Measurement of faradaic current during AFM local oxidation of magnetic metal thin films

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Abstract. Faradaic current during a local oxidation using an atomic force microscope was studied. The intensity of the measured faradaic current was increased with increasing bias voltage applied to a cantilever, resulting in fabrication of larger size of nano-oxide structures on Si substrates. On the other hand, an excess current (over current) that was considered not to contribute the oxidation reaction was observed noticeably in the local oxidation of NiFe thin films. It was found that the excess current could be suppressed by depositing insulating oxide layers on the surfaces. The surface oxide layers were also advantageous for stable existence of meniscus promoting the local oxidation because of their hydrophilic properties. This method of capped oxide layers is significant for stable performance of the local oxidation technique fabricating nanostructures and nano-devices.

1. Introduction

Lithography techniques using scanning probe microscopes have attracted much interest as novel tools for fabricating well-defined nanoscale devices and materials [1]. When negative-biased voltage is applied to a conductive atomic force microscope (AFM) cantilever, a metal thin film is oxidized locally by an electrochemical reaction between the metal and water in air. This anodic oxidation process is an electrochemical reaction between metal 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 semiconductor and metal surfaces. The fabrication of magnetic nanostructures is significant for developments of magnetic devices such as high-density recording system, memories and spin-related devices.

Size of fabricated nano-oxide depends on applied voltage to a conductive cantilever, which can be explained by introducing the threshold electric field for promoting oxidation [2]. A volume of the oxide can be theoretically deduced by integrating reaction current, called faradaic current specifically in this case, with time. Recently, Kuramochi et al. reported that the current was successfully measured and that the volume of fabricated nanodots of oxide agreed with the integrated current value [3]. In this paper, we report the measurement of faradaic current during the fabrication of nano-oxide with Si substrates and NiFe thin films.
2. Faradaic current during AFM local oxidation

2.1. Measurement of faradaic current
Nano-oxidation was performed by AFM equipment in an ambient air. The humidity was around 60%. A conductive cantilever coated with Au was used [2,4]. The vertical position of the cantilever was kept constant by maintaining the atomic force reference at 0.2 nN. The dc voltage from 6 V to 10 V was applied to the cantilever. A faradaic current during the nano-oxidation was measured. Nanowires of Si were fabricated by scanning the cantilever at 10 nm/s as shown by the AFM image of Fig. 1(a). P-type Si substrate of 9-12 Ωcm resistivity with a native oxide layer on the surface was used. The applied voltage to the cantilever was 8 V in this experiment. The width and height of the fabricated nanowires of oxide were about 150 nm and 3 nm, respectively. In order to confirm that the measured current was related to the oxidation, five nano-wires were fabricated sequentially from (1) to (5) as indicated in the figure [3]. Figure 1(b) shows the current-time sweep during the fabrication of 4th nano-oxide wire. The current of the order of 0.1 pA was successfully measured during the oxidation. When the cantilever crossed over the existing nano-oxide wires indicated by (1), (2) and (3) in Figs. 1(a) and 1(b), the current was drastically reduced to below 0.02 pA. This can be understood that the surface with the nano-oxide wires is not further oxidized. As it is observed that the height of the oxide at the crossing positions of nanowires is slightly higher than that at the single nanowires, the low current is detected at the crossing points due to the oxidation. From these results, it can be concluded that the detected current is attributed to the local oxidation and that the leak current, which is not related to the oxidation, is suppressed below the order of 0.01 pA.

2.2. Faradaic current during nano-oxidation of Si substrates
Nanodots of oxide were fabricated by applying pulse voltage to a cantilever. The sample was p-type Si substrate with a native oxide. Duration of the pulse was 50 s. Both of diameter and height of the fabricated nanodots were increased by increasing the applied voltage as shown by the AFM image in Fig. 2(a). Figure 2(b) shows the measured faradaic current during the oxidation. The current intensity was 0.1 to 0.5 pA, which became larger with increasing the applied voltage from 6 to 9 V. The waveform of the current indicates that the current decayed with time during the constant applied voltage for 50 s. The amount of charge actually supplied from the tip to the sample surface can be deduced by integrating the current waveform with time. On the other hand, the amount of charge that is attributed to the oxidation reaction can be calculated from the volume of the fabricated oxide. In this study the depth of the oxidized nanodot is assumed to be equivalent to its height. It has been confirmed that height and depth of nano-oxide fabricated by the AFM local oxidation are almost equivalent by etching the nano Si oxide. Figure 2(c) shows the relationship between the integrated charge (actually transferred from the tip) and calculated charge (attributed to the oxidation). In case that all of the detected current is used for the oxidation reaction, the integrated charge should be equivalent to the calculated charge. But, the figure indicates that the nearly half of the detected current is actually used for the oxidation. The dotted line in
the figure shows the current efficiency rate of 50%, which means the half of the current is attributed to the oxidation.

