

Schottky-barrier change by structural disorders at metal/Si interfaces: First-principles study

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Abstract—Schottky-barrier changes by structural disorders are studied using the first-principles calculation and adopting Au/Si interface. It is shown that the structural disorders prefer to locate near the interface, but the penetration depth of the MIGS into Si is about 5 Si layers similar to clean interface even when disorders exist. Reflecting such penetration, Schottky barrier for holes shows little change in cases of Si vacancy and Au substitution, while it increases in cases of Si and Au interstitials due to the presence of Si dangling bonds.

I. INTRODUCTION

It has long been known that the Schottky barrier height (SBH) on metal/semiconductor interfaces is evaluated using the charge neutrality level (CNL). In case of flat clean interfaces, CNL is determined by the density of state (DOS) of metal induced gap state (MIGS). MIGS is the evanescent wave in semiconductor, which is smoothly connected with wavefunction leaked from metal. Correspondingly, Tersoff proposed that the energy position of CNL is the point which changes the sign of propagation wave between valence and conduction bands[1], while Cardona and Christensen proposed to adopt the dielectric mid gap energy as CNL using one dimensional Penn model[2]. Their theoretical evaluations are reasonably in good agreement with experimental values.

In case of disordered interface, on the other hand, Hasegawa and Ohno considered that the dangling bonds of semiconductor atoms produced by structural disorders at metal/semiconductor interfaces decide the energy gap states of interface[3], which is called the disorder induced gap state (DIGS). They proposed that the CNL-like energy is obtained as an average of sp³-orbital energies of semiconductors which separates bonding and anti-bonding states

Fig.1 shows the CNL positions derived from MIGS and DIGS theoretical views, together with observed ones. Both theoretical CNLs show similar chemical trend with varying metals and semiconductors and roughly explain the observed variation. However, these CNLs derived from MIGS and DIGS correspond to different limit, clean and disorder interfaces. Moreover, these CNLs are estimated from different theoretical backgrounds, MIGS by non-empirical ab-initio calculation and DIGS by empirical tight-binding approximation. Therefore, it is unfair to compare both-theoretical estimates.

In this work, we theoretically investigate how Schottky barrier changes when the structural disorders are incorporated around metal/Si interfaces and clarify the connection between

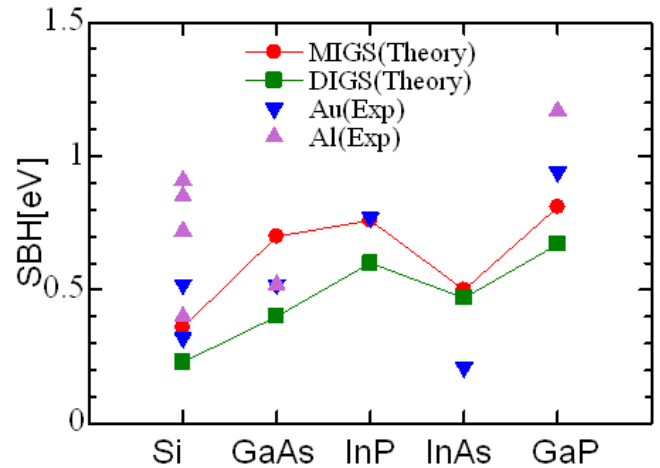


Fig. 1. Theoretical values of SBH at various Au and Al/semiconductor interfaces, estimated by MIGS and DIGS views[4][5]. Triangles are experimental values.

the MIGS and DIGS, based on the same theoretical framework, using the ab-initio calculation in the density functional theory.

II. METHOD OF CALCULATION

In order to simulate metal/Si interfaces, we select the Au/Si(111) interface and adopt the (2×1) and (2×2) repeated unit cells. Four kinds of defects (i.e., Si vacancy (V_{Si}), Si interstitial (Si_I), Au substitution at Si site (Au_{Si}), and Au interstitial (Au_I)) are produced in Si layers near the interface. V_{Si} and Si_I are generated when Si atoms are poorly and fully supplied in growth, respectively. On the other hand, Au_{Si} and Au_I are produced when Au atoms diffuse from the interface. In order to investigate the stability of defects and SBH variation, we calculated the formation energy and SBH when these disorders existed around Au/Si(111) interface.

