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Formation of Al_2O_3 Barrier in Magnetic Junctions on Different Substrates by O_2 Plasma Etching

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$Co/Al_2O_3/NiFe$ and $Co/Al_2O_3/Co$ tunnel junctions were fabricated by a radio frequency magnetron sputtering at room temperature with hard mask on glass and 4° tilt cut Si (111) substrates. The barrier layer was formed through two steps. After the Al layer was deposited, it was oxidized in the chamber of a reactive ion etching system (RIE) with O_2 plasma at various conditions. The dependence of the TMR value and junction resistance on the thickness of Al layer (before oxidation) and oxidation parameters were investigated. Magnetoresistance value of 7% at room temperature was obtained by optimizing the Al layer thickness and oxidation conditions. Circular shape junctions on 4° tilt cut Si (111) substrate showed 4% magnetoresistance. Photovoltaic energy conversion effect was observed with the cross-strip geometry junctions on Si substrate.

Key words : magnetic tunnel junction, magnetoresistance, Al_2O_3 magnetron sputtering

1. Introduction

Since the initial experimental discovery of magnetic tunnel junction (MTJ) with larger tunnel magnetorestance (TMR) [1], much attention has been focused on the technique of producing MTJ. The MTJ will possibly find their commercial applications in magnetic random access memory (MRAM) or reading heads, large arrays of sensors for imaging and ultra low-field sensors [2-4].

Tunneling between two ferromagnetic films although apparently simple was not successful in producing high values of TMR for 20 years. Several factors contributed to the failed attempts by many groups until 1995, and success still can be elusive [5]. The possibility of obtaining high TMR critically depends on the quality of the tunnel barrier. The current technique of forming with Al_2O_3 barrier consists of oxidizing a thin Al layer deposited on the ferromagnet with different methods. Major choices are thermal oxidation, reactive sputtering, plasma oxidation, and natural oxidation.

It has been shown that tunnel barrier with good insulating properties and well-controlled thickness can be formed by fixing a metallic film to the cathode of a standard sputtering system and generating RF Ar/O_2 plasma at the cathode [6-8]. In this paper the MTJ barrier layer was formed by O_2 plasma oxidation. The dependence of TMR and junction resistance on the Al layer thickness (before oxidation) and oxidation parameters were investigated.

2. Experimental Method

Junctions were grown at room temperature, in a three gun RF magnetron sputtering system without aligning magnetic field. The base pressure was 5×10^{-7} Torr. During sputtering, the Ar pressure was fixed at 3×10^{-3} Torr. The deposition rates are 0.22, 0.33, and 0.32 Å/s, for Co, Al, and NiFe, respectively.

The structures of the fabricated cross-strip geometry junctions are Glass/Co (180 Å)/Al_2O_3/$Ni_{80}Fe_{20}$ (180 Å)/Al (300 Å) and Si/Cu (300 Å)/Co (50 Å)/Al_2O_3/Co (100 Å)/Al (300 Å). The bottom electrode, barrier and top electrode were deposited on glass or Si 1×1 inch^2 wafer through successive metallic masks changed *ex-situ* to form 0.2×0.2 mm^2 wide junctions in a cross-strip geometry. Circular shape junctions with diameter of 0.3 mm were fabricated on Si substrate. The Si substrate is 4° tilt cut Si (111) wafer. Prior to put the Si substrates to the deposition chamber, they were cleaned with diluted HF solution and deionized water to remove the native oxide on the surface. Without using hard mask, some three layers blanket samples were deposited for magnetic characterization.

The 0.2 mm wide bottom electrode of the cross-strip geometry junction was formed with first hard mask. Then the vacuum was broken and the first mask was taken out. After the chamber was pumped down again, the Al layer ranged in 8-30 Å was deposited onto the bottom electrode and the whole wafer without any mask. The vacuum of the sputtering chamber was broken again and the Al_2O_3 barrier

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layer was formed by exposing the Al layer to O_2 plasma, obtained by biasing the substrates holder with RF power in the chamber of a reactive ion etching system (RIE). The base pressure of the RIE chamber was 5×10^{-6} Torr. The O_2 pressure was varied from 4×10^{-3} Torr to 2.5×10^{-1} Torr, and self bias voltage to the substrates holder was kept at −27 V. Exposure time was varied from 5 s to 240 s. After the oxidation process, the samples were put back into the chamber of the sputtering system and the top electrode capped with a 300 Å thick aluminum protective layer was deposited through the second hard mask. In each run, 24 cross-strip geometry junctions were prepared.

