First-principles study of iron segregation into silicon $\Sigma 5$ grain boundary

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(Received 27 November 2009; accepted 20 February 2010; published online 7 May 2010)

Using ab initio density functional theory total energy calculations, we have investigated the mechanism of Fe segregation into Si $\Sigma 5(310)$ grain boundary (GB). We find that the segregation is site selective at the GB—Fe will only segregate to specific sites. We further find that the choice of the segregation site is determined by the segregation-induced stress and effective crystal-field induce splitting of the Fe $d$ orbital at that site. Our results suggest that the revealed mechanism of Fe segregation into the GB should be general for other 3$d$ transition metals with partially filled 3$d$ orbits and for other grain boundaries. © 2010 American Institute of Physics. [doi:10.1063/1.3369390]

I. INTRODUCTION

To reduce the cost of Si solar cells, there is currently a steady interest to utilize less pure Si than what is currently used in the industry. A big challenge for utilizing these Si is to deal with their high density of impurities, particularly the 3$d$ transition metals. These impurities typically result in recombination centers, which reduces the minority carrier diffusion length and consequently the cell efficiency. Among the 3$d$ transition metal impurities, iron (Fe) is the most detrimental and dominant one in less pure Si. A number of methods such as nanoprecipitation, grain boundary (GB) gettering, and boron and phosphorus diffusion has been developed to reduce the detrimental effects of Fe impurities. Among them, GB gettering is an interesting approach because it involves both GBs and Fe impurities. Understanding how Fe segregates into grain boundaries in Si may help to develop new gettering process. However, so far, only Fe in bulk Si has received extensive attention. There are very few investigations on how Fe segregates into Si GBs.

The nature of Fe in bulk Si has been studied both experimentally and theoretically. It is found that the majority of individual iron impurities in Si are at interstitial sites and they can be at positively charged state (Fe$^+$) in p-type doped Si or charge neutral state (Fe$^0$) in undoped Si. The deep donor level is at about 0.4 eV above the top of the valence band of Si. Ludwig and Woodbury (LW) in the early 1960s proposed a model that can explain qualitatively very well the observed electron paramagnetic-resonance (EPR) (Refs. 10–12) of interstitial 3$d$ impurities in Si. Deep understanding of this model is further provided by more detailed theoretical calculations. These include the calculation of the reduction in hyperfine field of Fe in Si, which is consistent with the assumption of the LW model that two Fe 4$s$ valence electrons transfer into the 3$d$ shell, and the calculation of the energy level of Si:Fe by ab initio total energy calculations using a Green’s function technique and explanation of the energetic position based on the coupling with the host states.

In this paper, we investigate the mechanism of interstitial Fe segregation into a Si $\Sigma 5(310)$ GBs using the spin-polarized ab initio density functional theory. We find that the segregation energy depends sensitively on the GB site. We further find that the origin of this behavior is due to the site dependence of segregation-induced stress and the effective crystal field splitting of the Fe $d$ orbitals. Our results suggest that these effects that lead to Fe segregation into the GB should be general for other 3$d$ transition metals with partially filled 3$d$ orbits and for other grain boundaries.

II. METHOD

The density functional total energy calculations were performed using the VIENNA AB INITIO SIMULATION PROGRAM. We used the general gradient approximation for exchange correlation and the ultrasoft Vanderbilt-type pseudopotentials. For exchange correlation functional, we use the parameters proposed by Perdew and Wang known as PBE91. A cutoff energy of 320 eV was used for the plane-wave basis.

To build the $\Sigma 5$ GB, we adopted a super-cell including 128 atoms, which is small enough to simulate the doped GB and large enough to neglect the interaction of impurity iron. In addition, the super-cell had two twin GBs in order to guarantee the periodic boundary condition. The influence of different k-points was tested by a series of calculations and we find that calculations performed with $4 \times 1 \times 3$ Monkhorst–Pack k-point sampling are relatively converged. All atoms were relaxed until all force components at each atomic site is less than 0.01 eV/Å.

