Thin Al, Au, Cu, Ni, Fe, and Ta films as oxidation barriers for Co in air

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(Presented on 15 November 2002)

We have investigated the effectiveness of Al, Au, Cu, Ni, Fe, and Ta films with thicknesses up to 4 nm for protecting a Co surface from oxidation in air at room temperature. The distinct change in the $Co\,2p_{3/2}$ core-level line shape observed by x-ray photoelectron spectroscopy upon the oxidation of Co makes it a simple matter to identify the fractions of the Co that are in the metallic state and in the oxidized state. We find that the best choices for protecting Co from oxidation are Al and Ta. We found that Au, which is one of the most popular choices, is not particularly effective for protecting Co. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1543873]

INTRODUCTION

In the field of magnetic thin films, it is often necessary to transport films through air for certain measurements or for tests to be made. Very often, some protecting overlayer is needed to prevent oxidation of the magnetic thin film and any possible modification of the film properties. The purpose of the present work is to help provide a scientific basis for such choices.

In prior work, capping layers of Ag, Au, Al_2O_3, and metal silicides were investigated with varying degrees of success.[1–4] Ag provided the poorest protection and silicides the best protection. However, the silicides had to be grown at elevated temperature in SiH_4 gas, a procedure that is rarely compatible with magnetic thin-film deposition equipment. Our aim is to assess the degree of protection provided to magnetic thin films by metals that are likely to be readily available in a deposition system. In this work, we investigated capping layers of Al, Au, Cu, Ni, Fe, and Ta with thicknesses up to 4 nm. A capping layer thicker than 4 nm would probably provide additional protection, but x-ray photoelectron spectroscopy (XPS) cannot probe much deeper than ~4 nm.

EXPERIMENTAL PROCEDURE

The substrates used in this experiment are $1\,cm \times 2\,cm$ Si(100) with a 350-nm thermal oxide on the surface. The cleaning procedure was to immerse the substrate in detergent solution in an ultrasonic bath for a few seconds, rinse it with distilled water, blow it dry, introduce it into our vacuum chamber, and remove ~2 nm of the surface by ion milling. Next, a structure of 1-nm Ta, 5-nm Co, and a capping layer of the selected material was deposited at room temperature by dc magnetron sputtering in 0.4-Pa Ar. The structure is shown in Fig. 1. The base pressure of the system is $\sim 10^{-6}$ Pa, of which 90% is H_2. The Ta seed layer provides better adhesion for the Co films. Different thicknesses of six

metals, Al, Au, Cu, Ni, Fe, and Ta, were deposited as capping layers to protect against oxidation of Co in air. The films were investigated by XPS using $Al\,K_{\alpha}$ x-rays immediately after deposition and again after exposure to air for varying lengths of time. To obtain XPS data on CoO films of varying thickness, we reactively sputtered Co in 10^{-2} Pa O_2 on the thermal oxide. The thickness of deposited films was determined by two quartz-crystal oscillators adjacent to the substrate, and their estimated accuracy was ±10%.

RESULTS AND DISCUSSION

Our analysis of the oxidation of Co is based on the very different $Co\,2p_{3/2}$ core-level line shapes for metallic Co and CoO. This difference is illustrated in Fig. 2. Although the core-level intensity is attenuated by the capping layer, we found that we can collect useable spectra with capping layers as thick as 4 nm.

When the surface layers of a Co film are oxidized, the $2p_{3/2}$ core level has a characteristic line shape that can easily be resolved into metallic and oxidized components. Figure 3 illustrates our approach. The $Co\,2p_{3/2}$ core-level line shape for metallic Co is scaled and subtracted from the total signal to leave the line shape of the oxidized Co. The scaling is
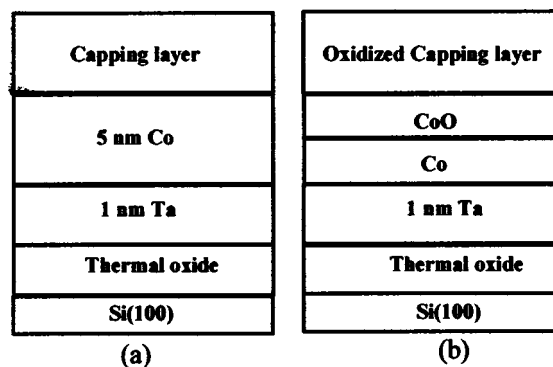

FIG. 1. The multilayer structure used in this experiment. The structure before exposure to air is shown in (a), and the structure after oxidation by air is shown in (b).

