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Materials

Interface structure between epitaxial $NiSi_2$ and Si

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Abstract: The interface structure between the Si and $NiSi_2$ epitaxially grown on the ($\bar{1}12$) Si substrate was studied using high resolution transmission electron microscopy and computer image simulation. The results showed that the interface between Si and $NiSi_2$ epitaxially grown on the ($\bar{1}12$) Si substrate has six different types: type A $NiSi_2$ ($\bar{1}11$)/($\bar{1}11$) Si, type A $NiSi_2$ (001)/(001) Si, type B $NiSi_2$ ($1\bar{1}\bar{1}$)/($1\bar{1}1$) Si, type B $NiSi_2$ ($\bar{1}12$)/($1\bar{1}2$) Si, type B $NiSi_2$ ($2\bar{2}1$)/(001) Si, and type B $NiSi_2$ ($1\bar{1}4$)/($1\bar{1}0$) Si. And there are one or more different atomic structures for one type of interface.

Key words: nickel silicide; interface; high resolution; image simulation; atomic structure

1. Introduction

Metal silicide is generally considered as a material for contact, gate, interconnection and so on in microelectronic devices. Due to their low sheet resistivity, self-alignment and high stability, silicides are widely used in very large and ultra large integrated circuits (VLSI/ULSI). Because of the lower temperature of formation, lower consumption of silicon and lower stress, nickel silicide has become an important material for advanced technologies with deep submicron geometries [1-3].

Si has diamond structure with a lattice constant of 0.543 nm. $NiSi_2$ possesses CaF_2 structure with a lattice constant of 0.54056 nm which is smaller than Si by 0.4%. Due to the good match between Si and $NiSi_2$ lattice, epitaxial $NiSi_2$ easily grows on the low index plane of Si substrate. It is well known that there are two types of epitaxial $NiSi_2$ on silicon. One is the type A $NiSi_2$ which possesses the same lattice orientation as Si and the other is the type B $NiSi_2$ which has twin relationship with type A $NiSi_2$ or Si. For cubic lattice, twin can be formed by the relative rotation of 70.53° along the common axis of [110].

The atomic structures of $NiSi_2$/(111) Si and type A $NiSi_2$/(001) Si interfaces had been studied by Chern *et al*. in 1982 [4] and 1984 [5], respectively. Werner *et al*. [6] investigated the $NiSi_2$/{111} Si interfaces bonding A type $NiSi_2$ islands on (111) Si in 1989. In 1990 Matthai *et al*. [7] found that the interface interplanar separation in type B case is less than type A from calculations of the energy of the $NiSi_2$/(111) Si interface. The fabrication, structure and properties of epitaxial $NiSi_2$ thin film had been examined by Tung in 1992 [8]. Chen *et al*. discussed the atomic faceting interfaces of $NiSi_2$/Si in 1993 [9] and 1995 [10], respectively. In 1994 Hesse *et al*. [11] presented the correlation between kinetic and structural observation during the $Ni+2Si \rightarrow NiSi_2$ reaction on the (111) Si interface. The microstructural characterization of ordered nickel silicide structures grown on (111) nickel silicide films had been studied by Ho *et al*. in 1996 [12]. In 2000 Schroeter *et al*. [13] summarized the understanding of structural and electronic properties of nickel silicide precipitate in silicon at that time.

In this work the interface structure between Si and $NiSi_2$ epitaxially grown on ($\bar{1}12$) Si substrate was studied by using high resolution transmission electron microscopy (HRTEM) and computer image simulation.

