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Structure of $NiSi_2$(111) Surface : An Atomic View

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$NiSi_2$(111) 표면의 구조 : 원자적 배율

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Abstract—The structure of $NiSi_2$/Si(111) has been studied by scanning tunneling microscopy. Atomically resolved STM images of this surface show an unreconstructed (1×1) structure with Si adatoms that tend to form trimers. The trimer can be used as a marker to differentiate type A and B interfaces. From the observed various defects, the surface is proven to be a simple bulk terminated layer.

요 약—$NiSi_2$(111)을 Si(111) 표면 위에 증착하여 그 구조를 STM으로 연구하였다. 실리사이드는 그 표면이 (1×1)의 구조를 띠고 여분의 trimer를 흡착 분자 구조로 가짐을 관찰하였다. 이 trimer로부터 실리사이드의 두 가지 구조 A, B를 구별할 수 있었다. 표면에 관찰된 결함으로부터 표면구조는 내부와 같음을 보았다.

1. Introduction

The mechanism and origin of Schottky barrier heights in metal/semiconductor interface have been an important issue in semiconductor physics for the last several decades[1, 2]. Depending on overlayer metal, metal-semiconductor interfaces reveal either ohmic contacts or Schottky barrier. Epitaxial metal overlayer on semiconductor surface has been a challenge for ohmic contact, Schottky diode and metal base transistor. Among metal metal semiconductor interfaces, the $NiSi_2$/Si(111) has unique properties; $NiSi_2$ has the cubic fluorite structure with a lattice constant that is 0.4% smaller than that of Si. Because of the good lattice match to Si, an epitaxial film of $NiSi_2$ can be grown on a Si(111) surface with abrupt and perfect interface[3]. As one of not many ideal metal-semiconductor interfaces, this interface has attracted much attention in semiconductor physics[4]. There have been many macroscopic studies on this system by photoemission[5], LEED[6], and Ruterford Back Scattering (RBS)[3]. Nanoscopic imaging of a metal-semiconductor interface and surface can provide crucial additional information to understand the geometric and electronic structures. Despite of the extensive studies, the surface and interface structures are not understood well. In this paper, the surface structure and the interface stacking sequence of the $NiSi_2$/Si(111) sy-

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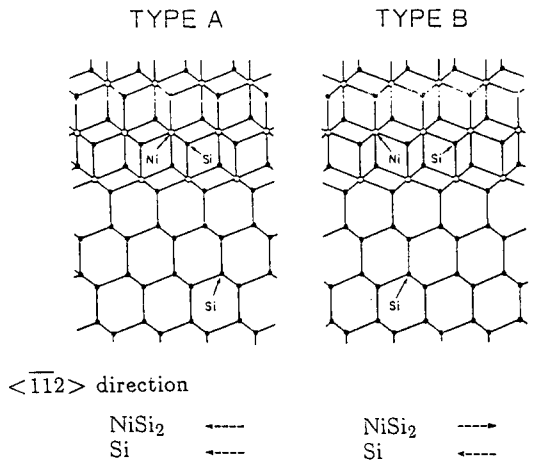

Fig. 1. Schematic side view model of the two types of the $NiSi_2$/Si(111) interface. Both $NiSi_2$ and Si(111) share the same crystallographic direction (a) in A-type silicide while they are rotated by 180° (b) in B-type.

stem have been resolved by STM and RBS. This is the second part of the relating papers[7] in which the surface and interface structure, the electron transport over the barrier, and nanoscopic electronic screening are described.

According to the relationship of the orientation of the two materials, there are two types of the interface: type A and B[3]. In case of the type A silicide, the silicide has the same orientation as the substrate. On the other hand, in case of type B silicide, the silicide shares the surface normal ⟨111⟩ axis with Si substrate but is rotated 180° about this axis (Fig. 1). The ⟨$\bar{1}$12⟩ directions of the Si substrate and silicides are shown in Fig. 1. While the directions are the same for the type A interface, those are opposite for type B. A, B or mixed type silicide interfaces was grown by the *template method*[3]. In addition, the Schottky barrier heights of these types of interface are known to differ by 0.14 eV.(Type A : 0.65 eV; Type B : 0.79 eV)[8]. This fact may shed new light on the formation mechanism of Schottky Barrier. In this paper, experimental procedure utilizing the template method will be described. Three types of defects were observed and used to justify the surface structure. The nanoscopic view of the interface by STM and BEEM (Ballistic Electron Emission Microscopy) will be published elsewhere[9].

