Enhanced activation of implanted dopant impurity in hydrogenated crystalline silicon

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(Received 5 March 1998)

We propose a physical model for enhanced activation of (implanted) dopant atoms in crystalline Si when the Si vacancy contains atomic hydrogen. Calculations of the potential barriers for inserting the interstitial phosphorus dopant into both hydrogenated and unhydrogenated vacancy sites of the crystalline Si dependent on the charge state of the hydrogenated vacancy, the hydrogen localization, and the transport direction of the interstitial atom to the vacancy are reported using the self-consistent field molecular-orbital linear combination of atomic orbitals technique in the neglect of diatomic differential overlap approach. The results suggest a decrease of the activation temperature for the phosphorus atoms by more than 300 °C.
[S0163-1829(98)05931-1]

It is well known that atomic hydrogen may effectively passivate donor[1] and acceptor[2–4] impurities and also various types of defects[5–8] in crystalline silicon. At present a significant number of simulations exists to explain the structure and properties of such hydrogen complexes.[9–11] It was shown[11–13] that an account of crystal lattice relaxation is essential in calculating both hydrogen localization within the silicon crystal lattice and its binding energy. In the case of impurity or defect passivation by hydrogen, heating results in breaking of the hydrogen bond and recovery of its electric activity.[14]

However, a second large class of phenomena exists in Si related to atomic hydrogen, but one in which hydrogen appears in the role of a process catalyst. These phenomena include the enhanced annealing of radiation defects[15,16] and reduction of activation temperature of implanted doping impurity[17,18] in silicon in the presence of hydrogen, an increase of radiation hardness of hydrogenated silicon,[19] and an increased oxygen diffusion rate in the silicon crystal lattice and enhanced formation of thermal donors by hydrogen plasma treatment.[20,21] So far there have not been many attempts to understand such catalytic behavior of hydrogen in Si.

In our earlier papers[16,18] we offered an explanation of enhanced annealing of vacancy defects and activation of implanted dopant impurity under a low-temperature rf hydrogen plasma annealing. We have attributed the effects to the relaxation of the crystal lattice in the vacancy region in the presence of hydrogen and the possible reduction of the potential barrier when an interstitial atom interacts with the hydrogenated vacancy. The quantum-chemical calculation presented in our paper[22] has shown that enhanced annihilation of a Frenkel pair in silicon occurs if the hydrogen atoms are localized near the vacancy. In this paper the effect of atomic hydrogen on the potential barrier height is calculated using the case of forcing a dopant (phosphorous, for example) from an interstitial site into a Si vacancy, i.e., on the process of electrical activation of a group-V impurity. The influence of localization and the charge state of hydrogen atoms on this process is analyzed and the possibility of verifying the model proposed in Refs. 16 and 18 for the reduction of implanted dopant activation temperature in the presence of hydrogen is discussed.

The calculations were performed using the self-consistent-field molecular-orbital linear combination of atomic orbitals technique in the neglect of diatomic differential overlap valence approach.[23] A cluster containing 51 silicon atoms and one vacancy site has been used, the total charge of which was reduced to zero by compensating for hydrogen atoms at the outer boundary of the cluster, so that a $[VSi_{51}H_{35}]$cluster was formed. The calculations of charged systems have been performed by a special technique, presented in Ref. 24.

In the interstitial of the cell adjacent to the vacancy the phosphorus atom was placed and the heights of potential barriers that should be overcome for ''building in'' the phosphorus impurity to the vacancy site of the crystal lattice were studied. The energy characteristics of the extremum points of the potential surface of the interaction of diffusing phosphorus atoms with free or hydrogenated vacancies were de-

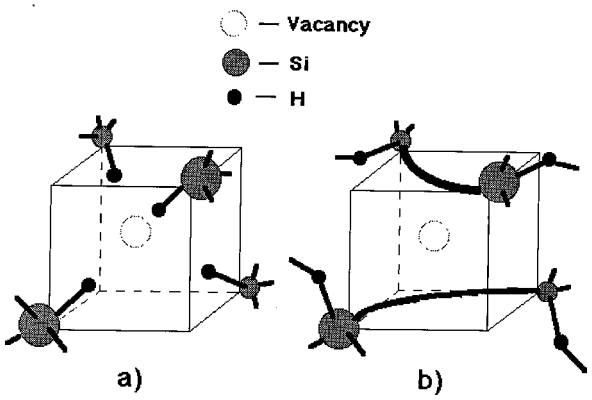

FIG. 1. Hydrogenated vacancy with hydrogen localized (a) inside and (b) outside the vacancy.

