Passivating effect of Si(111)-(√3×√3)Ag and Si₃N₄/Si(111)-(8×8) buffer layers

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Abstract. We have investigated the magnetic properties of iron deposited on Si(111)-(7×7), Si(111)-(√3×√3)Ag and Si₃N₄/Si(111)-(8×8) by x-ray absorption spectroscopy and x-ray magnetic circular dichroism measurements. By choosing the surface, it is possible to control the interaction of Fe atoms with Si atoms and to govern the spin magnetic moment of iron. The magnetic moment of 1.6 ML-Fe is almost lost on the clean surface, while that of 1.6ML-Fe on the Si₃N₄ surface remains completely. About a half of the magnetic moment of bcc-Fe is obtained by depositing Fe on the Ag modified Si(111) surface. In addition, it is found that the magnetic moment of Fe on the Ag modified Si(111) surface is lost easily by annealing at 500 K. On the other hand, that of Fe on the Si₃N₄ surface is sufficiently kept even when the sample is annealed at 500 K.

1. Introduction

It is important to control the magnetic properties of ferromagnetic transition metals on Si substrates because of the technological applications such as magnetic memories and spintronics. However, when Fe is deposited on a clean Si surface at room temperature (RT), Fe atoms form FeSi and/or FeSi₂ at low coverage due to strong interaction with Si atoms. Berling et al. reported that the magnetic moment of iron atoms in iron silicides depends on the chemical composition of iron silicides [1]. The Fe atoms in Fe-rich silicides carry the magnetic moment, while the Fe magnetic moment is zero in FeSi. Therefore, it is difficult to keep nonzero magnetic moments of Fe atoms at the interface between deposited Fe and the clean Si surface. In order to form ferromagnetic bare iron and/or magnetic iron silicides on the Si substrate, it is required to suppress the chemical interaction of Fe atoms with the clean Si surface.

One way to govern the magnetic moment of Fe on Si(111) is modifying the Si surface [2-9]. It has been attempted to suppress the formation of the iron silicide by inserting metals [3-8], semiconductors [4] and insulators [2, 9]. For instance, Eguchi et al. succeeded in effective suppression of the formation of iron silicides by nitridation of the clean Si(111) surface [9]. In this case, the Fe magnetic moments were measured by in situ x-ray magnetic circular dichroism (XMCD) and the magnetic moment of Fe atoms on the Si₃N₄ surface is fully maintained. In other cases that Fe deposited on metal coated Si surfaces, the iron silicidation is also suppressed somewhat [3, 6]. Zavaliche et al. have studied the suppression effect of the Au modified Si(001) surface and they observed the ferromagnetic behavior of 2.3 ML-Fe film on the Au modified Si surface by the magneto-optical Kerr effect [3].
Takagi et al. have reported that the magnetic property of Fe deposited on a Si(111)-(√3×√3)Ag by ex situ superconducting quantum interference device (SQUID) measurements. In their report, ferromagnetic iron silicide dots are obtained when Fe atoms deposited on the (√3×√3)Ag surface annealed at 500 K. Additionally, they concluded the chemical composition of the dots is close to Fe₃Si because the magnetic moment of dots is the same value as that of Fe₃Si [6]. Thus, it is clear that metal coated Si surface partially prevent silicidation reaction of Fe atoms. However, the magnetic moment of Fe has not quantitatively evaluated by an in situ measurement.

In this work, we investigated the magnetic property of Fe deposited on Si(111)-(√3×√3)Ag by in situ x-ray absorption spectroscopy (XAS) and XMCD measurements. Compared with the results of Fe deposited on clean Si(111) and Si₃N₄ surfaces, we have confirmed the passivation effect of the (√3×√3)Ag buffer layer. In addition, we investigated a thermal effect for the magnetic properties of Fe deposited on the Si₃N₄ surface and on the (√3×√3)Ag surface.

