Tunnel Magnetoresistance in the Magnetic Tunnel Junctions with an Amorphous Boron Nitride Barrier Formed via Nitrogen Diffusion

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ABSTRACT

Sputtering is the method widely used to fabricate thin films including nitrides in spintronic research fields. One of the issues to fabricate the nitride thin films via sputtering is the control of N deficiency. In this work, it was demonstrated that the use of atomic diffusion improved the insulating property of amorphous BN (a-BN): BN deposition caused the nitridation of Co underlayer, and the diffusion of N from Co-N into BN reduced the N deficiency of BN. The a-BN formed via this sequence showed flat interfaces and no pinholes, and could be used as a tunneling barrier layer. This provides an insight to synthesize stoichiometric BN thin films. A negative tunnel magnetoresistance (TMR) ratio of -0.2% was observed at room temperature. The TMR ratio increased with a decrease in temperature to -0.7% at 10 K. The effective thickness and height of the barrier were estimated to be 1.78 nm and 0.52 eV, respectively, for 2-nm-thick BN-MTJs based on the dependences of transport properties on the bias voltage and temperature.

KEYWORDS

Spintronics, Magnetic tunnel junction, Tunnel magnetoresistance, Boron nitride, Tunneling barrier

INTRODUCTION

Tunnel magnetoresistance (TMR) ratio can be used as a figure of merit to determine the performance of magnetic tunnel junctions (MTJs), which are fundamental components in spintronic research fields. MTJs with high TMR ratio pave the way for novel attractive applications such as neuromorphic computers, high-performance magnetic random-access memories, and magnetic field sensors. [1] Therefore, material developments for MTJs have been studied over two decades since the introduction of spintronics. Barrier materials have attracted immense attention recently. In fact, new crystalline barrier material systems, e.g., MgO-based materials, [2] spinel oxides, [3] CuIn(1-*x*)Ga*x*Se2 systems, [4] GaO, [5] LiF, [6, 7] and BN, [8 – 14] have been extensively studied. Among them, a BN barrier has been studied in particular because of its affinity to graphene and its new type of spin-filtering effects. [15] Because the high-quality h-BN films could be obtained by chemical vapor deposition (CVD) [9 – 11, 13] or exfoliation technique [12, 14], TMR ratios were observed in MTJs with h-BN, which have been improved year by year, and a TMR ratio as high as 160% was observed at low temperatures by using h-BN combined with van der Waals ferromagnet Fe3GeTe2. [14] Because the high potential of BN has been shown as mentioned above, rich BN polymorphs such as cubic (c-BN), wurtzite (w-BN), turbostratic (t-BN), and amorphous (a-BN) can be an interesting field to explore the TMR properties. In particular, amorphous phase do not require the high temperature to grow, and continuous flat films can be easily obtained on any underlayers. In fact, a-BN ultra-thin films were grown on various substrates including flexible ones by using pulsed laser deposition (PLD). [16] Although it was reported that a-BN thin films showed a band gap of ~ 5 eV, which was similar to that of h-BN, [17] and act as tunnel barriers, the TMR property of the MTJs with a-BN has not been reported so far. One of the important issues to use a-BN as the tunneling barrier is the reduction of N deficiency because the electric resistance of BN strongly depends on the stoichiometry. In this study, MTJs with an a-BN barrier were prepared by using reactive sputtering technique with N2 gas and the conventional photolithography process. The structural, magnetic, and spin-dependent transport properties of a-BN were investigated.