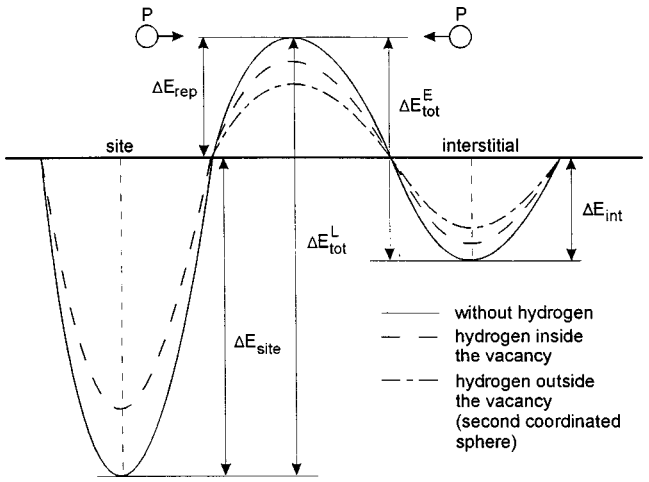

FIG. 2. Potential barriers for the impurity atom entering the vacancy region and exiting from the crystal lattice site.

termined using the technique of direct search for the extremum of the total energy functional, while taking into account the relaxation of all atoms in the model. The details of the calculation performed were presented in an earlier paper.[22]

In our study of the role of the hydrogen effect in building in the impurity atoms into the lattice site, two cases have been considered: (i) four H atoms are localized symmetrically inside the inner region of a vacancy [Fig. 1(a)] as demonstrated earlier in Ref. 14 and (ii) four H atoms are localized on the Si-Si bonds between silicon atoms with dangling bonds and neighboring atoms, so that the vacancy region remains free [Fig. 1(b)]. The second configuration of the hydrogenated vacancy is found to be more stable than the first one.[22]

At the first stage we consider the building in of the phosphorus atoms from the interstitial site in the vacancy site without the participation of hydrogen. The calculation was performed for the atoms moving in the directions along the axes [111], [110], and [100]. In order to be built into the vacancy site an atom should overcome the potential barrier $\Delta E^{E}_{\mathrm{tot}}$, which can be represented as the sum of the binding energy of the atom in the interstitial ΔE_{int} and of the energy of atom repulsion when an impurity enters the site $\Delta E^{E}_{\mathrm{rep}}$. The barriers that should be overcome by the impurity atoms in moving from the interstitial into the site of the crystal lattice and back are shown schematically in Fig. 2. The calculation has shown that full potential barriers for building in of the phosphorus atoms in the site of the silicon crystal lattice in the cases of motion along the ⟨111⟩, ⟨110⟩, and ⟨100⟩ directions are equal to 7.2, 9.5, and 8.6 eV, respectively. The results of the calculation are summarized in Table I. It is seen that the minimum potential barrier for the phosphorus atoms corresponds to the atomic motion along the ⟨111⟩ direction and the maximum one is in the ⟨110⟩ direction.

Let us consider now the effect of hydrogen on the building in of the phosphorus atoms. For localization of the four neutral hydrogen atoms in the inner region of the vacancy [Fig. 1(a)] or in the second coordination sphere out the vacancy region [Fig. 1(b)], the relaxation of the silicon crystal lattice leads to the expansion of the vacancy region due to the displacement of dangling-bond silicon atoms by 0.20 and 0.21 Å, respectively, from the equilibrium position.[22] This effect substantially lowers the potential barriers for atoms moving to the vacancy center. In the case of phosphorus atoms, the total height of potential barrier $\Delta E^{E}_{\mathrm{tot}}$ (Fig. 2) equals 5.1, 7.4, and 6.9 eV for the hydrogen localization inside the vacancy and 4.5, 6.9, and 6.2 eV for hydrogen localization outside the vacancy, with the phosphorus atoms moving in the ⟨111⟩, ⟨110⟩, and ⟨100⟩ directions, respectively. Thus hydrogen localization in the neutral charge state on a vacancy may result in the reduction of the potential barrier for building the phosphorus atom into the vacancy site by a factor ranging from 1.25 to 1.56 depending on the direction of atomic movement (Table I).

