Stability and Schottky barrier of silicides: First-principles study

T. Nakayama*, S. Sotome, and S. Shinji

Department of Physics, Chiba University, 1-33 Yayoi, Inage, Chiba 263-8522,
Japan

Abstract: Using first-principles calculations, we explain why some metal atoms such as Ni produce bulk silicides and the others like Au never produce silicides, why silicides with some stoichiometry are difficult to grow on Si substrate, and why Schottky barrier for electrons simply decreases as the Si ratio in silicides increases. It is shown that the key origins to answer these questions are the electron transfer from Si- p to metal-atom- d orbitals and the energy losses by the elastic strain and the bond-breaking at the interface.

KEYWORDS: silicide; silicide/Si interfaces; stability; Schottky barrier; first principles calculation

*Corresponding author. Fax: +81 43 290 2874.

Email address: nakayama@physics.s.chiba-u.ac.jp

1. Introduction

As promising candidates for source/drain metals in near-future nanoscale Si devices, a variety of silicides have again attracted intensive attention in these days. However, there remain many elementary questions concerning the stability and electronic properties of silicide systems [1]. For example, it is well known that most transition metals and rare earth metals like Ni produce metal silicides by mixing with Si, while sp-orbital metals like Al and a few transition metals such as Au and Ag have no silicide phases in their bulk phase diagrams [2]. In addition, some silicides like Mg_2Si and FeSi_2 become semiconductors. What physical origins distinguish such difference of silicide formation?

With respect to silicide/Si interfaces, though there exist many silicide phases like Ni_xSi_y in the bulk growth depending on the ratio of metal and Si atoms, only the silicides with specific stoichiometry of $(x,y)=(1,2)$, $(1,1)$, $(2,1)$ are allowed to grow on Si substrate [3]. What is the reason of such selective silicide formation? Moreover, it is often observed in a number of silicide/Si interfaces that the Schottky barrier for electrons simply decreases as the Si ratio in M_xSi_y (M=metal atom) increases [4]. Are there any obvious reasons for such Schottky-barrier variation with changing the silicide stoichiometry? The purpose of this work is to answer these questions using the first-principles theoretical calculations.

Theoretical calculations were performed using the standard first-principles method (TAPP code) based on the density functional theory. To simulate the interfaces, we adopted the repeated unit cell. The calculation

details are described in the literatures [5, 6].

2. Stabilization mechanism of bulk silicides

First, we consider why some metal atoms produce silicides and the others never produce silicides. Table I shows the calculated formation energies of NiSi_2 , TiSi_2 , AuSi_2 , and AlSi_2 , which all have a CaF_2 fcc structure. The formation energy is defined as the energy difference between a silicide phase and a metal/Si phase-separated one. It is seen that Ti and Ni silicides are stable, while Au and Al silicides are unstable, being in good agreement with the observation [2].

The reason of such formation-energy difference can be found by analyzing the band structures. Figures 1(a) and 1(b) show the calculated band structures of Ni and Au bulks, where the Fermi-energy position is selected as the energy origin, 0eV. Ni bulk has flat five d -orbital bands (-4 ~+0.5eV) and s -orbital bands (-9 ~+7eV), while Au has d (-7.5 ~-2eV) and s bands (-11~+4eV), respectively. The most important difference between Ni and Au is the electron occupation in d bands; all d bands are occupied by electrons in Au, while about a half electron is unoccupied in the top d band of Ni.

Figures 1(c) and 1(d) show the band structures of NiSi_2 and AuSi_2 . When the silicides are formed, one can see the deformation of metal-originated bands, which is caused by the production of covalent-like bonds between metal and Si atoms due to the hybridization of $s+d$ orbitals of metal atom and $s+p$ orbitals of Si, as seen in the case of metal/Si interfaces [7, 8].

However, we can roughly identify the relatively flat bands in NiSi_2 ($-9 \sim -3\text{eV}$) and in AuSi_2 ($-9 \sim -6\text{eV}$), which are mainly made of d orbitals of metal atoms. Moreover, we note that these d bands are located far below the Fermi energy in cases of silicides, compared to the cases of bulks. On the other hand, the electronic states around the Fermi energy are mainly made of Si p -orbitals. In fact, one can see three-folded degeneracy around $+2\text{ eV}$ at the center of the Brillouin zone, G, reflecting the Si p -orbital degeneracy. It should be noted here that such energy-band alignment reflects the atomic orbital energies; most d orbitals of transition-metal atoms have lower energies than the p orbitals of Si [8].