EXPERIMENTAL DETAILS

MTJ stacking structures composed of Ta(5)/ Ru(10)/ Ir22Mn78(10)/ Co(4)/ BN(*t*BN)/ Co(3)/ Ta(3)/ Ru(7) (thickness in nanometers) were deposited on Si/SiO2 substrates by using direct current (DC)/ radio frequency (RF) magnetron sputtering technique, and are referred to as BN-MTJs hereafter. *t*BN was varied in the range of 1.0 to 2.4 nm. A BN barrier layer was prepared by using reactive sputtering with a gaseous mixture of Ar and N2. The cathode for BN was arranged at 90° off-axis configuration with respect to the substrate plane. The sputtering power *P*s, Ar + N2 total gas pressure *P*tot, and N2 gas flow ratio *R*N2 defined as N2 gas flow / total gas flow × 100 (%) were varied to optimize the preparation conditions. All the films were deposited at room temperature (~290 K). The MTJ samples were annealed at 523–673 K in vacuum of < 1×10-4 Pa under a magnetic field of 2 kOe. The BN-MTJs were patterned into square shapes with the sizes of 10×10, 20×20, and 30×30 µm2 by using photolithography and Ar-ion milling techniques. As the reference MTJ samples, CoFeB/MgO/CoFeB-MTJs were also prepared. In the stacking structures, the buffer and capping layers were the same as in the BN-MTJs, i.e., Co and BN were replaced by CoFeB and MgO, respectively. CoFeB/MgO/CoFeB-MTJs could be used as reference of tunneling conduction because the MgO grown on CoFeB was reliable tunneling barrier. In the BN-MTJs, Co was used as the electrode material to avoid the formation of excess BN by nitriding B in CoFeB.

To investigate the transport properties, a DC 4-probe system, current-in-plane tunneling (CIPT) measurement system (CIPTech-M150, CAPRES), and physical property measurement system (PPMS, Quantum Design) were used. The CIPT technique was used to avoid the damage by microfabrication. The PPMS was used to investigate the temperature dependence of the TMR effect and the electric resistance in the BN-MTJs. A vibrating sample magnetometer was used to measure the magnetization of the samples. Si/ SiO2/ Ta(5)/ Ru(10)/ *A*/ Ta(5) structures were prepared in addition to BN-MTJs to investigate the magnetic properties of Co in detail, where *A* = Co(4), IrMn(10)/ Co(4), Co(4)/ BN(2), and BN(2)/ Co(4) (thickness in nanometers). The structural analysis of the BN-MTJs was performed by using transmission electron microscopy (TEM).

RESULTS AND DISCUSSIONS

First, the magnetic properties of BN-MTJs were investigated. In the as-deposited BN-MTJs, the magnetization of Co in the MTJ stacking was small with respect to bulk Co as shown in Fig. 1(c). The preparation conditions of the MTJ stacking in Fig. 1 were *P*s = 50 W, *P*tot = 0.1 Pa, and *R*N2 = 40%. The samples prepared under other conditions also showed a similar trend. To clarify the origin of the magnetization reduction in a Co layer, the samples separated in parts of MTJs, i.e., Co deposited on IrMn or BN, Co covered by BN, and Co single films were prepared. These samples are referred to as IrMn/Co, BN/Co, Co/BN, and Co single in Fig. 1(a), respectively. It was observed that the magnetization in Co/BN was small compared with that in other stacking structures, indicating the nitridation of bottom Co owing to the BN overlayer deposition. As the Co-N is unstable, [18] it is expected that N in the Co layer is easily removed via annealing. In fact, the magnetization of Co increased via annealing at > 523 K as shown in Fig. 1(b), which was comparable to that of bulk Co. This recovery of magnetization indicated the reduction of N-content in the bottom Co layer. Fig. 1(c) shows the annealing temperature *T*a dependence of the magnetization curves in the BN-MTJs. As in the case of the Co/BN sample, magnetization could be recovered by annealing at > 523 K. It was also observed that the magnetization of the bottom Co layer attached with the antiferromagnetic IrMn was pinned with the exchange bias field of ~120 Oe, i.e., antiparallel magnetization configuration could be obtained by annealing at > 523 K. The *T*a dependence of the saturation magnetization *M*s is plotted in Fig. 1(d). Here, the magnetization in the bottom and top Co in MTJ stacking was estimated from Fig. 1(c). The reduction of magnetization via high-temperature annealing can be observed in all films from Fig.1(d) in addition to a drastic improvement of the magnetization in Co/BN via annealing. In Co single films, interdiffusion between Co and Ru is the possible origin of the magnetization reduction because Co and Ru are soluble in each other. In contrast, the magnetization reduction in the bottom Co in MTJ stacking could be attributed to Mn-diffusion because the Co/BN without the IrMn layer, which is the imitation of the bottom electrode, did not show the reduction of magnetization. The top Co in MTJ showed a small magnetization relative to that in other stacking structures. Similarly, the magnetization of Co in BN/Co, which is the imitation of the top electrode, was small. A possible origin is the atomic diffusion from the BN layer owing to the non-stoichiometry of BN. In the non-stoichiometric BN, weakly bound B and/or N may diffuse into adjacent layers. Furthermore, as the crystal structure of BN in this study was amorphous, the chemical bond between B and N might not be as strong as that in crystallized BN phases. As Ta can act as the gettering material, which is well known in MTJ stacking, [19] B or N can be gotten in the nearest Ta, which was located on the top of Co. Consequently, in the MTJ stacking, B and/or N could diffuse into the top Co layer via annealing at a high temperature > 623 K. In the sample annealed at 523 K, less diffusion and clear antiparallel magnetization configuration could be obtained in the BN-MTJs, which were suitable to observe the TMR effect.

