Research Article

Systematic Investigation of Gettering Effects on 4th Row Element Impurities in Si by Dopant Atoms

Koji Sueoka, Ken Kamimura, and Seiji Shiba

Department of System Engineering, Okayama Prefectural University, 111 Kuboki, Soja, Okayama 719-1197, Japan

Correspondence should be addressed to Koji Sueoka, sueoka@cse.oka-pu.ac.jp

The gettering of 4th row element impurities (K, Ca, 3d transition metals, and Zn) in Si crystals by dopant atoms was systematically investigated by first-principles calculation through evaluation of the diffusion barrier and the binding energy. The dopant atoms considered include p-type dopants (B), n-type dopants (P, As, Sb), or light elements (C, O). It was found that (1) the diffusion barrier of impurity atoms decreases with an increase in their atomic number up to Ni, (2) B atom becomes an efficient gettering center for metals except for Ni, (3) most of the metals except for Fe and Co cannot be gettered by n-type dopants, and (4) C and O atoms alone do not become efficient 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 efficient gettering centers for Cu in n/n+ epitaxial wafers.

1. Introduction

There is an increasing demand on "impurity gettering" technology for removing metal impurities from the LSI active region. Various techniques are reported as impurity gettering [1, 2]. For example, a dopant atom forms a stable complex by the interaction with the metal atom under consideration. In this case, the dopant atom interacting with the metal is called "gettering center". Among the 4th element impurities, 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, which is used commonly as wiring, attracts attentions in the recent LSI fabrication [3]. However, there are limited reports on Ti, V, Cr, Mn and Co atoms that are newly in use for higher LSI performance.

First-principles calculation is the effective tool to simulate the gettering of the metals in Si crystals [3, 4]. To design the efficient gettering centers for new metals, the systematic investigations by first-principles calculation will be valuable. In this study, therefore, the gettering of 4th element impurities (K, Ca, 3d transition metals, and Zn) in Si crystals is systematically investigated by the first-principles calculation through evaluation of the diffusion barrier and the binding energy with p-type dopants (B), n-type dopants (P, As, Sb) or light elements (C, O). Efficient gettering centers for Cu in n/n+ epitaxial wafers are also investigated.

2. Calculation Methods

The calculation method is the first-principles calculation, 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 a given atomic configuration. The program package used in this study is CASTEP [5]. Wave function is expanded by plane-waves, and ultrasoft pseudopotential [6] is used to reduce a number of plane waves. The cutoff energy for the plane-wave expansion is 310 eV. The generalized gradient approximation (GGA) is used for the exchange-correlation term, and functional form is of PBE type [7]. The Γ and L points are used for the k sampling [8].

In the calculations, a Si 64-atoms supercell, that is, $2 \times 2 \times 2$ supercell constructed by conventional cell, is used. The lattice parameter of Si crystal is fixed as the experimental value of 5.431 Å. The Si atom at the center of the supercell is substituted with a dopant (B, P, As, Sb) or C atom. An O atom is located at the center of Si-Si bond. A metal atom is placed at the nearest interstitial positions to the dopant. The total energy of the supercell including various complexes is calculated with the geometrical optimization.
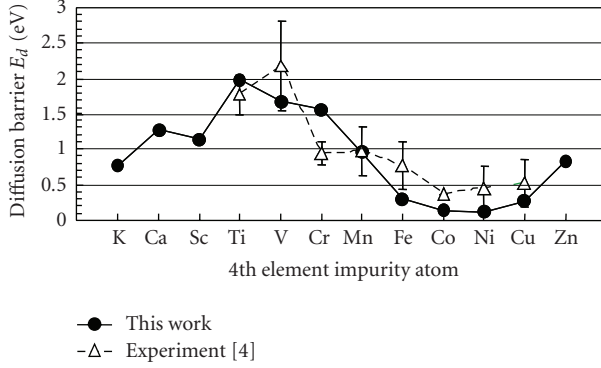
FIGURE 1: Calculated diffusion barrier E_d of 4th element impurity atoms in Si crystal.

3. Results and Discussion

The most stable position of K, Ca, Sc, Ti, V, Cr, Mn, Fe, Cu, and Zn atoms is determined as interstitial 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. The diffusion barrier E_d can be estimated by

$$E_d = |E_{tot}(\text{H-site}) - E_{tot}(\text{T-site})|. \qquad (1)$$

The calculated result of E_d is shown in Figure 1. It is found that the diffusion barrier of impurity atoms decreases with an increase in their atomic number up to Ni. The obtained E_d from Ti to Cu agrees with the experiments summarized in [4] quantitatively.

The binding energy E_b of B atom to the impurity atoms is calculated by

$$E_b = \{E_{tot}(\text{Si}_{63}\text{X}) + E_{tot}(\text{Si}_{64}\text{M})\} \\ - \{E_{tot}(\text{Si}_{63}\text{XM}) + E_{tot}(\text{Si}_{64})\}. \qquad (2)$$

In this equation, M indicates impurity atom and X gettering center. Here, X = B. The sign $E_b > 0$ means that the complex is stable. The calculated result of E_b of B to Fe, Co, Ni, or Cu atoms is summarized in Table 1. The values of E_b are in agreement with other calculations and experimental results quantitatively. It is well known that Fe and Cu atoms are efficiently gettered by B [1, 9], while Ni is not [1]. That the calculated E_b for Ni is smaller than E_b for Fe and Cu agrees with the experimental result qualitatively.

