

Relative concentrations of carbon related defects in silicon

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Abstract Irradiation induced defects in silicon are technologically important as they impact the electronic properties. Calculations based on density functional theory employing hybrid functionals have been previously used to investigate the structures and relative energies of defect clusters formed between vacancies, self-interstitials, carbon and oxygen atoms in silicon. In this study we employ a model to calculate the relative concentrations of carbon related defects in silicon. It is calculated that the carbon content has a significant impact upon the concentration of carbon-related defects. The C_iC_s defect is the most populous for all the conditions considered followed by the C_i , O_iSi_I and the C_iO_i defects. $C_iO_iSi_I$ and the C_iO_i become increasingly important for silicon with high carbon concentrations.

1 Introduction

For several decades silicon (Si) has been the key material used in a range of nanoelectronic, photovoltaic, and sensor devices. It is also a model system for the understanding of point defect processes in semiconductors. The detailed understanding of

many defect processes that can impact its material properties and consequently device operation is, however, not well established [1–4]. It should be stressed that defect processes are becoming increasingly important given that the characteristic dimensions of devices are a few nanometers.

Carbon (C) is incorporated in the Si lattice during crystal growth originating from the poly-crystalline starting material, the graphitic components in the equipment and from gaseous contaminants [5–7]. C is an isovalent impurity in the Si lattice and can occupy substitutional sites (C_s) that are electrically neutral. C in the lattice leads to local strains as it is smaller than Si. C atoms interact with O_i forming C–O complexes, and in particular C_s-O_i pairs [8]. In irradiated Si it is determined that most of the silicon interstitials (Si_I) are trapped by C_s , which are converted to C interstitials (C_i) via the Watkins displacement reaction $C_s + Si_I \rightarrow C_i$ [9, 10]. This is important from a technological viewpoint as C_i introduces in-gap states [11]. C_i at room temperature can interact with O_i and C_s to form C_iO_i and C_iC_s pairs respectively [8, 12–14]. Notably, both C_iO_i and C_iC_s defects introduce [8, 12–14] states within the Si band gap, impacting devices [15–17]. This has motivated the investigation of their structure and properties [18–22]. Importantly, the C_i , C_iO_i , and C_iC_s defects can act in the course of irradiation as nucleation centers for larger complexes such as for instance the $C_iO_iSi_I$ [23–27].

For completeness we need to consider the oxygen-vacancy defects. It is well established that the vacancy-oxygen pair (VO or A-center) is the most important defect in Czochralski grown Si (Cz–Si) [28]. A-centers form due to the introduction of a relatively high concentration of oxygen during the process of Czochralski crystal growth [28]. The oxygen interstitials (O_i) associate with vacancies (V) to form VO pairs via the reaction $V + O_i \rightarrow VO$ [28–30]. These VO pairs are technologically important as they are

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both electrically and optically active and therefore it may be necessary to control their formation and suppress their concentration [31, 32].

Defect clusters compete for point defects, and in that respect, we need to consider the formation of all defects and calculate their relative populations [33]. The aim of the present study is to calculate the relative concentrations of carbon-related defects within the mass action analysis framework.

2 Methodology

2.1 Definitions

Experiment can provide information on the thermal stability and formation of defect clusters and in that respect DFT can act synergistically through the calculation of the binding energies, E_b , defined by:

$$E_b = E_{\text{defectcluster}} - \sum E_{\text{isolateddefects}} \tag{1}$$

With this definition negative binding energies imply that a cluster is energetically favourable with respect to its constituent isolated components.

The concentration of an XY complex $[XY]$ with a binding energy E_b relative to the concentration of unbound defects X and Y (i.e. $[X]$ and $[Y]$ respectively) is given by:

$$\frac{[XY]}{[X][Y]} = \exp\left(-E_b/k_B T\right) \tag{2}$$

where k_B is Boltzmann’s constant and T is the absolute temperature.

Mass action techniques were previously used to calculate the relative concentrations of donor-vacancy clusters and the impact of codoping in germanium (Ge) [34, 35] and hydrogen related defects in amorphous Si [36]. The approach is predictive as it resulted in the first report of donor atom-vacancy clusters in Ge and the formation of fluorine clusters in Ge both of which were thereafter confirmed by experimental studies [35, 37]. In this approach the temperature dependence of defect concentrations at equilibrium conditions can be calculated. Nevertheless, kinetics may play a role, as will non-equilibrium conditions (i.e. irradiation). In the present work, the relative concentrations of carbon related defects are calculated under equilibrium conditions.

