Microstructural observation on effect of oxidation method of AlO_x in magnetic tunnel junction by high resolution transmission electron microscopy

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The formation of the insulating AlO_x tunnel barrier is a critical and sensitive process in magnetic tunnel junctions. Both the natural oxidation and the plasma oxidation methods were employed to fabricate the AlO_x insulating layer in this study. In the natural oxidation, the Al layer was exposed to pure oxygen gas at 20 Torr for up to 50 min to produce the AlO_x tunnel barrier. It was revealed by high resolution transmission electron microscopy that the oxidation occurred preferentially through the grain boundary of Al grains. Also, the AlO_x grains expanded isotropically when fully oxidized, thereby making the surface of the AlO_x layer modulated. In plasma oxidation, the oxygen plasma was used at 20 mTorr of pure oxygen gas for up to 30 s and the flat AlO_x layer formed uniformly on the Al layer. It had sharp interfaces with the underlying metallic Al and the rate of oxide layer growth decreased as the oxidation proceeded. © *2002 American Institute of Physics.*
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Research on magnetic tunnel junction (MTJ) that is composed of two magnetic layers separated by an insulating barrier has become active since the reports of high magnetoresistance (MR) at room temperature.[1,2] In the full layer sequence of MTJ, the insulating layer between two ferromagnetic layers plays an important and critical role in the reproducibility of stable magnetic properties such as magnetoresistance (MR) and resistance-area product $(R\times A)$. Julliere introduced Ge as a barrier.[3] Currently, however, insulators or semiconductors such as AlO_x, HfO, MgO, AlN,[4] and ZnS[5] are usually used as a tunnel barrier.

In general, the insulating layer is fabricated in the following way. First, a metal component such as Al is deposited as a layer on the bottom electrode. Then, the metal layer is oxidized *in situ* by pure oxygen gas, oxygen plasma, or ultraviolet light-assisted oxidation.[6,7] Depending on the oxidation method, the oxidized insulating layer shows different microstructures. Among the methods of oxidation, plasma oxidation[1] and natural oxidation[2] are mostly used. In the former, the oxygen plasma is induced at several mTorr of oxygen partial pressure over the already deposited Al thin layer and the Al layer is oxidized rapidly. In the latter, air or pure oxygen gas at a few tens of Torr is used at room temperature for oxidation.

In this work, both the natural oxidation and the plasma oxidation methods were employed to fabricate the AlO_x insulating layer. The oxidation behavior of the metallic Al film and microstructural evolution were mainly analyzed by high resolution transmission electron microscopy (HRTEM). In order to focus on the oxidation process of the insulating layer, the bottom and top electrodes which are composed of the ferromagnetic and antiferromagnetic layers were removed from the full layer sequence of MTJ, and only the thin Al layer was deposited directly on the Si substrate. The deposition of the Ta capping layer followed the oxidation of Al. The layer sequence in this study, therefore, is Si substrate/Al+AlO_x/Ta.

The Al(30 and 50 Å) and Ta(50 Å) layers were deposited in 6-gun dc magnetron sputtering at 5×10^{-3} Torr of argon and dc 40 W. In the natural oxidation, the chamber was held at 20 Torr of pure oxygen. It took about 24 min to reach 20 Torr from the base pressure of 5×10^{-7} Torr. The oxidation continued from 1 to 30 min. Oxygen plasma was used at dc 30 W and 2×10^{-2} Torr of pure oxygen for 10, 20, and 30 s in the plasma oxidation. Observations of the specimens were made with a JEOL JEM 3010 operated at 300 kV.

