Effect of Irradiation Atmospheres on the Film Growth of Iron Oxide on Si Substrate by Ion Beam Sputter Deposition Method

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(Received October 2, 2019)

Fe3O4 thin films of approximately 30 nm in thickness were grown on Si substrate at 573 K by means of ion beam sputter deposition (IBSD) technique, using oxygen or argon ions to sputter Fe3O4 solid target. The effect of these irradiation atmospheres on the chemical composition and crystallinity of the thin films was investigated using XPS (X-ray Photoelectron Spectroscopy), RHEED (Reflection High-Energy Electron Diffraction) and XRD (X-Ray Diffraction). We revealed that the oxygen atmosphere improves the crystallinity of the film as compared with argon atmosphere, but also causes the formation of iron oxide phases other than Fe3O4. On the other hand, the obtained results for Fe3O4 thin films prepared in argon atmosphere had poor crystallinity. Furthermore, the results of RHEED suggested that the preferential growth orientations of the film are different depending on the irradiation atmospheres.

1. Introduction

To deposit various materials on a Si substrate is of primary importance for various technological applications [1,2,3]. As such, Si based spintronics is a promising technology, where magnetic materials are deposited on Si, leading to development of next-generation devices which utilize both electronic charge and spin [4]. As a spintronics device material, Fe3O4 (magnetite) has a high Curie temperature of about 860 K, and since it is a half metal, it is theoretically predicted to have a 100% spin polarization near the Fermi level [5]. Many studies on high-quality thin film of Fe3O4 fabricated on single crystal metal oxide substrates, such as SrTiO3 [6], Al2O3 [7], MgO [8] and ZnO [9], have been reported. It is also formed on a semiconductor substrate, such as GaAs [10] and InAs [11]. There are also some reports on the fabrication of Fe3O4 thin films on Si substrates, but they are not so many [12, 13]. One likely reason may be that Si is more reactive than oxide substrates and may react with oxygen atoms in Fe3O4 to disturb the growth of high-quality thin film. Tiwari et al. reported that they grew highly (111)-oriented Fe3O4 film on a Si (100) substrate by PLD (Pulsed Laser Deposition) method [12]. The same result was obtained by Boothman et al. who employed DC magnetron sputtering method [13]. In the latter method, the film formation was conducted under the flow of O2 gas, so that oxygen may form oxide on the substrate. In fact, Boothman et al. refer to the presence of amorphous oxide layer between film and the substrate. In addition, it is well known that iron oxides form phases other than Fe3O4, so that precise control of oxygen partial pressure and temperature is necessary [14] to obtain single crystalline film. During ion beam sputter deposition (IBSD), irradiation atmosphere is governed by the residual gas flowing from the ion source, which reaches around 10−5 Pa. According to residual gas analysis with
a quadrupole mass spectrometer in this study, it is assumed that changing ion beams from oxygen (O$_2^+$) to argon (Ar$^+$) decreases oxygen partial pressure in the deposition chamber from 10$^{-5}$ Pa to < 10$^{-7}$ Pa. In other words, the IBSD method is an ideal technique to investigate the effect of irradiation atmospheres on the film growth processes on a substrate material. In this paper, as a preliminary study to understand the effect of chemical atmosphere on the complicated growth mechanism of Fe$_3$O$_4$ films on Si (100) substrate, the present study compares the properties of the film fabricated under oxidizing and reducing conditions.

2. Experimental

The ions are generated in the RF plasma ion source and transported through the beamline port equipped with mass-analyzing magnet, with the extraction voltage of around 35 kV. The ions then sputter the solid target facing the substrate. The ion irradiations were conducted at room temperature, where the ion flux can be varied by changing extraction voltage and/or ion current density. The target material employed in this study is a sintered compound of Fe$_3$O$_4$, which is installed in the vacuum vessel whose ultimate pressure is 3 × 10$^{-7}$ Pa. The thin films of Fe$_3$O$_4$ was fabricated as follows. A Si (100) disc specimen (The Nilaco Corporation) was cut into 1 cm × 1 cm in size, then cleansed in acetone and mounted on the sample holder in a vacuum vessel to be used as a substrate. This substrate was degassed at 973 K, which was radiatively heated by a tungsten filament and cooled down to room temperature. The temperature was measured with a pyrometer. After degassing, the substrate was irradiated with Ne$^+$ ions accelerated at 3 kV for 10 min at an ion current density of 1 μA cm$^{-2}$ in order to remove surface oxides and other impurities [15], followed by thermal annealing at 1073 K for 30 min to recover the crystallinity of the substrate irradiated by ion beam. Through this procedure, the Si (100) 2 × 1 pattern is confirmed by RHEED (Reflection High-Energy Electron Diffraction). On this substrate, Fe$_3$O$_4$ was deposited using O$_2^+$ ion beam (sample A) or Ar$^+$ ion beam (sample B). The substrate temperature was set between 473 and 773 K in a preliminary experiment by referring to Ref. 12, and it was found that the depositions at 573 K gave the best results with respect to RHEED measurements. The oxygen partial pressure was around 3×10$^{-6}$ Pa for sample A and < 10$^{-7}$ Pa for sample B. The film thickness measured by quartz thickness monitor was 30 nm for both samples. In addition to RHEED measurements, some film samples were taken out of the vacuum vessel for XRD (X-Ray Diffraction) and XPS (X-ray Photoelectron Spectroscopy) measurements to further investigate crystal structure and chemical composition of the film, respectively.