2. Experimental

The substrate ($\bar{1}12$) Si chip of 2 inch in diameter was cleaned by three steps: (1) the Si chip was sequentially cleaned in ethyl tri-chloride and acetone solution with supersonic vibration for 10 min and then rinsed by deionized water; (2) the Si chip was boiled for 10 min in acid solution (HNO_3:H_2SO_4=1:1) to grow a SiO_2 thin film and then rinsed by deionized water; and (3) the Si chip was dipped in HF solution

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(HF:H_2O=1:50) to remove the SiO_2 film and then immediately put into the chamber of electron gun evaporation-deposition system. The Ni film of about 30 nm in thickness was deposited on Si substrate (kept at room temperature) with a deposition rate of about 0.1 nm/s and a vacuum pressure below 2×10^{-6} torr.

After the Si chip deposited a Ni film was annealed for 20 min at 800°C in a furnace with N_2 atmosphere, it was then ground to a very thin sample for observation of lattice images in a transmission electron microscope (JEOL 4000 EX) operated at C_s=1.0 mm, Δf=15 nm, α=0.5 mrad, acceleration voltage=400 kV and allowed tilt angle = ±25°.

The atomic models of the interface between Si and $NiSi_2$ were produced using the Crystallcit software. In the process of model production' coordinates of unit cells were inputted into the software and the interface models were then established by defining the orientations of the two crystals and the direction of interfaces. The width of the interface and the rigid body translation between crystals (the relative displacement of the two crystals along the interface direction) can be adjusted and the location of each atom can be adjusted by changing its coordinates. After the atomic model of the interface was produced, the image simulation was carried out using the Mactempas software in which "multi-sliced method" was used for calculation.

At the last stage the simulation image was compared with the high resolution image of TEM (HRTEM image) using the "Adobe photoshop" software. In the comparison process the images were inputted into computer by scan and carried out for image treatment. The exact atomic model of the interface can be finally obtained after corrections once and again.

3. Results and discussion

In total there being six types of interfaces between epitaxial $NiSi_2$ and $(\bar{1}12)$ Si substrate were found in this work: type A $NiSi_2$ (001)/(001) Si, type A $NiSi_2$ $(\bar{1}11)/(\bar{1}11)$ Si, type B $NiSi_2$ $(2\bar{2}1)/(001)$ Si, type B $NiSi_2$ $(1\bar{1}\bar{1})/(1\bar{1}1)$ Si, type B $NiSi_2$ $(\bar{1}12)/(1\bar{1}2)$ Si, and type B $NiSi_2$ $(1\bar{1}\bar{4})/(1\bar{1}0)$ Si. Fig. 1 shows a TEM cross section image of the epitaxial $NiSi_2$ grown on the $(\bar{1}12)$ Si substrate, showing the epitaxial $NiSi_2$ has two different forms: type A $NiSi_2$ and type B $NiSi_2$. The high resolution transmission electron microscope (HRTEM) images of type A $NiSi_2$ and type B $NiSi_2$ on the $(\bar{1}12)$ Si substrate are shown in Figs. 2 and 3, respectively. From Fig. 2 it can be seen that there are two types of interfaces between type A $NiSi_2$ and $(\bar{1}12)$ Si substrate: type A $NiSi_2$ $(\bar{1}11)/(\bar{1}11)$ Si and type A $NiSi_2(001)/(001)$ Si. Fig. 3 shows the HRTEM images of type B $NiSi_2$ $(1\bar{1}\bar{1})/(1\bar{1}1)$ Si and type B $NiSi_2$ $(2\bar{2}1)/(001)$ Si interfaces. The HRTEM images of these two types of interfaces are also shown in Fig. 4. The HRTEM image of type B $NiSi_2$ $(1\bar{1}\bar{4})/(1\bar{1}0)$ Si is shown in Fig. 5. The interface of type B $NiSi_2$ $(\bar{1}12)/(1\bar{1}2)$ Si is shown in the right part of Fig. 6 and the interface in the left part is type A $NiSi_2$ $(\bar{1}11)/(\bar{1}11)$ Si.