The circular shape junctions were fabricated with one hard mask. After blanket Cu (300 Å)/Co (50 Å)/Al (20 Å) layers were deposited on 4^0 tilt cut Si (111) wafer without mask, the Al layer was oxidized in the RIE system chamber in the same way mentioned previously. Co (100 Å)/Al (3000 Å) two layers were deposited with hard mask to form circular shape top electrode. The diameter of the junctions is 0.3 mm, defined by the top Co/Al electrode. The distance between the junctions is about 1.5 mm. Hundreds of junctions were fabricated on one 1×1 inch^2 wafer.

The TMR of the samples were tested with a four-point arrangement and VSM at room temperature. It is easy to penetrate the Al_2O_3 layer and contact the bottom electrode for the measurements. The TMR of the circular shape junctions was measured in the probe station with two probes on the top of the junction and other two probes on the Cu buffer layer, as showed in Fig. 1. The room temperature I-V curve of the junctions was checked using the probe station.

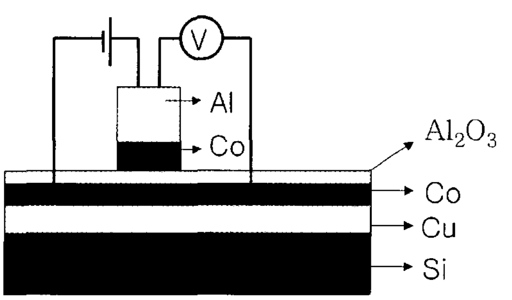

Fig. 1. Schematical drawing of the Circular shape junction on Si substrate and the TMR measurement.

3. Results and Discussion

3.1. Junctions on glass substrate

Most of the hundreds cross-strip geometry junctions on glass substrate from 15 different runs exhibited TMR. With a four terminal method, the measured resistance of the junctions ranged from tens of mΩ to tens of thousands Ω. Fig. 2 shows the typical R-H curves at room temperature for 0.2×0.2 mm^2 cross-strip geometry junctions with different Al layer thickness and oxidation condition. Magnetic decoupling of the electrodes was obtained. The magnetization of the Co bottom and the NiFe top electrodes were switched between parallel and antiparallel configurations with the applied magnetic field. The peak resistance corresponds to the antiparallel magnetization configuration; the minimum resistance related to the parallel magnetization configuration.

The structure of junction (a) was Glass/Co (180 Å)/Al (20 Å) (Oxidation)/NiFe (180 Å)/Al (300 Å). Al layer was oxidized for 180 s in 2.5×10^{-1} Torr oxygen plasma. TMR value is 6% and the junction resistance is 450 Ω, as showed in Fig. 2(a). One feature exhibited by ferromagnetic tunnel junctions is the DC bias dependence of TMR. During the four terminals measurement, when the voltage bias between the bottom and the top electrodes was below 10 mV, the TMR value increases with increasing the voltage bias, as shown in the inset of Fig. 2(a). While the bias voltage between the bottom and top electrodes was beyond 10 mV, the TMR decreases with increasing the bias voltage. The TMR decreases to a half of its maximum value at bias voltage V_h of 251.8 mV.