3 Results and discussion

3.1 Structure of defects

From an experimental viewpoint, the main defect species identified by FTIR spectroscopy are C_i , C_iO_i , C_iC_s , $C_iO_iSi_i$,

VO , V_2 , and VO_2 , (Ref. 38 and references therein). The relations for their formation are:



The structure of C_iC_s defects (known as G-centers) have been extensively investigated using DFT calculations [39, 40]. There are three structures of defects (refer to Fig. 1 of Ref. 40). To study the structure of the successive members of the $C_iO_i(Si_i)_n$ family of defects it is necessary to begin with the C_iO_i defect. The C_iO_i defect has two forms [19] the O-form (refer to Fig. 1a) and the R-form (refer to Fig. 1b) [19]. R denotes the ring formed by the O_i , C_i and two Si lattice atoms. The $C_iO_i(Si_i)$ defect forms by the attachment of a Si_i atom in the C_iO_i defect (refer to Eq. 6). There are at least three configurations of the $C_iO_i(Si_i)$ defect that have been previously investigated (refer to Fig. 1c–e) [20, 25, 41]. The first two configurations of the $C_iO_i(Si_i)$ can be formed by the two configurations of the C_iO_i pair (Fig. 1a,b) by the addition if a Si_i . The third configuration of the $C_iO_i(Si_i)$ (Fig. 1e), is the structure proposed by Estreicher and Backlund [25, 42] using DFT. In this structure the O and C atoms are again bonded in an R-form. Upon annealing an additional Si_i atom can be captured by the $C_iO_i(Si_i)$ defect to form a $C_iO_i(Si_i)_2$ structure, however, these larger defects are beyond the scope of the present study. Further DFT studies will be required to clarify the structure and energetics of these larger defects. The structure of VO , V_2 , and VO_2 defects is reported in previous studies [43].

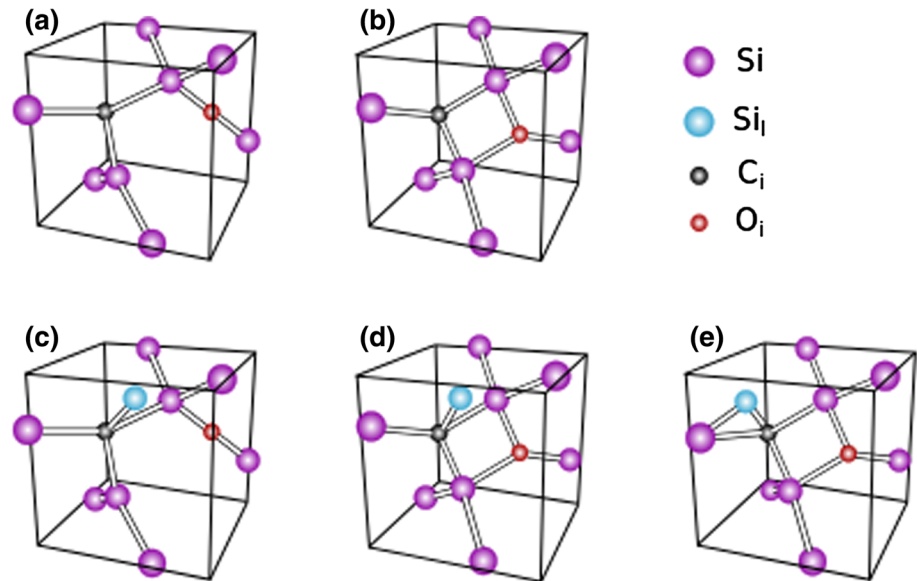
3.2 Model

To calculate the relative concentrations of the defects described by Eqs. 3–9, we have to solve simultaneously the following relations:

$$\frac{[C_i]}{[C_s][Si_i]} = \exp\left(2.34eV/k_B T\right) \tag{10}$$

$$\frac{[C_iO_i]}{[C_i][O_i]} = \exp\left(1.60eV/k_B T\right) \tag{11}$$

Fig. 1 Schematic representations of the C_iO_i (a, b) and $C_iO_iSi_i$ (c–e) defects



$$\frac{[C_iC_s]}{[C_i][C_s]} = \exp\left(\frac{1.68eV}{k_B T}\right) \quad (12)$$

$$\frac{[C_iO_iSi_i]}{[C_i][O_i][Si_i]} = \exp\left(\frac{3.14eV}{k_B T}\right) \quad (13)$$

$$\frac{[VV]}{[V][V]} = \exp\left(\frac{2.52eV}{k_B T}\right) \quad (14)$$

$$\frac{[VO_i]}{[V][O_i]} = \exp\left(\frac{2.21eV}{k_B T}\right) \quad (15)$$

$$\frac{[VO_2]}{[V][O_i][O_i]} = \exp\left(\frac{4.05eV}{k_B T}\right) \quad (16)$$

This is the mass action framework and can provide useful information within the approximations described above. Additionally, it is necessary to have accurate binding energies. The present binding energies in these relations were either derived by Wang et al. [26, 27], or by using the same state of the art hybrid functional DFT method. The thermal equilibrium concentration of Si_i and V is very low due to their relatively high formation energies. It is assumed here that under irradiation we must account for the formation of a highly athermal concentration of these defects which may interact and stabilize oxygen and carbon complexes. We consider here the impact of initial carbon concentration in Si on the relative concentrations of carbon related defects.