2. Experimental

The sample preparation and the XAS and XMCD measurements were carried out in an ultrahigh vacuum (UHV) chamber, of which the base pressure was ~10⁻⁸ Pa. The sample was degassed in a UHV chamber by direct heating at ~800 K for 5-12 hours. A reconstructed Si(111)-(7×7) surface was obtained by repeated flashing at 1200 K. Thermal nitridation was conducted at 1130 K with ammonia gas (1×10⁻⁴ Pa, 45 sec). Then, the substrate was subsequently cooled down slowly to room temperature, which leads to the formation of an Si₃N₄/Si(111)-(8×8) surface [9, 10]. Silver of 1 monolayer (ML) was deposited on the clean Si(111) at 800 K, which leads to the formation of a (√3×√3) reconstructed structure [11, 12]. The ordering and the cleanness of the Si₃N₄ and (√3×√3)Ag surfaces were verified by low energy electron diffraction and Auger electron spectroscopy. Fe was deposited on Si₃N₄/Si(111)-(8×8), Si(111)-(√3×√3)Ag and Si(111)-(7×7) substrates by using a commercial electron bombardment evaporator and the thickness was estimated by quartz crystal oscillator. In the present work, we define a unity monolayer for Fe as an atomic concentration of Fe of 1.217×10¹⁵ atoms/cm², which corresponds to the atomic density of bcc Fe(001) plane.

The in situ XAS and XMCD measurements were performed in the total electron yield mode by using the bending magnet Beamline 4B of UVSOR-II in Institute for Molecular Science (IMS). The details of the XMCD measurement system have been reported in the literature [13, 14]. The circular polarization factors were estimated to be P_c = 0.55 ± 0.71 from the storage ring parameters, which were verified by the XMCD measurements of a standard sample. The XMCD spectra were taken by switching the magnetic field of ±5 T applied to the sample in parallel and antiparallel geometries with respect to the x-ray beam, leaving the x-ray helicity unchanged. The x-ray incidence angles with respect to the surface normal were 0° (normal x-ray incidence) and 55° (grazing incidence).

3. Results and discussions

Figure 1(a) shows the circularly polarized Fe L₂,₃-edge XAS spectra of Fe deposited on Si(111)-(7×7), Si(111)-(√3×√3)Ag and Si₃N₄/Si(111)-(8×8) at RT at the incidence angle of 55°. The spectra were normalized by the edge jumps. The previous study on iron silicide has shown that additional peaks are observed at a higher photon energy of the main peaks [15, 16]. The spectral feature can be used as a fingerprint to confirm whether Fe atoms are bonded to Si atoms. In the present measurement, the shoulder structure does not appear in the spectrum of Fe on the Si₃N₄/Si(111)-(8×8), indicating that the Fe atom on the Si₃N₄ surface does not interact strongly with Si atoms. In contrast, that of Fe on Si(111)-(7×7) has an additional peak at a higher photon energy of the main L₃ peak. Namely, the iron silicide is formed on the clean Si(111) surface. For Fe on Si(111)-(√3×√3)Ag, although no additional satellite peak is observed in the spectrum, the peak width of the spectrum of Fe L₁ edge is broad in comparison with that of Fe on the Si₃N₄ surface. The full width of half minimum (FWHM) of the μ spectrum of Fe on the (√3×√3)Ag surface, actually, is 4.9 eV. This value is an intermediate one between 3.2 eV in the μ spectrum of Fe on the Si₃N₄ surface and 6.8 eV in that of Fe on the clean
surface. These features imply that the Fe atoms deposited on the (\(\sqrt{3}\times\sqrt{3}\))Ag surface chemically react with the Si atoms and partially become an iron silicide.