The structure of sample (b) was Glass/Co (180 Å)/Al (23 Å) Oxidation/NiFe (180 Å)/Al (300 Å). The Al_2O_3 barrier layer was formed by exposing the Al layer in 2.5×10^{-1} Torr O_2 plasma for 240 s. Because of the thick Al_2O_3 barrier and long oxidation time, the junction resistance is high (4900 Ω). The TMR is 1.4%. The inset of Fig. 2(b) is the I-V curve of the sample, which proves the existence of a

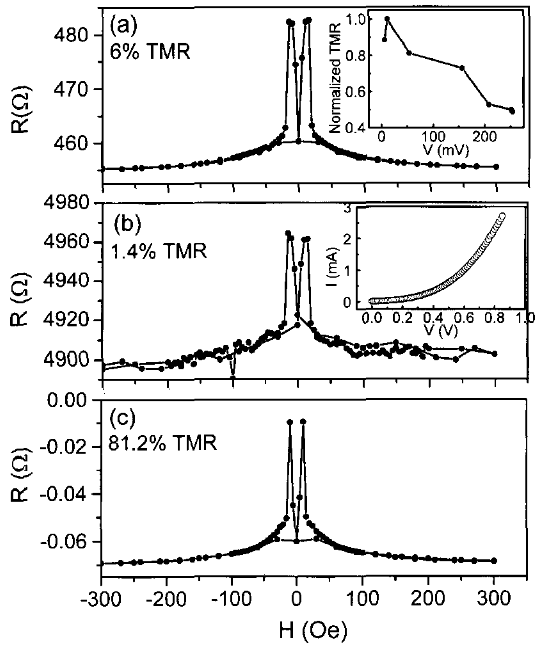

Fig. 2. Typical room temperature R-H curves of junctions with different structure and oxidation conditions. (a) Glass/Co (180 Å)/Al (20 Å) (Oxidation)/NiFe (180 Å)/Al (300 Å), the Al layer was oxidized for 180 s in 2.5×10^{-1} Torr O_2 plasma. (b) Glass/Co (180 Å)/Al (23 Å) (Oxidation)/NiFe (180 Å)/Al (300 Å), the Al layer was oxidized for 240 s in 2.5×10^{-1} Torr O_2 plasma. (c) Glass/Co (180 Å)/Al (11 Å) Oxidation/NiFe (180 Å)/Al (300 Å), the Al layer was oxidized for 30 s in 4×10^{-3} Torr O_2 plasma.

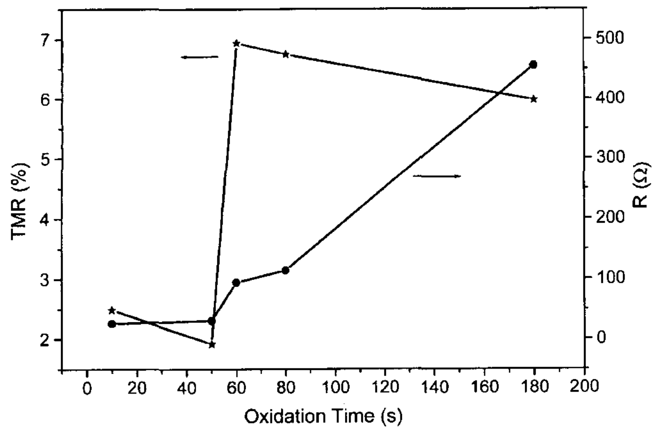

Fig. 3. Dependence of the Magnetotrsistance and junction resistance on the oxidation time of Al layer. The junctions structure is Glass/Co (180 Å)/Al (20 Å) Oxidation/NiFe (180 Å)/Al (300 Å). The 20 Å Al layer was oxidized in 2.5×10^{-1} Torr O_2 plasma.

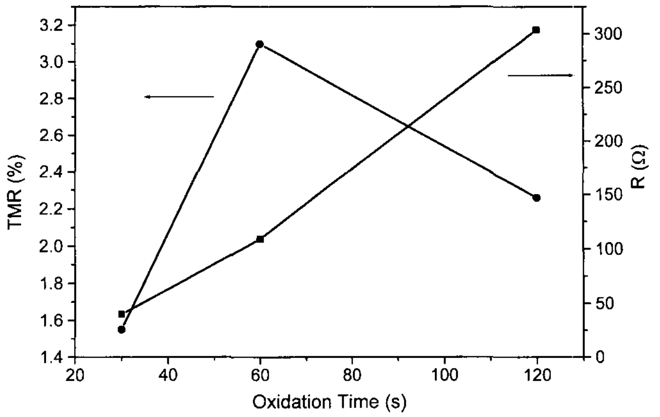

Fig. 4. Dependence of the Magnetotrsistance and junction resistance on the oxidation time of Al layer. The junction structure is Glass/Co (180 Å)/Al (15 Å) Oxidation /NiFe (180 Å)/Al (300 Å). The 15 Å Al layer was oxidized in 5×10^{-2} Torr O_2 plasma.

good tunnel barrier in the sample.

