First-Principles Calculation
of He–H Interaction in c-Si

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We used the density functional theory and *ab initio* pseudopotentials to investigate He–H interaction in crystalline silicon. It was shown that both hydrogen and helium stimulate the formation of vacancy complexes. The presence of hydrogen decreases the vacancy and divacancy formation energies by about 2 eV. The presence of one or two helium atoms reduces the divacancy formation energy by 0.3 and 0.4 eV, respectively. The influence of helium presence on hydrogen diffusion from silicon vacancies under high pressure depends on a helium concentration. Thus, according to our calculation, low concentrations of He increase the hydrogen out-diffusion.

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1. Introduction

According to experimental data [1] implantation of silicon with hydrogen and helium generates a huge number of point defects and their complexes as well as leads to the formation of so-called bubbles in the implanted areas. In these vacancy complexes implanted atoms accumulate.

Ab initio calculations also show that the presence of both helium and hydrogen in crystalline silicon stimulates the formation of vacancy complexes. Hydrogen is chemically active element and it interacts with Si atoms. When H_2 molecule moves from an interstitial site to a vacancy, it dissociates, and H atoms saturate the dangling silicon bonds. Being inert, helium does not interact chemically with other atoms and due to its high permeability evaporates completely at higher temperatures leaving the "empty" voids. According to experimental data [2] the

H concentration in silicon samples with co-implantation of He and H treated at high temperature – high pressure (1–1.1 GPa) is lower than the one treated under lower pressure. So at high-temperature treatment of a Si samples with implanted He and H under high pressure the increase in hydrogen out-diffusion is observed. In the present work quantitative estimations of He–H interaction in silicon under pressure and the process of hydrogen out-diffusion are considered.

2. Method and approaches

Our theoretical investigation is based on the density functional theory [3] with the local density approach [4, 5] combined with the pseudopotential method. The FHI96md computer code [6] was used to optimize atomic geometries of studied systems and to find their total energies. Our pseudopotentials were constructed and tested using the FHI98PP package [7]. The norm-conserving pseudopotentials for Si, He, and H were constructed in the frame of the Troullier–Martins [8] scheme in the fully separable form of Kleinman–Bylander [9].

The plane wave basis set was used with the energy cutoff of 12 Ry. To be sure that our results obtained at $E_{cut} = 12$ Ry are reliable we have carried out test calculations with some larger E_{cut} (16 and 20 Ry). We have calculated the formation energies of vacancy without hydrogen as well as with it. The differences of vacancy formation energies calculated with different E_{cut} are not larger than the accuracy of our calculation (0.1 eV).

To take into account lattice relaxation effects, all calculations were performed using a supercell containing 64 silicon atoms. The only one k-point of the Brillouin zone (Γ-point) was used because of the large size of supercell.

The nonlinear change in volume of a large number of solids as a function of applied hydrostatic pressure can be reproduced by the following equation [10, 11]:

$$P = \frac{B_0}{B_0' + 1} \left[\exp\left(\frac{(B_0' + 1)(V_0 - V)}{V_0} \right) - 1 \right], \tag{1}$$

V_0 and B_0 are the equilibrium volume and the bulk modulus at the zero pressure, and B_0' is the pressure derivative of B_0 at $P = 0$. We used the mean values ($B_0 = 98$ GPa and $B_0' = 3.4$) from the data taken from Ref. [12]. To simulate the pressure we decreased the supercell volume (i.e. corresponding lattice parameter $L = V^{1/3}$) by 1–5% that corresponds to the pressure of 1–5 GPa according to formula (1).

3. Results

3.1. Vacancies and divacancies in crystalline silicon

The vacancy and divacancy formation energies were calculated by using the following equations:

$$E_f(\text{vac}) = E_{Si64} - (E_{Si63} + E_{Si}), \tag{2}$$

$$E_f(\text{divac}) = E_{Si64} - (E_{Si62} + 2E_{Si}), \tag{3}$$

where E_{Si64} is the energy of the silicon supercell, E_{Si63} is the energy of the silicon

supercell with a vacancy, E_{Si62} is the energy of the silicon supercell with a diva-cancy, and E_{Si} is the chemical potential of silicon (the energy of one silicon atom in bulk silicon).

