First-Principles Prediction of Optical Absorption Enhancement for Si Native Defect Clusters under Biaxial Strain

Robert J. Bondi, Sangheon Lee, and Gyeong S. Hwang

Department of Chemical Engineering, University of Texas, Austin, Texas 78712, USA

We use density-functional theory calculations to qualitatively explore the effects of fourfold-coordinated vacancy (V4) and interstitial (I4) clusters on optical absorption spectra in crystalline Si (c-Si) under selected conditions of biaxial strain (ε = −3, 0, and 3%). While both native defect clusters enhance c-Si absorption by redshifting the absorption edge, we observe additional enhancement from biaxial strain. Increased strain magnitude tends to increase the absorption enhancement effect, but the optimal sign of strain exhibits a complementary relationship: compressive strain most effectively enhances V4 absorption, while tensile strain most effectively enhances I4 absorption. The absorption redshift as a function of strain correlates well with effective bandgap reduction, including the appearance of an intermediate band under certain conditions (ε = −3 and 0%) for V4. Our results suggest that manipulation of native defect distributions and their strain fields can be used to engineer the Si absorption spectra.

© 2010 The Electrochemical Society. DOI: 10.1149/1.3511714 All rights reserved.
Clusters shown embedded inside subsections of their respective 480-atom supercells. Light gray (gold) wireframe represents bulk Si atoms in the lattice. Dark gray spheres represent interstitial atoms comprising the cluster (I₄ only) as well as highly-strained atoms adjacent to the cluster cores (V₄ and I₄). The atoms representing the highest strain energy in each case (V₄, atom β; I₄, atom γ) are labeled and colored (red). The out-of-plane and in-plane directions for biaxial strain are depicted with the crystallographic axes.

Figure 1. (Color online) Strain-free representations of V₄ (a) and I₄ (b) clusters shown embedded inside subsections of their respective 480-atom supercells. Light gray (gold) wireframe represents bulk Si atoms in the lattice. Dark gray spheres represent interstitial atoms comprising the cluster (I₄ only) as well as highly-strained atoms adjacent to the cluster cores (V₄ and I₄). The atoms representing the highest strain energy in each case (V₄, atom β; I₄, atom γ) are labeled and colored (red). The out-of-plane and in-plane directions for biaxial strain are depicted with the crystallographic axes.

The relationship between out-of-plane and in-plane strain using tabulated elastic stiffness constants \( C_{ij} \):\(^{20} \) \( \nu^* = -\varepsilon_{\perp}/\varepsilon_{\parallel} = 2C_{12}/C_{11} \) = 0.771. The upper panel of Fig. 1 shows the biaxial strain scheme with crystallographic reference. Using \( \nu^* = 0.771, \quad \varepsilon_{\parallel} = (a_{\parallel} - a_{0})/a_{0}, \quad \varepsilon_{\perp} = (a_{\perp} - a_{0})/a_{0} \), we calculated values of out-of-plane \( a_{0}\) for each independent value of in-plane \( a_{0}\) to appropriately scale additional supercell dimensions representing ±3% biaxial strain. We numerically verified that minimum energy supercell dimensions occur as \( \nu^* \) converges to the theoretical value of 0.771.

Conditions of ±3% strain (tensile is positive) were chosen to best illustrate our results (±1, ±2, and ±4% strain were also studied). We investigated Si biaxial strain within the range of ±4% strain because 4% tensile strain is the limiting case of epitaxial Si grown on pure Ge.\(^{29} \) Compressive biaxial films could be realized on alloy substrates (Siₓ₋ₓGeₓ) of the diamond structure. Therefore, while ±3% strain conditions are large in high-density microelectronic integration (typical magnitudes are \( |\varepsilon| < 1\% \)),\(^{1, 2} \) these magnitudes are feasible in the laboratory. There is currently little precedence for strained c-Si in solar cells; however, strain engineering could be applied to photovoltaics. As in microelectronic fabrication, strategic material selection, such as the metal backplane in a conventional solar cell, or engineered process conditions, such as annealing treatments, could be used to implement strain in thin film c-Si absorption layers.

Improved descriptions\(^{2-34} \) of the aggregation and behavior of Si point defects following ion implantation were fueled by the development of microelectronic fabrication process simulators. Previous theoretical works by Makhov and Lewis\(^{35} \) (V₄ and I₄) proposed the importance of FC configurations for specific cluster sizes \( n \). The recent endeavors of Lee and co-workers\(^{37, 38} \) generalize the significance of FC Si native defect clusters by detailing their thermodynamic favorability through application of an integrated atomistic modeling procedure for small \( n \) (V₄, \( n = 48; \) I₄, \( n = 16 \)). Our recent work\(^{30, 38} \) describes the influence of uniform strain fields on the stability, structure, and orientation of these same clusters. We use the V₄ and I₄ clusters in this article to represent general FC cluster behavior. Based on our previous work,\(^{30, 38} \) only neutral-state clusters were considered because FC configurations are unlikely to ionize under intrinsic conditions. The embedded configurations of V₄ and I₄ are illustrated in Fig. 1a and b, respectively. For each structure, the atom representing the highest strain energy (degeneracy creates additional candidates), as calculated using a Keating-type parameterization of the Si network,\(^{29} \) is annotated for discussion.

