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Citation for published version (APA):

Fabrie, C. G. C. H. M., Knechten, C. A. M., Kohlhepp, J. T., Swagten, H. J. M., Koopmans, B., & Jonge, de, W. J. M. (2006). Real-time monitoring of plasma oxidation dynamics of subnanometer Al₂O₃ barriers for magnetic tunnel junctions. *Applied Physics Letters*, 88(3), 031909-1/3. [031909]. <https://doi.org/10.1063/1.2166696>

DOI:

[10.1063/1.2166696](https://doi.org/10.1063/1.2166696)

Document status and date:

Published: 01/01/2006

Document Version:

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

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
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Real-time monitoring of plasma oxidation dynamics of subnanometer Al_2O_3 barriers for magnetic tunnel junctions

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(Received 31 August 2005; accepted 23 November 2005; published online 19 January 2006)

We show that over-oxidation of sub-nm thin Al_2O_3 barriers of magnetic tunnel junctions can be observed in real time using *in situ* differential ellipsometry measurements. The change in ellipsometry signal of Al layers grown on CoFe films is proportional to the amount of oxidized metallic material. As a result, the derivative of this signal is a direct measure of the oxidation rate. Further analysis of this oxidation rate allows us to determine the onset of the CoFe oxidation. We found the onset to be proportional to the deposited Al layer thickness. The amount of CoO determined from *in situ* x-ray photoelectron spectroscopy data on identical samples was found to be proportional to that obtained from ellipsometry. © 2006 American Institute of Physics.

[DOI: 10.1063/1.2166696]

Magnetic random access memories (MRAMs) have the potential to replace the current RAM technologies and can lead to instant-on computers and longer battery lifetimes for mobile devices.¹ To replace the current RAM technologies by MRAMs, the surface area of the bits for information storage have to decrease to sub $0.01 \mu\text{m}^2$ in order to achieve a high enough areal density. Magnetic tunnel junctions (MTJs) can be used as bits for information storage, and serve as the basic elements of MRAMs. A MTJ consists of two ferromagnetic layers, which are separated by a thin insulating barrier, usually Al_2O_3 . The tunnel current that flows through the barrier depends on the relative alignment of the magnetization in the ferromagnetic layers,² which leads to a large magnetoresistance (MR) effect. For MTJs with a surface area of less than $0.01 \mu\text{m}^2$, the thickness of the Al_2O_3 barrier has to be typically thinner than a nanometer to ensure an appropriate tunnel current. If metallic Al is still present in the barrier, the spin polarization of the current will be reduced.³ On the other hand, if the bottom electrode is oxidized, the spins will be scattered by the ferromagnetic oxide that is formed. In both cases, the MR of the MTJ decreases.

In this letter we present *in situ* differential ellipsometry measurements, for studying the plasma oxidation dynamics of sub-nm Al layers. By analyzing the oxidation rate, we were able to mark the moment at which the over-oxidation of the Al_2O_3 barrier starts. To verify our conjecture, we performed *in situ* x-ray photoelectron spectroscopy (XPS) measurements of identical samples that were plasma oxidized for either 3 or 9 s. The results indicated that *in situ* real-time differential ellipsometry is in principle applicable for controlling the plasma oxidation of sub-nm Al layers to fabricate well defined Al_2O_3 barriers for MTJs.

To study sub-nm Al_2O_3 barriers, we used samples of the following composition: $\text{Si}(001)/\text{SiO}_x/50 \text{ \AA} \text{ Ta}/50 \text{ \AA} \text{ Co}_{90}\text{Fe}_{10}/d \text{ Al}$ (with d ranging from 4 to 9 \AA). The samples were grown in a sputtering system, with a base pressure of $<10^{-8}$ mbar. We grew the layers at a rate of approximately

0.5 \AA/s in $\sim 10^{-2}$ mbar argon gas. After growing the layers, the samples were transported to a plasma oxidation chamber connected to the system. There, the samples were plasma oxidized at a power of $\sim 5 \text{ W}$ in an oxygen background of about 0.1 mbar.

