Structural Analysis of Self-Assembled Platinum-Silicide Nanostructures on Si(001) Using Ion Scattering Spectroscopy*

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The structure of platinum (Pt) silicide products grown on Si(001) substrate by Pt deposition at 600°C was analyzed using coaxial impact collision ion scattering spectroscopy. The resulting surface always had two kinds of products, nanowires and islands. The Pt$_2$Si crystals with four low index surface planes were took up as candidates for the products, and it was found that the nanowires and islands of the Pt silicide were composed of Pt$_2$Si with (010) and Si-terminated (001) as surface planes, respectively. The surface energy calculation performed using density functional theory calculation indicated that the Si-terminated Pt$_2$Si(001) had the lowest energy among the examined surfaces, which is consistent with the fact that islands are the major products on the surface. [DOI: 10.1380/ejssnt.2018.66]

Keywords: Platinum; Silicide; Nanowire; Ion scattering spectroscopy

I. INTRODUCTION

Nanowires often have special physical properties different from thin films of the same material [1, 2], and their application for nanoscale devices has attracted attention [3, 4]. It is known that many metal silicides grow as nanowires on Si(001) [5–7], which are often studied as model materials of nanoscale wiring [8, 9]. Generally, the electrical resistivity of a crystal increases as the crystal size decreases due to the influence of surface scattering. Indeed, it has been demonstrated for several rare-earth silicides that the electrical resistivity of the nanowires is larger than that of the thin film [9, 10]. In the case of platinum (Pt) silicide, on the other hand, it has been reported that the electrical resistivity of the nanowire is as low as that of the thin film, indicating little surface scattering in the nanowire [11].

On a Si substrate, it is known that Pt silicide grows in different shapes such as nanowires and thin films, depending on the amount of Pt deposition and the substrate temperature [12–14]. It has been reported that the composition of Pt silicide thin films grown on Si substrate is mainly PtSi and Pt$_2$Si, depending on the substrate temperature [12]. Furthermore, for Pt$_2$Si thin films it is suggested that the surfaces with different plane indices appear depending on the film thickness and the substrate temperature [15].

According to the core-level photo emission spectroscopy study by Lim et al., the Pt silicide nanowires have a composition of Pt$_2$Si [13]. It has been reported that Pt$_2$Si is usually composed of a body-centered tetragonal structure represented by a space group $I4/mmm$ ($a = b = 3.94$ Å, $c = 5.96$ Å) [16, 17]. In the case of the nanowire, however, details of the structure, such as surface plane index and growth direction of the nanowire, have not been clarified, and therefore the reason for the low electrical resistivity described above is unknown. Thus, in this study, we performed structural analysis of Pt silicide nanostructures using ion scattering spectroscopy. It was found that the nanowires and islands of the Pt silicide were composed of Pt$_2$Si with (010) and Si-terminated (001) as surface planes, respectively.

II. EXPERIMENTAL

Pt silicide nanowires (NWs) were fabricated in an ultrahigh vacuum (UHV) chamber with a base pressure of $2 \times 10^{-7}$ Pa. In the growth process of the NWs, an n-type Si(001) substrate with dimension of $25 \times 25 \times 0.4$ mm$^3$ was first cleaned in UHV by flashing at 1200°C by electron bombardment (EB) from the reverse side of the sample. Pt was deposited onto Si(001) using a home-made EB evaporator. A typical deposition rate of Pt was 0.02 ML/min (1 ML = $6.8 \times 10^{14}$ atoms/cm$^2$), although the arrival rate of Pt atoms is unknown.

The analysis of the atomic arrangement of the Pt silicide was performed using co-axial impact collision ion scattering spectroscopy (CAICISS) in the UHV chamber connected with the Pt deposition chamber (base pressure: $1.3 \times 10^{-7}$ Pa). In the measurement, a pulsed beam of 2.0 keV helium ions (He$^+$) was made to impinge on the sample. The scattered particles (He$^+$ and neutral helium) were detected at a scattering angle of nearly 180° (almost perfect backscattering) using a time-of-flight analyzer [18]. The atomic structure can be determined by computer simulation of CAICISS measurement data, which is based on the commercial software program “COSCAT” from Shimadzu Corporation, Japan. In the simulation, only the large-angle scattering with two small-angle scatterings from each pair of atoms in a unit cell of a simulation model was taken into account [19]. The Ziegler Biersack Littmark potential was adopted as a screening function to calculate the differential scattering cross sections. The vibrational amplitude of surface atoms was assumed to be 0.25 Å. All CAICISS experiments were carried out at room temperature. After CAICISS experiments, the morphology of the sample surfaces was examined in air by commercially available amplitude modulation atomic force microscope (AFM).

