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Long-time-annealing and interdiffusion at AlO_X/Co-Fe/Ir-Mn interfaces

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Dual-spin-valve-type double magnetic tunnel junctions (double MTJs) of sputtered Ir-Mn/CoFe /AlO_x/CoFeNi/AlO_x/CoFe/Ir-Mn were fabricated using photolithography and ion-beam milling. The double MTJs were subjected to long-time annealing at various temperatures (185–400°C) in order to investigate the thermal stability due to the interdiffusion. The thermal changes of the magnetoresistance ratio are well-explained by considering three phenomena with effective activation energies of 2.6 eV, 0.26 eV, and 1.9 eV. These values are in good agreement with the activation energies of the interdiffusion based on the vacancy mechanism. The three phenomena with the effective activation energies are well-explained by considering the interdiffusion and redistribution of O and Mn at the AlO_x/Co-Fe/Ir-Mn interfaces. Based on the effective activation energies, it is evaluated that there would be no significant changes in the MR ratio in MTJs with CoFe(3nm)/IrMn pinned layers for a period of more than 10 years at 160°C.

Key words: Magnetic tunnel junctions, annealing temperature, annealing time dependence, activation energy, interdiffusion, AlO_x/CoFe/IrMn interfaces, electron transport in interface structures

1. INTRODUCTION

The discovery of large and reproducible magnetic tunnel junctions (MTJs) [1,2] at room temperature has led to a renewed interest in magnetic random access memory (MRAM) research. The high magnetoresistance (MR) ratio of single magnetic tunnel junction (single MTJ) devices, exceeding 40% at room temperature, can be utilized in a cross-point MRAM architecture in which each cell consists of a single MTJ device connected in series with a silicon diode or metal-oxide-semiconductor (MOS) switch [3]. For MRAM fabrication, the annealing temperature (T_A) dependence and thermal stability (long-time annealing and temperature dependences) of the MR ratio, which are governed by the interdiffusion at the interfaces, are important problems. MTJs should be thermally stable at up to 400–450°C for 1-2 hours for perfect CMOS compatibility during the fabrication process and also be thermally stable for a period of more than 10 years in a practical use environment. Many attempts [4-9] have been made to reveal the mechanisms for the decrease in the MR ratio above 320°C, and three different mechanisms have been proposed [6,7,9]. The first proposes that the decrease in the spin polarization at the CoFe/AlOx interfaces contributes to the decrease in the MR ratio [6,7]. Mn diffusion into the CoFe pinned layer above 300°C was observed by Rutherford backscattering (RBS) analysis in the CoFe/IrMn layers. The second proposes that a more subtle structural change at the CoFe/AlOx interfaces (at the level of 1-2 monolayers) observed in CoFe/AlOx multilayers by RBS after annealing at 435°C [6] possibly leads to the loss of interface polarization. The third proposes that the formation of an Al-Mn-O composite tunnel barrier is responsible for the decrease in the MR ratio. This barrier is formed by the diffusion of Mn through the CoFe layer and the redistribution of O followed by homogenization at above 300°C. The barriers have been observed by X-ray photoelectron spectroscopy (XPS) and cross-sectional transmission electron microscopy (TEM) measurements at the AlOx/CoFe/IrMn interfaces in MTJs with CoFe/AlOx/CoFe/IrMn [9]. However, we have not come across any studies on the long-term changes of the MR ratio (long-time annealing and temperature dependences) in MTJs. As reported in a previous paper, [10] estimation of the long-time annealing and temperature dependences is a good method for estimation of the lifetime and activation energy of interdiffusion, because resistance changes and the MR ratio are sensitive to interdiffusion. For memory applications in cars, memory elements should be thermally stable in practical use temperatures of more than 120°C for 10 years.