2. Experimental

The detailed design of the STM used in this study can be found elsewhere[10]. A As doped Si (111) wafer with resistivity of 0.1 Ω-cm was prepared by Shiraki cleaning[11] in order to obtain clean dry oxide layer. After being introduced into UHV-STM chamber, the sample was outgassed at 600℃ for several hours and then flashed at 850℃. A sharp (7×7) pattern was obtained without any trace of impurity in Auger spectrum. A samll e-beam deposition source was used to deposit Ni with a typical deposition rate of ~1 monolayer/min. $NiSi_2$ layer was grown on the Si(111) substrate by the deposition of Ni and subsequent annealing at about 450℃. The type of the interface grown by the method depends on the amount of Ni deposited on the substrate before annealing. $NiSi_2$/Si(111) sample with Type A or B interface was checked by RBS and STM as described in the next section. The deposition of Ni of 10 Å with subsequent annealing produces pure B type interface and of 20 Å produces A type interface. Subsequent deposition of Ni deposition resulted in the same type of structure as described earlier[3]. Deposition of 30 Å Ni results in A and B mixed type interface where each domain is of ~100 Å wide. The coverage of $NiSi_2$ was measured *in situ* by Auger spectra or by *exsitu* RBS after STM measurement.

3. Results

A single domain $NiSi_2$ with the thickness of 10~200 Å could be grown by template method. Once the silicide are formed, the surface is quite stable and surface diffusion was hardly observable. The silicide surfaces were imaged by STM with the bias voltages of from −3~3 V. An STM image of the $NiSi_2$ surface is shown in Fig. 2. A bright vertical line at the center of the image is a double layer step. A surface unit cell with 3.8 Å nearest neighbor distance is indicated. The base unit of the silicide surface is a (1×1) structure, while those of Si(111)

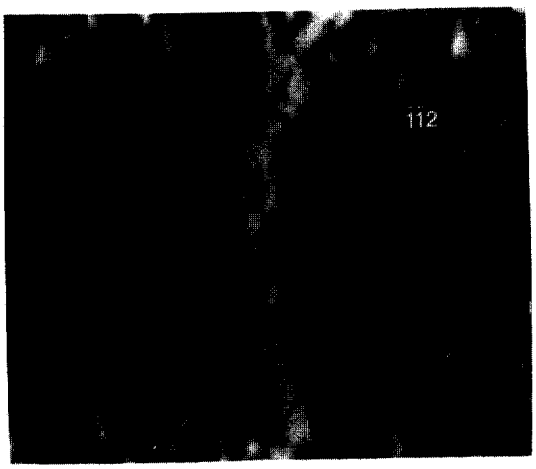

Fig. 2. 120×100 Å² image of a $NiSi_2$(111) surface. Individual Si atoms forming triangular lattice are 3.8 Å apart from each other. Trimers are aligned along the $\langle\bar{1}12\rangle$ direction. A double layer step is visible as a vertical bright line at the center.

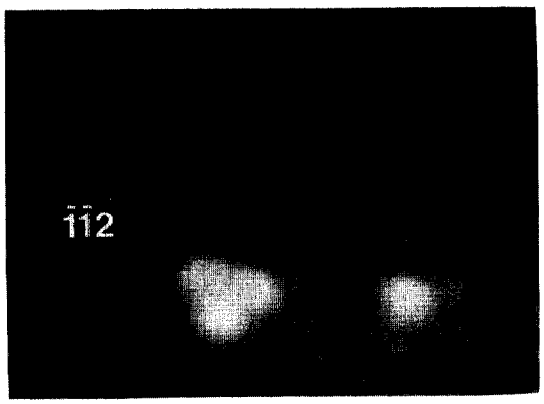

Fig. 3. 40×30 Å² image of $NiSi_2$(111) surface. The registry of a trimer is visible.

and Ge(111) is (2×2) structures. (Though there are some complication in Si(111)-(7×7) and Ge(111)-(2×8), the base unit is a (2×2) unit cell.) Only from STM images, it is difficult to determine whether the surface layer is a simple termination of bulk or not. Adatoms are observed on the surface and many of them form trimers with a shape of triangle. The trimers were proven to be Si adatoms from scanning tunneling spectroscopy (STS). The previous Auger study proved segregation of Si atoms