It should be noted that hydrogen localization outside the vacancy significantly lowers the repulsion energy of the doping impurity atom from the silicon atoms vis-à-vis the binding energy of the impurity atom located in the interstitial site, as compared to the case of hydrogen localization inside the vacancy. This situation is schematically shown in Fig. 2. It is related to the fact that if the hydrogen atom is situated inside the vacancy, it provides additional repulsion to the atom being built into the site.

If instead of neutral hydrogen atoms the H^+ or H^- ions are placed on the vacancy site, the heights of potential barriers for phosphorus atoms being built into the vacancy site will be substantially changed (see Table I). For example, if the four H^+ ions are located outside the vacancy, lattice relaxation leads to an increase of the distance from the vacancy center to the silicon atoms by 0.25 Å,[22] thus reducing the potential barrier for displacement of the phosphorus atom from the interstitial to the site along the ⟨111⟩, ⟨110⟩, and ⟨100⟩ directions to the values of 4.1, 5.9, and 5.6 eV, respectively. Localization of four hydrogen ions H^- outside the vacancy leads to an increase of the distance from the vacancy center to the dangling-bond silicon atoms by as little as 0.10 Å.[22] As a result, the potential barrier heights for the directions ⟨111⟩, ⟨110⟩, and ⟨100⟩ in the case of phosphorus atoms appear to be equal to 5.7, 7.6, and 7.1 eV, respectively. The complete results of the calculation are presented in Table I.

The calculations show that the reduction factor for the potential barrier encountered by the phosphorus atom being built into the vacancy reaches a maximum value of 1.8 when the vacancy is decorated with H^+ ions and the minimum value of 1.23 when the vacancy is decorated with H^-. Thus,

TABLE I. Hydrogen impact on the bonding energy in the interstitial position ΔE_{int} (eV), the energy of repulsion $\Delta E^{E}_{\text{rep}}$ (eV), and the total potential barrier $\Delta E^{E}_{\text{tot}}$ (eV) for the case in which the phosphorus atom enters the vacancy silicon site.

State of vacancy	⟨111⟩			⟨100⟩			⟨110⟩		
	ΔE_{int} (eV)	$\Delta E^{E}_{\text{rep}}$ (eV)	$\Delta E^{E}_{\text{tot}}$ (eV)	ΔE_{int} (eV)	$\Delta E^{E}_{\text{rep}}$ (eV)	$\Delta E^{E}_{\text{tot}}$ (eV)	ΔE_{int} (eV)	$\Delta E^{E}_{\text{rep}}$ (eV)	$\Delta E^{E}_{\text{tot}}$ (eV)
V	3.3	3.9	7.2	3.5	5.1	8.6	3.7	5.8	9.5
VH_4^0 hydrogen inside the vacancy	2.6	2.5	5.1	2.8	4.1	6.9	2.9	4.5	7.4
VH_4^0 hydrogen outside the vacancy	2.5	2.0	4.5	2.8	3.4	6.2	2.9	3.8	6.9
VH_4^+ hydrogen outside the vacancy	2.7	1.4	4.1	2.8	2.8	5.6	2.9	3.0	5.9
VH_4^- hydrogen outside the vacancy	2.7	3.0	5.7	2.9	4.2	7.1	2.9	4.7	7.6

in all states of the hydrogenated vacancy a substantial reduction of the potential barrier for the phosphorus atom being built into the vacant site of the silicon crystal lattice occurs, which should result in the reduction of the activation temperature for these doping impurities when implanted into silicon. The process of incorporating phosphorus atoms into the hydrogenated vacancy can be described by the reaction

$$\text{Si-H}+\text{P}_I \rightarrow \text{Si-P}+\text{H},$$

where P_I represents the interstitial phosphorus.