The structure of junction (c) was Glass/Co (180 Å)/Al (11 Å) (oxidation)/NiFe (180 Å)/Al (300 Å). The 11 Å Al was oxidized for 30 s in 4×10^{-3} Torr O_2 plasma. Because the resistance of junction (c) was comparable to that of the electrode (over the junction area) and this included inhomogeneous current distribution effect, the measured junction resistance was negative and the measured TMR value was 81.2%. When the junction resistance is comparable to the resistance of the electrode (over the junction area), with four terminal method the measured resistance is smaller than the actual resistance and the TMR value is enhanced [9].

For a given thickness of Al barrier layer, an optimum oxidation time is expected. The variations of junction resistance and TMR with plasma oxidation time for the Al layer is showed in Fig. 3. The junctions structure is Glass/Co (180 Å)/Al (20Å) Oxidation/NiFe (180 Å)/Al (300 Å). The pressure of O_2 plasma for Al oxidation was 2.5×10^{-1} Torr. Within the first 50 s oxidation, the measured junction resistances were lower than 50 Ω and the measured TMR is low. The TMR values increase rapidly after 50 s oxidation. The highest TMR value was obtained with 60 s oxidation. The TMR values are lower for samples with oxidation time less than 60 s, this is because the 20 Å thick Al was only partially oxidized. The unoxidized Al at the interface reduces the polarization and hence the TMR [10]. The Al layer was fully oxidized in 60 s, so the TMR reaches the maximum value of 7%. When the oxidation time is longer than 60 s, CoO_x may be formed on the bottom Co electrode. The CoO_x can lead to spin memory loss or spin scattering [10] and reduces TMR.

Al layers with different thickness (before oxidation) need to be oxidized in different conditions. Junctions with 15 Å Al layer were prepared. Fig. 4 shows the dependence of TMR value and junction resistance on oxidation time. The junction structure is Glass/Co (180 Å)/Al (15 Å) (Oxidation)/NiFe (180 Å)/Al (300 Å). The O_2 pressure was 5×10^{-2} Torr and the oxidation time ranged from 30 s to 120 s. The junction resistance increases with increasing oxidation time. A maximum TMR ratio of 3.1% was obtained with 60 s oxidation. The Al layer was not fully oxidized with 30 s and it was over oxidized in 120 s, the TMR values were reduced in the both conditions.

Fig. 3 and Fig. 4 show that the partially oxidized Al/Al_2O_3 barrier reduces TMR more radically than the over oxidized Al_2O_3/CoO_X barrier. In order to get high TMR, it is critical to fully oxidize the Al barrier layer, even to run the risk to slightly oxidize the bottom Co layer. Fig. 3 and Fig. 4 also show that the TMR is not sensitive to the oxidation time after 60 s. The result is similar to that in CoFe/Al_2O_3/CoFe system [11].

The thickness of the Al_2O_3 layer influences the TMR value. In our experiment, the junctions with 20 Å Al layer (before oxidation) yielded the highest TMR. With 15, 20 and 23 Å Al layer (before oxidation), the best TMR are 3.1%, 7% and 1.4%, respectively.

The junction resistance can be controlled by Al layer thickness, oxidation time and O_2 plasma pressure during oxidation. The resistances of the junctions with Al layer thinner than 15 Å were low and comparable to the electrode resistance (over the junction area). The measured TMR values of those junctions were high. If the Al barrier layer is thicker than 27 Å, it cannot be properly oxidized in our experiment; both the measured TMR and resistance were low.