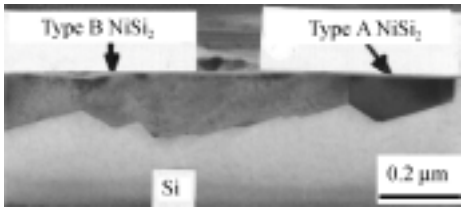

Fig. 1. TEM cross section image of the epitaxial $NiSi_2$ grown on the $(\bar{1}12)$ Si substrate.

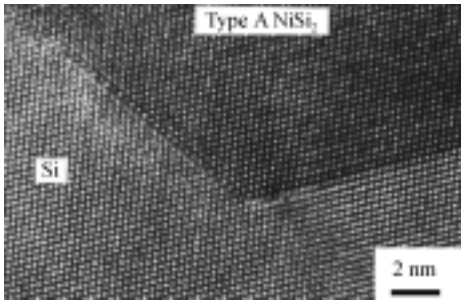

Fig. 2. HRTEM image of type A $NiSi_2$ on the $(\bar{1}12)$ Si substrate.

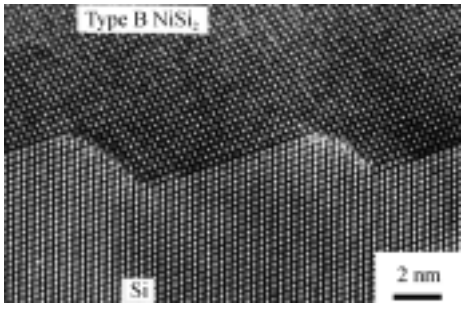

Fig. 3. HRTEM image of type B $NiSi_2$ on the $(\bar{1}12)$ Si substrate.

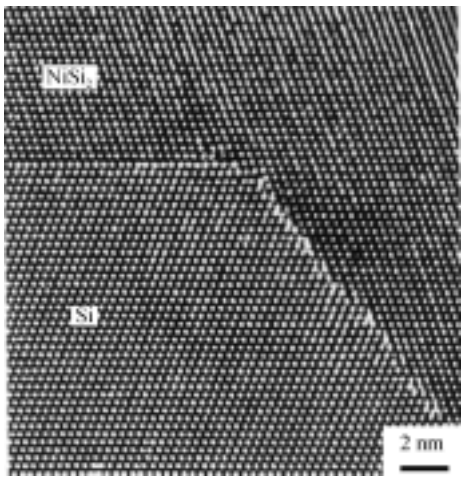

Fig. 4. HRTEM images of type A and B of the interfaces.

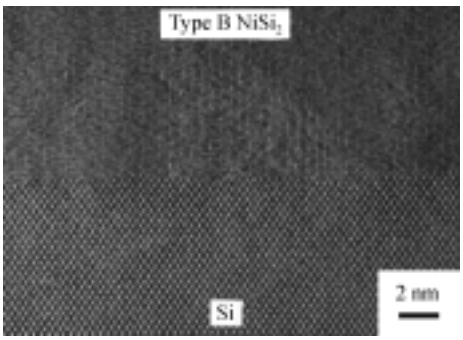

Fig. 5. HRTEM image of type B $NiSi_2$ $(1\bar{1}\bar{4})/(1\bar{1}0)$ Si interface.

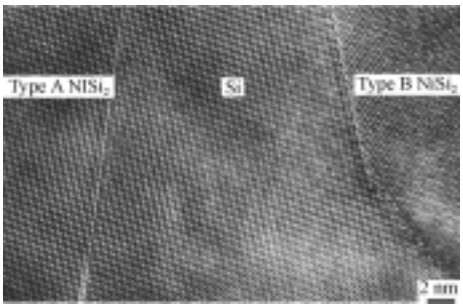

Fig. 6. HRTEM image of type A $NiSi_2$ $(\bar{1}11)/(\bar{1}11)$ Si and type B $NiSi_2$ $(1\bar{1}\bar{4})/(1\bar{1}0)$ Si of the interface.