3.3 Impact of carbon concentration

In Fig. 2 the dependence of carbon related defects with respect to the initial carbon content for two characteristic temperatures ($T = 500$ and 1000 K) is given. For both

temperatures considered it can be seen that the carbon-related defects are dominated by C_i and C_iC_s . The latter defect becomes more populous when the initial carbon concentration exceeds $3 \times 10^{18} \text{ cm}^{-3}$ (refer to Fig. 2).

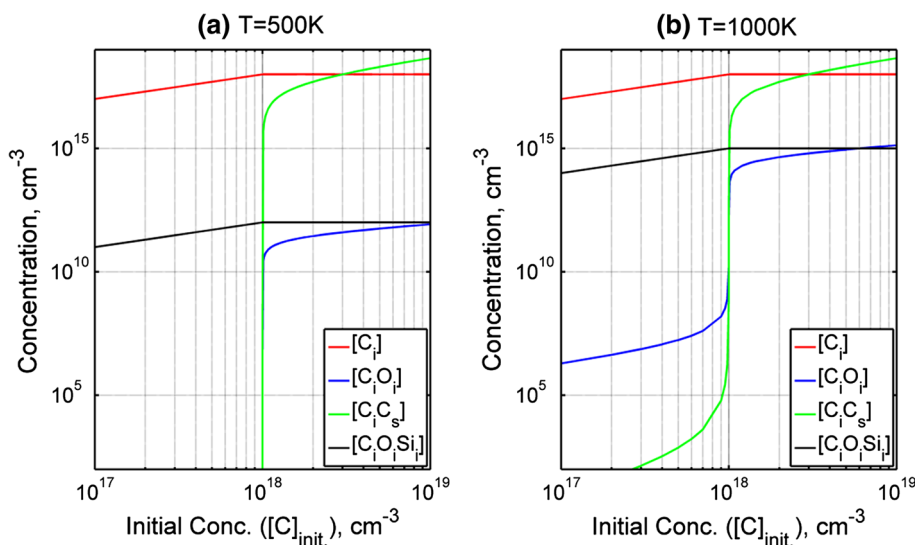
As it is expected the increase of the C concentration has a significant impact on the concentration of carbon-related defects. The concentrations of defect clusters considered are significantly increased with the increase of temperature. This is more profound for C_iO_i and $C_iO_iSi_i$. Notably, C_iC_s can be beneficial as it can be used to improve the Si optical emitters [17, 38], whereas C_iO_i and $C_iO_iSi_i$ can have a deleterious impact. Therefore we propose here that processing should be limited to lower temperatures to allow the formation of C_iC_s but avoid the formation of C_iO_i and $C_iO_iSi_i$ defects.

In the present study it is deduced that the carbon concentration has a limited impact on the concentration of the main oxygen-vacancy defects in Si. This is consistent to a recent model that considered the effect of isovalent doping (Ge, Sn, Pb) in Si [44]. Although carbon was not considered in that study it was demonstrated that only defects that had a strong interaction with vacancies (i.e. Sn and Pb) had a significant impact on the VO and VO_2 concentrations (refer to Fig. 4 of Ref. 44). Carbon has only a small interaction with vacancies and additionally the C_iO_i defect has a lower binding energy as compared to VO, therefore it is expected that carbon will have a limited impact upon the concentration of the oxygen-vacancy defects [38, 42].

3.4 Other considerations

It should be stressed that the present study involves the calculation of relative defect concentrations at equilibrium

Fig. 2 The dependence of carbon related defects with respect to the initial unbound carbon concentration for $T = 500$ K and $T = 1000$ K and initial $[O_i] = [Si_i] = [V] = 10^{18}$ cm^{-3}



conditions aiming to illustrate the impact of binding energies (i.e. mainly local strain relaxation). Most experiments typically involve irradiation and are under non-equilibrium conditions. Under these conditions kinetics will play a role as will extended defects and external sinks (i.e. surfaces). These effects are being considered and will be incorporated in future work.

$\text{Si}_{1-x-y}\text{Ge}_x\text{Sn}_y$ binary and ternary alloys are promising materials for numerous applications including detectors, photovoltaics, lasers and microelectronic devices [45, 46]. Although, mass action models have been used to other semiconducting materials such as Ge and $\text{Si}_{1-x}\text{Ge}_x$ it becomes increasingly difficult to model ternary materials [47–49] Considering the kinetics of the processes the picture becomes even more complicated in ternary semiconductors but forms a fruitful field for further experimental and theoretical investigations [50–53].

4 Summary

We present a model to describe carbon related defects in Si. The input parameters of the model are state of the art hybrid DFT binding energies. The model concerns equilibrium conditions and calculates the relative concentration of carbon related defects for a range of carbon concentrations. C_i and C_iC_s are the dominant carbon related defects, whereas $C_iO_iSi_i$ and C_iO_i defects become increasingly important for high temperatures and the higher initial carbon concentrations. It was previously calculated that the oversized (Pb and Sn) isovalent dopants impact the oxygen-vacancy defects [44], whereas here we showed that carbon does not. This is due to the limited formation of C_iO_i defects and the insignificant interaction of carbon atoms with vacancies. Therefore, carbon does not associate with both components of the oxygen-vacancy defects.

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