Applied voltage dependence of nano-oxidation of ferromagnetic thin films using atomic force microscope

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(Presented on 13 November 2002)

Nanodots of Ni, CoFe, and Cr oxide were fabricated by the nano-oxidation technique using atomic force microscope. The dot size was controlled from 40 to 200 nm by changing the pulse voltage applied to the cantilever from 2 to 10 V. In order to evaluate the size of the nanostructures quantitatively, the electric field emitted from the cantilever was calculated. The threshold electric field strength was defined as the minimum strength to promote the oxidation. The threshold field strength of the order of 10^7 V/m was derived by fitting the experimental results. The voltage dependence of the size of fabricated Cr-oxide dots was fitted well by the calculation. The dot size of the ferromagnet-based oxide was fluctuating and did not agree with the calculation. From the theoretical analysis, it was suggested that the size of the nanostructures did not depend on the distance between the cantilever and film surface, but significantly depended on the curvature radius of the cantilever. © 2003 American Institute of Physics. [DOI: 10.1063/1.1540046]

I. INTRODUCTION

Recent progress in lithography techniques has enabled us to fabricate nanoscale devices and observe quantum effects in nanostructures of magnetic materials as well as other electronic materials. Nanoscale fabrication techniques are significant for developments of magnetic devices such as high-density recording system, memories, and spin-related devices. The scanning probe microscopes (SPMs) such as the scanning tunneling microscope and atomic force microscope (AFM) have recently attracted much attention for fabricating electron devices with well-defined structures of a nanometer scale. The surface of metal thin film is selectively oxidized by applying a negative bias on the SPM tip. This anodic oxidation process is an electrochemical reaction between metals and water in air. As this fabrication technique does not require any pretreatments such as resist coating, it is a useful tool for direct modification of metal surface.¹⁻⁴

We have proposed planar-type magnetic tunnel junctions (MTJs) whose junction areas are smaller than those of the conventional multilayer-type MTJ.⁵ In a small MTJ with its charging energy larger than thermal energy, the tunnel magnetoresistance (TMR) is enhanced by Coulomb blockade.⁶⁻⁹ The planar-type MTJ is also advantageous because it allows a three-terminal configuration. The third electrode of the gate can control the current-voltage and TMR characteristics.¹⁰ Fabrication of a single electron transistor (SET) based on the planar-type tunnel junction by the AFM nano-oxidation technique has recently been reported. The electrical property related to the Coulomb blockade effect has been observed at room temperature.¹¹ The AFM nano-oxidation is a key technique to fabricate the barrier region of planar-type junctions.

The nano-oxidation of ferromagnetic thin films is studied in this article.

II. EXPERIMENTS

Figure 1(a) shows the schematic of the AFM nano-oxidation process. When a negative-biased voltage is applied

FIG. 1. Schematics of the nano-oxidation process using AFM (a) and planar-type Ni/Ni-oxide-based MIM diode (b). AFM topographic image (c) and current mapping image (d) of nanodot of Ni-oxide fabricated by AFM nano-oxidation.

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FIG. 2. Diameter of fabricated nanodots of Ni oxide (open circle) and CoFe oxide (solid circle) as a function of applied voltage to the cantilever. Solid and dotted lines indicate calculated values.

to the conductive AFM cantilever, the anodic oxidation of the electrochemical reaction between metals and water in air is promoted, resulting in the formation of the nanostructure of the oxide. We have reported the nano-oxidation of Ni (Ref. 12) and NiFe (Ref. 13) thin films as preliminary results on ferromagnetic thin films. By scanning the biased cantilever, the nanowire of oxide is fabricated, which can be utilized for the barrier region of planar-type MTJ [Fig. 1(b)]. The width of the nanowire of oxide is significant as the barrier width in MTJ. It is controlled by changing the scanning speed, applied voltage, thickness of the as-deposited metal thin films, and atmosphere (humidity).¹⁴ Among them, the applied voltage to the cantilever is a primary parameter. In order to exclude effects of other parameters, nanodots of oxide were fabricated by applying a pulsed voltage. The voltage dependence of their size was studied. Theoretical analysis was also performed by calculating the electric field emitted from the cantilever to the film surface.

Ni, CoFe, and Cr thin films of 20 nm thickness deposited on SiO₂/Si insulating substrates by rf magnetron sputtering were oxidized using the AFM nano-oxidation technique. The cantilever of Si₃N₄ coated with Au was used. Nanodots of oxide were fabricated on these films by applying the pulsed voltage of 100 ms duration to the AFM cantilever in normal air. Figure 1(c) shows the AFM topographic image of a fabricated nanodot of Ni oxide. In order to evaluate the conductivity of the nanodot, the current mapping image was measured using the AFM under the constant voltage mode. The insulating property of the nanodot due to oxidation was confirmed, as shown in Fig. 1(d).

