this end, the optical polarization modulation technique was adapted to provide a simple, fast, and flexible method for studying the growth characteristics of thin oxide layers, using $\text{Al}_2\text{O}_3$ as an example. The optical technique allows precise determination of the amount of remaining metallic Al as a function of the initial Al thickness, while scanning a laser spot across the wedge. Optical data suggest that the oxide growth rate for the ultrathin layers may be dependent on the specific microstructure. In situ x-ray photoelectron spectroscopy performed on homogenous samples confirmed the interpretation of the optical results. © 2000 American Institute of Physics.

To investigate the oxidation process as a function of oxidation time, homogeneous ultrahigh vacuum magnetron sputtered samples of Si(111)/Ta 50 Å/Co 50 Å/Al 60 Å were prepared and plasma oxidized for various times from 0–600 s in 0.1 mbar $\text{O}_2$. In order to judge the amount of “instantaneous” oxidation, samples were also exposed to 0.1 mbar for 10 s without plasma. The oxidation was performed in an incremental manner (i.e., a 20 s sample has been twice oxidized 10 s) to study the time evolution of the oxidation unambiguously. In addition, reference samples of Co, Al, $\text{CoO}_x$, and $\text{AlO}_y$ were prepared, with the oxides prepared by 600 s plasma oxidation of thick metal layers. In situ STM on Si/Ta/Co/Al samples indicated flat films with small grains and a mean roughness of $<3\,\text{Å}$ for all layers. XPS intensities of the Al 2$s$, Al 2$p$, and Co 2$p$ photoelectron lines were recorded with Mg $K_α$ radiation, while the O 1$s$ photoelectron line was recorded with Al $K_α$ radiation. Figure 1(a) shows the Al 2$s$ and 2$p$ spectra for samples with differing oxidation times, all for a nominal Al thickness of 22 Å. For the unoxidized sample, no peak at the oxidic binding energy is observed,7,8 while for only 10 s oxidation without plasma, significant Al oxide is clearly visible for both the 2$s$ and 2$p$ lines. With increasing oxidation time, the metallic Al XPS intensity monotonically decreases, while the oxidic Al XPS intensity monotonically increases. For 200 s oxidation, little metallic Al remains, and none is observable (≤1 ML) for 600 s.

Figure 1(b) shows the calculated O/(oxidized) Al ratio as a function of oxidation time, as obtained from the primary zero-loss intensities7,8 of the oxidic Al 2$p$ and O 1$s$ peaks, using a 600 s oxidized Al sample (where no metallic Al could be detected) of the same thickness as a reference. It is
evident that the 10 s exposure to O2 without plasma forms a significant amount of AlOx, with a further steep decrease of the O:Al ratio in the first 10–20 s of plasma oxidation. By 100 s, the AlOx is nearly stoichiometric, also evidenced by Fig. 1(a), which shows only a small amount of metallic Al remaining. The O 1 s XPS intensity is also plotted in Fig. 1(b), which exhibits an initial, rapid increase and becomes roughly constant beyond 100 s, in corroboration with the spectra and the O:Al ratio.

For experiments as a function of Al thickness, homogeneous samples of Si(111)/Ta 50 Å/Co 50 Å/Al dAl were prepared as previously, while for the optical experiments, 0–30 Å wedge shaped samples of 3–4 Å/mm were grown on Si(111) or oxidized Si(111). Both types of samples were plasma oxidized in 0.1 mbar O2 for 100 or 200 s, with several wedge samples air oxidized for several hours. Figure 2(a) shows the measured amount of unoxidized ("leftover") Al as a function of the deposited Al layer thickness as measured by XPS (circles) with the Al 2s (closed) or 2p (open) line. The XPS data show no metallic Al for thicknesses below 15 Å, with a continuously increasing amount of metallic Al observed beyond ~15 Å.

Figure 2(a) also shows the measured amount of unoxidized Al obtained from the optical measurements on oxidized Al wedges (lines). In order to determine the amount of remaining metallic Al from the optical measurements, model calculations were used to estimate the magnitude and dependencies of the 1f and 2f signals. These calculations were based on an idealized sample consisting of a linear Al wedge of 0 to 30 Å, which is homogeneously oxidized from the top [see Fig. 2(b)]. The two layers are placed on a Si substrate with a 20 Å SiO2 native oxide layer [inset to Fig. 2(b)]. The reflection coefficients of s- and p-polarized light at the top interface of the stack are obtained by solving the Maxwell equations in each layer and matching the E and B vectors at each interface. The 1f and 2f signals can then be calculated using the Jones Formalism9 for all optical components; the result is shown in Fig. 2(b). From the simulation it is clear that the 2f signal is approximately linear with the Al thickness, while the 1f signal is proportional to both the Al and the Al2O3 thickness.