III. RESULTS AND DISCUSSIONS

A. Atomic structure of Si $\Sigma 5(310)$ GBs

Si $\Sigma 5(310)$ GBs had been studied by the tight binding method and the first-principles method. The $\Sigma 5(310)$ GB composes alternating threefold and fivefold rings. There are

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**References**

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two types of $\Sigma 5$, the zigzag ($z$-type) and straight ($s$-type) ones, due to the different arrangement of $3\sim5$ units deduced from varied edge dislocation in the GB. We constructed the $\Sigma 5(310)$ GB structures by adapting the previously published models and calculated the GB energies $\sigma_{\text{GB}}$ using the first-principle method. To obtain $\sigma_{\text{GB}}$, we first calculate the GB formation energy defined as $E_{\text{form}}=\frac{1}{2}(E_{\text{GB}}-E_{\text{bulk}})$, where $E_{\text{GB}}$ is the total energy of a super-cell containing two GBs and $E_{\text{bulk}}$ is the total energy of bulk Si with an equivalent number of atoms. In the two total energy calculations, the cutoff energies were kept the same and the k-point grid was kept equivalent. The GB energy $\sigma_{\text{GB}}$ is then given by $E_{\text{form}}/A$, where $A$ is the area of the periodic unit cell of the boundary in the $(310)$ plane. Our calculations show that the interface energy of $z$-type ($0.368$ J/m$^2$) is smaller than the $s$-type ($0.444$ J/m$^2$). This result agrees with the high-resolution transmission electron microscopy experiment in Ge that the $z$-type was the stable structure. In the following discussions, we will use the stable $z$-type $(310)\Sigma 5$ model (Fig. 1) for investigation.

Considering the symmetry, we select six special sites (a-f in Fig. 1) to represent the GB and select the g site as the reference bulk site. We define the GB segregation energy as the total energy difference between iron at the GB sites and at the bulk site. Negative GB segregation energy indicates that Fe would like to segregate to the GB site. The calculated values are shown in Table I. We find that the interstitial iron has a negative GB segregation energy only at c site. In most Si solar cells, the concentration for Fe in bulk is around $10^{13}$ to $10^{14}$/cm$^3$. Because of the small segregation energy, the concentration for Fe in the GB should be around $10^{13}$ to $10^{14}$/cm$^3$.

To understand the calculated trend, we have calculated the bond length and bond angle distortion, $\Delta b_{\text{max}}$ and $\Delta a_{\text{max}}$.

![Image](http://jap.aip.org/jap-bin/abstract?f_id=2010093713-0062&f_name=fig1.png)

**FIG. 1.** (Color online) Structure model of $z$-type $(310)\Sigma 5$ GB. The label a-f indicate six possible GB sites for interstitial Fe. g is an interstitial site at the bulk region.

![Image](http://jap.aip.org/jap-bin/abstract?f_id=2010093713-0063&f_name=fig2.png)

**FIG. 2.** (Color online) Simplified energy level diagram for the tetrahedral interstitial Fe in silicon. (a) The atomic Fe $d$ single particle levels; (b) and (b') are the levels with the exchange splitting included; (c) and (c') include the effect of the crystalline field splitting; (d) and (d') include the resulting energy levels due to the coupling to the antibonding $p_t$ levels. For clarity, the coupling with bonding $p$ states is not shown.

when interstitial Fe is introduced at one of the GB sites. These distortion values are defined as the maximum differences between the nearest Si–Si bond lengths, bond angles of the doped sites and those in pure GB which are in the most stable structure. In general, larger strain means higher energy. Considering the changes of bond length and bond angle from Table I, we find that c, f, and e sites have one of the least length and angle change. This is consistent with the fact that the c site is the most stable one. Similarly, the f and e sites have lower energy because of their smaller angle and bond change. We also find that at a, b, and d sites the GB segregation energies are much higher because they are located at the vertex of the threefold ring, thus they have larger deviation from the standard tetrahedral symmetry. This can partly explain the energy trends of Fe in different GB sites. On the other hand, besides the strain, the electronic properties of Fe interstitial also plays role in determine the stability.

### B. Electronic structures

For Fe ($s^2d^6$) at the Si interstitial site, the coupling between the Fe 4$s$ orbital and the host pushes the 4$s$ orbital to a higher energy level, so the two $s$ electron transfer to the lower energy Fe 3$d$ orbital. Therefore, Fe in Si has a $(d^5)$ configuration. The energy levels of Fe 3$d$ states split into spin-up and spin-down level under the spin exchange interaction. The fivefold degenerated $d$ orbital further splits into triply degenerated $t_2$ and doubly degenerated $e$ states due to the crystal field of neighboring Si atoms (Fig. 2). In general, considering the electron Coulomb repulsion, the level should be below the $t_2$ level in a tetrahedral environment. However, for the interstitial iron atom because it is located at the antibonding site of the four nearest Si, the Coulomb repulsion between the $t_2$ state and the neighboring Si $s$ and $p$ electrons is weak. Moreover, the lobes of $e$ orbital point to the direction of the next nearest neighboring Si atoms, forming an octahedral environment, whose electron Coulomb repulsion pushes the $e$ level up. Consequently, the crystal field splitting between the $t_2$ and $e$ levels due to the overall Coulomb potential is small. On the other hand, the $d$ orbital hybridize strongly with the host $p$ orbital. The strong level repulsion between the Fe $t_{2g}$ $d$ level and the antibonding Si $p$ state pushes the Fe $t_2$ $d$ level down, so that the $t_2$ $d$ level is

