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VV and VO_2 defects in silicon studied with hybrid density functional theory

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Abstract The formation of *V*O (A-center), *VV* and VO_2 defects in irradiated Czochralski-grown silicon (Si) is of technological importance. Recent theoretical studies have examined the formation and charge states of the A-center in detail. Here we use density functional theory employing hybrid functionals to analyze the formation of *VV* and VO_2 defects. The formation energy as a function of the Fermi energy is calculated for all possible charge states. For the *VV* and VO_2 defects double negatively charged and neutral states dominate, respectively.

1 Introduction

Si is not only a key material for a range of nanoelectronic, photovoltaic, and sensor devices but also a model system for developing understanding of point defects and defect processes in other semiconductors. In particular, understanding of many defect processes, which can dominate the material and devices properties on the nanoscale, is limited [1–5]. The A-center is the archetypal O-related defect in Czochralski-grown Si (Cz-Si), having been characterized with numerous experimental techniques over the past 50 years. In Cz-Si an important impurity is O as it is introduced in high concentrations during the crystal growth. These O interstitials associate with vacancies (*V*) to form *V*O pairs [6, 7]. As A-centers are both electrically and optically active, it is technologically important to limit their formation. For example, A-centers can influence Si-based imaging and spectroscopy sensors (complementary metal–oxide–semiconductor sensors and charge-coupled device sensors) in space. The radiation in space in fact enhances the formation of A-centers, because high-energy particles (such as electrons, protons, neutrons, ions, and γ-rays) cause lattice displacements giving rise to a supersaturation of vacancies. The vacancies in turn diffuse through the lattice binding with O to yield A-centers, which are effective traps with deleterious impact on the device performance. In previous studies defect engineering strategies have been proposed including the introduction of large isovalent impurities [8]. From a theoretical point of view, recent state-of-the-art hybrid density functional theory (DFT) studies by Wang et al. [9, 10] have determined binding, formation and electronic structure details of *V*O defects in Si.

Divacancies are among the most prominent defects in irradiated Si and active recombination centers [11, 12] with a large influence on the carrier lifetime (an important parameter for the ideal operation of devices). The *VV* defect is formed in the course of irradiation either directly by the simultaneous displacement of two Si atoms at adjacent lattice sites or by the agglomeration of two single vacancies. It is the most prominent intrinsic defect in Si, since it is stable at room temperature in contrast to the monovacancy, which

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is very mobile even at relatively low temperatures. Technological importance of oxygen-vacancy defects also results from the thermal evolution of larger V_mO_n clusters. VO_2 is the main defect formed upon annealing of A-centers at temperatures of 300–400 °C. It has been proposed [13] that VO_2 plays an important role in O precipitation processes in irradiated Si, acting as nucleation species. It is formed by interaction of the migrating *V*O pair with an interstitial O atom. The aim of the present study is to employ hybrid DFT to investigate the formation energies of the *VV* and VO_2 defects for all reasonable charge states. The results are discussed in view of recent experimental evidence.

2 Methodology

All calculations were performed using the Vienna Ab-initio Simulation Package (VASP) [14] with pseudopotentials generated by the projector augmented wave method [15]. A 2 × 2 × 2 supercell containing 64 Si atoms is used with a 3 × 3 × 3 k-point mesh within the Monkhorst–Pack scheme [16] and the cutoff energy for the plane waves is set to 400 eV. The lattice constant of Si is optimized by the PBEsol [17] functional, giving results very close to those obtained by screened hybrid functional calculations [18–20]. A Gaussian smearing with a width of 0.05 eV is used. For each charged defect the lattice constant is kept at the value of pristine Si and the atomic positions are relaxed until the forces on all atoms amount to <0.01 eV/Å. The optimized structures are then used in Heyd–Scuseria–Ernzerhof calculations with Perdew–Burke–Ernzerhof local term and a screening parameter of $\mu = 0.206$ Å^{-1}. The correction approach by Freysoldt et al. [21, 22] for finite size supercell calculations is employed.

The formation energy of a defect is defined by [23].

$$\Delta H_{D,q}(\mu_e \mu_a) = E_{D,q} - E_H + \Sigma n_a \mu_a + q\,\mu_{e}, \quad (1)$$

where $E_{D,q}$ is the total energy of the defective cell with charge q and E_H is the total energy of the perfect cell. Moreover, n_a represents the numbers of atoms introduced or removed from the defective cell and μ_a their chemical potentials. The Fermi energy is denoted as μ_e and is measured from the valence band maximum (VBM), with values in the band gap ($E_{\mathrm{VBM}} \le \mu_e \le E_{\mathrm{VBM}} + E_{gap}$). The chemical potential of O is calculated using quartz SiO_2. While experiment can provide information on the thermal stability and formation of defect clusters, DFT can act synergistically by providing the binding energies.

$$E_b = E_{defect\ cluster} - \Sigma E_{isolated\ defects}. \quad (2)$$

Negative binding energies imply that a cluster is energetically favorable with respect to its components.

3 Results and discussion

Formation energies obtained for the *VV* defect show that the −2 charge state is favorable in almost the entire Fermi energy range, see Fig. 1 (left column). For very low Fermi energies the neutral and negatively charged states are competitive, whereas positively charges states have no significance. From an experimental point of view the *VV* defect appears in four charge states (+1, 0, −1, and −2) [24] and introduces [25–27] in the band gap three deep energy levels: a donor level at about $E_v-0.19$ eV, related to the transition (+/0), and two acceptor levels at about $E_c-0.42$ and $E_c-0.23$ eV, related to the transitions (−/0) and (−−/−), respectively. Infrared spectroscopy revealed [28–32] three major peaks at 3.9, 3.6 and 1.8 μm related to the *VV* defect. The 3.9 μm peak is attributed to electronic excitation between the valence band and states of the *VV* defect of charge −2, the 1.8 μm peak to an internal transition within the neutral *VV* defect, and the 3.6 μm peak to the *VV* defect of charge −1. This reflects consistency between the present hybrid DFT results and the experimental situation regarding the formation of the 0, −1, and −2 charge states of the *VV* defect.