To make the computer simulation images of interfaces, various interface models must be previously established. In this work a coincidence site lattice (CSL) method was used to establish the interface models. The unit cell of $NiSi_2$ can be formed by the interpenetration of three face center cubic (FCC) unit cells of Ni(0, 0, 0), Si (1/4, 1/4, 1/4) and Si (3/4, 3/4, 3/4). The unit cell of Si can also result from the interpentration of two FCC unit cells of Si (0, 0, 0) and Si (1/4, 1/4, 1/4). For the interface models of type A $NiSi_2$/Si, their coincidence site lattice can be obtained by connecting the coincidence atoms in the atomic array formed from the direct overlap of [110] projections of $NiSi_2$ and Si lattices. To obtain the coincidence site lattice for type B $NiSi_2$ /Si, the lattices of $NiSi_2$ and Si should be rotated 70.53° relative to each other before their [110] projections were overlapped.

Fig. 7 shows the four possible interface models for $NiSi_2$ $(\bar{1}12)/(1\bar{1}2)$ Si derived from the coincidence site lattice. All the bonds of Ni–Si and Si–Si have the same length (0.234 nm) in Figs. 7 (a) and (b). But in Figs. 7(c) and (d) the Ni–Si and Si–Si bonds in five-atom and six-atom rings have a lattice distortion. Figs. 8(a)-(d) show the computer simulation images under the defocusing of –32 nm and the thickness of 4 nm corresponding to Figs. 7(a)-(d), respectively. The common {111} lattice planes of $NiSi_2$ and Si are continuous in Figs. 8(a) and (b) and have a lattice displacement in Figs. 8(c) and (d) across the interface. From Fig. 9, a HRTEM image of type B $NiSi_2$ $(\bar{1}12)/(1\bar{1}2)$ Si interface, it can be seen that the common {111} lattice planes of $NiSi_2$ and Si have a little displacement across the interface which is similar with Fig. 8(c). The inset in the central part of Fig. 9 is Fig. 8(c), it is apparent that they match up very well.

For the interface of type A $NiSi_2$ (001)/(001) Si, there are four different coincidence site lattices, from which eight possible interface models can be derived. And eight computer simulation images can be formed in correspondence to these eight possible interface models. After comparing the computer simulation images with the HRTEM images, three types of atomic structures can be confirmed for the interface of type A $NiSi_2$ (001)/(001) Si. One of them had been studied by Cherns *et al*. [4], in which Ni atoms have six-fold coordination interface. Another type of atomic structure also has Ni atoms of six-fold coordination. This type of atomic structure is different from the six-fold coordination interface and can be called the corrected six-fold coordination interface. The third type of atomic structure of type A $NiSi_2$ (001)/(001) Si interface is one in which Ni atoms have alternate six-fold and eight-fold coordinations and can be called 2×1 reconstruction interface.

The procedure for determining the atomic structures of type A $NiSi_2$ $(\bar{1}11)/(\bar{1}11)$ Si interface is similar to type A $NiSi_2$ (001)/(001) Si interface. There are six possible interface models and six corresponding computer simulation images for type A $NiSi_2$ $(\bar{1}11)/(\bar{1}11)$ Si interface. After comparing the computer simulation images with the HRTEM images, the interface of type A $NiSi_2$ $(\bar{1}11)/(\bar{1}11)$ Si possesses one atomic structure in which Ni atoms have seven-fold coordination. This type of atomic structure can be called the seven-fold coordination interface which is the same with the result studied by Cherns *et al*. [5]. Besides the seven-fold coordination interface, there is still another atomic structure being found in this work, shown in Fig. 10(a). In this interface the Si–Si bonds are lengthened and distorted slightly and Ni atoms still have seven-fold coordination, so it can be called the corrected seven-fold coordination interface. The atomic structure for this interface does not belong to the six possible interface models stated above. It is shown in Fig. 10(b) and the computer simulation image corresponding to it is inserted in the central part of Fig. 10(a). It can be seen that the computer simulation image and the HRTEM image match up very well.