We have noticed that size of fabricated nanodots strongly depends on surface conditions of the films [5]. As for the surfaces covered with oxides, i.e. a Si substrate with native oxide and a metal surface capped with a thin oxide layer, their hydrophilic properties promote the local oxidation and the capped insulating layers reduce an influence of attractive Coulomb force between the tip and the conductive samples. Figure 3(a) shows the AFM image of nanowires of oxide fabricated on p-type Si substrate with native oxide on the surface. The cantilever was scanned at 10 nm/s. The width and thickness of the nanowires were increased with increasing the applied voltage to the cantilever. Figure 3(b) shows the detected current during the local oxidation of these nanowires. The current intensity was almost constant during the oxidation and was larger in the higher applied voltage. Figure 4(a) and 4(b) show the results on the similar experiment using a hydrogen-passivated p-type Si substrate. It was prepared with a buffered HF solution and the surface exhibited hydrophobic. The nanowires of oxide were successfully fabricated and their width and height depended on the applied voltage as similar to the p-type Si case with native oxide. But, the measured current was fluctuated during the oxidation. There was no correlation between the applied voltage and the current intensity. The fluctuated current was due to the conductive sample surface. It allows a current pass through the sample, which is not attributed to the local oxidation.

2.3. Faradaic current during nano-oxidation of NiFe thin films

The AFM local oxidation and measurement of faradaic current were also performed with NiFe thin films. The Ni$_{0.8}$Fe$_{0.2}$ thin films of 30 nm thickness were prepared on SiO$_2$/Si substrates by RF magnetron sputtering equipment. Figure 5(a) shows the AFM image of fabricated nanowires of oxide on NiFe thin films. Although the fabrication of nano-oxide structures on magnetic thin films was successfully achieved [2,4,5], the obtained result in this experiment was peculiar in the correlation between the AFM image and the measured current. Figure 5(b) shows the measured current during the oxidation. The current intensity of 200 to 500 nA was accidentally detected for the applied voltage of 6 V, but the fabrication of nano-oxide was not observed. This current of the order of nA-µA is an excess current (over current) that is considered not to contribute the oxidation reaction. NiFe thin films covered with Al$_2$O$_3$ cap layers were prepared. After depositing Al layers on the sputtered NiFe thin films of 30 nm thickness, the surface Al layers were oxidized in air. The thickness of the Al$_2$O$_3$ layer was 2.6 nm. The nanowires of oxide could be successfully fabricated on the Al$_2$O$_3$/NiFe thin film with all the employed applied voltage as shown in Fig. 6(a). The current intensity detected during the oxidation was varied from 0.03 pA (6V) to 1.5 pA. as shown in Fig. 6(b).
excess current of the order of nA measured in the oxidation of the NiFe film was not observed with the Al₂O₃/NiFe thin film. In case of the applied voltage of 6 V, the detected current intensity was 0.03 pA. This current intensity was enough for the fabrication of the nano-oxide wire of 50 nm width. Although

Fig. 3  AFM image of nanowires of oxide fabricated on p-type Si substrate (a) and measured faradaic current during local oxidation (b).

Fig. 4  AFM image of nanowires of oxide fabricated on H-passivated Si substrate (a) and measured faradaic current during local oxidation (b).

Fig. 5  AFM image of nanowires of oxide fabricated on NiFe thin film (a) and measured faradaic current during local oxidation (b).

Fig. 6  AFM image of nanowires of oxide fabricated on NiFe thin film capped by Al₂O₃ (a) and measured faradaic current during local oxidation (b).
most of the measured current during the oxidation at 7-10 V were not attributed to the oxidation, it was found that the surface oxide layer could suppress the excess current and realize stable performance of the local oxidation. The hydrophilic oxide layers supply stable meniscus on the sample surfaces, which promotes the local oxidation.

3. Conclusions
The faradaic current during the AFM local oxidation was studied. The measured current was due to the oxidation and the current intensity was increased with increasing the applied voltage to the cantilever. As for the local oxidation of p-type Si substrate with native oxide on the surface, the half of the detected current was used for the oxidation reaction. The excess current (over current) that was considered not to contribute the oxidation reaction was observed in the local oxidation of the samples with conductive surfaces. As for the samples covered with surface oxide layers, i.e. Si substrate with native oxide and NiFe thin film capped with thin Al₂O₃ layer, the excess current was suppressed. These surface oxide layers were also advantageous for stable oxidation because of their hydrophilic properties.

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