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Effect of vacancy charge state on positron annihilation in silicon*

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The charge-state-dependent lattice relaxation of mono-vacancy in silicon is studied using the first-principles pseudopotential plane-wave method. We observe that the structural relaxation for the first-neighbor atoms of the mono-vacancy is strongly dependent on its charge state. The difference in total electron density between with and without charge states in mono-vacancy and its relevant change due to the localized positron are also examined by means of first-principles simulation, demonstrating the strong interplay between positron and electron. Our calculations reveal that the positron lifetime decreases with absolute charge value increasing.

Keywords: vacancy, charge state, positron annihilation

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1. Introduction

Positron annihilation spectroscopy is widely used to study the defect properties in solids. Energetic positrons injected into a material will rapidly lose energy, then exist for a few hundred picoseconds in thermal equilibrium with the environment, before finally annihilating.[1–3] As a result, the positron lifetime or data related to the momentum of the annihilating electron–positron pair in a specific environment could be obtained from experimental and theoretical analysis. It has long been known that the probability of positron trapping in vacancy-related defects is directly dependent on its charge state.[4] At room temperature, trapping is expected for neutral or negative vacancy charge states; trapping to positive vacancies may occur but at a rate whose order of magnitude is below that for neutral vacancies.[3] Charge states could influence the electronic and geometrical structure of vacancies and also affect the associated positron annihilation parameters directly.

An efficient and convenient method to increase the electrical conductivity in a semiconductor is based on the doping method. The doping is directly responsible for material properties, and it has been known experimentally that thermal diffusion rate and luminescence quenching rate could be strongly dependent on the defect charge state in the semiconductor.[5] Introducing different types and concentrations of foreign atoms into the matrix could control not only the defect charging but also the defect local magnetic moments. As the capture center, the charge of these vacancy defects in semiconductors and its screening play a determinative role in determining the mechanism of positron trapping at vacancies. A strong enhancement in trapping cross section is also expected when a neutral defect becomes negatively charged. An understanding of the relationship between defect structures and its charge states is particularly important in semiconductor research.

However, under usual experimental conditions the time resolution of the positron annihilation lifetime spectrometer is limited, and it is very difficult to distinguish the positron lifetime between the substitutional defects and impurity-vacancy complexes due to their similar positron lifetime values. But theoretical analysis is successful in predicting or producing the positron annihilation properties.[6,7] Here the single vacancy in silicon is chosen to study the effect of vacancy charge state on positron annihilation. The lattice mono-vacancy in bulk silicon can support charge states of (2–), (1–), (0), and (2+).[8] It is worthwhile to mention that no evidence has been found for positron trapping in positive vacancies. Thus the present study only systematically examines those non-positive charge states related positron lifetime in cubic silicon within the framework of density functional theory. We hope that these calculation results will help to further understand the relationship between the vacancy charge states and positron annihilation parameters of silicon and related materials.

2. Method

Thermalized positrons are efficient in seeking for open-volume defect sites, owing to their large spatial extension. Description of the state of a thermal positron in a perfect bulk crystal or that of a positron trapped at a defect requires the solution of the Schrödinger equation. The electron density and the positron potential are calculated at each grid point of the three-dimensional mesh. Then, the positron annihilation rate λ, which is the reciprocal of the positron lifetime τ, can be

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calculated as

$$\lambda = \frac{1}{\tau} = \pi r_0^2 c \int \mathrm{d}r \cdot n_\mathrm{p}(r) \cdot n_\mathrm{e}(r) \cdot \gamma(n_\mathrm{e}) = \int \mathrm{d}r \cdot n_\mathrm{p}(r) \cdot \Gamma(n_\mathrm{e}), \quad (1)$$

where r_0 is the classical electron radius, c is the speed of light, n_e is the electron density, n_p is the positron density, $\gamma(n_\mathrm{e})$ is called the enhancement factor of the electron density at the positron, and $\Gamma(n_\mathrm{e})$ denotes the positron annihilation rate in a homogenous electron gas with density n_e, which we adopted in the following form (BN model):[9,10]