The magnetization (\(M-H\)) curves were also obtained by recording the electron yield with the photon energy fixed at the Fe \(L_3\) peak top for each sample (Fig. 1(b)). The amplitude corresponds to the difference in the \(L_3\) peak intensity of the normalized XAS spectra at \(\pm 5 \, \text{T}\). The data in the vicinity of \(H = 0\) are omitted due to strong suppression of the electron yield by the Lorentz force. Fe atoms are clearly magnetized on the Si\(_3\)N\(_4\) surface due to the effective suppression of reaction between Fe atoms and Si atoms. On the other hand, it is found that Fe atoms on the clean surface are not magnetized at all. In the case of Fe deposited on the (\(\sqrt{3}\times\sqrt{3}\))Ag surface, the saturation magnetization is somewhat smaller than that on the Si\(_3\)N\(_4\) surface. The magnetic moment of the iron atom decreases with increasing the composition ratio of silicon in iron silicides, and that is almost vanished at the Si:Fe=1:1 [1]. Therefore, the results indicate that Si-rich iron silicide is formed on the clean surface while Fe-rich iron silicide is formed on the (\(\sqrt{3}\times\sqrt{3}\))Ag surface.

![Figure 1](https://example.com/figure1.png) (Color online) (a) Fe \(L_{2,3}\)-edge circularly polarized XAS spectra of the Fe on each substrate. The Fe thickness on clean, (\(\sqrt{3}\times\sqrt{3}\))Ag and Si\(_3\)N\(_4\) surfaces are 1.6, 2.0 and 1.6 ML, respectively. The spectra are taken at \(T = 5 \, \text{K}, \mu_0H = \pm 5 \, \text{T}, \theta = 55^\circ\), \(\mu^+\) (red dashed line) and \(\mu^-\) (blue solid line) spectra correspond to the ones with the electron spin parallel and anti-parallel to the photon angular momentum, respectively. (b) Magnetization curves of Fe on each surface at \(T = 5 \, \text{K}\), obtained by recording the electron yield with the photon energy fixed at the Fe \(L_3\) peak top of 707 eV. This data are taken at normal x-ray incidence (\(\theta = 0^\circ\)).

Figure 2 shows the Fe \(L_{2,3}\)-edge XMCD spectra of Fe deposited on Si(111)-(7×7), Si(111)-(\(\sqrt{3}\times\sqrt{3}\))Ag and Si\(_3\)N\(_4\)/Si(111)-(8×8), taken at incident x-ray angles \(\theta = 0^\circ\) and 55°, a magnetic field of \(\pm 5 \, \text{T}\), and a temperature of 5 K. The XMCD signal of Fe become larger in order of Fe/Si(111), Fe/(\(\sqrt{3}\times\sqrt{3}\))Ag and Fe/Si\(_3\)N\(_4\). A sum-rule analysis was performed using the formula of the orbital magnetic moment (\(m_{\text{orb}}\)) and the effective spin magnetic moment (\(m_{\text{eff}}\)) [17, 18]. For the quantitative evaluation of the spin and orbital magnetic moments, the \(d\)-hole number \(n_d\) is experimentally estimated in a similar manner to the previous studies [13, 14]. In the present analysis, a XMCD spectrum (not shown) of bulk bcc Fe (\(n_d\) is assumed to be 3.40) was used as the standard. Then, the angle-dependent XMCD analysis at saturation was performed to eliminate the contribution of the spin dipole moment (\(m_T\)) and obtained the pure spin magnetic moment (\(m_{\text{spin}}\)) [19].

The results of the XMCD analysis are tabulated in Table 1. The spin magnetic moment is almost lost for Fe/Si(111). When small amount of Fe is deposited on the clean Si(111) surface, it is transformed into a nonmagnetic FeSi amorphous layer even at RT [20]. Additionally, the thickness of a magnetically dead layer is estimated as \(~2\) ML from photoelectron spectroscopic results [21]. The present XMCD result is consistent with the previous reports on the Fe/Si(111) system. On the other hand, the spin magnetic moment of Fe/Si\(_3\)N\(_4\)/Si(111) is 2.62 \(\mu_B\), which is larger than the bulk value of...
Table 1. Results of the Fe $L_{2,3}$-edge XMCD analysis for Fe on each substrate with/without annealing. For the orbital magnetic moment $m_{\text{orb}}$, surface parallel (\parallel) and normal (\perp) components are given separately.