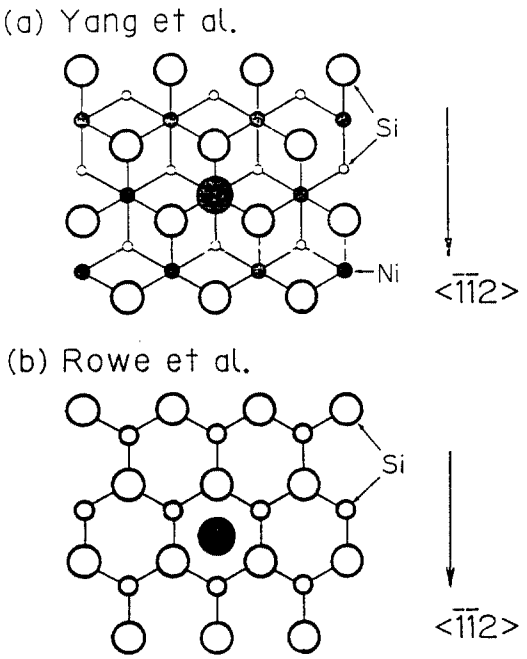

Fig. 4. Top views of $NiSi_2$ surface of Yang's and Rowe's models. The registry of Si adatoms are drawn as filled circles.

by annealing at high temperature[12]. As shown in Fig. 2 and Fig. 3, all trimers have the identical registry and point the same direction, $\langle\bar{1}12\rangle$.

One of important problems in the epitaxial growth of $NiSi_2$ on the Si(111)-(7×7) is how to determine and control the type of the silicide (A, B or mixed type). In the present, though STM images are mapping only surface layer, A unique method was devoloped to determine the type of the silicide in nanoscopic domain. Since the direction of the silicide can be determined by the adatom trimer, the type can be found if the crystallographic direction of Si(111) substrate is known. The crystallographic direction of substrate Si(111) can be easily determined by imaging a (7×7) image in which the faulted half points $\langle\bar{1}12\rangle$ direction. Once the Si (111)-(7×7) is imaged prior to the silicide growth, the type of silicide can be decided. This method is far more accurate than X-ray diffraction method or RBS since the latter measures an averaged quantity over macroscopic area and minor domains in it can be neglected. Even in an A and B mixed

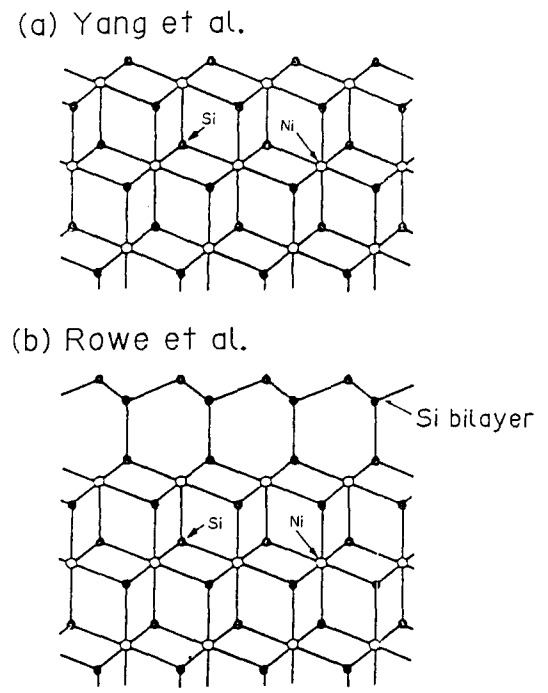

Fig. 5. Side views of $NiSi_2$ surface structures of Yang's and Rowe's model.

