

## ATOMIC STRUCTURE AND NONELECTRONIC PROPERTIES OF SEMICONDUCTORS

# Effects of Pressure and Hydrogen on the Formation of Vacancies and Divacancies in Crystalline Silicon

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**Abstract**—The electron-density functional and pseudopotential methods are used to study the effects of hydrogen and pressure on the formation of vacancies and divacancies in silicon. It is shown that the formation energy of vacancies can be reduced by 1.8–3.5 eV and that of divacancies by 2–5.4 eV in the presence of hydrogen. As a result, the spontaneous generation of vacancies and vacancy-containing complexes becomes possible at high concentrations of hydrogen. At the same time, the presence of hydrogen makes silicon less sensitive to pressure and, at high hydrogen concentrations, can completely suppress the tendency toward additional formation of vacancies in the sample exposed to pressure. © 2004 MAIK “Nauka/Interperiodica”.

## 1. INTRODUCTION

The presence of hydrogen in a silicon crystal lattice affects various properties of silicon. As it has high diffusivity, hydrogen (whose sources are many of the reactants used in semiconductor technology and water vapor) can easily penetrate silicon crystals even at room temperature and, thus, can interact with various defects of the crystal lattice. Hydrogen has a high chemical activity and reacts with impurities and crystal-lattice defects. Intrinsic point defects and their complexes with impurity atoms are formed in silicon crystals during technological treatment. Studying the interaction of these defects with hydrogen therefore has both scientific and practical significance.

Calculations from first principles show that hydrogen can be present in both atomic [1] and molecular [2, 3] states in silicon that is free of defects and other impurities. The molecular state is more favorable and yields an energy gain per hydrogen atom of 1.0 eV [4]. At the same time, the presence of hydrogen in silicon is conducive to the formation of vacancies [5, 6]. The difference between the energy of the Si–H bond and that of isolated interstitial hydrogen (2.2 eV) is sufficiently large to initiate the spontaneous formation of vacancies if four dangling silicon bonds are saturated simultaneously with hydrogen [7]. Even the formation of microvoids in silicon is possible if the hydrogen concentration is high [8]. In addition, it is well known that pressure also stimulates the appearance of vacancies in silicon by reducing their formation energy [9]. However, the combined effect of hydrogen and pressure on the formation of vacancies and vacancy-containing complexes has so far not been studied.

The objective of this study was to gain insight into the effect of pressure on the processes of formation of isolated vacancies and divacancies in crystalline silicon that contains hydrogen. We will not discuss issues related to the kinetics of these processes; i.e., we will not consider the diffusion of hydrogen molecules and atoms and that of silicon self-interstitials that appear as a result of the formation of vacancies. In other words, we will not consider the activation energies of the processes; we will only compare the energies of the initial and final states. Such an approach is justified in the case of high temperatures when we are interested only in the final result rather than in the process rate. Since we will compare our calculations with high-temperature (~1000°C) experiments [8], the approach above is completely justified. The effect of pressure on the diffusion-related processes will be considered in a separate publication.

## 2. METHOD AND PARAMETERS OF CALCULATION

The theoretical studies reported in this paper are based on the theory of the electron-density functional [10] in the local-density approximation [11, 12], which is combined with the pseudopotential method in the Troullier–Martins approximation [13].

For the calculations, we used the FHI96md software package [14], which made it possible to optimize the atomic configuration of the system and determine its total energy. Plane waves were chosen as the basis; the cutoff energy was varied from 8 to 20 Ry. In order to take into account the relaxation of the silicon crystal lattice around defects, we performed all the calcula-

tions for a silicon supercell composed of 64 silicon atoms. We used the  $\Gamma$  point of the Brillouin zone as the  $k$  point.

The equilibrium value of the silicon lattice constant was equal to 5.35 Å according to our calculations. In order to simulate the compression, we reduced the silicon lattice constant by 1–5%, which corresponded to a pressure of 1–5 GPa. These values are consistent with the pressures that actually exist in silicon and arise in semiconductor devices when they are used in conditions of dynamic loads and under the effect of thermoelastic stresses at the interfaces between silicon and other materials.