The Al layer was deposited 30 Å thick and both methods

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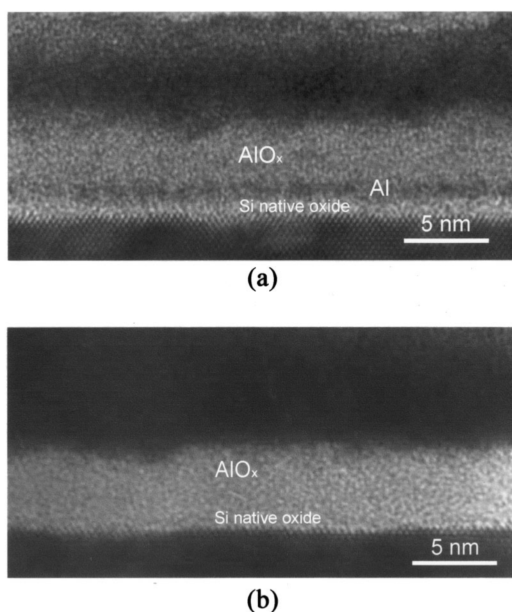

FIG. 1. HRTEM image (cross sectional) of Si/Al+AlO_x(30 Å)/Ta(50 Å), (a) natural oxidation for 20 min and (b) plasma oxidation for 30 s.

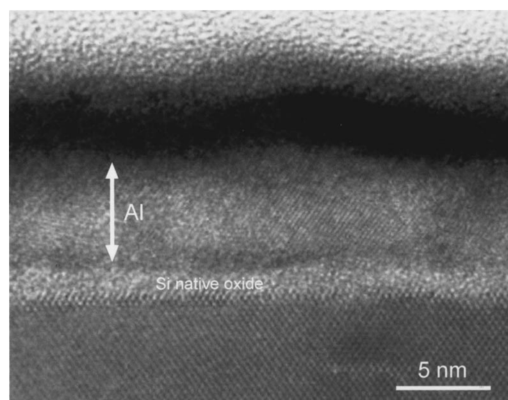

FIG. 2. HRTEM image (cross sectional) of as-deposited Si/Al(50 Å)/Ta(50 Å) before oxidation.

of oxidation were used. The metallic Al layer in the Si/Al(30 Å)/Ta(50 Å) structure was naturally oxidized at 20 Torr of pure oxygen gas for 20 min. The oxidized Si/Al +AlO_x(30 Å)/Ta(50 Å) structure is shown in Fig. 1(a). The upper area with bright contrast is amorphous AlO_x. Oxidation is almost complete. It is likely that the thin dark area between the oxidized layer and the Si native oxide is a nonoxidized Al layer. The remaining Al layer is too thin to examine in detail the interface between the Al and AlO_x layers. In Fig. 1(b), plasma oxidation was employed to fabricate the oxidized layer. In this case the chamber was held at 50 mTorr of the gas mixture of oxygen and argon at a 1:1 ratio. The Al layer was exposed to oxygen plasma for 30 s. Similar to what is shown in Fig. 1(a), oxidation proceeded so heavily that the nonoxidized Al layer was not present and it was even difficult to distinguish between the oxidized AlO_x layer and the Si native oxide layer. To observe more clearly the oxidation behavior and the interface between the Al and AlO_x layers the thickness of the Al layer on the Si substrate increased and was controlled at 50 Å.

Figure 2 shows the as-deposited Si/Al(50 Å)/Ta(50 Å) structure before oxidation, where the lattice images of Al are observed intermittently, especially clearly at the center, in the Al layer. Based on this observation, it is likely that the as-deposited Al layer is partially and intermittently crystalline. The layer above Si is a native oxide, SiO_2. Due to weak contrast, the boundary between Al grains is not clearly identified.