The atomic structures for the COSCAT simulation were prepared by surface relaxation from the typical surface

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planes of Pt$_2$Si using density functional theory calculations in the framework of the Vienna *ab initio* simulation program (VASP) developed at the Fakultät für Physik of the Universität Wien [20, 21]. The electron ion interaction was described by the projector augmented wave method [21, 22]. The electron-electron exchange-correlation interaction was treated using the Perdew-Burke-Ernzerhof function within the generalized gradient approximation [23, 24]. The plane-wave energy cutoff was set at 400 eV. The initial structures for the calculation are shown in Fig. 3. Each slab includes a vacuum region of $\sim$ 20 Å. Structural relaxation was performed until the Hellmann-Feynman forces were less than 0.01 eV/Å.

III. RESULTS AND DISCUSSIONS

Figure 1(a) displays an AFM image of the Si(001) surface after Pt deposition at 600°C for 40 min. Two types of the products, labeled “A” and “B”, are seen in the figure, and their line profiles are shown in Fig. 1(b) and Fig. 1(c), respectively. Here, the products having an aspect ratio of length to width more than 10 are defined as nanowires, whereas those smaller than 10 are defined as islands. From the line profiles of the two products, the nanowires, whereas those smaller than 10 are defined as islands to nanowires was estimated to be 4 : 1. In the CAICISS analysis, we first obtained a time-of-flight (TOF) spectrum at a He$^+$ incident angle ($\alpha$) of 90° (normal to the surface), which is shown in Fig. 2(a). In the spectrum, single backscattering signals from Pt and Si atoms can be confirmed, as indicated by pink and blue areas, respectively. Figure 2(b) shows an azimuth angle ($\varphi$) dependence of scattered signals from Pt ($\varphi$-dependence, hereafter) at $\alpha = 10^\circ$. Note that we used scattered signals from Pt in the analysis of the present study since the scattered signals from Si derived not only from the Pt silicides but also from bare Si surface. In Fig. 2(b), we can see the same shape appearing every 90° (fourfold symmetry) as well as a mirror symmetrical shape, as indicated by arrows. Since there are two domains rotated by 90° from each other on the Si(001) surface, the Pt silicides grow along two orthogonal directions, resulting in the fourfold symmetry in the $\varphi$-dependences in Fig. 2(b). On the premise that the composition of the products is Pt$_2$Si crystal, we will take up Pt$_2$Si with low index surfaces, (001), (010), (110), and (112) surface, as candidates for the products, whose structural models are shown in Fig. 3. All the above four surfaces have at least one mirror symmetrical plane, which is consistent with the experimentally obtained $\varphi$-dependence.

Next, we simulated the $\varphi$-dependences on the basis of the above four surfaces. Since the surface atoms would have a relaxed structure, we first performed the relaxation calculation of the four surfaces. In the case of Pt$_2$Si(001) and Pt$_2$Si(110) surfaces, there are two possible outermost layers; Si-termination and Pt-termination. The other two surfaces have only one kind of outermost layer, which includes both Si and Pt atoms. The surface unit cell of each surface was set based on the surface unit cell of Si(001), that is, $a \times a$ for Pt$_2$Si(001), $a \times 1.5a$ for Pt$_2$Si(101), $1.5a \times 1.5a$ for Pt$_2$Si(110), and $a \times 1.5a$ for Pt$_2$Si(112), where $a$ is the lattice constant of Si(001) (= 3.84 Å). Thus, we prepared six slab models shown in Fig. 3 and performed the relaxation calculation for each model with fixing only the bottom layer. The resulting structures were used as the base structures for the simulation of the $\varphi$-dependences. In the case of $\alpha = 10^\circ$, however, the simulations for all the surfaces did not coincide with the experimental $\varphi$-dependence (not shown here). Note that the relaxed structures of both Pt$_2$Si(010) and Pt$_2$Si(112) slabs are the same, so that we later take up (001), (010), and (110) surfaces of Pt$_2$Si.