<table>
<thead>
<tr>
<th>Fe site</th>
<th>Segregation energy (eV)</th>
<th>$\Delta b_{\text{max}}$ (Å)</th>
<th>$\Delta a_{\text{max}}$ (°)</th>
<th>$t_2$-$e$ splitting (eV)</th>
</tr>
</thead>
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<tr>
<td>a</td>
<td>0.20</td>
<td>0.644</td>
<td>12.97</td>
<td>1.45</td>
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<tr>
<td>b</td>
<td>0.25</td>
<td>0.121</td>
<td>14.67</td>
<td>0.76</td>
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<tr>
<td>c</td>
<td>-0.08</td>
<td>0.049</td>
<td>9.06</td>
<td>0.91</td>
</tr>
<tr>
<td>d</td>
<td>0.48</td>
<td>0.064</td>
<td>16.52</td>
<td>0.66</td>
</tr>
<tr>
<td>e</td>
<td>0.13</td>
<td>0.040</td>
<td>11.01</td>
<td>0.98</td>
</tr>
<tr>
<td>f</td>
<td>0.11</td>
<td>0.038</td>
<td>14.72</td>
<td>1.00</td>
</tr>
</tbody>
</table>

TABLE I. Segregation energy of Fe at different GB sites in $z$-type $\Sigma 5(310)$ GB. The bond length and bond angle distortions and the $t_2$-$e$ energy splitting of the Fe spin-down $d$ state are also given.
lower in energy than the $e$ level. Therefore, the exact energy position of the spin-up $t_2$ and $e$ states is determined by the effective crystal field splitting, consisting of overall Coulomb potential and $p$-$d$ coupling. Our calculation reveals that for Fe interstitial in Si, the spin-up $t_2$ and $e$ states are occupied, whereas the spin-down $t_2$ is occupied but the spin-down $e$ orbital is unoccupied (Fig. 2), meaning the $p$-$d$ coupling-induced splitting is larger than the Coulomb potential-induced splitting. The occupied spin-down $t_2$ level determines the position of the deep donor level, which can become a recombination center when it is partially ionized.

Because the spin-down $d$ level is closer to the conduction band minimum, the level repulsion between the occupied $t_2$ $d$ level and unoccupied $t_2$ antibonding $p$ level is larger in the spin-down channel than in the spin-up channel, so the effective crystal field induced $t_2$ and $e$ splitting is larger in the spin-down channel than in the spin-up channel (Fig. 2). This level repulsion lowers the energy of the occupied states and raises the energy of the unoccupied state, so it gains energy. This analysis indicates that when the effective crystal field splitting between $t_2$ and $e$ levels is large at a certain site, the Fe atom will tend to be more stable.

Figure 3 plots the total density of states (DOS) and partial DOS of interstitial Fe $d$ orbital in different GB sites. The average values of $t_2$-$e$ splitting of these sites are listed in Table I. These $t_2$-$e$ split values are calculated through weighted average of each $t_2$ and $e$ peaks as shown in Fig. 3. In Table I, Fe at d site has the smallest $t_2$-$e$ splitting, which is consistent with the fact that Fe in this site has the highest energy. On the other hand, the c, e, and f sites are all have relatively large $t_2$-$e$ splittings, which are consistent with the fact that they have relatively small GB segregation energy.

IV. CONCLUSIONS

Using ab initio density function theory total energy calculations, we have investigated the mechanism of Fe segregation into Si $\Sigma 5$(310) GB. We find that the segregation is site selective at the GB—Fe will only segregate to specific sites. We further find that the choice of the segregation site is determined by the segregation-induced stress and crystal-field-induce splitting of Fe $d$ orbital at that site. Our results suggest that the effects that lead to Fe segregation into the GB should be general for other 3$d$ transition metals with partially filled 3$d$ orbitals and for other grain boundaries.

ACKNOWLEDGMENTS

The work at Shanghai University was supported by the Natural Science Foundation of China (Grant No. 60876045) and Shanghai Leading Basic Research Project (Grant No. 09JC1405900). The work at NREL was supported by the U.S. Department of Energy (DOE), under Contract No. DE-AC36-08GO28308. Computing resources is provided by the High Performance Computing Center of Shanghai University.