In the slab model with vacuum region, we can't estimate the accurate the SBH because of inconvenient effect such as electric between surfaces. Therefore, we adopted superlattice geometry made by Si and Au layers (Fig.2). In this situation, SBH is evaluated using the local potential for electrons. We use the local potential difference between Au and Si layers (ΔV), the difference between local potential and Fermi energy (FE) in Au bulk ($\Delta\epsilon_1$), and the difference between local potential and top of the valence band in Si bulk ($\Delta\epsilon_2$), and

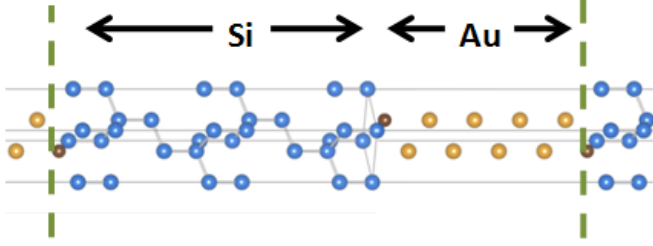


Fig. 2. Repeated superlattice model $(Si)_n (Au)_8$ for calculating SBH. Defects are formed near the Si/Au interface. The number of Si layers, n , is changed from $n = 16$ to $n = 28$ when defects are formed far from the interface.

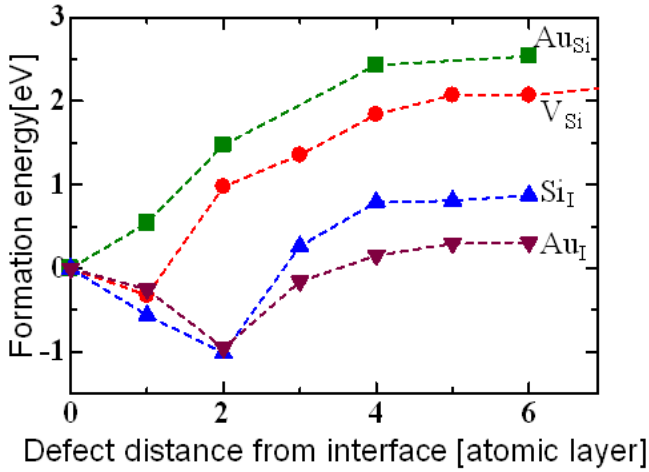


Fig. 3. Calculated formation energies of various defects as a function of the distance from Au/Si interface. The energy at the 0th layer (just at the interface) is set as zero. Defects are V_{Si} : Si vacancy, Si_I : Si interstitial, Au_{Si} : Au substitution at Si site, and Au_I : Au interstitial.

as $\Delta\epsilon_1 + \Delta V - \Delta\epsilon_2$ [6]. Namely, in this situation, the SBH is the value for hole carriers. In case of flat clean interfaces, the SBH at Au/Si is 0.39[eV]. In the following, we investigate how Schottky barrier changes when the structural disorders are incorporated around metal/Si interfaces.

III. STABILITY OF STRUCTURAL DEFECTS

First, we consider the stability of structural defects. Fig.3 shows the calculated formation energies of various defects as a function of the distance of defect from the interface. Here, the energy at the 0th layer, i.e., just at the interface, is set as zero. It is clearly seen that most defects are easily produced around the interface, within a few atomic layers from interface. This occurs in order to diminish the elastic energy loss in bulk Si layers, which is caused by the mismatch of atomic radius in cases of Si vacancy V_{Si} and Au substitution Au_{Si} , while by the atom insertion into the narrow tetrahedral interstitial site in cases of Si_I , Au_I . In cases of interstitials, Si_I and Au_I , the tetrahedral sites are located not at 0th and 1st layers but at 2nd layer. This is why Si_I and Au_I prefer to locate at 2nd layers from interface.

It is noted here that the formation energy of Au_{Si} is large while that of Au_I is small. This indicates the difficulty of

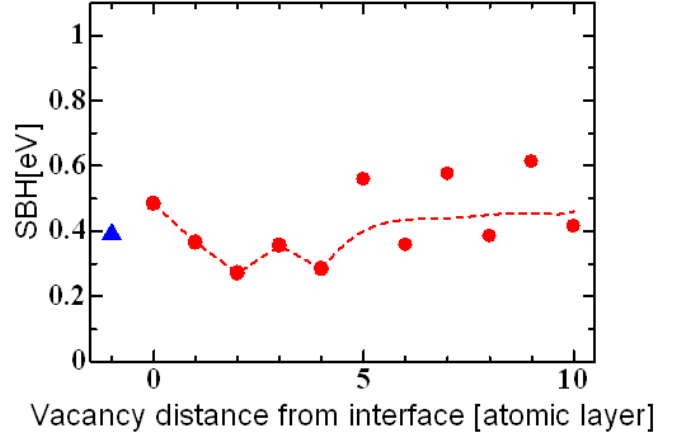


Fig. 4. Calculated Schottky barrier height (SBH) for hole carriers as a function of the distance of Si vacancy from Au/Si interface. The triangle shows the SBH at the flat clean interface. Dotted line is expected in a real system.