Typical micrographs of the Si/Al+AlO_x(50 Å)/Ta(50 Å) structure naturally oxidized for 1, 10, and 30 min are shown in Figs. 3(a)–3(c). The bright region covering the Al islands with dark contrast in Fig. 3(a) is amorphous AlO_x. It was observed that the oxidation proceeded by entirely surrounding the crystalline Al grains. Because the region between Al grains is an open structure, the oxidation must have proceeded heavily through the open grain boundary region, creating a modulated and repeated pattern of the oxide layer. Beneath the Al+AlO_x layer and above the Si wafer, the native Si oxide layer is still clearly observed. When the Al layer was oxidized for 10 min, the oxidation proceeded further as seen in Fig. 3(b). The preferred oxidation through the grain boundary is similar to Fig. 3(a) but the top surface of Al grains was oxidized more compared with Fig. 3(a). The Al grains that were not oxidized show the

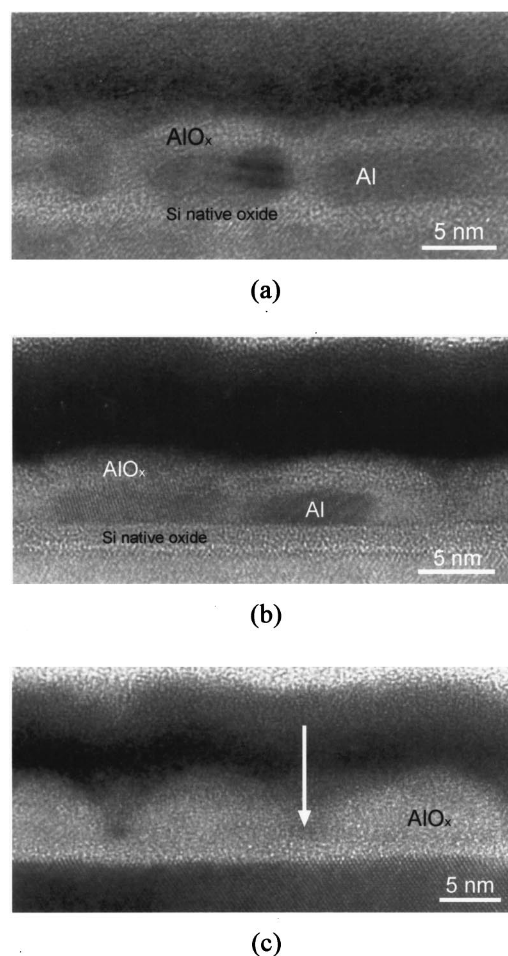

FIG. 3. HRTEM image (cross sectional) of naturally oxidized Si/Al +AlO_x(50 Å)/Ta(50 Å) at 20 Torr of pure oxygen for (a) 1 min, (b) 10 min, and (c) 30 min.

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crystalline lattice images. It was observed in both cases that the morphology of the AlO_x layer is rugged. It is concave at the location of the Al grain boundaries whereas it is convex at the top surface of the Al grains, which means that the oxide layer penetrates preferentially through the grain boundary but not completely through the top surface of the grain.

However, if the grain boundary regions are preferentially oxidized, they should become thicker than the Al grains due to lattice expansion with oxidation. In addition, the Al atomic volume in the grain boundaries is probably larger than in the grains, so the boundaries may end up thicker. What determines the final morphology may be more complex.

Figure 3(c) shows the structure oxidized for 30 min. The Al layer is now perfectly oxidized and the surface of the AlO_x is more rugged and clearly modulated. The metallic Al elements remaining inside the grain are reacted with oxygen during oxidation and there occurs a volume expansion, creating a fully modulated AlO_x surface. The oxidation path in the natural oxidation is primarily through the grain boundary at an early stage of oxidation and then through the grains at a later stage because of the faster grain boundary diffusion than volume diffusion. The path of oxidation described in Fig. 3(c) is shown by an arrow. It has been suggested that the oxygen will enter a metallic Al layer through the grain boundaries at an early stage of oxidation and diffuse into the grain afterwards[8] but it has not been verified in terms of oxide microstructures. Smith *et al.*[9] also proposed the grain boundary diffusion as a possible mechanism for different barrier height in the oxide layer but their interest was in the crystalline or amorphous nature of the oxide layer.

