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# Mechanism for hydrogen compensation of shallow-acceptor impurities in single-crystal silicon

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Experimental results are presented which identify the following chemical reaction as being responsible for compensation of shallow-acceptor impurities when single-crystal silicon is exposed to monatomic hydrogen: $A^- + h^+ + H^0 \rightarrow (AH)^0$, where $A^-$ represents an ionized shallow acceptor, $h^+$ is a (positively charged) free hole, and $H^0$ is a neutral hydrogen atom. Infrared absorption spectroscopy on boron-doped silicon, combined with recent defect-model calculations, reveals that the hydrogen atom forms a Si–H bond at the site of a substitutional boron atom; the absorption band for the stretch mode appears at 1870 $cm^{-1}$. Measurements by secondary-ion mass spectrometry of impurity profiles in deuterated silicon reveal that shallow-acceptor passivation is suppressed by counter doping to produce *n*-type conductivity. These new results identify both the defect complex responsible for hydrogen compensation of shallow acceptors and the essential role of free holes, or equivalently neutral acceptors, in the chemical reaction.

Shallow-acceptor impurities in single-crystal silicon can be compensated or neutralized by exposing the crystal to monatomic hydrogen. This conclusion has been well established from electrical measurements (e.g., spreading-resistance and capacitance-voltage measurements) of the change in apparent dopant concentration before and after hydrogenation.[1-5] Although models have been proposed, the specific chemical reaction and defect complex which are responsible for acceptor compensation have not yet been identified. In the first reports of this phenomenon, Sah, Sun, and Tzou[1,2] proposed that hydrogen diffuses into silicon and reacts with an acceptor impurity (e.g., boron) to form a $B^-H^+$ complex. Subsequently, Pankove, Carlson, Berkeyheiser, and Wance[3] proposed that the hydrogen atom specifically bonds to the silicon dangling orbital that is immediately adjacent to the substitutional trivalent acceptor impurity.[6] This qualitative model was further defined and theoretically examined by DeLeo and Fowler.[7] Their model involves a hydrogen-acceptor pair in a lattice vacancy with both the acceptor and hydrogen off center and situated along the $\langle 111 \rangle$ axis. The hydrogen passivates the single silicon dangling orbital in the $\langle 111 \rangle$ direction, which leaves the acceptor impurity to threefold coordinate with the remaining silicon neighbors. In addition, total-energy calculations predict that the hydrogen-boron pair is stable, at a separation of 1.62 Å, and will form spontaneously if an interstitial hydrogen atom approaches a neutral substitutional acceptor impurity. A different chemical model has been proposed by Hansen, Pearton, and Haller[4] based on electrical measurements of boron-doped silicon after treatment in $O_2$, $H_2$, and $H_2O$ plasmas. They concluded that acceptor compensation requires the rapid diffusion of monatomic oxygen as well as hydrogen which combine at the acceptor site to form a neutral acceptor-OH complex. However, by applying isotopic substitution it has recently been shown that oxygen does not diffuse into silicon under the conditions of shallow-acceptor passivation.[8] In the present study, the mechanism of hydrogen passivation of shallow-acceptor impurities is elucidated with new results from electrical, optical, and impurity-depth-profiling measurements. It is concluded that the defect complex is the hydrogen-acceptor pair and that free holes, or equivalently neutral acceptors, participate in the process of acceptor neutralization.

Specimens of single-crystal silicon were exposed to monatomic hydrogen or deuterium from a gas discharge. Details of sample preparation are described below in connection with the different measurement techniques. Deuterium was used as a readily identifiable isotope of low natural abundance which duplicates the chemistry of hydrogen. Secondary-ion mass spectrometry (SIMS) provided isotope separation and high sensitivity. The gas-discharge system and the application of SIMS for measuring depth profiles of deuterium have been described previously.[8-10] A particular feature of the system used here is the placement of specimens on a hot stage that is located downstream from the microwave plasma, with baffles for optical isolation. This arrangement permits anneals in monatomic hydrogen or deuterium without immersing the samples directly in the plasma. Therefore, any possible effect on the passivation process from charged particle bombardment or visible/uv illumination is minimized.

