X-ray photoelectron spectroscopy of SPE-grown bcc-Fe, polycrystal and β-FeSi2 phases on Si(111) surfaces

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Ultrathin films of iron silicides were grown on Si(111) surfaces by solid phase epitaxy (SPE); iron deposition and subsequent annealing, and analyzed using in situ high energy-resolution X-ray photoelectron spectroscopy (XPS). We analyzed peaks using Lorentzian and Doniach–ˇSunji´c curves and estimated the validity of both fittings. Under the sequence from bcc-Fe to polycrystal phase (the mixture of Fe3Si and β-FeSi2), and then β-FeSi2 phase with annealing process, the slight chemical shifts of Fe 2p3/2 toward higher binding energy (BE) and the reduction of peak asymmetry for Fe 2p3/2 and Fe 2p1/2 were observed. We attributed this behavior to the reduction of the metallicity in iron silicide films. Copyright © 2008 John Wiley & Sons, Ltd.

Keywords: iron silicides; β-FeSi2; XPS; Si segregation

Introduction

Fe silicide films on Si substrates have been widely studied for many years to gain an understanding of their fundamental properties, as well as for possible applications in microelectronics.1–8 These physical properties are no different from those of either single-crystal or polycrystal materials.9–13 However, some of the most severe limitations in the use of these materials in device technology come from the growth of thin films, which occasionally result in complex and ill-defined interfaces. Because of this, many researchers have studied the growth, thermal reaction, and crystalline structure of ultrathin iron silicide films on Si surfaces. So far, our group has studied structures and their properties of Si(111)–Fe system systematically and reported the schematic phase diagram,1 the relation between the structure and magnetic properties,14–15 and surface gas adsorption properties.16 In the Si(111)–Fe system, nine iron-silicide or iron phases formed by solid phase epitaxy (SPE), depending on Fe coverage and subsequent annealing temperature;11 above ∼1.0 nm-Fe deposition a bcc-Fe(111) phase appears at the deposition, and changes to a polycrystal phase at 670–770 K annealing and then to a β-FeSi2(101) or (110) phase at 770–870 K annealing. In the polycrystal phase, the existence of Fe3Si and β-FeSi2 was reported using an X-ray diffraction study. In the β-FeSi2 phase, the existence of a ferromagnetic iron-rich silicide interface layer between the β-FeSi2 thin film and the Si substrate has been reported using vibrating sample magnetometer and transmission electron microscopy studies.17 Recently, the reaction of the interface layer with annealing time has been suggested. According to Hattori et al.,15 the formation process from bcc-Fe phase to the β-FeSi2 phase is schemed in Fig. 1. For the formation process from bcc-Fe to β-FeSi2 through two intermediate states, polycrystal phase and β-FeSi2/disordered Fe-rich silicides/Si(111) heterostructure, the silicide formation should be achieved predominantly by Si diffusion. That is, the key process is the segregation of Si into Fe3Si and/or iron-rich silicide disordered phase to achieve the formation of the epitaxial β-FeSi2 films.

In this paper, we will present Fe 2p core spectra reflecting surface chemical states in each phase, through the growth process of SPE-grown iron silicides on Si(111) surface depending on annealing temperature, using in-situ high energy-resolution X-ray photoelectron spectroscopy (XPS) analysis. We discuss the changes of the electron state for each phase in SPE-grown Si(111)–Fe system, focusing on the chemical shifts of Fe 2p3/2 and peak asymmetry by fitting both Lorentzian and Doniach–Sunjić (DS) curves.17

Experimental

The sample preparation and reflection high-energy electron diffraction (RHEED) measurements were performed in an ultrahigh vacuum (UHV) system consisting of an air-lock chamber, a gas chamber, and a main chamber equipped with alumina crucible evaporators, a thickness monitor, a RHEED gun and a screen. The sample position is controlled by a four-axis (X, tilt-Y, Z, and azimuth φ) manipulator with a He refrigerator; the sample stage can be cooled at 40 K. The base pressures of the gas and the main chambers were less than 7 × 10−9 Pa. Si(111) mirror-polished wafers (0.5 mm in thickness, n-type, Sb-doped 0.02 Ω cm), cut in sizes of 4 × 26 mm2, were degassed in UHV over 12 h and flashed at 1520 K several times, below 2 ⋅ 3 × 10−8 Pa in the gas chamber. After transfer to the stage in the main chamber at 40 K, the samples were flashed again below 7 × 10−8 Pa. Clean 7 × 7 reconstructed patterns were confirmed with RHEED.