### 3. RESULTS AND DISCUSSION

#### 3.1. Vacancies and Divacancies in High-Purity Silicon under Atmospheric Pressure

The vacancy-formation energy was determined from the following formula:

$$E_f(\text{vac}) = E_{\text{Si}_{64}} - (E_{\text{Si}_{63}} + E_{\text{Si}}).$$

Here,  $E_{\text{Si}_{64}}$  is the energy of a silicon supercell,  $E_{\text{Si}_{63}}$  is the energy of a silicon supercell with a vacancy, and  $E_{\text{Si}}$  is the silicon chemical potential whose value was determined from separate calculations. Accordingly, we have the following expression for a divacancy:

$$E_f(\text{divac}) = E_{\text{Si}_{64}} - (E_{\text{Si}_{62}} + 2E_{\text{Si}}).$$

Here,  $E_{\text{Si}_{62}}$  is the energy of a silicon supercell with a divacancy. It is implied that the “excess” silicon atoms released as a result of the formation of vacancies and divacancies reach the surface and become incorporated into it; thus, one of the “surface” atoms is transformed into a “volume” atom, so that the number of volume atoms is conserved.

Different values of formation energy for vacancies and divacancies in silicon are reported in various publications [15–17]. The energy for a vacancy ranges from 3 to 4 eV; for a divacancy, 4–5 eV. Our calculations (with a cutoff energy of 8 Ry) yielded values of 3.0 and 4.2 eV, respectively, which are in good agreement with published data.

#### 3.2. Hydrogen in Silicon under Atmospheric Pressure

Since the molecular state of hydrogen in silicon that does not contain other impurities and intrinsic defects is more favorable than the atomic state, we will compare the energy of hydrogen in various defect structures with that of molecular hydrogen. In the absence of lattice defects, the tetragonal interstitial site is the most favorable site for molecular hydrogen in silicon [18, 19]. The formation energies for a vacancy and a divacancy in the presence of a hydrogen molecule decreases because a spontaneous dissociation of the  $\text{H}_2$  molecule and saturation of dangling silicon bonds with hydrogen occur

when hydrogen transfers from an interstitial site to a vacancy (divacancy). In this case, the formation energies are defined by the following formulas:

$$E_f(\text{vac}) = E_{\text{Si}_{64} + \text{H}_2} - (E_{\text{Si}_{63} + 2\text{H}} + E_{\text{Si}}),$$

$$E_f(\text{divac}) = E_{\text{Si}_{64} + \text{H}_2} - (E_{\text{Si}_{62} + 2\text{H}} + 2E_{\text{Si}}).$$

Here,  $E_{\text{Si}_{64} + \text{H}_2}$  is the energy of a system that consists of silicon and a hydrogen molecule at a tetragonal site,  $E_{\text{Si}_{63} + 2\text{H}}$  is the energy of a system that consists of silicon and two hydrogen atoms in a vacancy, and  $E_{\text{Si}_{62} + 2\text{H}}$  is the energy of a system consisting of silicon and two hydrogen atoms that reside in a divacancy.

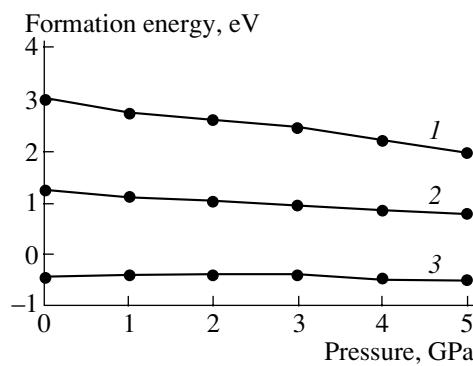
Our calculations yielded 1.2 eV for the formation energy for a vacancy in the presence of a hydrogen molecule and 2.3 eV for the case of a divacancy. Thus, the presence of a small amount of hydrogen in silicon reduces the formation energy for both vacancy and divacancy by about 2 eV. Only partial passivation of the internal dangling bonds of silicon occurs in this situation. Hydrogen can passivate all the dangling bonds if its concentration is higher. In that case, a vacancy attracts two hydrogen molecules, while a divacancy attracts three. A gain in the energy becomes so large that the formation energies become negative: –0.5 eV for a vacancy and –1.3 eV for a divacancy. Consequently, at high hydrogen concentrations, vacancies and divacancies can be formed spontaneously without any additional energy (for example, thermal) expenses, and they are immediately filled with hydrogen, which is consistent with experimental data [8].

