Magnetic properties of weak itinerant ferromagnetic $\zeta$-Fe$_2$N film

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Abstract

We have studied magnetic properties of $\zeta$-Fe$_2$N film deposited onto surface-oxidized Si (100) substrates by reactive dc magnetron sputtering with an argon–nitrogen atmosphere. At the temperature less than 120 K, the magnetic moment of the 120 nm-thick $\zeta$-Fe$_2$N film is hard to be saturated at magnetic fields up to 50 kOe, and the magnetic moment is weak. The inverse susceptibility linearly increases as the temperature increases between 65 and 160 K, and the change of the inverse susceptibility obeys the Curie–Weiss law. From the results of magnetization measurements, the magnetic parameter of the Curie temperature, the spontaneous magnetic moment at 0 K and the effective magnetic moment can be estimated to be 35 $^\circ$2.5 K, 0.028 $\mu_B$/iron atom and 0.70 $\mu_B$/iron atom, respectively. These parameters suggest that the $\zeta$-Fe$_2$N film is in the weak itinerant electron ferromagnetic state. These parameters can be also explained by self-consistently renormalization (SCR) theory.

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1. Introduction

Various iron nitride phases such as $\alpha'$-Fe$_x$N ($x \geq 8$), $\alpha''$-Fe$_{16}$N$_2$, $\gamma'$-Fe$_x$N, $\epsilon$-Fe$_x$N ($2 < x \geq 3$), $\zeta$-Fe$_2$N and FeN and their different magnetic properties have been reported in nano-order thin films and the fine powders [1--9]. The $\epsilon$-Fe$_x$N ($2 < x < 2.3$) [5], $\zeta$-Fe$_2$N [6--8] and FeN [8,9] phases are paramagnetic at the room temperature, but possesses the different magnetic state at the low temperature. The FeN phase with the NaCl-type crystal structure is an antiferromagnet whose Neél temperature is near a room temperature. The Fe$_x$N phase with the ZnS-type crystal structure is also non-magnetic over the whole temperature. The $\epsilon$-Fe$_x$N ($2 < x < 2.3$) phase is ferromagnetic below the room temperature, and the Curie temperature decreases as the iron content $x$ decreases. For the $\zeta$-Fe$_2$N phase, the different magnetic states have been reported: the $\zeta$-Fe$_2$N powder is an antiferromagnet whose Neél temperature is 9 K [9], while the powder and the film of $\zeta$-Fe$_2$N phase are weak itinerant electron ferromagnets, and the Curie temperatures of the film are higher than that of the powder [5,6]. The difference of the Curie temperature must be caused by the deviation from the stoichiometry in the $\zeta$-Fe$_2$N film as reported in Ref. [6]. In this study, we investigate the film structure and magnetic state of the $\zeta$-Fe$_2$N film prepared by the reactive dc magnetron sputtering using the mixture gas of argon and nitrogen. We measured the temperature dependence of the magnetic properties, determined the spontaneous magnetic moment at 0 K and the effective magnetic moment of the $\zeta$-Fe$_2$N film which were not determined in Ref. [6], and compared them with the reported values of the powder [5] and the film [6] of the $\zeta$-Fe$_2$N phase. The magnetic parameters also compare with those of the several typical itinerant electron magnetic materials [10--13].
the argon and the nitrogen gases were settled at 12 and 10 sccm (standard cc/min), respectively. The sputtering target was iron (3N5) disc (38.5 mm in a diameter and 1.0 mm in thickness). The sputtering power was 20 W. The deposition rate of the iron nitride films was 0.04 nm/s. The film thickness was fixed at 120 nm.

The structure of the iron nitride film was investigated by using an X-ray diffractometer (XRD) with Cu-Kα radiation and a transmission electron microscope (TEM). The composition of the iron nitride film was measured by using an X-ray photoelectron spectroscopy (XPS). The magnetization curves of the iron nitride film were measured by using a superconducting quantum interference device (SQUID) magnetometer with a maximum magnetic field of 50 kOe in the film plane. Changes of the magnetization with the temperature were also determined by using a SQUID magnetometer with the applied magnetic field of 10 kOe in the film plane. The magnetic properties were measured at the temperature range between 10 and 300 K.