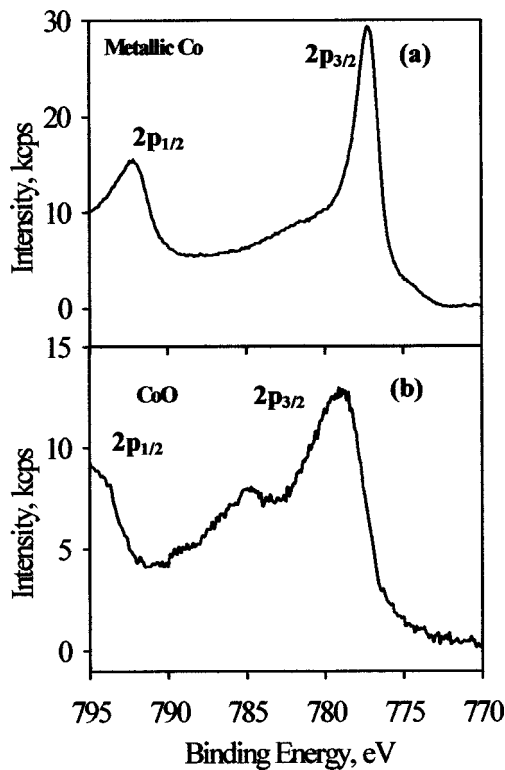[a)]Electronic mail: gan@glue.umd.edu

FIG. 2. The Co $2p_{3/2}$ core-level line shape for (a) 5 nm of Co and (b) 5 nm of CoO.
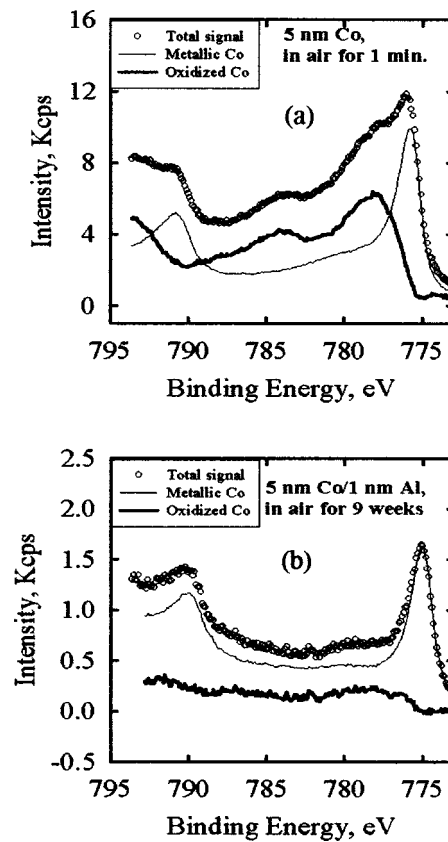

FIG. 3. Illustration of separation of the metallic Co and the CoO components of the Co $2p_{3/2}$ core-level signal: (a) a 5-nm Co film exposed to air for 1 min, and (b) a 1-nm Al capping layer on 5-nm Co exposed to air for nine weeks.

subject to little ambiguity because only minor changes in the optimum scaling leave a line shape that does not closely resemble the CoO line shape of Fig. 2(b). We estimate the uncertainties of the peak areas of Co and CoO determined in this manner to be ±10%.

In order to determine the thickness of CoO in a particular sample, we deposited CoO films of different thicknesses on Co, recorded the $2p_{3/2}$ line shapes, and resolved the spectra into the metallic and oxidized components. With such data as a reference, we can determine the thickness of CoO in an unknown sample to an estimated uncertainty of ±20%.

The relative intensities of the metallic and oxidized components in Fig. 3(a) correspond to an oxide thickness of 1.1 nm. While a more detailed analysis could improve our accuracy, our goal is not to obtain highly accurate estimates of the CoO thickness. Instead, our goal is to establish the onset of Co oxidation so that we know how effectively the capping layer protects the Co, and our simple approach seems adequate to meet our needs.

An underlying assumption in our analysis is that the CoO/Co interface is atomically flat and sharp. Support for this assumption comes from the well-known phenomenon in giant magnetoresistance samples that Co films scatter electrons more specularly after oxidization of the surface. Apparently, Co tends to oxidize in a layer-by-layer manner.[5,6]

The only capping layer for which the above assumptions do not work extremely well is Al. In that case, just before the onset of the characteristic CoO line shape in the spectra, a weak feature with a distinctly different line shape appears. Figure 3(b) illustrates this case. Instead of the characteristic two-peak line shape of oxidized Co in Figs. 2(b) and 3(a), a

single peak is observed at 779 eV. It is possible that this peak may represent Co atoms that are not fully oxidized, but that share O ions with Al ions. Support for this view comes from the fact that, whenever the single-peak state is observed, it is soon followed by observation of the characteristic two-peak CoO line shape. It seems that the oxidation front is moving steadily deeper into the sample. It is also possible that the one-peak state may be connected with the intermixing at the interface that occurs when Al is deposited on Co.[7] The oxidation of this alloyed region may somehow be connected with the single-peak state.