The phenomenon of hydrogen compensation of shallow-acceptor impurities is illustrated in Fig. 1. Specimens of heavily boron-doped Czochralski-grown silicon were ex-

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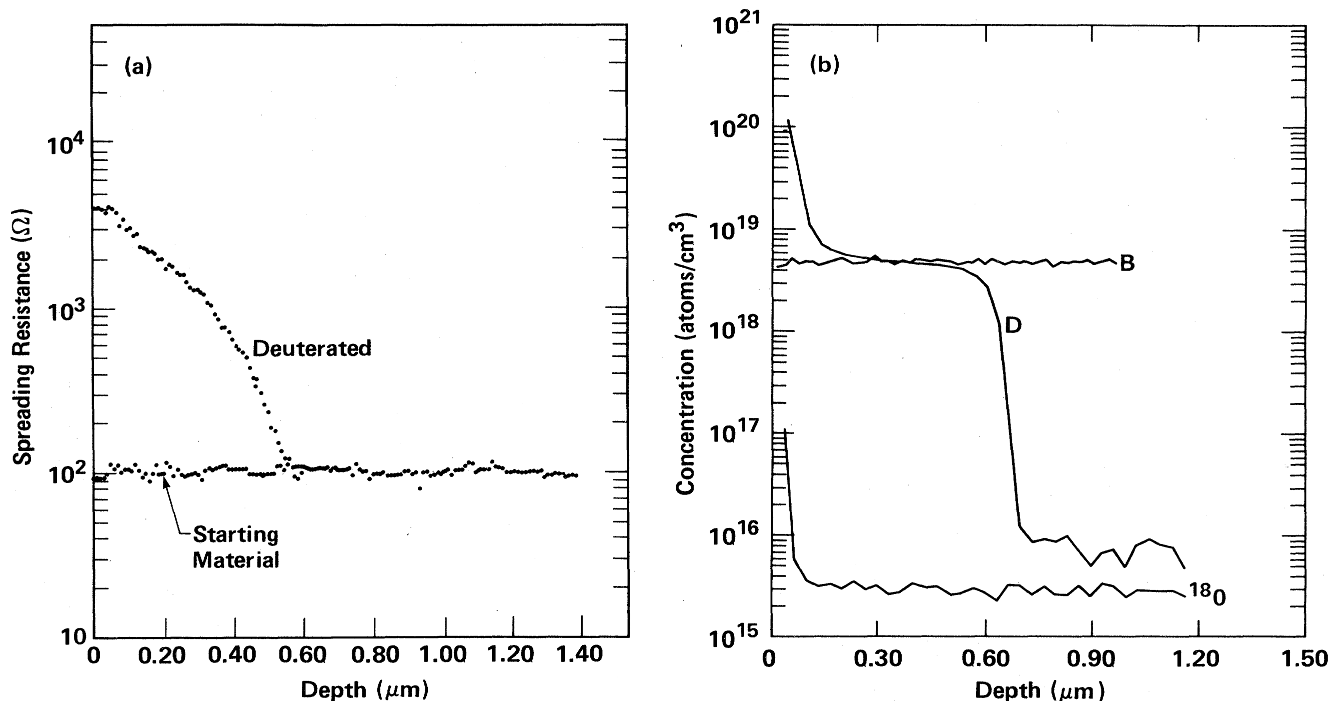


FIG. 1. Depth profiles of the spreading resistance (a) and deuterium (b) in boron-doped single-crystal silicon after deuteration at 150 °C for 30 min. In (b) profiles for boron and $^{18}O$ are also shown.

posed to monatomic deuterium at 150 °C for 30 min; the plasma also contained a controlled partial pressure of mass-18 oxygen, as described in Ref. 8. Figure 1(a) displays depth profiles of the spreading resistance before and after deuteration. The 100-Ω spreading resistance of the starting material corresponds to a uniform doping concentration of $5\times10^{18}$ cm$^{-3}$. After deuteration the spreading resistance increases in the region immediately beneath the exposed surface, which indicates an increase in the resistivity as a result of acceptor compensation. Similar results have been reported by Pankove, Carlson, Berkeyheiser, and Wance[3,5] who found that more than 99% of the boron near the surface could be neutralized by hydrogenation. In Fig. 1(b) are shown the depth profiles for D and $^{18}O$ as measured by SIMS; also shown is the uniform boron concentration. While deuterium readily diffuses into silicon at moderate temperatures, with the profile strongly influenced by the boron concentration, no $^{18}O$ is detectable above the background level; however, adding oxygen to a hydrogen plasma does increase the yield of monatomic hydrogen.[8] Comparing Figs. 1(a) and 1(b) reveals that the increase in resistivity is accompanied by the diffusion of deuterium into the silicon. Furthermore, the depth of penetration of deuterium as measured by SIMS is in good agreement with the acceptor-compensation depth as measured by the spreading-resistance technique.