The procedure for determining the atomic structures of type B $NiSi_2$ $(\bar{1}12)/(1\bar{1}2)$ Si interface can also be used for type B $NiSi_2$ $(1\bar{1}\bar{1})/(1\bar{1}1)$ Si interface. There are six possible atomic structure models and six

corresponding computer simulation images for type B $NiSi_2$ $(1\bar{1}\bar{1})/(1\bar{1}1)$ Si interface. But only one type of interface was found and confirmed in this work. In this interface Ni atoms have seven-fold coordination which is the same with the result published by Cherns *et al*. [5].

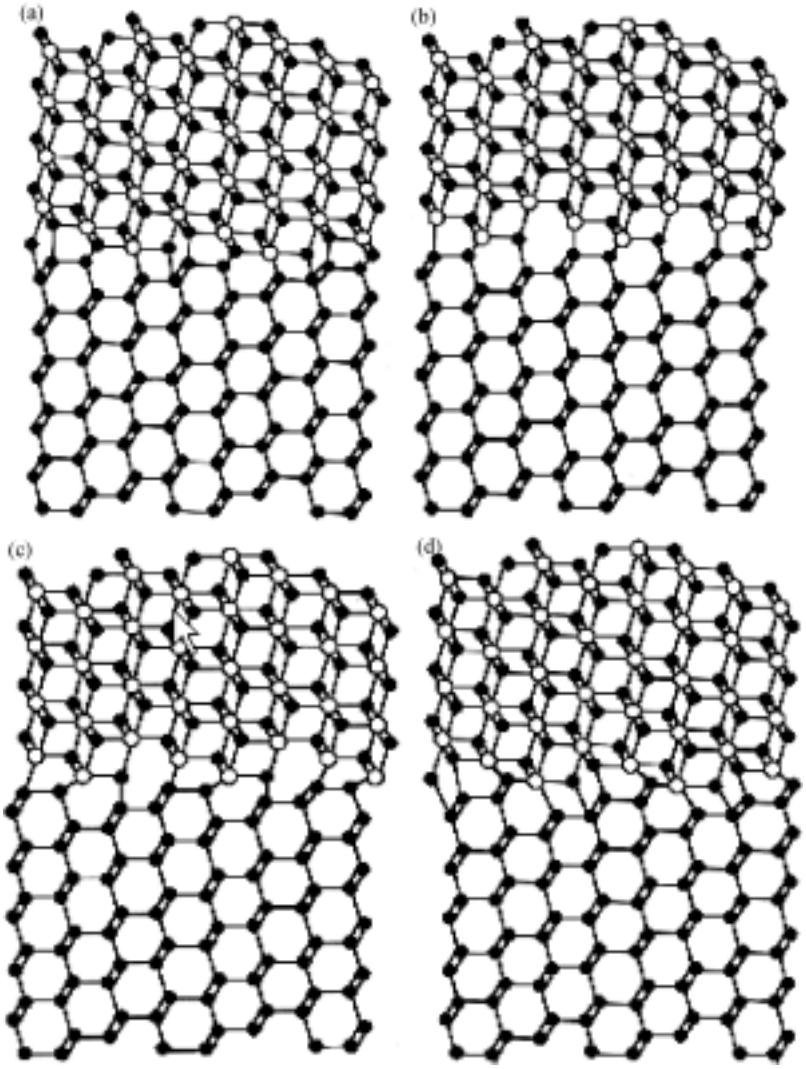

Fig. 7. Four possible interface models for $NiSi_2(\bar{1}12)/(1\bar{1}2)$ Si: (a) and (b) the bonds of Ni–Si and Si–Si having the same length; (c) and (d) the Ni–Si and Si–Si bonds in five-atom and six-atom rings having a lattice distortion.