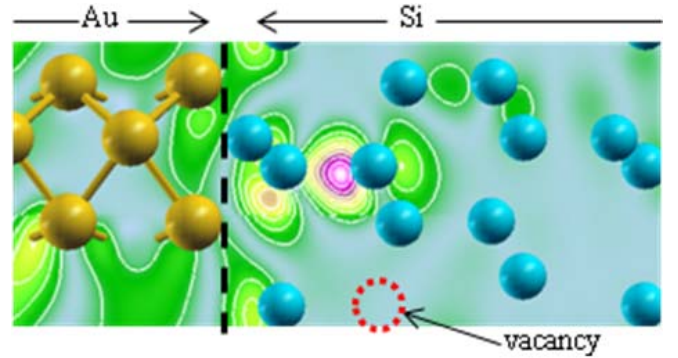


Fig. 5. Calculated MIGS wavefunction around Au/Si interface. Dotted circle indicates the position of Si vacancy.

making Au-Si silicide in inner Si layers and high ability of Au diffusion in Si layers as a interstitial atom. These results are consistent with the observation[7].

IV. SBH CHANGE BY DISORDER

A. In case of vacancy

Fig.4 shows the SBH for hole carriers, i.e., FE position of Au relative to the top of Si valence band, as a function of V_{Si} position, z , from the interface. The triangle shows the SBH at the flat clean interface, 0.39[eV].

The oscillation seen for $z > 5$, i.e., apart from interface, is artificially produced by the use of small (2×1) unit cell and Si(111) interface. When vacancy is formed at the 5th layer, for example, there appear three dangling bonds of Si at the 4th layer and one dangling bond at 6th layer. In order to vanish such dangling bonds by producing weak bonds, the electron at the 6th layer moves to the 4th layer. This electron transfer induces the dipole potential along the z direction and increases the Fermi-energy position of Au, thus the SBH increasing when V_{Si} is produced at the odd-number layers. When V_{Si} is produced at the even-number layer, on the other hand,

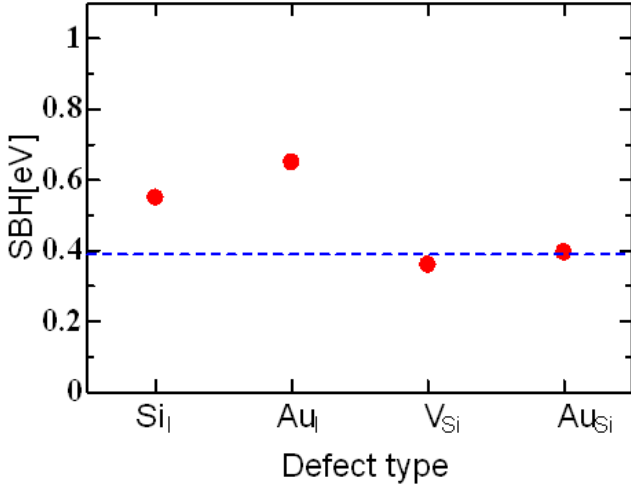


Fig. 6. Calculated Schottky barrier height (SBH) for hole carriers at disordered Au/Si (111) interfaces with four kinds of defects. The horizontal dashed line indicates the SBH at flat clean interface.

the opposite change occurs and the SBH decreases. In a real system, however, V_{Si} has the similar formation energy for both odd and even-number layers in inner Si, thus V_{Si} existing at both layers. Therefore, we expect the average SBH is realized as shown by a dotted line in Fig.4.

We also note that such SBH oscillation is not seen for $z < 5$. This reflects the penetration depth of the MIGS into Si layers. Fig.5 shows the square amplitude of metal wavefunction, i.e., the charge density, when the vacancy is formed at the 2nd layer. It is seen that the MIGS penetrates about five Si layer, similar to the case of flat clean Au/Si interface, even when V_{Si} exist. This penetration seems the SBH oscillation by metallic MIGS. From this result, we can expect that the MIGS view is applicable to the case of disordered interfaces.

Considering the formation energy of V_{Si} shown in Fig.3, most V_{Si} defects appear around the 1st layer. Therefore, we expect that the SBH at Au/Si interface with V_{Si} is around 0.37[eV], which is a little smaller than the case of clean interface.