3. Results

Fig. 1(a)–(c) show the high-angle X-ray diffraction profile, the electron diffraction pattern and the dark-field image by the diffraction ring of (121) and (102) planes for the 120 nm-thick iron nitride film. In Fig. 1(a), each broken line indicates the peak position of (102), (121), (202) and (221) planes derived from the \( \zeta \)-Fe\(_2\)N phase (\( Pbcn \), \( a = 0.44346 \) nm, \( b = 0.554 \) nm and \( c = 0.4842 \) nm), as reported in Ref. [14]. The (121) plane of the \( \zeta \)-Fe\(_2\)N phase is the close-packed plane (because the space group of this phase is \( Pbcn \)). As seen in Fig. 1(a), the diffraction peaks are observed at 2\( \theta \) of 42.7 and 56.3°. The diffraction line of the peak at 2\( \theta \) of 42.7° is symmetric. The peak at 42.7° corresponds to either (102) or (121) plane of the \( \zeta \)-Fe\(_2\)N phase. The diffraction line of the peak at 2\( \theta \) of 56.3° is asymmetric. The peak at 56.3° is caused by the overlap of two different peaks of the (202) and the (221) plane in the \( \zeta \)-Fe\(_2\)N phase. From this result, the structure of the 120 nm-thick iron nitride film is considered to be the structure of \( \zeta \)-Fe\(_2\)N phase.

The electron diffraction pattern reveals that the diffraction rings of (102), (121), (202) and (221) deriving from the \( \zeta \)-Fe\(_2\)N phase can be also observed as shown in Fig. 1(b). The existence of the \( \zeta \)-Fe\(_2\)N phase is coincident with that of the X-ray diffraction measurement. A lot of other diffraction rings resulting from the \( \zeta \)-Fe\(_2\)N phase can be also confirmed. In addition, the electron diffraction rings derived from the FeO phase can be observed. However, the FeO phase cannot be observed in the X-ray diffraction profile, probably because the FeO phase is not formed at the film deposition process but at the preparation process of the plane-view TEM specimen. From these results, it is apparent that the 120 nm-thick iron nitride film prepared in the present study is the polycrystalline \( \zeta \)-Fe\(_2\)N single phase. Henceforward, the specimen prepared in the present study is described as the \( \zeta \)-Fe\(_2\)N film.

As to the crystal grain size of the \( \zeta \)-Fe\(_2\)N film, the grain of various sizes is also found to distribute in the film plane widely (Fig. 1(c)). The average grain size can be estimated by using Fig. 1(c), and is around 20 nm.

Fig. 2 shows the magnetization curves of the \( \zeta \)-Fe\(_2\)N film at the various temperatures. The magnetic field is applied in the film plane. Above 120 K, the magnetization monotonically increases as the magnetic field increases. On the other hand, below 80 K, the magnetization curves cannot be saturated with the maximum magnetic field of 50 kOe. The magnetization is also enhanced as the temperature
decreases. This suggests that the magnetic state of the \( \zeta \)-Fe\(_2\)N film changes from a paramagnetic state to a ferromagnetic state as the temperature decreases. The behavior of the magnetic state in the \( \zeta \)-Fe\(_2\)N film is very similar to the results of Ref. [6,7], and can be considered to be due to the weak itinerant electron magnetic state.

In order to clarify that the magnetic state of the \( \zeta \)-Fe\(_2\)N film is in a weak itinerant electron ferromagnetic state, the most important magnetic parameters such as the Curie temperature, spontaneous magnetization, Curie constant and effective magnetic moment must be evaluated in detail. At first, the Curie temperature and spontaneous magnetization can be evaluated by using the \( M^2 - H/M \) plot (Arrott-plot) [15], as shown in Fig. 3. Each solid line indicates the extrapolation line to the \( M^2 - H/M \) plot. The intersection of the extrapolation line with the \( M^2 \)-axis changes from the negative side to the positive side at the temperature of 35 K, which is the Curie temperature of the \( \zeta \)-Fe\(_2\)N film. The spontaneous magnetization of the \( \zeta \)-Fe\(_2\)N film determined from the positive intersection with the \( M^2 \)-axis monotonically decreases as the temperature increases. Based upon the self-consistently renormalization (SCR) theory [16,17] for a weak itinerant electron ferromagnet, the linear relation seen in Fig. 4 suggests that the \( \zeta \)-Fe\(_2\)N film exhibits the weak itinerant electron ferromagnetic state. By the extrapolation of the straight line to \( T = 0 \) in Fig. 4, the spontaneous magnetization at 0 K can be estimated, and is 0.028 \( \mu_B \) per an iron atom where the \( \mu_B \) is Bohr magnetron.

