Nano-scale view of atom intermixing at metal/semiconductor interfaces

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Abstract. Atom intermixing processes at Au/Si(111), Al/Si(111), and Au/GaN(0001) interfaces are studied by using the first-principles calculations. It is shown that the motive force of intermixing is different between Au/Si and Al/Si interfaces; the production of Au-Si bonds causes the intermixing at Au/Si interface, while Al valence electrons screens Si-Si bonding and induces the intermixing at Al/Si interface. We show that the electronegativity and atomic radius are key quantities to control the intermixing at metal/semiconductor interfaces.

1. Introduction
Metal/semiconductor interfaces are essential structure to semiconductor physics and technology; e.g., metal layers are often used as electrodes and wirings. It has been known that the intermixing of metal and semiconductor atoms occurs at a number of metal/semiconductor interfaces, even around room temperature [1]. For example, Au shows the intermixing with lots of semiconductor substrates such as Si, Ge, InSb, InP, GaAs, GaP etc., while Si substrate exhibits the intermixing with many kinds of metals such as Au, Pd, Ag, Cu, Ni, Al etc. Such intermixing typically ranges from nm to μm and provides serious damages to nano-scale devices such as circuit shortening. Thus, it is important to understand how the intermixing proceeds and what the motive force of intermixing is.

In previous works [2,3], we investigated Au/Si(111) interfaces and showed that the intermixing starts by the thermal diffusion of interface Au atoms into Si substrate, with a small potential barrier around 0.6eV. This diffusion becomes possible due to a large electronegativity of Au compared to Si; the Au-Si bonds are produced during the diffusion by taking electron charge from Si-Si bonds. As a result, the Si-Si bonds are broken, which promotes the Si diffusion into Au layers and realizes the intermixing. The motivation of the present work comes from the questions whether such intermixing process can apply to other interfaces and what are relevant factors to determine intermixing. To answer these, we study the intermixing at Al/Si(111) and Au/GaN(0001) interfaces, particularly concentrating on the initial diffusion process of metal atoms. The former system is selected because Au is a transition metal while Al is a simple metal. On the other hand, the latter system is chosen because Au layers show intermixing at interfaces of most semiconductors but no mixing was observed on GaN substrate [4]. Thus, by clarifying reasons of no mixing, we expect to know relevant factors of intermixing.

2. Calculation method
When a few monolayer metal atoms are deposited on semiconductor substrate, no super structures have been observed in experiments. Moreover, we are interested in qualitative feature of intermixing.
Thus, in the present study, we employed the surface/interface unit models of Si(111) and N-polarity GaN(0001) (1\(\times\)1) structures for computational simplicity [2,3]. However, in some selected cases, the \((\sqrt{3} \times \sqrt{3})\) units were employed and we found that the results obtained in this work do not change. The repeated slab geometry was adopted for the surface/interface calculation, where the slab consists of five silicon layers or three GaN bilayers and the back surface is terminated by virtual hydrogens having fractional charges [5]. The vacuum region has thickness equivalent to eight Si layers. We deposited one to three monolayer metal atoms at the most stable positions on the slab surfaces. Valence charge densities and adiabatic potentials for the movements of Al and Au atoms were calculated using the standard first-principles method (TAPP code) based on density functional theory [3], where the Perdew-Zunger local exchange-correlation potential was employed. Norm-conserving separable pseudopotentials were used for Si, Al, and H atoms, while non norm-conserving ultrasoft pseudopotentials were adopted for Au (5d6s), Ga, and N atoms [5]. We have checked, for example, that the calculated lattice constants of bulk Si and Au are 10.15 and 7.60 a.u., respectively, which both reproduce observed values of 10.26 and 7.69 a.u. The wave functions are expanded by plane waves with the cut-off energy of 25.0 Ryd and the valence charge density is evaluated using \(8 \times 8\) k-points in the surface Brillouine zone. Atomic positions are optimized using Hellmann-Feynman forces. Calculational details are shown in the literatures [2,5].

3. Results and discussions

3.1. Diffusion at Au/Si and Al/Si interfaces

Figures 1(a) and 1(b) show the calculated adiabatic potentials of interface Au and Al-atom movements at Au/Si and Al/Si interfaces, respectively, from the stable surface positions, \(z = 0\), into Si substrate along (111). Here, ML indicates the number of monolayer deposited on Si surfaces. In the cases of Au and Al monolayer, as the metal atom moves into Si layers, the potentials monotonously increase and thus the diffusion does not occur because the metal atom can terminate dangling bonds of surface-top Si and largely stabilizes the interface when the metal atom is located on the surface, at \(z = 0\) [3]. On the other hand, when more than two metal layers are deposited on Si, the potentials change to have stable minimum positions at around \(z = -1.8\) Å for both Au/Si and Al/Si interfaces. Since the barriers are at most 0.4 eV, the diffusion of metal atoms becomes possible into Si layers.