Because the boundary planes of $NiSi_2$ and Si in type B $NiSi_2$ $(2\bar{2}1)/(001)$ Si interface do not belong to any common plane groups, this type of interface is viewed as the asymmetric heterogeneous twin interface. The interface of type B $NiSi_2$ $(2\bar{2}1)/(001)$ Si can be viewed as the composition of interfaces of type B $NiSi_2$ $(1\bar{1}\bar{1})/(1\bar{1}1)$ Si and type B $NiSi_2$ $(1\bar{1}2)/(\bar{1}12)$ Si. There are four possible atomic structure models and four corresponding computer simulation images for type B $NiSi_2$ $(2\bar{2}1)/(001)$ Si interface derived by the same CSL method as above. After comparing the computer simulation images with the HRTEM images, the interface of type B $NiSi_2$ $(2\bar{2}1)/(001)$ Si has two different structures. One of them is shown in Fig. 3 where the common {111} lattice plane of $NiSi_2$ and Si has a displacement across the interface. And in the other structure the common {111} lattice plane of $NiSi_2$ and Si is continuous as it crosses the interface.

Although the interface of type B $NiSi_2$ $(1\bar{1}\bar{4})/(1\bar{1}0)$ Si has been shown in Fig. 5, its atomic structure can not be easily determined. Because all the samples in TEM are observed from the <110> direction, not only type B $NiSi_2$ and Si with the same <110> direction but also type B $NiSi_2$ with the <114> direction and Si or type A $NiSi_2$ with the <110> direction can be observed. The atomic structure of the interface can be determined only as $NiSi_2$ and Si are in the same <110> direction. Therefore, the atomic structure of type B $NiSi_2$ $(1\bar{1}\bar{4})/(1\bar{1}0)$ Si interface was not determined in this work.

From the viewpoint of crystal theory, the relationship of lattice plane index between type B epitaxial $NiSi_2$ and Si can be derived out. The type B lattice can be formed by rotating $NiSi_2$ by 70.53° around [110] axis relative to the Si substrate. The rotation matrix ***R***

