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First Principles Calculations on CSL Grain Boundary Impurities in Multicrystalline Silicon

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1. Introduction

Currently, over half of all solar cells produced worldwide are made from multicrystalline silicon (mc-Si). While these devices have comparatively lower efficiencies mainly due to transition metal impurities (10^{14}–10^{16} cm^{-3}) in most of the mc-Si materials[1]. Metal silicide precipitate is observed to increase with decreasing atomic coincidence within the grain boundary (i.e. increasing Σ values)[2]. Point defects are precursor for metal silicide precipitation. The effect of impurity in the grain boundary (GB) of mc-silicon was studied using Σ 9 tilt boundaries by Fujita *et al*[3]. In the present study we used DFT method to understand relationship between sigma value and impurity precipitation. First we study the dopant position and the nature of interaction between the GB and transition metal. Finally we have studied the electronic changes that occurred up on doping the transition metal impurities in the GB region.

2. Results and discussion

Σ5 (210) and Σ9 (221) grain boundaries of mc-silicon were constructed using GB studio[4]. We used VASP code for geometrical optimization. The calculations were performed with monkhorst-pack of 4x4x4, using projector augmented wave (PAW) pseudopotentials with a wave cutoff of 240 eV. The Perdew – Wang (PW91) functional is used for the generalized gradient approximation (GGA)[5]. Periodic boundary condition was applied along x and y axis of the super cell containing 80 and 288 atoms for Σ 5 (210) and 9 (221) respectively with hydrogen termination along z-axis. This model is good enough to describe the GB property[7]. To validate our studies we used one Copper, Iron, Nickel and Chromium atom as point defect and compared our findings with the experimental results[2]. Σ 5 (210) and 9 (221) clean GBs do not show any states in the fundamental gap and their formation energy is -2.87 and -12.03 eV respectively. This shows that Σ9 (221) is more stable than Σ 5 (210) GB. To investigate the suitable position of dopant we optimized structures by placing dopants both at the interstitial and at the substitution sites. Up on complete relaxation atomic migrations of atoms were found to be minimal along the grain boundary plane, which is inline to the experimental results.

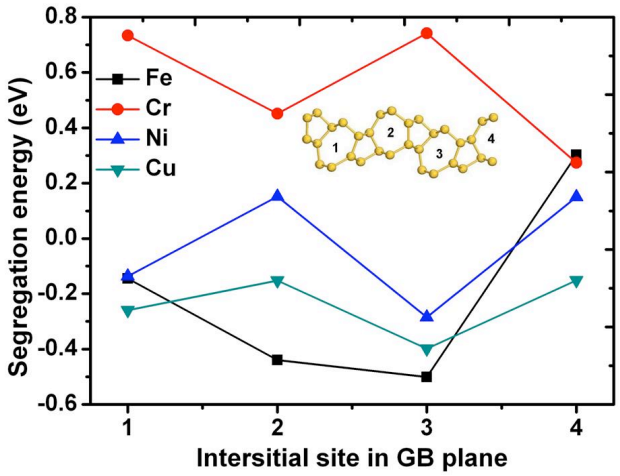
Table 1 show the segregation energy, Barder charge and local magnetic moment for both at the interstitial and substitution sites for the dopants in Σ5 GB. It is evident from the table substitution sites are favorable for doping compare to interstitial site. Among the metal impurity copper has highest segregation energy which is consistent with the experimental observation[6]. Bader analysis shows that charge transfer occurs from the metal to silicon for the Cr but in the other cases silicon to metal charge transfer was observed. Local magnetic moments are completely quenched in the case Ni and Cu due to Metal-Silicon covalence.

Table1. Bader charge, segregation energy and Fermi energy for metal doped in Σ5 GB of mc-Si
* - I – interstitial and S- substitution; *#SE = (1/2)*$[E_{MGB} - E_{SiGB}]$ *– (1/2)*$[E_{Mbulk} - E_{Sibulk}]$

System		Bader charge on metal (*e*)	Segregation Energy SE# (eV)	Local magnetic moment (μB)
M	Site			
Cr	I*	+0.8577	+0.29	4.0
	S*	+3.9865	-0.34	2.5
Fe	I	+0.0471	+0.41	1.7
	S	+5.9904	-0.18	2.5
Ni	I	-0.2117	+0.50	0.0
	S	+7.985	-0.12	0.0
Cu	I	+0.0196	+0.50	0.0
	S	+8.9846	-0.08	0.0

Figure 1 shows the segregation energy at interstitial and substitution site in the Σ9 (221) GB plane. Except chromium other metal favors segregation at both the sites.

(a)



(b)

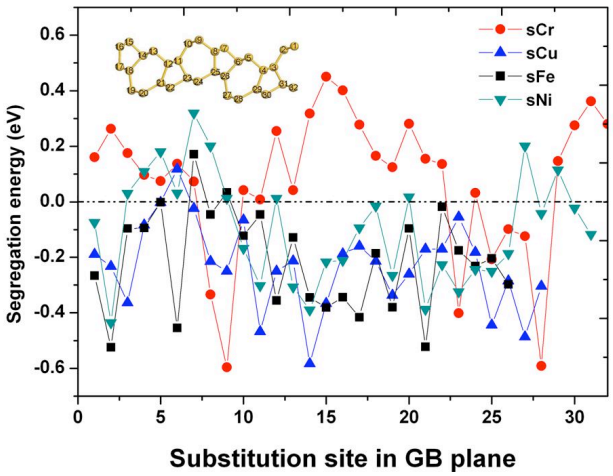


Figure 1 Segregation energy (a) at interstitial site (b) substitution site of Σ9 (221) GB plane.

3. Conclusions

In conclusion, we have carried out DFT studies on the Σ 5(210) and Σ9 (221) CSL GB of mc-silicon and its transition metal doped structures. Energy calculation shows substitution site is the preferred for the transition metals in the GB region of Σ 5(210) mc-silicon whereas, in the Σ9 (221) GB plane except chromium other metal favors segregation at both the sites. Local magnetic moments are completely quenched in the case Ni and Cu due to Metal-Silicon covalence. Clean GBs do not have any states in the fundamental gap whereas upon doping leads to deep states in the gap.

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