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We prepared various Fe silicides by the SPE method (annealing after deposition). Fe (99.997%) was deposited at $\theta_{Fe}$ = 5.0 nm on Si(111)−7×7 clean surfaces at 40 K below 3×10⁻8 Pa. The typical deposition rates were about 0.02 nm/min. The film thickness was calibrated by a quartz crystal monitor. Subsequently, the samples were annealed at $T_a$ between 470 and 820 K for five min, below 7×10⁻8 Pa. After cooling the sample to 40 K, RHEED measurements were carried out to confirm the surface structure of each phase.

The chamber described above was connected to the UHV transfer system[18] and the samples could be transferred to another UHV system (e.g. the XPS chamber[19]) without atmospheric exposure. After confirming the phases, the samples were transferred to the XPS chamber. In situ room temperature XPS measurements were performed with an electrostatic hemispherical analyzer (GAMMADATA-SCIENTA, SES 2002), using nonmonochromatized Al $K\alpha$ (hν = 1486.6 eV) X-rays. The spectra of Fe 2p core levels were obtained with a pass energy of 50 eV and X-ray spot size of ∼5 mm, giving a constant energy-resolution of <1.0 eV. The base pressure in the XPS analysis chamber was ∼3 × 10⁻8 Pa. The escape depth of photoelectrons is nearly 1-2 nm at the kinetic energy of 700-800 eV for the Fe 2p core electrons.

Results and Discussion

After the deposition of iron on Si(111)−7×7 surfaces at 40 K, RHEED patterns showed transmission diffraction spots of bcc-Fe(111) (bcc-Fe phase), as reported elsewhere.[11] At 470 K annealing for 5 min, the bcc-Fe spots changed to Debye rings, indicating fine polycrystals (polycrystal phase). Our group have confirmed that this polycrystal phase consists of Fe$_3$Si and β-FeSi$_2$ by X-ray diffraction measurements. At 820 K annealing for 5 min, the β-FeSi$_2$ streaky spots appeared instead of the Debye rings (β-FeSi$_2$ phase).[14] In this condition, it has been reported that β-FeSi$_2$ (∼20 nm)/disordered iron-rich silicide/Si(111) heterostructure forms.[15] Figures 2 and 3 represent XPS spectra of the Al Kα-excited Fe 2p core levels from (a) the bcc-Fe core, (b) the polycrystal phase, and (c) the β-FeSi$_2$ phase. The Fe 2p spectra consists of both 2p$_{3/2}$ peaks at about 708 eV in binding energy (BE) and 2p$_{1/2}$ at about 720 eV in BE. In Fig. 2 the spectra are fitted by Lorentzian peaks and the Shirley background.[20] Each asymmetric peak is fitted to two symmetric Lorentzian main and subpeaks. The fitting parameters for 2p$_{3/2}$-main peak, 2p$_{3/2}$-sub peak, 2p$_{1/2}$-main peak, and 2p$_{1/2}$-subpeak (red, green, blue and purple curves, respectively, in Fig. 2) are presented in Table 1.

In the Lorentzian fitting (Fig. 2 and Table 1), we notice the BE increase of Fe 2p$_{3/2}$-main peak with decreasing Fe concentration and metallicity (from bcc-Fe to the peak shift of +0.09 eV (toward higher BE) from the bcc-Fe phase to the polycrystal phase, and +0.23 eV to the β-FeSi$_2$ phase. A similar tendency is reported for thin Fe$_3$Si$_{100-x}$ amorphous and polycrystal films (0≤x≤75); the chemical shifts of Fe 2p$_{3/2}$ increase almost monotonically with decreasing Fe content.[21] The similar tendency is also reported for epitaxial Fe or Fe silicide system[22] where the chemical shift has been explained by a plasmon loss effect due to metallization. Our chemical shift of 2p$_{3/2}$ main peak value for the semiconductor β-FeSi$_2$ (+0.23 eV) is in good agreement with the previous reports.[23-26] Table 1 shows new information of the chemical state in polycrystal phase (the mixture of Fe$_3$Si and β-FeSi$_2$). The chemical shift value (+0.09 eV) for the polycrystal is the intermediate value between bcc-Fe and β-FeSi$_2$ phases. We have not confirmed the abundance ratio of Fe$_3$Si and β-FeSi$_2$ yet, however, qualitatively we could discuss the tendency of the components of elements at the surface. It is well known that epitaxial Fe$_3$Si could not form directly on the Si surface. The problem is the formation of interfacial compounds like FeSi due to the diffusion of Si atoms from the substrate into the film.[27] Therefore, so far there are a few reports about the chemical state of Fe$_3$Si films.[21,28] Compared with these results (2p$_{3/2}$ shift to +0.1-0.2 eV toward higher BE), our results are quite reasonable for the mixture of Fe$_3$Si and β-FeSi$_2$.