B. In cases of other defects

Fig.6 shows the calculated SBH for hole carriers at disordered Au/Si interface when various defects are located at most stable positions. It is seen that the SBH increases compared to the case of clean interface when Si and Au interstitials are produced. These increases originate from the appearance of Si dangling bonds. In case of Si_I , the interstitial Si cannot make covalent bonds with surrounding Si atoms because the latter Si atoms already form covalent bonds. Therefore, the dangling bonds of the Si interstitial survive and the CNL around the Si_I has the high energy position. In case of Au_I , the Au interstitial produces strong covalent bonds with surrounding Si atoms and promote dangling bonds of Si atoms, which also increases the CNL.

In case of Au_{Si} , the SBH shows no deviation from the case of clean interface. This is because the Au substitution occurs

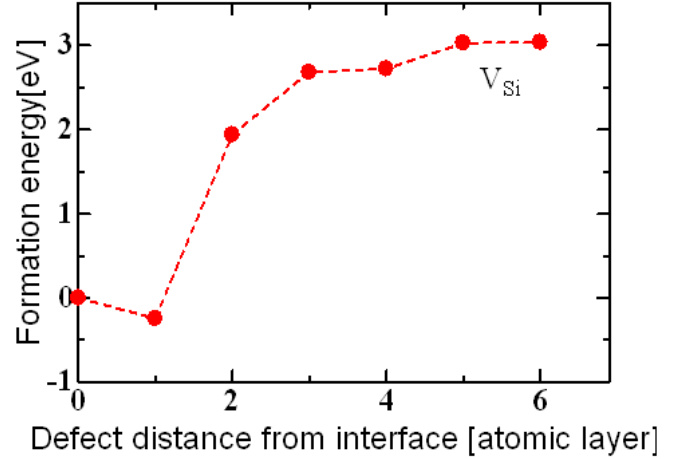


Fig. 7. Calculated formation energies of Si vacancy as a function of the distance from Au/Si interface, when the (2×2) unit cells adopted. The energy at the 0th layer, i.e., just at the interface, is set as zero.

just at the interface and such substitution simply shifts the position of Au/Si interface. In case of V_{Si} , dangling bonds are produced around the vacancy. In case of V_{Si} near the interface, the electron transfer occurs from Au to Si to fill such dangling bonds. Therefore, the SBH slightly decreases.

C. In case of (2×2) unit cell

Fig.7 shows the formation energy of Si vacancy and Fig.8 shows the SBH change, as a function of V_{Si} position in case of (2×2) unit cell. Comparing with the case of (2×1) unit cell shown in Fig.3, the formation energy shows the similar tendency; the most stable site is located at the 1st layer and it is difficult to produce V_{Si} inside of Si. Moreover, the similar tendency is also seen for the SBH variation, as shown in Figs.4 and 8. However, the variation is small for the (2×2) unit. This is because the V_{Si} concentration in the (2×2) unit is low compared to the case of (2×1) .

V. CONCLUSION

In this work, we studied the formation energy and the SBH variation of structural defects by using the first principles calculation in order to study MIGS and DIGS. The main results are summarized as follows.

(1) Most defects prefer to locate near the interface. This occurs in order to diminish the elastic energy loss by producing defects.

(2) In cases of Si_I and Au_I , the SBH increase from the case of clean interface. This increase is caused by the appearance of Si dangling bonds. In cases of V_{Si} and Au_{Si} , on the other hand, the SBH change is small. This is because the MIGS penetrates around the defects and screens the electronic changes.

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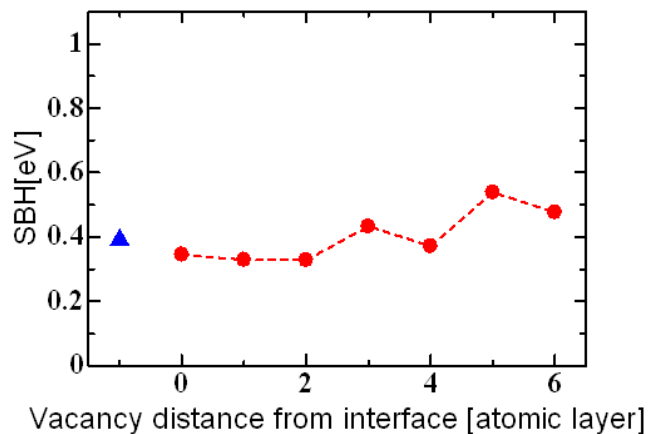


Fig. 8. Calculated Schottky barrier height (SBH) for hole carriers as a function of the distance of Si vacancy from Au/Si interface, when the (2×2) unit cell is adopted.

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