The most remarkable feature is that the d bands of Ni, which are partially unoccupied in bulk, become fully occupied in NiSi_2 . This feature indicates that the electron-charge transfer occurs from Si p orbitals to Ni d orbitals in NiSi_2 due to the orbital hybridization. However, in case of AuSi_2 , since the d bands are already fully occupied by electrons in bulk Au, such transfer never occurs. In this view, we can expect that the stability of metal silicides is realized by the charge transfer from Si to unoccupied d -orbital states of transition-metal atoms. This stabilization scenario of metal silicides well explains why transition metals have stable silicide phases except Au and Ag and why Al having no d -orbital states never produces silicides.

Finally, we shortly comment on the electronic structures of semiconductor silicides. In spite of the same stoichiometry, some silicides such as Mg_2Si and $\beta\text{-FeSi}_2$ show semiconducting properties. The key is the crystal structures of these systems that reflect the valency of metal atoms.

For example, most M_2Si metal silicides have orthorhombic Co_2Si structure, while Mg_2Si has cubic CaF_2 one. Figures 2(a) and 2(b) show the calculated band structures of Mg_2Si and Si. Since Mg_2Si is a compound made of Mg and Si, one can see the band splitting at the Brillouin-zone boundaries around X and L points similar to the case of GaAs. However, it is surprising that overall band structures are similar between Mg_2Si and Si. This occurs because the basic crystal structure and the number of valence electrons in a unit cell are similar between these systems.

3. Stability of silicides on Si substrate

Next, we study the stability of silicides on the Si substrate. Figures 3(a) and 3(b) show the calculated phase diagrams of Ni_xSi_y as a function of chemical potentials of Ni and Si, in cases of (a) the bulk growth and (b) the growth on the Si substrate, respectively. Here, we consider $NiSi_2$, $NiSi$, Ni_2Si , and Ni_3Si phases with observed cubic- CaF_2 , ortho-MnP, ortho- Co_2Si , and cubic- $AuCu_3$ structures. Considering the crystal symmetry and the lattice constant, $NiSi_2$ and Ni_2Si are located on Si(111) surface, while $NiSi$ and Ni_3Si are on Si(100). These diagrams denote the most stable phase judged by comparing the formation energies of four phases as a function of chemical potentials. Chemical potentials represent the supply ratios of Ni and Si atoms and the grey regions correspond to allowed regions to grow in thermal equilibrium without phase separation. It is clearly seen that all $NiSi_2$, $NiSi$, Ni_2Si , and Ni_3Si phases are realized in the bulk growth depending on the growth condition. However, Ni_3Si phase becomes difficult to grow on the Si

substrate, being in good agreement with experiments [3]. Similar results are also obtained when we consider Ti_xSi_y silicides.

The instability of Ni_3Si occurs due to the shift of vertical phase boundary lines in diagrams and such shift is found caused by two factors. One is the elastic strain in Ni_xSi_y . As the ratio of Ni increases, the lattice constant of Ni_xSi_y increases and the compressed strain in Ni_xSi_y increases, which pushes Ni_3Si phase out of the stable region. In fact, NiSi_2 , NiSi , Ni_2Si , and Ni_3Si phases receive about 0, 1, 4, and 8 percent compressed strains and have about 0, 0.08, 0.35, and 0.52 eV elastic energy losses per unit cells, respectively. The other factor is the energy loss of the interface bonding. With increasing Ni, the number of stable Si-Si covalent bonds decreases at the interface, which also promotes the instability of Ni_3Si . In fact, NiSi_2 , Ni_2Si , and Ni_3Si have about 0.4, 0.3, and 0.7 eV bonding-energy losses at the interface, compared to the NiSi/Si interface.

Although Fig. 3(b) represents the thermal equilibrium property, it is interesting to estimate how the silicidation occurs at Ni/Si interfaces using this diagram. Ni-silicide source/drain electrodes are often produced by first stacking Ni metals on Si substrate and then heating the system to realize the intermixing between Ni and Si. During this silicidation, the Ni chemical potential proceeds to decrease from the bulk value around $\mu_{\text{Ni}} = -41.3$ eV by consuming Ni atoms, while the Si chemical potential remains around the bulk value of $\mu_{\text{Si}} = -3.95$ eV because of a large amount of Si atoms in the substrate. Thus, we can expect that the Ni_2Si is first produced at the interface, then NiSi phase appears, and finally one obtains NiSi_2 .

4. Schottky barrier on Si substrate

Then, we consider the Schottky barrier at metal-silicide/Si interfaces. Even in case of well-studied Ni_xSi_y /Si interfaces, the observed values scatter with an error of about 0.2 eV and there is no consensus. Such scatter is believed caused by the polymorphic Ni_xSi_y structures around the interface [4]. Thus, it is interesting to clarify the intrinsic values of Schottky barrier. Figure 4(a) and 4(b) respectively show the calculated Fermi energy positions of various Ni_xSi_y and Ti_xSi_y at the Si interfaces. It is seen that the work function of silicides decreases as the ratio of Si increases, which tendency is consistent with the observations at oxide interfaces such as SiO_2 . Thus, we can conclude that the observed Schottky-barrier variation is intrinsic not to the interface property but to the silicide property.