Figure 2 shows the \( \alpha(\omega) \) spectra for c-Si, V₄, and I₄ subjected to various biaxial strain conditions. Note that the absorption edge in the \( \alpha(\omega) \) plots is modified from the fundamental \( E_g \) in two ways: (1) the indirect nature of Si precludes significant optical transitions from occurring at the 1.11 eV bandgap, so the main transitions begin at higher energies where the first direct transitions are possible,\(^{1} \) and (2) DFT \( E_g \) underestimation tends to reduce calculated direct transition energies. In Fig. 2a, it is apparent that biaxial strain redshifts the onset of absorption \( (E_g, \text{transition}) \),\(^{3} \) where the greater absorption enhancement is seen for the tensile case. We observed similar behavior at other strain magnitudes (±1, ±2, and ±4%) and verified that the magnitude of redshift (enhancement) in absorption onset correlates with the applied strain magnitude. In Fig. 2b and c, the inception of low-energy optical absorption is redshifted by nearly 2 eV in the presence of either FC cluster embedded in strain-free Si. In Fig. 2b, incipient absorption for strain-free V₄ occurs at 0.48 eV, which reduces to 0.23 (0.17) eV under 3% tensile (compressive) biaxial strain. Similarly, in Fig. 2c, incipient absorption for strain-free I₄ occurs at 0.55 eV, which reduces to 0.37 (0.10) eV under 3% compressive (tensile) biaxial strain. Note that the observed optical response is complementary with respect to the structural strain configuration: V₄ imparts a tensile local strain field on the lattice and is consequently stabilized by applied compression; likewise, I₄ imparts a compressive local strain field on the lattice and is consequently stabilized by applied tension. These results suggest that characteristic optical absorption in c-Si can be modulated through manipulation of the comprehensive strain field profile.

To better understand the complementary behavior exhibited in optical absorption, we examined the LDOS of atoms selected through inspection of atomistic strain profiles. Searching for a po-
potential structural connection to the observed absorption phenomena, we reviewed the LDOS character at the compressive and tensile extrema (atomic sites) for both clusters; however, a complementary LDOS relationship between dominant valence band (VB) and conduction band (CB) character was not readily apparent within the same structure. Instead, we proceeded to analyze the effect of variable applied strain conditions on the atomic site representing the highest strain energy in each structure. These results are collectively presented in Fig. 3 for each case. The complementary LDOS behavior originally anticipated is present when the $V_4$ LDOS at atom $\beta$ is compared to the $I_4$ LDOS at atom $\gamma$. Consistent with the results of Pan et al.,$^{12}$ increased CB character is observed with the longer bonds associated with the locally-tensile strain field around $V_4$, while increased VB character is observed with the shorter bonds associated with the locally-compressive strain field around $I_4$.

Furthermore, evaluation of the LDOS dependence on applied strain reveals that the primary reason for increased optical absorption in each case is an effectively shrinking $E_g$ that correlates with observed redshifting in $\alpha(\omega)$. For $V_4$, we also observe a prominent distribution of IB states, which can be manipulated by strain, that can reduce the minimum energy required to absorb an incident photon and lower the effective $E_g$ similar to studies of IB solar cell materials that rely on transition metal doping.$^{4,5}$ In both $V_4$ cases ($\epsilon = -3$ and 0%) containing the IB peak, the Fermi level is also located at the IB peak, which suggests partial band occupation that satisfies one requirement for multistage photon absorption.$^4$ With this multigap perspective, the smallest $E_g$ gating $V_4$ absorption among the three strain cases is observed under compressive strain.
between the VB and prominent IB peak, while the smallest $E_g$ in both the c-Si and $I_4$ cases occurs under tensile conditions.

In summary, our DFT calculations predict optical absorption enhancement (redshift) in c-Si in the presence of either vacancy ($V_{\text{d}}$) or interstitial ($I_4$) FC clusters that can be further enhanced by biaxial strain. Although applied strain improves absorption in all cases studied ($\varepsilon = -3$, 0, and 3%), compressive strain exhibits the largest enhancement on $V_{\text{d}}$, while tensile strain exhibits the largest enhancement on $I_4$. LDOS examination of the most-strained atom in each structure reveals that the primary reason for increased absorption correlates with a decreased bandgap, including an IB for $V_{\text{d}}$ under certain strain conditions.

Acknowledgments

We acknowledge the National Science Foundation (CAREER-CTS-0449373) and the Robert A. Welch Foundation (F-1535) for their financial support. S. L. is grateful for support from the Donald D. Harrington Graduate Fellows Program. We would also like to thank the Texas Advanced Computing Center for use of their computing resources.

The University of Texas at Austin assisted in meeting the publication costs of this article.

References