In this paper, the annealing time and temperature dependences of the MR ratio and resistance in double tunnel junctions (double MTJs) after annealing at 325°C for 1 hour were investigated. We have recently achieved MRAM operation of ≥90% [11] in MTJs by using double MTJs [12, 13]. The dependence of the MR ratio

on the bias voltage (V_B) for double MTJs is favorable in terms of the signal voltage compared to that for single MTJs [12,13], because the voltage across each barrier in double MTJs is half of the external V_B. Physically, there is no difference between single and double MTJs for investigating the thermal stability of the MR ratio, i.e., the interdiffusion at the interfaces. In this paper, we show that the thermal changes in the MR ratio of MTJs with CoFe/IrMn pinned layers are well-explained by considering three phenomena with effective activation energies. The values of the effective activation energies can be understood in terms of interdiffusion. Based on the effective activation energy values, the long-term stability of the MR ratio at practical-use temperatures is estimated.

2. EXPERIMENTAL METHOD

The samples were fabricated on oxidized Si substrates by ultra-high vacuum sputtering deposition and oxidization. The base pressure was less than 5×10^{-9} torr. Double MTJs of $Ni_{81}Fe_{19}$ (3nm)/Ir-Mn(12nm)/$Co_{90}Fe_{10}$(3nm)/AlO_x/$Co_{20}Fe_{1}$ $_5Ni_{65}$(3nm)/AlO_x/$Co_{90}Fe_{10}$(3nm)/Ir-Mn(12nm)/Ni_{8} $_1Fe_{19}$ (3nm) were prepared in order to investigate the long-time annealing of double MTJs. Multilayers of NiFe/Ir-Mn/CoFe/AlO_x/CoFeNi/ AlO_x/CoFe/Ir-Mn/NiFe and NiFe/Ir-Mn/CoFe/ AlO_x/CoFeNi having the same layer thickness and composition with double MTJs were prepared in order to clarify the structural changes by using cross-sectional transmission electron microscopy (TEM) measurements, and in order to confirm there were no significant changes in the anti-parallel alignment of the magnetic moment between the pinned layers and free layers by vibrating sample magnetometer (VSM) measurements. The detailed preparation conditions have been specified in a previous paper [12]. The cross-sectional TEM images revealed the existence of uniform single- and double-tunneling barriers and a uniform CoFeNi central layer in double MTJs, and a reproducible MR ratio was observed. A photolithographic patterning procedure and ion-beam milling were used to fabricate double MTJ devices with a 4×4 μ m^2 junction area. A Ti(50nm)/Au(200 nm) bilayer was used as the contact for the top electrode. Initial thermal treatment was performed in a vacuum (less than 1×10^{-6} torr) for 1 hour at 325°C (T_A at which the MR ratio has a maximum), with a rise time of 1.5 hours. A magnetic field of 6500 Oe was applied along the easy direction of magnetization during the annealing and furnace cool down.

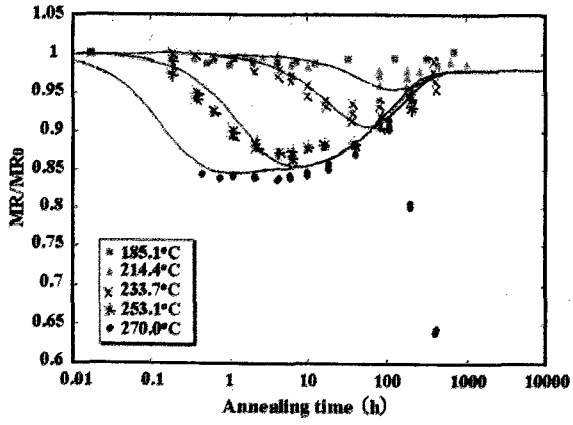

Fig.1. Annealing time dependence of the normalized MR ratio for various annealing temperatures. The solid lines are results fitted by using Eq. (1) in MTJs with the constant resistance of Fig. 2.