$$\Gamma(n_\mathrm{e}) = \pi r_0^2 c n_\mathrm{e}(1 + 1.23 r_\mathrm{s} + 0.8295 r_\mathrm{s}^{1.5} - 1.26 r_\mathrm{s}^2 + 0.3286 r_\mathrm{s}^{2.5} + (1 - 1/\varepsilon) \cdot (r_\mathrm{s}^3/6)), \quad (2)$$

where ε is the high-frequency dielectric constant and r_s is the electron density parameter,

$$n_\mathrm{e} = 3/(4\pi r_\mathrm{s}^3). \quad (3)$$

The first-principles pseudopotential plane-wave method is used to study the lattice relaxation of silicon mono-vacancy in different charge states. When dealing with charged vacancies, a compensating uniform background charge density is introduced to maintain the charge neutrality. The generalized gradient approximation (GGA) within the scheme due to Perdew–Burke–Ernzerhof (PBE)[11] is chosen for the exchange–correlation interactions. The valence electron configuration is $3s^2 3p^2$ for silicon. A cutoff energy of 400 eV and a $6 \times 6 \times 6$ grid of Monkhorst–Pack k points are chosen in this study to ensure a good convergence of the calculated structure.

3. Results and discussion

The structural optimization results show that the bond length between the nearest two Si atoms is $d_0 = 2.368$ Å which is slightly larger than the 2.352 Å bond length observed in crystalline silicon.[12] It is common for DFT–GGA calculations to suffer from insufficient electron correlation to both underestimate the bond energy and overestimate the lattice constant. As shown in Fig. 1, for the cubic structure silicon, four dangling bonds could be left when one atom is removed from the perfect crystal lattice. In this configuration each of these dangling or broken bonds contains one unpaired valence electron, and the interesting consequences of the re-bonding effect could occur to eliminate these dangling bonds.[13] In the process, the structural relaxation or nuclear displacements can be achieved in order to minimize the total energy of the system, and the relevant tetragonal John–Teller distortion could reduce the symmetry of the original configuration and break the tetrahedral (T_d) symmetry of the system.

To evaluate the effect of the charge states in this structure, we perform structural relaxation of the systems with different charge states. The relative changes of the internal atomic positions are summarized in Table 1. The geometrical relaxation arises from the evolution of electrostatic forces between the surrounding atoms and the negatively charged vacancy. Once the silicon mono-vacancy becomes negatively charged by adding one or two electrons, the surrounding silicon interacts more strongly. The direct consequence is the obvious inward-relaxation of silicon tetrahedron. The largest displacement is up to 14.81% of the nearest-neighbor distance for a doubly negative vacancy. Lento and Nieminen[14] observed a similar result and explained it in terms of Jahn–Teller distortion and negative effective-U effect with a lower symmetry and total energy.

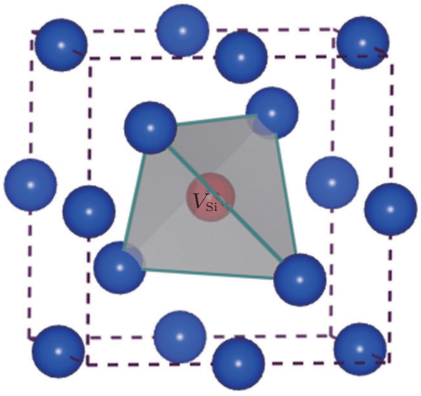

Fig. 1. (color online) Atomic geometry of the mono-vacancy in cubic silicon. The four associated neighboring silicon atoms are located at the vertices of a tetrahedron.

Table 1. Values of displacement (Δ_d in Å) of the nearest-neighbor Si atoms surrounding the vacancy. Negative values denote inward relaxation. The corresponding positron annihilation lifetime $\tau(V_\mathrm{Si})$ is also provided for comparison.

