DFT calculation of the stability and mobility of noble gas atoms in silicon

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ABSTRACT

We have investigated the stability and the migration of single noble gas atoms (He, Ne, Ar, Kr) in bulk silicon, by performing first-principles calculations. Our results indicate that all noble gas interstitials were found to be preferentially located in a tetrahedral site. Other possible sites have been studied too, like the hexagonal one which becomes unstable for large noble gas atoms such as Ar and Kr. Using nudged elastic band technique, we have determined the minimum energy path, and the associated migration energies. Our results are discussed and compared to other works.

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1. Introduction

Ion implantation in a material is particularly interesting as a tool to modify its microstructure, leading to significant changes of its electrical and mechanical properties. For instance, the implantation of He atoms in a semiconductor like silicon may produce bubbles, which evolve into cavities after a thermal treatment [1]. These voids are found to be active to trap metallic impurities [2], and can then be used to improve the quality of silicon-based devices. Other noble gas (NG) atoms such as Ne, Xe have also been considered [3,4].

Bubbles formation due to implantation and aggregation of the implanted ions is a complicated dynamic process, whose details remain largely unknown. To improve our knowledge, it is first necessary to understand and characterize the behavior of a single NG atom in a Si crystal. As far as we know, very little information is available. For He, two different migration energy values, 1.34 eV [5] and 0.80 eV [6] have been reported. To our knowledge no experimental values are available for the other NG atoms. From the theoretical point of view only two calculations have been done for studying the stability and the migration of NG atoms in Si [7,8]. In this work we have carried out first-principles calculations to investigate the stability and the mobility of He, Ne, Ar and Kr single atoms in silicon. Different configurations have been considered to determine NG stable positions, and formation energies. We have also investigated the migration of NG atoms, by computing both the migration mechanism and the associated energy. Finally we discussed our results in comparison with experiments.

2. Methods

Our calculations have been done in the framework of density functional theory (DFT) [9,10], using a plane-wave self consistent field code (PWscf) [11]. The interaction of valence electrons with the ions has been described with ultrasoft pseudopotentials [12]. The Brillouin zone was sampled with a $3 \times 3 \times 3$ grid of k-points [13]. The Perdew–Burke–Ernzerhof generalized-gradient approximation (GGA-PBE) [14] has been used for describing exchange and correlation, since it allows an overall better description of weak bonding than local density approximation [15]. We found that the electronic structure was accurately converged with a plane-wave cutoff energy of 35 Ry. Using these parameters, we have determined the lattice constant of silicon a_0 to be equal to 5.468 Å, close to the experimental value of 5.43 Å.

We used periodic boundary conditions and a 64-atom supercell ($2a_0 \times 2a_0 \times 2a_0$), for modelling an infinite crystal. We have checked that this size is large enough to avoid a significant interaction between an interstitial NG atom and its replicated images. In order to compute a NG atom migration in Si, the nudged elastic band technique (NEB) has been used with three intermediate images between initial and final configurations [16,17]. Atomic structures were considered relaxed when forces were below 10^{-4} eV/Å.

3. Stability

The most stable configuration for a NG interstitial in the Si lattice has been investigated by considering different positions. Among possible candidates were the tetrahedral (T) and hexagonal (H) sites, since they correspond to positions that offer the more

room for an interstitial atom in the lattice, in which extra atoms are likely to be accommodated (Fig. 1). Both have already been considered in previous works [7,8]. We have also tried another possible NG position, in between two Si atoms (bond centered), but such a configuration is not energetically favored. The formation energies E_f, reported in Table 1 for T and H configurations, are computed according to

$$E_f = E_{Si+NG} - n_{Si}\ \mu_{Si} - \mu_{NG} \tag{1}$$

where μ_{Si} is calculated from a 64-atom bulk calculation, and μ_{NG} is simply the energy of a single NG atom in the empty reference supercell.

