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Numerical simulations and modeling of the stability of noble gas atoms in interaction with vacancies in silicon

L. Pizzagalli [a,*], A. Charaf-Eddin [b], S. Brochard [a]

[a] Institut P', CNRS UPR 3346, Université de Poitiers, SP2MI, BP 30179, Boulevard Marie et Pierre Curie, 86962 Futuroscope Chasseneuil Cedex, France
[b] CEISAM CNRS UMR 6230, Université de Nantes, 2 rue de la Houssinière, BP 92208, 44322 Nantes Cedex 3, France

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ABSTRACT

In order to identify the main actors during the initial steps of the formation of noble gas filled bubbles, we have performed an extensive investigation of a single noble gas atom (helium, neon, argon, krypton, xenon) as interstitial or in interaction with a monovacancy and a divacancy in silicon. Density functional calculations in the generalized gradient approximation allowed us for determining the structure and stability of various configurations. We found that interstitial configurations are especially relevant for helium, and to a lesser extent for neon. Heavy noble gas species are predicted to form complexes with vacancies, except in out-of-equilibrium situations where an original bond-centered interstitial configuration is favored. Besides, we propose a model combining a repulsive interaction between the host local electronic density and the noble gas atom, and an elastic description of this atom as a deformable spherical inclusion into an homogeneous isotropic medium. This model is shown to provide an appropriate description, especially for light noble gas species such as helium and neon.

1. Introduction

Chemical elements located in the rightmost column of the periodic classification constitute the group of so-called noble gas (NG) species. They are, among other specific properties, characterized by the quasi absence of chemical reactivity, because of their completely filled electronic shells. Being inert, NG exhibit unique behaviors when interacting with many materials [1]. For instance, NG can be used for processing semiconductors, yielding inert atmosphere during growth, ion beam milling of surfaces, or plasma etching. In electronics, light NG such as He or Ne are also potentially useful in the gettering process for electronic devices [2]. NG atoms are initially implanted in the material, far from the active layers of the future device. Subsequent treatments lead to the formation of cavities [3], which are then used to trap undesirable impurities migrating from active layers. The formation of these extended defects is beneficial for relaxing strain in pseudomorphic SiGe/Si heterostructures, and is also an essential step in the smart-cut process used in the production of silicon-on-insulator wafer substrates. In a spatial context, embedded NG atoms have been found in interstellar dusts [4], and can be used as marker for models attempting to describe stars evolution. Finally, the effects of the presence of NG into materials are also extensively investigated in the context of nuclear applications. In fact, NG like helium are produced in large quantities coming from neutron-induced transmutation reactions and from the coolant. In fusion reactors, the plasma is also generating a high flux of helium which will interact with the wall. The accumulation of helium into structural, confining or fuel cladding materials leads to the formation of extended defects like bubbles [1,5], potentially resulting in swelling, embrittlement, surface roughening, blistering, all processes that can dramatically degrade the mechanical properties.

Extended defect formation due to the presence of helium is largely documented in metals [6,7], covalent systems like silicon [8–14], silicon carbide [15–19], gallium nitride [20], or disordered materials [21]. However a similar outcome has been observed when other NG species such as neon [22,23], argon [24–28], krypton [29,30], and xenon [26,31–33] are inserted into materials. The formation of extended defects such as bubbles or platelets is then clearly a general feature caused by the presence of NG atoms into materials.

The generally accepted driving force behind defects formation is the non-solubility of NG atoms in most materials because of their chemical inertness. NG atoms tend to aggregate to lower the energy cost, occupying available space at defects or generating some if possible. As a result, the formation of NG-filled extended defects such as platelets and bubbles is generally favored.

* Corresponding author.
E-mail address: Laurent.Pizzagalli@univ-poitiers.fr (L. Pizzagalli).

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Nevertheless, the different and possibly complex mechanisms leading to the formation of these defects are not fully understood yet. For instance NG-filled bubbles can grow through continuous supplies of NG atoms and vacancies, by coalescence of existing bubbles, or by emission of dislocation loops [6,34]. Determining the properties and evolution of NG-filled bubbles was the motivation of a large number of dedicated studies. A key property in all proposed models is the NG density into the bubble, which can be obtained thanks to experiments [32,35–40] and numerical simulations [41–50].

To understand bubbles formation, it is also equally important to determine the very first steps leading to the formation of bubbles precursors. Then elementary properties such as formation and migration energies associated with single NG atoms need to be characterized. Furthermore, one has to consider the interaction of NG atoms with vacancies. In fact, NG atoms can be introduced into materials only as energetic particles. A large part of this energy is dissipated through inelastic collisions of the impinging particle with electrons, and the remaining part as elastic collision with ions of the host material. When the energy transmitted to one of these ions is higher than the threshold displacement energy [51–54], there is formation of both an interstitial and a vacancy defect (a Frenkel pair). A large proportion of those recombine during the irradiation process [55,56]. Nevertheless, it is assumed that a non negligible amount of vacancy defects remain, whose interaction with NG atoms could play the role of precursors for bubbles formation. This is especially true for the heaviest NG species, for which a larger amount of damage is created in the host lattice.