There are two explanations for the main and subpeaks; one is the difference of iron chemical states (Fe$^{3+}$ and Fe$^{2+}$, bulk and surface Fe, and so on) and another is the intrinsically asymmetric feature of the peak. For iron oxide system,[29,30] some previous works suggested two iron states Fe$^{3+}$ and Fe$^{2+}$ (BE for Fe$^{3+}$ is ∼1 eV higher than that for Fe$^{2+}$). In our case, the energy differences between the main and sub peaks are scattered (∼1.3-2.1 eV) and higher than ∼1 eV (Table 1), while we expect fixed values of ∼1 eV in the different ionic states. Moreover, the ratio of the intensities A between the main and sub peaks did not drastically change in bcc-Fe, polycrystal and β-FeSi$_2$ phases, which should be changed drastically if we assume the different chemical states. In addition, our Lorentzian fitting results (Table 1) show no coincidences behavior of the chemical shift of the 2p$_{3/2}$-main and sub peaks with those of the 2p$_{1/2}$ peaks for the phase change. Thus, the explanation by the different chemical states would have low possibility. Here, we suggest the peak fitting with an asymmetric shape function, the so-called DS function,[17] instead of two (main and sub) symmetric shape functions. The asymmetry in the DS function is explained by the singular electron-hole scattering with a transient and singular re-adjustment of the ground state of the Fermi gas to the creation of the effective potential of the core hole.[31]

So far, parameter $\gamma$[32] were discussed in the DS fitting for the various materials. The metals which show the stronger tendency towards magnetism and have higher density of states at the Fermi level have the larger value of $\alpha$. The larger value of $\alpha$ is due to the stronger electron–electron interaction in these metals.
The α represents the scattering of Fermi energy electrons by the hole potential and hence it depends upon the number of available electrons at the Fermi level. Hüfner and Wertheim[33] have reported that the values of α are as high as 0.3 for metals and close to zero for insulators and semiconductors. Indeed, α value of 0.04 was reported for Zn 2p3/2 in ZnO.[34]

The obtained experimental data can be fitted to the DS line shape, as shown in Fig. 3. The estimated values are also summarized in Table 1. In the DS fittings, the values of 2p3/2 and 2p1/2 peaks position are very close to those of the main peaks in the Lorentzian fitting. We confirmed, however, the coincidence behavior of the chemical shift for both 2p3/2 and 2p1/2 peaks, increasing BE with decreasing the metallicity: 2p3/2 (2p1/2) of +0.15 (+0.12) eV and +0.25 (+0.23) eV for the polycrystal and the β-FeSi2 phase, respectively, in contrast to the Lorentzian fitting. This tendency is also observed in the other systems[21,22] as discussed above. In addition, the asymmetry parameter α decreases with decreasing metallicity 0.31 (0.30), 0.30 (0.25) and 0.19 (0.21) for 2p3/2 and 2p1/2 peak in the bcc, polycrystal, and β-FeSi2 phases, respectively. Here, we emphasize that the α values for the 2p3/2 and 2p1/2 peaks are almost the same or very close in the same phase. Figure 4 shows the residual standard deviation.

Figure 2. XPS spectra (square dots) for (a) the bcc-Fe phase, (b) the polycrystal phase, and (c) the β-FeSi2 phase. Each spectrum is fitted (a black curve) with four peaks of the Lorentzian function, 2p3/2-main, 2p3/2-sub, 2p1/2-main and 2p1/2-subpeaks (red, green, blue, and purple curves, respectively), and the Shirley background (a black dashed curve). This figure is available in colour online at www.interscience.wiley.com/journal/sia.

