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Difference between chemical structures of the interface at the Al-oxide tunneling barrier prepared by plasma or by radical oxidation

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Abstract

We have studied chemical structures of the interface between the Al-oxide tunneling barrier and the underlying $Co_{90}Fe_{10}$ layer in magnetic tunnel junctions when a 1-nm thick metallic Al barrier was oxidized by two different methods: plasma oxidation and radical oxidation. Our chemical analyses confirmed that the underlying CoFe layer was unavoidably attacked by oxygen during the oxidation and that this left different oxide states at the AlO_x/CoFe interface, depending on the oxidation method. The radical oxidation required long oxidation time for optimizing tunneling performance and resulted in a large amount of oxygen at the interface, which, in turn, resulted in the formation of mostly α-Fe_2O_3 and Al_2O_3. Conversely, the plasma oxidation required a relatively short oxidation time for optimization and left FeO as a dominant phase at the interface. Our results also show that the thermal treatment helped AlO_x, an oxygen-deficient phase, to be re-oxidized and transformed into Al_2O_3, the thermodynamically stable stoichiometric phase. The oxygen that diffused from the reduced CoFe layer into the barrier is likely responsible for this oxygen enrichment. We show that such differences in the chemical structure of the interface are critical clues to understanding what causes the change in tunneling properties of magnetic tunnel junctions.

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1. Introduction

Magnetic tunnel junctions (MTJs) have become promising candidates for novel electronic applications, such as magnetic read sensors and non-volatile memory elements, due to their high values of tunneling magnetoresistance (TMR) at room temperature [1]. One of the keys to obtain a large TMR value is to keep the magnetic layers intact throughout the process of fabrication of MTJs. However, it has been extremely difficult to avoid oxidation of an underlying magnetic layer because the process first deposits an ultra-thin metallic layer, for example 1-nm thick Al, and then oxidizes the layer to make a tunneling barrier. This has led to TMR values lower than expected. Another key to large TMR value is to achieve an oxide tunneling barrier that is pinhole free and very smooth because the quality of the barrier is critical to determining the characteristics of MTJs. In MTJs small variations in the barrier thickness result in large variations in tunneling resistance since the resistance exponentially increases with the thickness of the barrier [2].

Various oxidation methods, such as natural oxidation [3], radio frequency (RF) plasma oxidation [4,5], and radical oxidation [6,7], have been explored to obtain an Al-oxide tunneling barrier of high quality. Of those methods, plasma

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oxidation has been the most popular to fabricate the Al-oxide barrier because it requires less oxidation time and produces MTJs with better characteristics than those fabricated by natural oxidation [5]. However, the energy of oxygen ions in plasma seems too high to uniformly oxidize 1-nm thick Al alone. Furthermore, the short oxidation time has made the oxide barrier non-uniform and the process control difficult over an entire film. The results have often been a source for noise [8] and low dielectric breakdown [9] of the MTJ. On the other hand, recent reports suggest that large TMR can also be achieved if the barrier is prepared by radical oxidation, a process that involves energetically weak oxygen radicals [6]. This can be especially the case when the metallic barrier is ultra-thin.

In this article, we present our investigation of the causes for the significant difference between the properties of MTJs prepared by radical oxidation and by plasma oxidation, on the basis of chemical fine structures obtained by near-edge x-ray absorption fine structure (NEXAFS) spectroscopy and x-ray photoelectron spectroscopy (XPS). We review and contrast the properties and the chemical fine structures of the interface of MTJs prepared by radical oxidation with those of MTJs prepared by plasma oxidation, which we reported earlier [10].

2. Experiments

We prepared two kinds of films in an ultrahigh-vacuum sputtering system: (1) Si substrate/SiO_2 200/Ta 5/NiFe 2/PtMn 15/CoFe 1.8/Ru 0.9/CoFe 2.8/Al 1/oxidation/CoFe 1.5/NiFe 3/Ta 10 (nm) for MTJs and (2) Si substrate/SiO_2 200/Ta 5/Cu 10/CoFe 3/Al 1/oxidation/Ta 4 (nm) for chemical analyses, where the alloy compositions were $Co_{90}Fe_{10}$, and $Ni_{80}Fe_{20}$. For chemical analyses, the seed layer of Cu was deposited to provide a (1 1 1) texture, to increase the sample current for the absorption experiment, and to distinguish the Fe signal of the NiFe underlayer from that of the CoFe pinned layer of MTJs. In addition, Ta was used as a cap to prevent further oxidation of the underlying AlO_x barrier and CoFe by air. The base pressure of the deposition chamber was less than 3.0×10^{-7} Pa and a magnetic field of ~150 Oe was applied to induce uniaxial anisotropy during the deposition. All the films were annealed at a temperature of 270 °C for 5 h under a field of 8 kOe at a pressure of less than 5.0×10^{-5} Pa. The MTJ was fabricated by photolithography and its junction size was 30 μm × 30 μm.