The available published theoretical data are also consistent with our results. For example, Van der Walle *et al.* [4] showed that the energy of a silicon crystal is reduced by ~2.2 eV owing to the passivation of a single dangling bond when an isolated hydrogen atom is transferred from an interstitial site to a vacancy; two hydrogen atoms reduce the crystal energy by 4.4 eV if these atoms passivate two dangling bonds. Since we are considering molecular hydrogen (rather than atomic hydrogen) as the initial state, we should subtract the dissociation energy of a hydrogen molecule (equal to 2 eV [4]) from 4.4 eV in order to compare the data of [4] with our results. Thus, according to [4], the formation energy for a vacancy in the presence of a hydrogen molecule is reduced by 2.4 eV, which is not very different from our value of 2 eV.

#### 3.3. The Combined Effect of Pressure and Hydrogen

We studied the effect of pressure on the formation of vacancies and divacancies in silicon that contains and does not contain hydrogen. In this case, the formation energy for a vacancy was determined from the expression

$$E_f^P = (E_{\text{Si}_{63}}^P + E_{\text{Si}}^P) - E_{\text{Si}_{64}}^P,$$



**Fig. 1.** Dependences of the vacancy-formation energy on pressure in silicon (1) without hydrogen, (2) in the presence of a hydrogen molecule, and (3) in the presence of three hydrogen molecules.

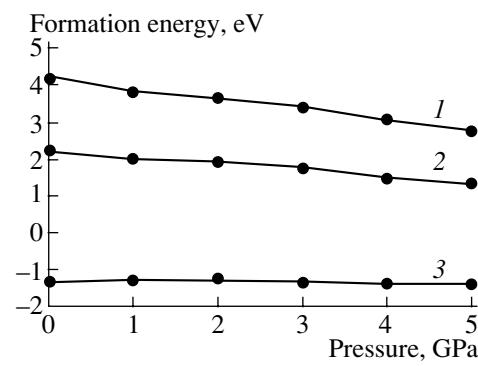
where the superscript  $P$  indicates the dependence of corresponding parameters on pressure.

The formation energy for a vacancy in silicon that contains hydrogen and is subjected to pressure was determined from the formula

$$E_f^P = (E_{\text{Si}_{63} + 2\text{NH}}^P + E_{\text{Si}}^P) - E_{\text{Si}_{64} + \text{NH}_2}^P,$$

where  $N = 1, 2$  is the number of hydrogen molecules.

In Fig. 1 we show the calculated dependences of the formation energies for a vacancy  $E_f$  on pressure in silicon that contains and does not contain hydrogen. The value of  $E_f$  decreases linearly with increasing pressure in silicon without hydrogen: as the pressure increases to 5 GPa, the value of  $E_f$  decreases by 1 eV. This result is qualitatively consistent with the data reported previously [9] but differs from these data quantitatively: according to [9], the vacancy-formation energy decreases by only 0.2 eV as the pressure increases to 5 GPa. In our opinion, this discrepancy is caused by the fact that a cell with 32 silicon atoms was used in [9] to simulate the behavior of a vacancy, whereas we used a cell composed of 64 atoms. As shown previously [20], it is necessary to use a cell with no less than 70 atoms in order to describe realistically the relaxation properties of a vacancy in silicon (these properties are important in studying the effect of pressure). As the number of atoms decreases, the error increases drastically. This behavior is understandable since the boundary atoms in the cell are fixed during simulation and cannot contribute to the relaxation. At the same time, there are a relatively large number of boundary atoms in cells with a small number of atoms. Specifically, 26 atoms are involved in relaxation around a vacancy in a cell composed of 64 atoms, whereas only 4 atoms are involved in this relaxation in a cell composed of 32 atoms. The result we obtained indicates that pressure has a relatively strong effect on vacancy formation and is implicitly consistent with the results reported in [21], where the effect of pressure on the activation energy of As diffusion (with a vacancy-