Figure 3. XPS spectra (square dots) for (a) the bcc-Fe phase, (b) the polycrystal phase, and (c) the β-FeSi2 phase. Each spectrum is fitted with two peaks of the Doniach–Sunjić function, 2p3/2 and 2p1/2 peaks (red dashed curves), on two constant backgrounds (black dashed lines). This figure is available in colour online at www.interscience.wiley.com/journal/sia.
Table 1. Fitting parameters (binding energy (BE), full-width at half maximum (FWHM), intensity (A) and asymmetric factor (\(\alpha\))) in the Fe 2p spectra for bcc-Fe, polycrystal, and \(\beta\)-FeSi\(_2\) phases, assuming Lorentzian and Doniach–Šunjić functions

<table>
<thead>
<tr>
<th>Phase</th>
<th>Parameter</th>
<th>Lorentzian fitting</th>
<th>Doniach–Šunjić fitting</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(2p_{3/2})-main</td>
<td>(2p_{3/2})-sub</td>
<td>(2p_{3/2})-main</td>
</tr>
<tr>
<td>bcc-Fe</td>
<td>BE (eV)</td>
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<td>708.09</td>
</tr>
<tr>
<td></td>
<td>FWHM (eV)</td>
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<tr>
<td></td>
<td>A (%)</td>
<td>65</td>
<td>35</td>
</tr>
<tr>
<td></td>
<td>(\alpha)</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>polycrystal</td>
<td>BE (eV)</td>
<td>706.32</td>
<td>708.19</td>
</tr>
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<td>FWHM (eV)</td>
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<td>(\alpha)</td>
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<tr>
<td>(\beta)-FeSi(_2)</td>
<td>BE (eV)</td>
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<td>707.72</td>
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<td>FWHM (eV)</td>
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<tr>
<td></td>
<td>A (%)</td>
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<td>34</td>
</tr>
<tr>
<td></td>
<td>(\alpha)</td>
<td>–</td>
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</table>

Figure 4. The residual errors of Fe 2\(p_{3/2}\) peaks for (a) the bcc-Fe phase, (b) the polycrystal phase, and (c) the \(\beta\)-FeSi\(_2\) phase. The red and blue curves represent the residual error for Doniach–Šunjić and Lorentzian fittings, respectively. Here, the residual error is defined as (measured intensity/peak height - fitted intensity)/peak height respectively. Here, the residual error is defined as (measured intensity - fitted intensity)/peak height. This figure is available in colour online at www.interscience.wiley.com/journal/sia.

deviation for the fitting of the DS (red) and Lorentzian (blue) functions. We can confirm that the residual in the DS fitting is almost half as large as those in Lorentzian fitting. This also indicates that the DS explanation is preferred than the Lorentzian one. According to the previous reports about the asymmetry parameter \(\alpha\) in thin Fe\(_2\)Si\(_{100-x}\) amorphous and polycrystal films\[21\], \(\alpha\) decreases (symmetric property increases) with decreasing the Fe concentration in the alloy, and \(\alpha\) is strongly reduced for semiconductor \(\beta\)-FeSi\(_2\) phase; \(\alpha\)\(\sim\)0.4 for Fe, \(\sim\)0.3 for Fe\(_3\)Si and \(\sim\)0.1 for FeSi\(_2\) in both amorphous and crystalline 20 nm-Fe\(_2\)Si\(_{100-x}\) films onto sapphire substrates\[21\]. The \(\alpha\) tendency of these results is consistent with ours.

Conclusions

The formation process of SPE-grown Si(111)–Fe system, from bcc-Fe to \(\beta\)-FeSi\(_2\) through polycrystal phase, has been studied in situ high energy-resolution XPS. The obtained peaks of Fe 2\(p_{3/2}\) were fitted by two different model functions: Lorentzian and Doniach–Šunjić functions. The DS fitting indicated the excellent coincidence behavior of the chemical shift for both 2\(p_{3/2}\) and 2\(p_{1/2}\) peaks while the Lorentzian fitting had poor coincidence for 2\(p_{3/2}\) and 2\(p_{1/2}\) (and also main and sub) peaks. Thus, we consider that the DS fitting is better than the Lorentzian fitting in this system. In the DS fitting we obtained the monotonic peak-shift toward higher BE and decreasing asymmetry parameter \(\alpha\) value with decreasing the metallicity (from bcc-Fe to polycrystal and then \(\beta\)-FeSi\(_2\) phases). Here we can understand the decreasing trend of \(\alpha\), which reflects the asymmetricity of the spectrum arising from the scattering of Fermi-energy electrons by the transient core-hole potential. This paper also shows the chemical shift and \(\alpha\) values for the polycrystal phase (the mixture of Fe\(_3\)Si and \(\beta\)-FeSi\(_2\)), as new information.

References