RF plasma oxidation was carried out at a bias power of 20 W, and the oxygen pressure was 0.07 Pa during the oxidation. For the radical oxidation, RF power was also applied to generate oxygen radicals in a separate oxidation chamber, but an Al grid was set up between the Al target and the film and it was grounded to reduce the flux of energetic oxygen ions. The applied power was 500 W and the oxygen pressure was 1.5 Pa. We measured the electrical and magnetic properties of the MTJs in the field range of −10 kOe to 10 kOe with a four-point probe at room temperature.

To study the chemical structures of the interface between the Al-oxide barrier and the underlying magnetic CoFe layer, we carried out the NEXAFS measurements on the U7 beamline at the Pohang Light Source, which provided a highly brilliant and monochromatic linear-polarized soft x-ray for high-resolution spectroscopy. The area of the x-ray beam was 0.5×1.0 mm^2. Since our data are averaged over that area, our NEXAFS analyses represent our film or interfacial properties on average. We took the *L*-edge x-ray absorption spectra of Fe and Co in a total electron yield (TEY) mode, recording the sample drain current. The base pressure of the experimental chamber was less than 5.0×10^{-7} Pa. To calibrate the absolute energies of the *L*-edges we referenced the spectra of metals to those reported [11]. We scanned the NEXAFS spectra with a step size of 0.1 eV. We also investigated chemical states of the AlO_x barriers by XPS using a monochromated Al *K*α source at 1487 eV. The base pressure of the experimental chamber was less than 3.0×10^{-7} Pa.

3. Results and discussion

Fig. 1 shows the variations in the TMR values and the resistance-area (RA) products of MTJs with oxidation time when they were prepared by radical or by plasma oxidation. As similarly observed by others [6], radical oxidation took longer than plasma oxidation to achieve the optimal TMR. Our optimum TMR value of MTJs prepared by radical oxidation was higher than that of MTJs prepared by the plasma oxidation: 30.0% versus 24.5%. In addition, other properties were also improved. For example, the RA product was decreased by

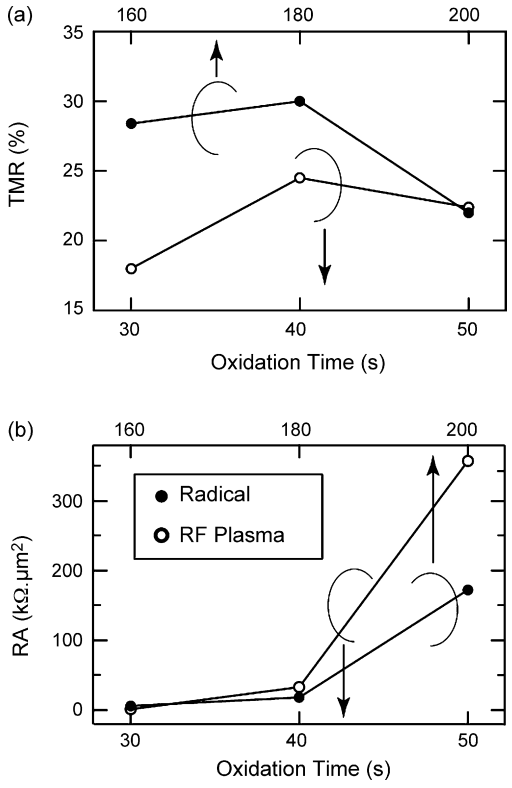

Fig. 1. Variations in (a) TMR values and (b) RA products of MTJs with oxidation time when they were prepared by radical oxidation or by plasma oxidation: The closed circles (●) correspond to the radical oxidation and the open circles (○) correspond to the plasma oxidation.