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Effect of NH_3-Free Silicon Nitride for Protection Layer of Magnetic Tunnel Junction on Magnetic Properties of Magnetoresistive Random Access Memory

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1. Introduction

Magnetoresistive random access memory (MRAM) is the first candidate of non-volatile memory in the next generation. The core of memory bit consists of a magnetic tunnel junction (MTJ) with a tunnel dielectric layer sandwiched between magnetic layers as shown in Fig. 1. Since magnetic properties of the MTJ are degraded by moisture from inter-metal dielectric films and deteriorate at temperatures in excess of 300 ℃, a protection layer of the MTJ deposited below 300 ℃ is required [1-3]. Low-temperature silicon nitride (LT-SiN) film deposited using plasma-enhanced techniques is suitable for the protection layer of the MTJ [1]. However, we first observed the magnetic properties degradation of the MTJ free layer during the LT-SiN film deposition. In general, the LT-SiN film deposited below 300℃ tends to have low quality, resulting in higher leakage current [4]. The LT-SiN film with low leakage current is required.

In this study, we have observed degradation of the magnetic properties of the MTJ free layer by NH_3 plasma exposure and have investigated film characteristics of an NH_3-free LT-SiN film for the MTJ protection layer in MRAM. Finally, we demonstrate that electrical properties of 8-Kbit MRAM arrays have been improved by using the optimized NH_3-free LT-SiN film.

2. Experimental

LT-SiN films discussed in this paper were prepared in a conventional plasma-enhanced chemical vapor deposition (PECVD) apparatus. In order to evaluate the effect of plasma and precursors during the LT-SiN film deposition on magnetic properties of the CoFeB film, which is the MTJ free layer, four kinds of CoFeB blanket film were prepared. The first sample is non-exposed CoFeB blanket film as a control sample (Sample-A). The second, third, and fourth samples are CoFeB blanket films processed by NH_3 plasma (Sample-B), SiH_4 soak (Sample-C), and N_2 plasma (Sample-D), respectively. These three samples were processed at 275 ℃ using the PECVD apparatus. Kerr rotation angles (θ_{KLA}) were measured using magnetic optical Kerr effect (MOKE) method for the magnetic properties of these samples. In the MOKE measurement, magnetic fields were applied from –60 to 60 Oe in the direction parallel to the magnetic easy axis in the CoFeB film. Five points in each sample were measured. Compositions of the CoFeB film were measured using X-ray photoelectron spectroscopy (XPS).

To suppress the degradation of magnetic properties in the CoFeB film by the NH_3 plasma exposure, NH_3-free LT-SiN films were evaluated using SiH_4-N_2-He (He diluted) and SiH_4-N_2-Ar (Ar diluted) gas mixtures in temperature of 275 ℃. In both gas mixtures, the flow ratio of He or Ar gas flow rate to total gas flow rate was defined as R, and was optimized from 0 to 55 %. The leakage currents, compositions, atomic structures, and densities of the LT-SiN film were measured using a mercury probe method, XPS, Fourier transform infrared spectroscopy (FTIR), and X-ray reflectivity (XRR), respectively.

The effects of the optimized NH_3-free LT-SiN film on electrical properties for MRAM were evaluated using 8-Kbit MRAM arrays. In this evaluation, MR ratio, switching current deviation (3σ), low resistance deviation (3σ), and high resistance deviation (3σ) were compared between the NH_3-free LT-SiN film by SiH_4-N_2-He gas mixture and the conventional LT-SiN film by SiH_4-NH_3-N_2 gas mixture for the MTJ protection layer.

3. Results and Discussion

3.1 Effect of plasma and precursors during LT-SiN film deposition on magnetic properties of CoFeB film

Figure 2 shows the effect of plasma and precursors during the LT-SiN film deposition on magnetic properties of CoFeB film measured by MOKE method. The hysteresis loops of the Sample-B were not square in contrast with those of the Sample-A. This means that the NH_3 plasma exposure degrades the magnetic properties of the CoFeB film. The hysteresis loops of the Sample-C and -D were square in common with those of the Sample-A. The exposures of SiH_4 soak and N_2 plasma didn't cause the degradation of the magnetic properties of the CoFeB film. In order to investigate the degradation of the magnetic properties by the NH_3 plasma exposure, compositions of the Sample-B and -A were compared. The boron density of the Sample-B was less than that of Sample-A, and nitrogen was detected in the Sample-B. These results indicate that excited species in the NH_3 plasma diffuse boron from the CoFeB film and nitride the CoFeB film, resulting in distributions of the magnetic anisotropy in the CoFeB film. Therefore, the LT-SiN film deposition using NH_3 gas degrades the magnetic properties of the CoFeB film.