III. RESULTS AND DISCUSSION

The diameters of the fabricated nanodots of Ni oxide (indicated by open circles) and CoFe oxide (solid circles) are plotted as a function of the applied pulse voltage to the AFM cantilever in Fig. 2. With increasing the applied voltage, the diameter was increased in the range from 40 to 200 nm. The nanostructures of the oxide were not obtained at applied voltage below 3 V for Ni and 2 V for CoFe thin films, respectively. The electric field emitted from the cantilever to film

FIG. 3. Diameter of fabricated nanodots of Cr oxide as a function of applied voltage to the cantilever. Solid and dotted lines indicate calculated values.

surface was calculated in order to evaluate these results quantitatively, as shown in the inset of Fig. 4. The curvature radius of the cantilever of 20 nm was assumed, which was a typical value of commercial products used in this study. The perpendicular distance between the cantilever and film surface was assumed to be 1 nm. Threshold electric field, E_t , is defined as a minimum field strength to promote the electrochemical reaction of nano-oxidation. The diameter of the nanodots of the oxide was calculated as functions of applied voltage and threshold electric field of E_t as parameters. Experimental results for Ni- and CoFe-oxide nanodots could be fitted with the calculation using E_t from 5×10^6 to 5×10^7 V/m. Figure 3 shows the experimental results on nano-oxidation of Cr thin films. The Cr oxide was not obtained at the applied voltage below 3 V. The diameter of the nanodots of Cr oxide was also increased with increasing the applied voltage. Its voltage dependence was fitted well with

FIG. 4. Electric field strength at the film surface calculated for various distances between the cantilever and film surface. Inset shows the schematic of the model for calculation of electric field emitted from the cantilever to the film surface.

the calculation using E_t around 4×10^7 V/m. Figure 4 shows the electric field strength at the film surface under the applied voltage of 5 V plotted as a function of the in-plane distance from the position of the cantilever. The electric field was calculated for three cases of different perpendicular distances between the cantilever and film surface, noted as d in the inset of Fig. 4. It is found that the diameter of the nanodots of the oxide does not strongly depend on the perpendicular distance between the cantilever and film surface for $E_t = 4 \times 10^7$ V/m. This independence partially contributes to the good uniformity in the diameter of Cr-oxide dots.

The applied voltage dependence of the diameter of Ni- and CoFe-oxide nanodots was fluctuating and could not be fitted by the calculation using any constant values of E_t as shown in Fig. 2. It was presumably attributed to the Lorentz force generated at the surface of the ferromagnetic thin films. When the current flows from the cantilever to the ferromagnetic metal surface, the cantilever is forced by the Lorentz force. The position of the cantilever is possibly shifted towards both the in-plane and perpendicular directions to the film surface, which results in the fluctuation of the diameter of nano-oxide dots. The smaller threshold field for Ni and CoFe is another cause of the poor uniformity in size. E_t of around 1×10^7 V/m for nano-oxidation of Ni and CoFe is derived from Fig. 2, whereas E_t is about 4×10^7 V/m for that of Cr. The diameter of nanodots fabricated under E_t of 1×10^7 V/m strongly depends on the perpendicular distance between the cantilever and film surface, as shown in Fig. 4. This dependence, cooperated with the cantilever shift by the Lorentz force, degrades the uniformity in size of ferromagnet-based nano-oxides.

The minimum diameter of the nanodots obtained in this study was 40 nm for CoFe oxide at the applied voltage of 2 V. Figure 5 shows the electric field at the film surface calculated using different curvature radius of the cantilever, R_c , under the applied voltage of 2 V. The perpendicular distance between the cantilever and film surface was assumed to be 1 nm. The calculation suggests that the size of nanodots as small as a few nm can be fabricated with using the cantilever of $R_c = 1$ nm, which is achieved by using a cantilever with a carbon nanotube.

IV. CONCLUSION

Nanodots of NiFe, CoFe, and Cr oxides were fabricated by the AFM nano-oxidation technique. The dot diameter was

FIG. 5. Electric field strength at the film surface calculated for various curvature radii of the cantilever.

increased with increasing the applied voltage to the cantilever. The voltage dependence of the diameter agreed with the calculation by introducing the threshold electric field. The size of the fabricated Cr-oxide dots exhibited a good uniformity, and its voltage dependence was fitted well by the calculation. The dot size of Ni- and CoFe-based oxides fluctuated. Theoretical analysis suggested that the size of the nanostructures did not depend on the distance between the cantilever and film surface, but significantly depended on the curvature radius of the cantilever.

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