Such variation of work function is a natural result expected from the stability mechanism of silicides. Since the valence energy states of Si are located above those of Ni and Ti, the charge transfer occurs from Si to Ni and Ti in M_xSi_y and lowers the Fermi energy positions originated from Si electronic states. As the Si ratio of M_xSi_y increases, since there are many Si-like electronic states around the Fermi energy, such charge-transfer hardly contributes to lower the Fermi energy.

Finally, we consider how the Schottky barrier changes when some dopants are incorporated into the silicides. Manabe *et al.* showed for NiSi_2 structures that the doping of B and P atoms into NiSi_2 silicide increases and decreases the NiSi_2 workfunction, respectively, thus the doping becomes one

of effective method to control the workfunction, although the electronegativity is large for P compared to B [9]. This result is easily explained by considering the electronic structure of silicides. If we assume that these dopants are incorporated at Si sites as substitutional impurities, since B and P have less and more valence electrons than Si, respectively, the B and P-doped silicides effectively correspond to the silicides with less and more Si atoms. Therefore, the B-doped silicide has the lower Fermi-energy position, while the P-doped one possesses the higher Fermi-energy position.

5 Conclusions

We have studied the stability and Schottky barrier of various silicides by the first-principles calculations. We first clarified that the transition-metal silicides stabilize by the electron transfer from p -orbital states of Si to d -orbital states of transition-metal atoms, which explains why transition metals except Au and Ag produce silicides. Then, we showed that some stoichiometric silicides are forbidden to grow on Si substrate due to the elastic-energy loss caused by the lattice mismatch on Si and the interface-bond energy loss. Moreover, we found that the Schottky barrier at silicide/Si interface is closely related to the stabilization mechanism of silicide and changes monotonously with varying the stoichiometry and incorporating the dopants such as B and P.

Acknowledgements

This work is supported by the Ministry of Education, Culture, Sports,

Science and Technology (No. 18360017, 18083003, and 17540291), the CREST program of JST, and the GCOE program of Chiba University. We also thank Super Computer Centers, ISSP, University of Tokyo, and Chiba University for the use of facilities.

References

- [1] T. Nakayama, S. Shinji, S. Sotome, *ECS trans.* **16** (2008) 787.
- [2] Landolt-Boerenstein New Series, *Group IV Physical Chemistry*, Vol. 5C, I, J, Springer-Verlag, New York (1997).
- [3] A. Hiraki, *J. Electrochem. Soc.*, **127** (1980) 2662, and references therein.
- [4] Y. Chang, J. L. Erskine, *Phys. Rev. B*, **28** (1983) 5766.
- [5] S. Sakurai, T. Nakayama, *Jpn. J. Appl. Phys.*, **41** (2002) 2171.
- [6] Y. Takei, T. Nakayama, to be published in *Jpn. J. Appl. Phys.*, (2009).
- [7] M. Murayama, T. Nakayama, A. Natori, *Jpn. J. Appl. Phys.*, **40** (2001) 6976.
- [8] T. Nakayama, S. Itaya, D. Murayama, *J. Phys. Conf. Ser.*, **38** (2006) 216.
- [9] K. Manabe, K. Masuzaki, T. Ogura, T. Nakagawa, M. Saitoh, H. Sunamura, T. Tatsumi, H. Watanabe, *Symp. on VLSI Tech.* (2006) p.46.

Table I. Calculated formation energies of MSi_2 bulk silicides, per MSi_2 unit, where M denotes metal atoms.

Silicides	Formation energy [eV]
TiSi_2	-1.2
NiSi_2	-0.3
AuSi_2	+0.8
AlSi_2	+1.3

Figure captions

Fig. 1. Calculated band structures of (a) Ni and (b) Au bulks, and (c) NiSi₂ and (d) AuSi₂ silicides. Horizontal lines at 0 eV denote the Fermi-energy positions.

Fig. 2. Calculated band structures of (a) Mg₂Si silicide and (b) bulk Si. Band gaps are seen around 0 eV.

Fig. 3. Calculated phase diagrams of Ni_xSi_y as functions of Ni and Si chemical potentials, in cases of (a) bulk growth and (b) growth on Si substrate. Grey regions are regions where Ni_xSi_y is allowed to grow in thermal equilibrium without phase separation.

Fig. 4. Calculated Fermi-energy positions of various (a) Ni_xSi_y and (b) Ti_xSi_y silicides in the band gap of bulk Si. The values are relative to the valence-band top of Si.

Fig. 1.

Fig. 2.

Fig. 3.

Fig. 4.