|                  | $m_{\text{spin}}$ ($\mu_B$) | $m_{\text{orb}}(\parallel)$ ($\mu_B$) | $m_{\text{orb}}(\perp)$ ($\mu_B$) |
|------------------|-----------------------------|--------------------------------------|----------------------------------|
| clean            | 0.17                        | 0.15                                 | 0.00                             |
| $(\sqrt{3}\times\sqrt{3})\text{Ag}$ | 1.25                        | 0.17                                 | 0.11                             |
| $\text{Si}_3\text{N}_4$ | 2.62                        | 0.15                                 | 0.18                             |
| annealed $(\sqrt{3}\times\sqrt{3})\text{Ag}$ | 0.32                        | 0.03                                 | 0.01                             |
| annealed $\text{Si}_3\text{N}_4$ | 2.19                        | 0.11                                 | 0.13                             |

2.2 $\mu_B$. It is found by the scanning tunneling microscopy (STM) measurements that the uniform nanoparticles of Fe grow on the $\text{Si}_3\text{N}_4$ surface at the initial stage [9]. Thus, the large magnetic moment can be explained by the less chemical interaction of Fe atoms with silicon atoms and the enhancement of the magnetic moment due to the size effect.

![Figure 2](image.png)

**Figure 2.** (Color online) Normalized Fe $L_{2,3}$-edge XMCD spectra of Fe on each substrate, taken at $T = 5$ K and $\mu_0H = \pm 5$ T. The Fe thickness is the same as that in figure 1.

The spin magnetic moment of Fe deposited on the $(\sqrt{3}\times\sqrt{3})\text{Ag}$ is 1.25 $\mu_B$, which indicates that the magnetic Fe-rich iron silicide is formed on the $(\sqrt{3}\times\sqrt{3})\text{Ag}$ surface. Compared to the Fe/Si(111) result, it is clear that the $(\sqrt{3}\times\sqrt{3})\text{Ag}$ surface suppress a silicidation reaction between deposited Fe atoms and the silicon substrate. However, the magnetic moment is smaller than that of Fe$_2$Si (1.6 $\mu_B$) [22] and is almost equal to that of Fe$_2$Si [1]. Therefore, the chemical composition of iron silicide grown on the $(\sqrt{3}\times\sqrt{3})\text{Ag}$ surface is close to Fe$_2$Si. This means that the passivation of $(\sqrt{3}\times\sqrt{3})\text{Ag}$ is not strong enough to prevent the silicidation completely.

We also investigated the annealing effect. The XAS spectra of Fe deposited on the $(\sqrt{3}\times\sqrt{3})\text{Ag}$ and $\text{Si}_3\text{N}_4$ surfaces annealed at 500 K are shown in Figure 3(a). The peak profile of Fe on the $\text{Si}_3\text{N}_4$ surface is similar to that of Fe deposited on the surface at RT and the FWHM of the $\mu$ spectrum of annealed Fe is 0.2 eV wider than that of the $\mu$ spectrum of the Fe without annealing. On the other hand, a shoulder structure is clearly seen at a higher photon energy side of the main peak in the spectra of Fe on the $(\sqrt{3}\times\sqrt{3})\text{Ag}$ surface. The silicidation of the Fe atoms on the $(\sqrt{3}\times\sqrt{3})\text{Ag}$ surface proceeds by annealing, which means that thermal resistance of the $(\sqrt{3}\times\sqrt{3})\text{Ag}$ surface is not strong enough to prevent the silicidation reaction at high temperature.