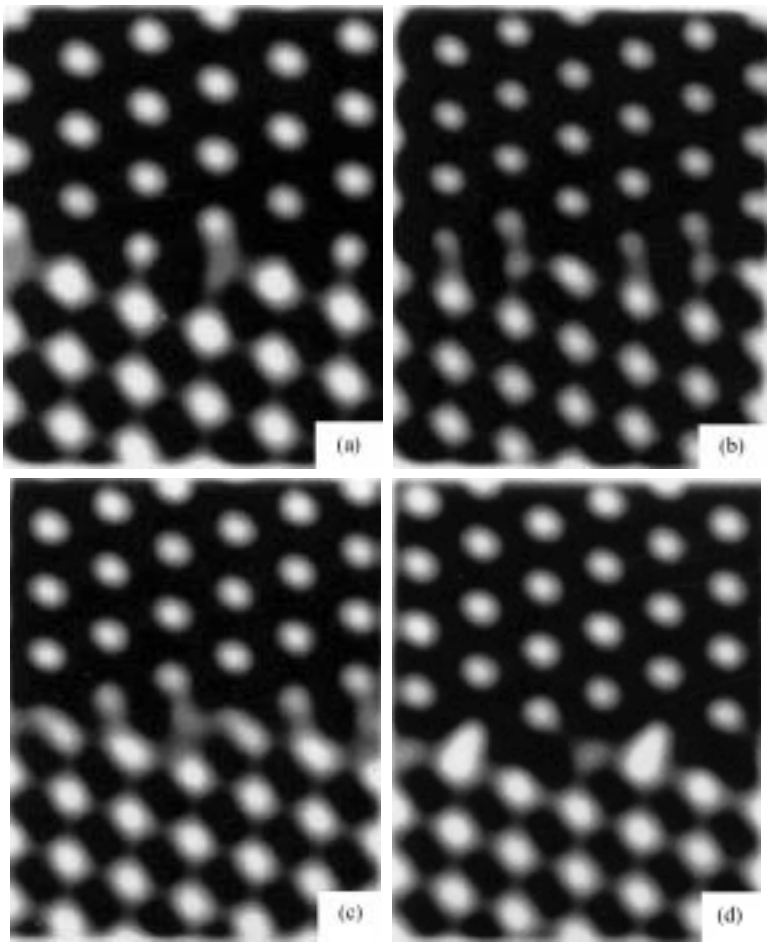

Fig. 8. Computer simulation images corresponding to Figs. 7(a)-(d): (a) and (b) the common {111} lattice planes of $NiSi_2$ and Si being continuous; (c) and (d) they having a lattice displacement across the interface.

for the transformation of cubic lattice is given as the following:

$$\boldsymbol{R}=\cos\theta\begin{bmatrix}1&0&0\\0&1&0\\0&0&1\end{bmatrix}+(1-\cos\theta)\begin{bmatrix}C_1C_2&C_1C_2&C_1C_3\\C_2C_1&C_2C_2&C_2C_3\\C_3C_1&C_3C_2&C_3C_3\end{bmatrix}+\sin\theta\begin{bmatrix}0&-C_3&C_2\\C_3&0&-C_2\\-C_2&C_1&0\end{bmatrix}$$

where C_1, C_2 and C_3 are the components of unit direction $[C_1\ C_2\ C_3]$ of the rotation axis; θ is the rotation angle.

For $NiSi_2$/Si system, $[C_1\ C_2\ C_3]=\left[\frac{1}{\sqrt{2}}\ \ \frac{1}{\sqrt{2}}\ \ 0\right]$ and θ=70.53°. Therefore, $\boldsymbol{R}=\begin{bmatrix}\frac{2}{3}&\frac{1}{3}&\frac{2}{3}\\\frac{1}{3}&\frac{2}{3}&\frac{-2}{3}\\\frac{-2}{3}&\frac{2}{3}&\frac{1}{3}\end{bmatrix}$.

Letting $[h\ k\ l]$ and $[H\ K\ L]$ be the indices of Si and $NiSi_2$ lattice plane, respectively. The $[h\ k\ l]$ and $[H\ K\ L]$ have the following relationship:

$$[H\ K\ L]=\begin{bmatrix}\frac{2}{3}&\frac{1}{3}&\frac{2}{3}\\\frac{1}{3}&\frac{2}{3}&\frac{-2}{3}\\\frac{-2}{3}&\frac{2}{3}&\frac{1}{3}\end{bmatrix}\begin{bmatrix}h\\k\\l\end{bmatrix}.$$

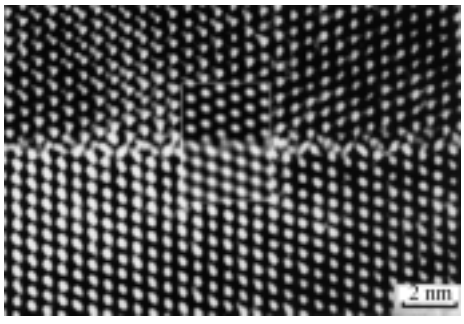

Fig. 9. HRTEM image and simulation image inset in the central part of type B $NiSi_2$ $(\bar{1}12)/(1\bar{1}2)$ Si interface.

After calculation, all possible type B $NiSi_2$ $(H\ K\ L)$/$(h\ k\ l)$Si interfaces with the planes of low Miller indices can be obtained: $(2\bar{2}1)/(001)$, $(1\bar{1}\bar{4})/(1\bar{1}0)$, $(1\bar{1}\bar{1})/(\bar{1}\bar{1}1)$, $(\bar{1}1\bar{5})/(1\bar{1}\bar{1})$, $(1\bar{1}2)/(\bar{1}12)$, $(\bar{1}1\bar{1})/$

$(1\bar{1}\bar{5})$ and $(1\bar{1}1)/(\bar{1}15)$.

