Interstitial Hydrogen and Neutralization of Shallow-Donor Impurities in Single-Crystal Silicon

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It is demonstrated for the first time that hydrogen can passivate shallow-donor impurities in *n*-type single-crystal silicon, and a novel chemical-bonding model is proposed to explain the phenomenon. Phosphorus greatly slows the bulk diffusion of hydrogen at ~ 150 °C. Conductivity and Hall measurements show that the room-temperature electron density is decreased by hydrogenation, but the mobility is *increased,* so that compensation is ruled out. Total-energy calculations predict an energy minimum for H at the antibonding site of a silicon nearest neighbor of substitutional P. Known solubilities imply ~ 1-eV binding for atomic H in pure silicon.

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The current intense interest in the properties of hydrogen in semiconductors derives from its ability to passivate shallow-level, as well as deep-level, defects at moderate temperature (e.g., $\leq 400\,°\mathrm{C}$). In single-crystal silicon it has been established that shallow-acceptor impurities (e.g., B) are passivated by insertion of a hydrogen atom between the substitutional acceptor and an adjacent silicon atom so as to form a Si—H bond and a neutralized, threefold-coordinated acceptor.[1-5] On the other hand, several studies[6-8] have concluded that shallow-donor impurities in silicon (e.g., P) cannot be passivated. Contrary to these previous conclusions, this Letter experimentally demonstrates that hydrogen neutralizes shallow donors in *n*-type silicon. In addition, hydrogen passivation of shallow donors is theoretically established with total-energy calculations which place the interstitial hydrogen atom at the antibonding site of a silicon atom that is adjacent to the substitutional donor impurity.

Hydrogen diffusion in *n*-type silicon is strongly dependent on donor concentration. This is demonstrated in Fig. 1 with depth profiles of deuterium (D) in specimens of single-crystal silicon that possess different uniform phosphorus concentrations [P]. The specimens were exposed at 150 °C for 10 min to monatomic deuterium, which was generated in a gas discharge.[9] Deuterium was used as a readily identifiable isotope of low natural abundance which duplicates the chemistry of hydrogen and is detectable with high sensitivity by secondary-ion mass spectrometry (SIMS).[10] The depth profiles in Fig. 1 demonstrate conclusively that hydrogen and deuterium diffusion in silicon is greatly slowed by the presence of phosphorus. In addition, the areal density of D strongly increases with [P], which disproves the recent claim[11] that free holes in the surface layer are needed to permit the entry of atomic hydrogen. Furthermore, the fact that the D profiles cross over establishes that the effective (bulk) diffusion coefficient depends on [P]. However, the results in Fig. 1 alone do not distinguish between a direct trapping of H by P and an indirect effect such as a dependence of the charge state of H on the dopant-controlled Fermi energy. Moreover, quantitative analysis of the SIMS profiles has to date been hindered by the need for more complete information on surface boundary conditions and on the coalescence of hydrogen atoms into inert H_2 molecules.

Combined resistivity and Hall-effect measurements have now provided not only further evidence of hydrogen-donor interaction, but also a demonstration that hydrogen can passivate donors by associating with them to form neutral complexes, rather than by producing spatially unrelated acceptors. Polished wafers of *p*-type silicon ($[\mathrm{B}] \simeq 2\times10^{16}\ \mathrm{cm}^{-3}$) were implanted with phosphorus to form a surface layer of *n*-type elec-

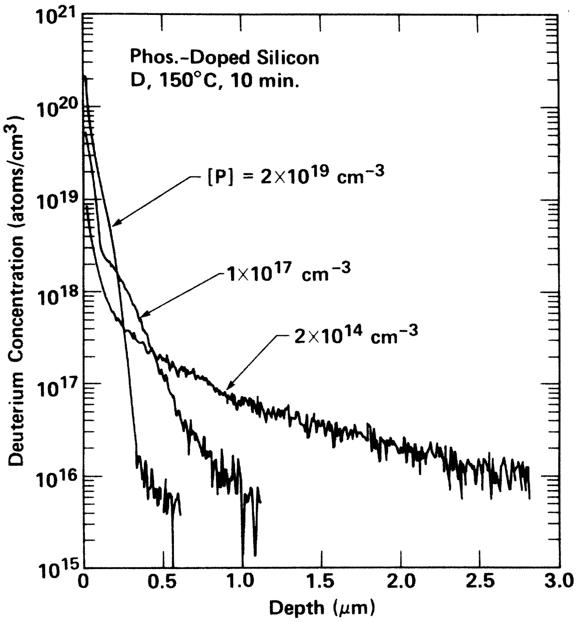

FIG. 1. Dependence of the depth profile of diffused deuterium on the uniform phosphorus concentration [P] in *n*-type single-crystal silicon.