It has been reported that Pt deposition on Si(001) at 600–900°C induces c(4×6) reconstruction [25–27]. This reconstruction was reported to coexist with Pt silicide nanostructures [13]. Therefore, the signals in the $\varphi$-dependences must be derived both from the Pt silicide nanostructures and the c(4×6) reconstruction. To compare the $\varphi$-dependences of the two, we prepared a surface covered only with c(4×6) reconstruction by Pt deposition onto Si(001) surface at 800°C. Figures 4(a) and 4(b) show the $\varphi$-dependences at $\alpha = 10^\circ$, $20^\circ$, $30^\circ$, and $40^\circ$ experimentally obtained from the Pt/Si(001) surfaces formed by Pt deposition at 600°C and 800°C, respectively. Note that the $\varphi$-dependences at $\alpha = 30^\circ$ and $40^\circ$ are average of several measurements. It can be seen that the shapes of the $\varphi$-dependences of the two are quite similar at $\alpha = 10^\circ$ and $20^\circ$. This result suggests that the $\varphi$-dependences of the Pt/Si(001) surface obtained at low incident angles are almost derived from c(4×6) reconstruction.
FIG. 3. Structural models of various Pt$_2$Si surfaces; Si-terminated Pt$_2$Si(001) (a), Pt-terminated Pt$_2$Si(001) (b), Pt$_2$Si(010) (c), Si-terminated Pt$_2$Si(110) (d), Pt-terminated Pt$_2$Si(110) (e), and Pt$_2$Si(112) (f). The upper illustration in each figure shows the top view, whereas the lower one is the slab model of the initial structure for the relaxation calculation of each surface.

The $\varphi$-dependences at $\alpha = 30^\circ$ and $40^\circ$ after the subtraction are shown in Fig. 5(a). The simulated $\varphi$-dependences based on the five surface termination models exhibited in Fig. 3(a–e) are shown as Fig. 5(b–f), respectively. First, we compare the experimental result of $\alpha = 30^\circ$ with each simulation result. Regarding the main peak around $\varphi = 35^\circ$ (and 55$^\circ$) of the experimental result, which are indicated by blue dotted line, neither Si-terminated nor Pt-terminated Pt$_2$Si(110) can reproduce the peaks [Fig. 5(e, f)]. Out of the remaining four surface termination models, only the simulation results based on the Si-terminated and Pt-terminated Pt$_2$Si(001) [Fig. 5(b, c)] reproduce the main peak around $\varphi = 20^\circ$ (and $60^\circ$) as in the experimental result of $\alpha = 40^\circ$, indicated by blue dotted line. Furthermore, there is another peak at $\varphi = 30^\circ$ (and $60^\circ$) in the simulation result of the Pt-terminated Pt$_2$Si(010) [Fig. 5(c)], which is not seen in the experimental result. Therefore, the Si-terminated Pt$_2$Si(001) is the most plausible surface for the Pt silicide formed in the present study. However, the peak around $\varphi = 10^\circ$ (indicated by green dotted lines) observed in the experimental results of $\alpha = 30^\circ$ and $40^\circ$ were not reproduced even in the simulation of the Si-terminated Pt$_2$Si(001) [Fig. 5(b)].

As mentioned in Fig. 1(a), two types of Pt silicide products, nanowires and islands, were formed on the Pt/Si(001) surface formed at 600$^\circ$C. It is known that nanowires tend to grow when the lattice mismatch with the substrate in the longitudinal direction is smaller and that in the short axis direction is larger [28]. However, the lattice constants in the two orthogonal directions of Pt$_2$Si(001) are the same. Therefore, the Si-terminated Pt$_2$Si(001) is considered to be the surface of the islands. It is also considered that the surface of the nanowire is
FIG. 4. Experimentally obtained azimuth angle (φ) dependences of Pt intensity; Pt/Si(001) surface (a) and c(4 \times 6) reconstruction (b).

FIG. 5. (a) Azimuth angle (φ) dependences of Pt intensity at α = 30° and 40° constructed by the subtraction of Fig. 4(b) from Fig. 4(a). The simulated φ-dependences obtained based on Si-terminated Pt$_2$Si(001), Pt-terminated Pt$_2$Si(001), Pt$_2$Si(010), Si-terminated Pt$_2$Si(110), and Pt-terminated Pt$_2$Si(110) are shown in (b)–(f), respectively.

FIG. 6. (a) Azimuth angle (φ) dependence of Pt intensity at α = 30° and 40° [identical to Fig. 5(a)]. (b) The φ-dependence created by adding simulation results of Si-terminated Pt$_2$Si(001) and Pt$_2$Si(010) in 4 : 1.

Finally, we discuss the surface energy $E_s$ of each termination with the bulk lattice constant (Si substrate was not taken into account). In the case of Pt$_2$Si(010), the $E_s$ is defined as,

$$E_s = (E_{\text{slab,r}} - n_{\text{unit}}E_{\text{bulk}})/2S + (E_{\text{slab,f}} - E_{\text{slab,f}})/S = (2E_{\text{slab,r}} - E_{\text{slab,f}} - n_{\text{unit}}E_{\text{bulk}})/2S,$$

where $E_{\text{slab,r}}$, $E_{\text{slab,f}}$, $E_{\text{bulk}}$, $n_{\text{unit}}$, and $S$ are the total energy of the relaxed slab model, that of the non-relaxed slab model, that of the bulk Pt$_2$Si per primitive unit cell, the number of primitive unit cell included in the slab, and the surface area of the slab, respectively. In the case of Pt$_2$Si(001) and Pt$_2$Si(110), the $E_s$ for Si termination is defined as,