The samples were long-time-annealed at various temperatures (185.1-400°C) under a magnetic field of 500 Oe in a vacuum (less than 1×10^{-6} torr) in order to introduce interdiffusion without distribution of magnetic moments between the pinned and free layers. The MR ratio and resistance were measured before and after annealing. The MR was measured using the conventional four-point probe method with the magnetic field applied in the plane along the easy direction of magnetization of the pinned layer. For all the MTJs in this study (annealed at the various temperatures shown below), the VSM measurements revealed no significant changes in the anti-parallel alignment of the magnetic moment between pinned layer and free layer.

3. RESULTS AND ANALYSIS

Figure 1 shows the annealing time dependence of the normalized MR ratio in double MTJs at various annealing temperatures (185.1-270°C). The MR ratio was normalized against the value of 37.0 % obtained after the initial pinned annealing (T_A=325°C; 1 hour). The annealing time dependence of the MR ratio has a minimum for the MTJs annealed between 214.4°C and 270°C. The time at which the MR ratio is minimum increases as T_A decreases. For the MTJs annealed at 270°C, the annealing time dependence of the MR ratio decreased greatly over 100 hours. On the other hand, significant changes in the MR ratio were not observed till 700 hours for annealing of the MTJs at 185.1°C. The results for the MTJs annealed at 270°C suggest that at least three factors of interdiffusion, which change the MR ratio, exist. The first is the interdiffusion of atoms that causes a slight decrease in the MR ratio in the period up to 10 hours in Fig.1 (factor I). The second is the interdiffusion that causes a slight increase in the MR ratio in the period between 10 and 100 hours (factor II). And the third is the interdiffusion that causes a large decrease in the MR ratio in the period beyond 100 hours (factor III). These factors should correlate with previously proposed mechanisms for explaining the annealing temperature dependence of the MR ratio [6,7,9]. Factor I is thought to be related to the diffusion of Mn into the CoFe pinned layer, which decreases the spin polarization at the CoFe/AlOx interfaces and contributes to the loss of the MR ratio[6,7]. Factor II is thought to be related to oxygen distribution and homogenization in the barrier (RBS [4] and XPS [14] measurements below 300°C indicate that oxygen incorporated in the electrode (magnetic layer) at the interface tends to move into the barrier). Factor III is

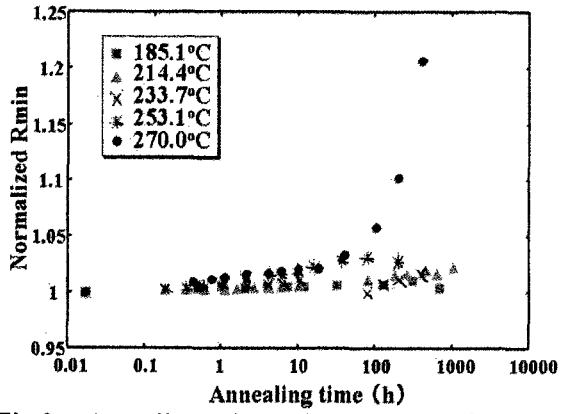

Fig.2. Annealing time dependence of the normalized resistance for various annealing temperatures.

thought to be related to the formation of an Al-Mn-O composite tunnel barrier due to diffusion of Mn through the CoFe layer and O redistribution and homogenization [9].

Figure 2 shows the annealing time dependence of resistance in double MTJs at various annealing temperatures (185.1-270°C). The resistance was normalized against the value of 4.8 k Ω μ m^2 obtained after initial pinned annealing (T_A=325°C; 1 hour). The resistance is almost constant except for the MTJs annealed at 270°C, whose resistance increases when the annealing time is increased to more than 100 hours. This increase in resistance is consistent with the observed annealing temperature dependence of resistances at annealing temperatures of above 325°C [9]. The increase in resistance is thought to be caused by the barrier nature of the interface resulting from the formation of an Al-Mn-O composite tunnel barrier due to the diffusion of Mn [6,7] through the CoFe layer and O redistribution and homogenization [9]. In fact, the cross-sectional TEM images and XPS results confirmed the existence of a uniform tunnel barrier below 100 hours and the absence of such a barrier at 402 hours and existence of an Al-Mn-O composite tunnel barrier at 402 hours [15].