We found that the configuration T is the most stable one for all considered NG atoms. In all cases, the formation energy of the H configuration is higher. Moreover, a Ar or a Kr atom located in the H site is not stable, and moves towards the nearest T site during the relaxation.
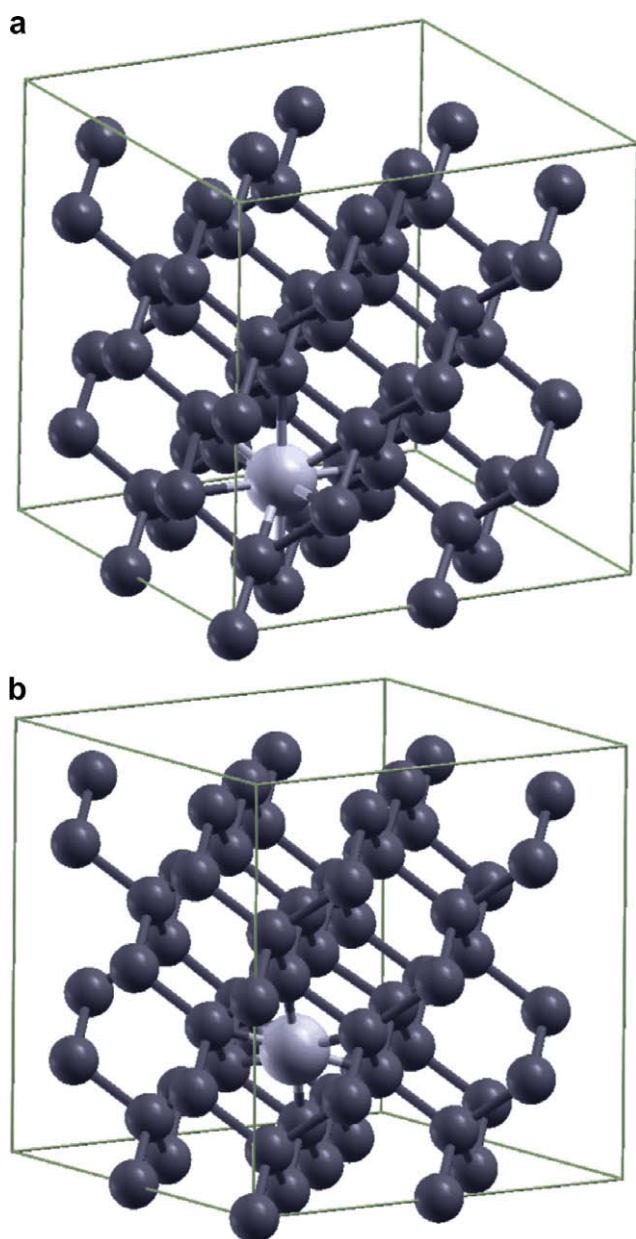
Table 1
Formation and migration energies (in eV) of different NG impurities

	He	Ne	Ar	Kr
Covalent radius	0.4–0.6	0.70	0.94	1.10
T interstitial	1.17	2.59	6.07	7.92
H interstitial	1.87	3.57	→ T	→ T
Substitutional NG	5.40	5.39	6.25	6.46
Migration energy	0.71	1.00	1.21	1.08

The covalent radii (in Å) are obtained from [8].

A possible explanation comes from the analysis of the crystal geometry, assuming that a NG interstitial may be considered as a hard sphere inserted into the Si lattice. Even for the smallest NG, He, we observed a deformation outward of the Si atoms surrounding the T and H sites. Since the available volume is larger around the T site than the H one, it seems reasonable that a lower energy is required to form a NG interstitial in the former than in the latter. In the case of Ne, bonds between first-neighbors Si expand by 2.4% for a T interstitial, and by 5.5% for a H interstitial.

The formation energy increases dramatically for the heaviest and the largest NG interstitial. Fig. 2 shows the formation energy variation as a function of the theoretical NG covalent radius (given in Table 1). In a previous study, Estreicher et al. have determined a similar variation, albeit with a much larger increase rate [8]. For instance, our calculated formation energy for a Kr interstitial is half their value. This difference could be explained by their use of a very small 14 atom hydrogenated cluster, yielding a stiffer silicon structure. In fact, for He, which is small enough and does not significantly deform the lattice, we computed a very similar formation energy.

4. NG atom in a Si vacancy

We have also considered that a NG atom could be located in a Si vacancy. The formation energies E_f, calculated using expression (1) and $n = 63$, are reported in Table 1. In all cases, a NG atom in a Si vacancy is a stable configuration. The energy variation is represented in Fig. 2. For the lightest NG atoms like He and Ne, the formation energy is high, and only slightly increases for the heaviest. This can be due to different causes. First the formation of the Si vacancy involves the breaking of four covalent bonds which is energetically expensive. In addition, the presence of the NG atom
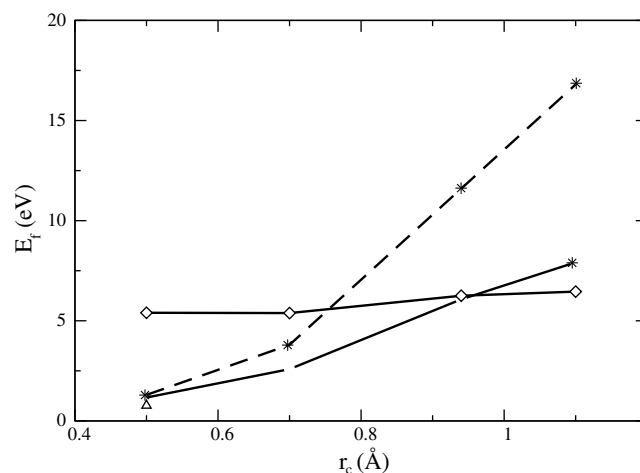

Fig. 1. Ball and stick representation of a Ne interstitial in a tetrahedral site T (a), and in a hexagonal site H (b).

