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The $C_iO_i(Si_I)_2$ defect in silicon: density functional theory calculations

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Abstract Carbon–oxygen-self-interstitial defects in silicon (Si) are technologically important as they can impact the operation of devices through the concentration of intrinsic point defects. In irradiated Si the C_iO_i defect attracts self-interstitials (Si_I's) and leads to the formation of the $C_iO_i(Si_I)$. Experimental studies have determined that annealing at 150 °C results in the capturing of more Si_I's leading to the formation of the $C_iO_i(Si_I)_2$ defect. Recent experimental studies proposed that the $C_iO_i(Si_I)_2$ defect is bistable and considered possible configurations. In the present study we aim to clarify the structure of the $C_iO_i(Si_I)_2$ defect and use density functional theory calculations to gain insights on the formation and stability of the $C_iO_i(Si_I)_2$ defect in Si. It is calculated that two configurations are energetically favourable differing in energy by only 0.19 eV.

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1 Introduction

Throughout the evolution of microelectronics silicon (Si) was the dominant material, however, there is a recent technological requirement to replace Si with higher mobility substrates [1–10]. At any rate Si will continue to be technologically important as it is the mainstream material for photovolatics and sensors.

Point defects and defect clusters are important in devices as they can influence their properties. To optimise devices the control of oxygen-related defects such as the A-center (vacancy-oxygen interstitial pairs, *V*O) and the carbon-related defects (such as $C_iO_i(Si_I)_n$, $n=1, 2,\ldots$) is required [11–18].

Irradiation in Si leads to the association of O and C to form the C_iO_i defect (C_3) [19, 20]. When considering high irradiation dose the C_iO_i may attract a Si_I's to form the $C_iO_i(Si_I)$ complex (C_4) and thereafter even larger complexes such as the $C_iO_i(Si_I)_2$ [16, 20–23]. In a recent study Angeletos et al. [15] introduced a model concerning a transformation of the $C_iO_i(Si_I)$ complex to the formation of $C_iO_i(Si_I)_n$ ($2 \le n \le 4$) complexes. In particular, Angeletos et al. [15] proposed that $C_iO_i(Si_I)_2$ exhibits a bistable behavior switching between two configurations depending on the temperature. In the present study we employ density functional theory calculations to investigate the structure of the $C_iO_i(Si_I)_2$ defect.

2 Methodology

2.1 Details of calculations

In the present study we employed the plane wave density functional theory code CASTEP [24, 25]. Exchange and

correlation interactions were implemented within the corrected density functional of Perdew, Burke and Ernzerhof (PBE), [26] using the generalized gradient approximation (GGA) and with ultrasoft pseudopotentials [27]. The plane wave basis set cut-off was 350 eV, a 2×2×2 Monkhorst–Pack (MP) [28] k-point grid was used, in conjunction with a 250-atom supercell. The convergence and efficacy of this theoretical methodology has been discussed in previous studies [29, 30].

2.2 Definitions of binding energies

The criterion we set to compare the stability of the different configurations of the $C_iO_i(Si_I)_n$ defect is the binding energy. For example, the binding energy to form a $C_iO_i(Si_I)_2$ defect in Si is given by:

$$E_b(C_iO_i(Si_I)_2Si_N) = E(C_iO_i(Si_I)_2Si_N) - E(C_iSi_N) - E(O_iSi_N) - 2E(Si_ISi_N) + 3E(Si_N) \quad (1)$$

where $E(C_iO_i(Si_I)_2Si_N)$ is the energy of a N lattice site supercell (here $N=64$) containing N Si atoms, a C_i, one O_i atom, two Si_I and N Si atoms; $E(C_iSi_N)$ is the energy of a supercell containing a C_i and N Si atoms; $E(O_iSi_N)$ is the energy of a supercell containing one O_i atom and N Si atoms; $E(Si_ISi_N)$ is the energy of a supercell containing a Si_I and N Si atoms; and $E(Si_N)$ is the energy of the N Si atom supercell. With this definition a negative binding energy implies that the defect cluster is stable with respect to its constituent point defect components.

3 Results and discussion

In the present study we have employed extensive DFT calculations calculate the lowest energy structures of the $C_iO_i(Si_I)_2$ defect. We have used a step by step approach starting with the formation of the C_iO_i defect and then we have gradually added Si interstitials. In the process we have performed more than 4000 calculations exploring different geometries.