Solid lines in Fig. 1 show the fitted results for the MTJs with constant resistance in Fig. 2, which are thought to be related to factors I and II. The experimental data were fitted using the following equation [16]:

$$MR(t)= \delta_{I\text{-}II}+ \delta_1 \exp(-t/\tau_1)+ \delta_2(1-\exp(-t/\tau_2)), \quad (1)$$

where $\tau_i^{-1}(T) \propto D_i \exp(-Ea_i/k_BT)$ (i=1,2), τ_i is the time constant for the relaxation term, Ea_i is the effective activation energy, and D_i is the pre-exponential factor. The term $\delta_{I\text{-}II}+\delta_2$ is the saturation value of the MR ratio. The second term is the deterioration of the MR ratio caused by the diffusion of Mn (factor I). The third term is increase of the MR ratio caused by oxygen distribution and homogenization in the barrier (factor II). The saturation value of the MR ratio $\delta_{I\text{-}II}+\delta_2$ and the factor δ_1 should be the same for all annealing temperatures. As shown in Fig. 1, the experimental data were well-fitted by Eq. (1).

To clarify the deterioration of the MR ratio observed in the period beyond 100 hours for annealing at 270°C in Fig. 1, we investigated the annealing time and temperature dependences of MR ratio above 270°C as shown in Fig. 3. The MR ratio was normalized against the saturation value obtained by the least square fitting for Fig.1 ($\delta_{I\text{-}II}+\delta_2 \times 37.0$ %). The solid lines in Fig. 3 are obtained by least-squares fitting for the following equation [16]:

$$MR(t)= \delta_{III}+ \delta_3 \exp(-t/\tau_3), \quad (2)$$

where $\tau_3^{-1}(T) \propto D_3 \exp(-Ea_3/k_BT)$. δ_{III} is the saturation value of the MR ratio for annealing above 270°C. The second term in Eq. (2) is the deterioration of the MR ratio resulting from the barrier nature of the interface due to the diffusion of Mn through the CoFe layer and O redistribution and homogenization (factor III). As shown in Fig. 3, the experimental data were well-fitted by Eq. (2).

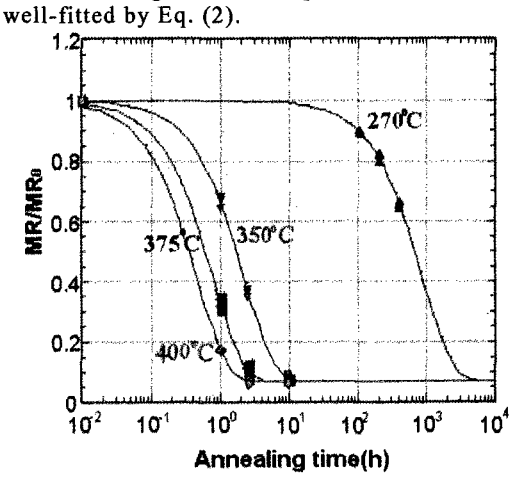

Fig.3. Annealing time dependence of the normalized MR ratio for temperatures greater than 270°C. The MR ratio is normalized against the saturation value of the MR ratio shown in Fig. 1. The solid lines are results fitted by using Eq. (2).

4. DISCUSSIONS

Figure 4 shows the plots of the relaxation time τ_i versus the inverse of the annealing temperature. The inclinations of the solid lines corresponding to τ_1, τ_2 and τ_3 respectively represent the effective activation energies Ea_1, Ea_2 and Ea_3, that are respectively correlated to factor I, factor II and factor III. The effective activation energies are estimated by the least-squares method to be Ea_1=2.63 eV, Ea_2=0.26 eV, and Ea_3=1.90 eV as shown by the solid lines in Fig. 4. The value of Ea_2 is an order of magnitude smaller than those of Ea_1 and Ea_3.

