First principles calculation on gettering mechanism of transition metals in Si crystal

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Abstract

The binding energy between 4th periodic metals (K, Ca, Zn and 3d transition metals) and p-type dopants (B, Al, Ga), n-type dopants (P, As, Sb) or light elements (C, O) in Si single crystals was estimated by first principles calculation. It was found that the p-type dopants become effective gettering centers for metals except for the Ni atom. On the other hand, in the n-type dopants, it was found that (1) P atom can be an effective gettering center for Fe and Co atoms, and (2) As and Sb atoms can be effective gettering centers only for Co atom. Furthermore, in the light elements, it was found that C and O atoms do not become effective gettering centers for the metals used in actual LSI processes. The vacancy \( V_c \) and n-type dopant complexes (\( PV_c \), \( AsV_c \), \( SbV_c \)) can be effective gettering centers for Cu in n/n+ epi wafers.

1. Introduction

There is an increasing importance of “impurity gettering” technology for removing transition metals from the LSI active region [1]. Various techniques are reported as impurity gettering [2][3]. For example, a dopant atom forms a stable complex by the interaction with transition metal atoms. In this case, the dopant atom interacting with a transition metal is called “gettering center”. Among the transition metals, there are many reports on the gettering of the Fe and Ni incorporated to Si wafer mainly from the plumbing for heat-treatments [1][2]. Furthermore, gettering of Cu used mainly as wiring attracts attentions in recent LSI fabrication [1][3]. However, there are few reports on Ti, V, Cr, Mn and Co atoms that are newly in use for higher LSI performance. In this study, therefore, the binding energies between these transition metal atoms and the dopant atom were estimated by the first principles calculation to design the effective gettering centers. Furthermore, the binding energy between 4th periodic metal atoms except for the above, that is K, Ca, Sc, Zn, and gettering center was examined systematically in order to understand the gettering mechanism deeply. Effective gettering centers for Cu atom in n/n+ epi wafers were also investigated.


The calculation method is the first principles calculation based on the density functional theory, in which the ground state of the system is found by solving the Kohn-Sham equation that is a rule equation of the electronic system for given atom placement. The program package used in this study is CASTEP. Wave function is expanded as plane-waves, and ultrasoft pseudopotential is used to reduce a plane-wave number. The cutoff energy for the plane-wave expansion is 310 eV. The generalized gradient approximation (GGA) is adopted in the evaluation of the exchange-correlation term, and function form suggested by Perdew and Zunger is used. The \( \Gamma \) and \( L \) points are used for \( k \) sampling [5]. In the calculations, a Si 64-atoms supercell of 2\( \times \)2\( \times \)2 times as large as the conventional cell
is used. The lattice parameter of Si crystal is fixed as the experimental value of 5.34 Å. The Si atom at the center of
the supercell is substituted with dopant (B, Al, Ga, P, As, Sb) or C atom. A metal atom is placed at each the nearest
interstitial positions to the dopant. The total energy of the supercell including various complexes is calculated with
the geometry optimization.

3. Results and discussion

The most stable position of K, Ca, Sc, Ti, V, Cr, Mn, Fe, Cu and Zn atoms is determined as T site from the
calculated total energies. On the other hand, the most stable position of Co and Ni atoms is H site. Here, we
assume that the metal atom diffuses as T → H → T sites. In this case, the diffusion barrier $E_d$ can be estimated by

$$ E_d = | E_{tot} \text{(H-site)} - E_{tot} \text{(T-site)} |. $$

The calculated result of diffusion barrier $E_d$ is shown in Fig.1. It is found that diffusion barrier decreases with an
increase in the atomic number up to Ni atom. This result well agrees with the calculation reported by Matsukawa \cite{1},
qualitatively.

![Fig.1 The calculated diffusion barrier $E_d$ of 4th periodic metal atoms in Si crystal.](image)

The binding energy $E_b$ of p-type dopant (B, Al, or Ga) and metal atoms is calculated by eq.(2) with using the
calculated total energy including each complex.

$$ E_b = \left\{ E_{tot} \left( \text{Si}_{63} X_1 \right) + E_{tot} \left( \text{Si}_{64} M_1 \right) \right\} - \left\{ E_{tot} \left( \text{Si}_{63} X_1 M_1 \right) + E_{tot} \left( \text{Si}_{64} \right) \right\} $$

In this equation, M indicates metal atom and X gettering center. Here, $E_b > 0$ means that the complex is stable.
The calculated result of $E_b$ between B atom and Fe, Co, Ni or Cu atoms is summarized in Table 1. The previous
works of the first principles calculation and the experiments are also summarized in this table. The values of the
binding energies between these metal atoms and B atom are almost in agreement with other calculations and
Experimental results quantitatively. Furthermore, it is found that the binding energy between Ni and B atoms is lower than the other metals. This tendency is in agreement with previous works.

Table 1  The binding energy $E_b$ between B atom and Fe, Co, Ni, and Cu atoms.