The calculated result of E_b of B to 4th element impurity atoms is shown in Figure 2. The E_b of B to all the impurity atoms listed possesses a positive value, which indicates the formation of stable complexes. If we use the E_b for Fe as the critical energy for efficient gettering, the calculated results in Figure 2 suggest that the 4th element impurities except for Ni can be gettered by B atom. In Si crystals, a substitutional B atom is negatively charged and most interstitial metal atoms are positively charged except for Ni. Since the Ni atom exists in electronically neutral state in Si crystal [1], E_b of B to Ni should be smaller than E_b for the other metals.

TABLE 1: Binding energy E_b of B to Fe, Co, Ni, and Cu atoms.

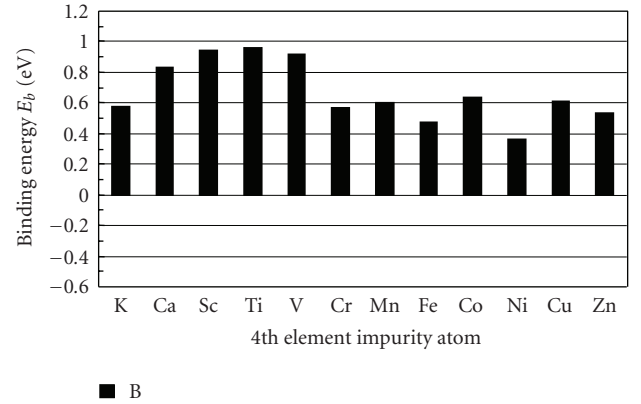|		E_b (eV)
Fe-B	This work	0.48
		0.64 (Cal. [4]), 0.47–0.73 (Exp.[9, 10])
Co-B	This work	0.64
		0.65 (Cal. [4]), 0.61 (Exp. [11])
Ni-B	This work	0.36
		0.44 (Cal. [4]), 0.52 (Exp. [12])
Cu-B	This work	0.61
		0.57 (Cal. [4]), 0.43 (Exp. [9, 10])

FIGURE 2: Calculated binding energy E_b of B to 4th element impurity atoms.

The calculated result of E_b of n-type dopants (P, As, or Sb) to impurity atoms is shown in Figure 3. It is found that E_b of P to Fe (or Co) atom, and E_b of As (or Sb) to Co atom are as high as E_b of B to Fe atom. As a result, it can be said that (1) P atom can be an efficient gettering center for Fe and Co atoms, and (2) As and Sb atoms can be efficient gettering centers only for Co atom.

The calculated result of E_b of C (or O) to impurity atoms shows that (1) C atom does not become an efficient gettering center for any 4th element impurities, and (2) O atom has negative or small positive binding energies with impurity atoms except for K and Ca atoms. Thus it is concluded that C and O atoms alone do not become efficient gettering centers for the metals used in actual LSI processes.

In order to find an efficient gettering center for Cu in n/n+ epitaxial wafers, we have considered the complexes of vacancy V_c and n-type dopant (PV_c, AsV_c, SbV_c). In the calculation, first, we have evaluated the binding energy of V_c + Cu^i → Cu$_s$. Here, Cu^i and Cu$_s$ indicate the interstitial and the substitutional Cu atom, respectively. Then, the binding energy of V_c + Cu^i → Cu$_s$ is taken as the reference energy for the binding energy E_b of PV_c, AsV_c, SbV_c complexes to Cu atom. It was found in Table 2 that these complexes can be efficient gettering centers for Cu with forming the complexes of PCu$_s$, AsCu$_s$, and SbCu$_s$. This result suggests a new Cu gettering technique in n/n+ epitaxial wafers with using gettering centers of PV_c, AsV_c, and SbV_c complexes as the gettering center.
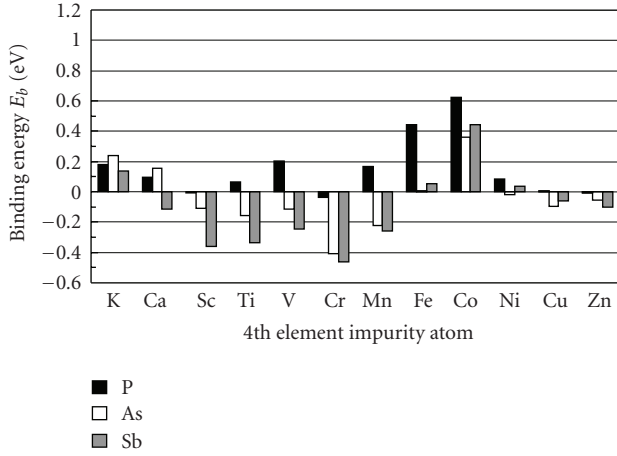
FIGURE 3: Calculated binding energy E_b of n-type dopants to 4th element impurity atoms.

TABLE 2: Calculated binding energy E_b of PV_c, AsV_c, SbV_c to Cu.

Formed Complex	E_b (eV)
PCu_s	1.34
$AsCu_s$	1.25
$SbCu_s$	1.09

4. Summary

We have systematically investigated the gettering of 4th element impurities (K, Ca, 3d transition metals, and Zn) in Si crystals by first-principles calculation through evaluation of the diffusion barrier and the binding energy with p-type dopants (B), n-type dopants (P, As, Sb), or light elements (C, O). It was found that (1) the diffusion barrier of impurity atoms decreases with an increase in their atomic number up to Ni, (2) B atom becomes an efficient gettering center for metals except for Ni, (3) the most of the metals except for Fe and Co cannot be gettered by n-type dopants, and (4) C and O atoms alone do not become efficient 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 efficient gettering centers for Cu in n/n+ epitaxial wafers.

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