3.2. Junctions on 4° tilt cut Si (111) wafer

It has been reported that Co thin film with Cu buffer layer on 4° tilt cut Si (111) wafer showed strong uniaxial magnetic anisotropy [12, 13]. The cross-strip geometry junctions on 4° tilt Si (111) substrates with the structure of Si/

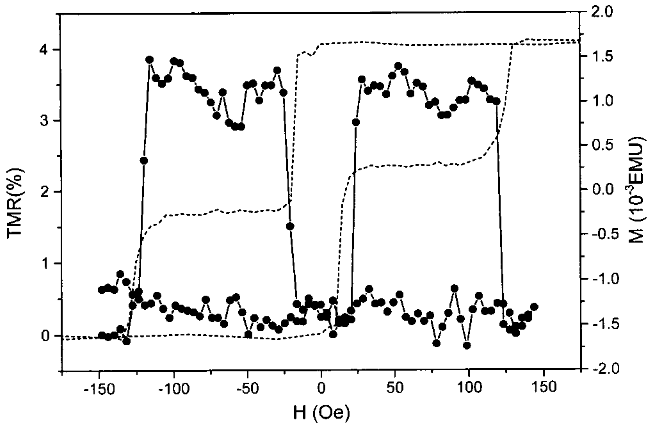

Fig. 5. The TMR (straight line) and M-H curves (dotted line) of round shaped junctions. The structure is Si/Cu (300 Å)/Co (50 Å)/Al (20 Å) (oxidation)/Co (100 Å)/Al (3000 Å). The Al layer was oxidized for 60 s in 2.5×10^{-1} Torr O_2 plasma.

Cu (300 Å)/Co (50 Å)/Al (20 Å) (oxidation)/Co (100 Å)/Al (300 Å) did not show TMR in room temperature. They were kind of photovoltaic energy converters. The voltage between the bottom and top electrode was measured in probe station without current source. When the junction was illuminated with the light of the microscopy of the probe station, the measured voltage was about 50 mV. The potential of the bottom electrode (Cu/Co) was higher than that of the top electrode (Co/Al). When the light of the microcopy was turned off, the voltage was only 0.2 mV. The photovoltaic energy conversion effect was due to the Si substrate and the geometry of the junction.

To avoid the photovoltaic energy conversion effect, the circular shape junctions were prepared. The structure of the junctions is Si/Cu (300 Å)/Co (50 Å)/Al (20 Å) (oxidation) /Co (100 Å)/Al (3000 Å). The 3000 Å Al cap layer protected the junction from the probe penetrating during the measurement. The typical R-H and M-H curves of the circular shape junctions are shown in Fig. 5. The 20 Å Al layer was oxidized in 2.5×10^{-1} Torr oxygen plasma for 60 s. TMR value of 4% was obtained with junction resistance 118 Ω. The M-H and R-H curves were measured along 4° tilt cut Si <112> direction, and details of the measurement have been published elsewhere [12, 13]. The magnetization reversal of the sample consists of two-step process, and interlayer coupling between the top and bottom electrodes is negligible. The reversal process in the small magnetic field is contributed by the top Co layer and that in a large magnetic field is due to the bottom Co layer. The measured coercivities of the top and bottom electrodes were about 25 Oe and 125 Oe, respectively. Comparison of Fig. 2 and Fig. 5 shows that the covercivity of the bottom Co layer on Si substrate was significantly increased. The circular shape junctions on Si substrate shows no photovoltaic energy conversion effect.

Because the masks were exchanged *ex-situ* in our experiment, a very thin CoO_x layer could be formed on the bottom Co electrode. The CoO_x can reduce the TMR. Higher TMR value is expected for *in-situ* masks exchanging and patterning of junctions by lithography.

4. Conclusions

In this study, series of cross-strip geometry and circular shape magnetic tunnel junctions were successfully fabricated with vacuum break. The barrier oxidation technique is based on RF O_2 plasma etching of aluminum at room temperature. The TMR value of 7% was obtained by optimizing the Al layer thickness and oxidation conditions. Circular shape junctions on 4° tilt cut Si (111) substrate showed about 4% TMR. Photovoltaic energy conversion effect was observed with the cross-strip geometry junctions on Si substrate.

Acknowledgment

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