The oxidation chamber is equipped with an *in situ* differential ellipsometer to monitor the plasma oxidation dynamics of Al layers in real time. Details of the implementation, using a photoelastic modulator operating at frequency f , have been reported before.⁴ Explicit modeling of the optical response of the multilayered system revealed that the signal at $2f$ is approximately linearly proportional to the amount of oxidized metallic material. More specifically, the proportionality factor deviates by no more than $\pm 5\%$ for the sub-nm films discussed here. Figure 1(a) shows the ellipsometry sig-

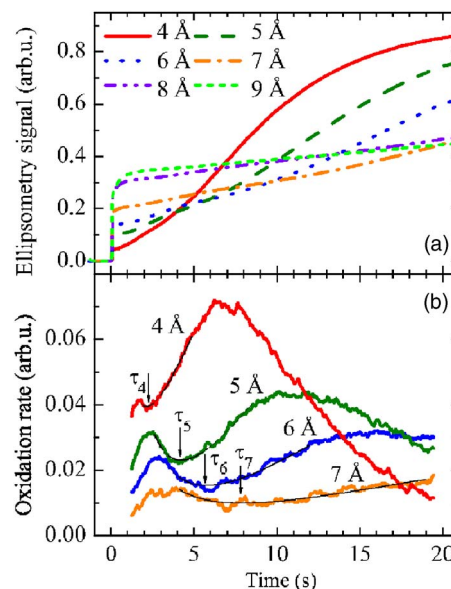


FIG. 1. (Color online) Ellipsometry measurements of the plasma oxidation for samples with 4–9 \AA Al grown on $50 \text{ \AA} \text{ Ta}/50 \text{ \AA} \text{ CoFe}$ (a). Oxidation rate of the samples with Al layers $\leq 7 \text{ \AA}$ on $50 \text{ \AA} \text{ Ta}/50 \text{ \AA} \text{ Co}_{90}\text{Fe}_{10}$ (b). The curves are polynomial fits used to determine the start of the CoFe oxidation $t = \tau_i$, with i an index number indicating the Al thickness in \AA .

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nal (ES) as a function of oxidation time for samples with Al layers ranging from 4 to 9 Å. At time $t=0$ s the oxygen gas is let into the chamber. Within a few tenths of a second the ES rises distinctly, indicating a high initial oxidation rate. After a few seconds, the ES for the samples with Al layers ≤ 6 Å clearly show a point of inflection, indicating a change in the oxidation rate. This can be interpreted as the start of the CoFe oxidation, because the oxidation rate of a single layer decreases monotonously.⁵

The changes in the oxidation rate can be studied in more detail by analyzing the derivative of the ES, because the ES is linearly proportional to the amount of oxidized metallic material. For the samples with Al layers ≤ 7 Å, the oxidation rate as monitored by the ellipsometry measurements is shown in Fig. 1(b). The start-up phase, in which the gas is let into the chamber and the plasma is ignited, is not included in Fig. 1(b). In this phase, which lasts about 1.5 s, an instantaneous thermal oxidation of the Al surface and plasma stabilization takes place.⁶

Kuiper *et al.* developed a model that distinguishes separate steps in the plasma oxidation of a thin Al layer. After instantaneous oxidation of the surface, oxygen diffuses through the Al grain boundaries to the CoFe/Al interface. When the oxygen has reached the interface, a conversion from substoichiometric AlO_x to stoichiometric Al_2O_3 takes place due to Al diffusion to the oxygen at the grain boundaries. After stoichiometric Al_2O_3 is formed, oxygen accumulates at the CoFe/Al interface and when there is an excess of oxygen, the CoFe starts to oxidize.⁷ The features of the oxidation rate in Fig. 1(b) are analyzed in terms of this stepwise oxidation model.