Figs. 2(a)–(c) show the preparation condition dependences of the resistance–area (*RA*) products, which were estimated by using the CIPT technique. CIPT is the effective method to evaluate the tunnel junctions with low *RA* because the microfabricated barrier would show the resistance of < 1 Ω. In the MTJs, since the bottom ferromagnets were pinned by IrMn layer, the magnetization direction could be defined without shape magnetic anisotropy caused by microfabrication. It was observed that a relatively high electric resistance can be obtained in the sample prepared under low-pressure and low-power conditions. In the BN thin films prepared using the PLD technique, the bombardment of N-plasma could reduce the content of N in the BN films. [20] Therefore, low density of N-plasma and low energy deposition are more suitable to obtain the stoichiometric BN, which correspond to low-pressure and low-power conditions. In Fig. 2(a)–(c), the estimated *RA* values in the sample annealed at 523 K and the as-deposited samples are plotted. It can be observed that the *RA* values in the sample annealed at 523 K were 2–3 orders of magnitude greater than those in the as-deposited samples. As N could move from Co-N formed on the bottom Co to the upper films as shown in the magnetization measurements, N could be supplied into the BN layer via annealing at 523 K, resulting in the reduction of N deficiency in BN. As the insulating property of BN depends on the composition, the annealed BN-MTJs showed a high *RA* product. Fig. 2(d) shows the *T*a dependence of the *RA* product and the sheet resistance of the top (*R*t) and bottom (*R*b) electrodes. In contrast to *R*t and *R*b, which are constant as the annealing temperature changed, the *RA* product increased exponentially with an increase in *T*a. An increase in N-content in BN is a possible origin of the increasein *RA* products. However, in the magnetization measurements, the magnetization of Co was almost recovered via annealing at 523 K. Therefore, other contributions to *RA* products may exist. For instance, Mn diffusion from IrMn, which is indicated by the magnetization measurements, also contributes to the increase in *RA* product in the high *T*a region. This acts as an impurity, causing scattering. Therefore, as shown in the magnetization measurements, a relatively low annealing temperature, e.g., 523 K was suitable for the BN-MTJs. The magnetization and transport measurements suggested that insulating BN could be obtained by utilizing N-diffusion from unstable Co-N, which may be suitable to synthesize the stoichiometric BN films. This provides a new insight into the synthesis of BN thin films because the stoichiometry of BN is important for the physical properties of BN and the difficulty of preparation of stoichiometric BN. In this work, the N diffusion was speculated from magnetization and electric resistance measurements without direct measurements of N composition by using other techniques such as X-ray photoelectron spectroscopy (XPS) because the etching process in the measurement of depth-resolved XPS may destruct the as-deposited condition due to unstable nature of Co-N. The *t*BN dependences of *RA* products of BN-MTJs are plotted in Fig. 2(e) with the reference data of CoFeB/MgO/CoFeB-MTJs, where the CoFeB/MgO/CoFeB-MTJs were not annealed for comparison to amorphous barrier without coherent tunneling nature. The annealed BN-MTJs exhibited *RA* products comparable to those of CoFeB/MgO/CoFeB-reference samples, suggesting that the N-content in BN was sufficient to separate the bottom and top electrodes electrically. Furthermore, the slopes in Fig. 2(e) for CoFeB/MgO/CoFeB-MTJs and BN-MTJs were similar, confirming that the conduction mechanism in the BN-MTJs was tunneling.