$$E_s = [2E_{\text{slab,r}} - E_{\text{slab,f}} - n_Si\mu_{Si} - n_{Pt}(\mu_{Pt} + \Delta H_f/2)]/2S,$$

different from Pt$_2$Si(001), which must be the reason why Fig. 5(b) shows the inconsistency with the experimental results of Fig. 5(a). The minor peak (green dotted line) around φ = 10° seen in the experimental result of α = 40° in Fig. 5(a) can be reproduced by the simulation result of the Pt$_2$Si(010) surface [Fig. 5(d)]. On the Pt$_2$Si(010) surface, the lattice constants in two orthogonal directions are different, 2.6% in the [100] direction and 3.5% in the [001] direction, which is consistent with the growth mechanism of the nanowires above mentioned. Furthermore, the two simulation results, based on Pt$_2$Si(010) and Si-terminated Pt$_2$Si(001), were added together at a ratio of 1 : 4 [Fig. 6(b)], which shows good agreement with experimental results [Fig. 6(a)].
direction in the case of Pt2Si(010) as a top surface. Consequently, the surface of the side walls along the nanowire is composed of Pt2Si(001), which must decrease the energy of the nanowire. Thus, the present study strongly indicates that the nanowires and islands of the Pt silicide were composed of Pt2Si with (010) and Si-terminated (001) as surface planes, respectively.

IV. CONCLUSIONS

We analyzed the structure of Pt silicides grown on a Si(001) substrate by Pt deposition less than 1 ML at 600°C using CAICISS. The resulting surface always had two products, mainly islands, and nanowires. The structural analysis of the products was performed with taking up low index surface planes of Pt2Si as candidates. As a result, it was found that the nanowires and islands of the Pt silicide were composed of Pt2Si with (010) and Si-terminated (001) as surface planes, respectively. The surface energy determined by DFT calculation indicated that the Si-terminated Pt2Si(001) has the lowest energy among the examined surfaces. Although the surface energy of the Pt2Si(010) is larger than that of the Si-terminated Pt2Si(001), the energy of the nanowire would decrease by the side wall composed of Pt2Si(010). On the other hands, the surface energy of both Si-terminated and Pt-terminated Pt2Si(110) were much larger than those of Pt2Si(001) and Pt2Si(010). Thus, the calculation supports the experimental results.

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TABLE I. Lattice mismatch and the calculated surface energy of various surface termination of Pt2Si.

| Surface termination | Lattice mismatch (a, b) | Surface energy (eV/nm²) |
|---------------------|-------------------------|-------------------------|
| Pt2Si(001)-Si       | +2.6%, +2.6%            | 5.9                     |
| Pt2Si(001)-Pt       | +2.6%, +2.6%            | 8.2                     |
| Pt2Si(010)          | +2.6%, +3.4%*           | 9.3                     |
| Pt2Si(110)-Si       | -3.3%, +6.2%*           | 11.4                    |
| Pt2Si(110)-Pt       | -3.3%, +6.2%*           | 11.1                    |

* Lattice mismatch compared with 1.5 times the lattice constant of Si(001).

while for Pt termination is defined as,

\[ E_s = \frac{[2E_{slab,f} - E_{slab,i} - n_{Si}(\mu_{Si} + \Delta H_t) - n_{Pt}(\mu_{Pt})]}{2S}, \]

where \( n_{Si} \) and \( n_{Pt} \) are the numbers of Si and Pt atoms in the slab, respectively, and \( \mu_{Si} \) and \( \mu_{Pt} \) are the energy per atom in the Si and Pt bulks, respectively. \( \Delta H_t \) is a generation energy of Pt2Si bulk from Si and Pt bulks, and defined as,

\[ \Delta H_t = E_{bulk} - (\mu_{Si} + 2\mu_{Pt}). \]

For estimating the \( E_{slab,f} \), only top four [for Pt2Si(010)] and five [for Pt2Si(001) and Pt2Si(110)] layers in each slab model shown in Fig. 3 were relaxed.

The result is shown in Table I. It was found that the Si-terminated Pt2Si(001) has the lowest surface energy of 5.9 eV/nm², which is consistent with the experimental result that the surface of the Pt silicide islands are Si-terminated Pt2Si(001). On the other hand, the surface energy of the Pt2Si(010), which is considered to be the surface of Pt silicide nanowires, is 9.3 eV/nm². Although the value is larger than that of the Si-terminated Pt2Si(001), this surface energy is much smaller than those of both the Si-terminated and Pt-terminated Pt2Si(110). It is worth to be mentioned that the nanowire would grow along [100] direction.
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