<table>
<thead>
<tr>
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<th>$E_b$ (eV)</th>
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<tbody>
<tr>
<td>Fe-B</td>
<td>This work 0.48</td>
</tr>
<tr>
<td></td>
<td>Other calc. $[1]$ 0.64</td>
</tr>
<tr>
<td></td>
<td>Exp. $[6][7]$ 0.47-0.73</td>
</tr>
<tr>
<td>Co-B</td>
<td>This work 0.64</td>
</tr>
<tr>
<td></td>
<td>Other calc. $[1]$ 0.65</td>
</tr>
<tr>
<td></td>
<td>Exp. $[8]$ 0.61</td>
</tr>
<tr>
<td>Ni-B</td>
<td>This work 0.36</td>
</tr>
<tr>
<td></td>
<td>Other calc. $[1]$ 0.44</td>
</tr>
<tr>
<td></td>
<td>Exp. $[9]$ 0.52</td>
</tr>
<tr>
<td>Cu-B</td>
<td>This work 0.61</td>
</tr>
<tr>
<td></td>
<td>Other calc. $[1]$ 0.57</td>
</tr>
<tr>
<td></td>
<td>Exp. $[6][7][10]$ 0.43</td>
</tr>
</tbody>
</table>

The calculated result of the binding energy between the metal atoms and the p-type dopants (B, Al or Ga) is shown in Fig.2. The binding energy between the p-type dopants and all metal atoms takes a positive value, and results in the formation of stable complexes. However, the binding energy between Ni and Al or Ga is also low similar to B. This result indicates that Ni atom is not effectively gettered by the p-type dopants. One of the possible reasons is that Ni atom exists in electronically neutral state in Si crystal $[2]$.  

![Graph showing calculated binding energy $E_b$ between p-type dopants and 4th periodic metals.](image_url)  

**Fig.2** The calculated binding energy $E_b$ between p-type dopants and 4th periodic metals.
The calculated result of binding energy between the metal atoms and the n-type dopants (P, As or Sb) is shown in Fig. 3. It is found that the binding energies between P atom and Fe or Co atoms are relatively high. Furthermore, it is found that the binding energies between As or Sb atoms and Co atom are relatively high. As a result, it can be said that (1) P atom can be an effective gettering center for Fe and Co atoms, and (2) As and Sb atoms can be effective gettering centers only for Co atom.

![Fig. 3 The calculated binding energy $E_b$ between n-type dopants and 4th periodic metals.](image)

The calculated result of binding energy for metal atoms and light elements (C or O) showed that (1) C atom does not become an effective gettering center for any 4th periodic metals, and (2) O atom has negative or small positive binding energies with metals except for K and Ca atoms. Thus it is concluded that C and O atoms do not become effective gettering centers for the metals used in actual LSI processes.

In order to find an effective gettering center for Cu in n/n+ epilayers, we have considered the vacancy $V_c$ and n-type dopant complexes ($P_{V_c}$, $As_{V_c}$, $Sb_{V_c}$). It was found that these complexes can be effective gettering centers for Cu as summarized in Table 2. Interstitial Cu interacts with $V_c$, then forms complexes of $PCu_{us}$, $AsCu_{us}$, and $SbCu_{us}$. Here, $Cu_{us}$ indicates substitutional Cu atom. Figure 4 shows the stable configurations and valence electron density of $SbCu_{us}$ complex. It is obvious that covalent bonding is formed between Sb and $Cu_{us}$ atom. This calculation proposes a new Cu gettering technique in n/n+ epilayers with using the gettering centers of $P_{V_c}$, $As_{V_c}$ and $Sb_{V_c}$ complexes.

<table>
<thead>
<tr>
<th>Formed Complex</th>
<th>$E_b$ (eV)</th>
<th>Distance of Cu and dopant (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$PCu_{us}$</td>
<td>3.32</td>
<td>2.27</td>
</tr>
<tr>
<td>$AsCu_{us}$</td>
<td>3.18</td>
<td>2.33</td>
</tr>
<tr>
<td>$SbCu_{us}$</td>
<td>2.85</td>
<td>2.45</td>
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</table>
Fig.4 Stable configurations and valence electron density of Sb and substitutional Cu (SbCu₄) complex in Si (110) plane. The maximum contour of the density is set to 0.8 electron/Å³.

4. Summary

In order to search the effective gettering center to the metal impurities in Si single crystal, we have estimated the binding energy between 4th periodic metals and p-type, n-type dopants or light elements by first principles calculation. It was found that the p-type dopants become effective gettering centers for metals except for the Ni atom. On the other hand, in the n-type dopants, it was found that (1) P atom can be an effective gettering center for Fe and Co atoms, and (2) As and Sb atoms can be effective gettering centers only for Co atom. Furthermore, in the light elements, it was found that C and O atoms do not become effective gettering centers for the metals used in actual LSI processes. The vacancy Vₓ and n-type dopant complexes (PVₓ, AsVₓ, SbVₓ) can be effective gettering centers for Cu in n/n+ epi wafers.

REFERENCES