TEM observations were obtained to investigate the structure of BN-MTJs. Fig. 3 shows the cross-sectional TEM images for the as-deposited BN-MTJs. A relatively flat surface could be observed in the sample prepared with low power, which may contribute to the high resistance in Fig. 2(c). The BN films were continuous without any pinholes, and can act as the tunnel barrier. The BN film thickness was consistent with the designed value of 2 nm. No evident structural ordering was observed in the BN layer, indicating that the crystal structure of BN was amorphous. Both the bottom and top interfaces across the BN layer show < 1 nm roughness. From these TEM images, it was suggested that a large-scale MTJ structure using a-BN could be formed by using the sputtering technique.

Fig. 4(a) shows the current density *J* as a function of the bias voltage *V* of the MTJ with the 2-nm-thick BN barrier under the magnetic field of 1 kOe, which is sufficiently large to saturate the magnetization of the pinned layer. The *J–V* measurements were performed at room temperature. Symmetric non-linear dependence of the current density on the bias voltage can be observed in Fig. 4(a). By fitting the *J–V* curve into the Simmons formula assuming a simple rectangular-shaped barrier, [21] the effective thickness and barrier height were estimated to be 1.78 nm and 0.52 eV, respectively. The effective thickness of 1.78 nm was comparable to the designed thickness of 2 nm, suggesting that the fitting was reasonable. However, the estimated barrier height of 0.52 eV was lower than that of h-BN. [9, 10, 22] In the amorphous structure, energy bands could be smeared, causing a reduction in the bandgap, i.e., barrier height. Hopping conduction may also be an origin of the low barrier height. This could be one of the differences between the amorphous and hexagonal phases. Fig. 4(b) shows the bias voltage dependence of the TMR ratio, which was estimated from the difference between *J–V* curves in parallel configuration (under 1 kOe) and antiparallel configuration (under -200 Oe). Zero-bias anomaly is the artifact originating from the current density of ~ 0 at zero-bias in the antiparallel configuration. The TMR ratio around zero-bias was ~ -0.2% at room temperature. Notably, the sign of the TMR ratio was negative. The possible origin of the negative TMR could be the contamination in Co by N. The first-principle calculation indicated that Co-N possesses negative spin polarization similar to an Fe-N system. [23] In the BN-MTJs in this study, Co-N might be formed in the bottom and/or top Co layers as suggested from the magnetization measurements. The Co-N formation was considered from the asymmetric behavior in the bias dependence of TMR. Such an asymmetric bias dependence with negative TMR was also observed in the MTJs with the Fe4N electrode. [24] In the bias dependence, the positive direction was defined as the top electrode connected to the positive terminal, which is the same as in ref. [24]. The highest TMR could be observed at ~+0.05 V in our BN-MTJs, which was in contrast to Fe4N/MgO/CoFeB-MTJs. Assuming similarity in the electronic structures of Fe4N and Co-N, Co-N in the BN-MTJs might be formed on the top electrode. This is consistent with the magnetization measurements showing a reduction of magnetization of the top Co after high-temperature annealing in the BN-MTJs. The inhomogeneous distribution of Co-N in the Co may decrease the TMR ratio, because the positive TMR in the Co/BN/Co and the negative TMR could be canceled out each other. Therefore, further optimization of stacking structure and preparation conditions may increase the TMR ratio in the BN-MTJs.

Fig. 5 shows the temperature dependence of the TMR properties in the BN-MTJ. The TMR ratio changed from -0.2% to -0.7% with a decrease in the temperature from 300 to 10 K, i.e., the absolute value of TMR ratio gradually increased with a decrease in the temperature as observed in typical MTJs. This indicated that the inelastic tunneling process could be suppressed by a decrease in the temperature. In the BN-MTJs, inelastic tunneling appeared to relate to the contribution of hopping conduction as suggested from the temperature dependence of the resistance. In the case of ideal tunnel conduction, the temperature dependence of resistance should be small, e.g., with a variation of 10%, which mainly originates from the smearing of the energy band. However, the resistance of the BN-MTJ at 10 K was three times larger than that at 300 K as shown in Fig. 5(b). This kind of temperature dependence could be described by inelastic tunneling owing to the hopping conduction in the MTJs with an amorphous barrier. [25] The temperature-dependent electric conductance *G*(*T*) of the tunnel junction is given by