Fig. 2. Calculated formation energies of NG interstitials in T sites (circles, our results, and stars [8]), and substitutional NG (diamond), as a function of the covalent radius. For a He interstitial in T site, the value from [7] is represented by a triangle.

prevents the lattice relaxation around the Si vacancy. For all NG atoms, we have observed a noticeable deformation at the level of the first-neighbors, i.e. Si–Si bonds contract by 2–3%. Because of the slow increase of the formation energy, this configuration becomes competitive compared to an interstitial in T site for Ar and Kr.

5. Migration

To study the diffusion properties of NG atoms in silicon, we have investigated the migration of a single NG interstitial in the lattice. For this purpose, we have used the NEB method to determine the minimum energy path, allowing to pass from a stable position to another. Our NEB calculations have been performed with the same parameters than before, with a band including three relaxed images. Initially, it is reasonable to consider a path linking two stable T sites through the H configuration. We found that for all cases, the final relaxed paths remained close to the initial T–H–T guess. Fig. 3 shows the minimum energy paths as a function of the NG atom position after relaxation. It is clear that for all NG atoms, the diffusion mechanism involves successive hoppings of the NG atom between H and T site. On the figure, one can remark that an H configuration appears to be saddle for He and Ne, in apparent contradiction with our previous results. However, this can be explained by the low number of images in our NEB calculation, which does not allow a good resolution in the vicinity of the H configuration. NEB calculations with a larger number of images have been performed for Ne (Fig. 3), without providing further information. It is then likely that a NG impurity located in the H site is only weakly stable, this stability vanishing for large atoms such as Ar and Kr. The migration energies were obtained as the difference between the lowest, i.e. T configuration, and the highest, i.e. H configuration, energies along the minimum energy path. Note that in the case of He and Ne, we obtained almost similar migration energies by computing directly $E_f^H - E_f^T$ in Table 1. The migration energies are shown in Fig. 4 as a function of the NG atom covalent radius. The migration energy increases according to the size of the NG atom, except for the Kr atom. Estreicher et al. computed the migration energies as $E_f^H - E_f^T$ (Fig. 4) [8]. Surprisingly, they reported that Ar and Kr atoms were stable in the H site. Compared to our results, they found much larger migration energies, due to the small size of their computational system, leading to very high E_f^H. Alatalo et al. have also computed the migration energy for He [7], but using a larger supercell, similar to ours, and they found a value in agreement with our results.
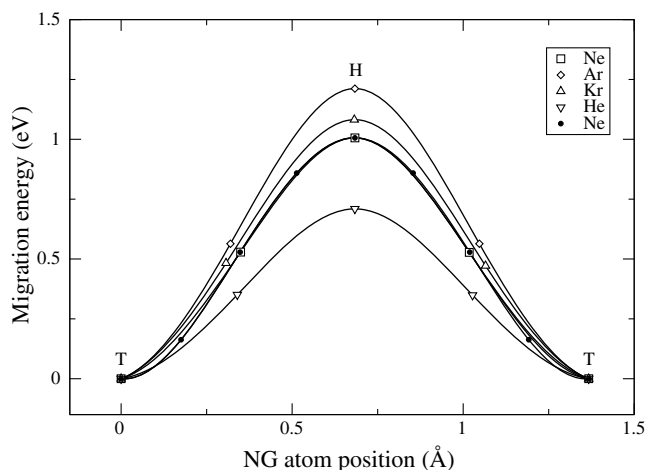
6. Discussion

Our computed energies are lower than those given by Estreicher et al., especially for the heaviest NG atoms such as Ar or Kr for which formation and migration energies are about half and 25% of values in [8], respectively. The most likely explanation for such a discrepancy is the very small size of the cluster used in their ab initio calculations, i.e. 14 atom, that may lead to a very stiff silicon lattice. Contrary to their conclusions, our results suggest that diffusion of species such as Ar or Kr should be possible in silicon. Nevertheless, we have only investigated the migration of a NG atom starting from an interstitial T site. However, our results indicate that a Kr atom located in a silicon vacancy is energetically less expensive. In that case, starting from a lowest energy configuration, migration energies are expected to be higher, with a more complicated diffusion mechanism involving concerted migration of Si and Kr atoms. Such an investigation is out of the scope of the present study.