**Fig. 2.** Dependences of the divacancy-formation energy on pressure in silicon (1) without hydrogen, (2) in the presence of a hydrogen molecule, and (3) in the presence of three hydrogen molecules.

related origin) in silicon was studied and a decrease in  $E_f$  by 0.7 eV was observed under a pressure of 6 GPa.

A decrease in the vacancy-formation energy as a result of exposure to pressure is attributed to the fact that pressure reduces the distances between atoms, specifically, between the atoms that have dangling bonds and surround the vacant site in the crystal lattice. As a result, we have an increased overlap of the wave functions that correspond to dangling bonds and an increase in the exchange (covalent) interaction. Simultaneously, a partial (proportional to the pressure) saturation of dangling bonds occurs, the vacancy energy decreases, and the vacancy-formation energy decreases.

Hydrogen reduces the vacancy-formation energy by saturating (passivating) the dangling bonds. Therefore, one would not expect the pressure to have a significant effect on the formation energy for vacancies with completely passivated dangling bonds. The effect of pressure is expected to be less in the case of incomplete passivation than in the case of the absence of hydrogen. Indeed, as can be seen from Fig. 1, the curve representing the dependence of  $E_f$  on pressure in the presence of a single  $\text{H}_2$  molecule has slope that is smaller by a factor of two in the absence of hydrogen. Two hydrogen molecules completely neutralize the effect of pressure (within the accuracy of the calculation and simulation methods used). Similar results were also obtained for a divacancy (Fig. 2). A pressure of 5 GPa applied to silicon devoid of hydrogen reduces the divacancy-formation energy by 1.4 eV. In the presence of a single hydrogen molecule, the formation energy decreases by 2 eV, continues to decrease with increasing pressure, and attains a value of 1.3 eV at 5 GPa. At higher hydrogen concentrations (three hydrogen molecules per divacancy), in which case all the dangling bonds are saturated, the divacancy-formation energy at the zero pressure is equal to -1.3 eV. The divacancy-formation energy remains nearly constant as pressure increases further (Fig. 2, curve 3).

The values of the vacancy- and divacancy-formation energies (in eV) in relation to the cutoff energy  $E_{\text{cut}}$

Energy	$E_{\text{cut}} = 8 \text{ Ry}$	$E_{\text{cut}} = 16 \text{ Ry}$	$E_{\text{cut}} = 20 \text{ Ry}$
$E_f(\text{vac})$	3.0	2.9	3
$E_f(\text{vac}, \text{H}_2)$	1.2	1.1	1.1
$E_f(\text{divac})$	4.2	4.0	4.0

In order to estimate the reliability of the results reported here, we performed test calculations at higher cutoff energies (16 and 20 Ry). The results obtained are listed in the table.

The difference in the vacancy-formation energies calculated at various values of the cutoff energy is within the error of the calculation method (0.1 eV). For a divacancy, the difference in energies represents an error within 0.2 eV, which is within the range of the spread in the available published data.

#### 4. CONCLUSION

Calculations from first principles show that pressure stimulates significantly the appearance of vacancies and divacancies in silicon by decreasing the energy of their formation owing to the fact that atoms with dangling bonds are forced closer to each other and that exchange interaction between these atoms increases. As hydrogen is introduced into silicon, the effect of pressure is reduced, as hydrogen atoms passivate the dangling bonds. If the amount of hydrogen is insufficient to passivate all the dangling bonds, the pressure has almost no additional effect on the formation of vacancies and divacancies.

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