Figures 4(a)–4(d) present plots of the CoO thickness versus time-in-air for four different capping layers. For an uncapped Co film, 1 nm of CoO forms immediately in air (in fact, even 10^{-2} Pa O_2 forms 1 nm of CoO almost immediately). Subsequent oxidation proceeds at an exponentially slower rate.

In most cases, subnanometer films of the capping layer significantly reduce the Co oxidation rate. However, more than 1 nm is required for most capping layers to provide protection for any significant length of time; that is, one day.

Surprisingly, Au is not a particularly good capping layer. Its inertness to oxygen would suggest it might be the best. Although we could not find any published references to its use as a capping layer, we know from personal contacts that it is a common choice in protecting magnetic thin films. One advantage of using Au as a capping layer is that it does not
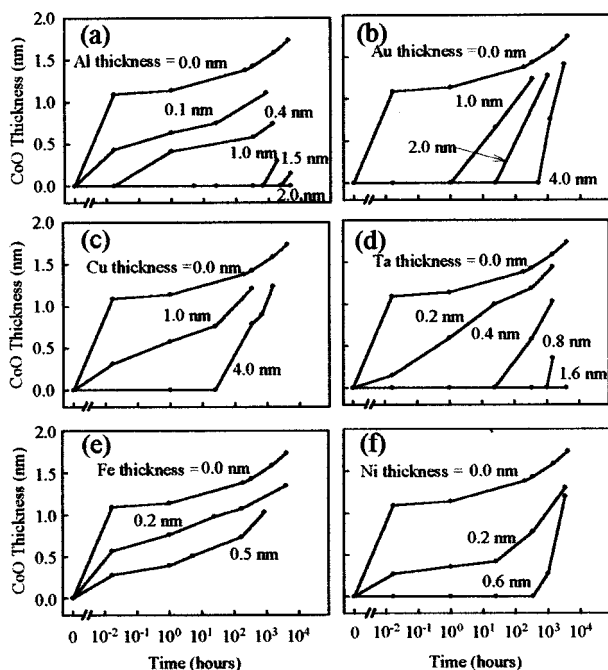
FIG. 4. Plots of the thickness of CoO versus time in air for the indicated thickness of (a) Al, (b) Au, (c) Cu, (d) Ta, (e) Fe, and (f) Ni.

intermix extensively with the magnetic metal on which it is deposited, unlike Al capping layers.[7] Cu also has the advantage of not intermixing extensively with magnetic thin films, but, as seen in Fig. 4(c) it is even less successful in protecting the Co than Au. Perhaps Au layers thicker than 4 nm would be successful, but 4 nm is about the upper limit of what we can use in an XPS study. Nevertheless, an extrapolation from our data gives an important suggestion for cases in which Au cap layers are highly desirable. As seen in Fig. 4(b), there is a 20-fold increase in the time to the onset of Co oxidation in going from 1- to 2-nm Au and also in going from 2- to 4-nm Au. This result suggests that if 10 000 h of protection were needed, a plausible guess at the Au thickness required would be 8 nm.

Although Al and Ta seem to give the best protection from oxidation, they are not entirely benign as capping layers. In other studies, we have found that an Al capping layer forms an intermixed layer with approximate thicknesses of

0.6 nm on Fe, 0.9 nm on Co, and 2 nm on Ni.[7] We have not performed a thorough study of intermixing with Ta capping layers, but our studies of magnetization versus Co thickness indicate that when a Ta capping layer is deposited on Co, the top 0.5 to 1 nm of the Co is no longer ferromagnetic.[8] Thus, it seems likely that Al and Ta intermix to similar extents on magnetic thin films.

In Figs. 4(e) and 4(f), we present similar data for Fe and Ni. Fe and Ni are unlikely to be desirable as protection layers for magnetic thin film because of complications they would create in the magnetic films they were protecting. However, we present the data for the insight it provides into the time dependence of the oxidation of Fe and Ni films in air. We note in passing that the reason no more than 0.5-nm Fe was investigated as a capping layer is that an Fe Auger peak overlaps the $\mathrm{Co}\,2p_{3/2}$ peak and then interferes with the analysis for thicker Fe capping layers. This problem could be avoided with $\mathrm{Mg}\,K\alpha$ radiation, but this source was not available in our system.

CONCLUSIONS

The major conclusions of this work are:

(1) XPS is a useful method of observing the onset of oxidation of Co films that are protected by thin capping layers;
(2) Al and Ta capping layers provide the best long-term protection from oxidation in air, but suffer from the disadvantage that they intermix with the Co to a depth on the order of 1 nm; and
(3) Au and Cu capping layers do not intermix extensively with Co, but only provide rather short-term protection from oxidation in air.

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