In general, atomic diffusion in metals proceeds by the vacancy mechanism [17]. The reported values of the activation energies for self-diffusion or interdiffusion and for boundary diffusion are shown in Table I [16]. The reported values of the activation energy for self-diffusion or interdiffusion for Mn atoms in the host transition

metal matrix fcc Co is 2.409 eV, and that for O atoms in the host transition metal matrix fcc Cu is 0.33-0.47 eV, but there is no data for the case of an Al or AlOx host matrix. The effective activation energies Ea_1=2.63 eV, Ea_2=0.26 eV, and Ea_3=1.90 eV observed in MTJs with CoFe/IrMn pinned layers are consistent with those for interdiffusion shown in Table I. These surprising agreements lend support to the proposed mechanisms of the interfacial mixing of Mn in the CoFe host matrix (factor I); the oxygen diffusion from $CoFeO_x$ to AlO_x (factor II), which increases the MR ratio; and the oxygen diffusion from AlO_x to Mn (factor III), which greatly decreases the MR ratio.

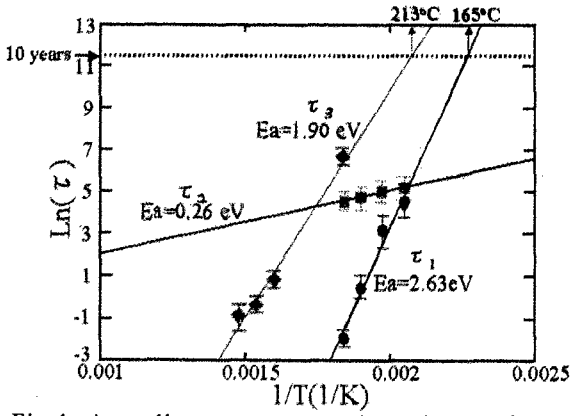

Fig.4. Annealing temperature dependence of the relaxation times τ_1, τ_2 and τ_3. The solid lines are results fitted by using the equation $Ln[\tau_i(T)]=Ea_i/k_BT-Ln[D_i]$.

For memory applications in cars, memory elements should be thermally stable in practical use temperatures of more than 120°C for 10 years. The effective activation energies of the decrease in the MR ratio due to the atomic diffusion of Mn to the CoFe/AlOx interfaces (factor I) and the oxygen redistribution to the diffused Mn from AlOx (factor III) are estimated to be 2.63 eV and 1.90 eV, respectively. Based on the activation energies, it was found that the TMR characteristics in MTJs with CoFe/IrMn pinned layers are stable for a period of 10 years at 165°C as shown in Fig. 4. These results indicate that the MTJs with CoFe/IrMn pinned layers are extremely stable with respect to interdiffusion even in the practical use temperature range.

5. CONCLUSIONS

The annealing time and temperature dependences of the MR ratio in MTJs were investigated in detail. Thermal changes of the MR ratio are well-explained by considering three phenomena. The first is the deterioration of the MR ratio due to Mn interdiffusion (effective activation energy; 2.6 eV), the second is the interdiffusion of oxygen from CoFe pinned layers to the AlOx layers (effective activation energy; 0.26 eV), the third is oxygen redistribution and homogenization between AlOx and Mn (effective activation energy of 1.9 eV), which causes the largest deterioration of MR ratio. These effective activation energies indicated that there would be no significant changes in the MR ratio in MTJs with CoFe(3nm)/IrMn pinned layers for a period of more than 10 years at 160°C.

Table I. Activation energies of interdiffusion and boundary diffusion.

Solute/tracer	Host matrix	Ea(eV) Self-diffusion/interdiffusion	Ea(eV) boundary diffusion
Co	Cu(fcc)	2.348	no data
Mn	Cu(fcc)	2.117	no data
Ni	Cu(fcc)	2.452	0.808-1.524
Fe	Co(fcc)	2.961	1.358
Mn	Co(fcc)	2.409	no data
O	Fe(bcc)	0.89-1.63	no data
O	Cu(fcc)	0.33-0.47	no data

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