In diluted state, NG atoms are hardly detected by most of experimental techniques because of the lack of interaction with the host lattice. Then, available information concerning NG interstitials alone or in interaction with vacancies is often obtained from theoretical studies. Helium impurities have been the most studied, especially in metals [57–67], but also in more complex materials such as oxide [68] and MAX phases [69]. In covalent materials, single NG atom properties have been investigated especially for helium in several group IV materials such as silicon [70–74], silicon carbide [75–78], and diamond [79]. In these studies, it appears that it is usually favorable for helium to bind to existing vacancies. For heavier NG species, such as Ne, Ar, Kr and Xe, both experimental and theoretical data are scarce. Further investigations are then needed to extend the current state of the art.

In this paper, we report density functional theory (DFT) calculations of the properties of single NG atoms (He, Ne, Ar, Kr, and Xe) as interstitial or in interaction with mono- and divacancy in silicon. The latter was chosen since it is considered as a covalent model material, for which one can hope that the results presented here will be quite general. In a first part, we describe our calculations of the stability and structure of a NG atom as interstitial and in presence of vacancies. In a second part, we propose a simple model combining an elastic description and an electronic embedding contribution, which allows for reproducing the results of numerical simulations.

2. Methods

The calculations reported in this work were performed with the PWscf code [80] from the Quantum-ESPRESSO project [81], therefore in the framework of DFT [82,83], and using the Perdew–Burke–Ernzerhof (PBE) [84] generalized gradient approximation for the description of exchange and correlation. The use of a DFT-PBE framework is justified here because the interactions between the NG atoms and the host materials are essentially repulsive. Furthermore, PBE has been shown to allow an overall better modeling of weak bonding than other usual exchange–correlation approximations [85]. The interaction between valence electrons and ions was described using ultrasoft pseudopotentials [86]. Wave functions were expanded on a plane-wave basis, with an energy cutoff of 15 Ry. Within these conditions, the computed lattice parameter of silicon a_0 was found to be equal to 5.468 Å, in good agreement with the experimental value of 5.43 Å. The calculation of the electronic density was made by sampling the Brillouin zone with a $\frac{1}{2}$-shifted 2^3 Monkhorst–Pack grid of k-points [87], equivalent to a set of 4 irreducible k-points.

A $3a_0 \times 3a_0 \times 3a_0$ periodically repeated cubic supercell, including 216 atoms for a perfect silicon crystal, was used for all simulations. A NG atom was initially positioned at different locations in the perfect lattice, or relative to a mono- or a divacancy. Forces were relaxed using the Broyden-Fletcher-Goldfarb-Shanno quasi-Newton algorithm, stopped when residual forces were below 10^{-3} eV Å^{-1} to ensure well converged final structures.

Several sources of errors are possible when dealing with finite size density functional calculations. An important one is related to the convergence of the electronic structure calculation. Here we found that both the chosen energy cutoff and k-points set were appropriate to obtain well converged energies, with errors likely to be much lower than the influence of the exchange correlation approximation selected in our work. Another important source of error is coming from the use of a finite size cell, especially for the heaviest NG species which can induce important lattice deformations. The influence of using fixed volume calculations can be estimated by computing an Eshelby type elastic correction, following Hepburn et al. [66]. For Xe in tetrahedral interstitial position, for which the lattice distortions are the largest among investigated configurations, we calculate a correction of 0.3 eV, thus only 3% of the 10.22 eV formation energy (see Table 1). Corrections will be much lower for lighter NG species or configurations involving NG in vacancies. Finally, zero point energy contributions have not been computed in this work, since they have been shown to change excess energies by about 0.01 eV [66]. Overall, we estimate the errors on our computed excess energies to be at least 0.05 eV and at most 3%.

The validity of our computational setup was finally assessed in the case of the mono and divacancy in silicon. The formation energies in both cases are

$$E_f(V_1) = E(V_1) - \frac{N-1}{N}E_0 \quad (1)$$

$$E_f(V_2) = E(V_2) - \frac{N-2}{N}E_0 \quad (2)$$

where $E(V_1/V_2)$ is the total energy of the defected configuration, N the total number of atoms and E_0 the total energy of the pristine system. These definitions allow for an appropriate cancelation of errors associated with the finite size of supercells. We calculated a formation energy of 3.33 eV for the monovacancy, in excellent agreement with previous investigations [88–90]. The relaxed

Table 1
Energies (in eV) required to introduce a single NG atom into the silicon lattice according to different configurations (see the text for labels meaning). The '–' symbol indicates unstable or untested configurations.

	He	Ne	Ar	Kr	Xe
T	1.00	2.50	5.83	7.14	10.22
H	1.66	3.37	6.86	8.02	10.82
BC	–	–	5.81	5.82	7.14
SP	–	–	7.13	6.96	–
V_1S	1.82	1.98	2.63	2.29	3.34
V_1T	1.15	1.65	–	–	–
V_2S	–	–	1.63	1.24	2.30
V_2C	0.49	0.89	–	1.94	2.54