trical conductivity. The total dose of implanted phosphorus was 1.6×10^{14} cm^{-2}, and the implanted dopants were electrically activated with a furnace anneal at 1000 °C for 35 min in flowing N_2. SIMS analysis[10] showed that [P] decreases monotonically with depth from a surface concentration of $\sim7\times10^{18}$ cm^{-3} to $\sim2\times10^{16}$ cm^{-3} at 0.6 μm. A circular van der Pauw device geometry[12] was defined by acid etching to create a mesa structure with four peripheral thin-film Al contacts. The resistivity and Hall voltage were measured at room temperature with a constant-current source, and the measured voltages were linear with respect to both current and magnetic field. The Hall data were used to compute the areal density of free electrons, n_S, and combining resistivity and Hall data yielded the Hall mobility for electrons, $\mu_{\mathrm{H}n}$, in the n-type conducting layer.[12,13] Results are summarized in Table I. Since the entire sequence of treatments was performed on each device, the relative accuracy of the measurements was set by electronic instrumentation and is estimated to be $\sim1\%$. On the other hand, the absolute accuracy is only $\sim50\%$ as a result of uncertain corrections for electrode geometry[12] and the uncertainty of the Hall factor, the ratio of $\mu_{\mathrm{H}n}$ to the conductivity mobility, which depends on anisotropies and scattering processes. The results in Table I clearly demonstrate that deuteration reduces the free-electron concentration and that the passivation is thermally reversible and cyclic. Exposure to D_2 instead of D had no effect. In addition, the Hall mobility and n_S vary in opposite directions. Similar changes in electrical conductivity were obtained with monatomic hydrogen and with arsenic-implanted n-type layers.

Since most of the electrons drift in the region where the donor concentration is $>10^{18}$ cm^{-3}, the electron mobility is limited by ionized-donor scattering.[13] Indeed, the increase in Hall mobility agrees, within measurement accuracy, with the expected increase in the conductivity mobility as the donor concentration decreases. Thus, the increase in $\mu_{\mathrm{H}n}$ after deuteration is consistent with reduced ionized-impurity scattering due to neutralization of donor dopants. The alternative explanation that the donor passivation observed in this experiment was due to generation of physically separate H-associated compensating defects (i.e., deep-acceptor levels) is untenable since such centers would contribute to ionized-impurity scattering and thereby further decrease the mobility.

For comparable hydrogenation conditions, passivation of shallow donors is less pronounced than for shallow acceptors (e.g., Ref. 4). This may be due to a lower dissociation energy for passivated donors and may account for the failure to detect donor passivation in previous studies.

TABLE I. Effect of deuteration on electron concentration and Hall mobility in phosphorus-implanted silicon.

Treatment	n_S (cm^{-2})	$\mu_{\mathrm{H}n}$ (cm^2/V-s)
Starting material	9.0×10^{13}	309
D, 156 °C, 30 min	4.8×10^{13}	362
200 °C, 30 min, *in vacuo*	8.9×10^{13}	315
D, 156 °C, 30 min	5.9×10^{13}	361

We now turn to the energetics of interstitial atomic hydrogen in silicon. Here an important number is the energy difference $E_{\mathrm{H}}^{S}-E_{\mathrm{H}}^{O}$ between a state "O" with a hydrogen atom at rest in vacuum and a state "S" with the hydrogen at a minimum-energy interstitial position inside the crystal. This difference is important for understanding equilibria and kinetics at the crystal-plasma boundary and will provide a useful check on the quantum-mechanical calculations to be discussed below. The most reliable information for its calculation comes from measurements of the equilibrium solubility of hydrogen in silicon at high temperatures T, where the dissolved hydrogen is known to be monatomic because its concentration varies as the square root of the external gas pressure.[14] The chemical potential μ_{H} of atomic hydrogen (per atom) must be the same in the gaseous and dissolved phases. In the gas, dissociative equilibrium gives $\mu_{\mathrm{H}}=\frac{1}{2}\mu_{\mathrm{H}_2}$, where the chemical potential μ_{H_2} of hydrogen molecules can be obtained, relative to the ground-state energy $E_{\mathrm{H}_2}^{O}$ of a molecule at rest, from tables of thermodynamic properties of hydrogen.[15] Specifically,