Different researches give different values for vacancy and divacancy formation energies [13–15]. These values lie in the region of 3–4 eV for a vacancy and of 4–5 eV for a divacancy. Our calculations (with E_{cut} of 12 Ry) give 2.8 eV for a vacancy and 3.7 eV for a divacancy, which are in good accordance with literature data.

3.2. Hydrogen influence on the vacancy complexes formation in silicon

Ab initio calculations show that hydrogen can exist in perfect silicon in two forms: atomic [16] and molecular [17, 18]. The molecular state is more favorable than the atomic one. In the absence of defects the most preferable position for the molecular hydrogen is the tetragonal interstitial site [19, 20]. Moving from silicon interstitial to a vacancy or divacancy, the hydrogen molecule dissociates for atoms which interact with silicon atoms and saturate its dangling bonds. The hydrogen presence in small concentration decreases the formation energy of both a vacancy and a divacancy by the value of about 2 eV. But at the high hydrogen concen-trations vacancies and divacancies have to be formed and to fill with hydrogen spontaneously in accordance with our calculation [21] and experimental data [22].

3.3. Helium atoms in silicon lattice and their influence on the divacancy formation

In the absence of defects the most preferable position for helium atoms is the tetragonal interstitial site of silicon lattice [23], which is also confirmed by our calculations. But at the presence of vacancy defects helium atoms will aspire to proceed in divacancies or larger complexes of vacancies. Therefore the divacancy can be considered as the minimal model of a cavity in silicon which serves as the accumulation center for He atoms.

The divacancy formation energy is equal to 3.7 eV in the absence of external pressure. It decreases linearly by 1 eV with increasing pressure from zero to 5 GPa. The presence of one helium atom reduces the divacancy formation energy by 0.3 eV, and the presence of two helium atoms — by 0.4 eV. The influence of pressure on divacancy formation does not vary; in both cases the pressure of 5 GPa reduces the formation energy by about 1 eV.

3.4. Pressure and helium presence influence on hydrogen out-diffusion

Both helium and hydrogen, implanted in a silicon sample, stimulate the formation of vacancy complexes. Hydrogen is chemically active element in contrast to inert helium. Leaving silicon interstitial sites for divacancies, H_2 molecules dissociate and passivate silicon dangling bonds with some energy profit which is calculated in the following way:

$$E_{mov} = (E_{Si62-H4} + E_{Si64-H2}) - (E_{Si62-H6} + E_{Si64}), \tag{4}$$

where $E_{Si64-H2}$ is the energy of the silicon supercell with the H_2 in tetrahedral

interstitial, $E_{Si62-H4}$ is the energy of the "four H atoms in divacancy" system, $E_{Si62-H6}$ is the energy of the "six H atoms in divacancy" system. According to our calculation this value is equal to 1.6 eV.

In the case of the presence of He atoms (one or two) in "H-decorated" divacancy this energy profit is defined similarly:

$$E_{mov} = (E_{Si62-H4-He(1,2)} + E_{Si64-H2}) - (E_{Si62-H6-He(1,2)} + E_{Si64}). \qquad (5)$$

In the case of the presence of one as well as two helium atoms reduces this profit by 0.1 eV. But additional pressure influence in the presence of one helium atom and two ones is different. At low He concentration (one atom per divacancy) the 5 GPa pressure decreases this energy additionally by 0.2 eV and makes hydrogen less bonded and more mobile in silicon which is in accordance with experimental data [2]. In the case of high He concentration (two atoms per divacancy) the same pressure increases the H_2 binding energy by 0.2 eV. Thus, high concentrations of He reduce the hydrogen out-diffusion.

4. Conclusion

The first principles calculations show that pressure as well as the embedding of hydrogen and helium stimulate the appearance of vacancy complexes in silicon. The presence of hydrogen assists the vacancy formation more significantly in comparison with the helium presence. But hydrogen bonds with silicon atoms complicate hydrogen out-diffusion. Our calculations in accordance with experimental data show that the presence of helium atoms (in a low concentration) in an "H-decorated" vacancy complex increases the probability of hydrogen out-diffusion at the high pressure treatment.

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