To analyze the origin of such potential change, we show in figures 2(a) and 2(b) the valence charge densities of Au/Si and Al/Si systems, respectively, in cases when metal atoms are moved to locate around \(z = -1.8\) Å. In the case of Au/Si system, it is clearly recognized that the diffused innermost Au atom produces Au-Si bonds with the second-top-layer Si as well as the top-layer Si. The creation of Au-Si bonds is also confirmed by finding new Au-Si bands in lower energy region of Si valence bands.
In addition, note that the charge density of Si-Si bond between top and second-top layers is smaller than that of Au-Si bonds. Namely, the charge on Au-Si bonds is mainly supplied from the nearest Si-Si bonds. This charge transfer occurs because the electronegativity of Au, 2.5 (Pauling's value), is much larger than that of Si, 1.9, and the Au-Si bonding state has the lower energy than the Si-Si one. Since such bond rearrangement apparently stabilizes the system and produces the potential minima, one can say that the rebonding is the motive force of the Au diffusion and thus the intermixing. Once such rebonding weakens the interface Si-Si bonds, the interface Si atoms can easily diffuse into Au layers with a small potential barrier around 0.2 eV [3].

On the other hand, in the case of Al/Si system, we cannot see the creation of Al-Si bonds in figure 2(b). In fact, the charge density between innermost Al and Si atoms is smaller than that of Si-Si bond between top and second-top layers. However, the charge density of Si-Si bond between top and second-top layers is much smaller than that of Si-Si bonds in inner layers. We note that the charge density has almost constant values in the region surrounded by Al and Si atoms. This can be explained as follows; since the electronegativity of Al atom, 1.6, is small compared to that of Si, 1.9, the interface Al atoms partially present their valence electrons toward Si atoms and spread their valence-electron density widely over the Si substrate. As a result, the electron density increases around Si atoms, and such increase screens up and decreases the charge density of Si-Si bond. Once such screening weakens the interface Si-Si bonds, the interface Si atoms can diffuse into Al layers. In fact, the calculated barrier of Si diffusion is small, around 0.2 eV. Therefore, one can say that the screening due to charge extension is the motive force of intermixing for Al/Si interfaces. In this way, the motive force of intermixing is quite different between Au/Si and Al/Si interfaces.

Finally, we shortly comment on the potential minima around z = –3.3 Å in figures 1(a) and 1(b). The region around z = –3.3 Å corresponds to the diffusion in bulk Si rather than at interface. Thus, the existence of these minima is not a necessary condition for the intermixing because, as explained above, the Si diffusion easily occurs at z = –1.8 Å before the metal atoms reach to the point, z = –3.3 Å.

3.2. Diffusion at Au/GaN interface

Figure 3 shows the calculated adiabatic potentials of interface Au-atom movements at Au/N-polarity GaN interface, in the case when two-monolayer Au are deposited. Potential #1 is obtained when we simply move the innermost Au atom from the stable position of z = 0 into GaN substrate along (0001). It is seen that this potential monotonously and largely increases as the Au atom moves into GaN layers, which indicates that the Au diffusion is impossible being consistent with the experiment [4]. Such increase occurs as follows; since the atomic radius of Au, 1.44 Å, is much larger than the averaged atomic radius of Ga and N, 1.0 Å, the movement of Au pushes the GaN substrate to realize simple
compression deformation of GaN layers and produces the elastic energy loss. This result points out that the atomic radius of metal and semiconductor atoms become one of important factors to judge the realization of intermixing. For example, Pb metal layers were observed not showing intermixing on Si substrate, which might be explained by this scenario because the atomic radius of Pb, 1.8 Å, is much larger than that of Si, 1.1 Å.

Potential #2 in figure 3 is obtained when we assume that Au atom moves between top-layer Ga and second-top-layer N by some atom exchange process. We can see that the quasi-stable position exists around \( z = -1.3 \) Å. However, the energy at this position is much larger, around 1 eV, compared to the cases of Au/Si and Al/Si systems, around 0.0 eV. Such increase of energy is explained as follows; since the electronegativities of Ga, Au, and N atoms are 1.6, 2.4, and 3.0, respectively, Ga atoms prefer locating among N atoms to Au atoms. When the Au atom is located on GaN surface, the top-layer Ga is surrounded by Au and N. On the other hand, when the Au atom moves between Ga and N, the top-layer Ga is surrounded only by Au atoms, thus losing the Ga-N bonding energy gain. From this result, to realize the intermixing, we expect that the electronegativity of metal atom should be smaller or larger than those of semiconductor constituent atoms. In fact, the intermixing was observed at Au/GaAs interface [1], which is due to the larger negativity of Au, 2.4, compared to those of Ga and As, 1.6 and 2.1.

4. Conclusions
We have studied atom intermixing processes at Au/Si(111), Al/Si(111), and Au/GaN(0001) interfaces, by using the first-principles calculations and analyzing diffusion adiabatic potentials. We found that the motive force of intermixing is different between Au/Si and Al/Si interfaces. The production of Au-Si bonds causes Au diffusion and breaks Si-Si bonds at Au/Si interface, while the Al electrons extend over Si sites and weaken Si-Si bonds by screening. Such difference originates from large and small electronegativity of Au and Al metal atoms compared to Si. Moreover, we showed that the small atomic radius and the larger/smaller electronegativity of metal atoms are relevant factors to realize the intermixing. We believe that the present model is one of promising mechanisms for intermixing.

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