Next, in order to estimate the Curie constant and the effective magnetic moment of the 120 nm-thick \( \zeta \)-Fe\(_2\)N film, we measured the temperature dependence of susceptibility \( \chi \) and plot \( 1/\chi \) against temperature with the SCR theory [18]. As shown in Fig. 5, the inverse susceptibility \( 1/\chi \) gradually increases as the temperature increases at the range of 10–60 K. This behavior is considered to be due to the effect of the spin fluctuation at the zero point and the thermal spin fluctuation, as reported [19]. At the temperature range of 65–160 K, the inverse susceptibility linearly increases as the temperature increases. This result is considered to be due to the saturation of the thermal spin fluctuation, and so the inverse susceptibility obeys the Curie–Weiss law. From extrapolating to this result by the Curie–Weiss law, the Curie constant and the effective magnetic moment are estimated.
magnetic moment can be estimated, and is 0.11 emu·K/cc (0.016 emu·K/g) and 0.70 μB per an iron atom, respectively. In addition, for the temperature above 170 K, the inverse susceptibility slowly increases. This behavior cannot be explained in the present study.

4. Discussion

The magnetic parameters of the ζ-Fe₂N film can be obtained as described above, and are summarized in Table 1. For comparison, those parameters of other ζ-Fe₂N and typical weak itinerant electron magnetic materials are represented. The Curie temperature of our film specimen is higher than that of the ζ-Fe₂N powder [6]. There is a possibility that is a slight deviation from the stoichiometry. In order to clarify the composition of the ζ-Fe₂N film prepared in this study, we measured the XPS. The composition of the ζ-Fe₂N film is slightly deviated from the stoichiometry into the iron-rich composition, and the value of the nitrogen composition is about 32.7 at.% [7]. The spontaneous magnetization at 0 K is 0.028 B per an iron atom, and this value is lower than that of the ζ-Fe₂N powder [6]. The difference of the spontaneous magnetization at 0 K is also considered to be mainly due to a slight deviation from the stoichiometry. The ratio of the effective moment to the spontaneous magnetic moment at 0 K is much larger than those of the ζ-Fe₂N powder [6] and the bulk materials [10–13]. This suggests the strong effect of spin fluctuation in our film specimen: the thermal spin fluctuation amplitudes increase with temperature above Tc according to the SCR theory, as reported in Ref. [19]. From these magnetic parameters, it can be concluded that the magnetic state of the ζ-Fe₂N film is in a weak itinerant electron ferromagnetic state with the Curie temperature of 35 K.

5. Conclusions

We have studied magnetic properties of the 120 nm-thick ζ-Fe₂N film prepared onto surface-oxidized Si (100) substrates by reactive dc magnetron sputtering in an argon–nitrogen atmosphere. The crystal structure of the ζ-Fe₂N film is found to be the polycrystalline with the grain size of about 20 nm. The magnetization of the ζ-Fe₂N film cannot be saturated as the temperature decreases though the external field of 50 kOe is applied in the film plane. This reason should be that the magnetic moment is weak and fluctuates in the 120 nm-thick ζ-Fe₂N film. The inverse susceptibility increases linearly at the temperature range between 65 and 160 K, and is found to obey the Curie–Weiss law. From the results of magnetization measurements, the magnetic parameters of the ζ-Fe₂N film can be determined: the Curie temperature, spontaneous magnetic moment at 0 K and effective magnetic moment are 35 ± 2.5 K, 0.028 μB/iron atom and 0.70 μB/iron atom, respectively. From these results, it can be concluded that the ζ-Fe₂N film is the weak itinerant electron ferromagnet. Based on the self-consistently renormalization (SCR) theory, we can also explain the magnetic parameters of the ζ-Fe₂N film.

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