Comparing the theoretical derivation and experimental observation, the three interfaces of type B $NiSi_2$ $(\bar{1}1\bar{5})/(1\bar{1}\bar{1})$ Si, type B $NiSi_2$ $(\bar{1}1\bar{1})/(1\bar{1}\bar{5})$ Si and type B $NiSi_2$ $(1\bar{1}1)/(\bar{1}15)$ Si had not been found in this work.

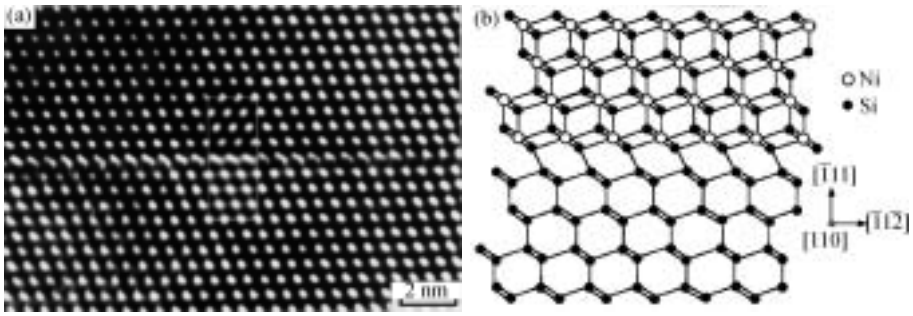

Fig. 10. (a) HRTEM image and the simulation image inset in the central part of type A $NiSi_2$ $(\bar{1}11)/(\bar{1}11)$ Si interface and (b) the atomic structure model for the interface of (a).

4. Conclusions

(1) After the $(\bar{1}12)$ Si chip deposited a film of Ni was annealed for 20 min at 800°C in a furnace with N_2 atmosphere, there was epitaxial $NiSi_2$ grown on the surface of the Si substrate. Between the epitaxial $NiSi_2$ and Si substrate there are six types of interfaces: type A $NiSi_2$ (001)/(001) Si, Type A $NiSi_2$ $(\bar{1}11)/(\bar{1}11)$ Si, type B $NiSi_2$ $(2\bar{2}1)/(001)$ Si, type B $NiSi_2$ $(1\bar{1}\bar{1})/(1\bar{1}1)$ Si, type B $NiSi_2$ $(\bar{1}12)/(1\bar{1}2)$ Si and type B $NiSi_2$ $(1\bar{1}4)/(1\bar{1}0)$ Si.

(2) The interface of type A $NiSi_2$ (001)/(001) Si has three different atomic structures: six-fold coordination interface, corrected six-fold coordination interface, and 2×1 reconstruction interface. The six-fold coordination and corrected six-fold coordination structures may coexist in one interface.

(3) The interface of type A $NiSi_2$ $(\bar{1}11)/(\bar{1}11)$ Si has two atomic structures: seven-fold coordination interface and corrected seven-fold coordination interface. In the interface of type B $NiSi_2$ $(\bar{1}12)/(1\bar{1}2)$ Si the Ni–Si and Si–Si bonds in the five-atom and six-atom rings have a little distortion. Only one structure for type B $NiSi_2$ $(1\bar{1}\bar{1})/(1\bar{1}1)$ Si interface was found and the Ni atoms in this interface have seven-fold coordination.

(4) The interface of type B $NiSi_2$ $(2\bar{2}1)/(001)$ Si can be viewed as the composition of the interfaces of type B $NiSi_2$ $(1\bar{1}\bar{1})/(1\bar{1}1)$ Si and type B $NiSi_2$ $(1\bar{1}2)/(\bar{1}12)$ Si. There are two structures for this type of interface. In one structure the common {111} lattice planes of $NiSi_2$ and Si have a displacement and in the other structure they are continuous across the interface.

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