Overall, we found that both formation and migration energies increase when considering the heaviest NG atoms, except for the migration energy of the Kr interstitial. For the latter, we have not been able to find the cause of this behavior, since an examination of the lattice structure during the migration did not reveal any significant differences with Ar for instance. However, it is noteworthy that Estreicher et al. also found a strong reduction of the migration energy increase rate from Ar to Kr [8]. Leaving aside Kr, a straightforward explanation for the formation and migration energy increase is a steric effect, since a larger volume can be attributed to the heavier NG atoms. This assumption of a 'hard sphere' located and diffusing into the silicon lattice is also supported by an analysis of the electronic density, showing that there is only electronic repulsion between the fully populated orbitals of the NG interstitial and the Si atoms, as expected. In the case of a small hard sphere diffusing into a rigid lattice, one may expect that the migration energy increases as the square of the sphere radius [18]. This is not the case here, simply because NG interstitials are equivalent to large spheres and the silicon lattice is severely deformed during the NG interstitial migration.

In conclusion, we have performed first-principles calculations of the stability and migration of a single NG interstitial in a silicon lattice. For He, our computed energies are in good agreement with available data, whereas we found much lower formation and migration energies for the other NG atoms, compared to a previous theoretical work.
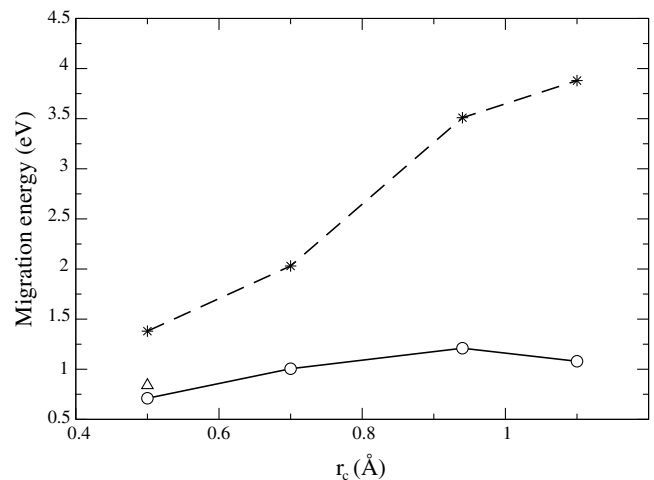

Fig. 3. Minimum energy paths for a single NG atom in the Si crystal (empty symbols T → T with three relaxed images, and filled circle T → H with three relaxed images).

Fig. 4. Calculated migration energies of NG atoms (circles, our results, and stars [8]) as a function of the covalent radius. For a He atom, value from [7] is represented by a triangle.

References

[1] V. Raineri, S. Coffa, M. Saggio, F. Frisina, E. Rimini, Nucl. Instrum. Meth. Phys. Res. B 147 (1999) 292–297.

[2] V. Raineri, A. Battaglia, E. Rimini, Nucl. Instrum. Meth. Phys. Res. B 96 (1995) 249–252.

[3] E. Oliviero, S. Peripolli, P.F.P. Fichtner, L. Amaral, Mater. Sci. Eng. B 112 (2004) 111–115.

[4] G. Faraci, A.R. Pennisi, F. Zontone, B. Li, I. Petrov, Phys. Rev. B 74 (2006) 235436.

[5] A. Weringen, N. Warmoltz, Physica 22 (1956) 849.

[6] P. Jung, Nucl. Instrum. Meth. Phys. Res. B 91 (1994) 362.

[7] M. Alatalo, M.J. Puska, R.M. Nieminem, Phys. Rev. B 46 (1992) 12806–12809.

[8] S.K. Estreicher, J. Weber, A. Derecskei-Kovacs, D.S. Marynick, Phys. Rev. B 55 (1997) 5037.

[9] P. Hohenberg, W. Kohn, Phys. Rev. 136 (1964) B864–B871.

[10] W. Kohn, L.J. Sham, Phys. Rev. 140 (1965) A1133–1138.

[11] http://www.pwscf.org/.

[12] D. Vanderbilt, Phys. Rev. B 41 (1990) 7892–7894.

[13] H.J. Monkhorst, J.D. Pack, Phys. Rev. B 13 (1976) 5188–5192.

[14] J.P. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. Lett. 77 (1996) 3865–3868.

[15] D.C. Patton, M.R. Pederson, Phys. Rev. A 56 (1997) R2495–R2498.

[16] G. Henkelman, H. Jónsson, J. Chem. Phys. 113 (2000) 9978.

[17] H. Jónsson, G. Mills, K.W. Jacobsen, Classical and Quantum Dynamics in Condensed Phase Simulations, World Scientific, 1998.

[18] J.M. Rickman, J. Vinals, R.F. Sekerka, Phys. Rev. B 43 (1991) 8251–8263.