Returning to the optical data of Fig. 2(a), no measurable Al is visible for thicknesses below ~15 Å as with the XPS data. For all oxidation times, the amount of leftover metallic Al increases (approximately) linearly for thicknesses beyond ~15 Å also in agreement with the XPS data. The nominal thickness of leftover Al obtained from the model calculations is in rough agreement with the behavior of the XPS signals, and it can be seen that monolayer amounts of metallic Al may be observed, confirming that this method may in principle be used to observe the oxidation process in ultrathin metallic layers. As expected, the 200 s oxidized sample shows less leftover Al than 100 s or air oxidized samples. Surprisingly, however, the onset of unoxidized Al occurs at approximately the same thickness for all samples.

The amount of Al2O3 was also determined by both methods. Figure 3(a) shows the intensity of the Al–O 2s (closed) and 2p (open) oxidic binding peaks determined by XPS. The amount of oxide increases with increasing Al thickness, showing a decreasing slope between 15–25 Å though it is not constant in this region. The amount of Al2O3 was also determined via the optical method, and although it showed some interesting features, they were found to depend sensitively on specific assumptions in the model (e.g., εAl2O3, tSiO2, etc.). A detailed discussion of this data is therefore postponed to a future publication.

Figure 3(b) shows the Co 2p XPS spectra for samples of 23 Å Al and 5 Å Al after 200 s oxidation, as well as reference Co and CoO spectra. For 23 Å Al, it is clear that only metallic Co is present, while for 5 Å, the Co oxidic satellite peaks are visible as well as a shift of the Co 2p lines, indicating oxidation of the underlying electrode. For all thick-
nesses below ~15–20 Å with 200 s oxidation, CoO was observed; the vertical line in Fig. 2~a! indicates the maximal thickness for which CoO was observed. This thickness is nearly the same thickness at which metallic Al began to be observed, indicating that disappearance of Co oxides and onset of leftover metallic Al are nearly coincident. The observation of Co oxides only after nearly all metallic Al is oxidized is not unexpected even in the presence of interface roughness, given the large difference in the free energy of formation for Al 2O 3 (~DG f o = −378 kcal/mol) and CoO (~DG f o = −51.5 kcal/mol) or Co 3O 4 (~DG f o = −184 kcal/mol). 6 The region of minimal CoO and metallic Al is the desired regime for formation of high TMR magnetic tunnel junctions. 1

Returning now to the optical data of Fig. 2~a!, the onset of leftover Al is nearly identical for 100 or 200 s oxidation, though the slopes of the curves show significant disparity between 100 and 200 s oxidized samples. This may indicate that the simple model of oxidation proceeding uniformly through the Al layer [see inset to Fig. 2~b!] may be too simplistic. Rather, it may be consistent with an initial, rapid oxidation via grain boundaries, 10 while longer times are needed to fully oxidize grain interiors. The unoxidized grain interiors would represent a relatively small volume fraction compared to the total amount of Al, and therefore, a small XPS or optical signal, but would require much longer times to fully oxidize. The thickness at which leftover Al is observed would then only differ in each case by the (small) amount of metallic Al remaining in the grain interiors. Further, the amount of metallic Al would also exhibit a smaller slope as a function of Al thickness for longer oxidation times, since the grain interiors are then more fully oxidized. More detailed microstructural data, as well as measurements for Al layers with differing microstructures, could clarify the mechanism(s) involved.

In summary, an optical polarization modulation technique was combined with in situ XPS to investigate the plasma oxidation of ultrathin Al layers. The optical technique allows precise determination of the amount of unoxidized Al with the use of wedge-shaped Al layers, confirmed by XPS measurements. The optical technique shows great potential for simple, flexible, and rapid optimization of oxidic tunnel barriers, and may be easily adapted for in situ use.

P. L. is supported by the Technology Foundation STW, and A. A. S. is supported by the foundation for Fundamental Research on Matter (FOM).