$$N_{\mathrm{A}}(\mu_{\mathrm{H}_2}-E_{\mathrm{H}_2}^{O})=H-TS, \qquad (1)$$

where N_{A} is Avogadro's number and H and S are the molar enthalpy (relative to separate ground-state molecules) and the entropy, respectively.[16] In the solid μ_{H} is related to the volume concentration n_{H}^{S} of interstitial hydrogen by

$$n_{\mathrm{H}}^{S}=(\nu Z_S/\Omega_0)\exp[(\mu_{\mathrm{H}}-E_{\mathrm{H}}^{S})/kT], \qquad (2)$$

where we assume for simplicity that only a single type of interstitial site is populated, there being ν of these in each unit cell of volume Ω_0; Z_S is the vibrational partition function of a single site. The above equations combined with the dissociation-energy relation, $2E_{\mathrm{H}}^{O}=E_{\mathrm{H}_2}^{O}+4.476$ eV, give

$$E_{\mathrm{H}}^{S}-E_{\mathrm{H}}^{O}=-2.238\ \mathrm{eV}+(H-TS)/2N_{\mathrm{A}}-kT\ln[n_{\mathrm{H}}^{S}\Omega_0/\nu Z_S]. \qquad (3)$$

Van Wieringen and Warmholtz[14] reported solubilities at 1 atm of 2.24×10^{15} cm^{-3} at 1473 K and 6.8×10^{14} cm^3 at

1365 K. If all the dissolved hydrogen is neutral, then with the H_2 data of Ref. 15, Eq. (3) gives

$$E_H^S - E_H^Q = \begin{cases} -1.31+0.127\ln(\nu Z_S)\ \text{eV} \quad (T=1473\ \text{K}), & (4)\\ -1.22+0.118\ln(\nu Z_S)\ \text{eV} \quad (T=1365\ \text{K}). & (5) \end{cases}$$

Note that Z_S increases with temperature. If hydrogen in pure Si is mostly charged, then the binding energy for neutral interstitial H would be more positive by half the band-gap energy (i.e., ~0.3 eV at 1400 K) than the right-hand side of Eq. (4) or (5). The values from Eqs. (4) and (5), which of course should be equal, differ by more than can reasonably be attributed to the temperature dependence of Z_S. This difference may be due to inaccuracy of the transient-analysis procedure[14] used to extract the solubility from permeation data. While such errors may be appreciable and may cause Arrhenius slopes to be misleading, it seems fairly certain that $E_H^S - E_H^Q$ is close to -1 eV. Comparable numbers were obtained from analysis of similar experiments[17] on the permeation of H in germanium.

An empirical tight-binding calculation,[18] augmented by correlation corrections fitted empirically to configurations identifiable as having specific sets of bonds, was used to determine the total energy and electronic structure of H in both pure and P-doped Si. Hamiltonian matrix elements between Si and H orbitals and other parameters were determined from the electronic structure and from the average Si-H binding energy of silane (SiH_4).[19] A repulsive core-core term[18] U_0 of magnitude 3.8 eV for each Si—H bond is required to obtain the correct binding energy in SiH_4, and this value was used in all of the calculations reported below. The accuracy of the predictions was tested by comparison of the calculated H-SiH_3 and H-Si binding energies in SiH_4 and SiH molecules, respectively, with experiment. The calculations (experiment) give binding energies of 4.12 (4.09) eV and 3.12 (3.09) eV for H-SiH_3 and SiH, respectively.[20] For H in bulk Si, the calculations used a 65-atom cubic unit cell (with dimensions 2×2×2 larger than a normal cubic cell) consisting of 64 Si atoms (or 63 Si atoms and a substitutional P atom) and a single H atom. Periodic boundary conditions were imposed to eliminate edge effects. The large unit cell minimized interactions of H or P atoms in neighboring unit cells.

For hydrogen in pure Si, the tight-binding calculations indicate that the bonding of H to Si in an "antibonding" site along the (111) axis is energetically favorable. Minimizing the total energy with respect to bond length gives a Si-H distance of 1.61 ±0.01 Å and a relaxation energy of ~0.23 eV. The variation of total energy with bond length is very similar to that shown in the lower curve of Fig. 2. This bond length is 9.2% larger than the value of 1.48 Å in SiH_4 and is in excellent agreement with the 1.6-Å separation determined experimentally by Picraux and Vook[21] for the D center in H-implanted Si, which they assigned to H in the antibonding position. The calculated Si-H stretch vibrational frequency of the D center is 96.7% of the normal Si-H frequency[21] of 2162 cm^{-1} which yields 2090 ±10 cm^{-1}. Several vibrational modes of disputed origin[22] (including a doublet at 2107 and 2083 cm^{-1}) are observed in both H-implanted crystalline Si and hydrogenated amorphous Si.[23] Our calculations suggest that a new type of Si—H bonding (i.e., the D center) is responsible for these modes in both systems. The tight-binding calculations suggest that the antibonding site is energetically favorable as compared to the often-studied[24-26] T_d interstitial site where the (charge-neutral) H atom is too far away from the Si atoms for effective bonding.[27] In comparison with the thermodynamically deduced binding energy given above for interstitial H in pure Si, the tight-binding results overestimate by ≥50% the binding energy in

