Study of the effect of natural oxidation and thermal annealing on microstructures of AlO_x in the magnetic tunnel junction by high-resolution transmission electron microscopy

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In a magnetic tunnel junction, the formation of an insulator is sensitive and critical to the stable performance and reproducibility of the junction. The oxidation path and the microstructural change with time of the insulator in natural oxidation have been studied by the high-resolution transmission electron microscopy. It has been observed that the oxidation path is primarily through the grain boundary at an early stage of oxidation and then through the grains at a later stage. The morphology of the oxide layer was rugged and modulated. There also occurred an isotropic volume expansion with increased oxidation. It was observed that the ferromagnetic Co layer below an insulator was partially oxidized because of the preferred grain boundary oxidation. When this multilayer was annealed, the locally oxidized Co layer was reduced and the metallic layer formed as a continuous film type, thereby improving the interface.
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Since the recent reports on the high magnetoresistance (MR) at room temperature,[1,2] the research on tunneling magnetoresistance (TMR) has become more active as it can be applied to nonvolatile magnetic random access memory (MRAM).[3,4] There are several reports on the MR ratio as high as or over 40%.[4,5] The layer sequence of the TMR junction is substrate/antiferromagnet/ferromagnet/insulator/ferromagnet. In this junction structure, the formation of an insulator is very sensitive and critical to the stable performance and reproducibility of the junction.[6,7] If the procedure of metal deposition and oxidation is not controlled accurately and not optimized properly, it is difficult to avoid the fluctuation of the tunnel resistance along the barrier. AlO_x is mostly used as the tunnel barrier. After depositing Al, two methods of oxidation are generally adopted, plasma oxidation[1] and natural oxidation.[2] In the former, oxygen plasma is used to oxidize the Al film and was first introduced by Moodera.[1] In the natural oxidation process, the deposited Al is exposed to air at room temperature.[2] According to recent experiments[8,9] the Al film is oxidized in pure oxygen at a few tens of Torr for several hours. However, the oxidation mechanism or path that is critical to the formation of an insulator is not understood clearly at present.

In this study, natural oxidation was used because another parallel study of the authors covered the plasma oxidation.[10] As the focus was on the insulator, the antiferromagnetic and ferromagnetic layers in the real TMR junction were removed from the full layer sequence and only the AlO_x layer was deposited. The multilayer consisted of Si/Al $+AlO_x(50\ \text{Å})/Ta(50\ \text{Å})$. The oxidation behavior of the metallic Al film and the oxidation path were mainly analyzed with a cross-sectional high resolution transmission electron microscope (HRTEM). The ferromagnetic layer adjacent to the insulator in the real TMR junction may be partially oxidized during the oxidation of Al, thereby degrading the junction performance. In this case the MR ratio may be improved by thermal annealing although the mechanism has not been clearly explained.[7,11–13] This was assumed to occur because of the movement of oxygen atoms in the Co layer to Al by annealing.[13] Ando *et al.*[7] explained it by taking into account both an increased homogenization of the insulator and a small fluctuation of the tunnel resistance. In this analysis, the stacking sequence was $Si/Co(20\ \text{Å})/Al+AlO_x(30\ \text{Å})/Ta(50\ \text{Å})$. This specimen was examined by HRTEM under both conditions of as-deposition and thermal annealing.

The Co, Al, and Ta layers were deposited in 6-gun dc magnetron sputtering at 5×10^{-3} Torr of argon. The Al film was naturally oxidized at 20 Torr of pure oxygen before Ta capping. It took about 24 min to reach 20 Torr from the base pressure of 5×10^{-7} Torr. The oxidation continued for 1, 10, and 30 min. As the oxygen can react to Al surface at the start of introduction of oxygen, the real oxidation times might be 25, 34, and 54 min. Annealing was performed in a rapid thermal annealing (RTA) furnace. In a vacuum condition of about 10^{-6} Torr, it was ramped up to 300 °C for 10 s and