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where, *G*0, *β*, and *γ* are the fitting parameters, *T* is the temperature in K, and *C* = 1.387×10-3*dφ*1/2. *d* and *φ* are the thickness of the barrier (nm) and the barrier height (eV), respectively. The fitting parameters *G*0, *β*, and *γ* were estimated to be 0.006 Ω-1, 2.5×10-6, and 1.47, respectively. It was known that *γ* could be given as *n*-2/(*n*+1) for hopping order *n*. [25] When the hopping order was 2, *γ* was 1.33, which was smaller than the estimated value of 1.47. Therefore, a higher hopping order i.e., larger than 2 could also contribute to the electric conduction in addition to the direct tunneling in the BN-MTJ. This extra contribution could degrade the barrier height and the TMR properties because the spin-independent hopping conduction could be considered to be the additional path to the spin-dependent tunnel conduction. Thus, Co-N in the top Co and inelastic tunneling in the BN are important to improve the device qualities, which relate to the diffusion of N and the gettering effect of Ta. Therefore, it is expected that the further optimization of stacking structure and preparation conditions can improve the TMR ratio of the a-BN MTJs. This is the first step to explore the TMR properties of the MTJs with BN which possesses the many polymorphs even though the issues such as the purity of BN sputtering targets as well as the stacking structures and preparation conditions are remaining to improve the TMR ratios of the MTJs with the BN barrier.

CONCLUSION

The a-BN thin films deposited by using sputtering showed flat interfaces and no pinholes, and could be used as the tunneling barrier layer of MTJs. The use of the atomic diffusion of N from Co-N formed by the deposition of a BN overlayer reduced the N deficiency of BN, resulting in a drastic increase in the *RA* products in the BN-MTJs. Low-temperature annealing suppressed the excess diffusion. A negative TMR ratio of -0.2% was observed at room temperature. The dominant conduction mechanism in the BN-MTJs was tunneling, whereas the contribution of hopping with a higher order > 2 was indicated from the temperature dependence of resistance. It is expected that the further optimization of stacking structure and preparation conditions will improve the nitridation of ferromagnet and defects in the BN barrier, resulting in high TMR ratio.

FIGURES

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**Figure 1.** (a) Magnetization curves for various stacking structures. Co covered by BN referred to as Co/BN showed the small magnetization compare with other structures. (b) The annealing temperature *T*a dependence of magnetization curves in Co/BN stacking. The magnetization of Co was recovered by annealing > 523 K. (c) The annealing temperature *T*a dependence of magnetization curves in MTJ stacking. The anti-parallel configuration could be clearly observed in annealed MTJs. The magnetization curve of the Co single film was denoted by Ref. (d) The annealing temperature *T*a dependence of saturation magnetization *M*s.

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**Figure 2.** (a) N2 ratio *R*N2, (b) pressure *P*tot, (c) power *P*s dependence of the resistance-area (*RA*) product. The samples prepared under low-pressure and low-power showed high resistance. Resistance of BN increased by annealing at 523 K. (d) The annealing temperature *T*a dependence of the *RA* product, and sheet resistance of top and bottom electrodes. The *RA* product increased with *T*a. (e) The thickness dependence of the *RA* product. The *RA* product of BN-MTJs increased exponentially with an increase of thickness similar to CoFeB/MgO/CoFeB-MTJs.

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**Figure 3.** The cross-sectional TEM images for BN-MTJs prepared under sputtering power *P*s of (a) 50 W, and (b) 22 W.

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**Figure 4.** (a) The current density and (b) the TMR ratio as a function of the bias voltage. The fitting curve for the bias dependence of the current density is shown as black line in (a). The effective thickness and barrier height were estimated to be 1.78 nm and 0.52 eV, respectively.

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**Figure 5.** (a) The temperature dependence of TMR curves in the BN-MTJ. (b) The resistance and the TMR ratio as a function of temperature ranging from 10 to 300 K. The fitting curve for the temperature dependence of the resistance is shown as black line in (b).

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Author Contributions

T.I. and S.M. prepared the samples and measured the magnetic and transport properties. K.E. and A.H. performed transmission electron microscopy. T. I. wrote the manuscript and all authors have given approval to the final version of the manuscript.

Note

The authors declare no competing financial interest.

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