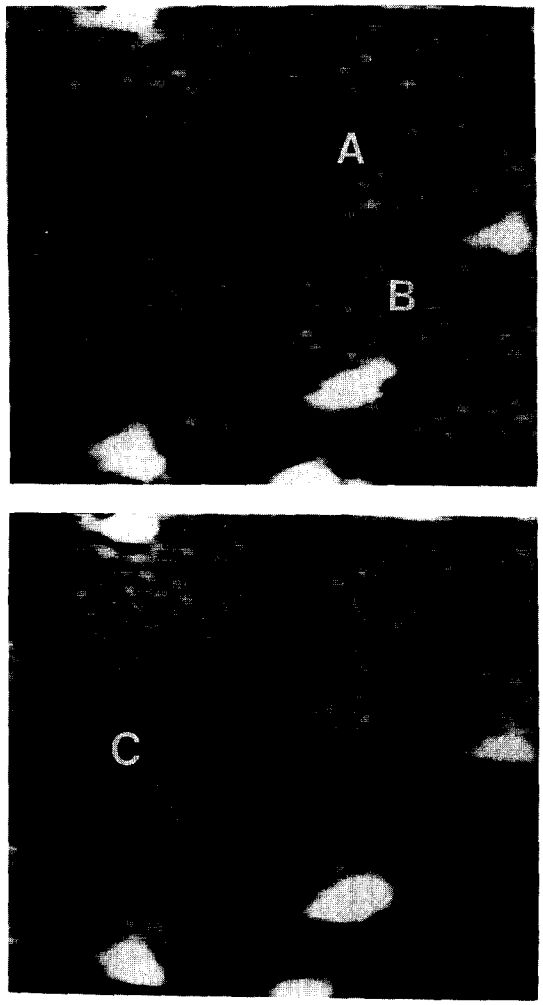

Fig. 6. 60×50 Å^2 images of $NiSi_2$ at the sample bias voltage of a) −1.2 V and b) 1.2 V. A, B, C defects are indicated by arrows.

type $NiSi_2$ film, the type of nanoscopic domain can be determined by this method. In our measurement, we often found small area B type silicide domain in "pure" A type silicide film grown by the template method. Fig. 4 shows the registry of the adatoms on $NiSi_2$(111)-(1×1) surface. All Si adatoms are located at 3-fold hollow sites on the surface. There are two different 3-fold hollow sites on the surface: on the center of a triangle pointing along the $\langle\bar{1}12\rangle$ or $\langle 11\bar{2}\rangle$. All adatoms are proven to be located at the latter sites.

Though the surface of $NiSi_2$ reveals (1×1) structure in STM and LEED, the subsurface many have a different stacking sequence. Two structural models have been proposed[5, 6]; In a LEED study, a bulk like termination with the first interlayer contracted by ~25% has been suggested by analyzing intensity vs. energy dependence. In a recent photoemission study[5], Rowe *et al.* measured 2 different surface states and concluded that there exsists additional silicon double layer with a stacking fault and additional random adatoms on the surface as shown in Fig. 5(b). The registry of the trimer adatom for this model is shown in Fig. 4(b). The spacing between the adatoms forming trimer is 1 unit length of the surface, different from that of the adatoms of the (7×7) structure, in which (2×2) is a base unit. For the model by Rowe *et al.*, the adatom site is above H3 site, different from T4 site of the adatoms of the (7×7) structure. Although the adatoms in the (7×7) structure are explained by saturation of the dangling bonds of the surface, the adatoms on $NiSi_2$ cannot be explained by this

mechanism. In Yang's model in the LEED study[6], the adatoms would be located on top of T4 site, while the second layer atom is Ni. Considering 6-fold bonding of Ni in the $NiSi_2$, this site would lower the surface energy. The surface states observed in the photoemission study can be originated from the trimer adatom states and additional adatoms which do not form trimers.

Three types of defects, which may be related to the Ni substitution, are observed in dual volatge images in Fig. 6, taken simulataneously with 2 bias voltages. The defects marked as A appear dark at the sample biases of -1.2 and 1.2 V, indicating that they are vacancy defects. At any bias volatge of $-3 \sim 3$ V, A defect appears dark. The B defects in Fig. 6 appear dark in the filled state image but similar with other atoms in the empty state image. From STS, Ni substitution of the surface Si atom would appear dark in the filled state image due to lower state density. At unoccupied state, the state density on top of Si is similar to that on top of the substituted Ni atoms. The C defects are a little darker than other surface atoms in both images. There is a little darker ring around the defect. If the second layer Ni atom is substitued by Si, this image can be explained. Similar kinds of defect were observed in the Si(111)-Al chemisorbed system[13]. The appearance of the three defects confirms the surface structure concluded from the adatom trimer registry; The $NiSi_2$(111) is a simple bulk termination with the first layer of Si and trimer adatoms.

4. Summary

The geometric and electronic structure of $NiSi_2$ (111) surface were studied. By using the trimer adatom as a marker, the type (A or B) of the silicides grown on Si(111) was determined. This method is applicable to a nanoscopic domain, therefore far more accurate than any other macroscopic methods. The template method to grow a single domain seems to work well in $NiSi_2$/Si(111) system. The surface energy of the $NiSi_2$ is lowered by having Si adatom trimers. By analyzing 3 types of vacancies, Yang's model (bulk-like termination) is more favorable than Si double layer for the surface structure.

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