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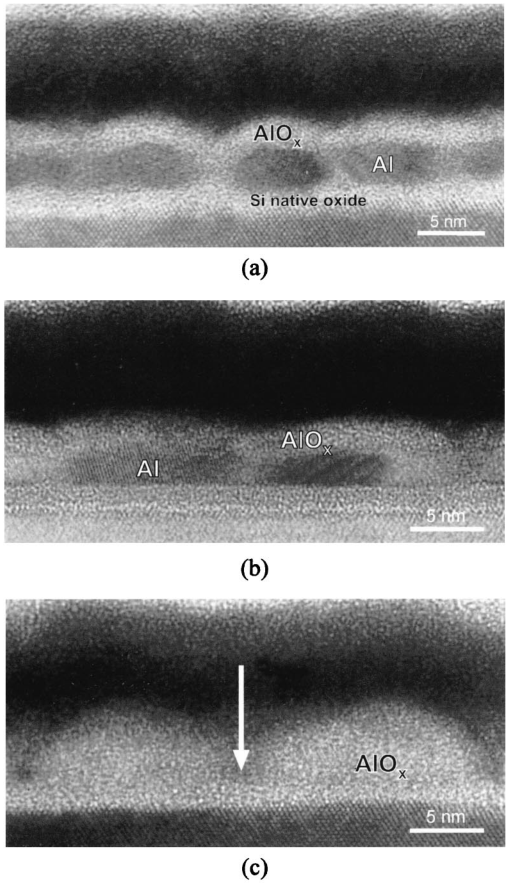

FIG. 1. Cross-sectional HRTEM image of Si/Al+AlO_x(50 Å)/Ta(50 Å) naturally oxidized at 20 Torr of pure oxygen for (a) 1 min, (b) 10 min, and (c) 30 min.

held for 10 s. Observations of the specimen were made with JEOL JEM 3010 operated at 300 kV.

Figures 1(a)–1(c) represent typical micrographs of the Si/Al+AlO_x(50 Å)/Ta(50 Å) structure at oxidation times of 1, 10, and 30 min. Figure 1(a) shows that the specimen is naturally oxidized for 1 min, and the bright region covering the Al islands with dark contrast is an amorphous AlO_x. It was found that the oxidation proceeded by entirely surrounding the crystalline Al grains. As the region between Al grains must be an open structure, the oxidation proceeded heavily through the open grain boundary region, creating a modulated and repeated pattern of the oxide layer. The native silicon oxide layer is still clearly observed beneath the Al +AlO_x layer and above the Si wafer. When the Al layer was oxidized for 10 min, the oxidation proceeded slightly more as seen in Fig. 1(b). The preferred oxidation through the grain boundary is similar to Fig. 1(a) and the grain size of metallic Al seems to be larger in comparison with Fig. 1(a). The Al grains that have not been oxidized show the 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 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. Figure 1(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 an isotropic volume expansion, creating a fully modulated AlO_x surface. The oxidation path in this natural oxidation study 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. 1(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[7] but it has not been verified in terms of oxide microstructures. Smith *et al.*[14] 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.

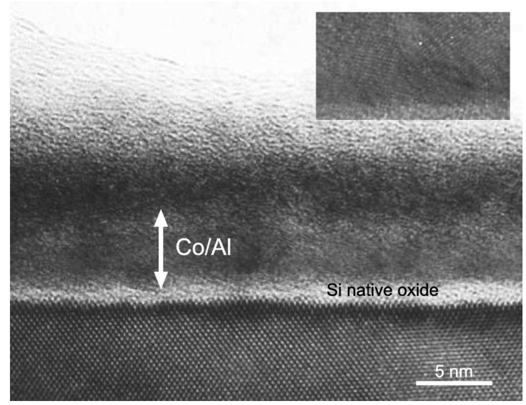

FIG. 2. Cross-sectional HRTEM image of as-deposited Si/Co(20 Å)/Al(30 Å)/Ta(50 Å) before oxidation.