Consistently with previous DFT studies [14, 31, 32] the energetically favourable structure of the C_iO_i defect is the ring configuration (known as R-form) rather than the configuration where the O_i is occupying an interstitial site in between two Si (known as O-form) atoms that effectively resembles its position in undoped Si. The energy difference between these two configurations is 0.003 eV. In the ring configuration the C and O interstitials form with Si a ring, with the O–Si bond lengths being 1.79, 1.88, 1.75 Å, whereas the C–Si bond lengths being 1.77, 1.78 and 1.79 Å. The corresponding Si–O–Si and Si–C–Si angles are (139.9°, 131.5°, 88.6°) and (92.5°, 141.1°, 126.4°), respectively.

The second step in this process was to form the $C_iO_i(Si_I)$. This defect has been previously investigated by DFT [33] and hybrid functional DFT calculations [14]. Here we added the Si_I not only to the energetically favourable R-form but also to the O-form. The extensive search was not confined to configurations with the Si_I being close to the C_iO_i defect, however, it was calculated that these are prevalent in agreement with previous theoretical studies (Ref. [14] and references therein). The R-form $C_iO_i(Si_I)$ configuration is energetically fabourable as compared to the O-form $C_iO_i(Si_I)$ configuration by 0.18 eV. This is in agreement to the study of Backlund and Estreicher [33] where it was calculated that the difference between the two configurations is 0.27 eV. Comparing these two configurations it can be observed that the distinctive C_iO_i ring features have been rectified by the Si_I. This is expected as in both configurations the local relaxation induced by the introduction of the third and more substantial interstitial is bound to lead to similar structures breaking the symmetry.

The third step of the process is to add a further Si_I forming the O-form and R-form $C_iO_i(Si_I)_2$ configurations, Fig. 1a, and b respectively. In Fig. 1b the characteristics of the ring are now completely rectified. Therefore, one may consider these two configurations as being O-form. The configuration represented in Fig. 1b is energetically fabourable but by only 0.19 eV. Comparing to the recent phenomenological configurations proposed by Angeletos et al. [15] it can be observed that they have resemblances. This small energy difference will imply that there will be a non-negligible concentration of both $C_iO_i(Si_I)_2$ configurations.

In a simplified mass action analysis [34] approach where we consider that both $C_iO_i(Si_I)_2$ configurations effectively compete for the same C_i, O_i and Si_I defects their relative concentration will be given by the temperature dependent factor $\exp(0.19\ \text{eV}/k_BT)$. This is an important factor as for example at 479 K there will be a hundred $C_iO_i(Si_I)_2$ with the Fig. 1b configuration for every $C_iO_i(Si_I)_2$ with the Fig. 1a. This ratio will become ten to one at 958 K and 3.55 to one near the melting temperature. Therefore, based on a simple mass action argument it is anticipated that both configuration will be present particularly at higher temperatures. This of course assumes that migration barriers will be similar and that competing structures will not readily form at higher temperatures. At any rate though it is demonstrated that the $C_iO_i(Si_I)_2$ cluster forms and that two configurations can acquire significant concentrations in good agreement with a recent experimental study [15].

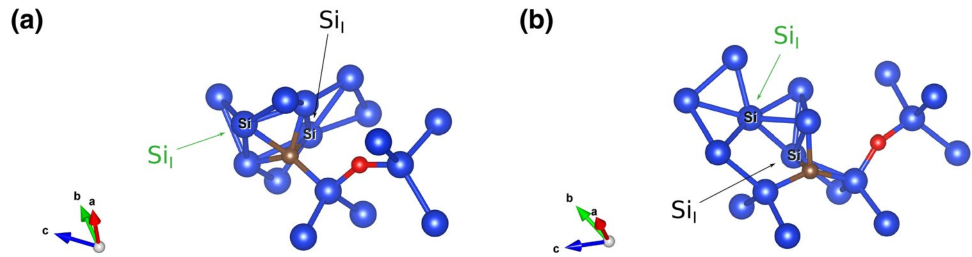

Fig. 1 Schematic representation of the energetically favourable $C_iO_i(Si_I)_2$ configurations

4 Conclusions

Density functional theory calculations were used to calculate the relative stability and structure of the $C_iO_i(Si_I)_2$ defect. We propose that the formation of two O-form like $C_iO_i(Si_I)_2$ configurations with relative energies differing by only 0.19 eV. This is important as both will have comparable concentrations, particularly at higher temperatures. Here the systematic investigation focuses on the binding energies of the defects, however, kinetics may play a role on the formation of the $C_iO_i(Si_I)_2$ defect and this is presently under investigation. Finally, further computational studies are required to calculate competing carbon-related defects (such as $C_iO_i(Si_I)_n$ and $C_iC_s(Si_I)_n$), the local vibration modes of the configurations proposed here and how these can be related with experiment.

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