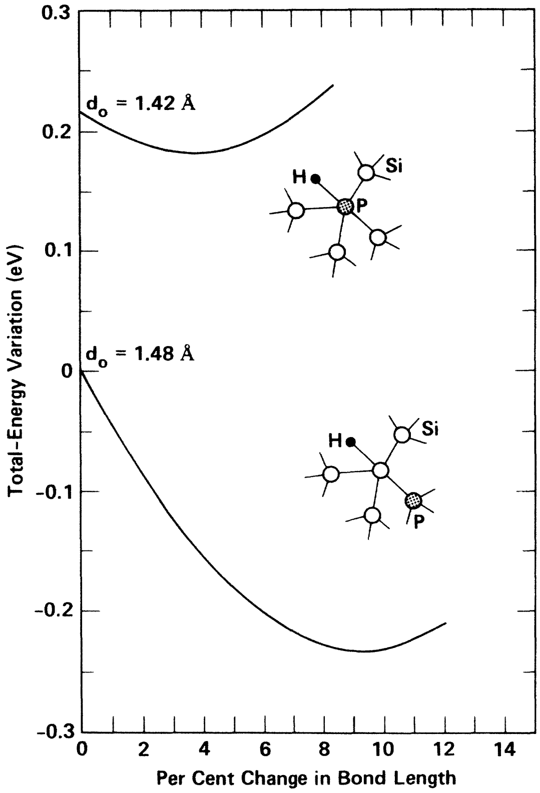

FIG. 2. Bond-length dependence of the relative binding energies for H in an antibonding position of (1) a substitutional P atom (upper curve) and (2) a Si atom that is a nearest neighbor of the substitutional P (lower curve). The distances d_0 are the P—H and Si—H bond lengths in phosphene (PH_3) and silane (SiH_4), respectively.

the antibonding site. Structural parameters are generally more accurately determined than binding energies within the semiempirical tight-binding approach.

The electronic structure found for this antibonding position of H in pure Si is interesting: It turns out to be an acceptor, the H-Si complex becoming negatively charged and creating a hole some distance away. We do not yet have a reliable estimate of the hole binding energy. The fact[28] that no EPR signal has been observed from H in Si may be a result of this spin-paired configuration, although it is not yet reliably known what fraction of the hydrogen remains unassociated under the conditions of typical EPR experiments. Similarly, no EPR signal is expected if H bonds to a Si dangling orbital or to another H atom. While the antibonding site appears to be the lowest-energy state for interstitial H, we have not yet fully explored other possibly accessible metastable states.

For P-doped Si, calculations were performed for H bonded to either a substitutional P atom or a Si atom that is adjacent to the P atom. In each case the H atom was placed in an antibonding position and allowed to relax.[29] The relative binding energy of H in the two sites is shown in Fig. 2. For H bonded to a neighboring Si, the optimal bond length and the overall shape of the total-energy curve are the same as in pure Si, that is, the bond length is stretched by 9.2% from its value of 1.48 Å in SiH$_4$. For H bonding to P, the total energy has a minimum at a H—P bond length of 1.48 Å which is 4% larger than the distance of 1.42 Å in phosphene (PH$_3$). Our calculations reveal that at equilibrium the Si—H bond is 0.41 ± 0.25 eV more stable than the P—H bond. However, *both* configurations lead to the passivation of P. The Si-H stretch frequency is predicted to be $\sim 2145 \pm 10$ cm^{-1}, which is essentially identical to the Si-H frequency in pure Si. An alternative Si antibond-site geometry which places H in the proximity of the P atom was not found to be energetically favorable. The energetics of H bonding to Si in an antibonding site are improved by passivation of a shallow donor because of the electrostatic attraction of the negatively charged H-Si complex to the positive donor center.

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[1] J. I. Pankove, D. E. Carlson, J. E. Berkeyheiser, and R. O. Wance, Phys. Rev. Lett. **51**, 2224 (1983).