3.2 Film characteristics of NH_3-free LT-SiN film

Figure 3 shows leakage current versus R for the LT-SiN films using He diluted gas mixture and Ar diluted one. The leakage current of the film using He diluted gas mixture of R = 55 % decreased less than $1x10^{-9}$ A/cm^2. In the case of the Ar diluted gas mixture, leakage currents were as high as $1x10^{-3}$ A/cm^2 at all R points. From these results, highly dilute helium gas flow condition decreases leakage current of the film. The compositions of the films deposited at R = 0 % and R = 55 % in the He diluted gas mixture were compared. The N/Si ratios of the films of R = 0 % and R = 55 % were 1.00 and 1.22, respectively. Oxygen densities in the films of R = 0 % and R = 55 % were 15 at% and 0 at%, respectively. Since oxidation gases were not used in the LT-SiN film deposition, the film of R = 0 % was oxidized due to moisture absorption in the air. These results indicate that highly dilute helium flow condition prevents the LT-SiN film from the oxidation.

Figure 4 shows the Si-N stretching-mode frequency as a function of R for the LT-SiN films using He diluted gas mixture and Ar diluted one. The Si-N frequency decreased with increasing R in both gas mixtures, and the frequency of this mode in the film using He diluted gas mixture approached the frequency of 835 cm^{-1} that is found in Si_3N_4 film. These results indicate that helium dilution has an effect on the formation of the near stoichiometric Si-N bond network.

Figure 5 shows the dependence of the density of the LT-SiN films using He diluted gas mixture and Ar diluted one on R. The density increased with increasing R in both gas mixtures. The densities of the films using He diluted gas mixture were higher than those of the films using Ar diluted gas mixture at each R. These results indicate that helium dilution condition contributes to the deposition of the high density LT-SiN film. Therefore, we speculate that helium enhances nitridation of silicon source during the LT-SiN deposition and promotes the formation of near stoichiometric Si-N bond network, resulting in the deposition of higher density LT-SiN film.

Figure 6 shows the magnetic properties of the CoFeB film exposed by He plasma measured by the MOKE method. The hysteresis loops were almost equal to those of the non-exposed sample in Fig. 2 (A). From these results, SiH_4-N_2-He gas mixture exhibits non-degradation of the magnetic properties of the CoFeB film.

3.3 Effect of NH_3-free LT-SiN film on electrical properties

Figure 7 shows the comparison of electrical properties of the MTJ cells in 8-Kbit MRAM arrays between the NH_3-free LT-SiN film using He diluted gas mixture (R = 55 %) and a conventional LT-SiN film using SiH_4-NH_3-N_2 gas mixture for the MTJ protection layer. The MR ratio with the NH_3-free LT-SiN film was slightly higher than that with the conventional LT-SiN film. The Deviations of switching current (I_{sw}), low resistance (R_{low}), and high resistance (R_{high}) with the NH_3-free LT-SiN film were lower than those of the conventional LT-SiN film. From these results, the NH_3-free LT-SiN film improves the electrical properties of the MTJ cells.

4. Conclusion

We demonstrated that the NH_3 plasma exposure on the CoFeB film distributes the magnetic anisotropy of the CoFeB film. We have successfully obtained an NH_3-free LT-SiN film with low leakage current and high density using SiH_4-N_2-He gas mixture. For this process, the key technology is highly dilute helium gas flow condition. It is concluded that helium enhances nitridation of silicon source during the deposition and promotes the formation of near stoichiometric Si-N bond network. Finally, electrical properties of 8-Kbit MRAM arrays have been improved using the NH_3-free LT-SiN film for the protection layer of the MTJ.

Acknowledgements

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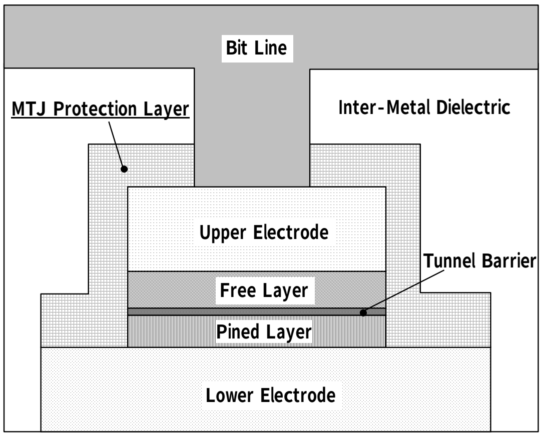

Fig. 1 Schematic Cross section of MTJ.