Figure 1(b) shows that the overall oxidation rate is higher with decreasing Al thickness. This is likely due to variations in the morphology of such thin Al layers. As has been reported, the initial grain size depends on the deposited layer thickness.⁸ Thinner layers have a higher density of grain boundaries due to the reduced grain size. Besides that, Fig. 1(b) shows that the oxidation rate of all samples initially increases. We tentatively explain this by heating of the top layers by the oxygen plasma, causing an increase of oxidation rate. Furthermore, the oxidation rate of all samples displays a maximum after a few seconds. We believe that, in accordance with the results by Kuiper, the oxidation front has reached the CoFe/Al interface at that time. Thereafter, the oxidation rate slows down until a minimum is reached at time $t = \tau_i$, with i an index number indicating the Al thickness in Å. During this phase, the AlO_x is supposed to convert to Al_2O_3 . The oxidation rate increases again after time τ_i , as a signature of the CoFe oxidation. As a surprising feature, the apparent oxidation rate of the CoFe is found to be higher than that of Al for layers thinner than 6 Å. In contrast, our explicit modeling shows that the change in ES for Al oxidation is larger than that for Co oxidation, unless strong deviations of the refractive indices of the ultrathin films with respect to bulk values are assumed. Such deviations could indeed be expected for the sub-nm film, and noncontinuous films.⁹

In Fig. 2 we plotted the onset of the CoFe oxidation, τ_i , as a function of the Al thickness. We concluded that the onset of CoFe oxidation is linearly proportional to the Al thickness and, moreover, that initially (2.9 ± 0.1) Å of the Al is already oxidized.

For further investigation we used *in situ* XPS measure-

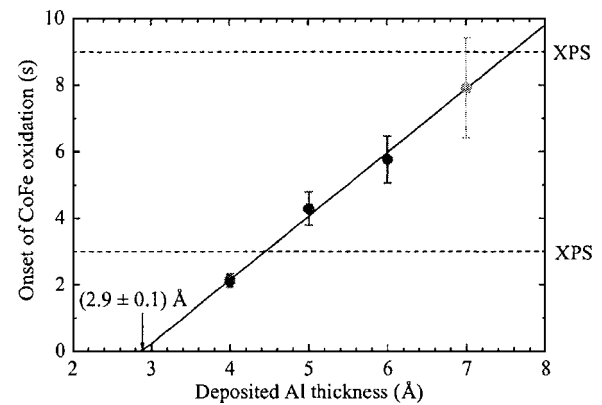


FIG. 2. Onset of the CoFe oxidation as a function of the deposited Al thickness. The dashed lines indicate the times at which XPS measurements are performed.

ments (Mg $K\alpha$ to confirm the ellipsometry results, and specifically examine the CoFe oxidation. XPS, a surface-sensitive analysis method with an information depth of a few nanometers, has been applied to study thin AlO_x based tunnel barriers before.¹⁰ For the XPS measurements we transported identical samples that were plasma oxidized for either 3 or 9 s to the connected XPS chamber. Figure 3 shows spectra around the Co $2p_{3/2}$ peak after 3 and 9 s plasma oxidation, as well as a reference spectrum of an unoxidized sample, that was transported to the XPS chamber directly after growing the Al layer. The amount of CoO can be determined from the ratio of the oxidic and metallic Co $2p_{3/2}$ peak areas in the spectra. To obtain the Co $2p_{3/2}$ peak areas, we subtracted a Shirley background and, while taking the escape depth of the electrons into account, used a standard Gauss + Lorentz curve fitting of the Co $2p_{3/2}$ peaks.

The XPS spectra in Fig. 3(a) of the samples that were oxidized for 3 s show no clear shift of the Co $2p_{3/2}$ peak in comparison to the reference spectrum. However, in the spectrum of the sample with 4 Å Al, the peak is asymmetrically broadened towards a higher binding energy,¹¹ indicating that the CoFe oxidation has indeed started, in accordance with the ellipsometry data. Figure 3(b) shows the spectra of samples that were oxidized for 9 s. The spectrum of the 7 Å Al shows an asymmetrically broadened peak towards a higher binding energy. Furthermore, the spectra of the 4, 5

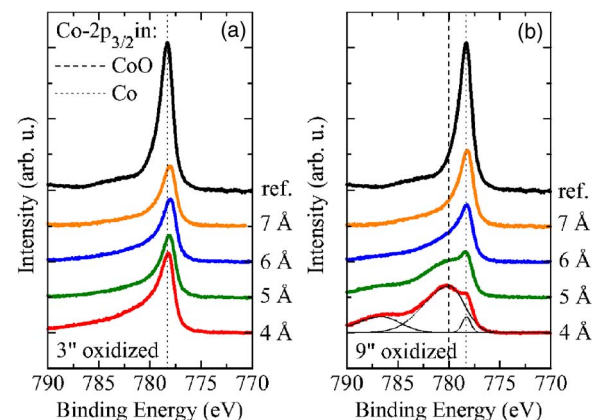


FIG. 3. (Color online) Co $2p_{3/2}$ XPS spectra for samples with 4–7 Å deposited Al after 3 s (a) and 9 s (b) oxidation. As a reference also the spectrum of an unoxidized sample is plotted. The arrow indicates the position of the shake-up peak.