[2] G. G. DeLeo and W. B. Fowler, J. Electron. Mater. **14a**, 745 (1985).

[3] J. I. Pankove, P. J. Zanzucchi, C. W. Magee, and G. Lucovsky, Appl. Phys. Lett. **46**, 421 (1985).

[4] N. M. Johnson, Phys. Rev. B **31**, 5525 (1985).

[5] G. G. DeLeo and W. B. Fowler, Phys. Rev. **31**, 6861 (1985).

[6] C.-T. Sah, J. Y.-C. Sun, and J. J.-T. Tzou, J. Appl. Phys. **54**, 5864 (1983).

[7] W. L. Hansen, S. J. Pearton, and E. E. Haller, Appl. Phys. Lett. **44**, 606 (1984).

[8] J. I. Pankove, R. O. Wance, and J. E. Berkeyheiser, Appl. Phys. Lett. **45**, 1100 (1984).

[9] N. M. Johnson and M. D. Moyer, Appl. Phys. Lett. **46**, 787 (1985).

[10] N. M. Johnson, Appl. Phys. Lett. **47**, 874 (1985).

[11] J. I. Pankove, C. W. Magee, and R. O. Wance, Appl. Phys. Lett. **47**, 748 (1985).

[12] L. J. van der Pauw, Philips Res. Rep. **13**, 1 (1958).

[13] S. M. Sze, *Physics of Semiconductor Devices* (Wiley, New York, 1981), 2nd ed., Chap. 1.

[14] A. Van Wieringen and N. Warmholtz, Physica (Utrecht) **22**, 849 (1956).

[15] D. R. Stull and H. Prophet, *JANAF Thermochemical Tables,* U.S. National Bureau of Standards NSRDS-NBS37 (U.S. GPO, Washington, D.C., 1971), 2nd ed.

[16] These are tabulated in the preceding reference with neglect of nuclear-spin degrees of freedom, and so for consistency they are neglected in the solid as well.

[17] R. C. Frank and J. E. Thomas, Jr., J. Phys. Chem. Solids **16**, 144 (1960).

[18] D. J. Chadi, Phys. Rev. B **29**, 785 (1984), and Phys. Rev. Lett. **41**, 1062 (1978).

[19] The parameters for Si are given in Ref. 18. The additional Si-H parameters are $E_s(\mathrm{H}) = -4.15$ eV, $V_{ss\sigma} = -3.46$ eV, and $V_{sp\sigma} = 1.855$ eV.

[20] It is to be noted that the H—SiH$_3$ bond energy of 4.09 eV is approximately 0.9 eV larger than the *average* Si—H bond energy in SiH$_4$. The tight-binding method accurately predicts this difference.

[21] S. T. Picraux and F. L. Vook, Phys. Rev. B **18**, 2066 (1975); S. T. Picraux, F. L. Vook, and H. J. Stein, in *Defects and Radiation Effects in Semiconductors, 1978,* edited by J. H. Albany (Institute of Physics and The Physical Society, London, 1979), p. 31.

[22] W. Paul, Solid State Commun. **34**, 283 (1980).

[23] H. J. Stein, J. Electron Mater. **4**, 159 (1975).

[24] W. E. Pickett, M. L. Cohen, and C. Kittel, Phys. Rev. B **20**, 5050 (1979).

[25] N. Sahoo, S. K. Mishra, K. C. Mishra, A. Coker, T. P. Das, C. K. Mitra, and L. C. Snyder, Phys. Rev. Lett. **50**, 913 (1983).

[26] H. Katayama-Yoshida and K. Shindo, Phys. Rev. Lett. **51**, 207 (1983).

[27] V. A. Singh, C. Weigel, J. W. Corbett, and L. M. Roth, Phys. Status Solidi (b) **81**, 637 (1977); J. W. Corbett, S. N. Sahu, T. S. Shi, and L. C. Snyder, Phys. Lett. **93A**, 303 (1983); S. Tiansheng, S. N. Sahu, J. W. Corbett, and L. C. Snyder, Sci. Sin., Ser. A (Engl. Ed.) **27**, 98 (1984).

[28] R. L. Kleinhenz, Y. H. Lee, V. A. Singh, P. M. Mooney, A. Jaworowski, L. M. Roth, J. C. Corelli, and J. W. Corbett, in *Defects and Radiation Effects in Semiconductors, 1978,* edited by J. H. Albany (Institute of Physics and The Physical Society, London, 1979), p. 200.

[29] Relaxation of the silicon lattice around the phosphorus dopant was also taken into account.