Figure 3(b) shows the normalized XMCD spectra for the Fe atoms deposited on the both substrates and annealed at 500 K, and the results of the XMCD analysis are also tabulated in Table 1. The XMCD intensity of Fe on the $\text{Si}_3\text{N}_4$ surface becomes slightly weaker and the spin magnetic moment of the Fe atom decreases from 2.62 $\mu_B$ to 2.19 $\mu_B$. The value is, however, still similar to that of the bulk...
Fe. Two possible reasons for the decrease in the magnetic moment can be proposed. One reason is that the iron silicide is formed at defects of the Si$_3$N$_4$ buffer layer, e.g. steps and pits. Another one is that Fe nanoparticles are coalesced with each other and make larger nanoparticles by annealing to suppress the size effect. We will here emphasize that the passivation of the Si$_3$N$_4$ buffer layer is efficient to avoid the silicidation reaction between the Fe atoms and the Si atoms at least 500 K.

In contrasted to the magnetic moment of Fe on the Si$_3$N$_4$ buffer layer, that of Fe on the (√3×√3)Ag surface after annealing decreases significantly in comparison with that before annealing. It is found that the passivation effect of the (√3×√3)Ag surface is rather sensitive to the heating than that of the Si$_3$N$_4$ surface. However, it is noted that Fe atoms on the annealed (√3×√3)Ag surface carry the nonzero magnetic moment, although it is completely vanished for the Fe atoms deposited on the clean Si(111) surface annealed at 500 K (not shown). In addition, we also note that the small magnetic moment (0.32 $\mu_B$) is inconsistent with previous study on Fe/Si(111)-(√3×√3)Ag at annealed 500 K, which reported that the nano dots whose composition ratio is Fe$_3$Si (1.6 $\mu_B$) grow on the (√3×√3)Ag surface [6]. This discrepancy is explained by the difference of the measurement method. The magnetic moment of Fe atoms estimated by SQUID was calculated by dividing the whole magnetic moment with the volume of the dots estimated by STM. In this method, they only took account of the Fe atoms above the surface. Consequently, the average magnetic moment is estimated highly in comparison with the XMCD measurement because the value excludes the contribution from nonmagnetic iron atoms which diffuse into the Si substrate.

The difference of thermal resistance between Si$_3$N$_4$ and (√3×√3)Ag can be interpreted as the difference of the decomposition temperature. Si$_3$N$_4$ is thermally stable even above 2000 K, whereas the Si(111)-(√3×√3)Ag structure breaks at 900 K [23]. This means that the silicidation reaction is enhanced on the (√3×√3)Ag surface than on the Si$_3$N$_4$ surface. The Si$_3$N$_4$ surface is superior to the (√3×√3)Ag surface as a buffer layer to suppress the iron silicide formation.

Figure 3. (Color online) (a) Fe L$_{2,3}$-edge circularly polarized XAS spectra of the Fe on (√3×√3)Ag and Si$_3$N$_4$ surfaces annealed at 500 K. (b) Normalized Fe L$_{2,3}$-edge XMCD spectra of Fe on each substrate annealed at 500 K. The XAS and XMCD spectra are taken at $T = 5$ K and $\mu_0H = \pm 5$ T.
4. Summary

We investigated the magnetic properties of Fe grown on the Si₃N₄/Si(111)-(8×8) and Si(111)- (√3×√3)Ag substrates with and without annealing at 500 K by XAS and XMCD measurements. The spin magnetic moment of Fe can be controlled by modifying the Si surface; those of Fe atoms without annealing are 0.17, 1.25 and 2.62 μB on the clean, (√3×√3)Ag, and Si₃N₄ surfaces, respectively. Moreover, the annealing effect was studied for Fe on Si₃N₄ and (√3×√3)Ag surfaces. The iron silicidation is effectively suppressed on the Si₃N₄ surface even when the sample is annealed at 500 K. On the (√3×√3)Ag surface, the iron silicide are formed easily by annealing at 500 K and the spin magnetic moment of Fe atom is almost lost on the (√3×√3)Ag surface.

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