For the VO_2 defect the charge neutral state is preferred for the whole Fermi energy range, see Fig. 1 (left column). This is consistent with the structure and the experimental evidence associated with VO_2. In particular, the VO_2 defect comprises two O atoms (equivalent within its structure) that bridge all four dangling bonds of the Si vacancy and therefore is electrically inactive. There is no experimental evidence for electronic levels in the band gap of Si associated with the VO_2 defect. For completeness, there is experimental evidence [33, 34] of another defect configuration in which only one O atom occupies the vacancy site, whereas the second O atom is in a back bond position. An acceptor level at $E_c-0.05$ eV was assigned to this case.

Total DOSs of pristine Si and the two defects are shown in the right column of Fig. 1. For the *VV* defect the filled area indicates six electrons, as required to saturate the six dangling electrons of the two vacancies. The two unpaired electrons correspond to the sharp peak seen in the figure just below the Fermi energy. The calculated formation energies indicate that the *VV* defect would like to accept two electrons to saturate the two unpaired electrons rather than to donate them. In the VO_2 defect all dangling bonds are saturated by O interstitials so that this defect neither prefers to accept nor to donate electrons.

Table 1 reports the calculated binding energies from Eq. (2). In previous hybrid DFT work [9] it was found that the *V*O defect has a binding energy of −2.21 eV, which is the energy of the association of the *V* to the interstitial O. The association of two *V* to form a *VV* defect results in a binding energy of −2.52 eV. For the *V*O defect to trap an

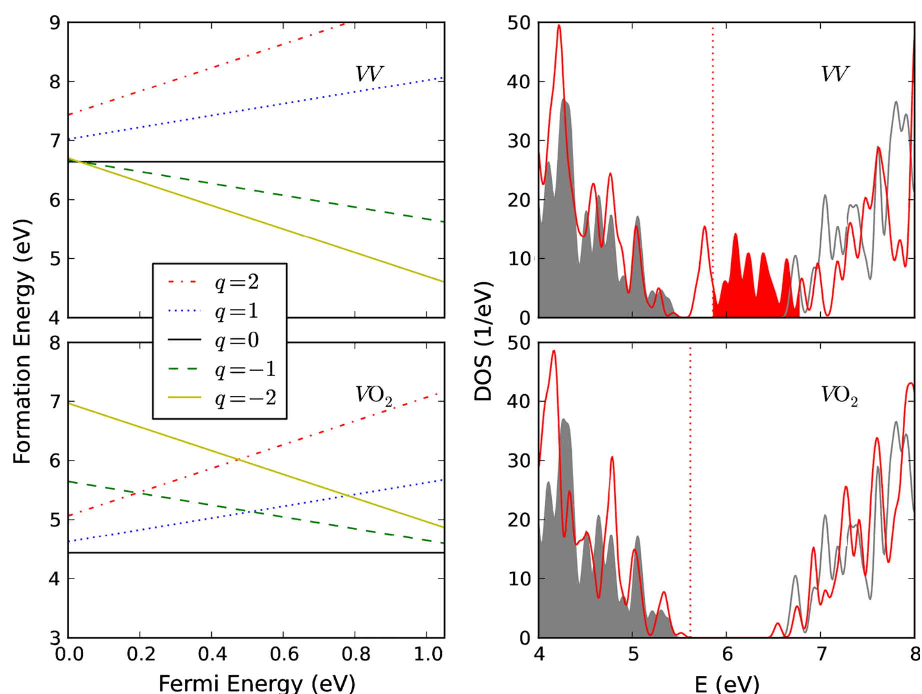

Fig. 1 Formation energies of the *VV* and VO_2 defects in different charge states, as functions of the Fermi energy, and total DOS of pristine Si (*gray*) and defects (*red*). The states below the *dotted line* are occupied (Color figure online)

Table 1 DFT derived binding energies (eV) of the *VO*, *VV* and VO_2 defects in Si

Reaction	Binding energy
$V + \mathrm{O} \rightarrow VO$	−2.21[a]
$V + V \rightarrow VV$	−2.52
$VO + \mathrm{O} \rightarrow VO_2$	−1.83

[a] Reference [10]

interstitial O atom the binding energy is −1.83 eV. The calculated high binding energies are reflected by the experimental result that the defects form in considerable concentrations in Si. Indeed, the main species identified by Fourier transform infrared spectroscopy up to 450 °C are *VO*, *VV*, and VO_2 [35, 36].

4 Summary

Using hybrid DFT, we have calculated the DOS, formation energies and binding energies of the *VV* and VO_2 defects in Si. We have demonstrated consistency between the numerical results and the experimentally determined charge states of both defects. The calculations suggest that the neutral VO_2 defect will be prevalent for any Fermi energy, whereas the −2 charged *VV* defect will be energetically favorable for most values of the Fermi energy (at low Fermi energy the neutral and −1 charged *VV* defects are competitive). The binding energies for two *V* to form a *VV* defect and for the *VO* defect to trap an interstitial O atom amount to −2.52 and −1.83 eV, respectively.

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