The balance of energy for the phosphorus atoms moving on the direction ⟨111⟩ to the hydrogenated vacancy (when the neutral hydrogen atom is localized out of it) can be assessed in the following way. Since the binding energy for the phosphorus atom localized in a site of the lattice for the case of trapped hydrogen (H^0) in the second coordination sphere is 19.8 eV (our calculation) and the potential barrier value for inserting the interstitial phosphorus into the site for this case equals 4.5 eV (see Table I), the energy being released to incorporate the phosphorus atom into the site, per one bond, equals $\{(19.8\text{ eV}-4.5\text{ eV})/4\}=3.83$ eV. If the binding energy of the Si-H bond at the vacancy equals 2.21 eV,[22,25] the above reaction comes with the release of energy on the order of 1.6 eV. That is, resulting from the reaction we can expect the hydrogen separation from this bond in the reaction region with either its trapping by a neighboring vacancy or the creation of the interstitial molecule H_2. Taking into account that in the building of the phosphorus atom into the lattice site the binding energy of the Si-H bond in the structure P-Si-H-Si decreases to the value of 1.87 eV, one can expect the above reaction to become more efficient.

Figure 3 shows qualitatively the model of the phosphorus atom building into the hydrogenated vacancy. The three principal steps involved are as follows. (i) Trapping of the hydrogen atom by the vacancy leads to substantial relaxation of the crystal lattice near the vacancy, which results in an essential expansion of the inner region [Figs. 3(a) and 3(b)].

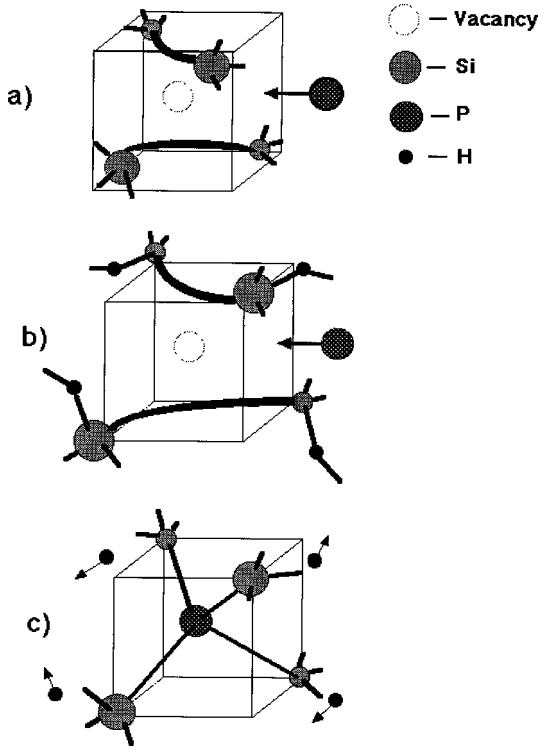

FIG. 3. Illustration of the model of enhanced activation of the doping impurity: (a) The impurity atom moves toward the nonhydrogenated vacancy, (b) the impurity atom moves toward the hydrogenated vacancy, and (c) impurity atom is being built into the crystal lattice site and hydrogen leaves the place of reaction.

(ii) Enlargement of the inner vacancy region reduces the potential barrier for the impurity being built into the lattice site (Fig. 2). (iii) The impurity is incorporated into the lattice site, with breaking of the Si-H bond and release of the hydrogen [Fig. 3(c)] for possible trapping at the neighboring vacancies or formation of the H_2 molecule. It is seen that the hydrogen in this process acts as a catalyst and at the final stage it leaves the reaction region, with a high probability of repeating the process at another site.

Let us consider how the activation temperature can be reduced in the case of hydrogenated silicon. Since the probability of impurity building into the site is proportional to the magnitude $\exp(-\Delta E^E_{\rm tot}/kT)$, the reduction of the potential barrier $\Delta E^E_{\rm tot}$ by the factor ranging from 1.25 to 1.56, calculated for the vacancy saturated by the neutral hydrogen, should result in the reduction of the annealing temperature T by the same factor, for equal dopant activation probability. Thus, if the annealing temperature in hydrogenated phosphorus implanted crystalline silicon is 400 °C (i.e., 673 K), then for the same dopant activation efficiency in conventional silicon the temperature should range over 840–1050 K (i.e., over 568 °C–777 °C). The mean value of this range corresponds to the experimental results[17,26] and attests that atomic hydrogen incorporation into implanted silicon can reduce the activation temperature more than 300 °C. The presented model can be valid for different kinds of impurities in silicon and demonstrates the enhanced transformation for vacancy defects in crystalline hydrogenated silicon.

The research described in this paper was made possible in part by Grant No. UP2-291 from the Government of Ukraine and the U.S. Civilian Research & Development Foundation for the Independent State of the Former Soviet Union (CRDF).