In the real TMR junction a ferromagnetic layer such as Co, CoFe, or NiFe is located below the AlO_x layer. Due to preferred grain boundary oxidation of Al, it is supposed that this ferromagnetic layer may be oxidized locally below the grain boundaries of Al. To investigate this assertion, a nonoxidized Si/Co(20 Å)/Al(30 Å)/Ta(50 Å) multilayer was deposited as a reference structure and observed by HRTEM. As shown in Fig. 2 the Co/Al layer with gray contrast is located above the bright native silicon oxide and below the dark capped Ta layer. As the atomic number of Co is higher than that of Al, the Co layer is supposed to show darker contrast than Al but it is not clearly revealed in this observation. The image in the upper-right-hand side of Fig. 2 is an enlarged view of the Co/Al layer at the marked region and the lattice pattern of crystalline Co and Al is observed. The grain boundaries are hard to identify in this condition. Then, this multilayer was oxidized for 1 min after reaching the oxygen pressure of 20 Torr and is shown in Fig. 3. The bright region below Ta is an AlO_x layer. In addition to the oxidized area at the top surface of the Co/Al layer there are seemingly intermittent bright regions along the Co/Al layer, implying grain boundary oxidation. Nonoxidized Co/Al grains with dark contrast are separated from each other by a modulated oxide layer with bright contrast. The oxidation path suggested by an arrow mark is same as that of Si/Al +AlO_x(50 Å)/Ta(50 Å) which is shown in Fig. 1. It was observed that the modulated oxide layer reached the SiO_2 layer and therefore the Co layer was at least partially oxidized during oxidation.

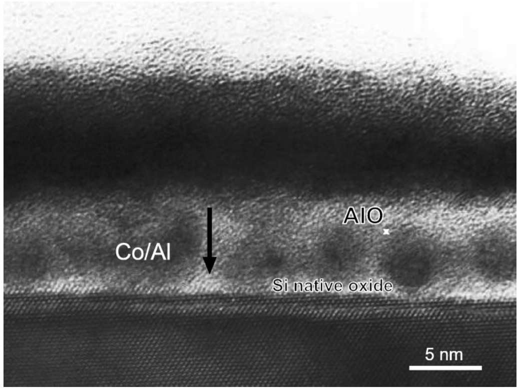

FIG. 3. Cross-sectional HRTEM image of Si/Co(20 Å)/Al + AlO_x(30 Å)/Ta(50 Å) naturally oxidized at 20 Torr of pure oxygen for 1 min.

The magnetic properties of the TMR junction such as MR can suffer from local oxidation of the ferromagnetic layer. This structural damage has been shown to recover by thermal annealing. When this multilayer was annealed, the locally oxidized Co layer was reduced and the metallic grains are connected as a continuous film layer as observed in Fig. 4. The thickness of the Co/AlO_x layer decreased slightly after annealing and the thickness of AlO_x is smaller than that of Co suggesting that metallic Al remains below AlO_x. On the upper-right-hand side the magnified image of the recovered Co/Al layer shows the distinct crystalline lattice image, implying recovery of the crystalline Co layer. The enhancement of the magnetic properties such as MR by means of thermal annealing in the real TMR junction[4,7,11–13] is in good agreement with the current microstructural observation. Parkin *et al.*[4] suggested that the increased MR during annealing is related to homogenization of the tunnel barrier or, more likely, by an improved interface with the ferromagnetic layer. As clearly observed in Fig. 4 the insulating tunnel barrier became homogeneous and flat, and the interface with the ferromagnetic layer was improved as well. Ando *et al.*[7] assumed that the high MR after annealing might come from increased homogenization of the insulator and was verified by HRTEM in this study. The homogeneous distribution of oxygen after annealing measured by Rutherford backscattering analysis[11] was also expected from the homogenized flat oxide layer of this work. The assumed movement of oxygen atoms in the Co layer to Al by annealing[13] was verified by the current microstructural observation.

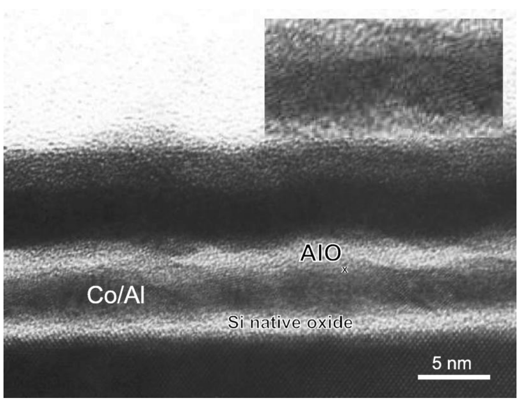

FIG. 4. Cross-sectional HRTEM image of Si/Co(20 Å)/Al + AlO_x(30 Å)/Ta(50 Å) after the rapid thermal annealing (RTA) treatment.

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