3. Results and Discussion

3.1 Growth orientation

Figure 1 represents 0-20 XRD patterns for sample A and B using Cu-K$\alpha$ as the source. The XRD patterns show significant difference between the two samples. In particular, the diffraction peaks of Fe$_3$O$_4$ (222) and (333) planes were observed at 2θ = 34° and 56°, respectively, in the spectrum of the sample deposited with the O$_2^+$ ion beam. Therefore, it is suggested that the Fe$_3$O$_4$ (111) phase is preferentially grown on Si (100) substrate. This result is similar to that reported in Refs. 12 and 13 as mentioned in a previous section. However, the intensity of diffraction peak is weak and its width is wide, so that the crystal size is considered to be small. In sample A, while preferential growth of Fe$_3$O$_4$ (111) is confirmed, growth of α-Fe$_2$O$_3$ phase is also observed, the formation of Fe$_3$O$_4$ phase together with Fe$_3$O$_4$ is not reported in the literature. On the other hand, no XRD peak corresponding to Fe$_3$O$_4$ was observed when the film is fabricated with the Ar$^+$ beam, indicating that the film is not sufficiently crystallized.
3.2 Chemical compositions

Figure 2 shows the Fe2p XPS spectra for sample A and B. XPS spectra show no significant difference between these samples, while XRD showed a difference in the pattern for both samples. Both position of Fe2p1/2 and Fe2p3/2 in Fig. 2 is identical to the result reported in Ref. 17. The obtained results indicate that they contain Fe3O4 on the surface of deposited film. The fact that no peaks corresponding to Fe2O3 were observed may indicate that Fe2O3 exists in deeper region towards the film / substrate interface.
3.3 Surface crystallinity

The RHEED pattern corresponding to Si (100) 2 × 1 structure was observed to soon disappear after 3 nm of film deposition for both samples. After we deposited 15 nm of films, the streak patterns were observed. Figures 3 (a) and (b) are the RHEED patterns for sample A and B, respectively, where the direction of incident electron beam is parallel to Si <0-11>. When the film was formed with an O\textsuperscript{2-} ion beam, a pattern in which bright and wide streaks and dark and narrow streaks appear alternately was observed. On the other hand, only a streak with the same width and brightness was observed when the film was formed with an Ar\textsuperscript{+} beam, although the XRD peaks corresponding to Fe\textsubscript{3}O\textsubscript{4} were very weak in intensity. The distances between the streaks in A and B were different. Although we did not find in literature which shows clear RHEED patterns of Fe\textsubscript{3}O\textsubscript{4} fabricated on Si substrate, Fig. 3(a) is similar to that of a (111)-oriented Fe\textsubscript{3}O\textsubscript{4} film on α-Al\textsubscript{2}O\textsubscript{3} substrate (e-beam // Fe\textsubscript{3}O\textsubscript{4} <110> [16]). So we consider that Fe\textsubscript{3}O\textsubscript{4} thin film grows preferentially along (111) direction on Si (100) under the condition of O\textsuperscript{2-} ion beam irradiation as confirmed by XRD. On the other hand, the pattern shown in Fig. 3 (b) was similar to that of Fe\textsubscript{3}O\textsubscript{4} (111) on α-Al\textsubscript{2}O\textsubscript{3} substrate (e-beam // Fe\textsubscript{3}O\textsubscript{4} <=211>). At present, it can be said that growth direction of the sample B may be different from that of sample A.

![Fig.3 RHEED pattern for (a) sample A (b) sample B](image)

4. Conclusion

We employed IBSD method to fabricate thin film of Fe\textsubscript{3}O\textsubscript{4} (magnetite) on Si (100) substrate, under two different kinds of ion irradiation atmospheres to sputter Fe\textsubscript{3}O\textsubscript{4} target. It was expected that choice of ion beam will change the chemical atmosphere of film formation. The results of XRD, RHEED and XPS measurements revealed that when O\textsuperscript{2-} beam was employed in IBSD the Fe\textsubscript{3}O\textsubscript{4} phase was observed to grow preferentially in (111) direction, but also accompanied by Fe\textsubscript{2}O\textsubscript{3} phase. In other words, while an employment of O\textsuperscript{2-} ion beam during IBSD process improved the crystallinity of film, it also caused excessive oxidation of film. Therefore, it may be difficult to fabricate single phase Fe\textsubscript{3}O\textsubscript{4} films by O\textsuperscript{2-} ion beam irradiation without more precise control of chemical atmosphere. On the other hand, when Ar\textsuperscript{+} ion beam was employed so that the film deposition was performed in more reducing conditions, the formation of Fe\textsubscript{3}O\textsubscript{4} phase was considered to be very small. The observed difference in the crystal structures and chemical compositions of the films may indicate that sufficient supply of oxygen is needed to form highly crystalline Fe\textsubscript{3}O\textsubscript{4} phases on Si substrate.

Acknowledgment

Authors would like to acknowledge Dr. S. Sakai of QST and Prof. H. Udono of Ibaraki University for fruitful discussions.
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