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[1] N. M. Johnson, C. Herring, and D. J. Chadi, Phys. Rev. Lett. **56**, 769 (1986).
[2] J. I. Pankov, R. O. Warn, and J. E. Berkeyheyser, Appl. Phys. Lett. **45**, 1100 (1984).
[3] A. J. Tavendale, D. Alexiev, and A. N. Williams, Appl. Phys. Lett. **47**, 316 (1985).
[4] C. T. Sah, S. C.-S. Pan, and C. C.-H. Hsu, J. Appl. Phys. **57**, 5148 (1985).
[5] J. L. Benton, C. J. Doherty, S. D. Ferriss, D. L. Flamm, L. C. Kimerling, and H. J. Leamy, Appl. Phys. Lett. **36**, 670 (1980).
[6] S. J. Pearton, Phys. Status Solidi A **72**, K73 (1982).
[7] V. V. Kveder, R. Labusch, and Y. A. Ossipyan, Phys. Status Solidi A **84**, 149 (1984).
[8] S. M. Myer, M. I. Baskes, H. K. Birnbaum, J. W. Corbett, G. G. DeLeo, S. K. Estreicher, E. E. Heller, P. Jena, N. M. Johnson, R. Kirchheim, S. J. Pearton, and M. J. Stavola, Rev. Mod. Phys. **64**, 559 (1992).
[9] G. G. DeLeo and W. B. Fowler, Phys. Rev. B **31**, 6861 (1985).
[10] P. Deak, M. Heinrich, L. C. Snyder, and J. W. Corbett, Mater. Sci. Eng., B **4**, 57 (1989).
[11] C. G. Van de Walle, P. J. H. Denteener, Y. Ber-Yam, and S. T. Pantelides, Phys. Rev. B **39**, 10 791 (1989).
[12] P. J. H. Denteener, C. G. Van de Walle, and S. T. Pantelides, Phys. Rev. B **39**, 10 824 (1989).
[13] G. C. Van de Walle and N. H. Nickel, Phys. Rev. B **51**, 2636 (1995).
[14] S. J. Pearton, J. W. Corbett, and T. S. Shi, Appl. Phys. A: Solids Surf. **A43**, 153 (1987).
[15] Qin Guayang and Hua Zongla, Solid State Commun. **53**, 975 (1985).
[16] V. S. Lysenko, A. N. Nazarov, S. A. Valiev, I. M. Zaritskii, T. E. Rudenko, and A. S. Tkachenko, Phys. Status Solidi A **113**, 653 (1989).
[17] R. Singh, S. J. Fonash, A. Rohatgi, P. R. Choudhary, and J. Gigante, J. Appl. Phys. **55**, 867 (1988).
[18] M. Ya. Valakh, V. S. Lysenko, A. N. Nazarov, G. Yu. Rudko, A. S. Tkachenko, and N. I. Shakhraychuk, Nucl. Instrum. Methods Phys. Res. B **44**, 146 (1989).
[19] S. V. Koveshnikov, S. V. Nosenko, and A. M. Surma, Solid State Phenom. **19**, 165 (1991).
[20] H. J. Stein and S. K. Hahn, Appl. Phys. Lett. **56**, 63 (1990).
[21] R. Murray, Physica B **170**, 115 (1991).
[22] A. N. Nazarov, V. M. Pinchuk, V. S. Lysenko, and T. V. Yanchuk, Modell. Simul. Mater. Sci. Eng. **4**, 323 (1996).
[23] J. A. Pople, D. P. Santry, and G. A. Segal, J. Chem. Phys. **43**, 129 (1965).
[24] E. F. Sheka, V. D. Khavryuchenko, and V. A. Zayets, Phys. Low-Dim. Struct. **2/3**, 59 (1995).
[25] A. N. Nazarov, V. S. Lysenko, V. M. Pinchuk, and T. V. Yanchuk, in *The Physics of Semiconductors,* edited by M. Scheffler and R. Zimmermann (World Scientific, Singapore, 1996), Vol. 4, p. 2585.
[26] M. Ya. Valakh, V. S. Lysenko, A. N. Nazarov, G. Yu. Rudko, and N. I. Shakhraychuk, Phys. Status Solidi A **130**, 45 (1992).