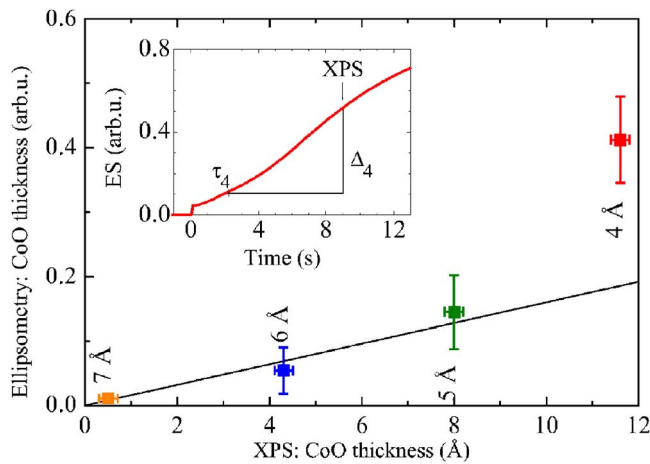


FIG. 4. (Color online) CoO thickness after 9 s oxidation, determined from the ellipsometry measurements, vs the amount of CoO that was determined from the XPS data of 9 s oxidation. The inset shows how the amount of CoO, Δ_4 is determined from the ellipsometry measurements of the 4 Å Al sample.

and 6 Å Al show a distinct double peak, indicating the progressive oxidation of the CoFe. This is confirmed by the appearance of a shake-up peak around 787 eV for the sample with 4 Å Al, and, although to a lesser degree, for the 5 Å Al. The shake-up peak, marked with an arrow, is attributed to the CoO and is included in the total oxide intensity.

Once the amount of CoO is determined from the XPS data, our implication of the onset of the CoFe oxidation can be verified. For this verification, we had to determine the CoO thickness from the ellipsometry data. The amount of CoO, Δ_i , can be determined by the difference in the ES at time $t=9$ s and τ_i , as shown in the inset of Fig. 4 as shown for the 4 Å Al sample. For the samples with 4–7 Å Al, the XPS data of 9 s oxidation and the ellipsometry data are shown in Fig. 4. A linear relationship through zero is expected between the amount of CoO determined from the XPS data and the ellipsometry data. Except for the data point of 4 Å Al, the fit through zero displays a good linear relationship, and therefore confirms the validation of the ellipsometry outcome.

The deviation of the 4 Å Al data point from the fit cannot be explained by the initially oxidized Al of about 3 Å because it only generates an offset in the ES. The uncertainty

in the thickness and morphology of the extremely thin Al layer is a more plausible reason, as separate samples had to be used for the ellipsometry and XPS measurements. Taking into account that the CoFe oxidation rate is strongly dependent on whether or not the Al₂O₃ layer forms a closed film, then even the slightest deviation in original Al thickness or morphology has a significant influence on the amount of CoO formed after 9 s. In addition, given the slope of the oxidation rate curve around 9 s for the 4 Å Al sample in Fig. 1(b), a slight inaccuracy in the onset time τ_4 can cause a substantial error in the estimation of the amount of CoO. This adds to the unreliability of the 4 Å data point.

Taking this into account, we conclude that over-oxidation of the sub-nm thin AlO_x barriers of MTJs can be observed by recording the derivative of the ES. Furthermore, specific features in our ellipsometry traces confirmed the oxidation model proposed by Kuiper. We conclude that *in situ* real-time differential ellipsometry can be applied for monitoring the plasma oxidation dynamics in sub-nm Al layers and is potentially applicable as industrial process control.

This project is supported by NanoNed, a nanotechnology programme of the Dutch Ministry of Economic Affairs.

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