The same layer sequence of $Si/Al+AlO_x(50\ Å)/Ta$ $(50\ Å)$ in Fig. 3 was adopted in Fig. 4, but this structure was oxidized by plasma. The plasma oxidation was performed in a chamber of 20 mTorr of pure oxygen. The metallic Al layer was exposed to oxygen plasma of dc 30 W for 10, 20, and 30 s. According to Fig. 4(a) that shows the specimen exposed for 10 s, the bright layer above the dark Al layer is amorphous AlO_x. The nonoxidized Al layer with dark contrast still remains below AlO_x and above the Si oxide. It occasionally shows crystalline lattice images. Different from natural oxidation, the preferred grain boundary oxidation was not observed in this case and the oxidation proceeded rapidly and uniformly through the metallic Al layer and it resulted in a flat and sharp interface between AlO_x and Al. A specimen exposed to oxygen plasma for 20 s is shown in Fig. 4(b). The oxidized depth and the interfacial morphology are similar to Fig. 4(a). Figure 4(c) is true for 30 s. The interface between the AlO_x and Al layers also remained flat. According to Figs. 4(a)–4(c) the thickness of the oxidized layer did not change significantly with time, which implies that the growth of the oxide layer was retarded under the current experimental condition. It is likely that the oxide layer became saturated and oxidation did not proceed further with time. In the plasma oxidation the oxidation did not go on through the grain boundary of Al grains but uniformly throughout the Al layer.

The growth of the Al layers directly onto the native Si oxide may raise questions of the true applicability to actual MTJ. The additional layers that would be present in a real device can be expected to influence the Al layer microstructure, which would in turn influence how the oxidation front proceeds through the layer. As a parallel study,[10] the microstructures of the Al layer grown on ferromagnetic Co were investigated before and after natural oxidation. The crystalline nature of the Co/Al layer was observed and the oxidation behavior was similar.

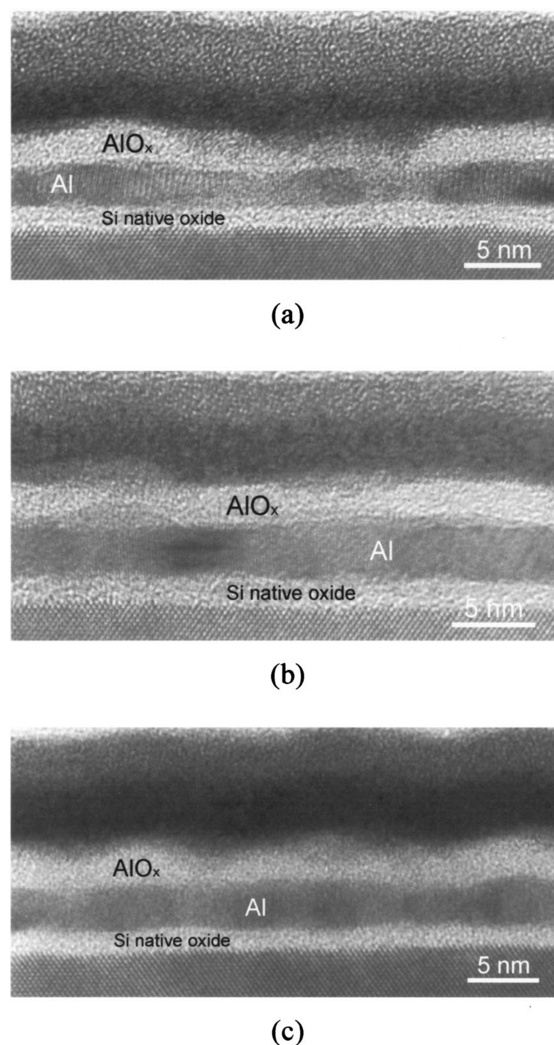

FIG. 4. HRTEM image (cross sectional) of $Si/Al+AlO_x(50\ Å)/Ta(50\ Å)$ oxidized by plasma oxidation for (a) 10 s, (b) 20 s, and (c) 30 s.

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