Charge state	Δ_d/Å	(Δ_d/d_0)/%	$\tau(V_\mathrm{Si})$/ps
0	–0.144	–6.06	257
1–	–0.256	–10.80	240
2–	–0.351	–14.81	230

Trapped positrons, in comparison to delocalized Bloch state positrons, are likely to annihilate with a low momentum valence electron. Changing the charge states number to a different value must result in a different electron density distribution around the mono-vacancy. Therefore, the positron annihilation parameters will also be affected. The difference in distribution of total electron density between with and without (1–) charge state in V_Si is shown in Fig. 2(a). The visualized electron density isosurface shows that the excess electron state is localized near the vacancy. Different vacancy charge states could yield distinctly different positron annihilation probability distributions. In contrast, the localized positron state at the vacancy site will also affect the electron density distributions as shown in Fig. 2(b), although such a change magnitude is usually very small. The magnitude reflects the enhanced density of the bonding electrons around the positron, and from

some aspect it also dominates the process in which positrons and electrons are mutually influenced.

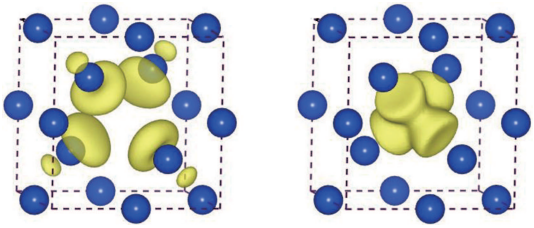

Fig. 2. (color online) Calculated difference in total electron density between with and without (1–) charge state in V_{Si} (a), and the localized positron state enhanced the electron accumulation (b). The isosurface values are taken to be 1.4×10^{-2} electron/Å^3 (a) and 7×10^{-8} electron/Å^3 (b).

The calculated value of $\tau_b = 211$ ps for the positron lifetime characteristic of the bulk silicon is in agreement with the experimental value of about 216 ps in defect-free silicon.[15,16] The difference in lifetime between positron bulk and defect is also the most important criterion for judging the computational results, and the value of $\Delta = 46$ ps for the charge-free mono-vacancy is also consistent with previous experimental results and the ratio Δ/τ_b in a reasonable error range.[16] After relaxation with the negative charge state, the positron lifetime decreases and becomes close to the bulk lifetime. This is not surprising since the inward relaxation of the first-neighbor atoms is large. It is also interesting to mention that the change of the charge state to a more negative one, which leads to the decrease of the positron lifetime, has also been observed in other semiconductors, such as GaAs.[17]

Table 2. Calculated values of positron lifetime and the relative positron energy eigenvalue (ΔE) in the un-relaxed mono-vacancy systems with different charge states.

Excess charge (e)	Lifetime/ps	ΔE/eV
0	258	0
1–	250	–0.126
2–	245	–0.240

To clarify the predominant influence on the difference in positron annihilation between the defect charging and lattice relaxation, we calculate the positron lifetime in an un-relaxed mono-vacancy system with different charge states. The results show that positron lifetime is mainly affected by the inward-relaxation surrounding atoms. This situation is quite similar to the case for the two negatively charged structures. Through more quantitative analysis, we can find that the positron energy eigenvalue could decrease in the trapping process more in the more negatively charged state vacancies. This in turn reflects the additional strong Coulomb interaction between the positron and the excess electrons when the vacancies are charged.

4. Conclusion

The relaxation structure of the mono-vacancy in cubic silicon with different charge states is investigated using the pseudopotential plane-wave method. The results show that ions surrounding the vacancy relax largely towards the center of the vacancy. The relaxation of the charge state vacancy leads to a reduction of the symmetry with tetragonal John–Teller distortion. The specific distributions of the excess electrons and the localized positrons reveal the strong lattice dynamic process of the mono-vacancy trapped positron. The lifetimes of the positron trapped at mono-vacancy with different charge states are calculated. A comparison between experimental data and theoretical results clearly shows that the calculated positron lifetime in bulk silicon is consistent with experimental values. Also the variation of the positron lifetime with vacancy charge state shows that the positron has a great charge-state-dependent annihilation characteristic.

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