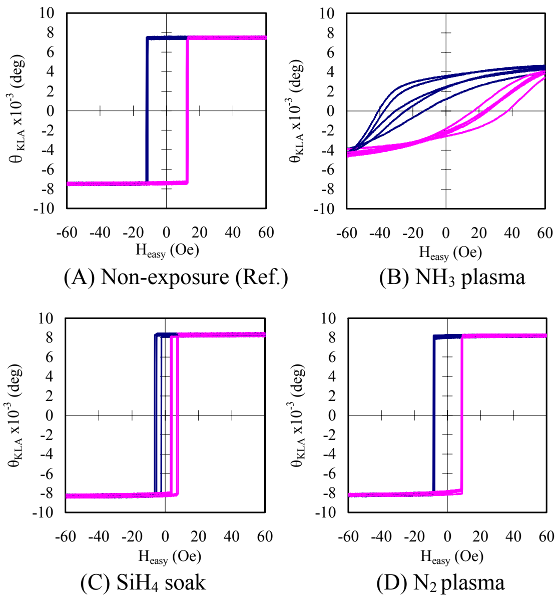

Fig. 2 Effect of the various exposures on the Kerr rotation angles of CoFeB films measured by MOKE method.

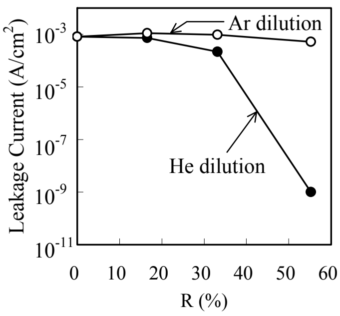

Fig. 3 Leakage current versus R for the LT-SiN films using SiH_4-N_2-He and SiH_4-N_2-Ar gas mixture.

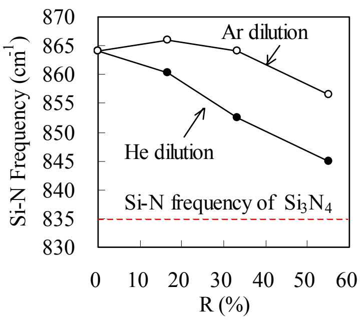

Fig. 4 Si-N stretching-mode frequency versus R for the LT-SiN films using SiH_4-N_2-He and SiH_4-N_2-Ar gas mixture.

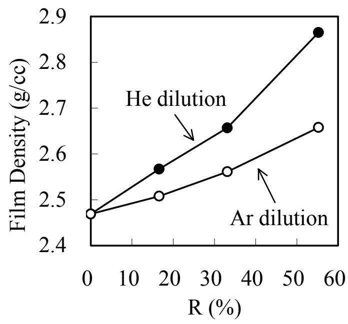

Fig. 5 Dependence of the density of the LT-SiN films using SiH_4-N_2-He and SiH_4-N_2-Ar gas mixtures on R.

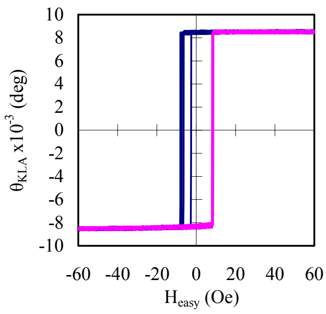

Fig. 6 Effect of the He plasma on the Kerr rotation angles of CoFeB film measured by MOKE method.

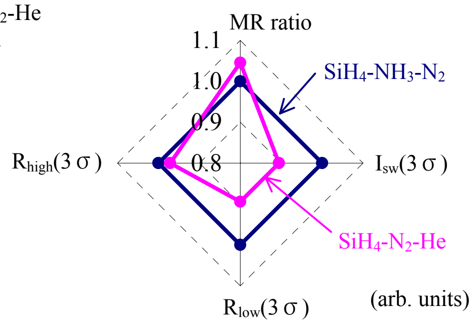

Fig. 7 Comparison of electrical properties of MTJ cells in the 8-Kbit MRAM arrays between the LT-SiN films using SiH_4-N_2-He and SiH_4-NH_3-N_2 gas mixture.