Direct experimental evidence for the bonding of a hydrogen atom at a boron site is presented in Fig. 2 with results from Fourier transform infrared absorption (IR) spectroscopy. Wafers of initially undoped float-zone silicon, with both surfaces polished, were implanted with boron ions at several accelerating voltages to obtain a heavily doped layer adjacent to each surface. The total fluence of implanted boron was $1.3\times10^{16}$ cm$^{-2}$ and the dopants were electrically activated with a furnace anneal at 1000 °C for 35 min in flowing $N_2$; the boron depth profile was measured by SIMS, and electrical activation was verified by sheet-resistance measurements. The IR spectrum for the implanted material, prior to passivation, was dominated by free-hole absorption. The spectra shown in Fig. 2 are for specimens that were passivated at 150 °C for 1 h (per surface) in either monatomic hydrogen or deuterium. (Consistent with acceptor compensation, this greatly reduced free-hole absorption.) A single well-resolved absorption peak is evident in each spectrum. In the hydrogenated sample the peak is located at 1870 cm$^{-1}$, with a full width at half maximum intensity of ~37 cm$^{-1}$. This absorption band has recently been reported.[11] However, Fig. 2 reveals for the first time that

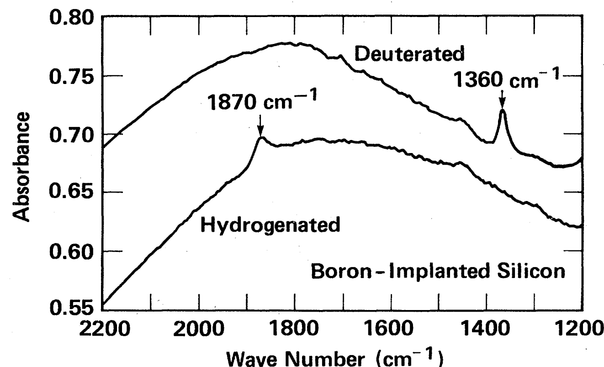


FIG. 2. Infrared absorption spectra for boron-implanted silicon after passivation in either monatomic hydrogen or deuterium. The specimens were passivated at 150 °C for 1 h (per surface), and the spectral resolution is 4 cm$^{-1}$.

deuterium compensation shifts the peak to 1360 $cm^{-1}$. The two peaks are shifted with respect to each other by a factor of 1.375. This is exactly the isotopic frequency shift for hydrogen versus deuterium bonding to silicon that was experimentally determined by Stein[12] from IR studies of implanted hydrogen and deuterium in silicon; the shift approximately agrees with the square root of the reduced mass ratio of 1.394 which is expected for Si-H relative to Si-D vibrations in a simple diatomic molecule. The isotope shift establishes that H(D) is bonded to silicon rather than to boron, which would have a different shift. For comparison, an optical-absorption band at 1985 $cm^{-1}$, observed in both *a*-Si:H and hydrogen-implanted crystalline silicon, has been assigned to the Si-H stretch mode for monohydride (SiH) bonding; dihydride ($SiH_2$) formation is responsible for a band at 2085 $cm^{-1}$, and a band at 2110–2120 $cm^{-1}$ is attributed to the trihydride ($SiH_3$).[13,14] As discussed below, the absorption peak at 1870 $cm^{-1}$ is consistent with, and indeed may be considered the IR signature of, the stretch mode for a Si–H bond in which the hydrogen atom is weakly interacting with an adjacent boron atom.

The effect of counter doping (i.e., introducing an *n*-type dopant) on deuterium diffusion and boron neutralization is shown in Fig. 3. Specimens of Czochralski-grown (100)-oriented silicon, which were doped in the melt with phosphorus to a uniform concentration of either $4\times10^{15}$ $cm^{-3}$ or $2\times10^{19}$ $cm^{-3}$, were implanted with boron ions at an accelerating voltage of 200 kV to a fluence of $1\times10^{14}$ $cm^{-2}$. The implanted dopants were electrically activated and the displacement damage was removed with a rapid thermal anneal at 1100 °C for 10 sec in flowing Ar; electrical activation and damage removal were verified with spreading-resistance measurements and transmission electron microscopy, respectively. The boron-implanted specimens were exposed to monatomic deuterium, and then deuterium-depth profiles were measured with SIMS for comparison with the boron distribution. Results for isochronal deuterations at 150 and 120 °C are shown in Figs. 3(a) and 3(b), respectively. In the lightly P-doped material, the boron concentration greatly exceeds the phosphorus density to a depth of $\sim 1.2$ $\mu$m, so that the boron implantation converted the surface layer to *p*-type conductivity, with a range of low resistivities relative to the *n*-type substrate. For both deuteration temperatures, the deuterium profiles superimpose, within experimental accuracy, on the boron distribution to the depth of deuterium penetration; spreading-resistance profiles confirmed the increase in resistivity as a result of boron neutralization. In sharp contrast to this now well-documented phenomenon, in the heavily phosphorus-doped material the deuterium profiles are unaffected by the presence of boron. In this material the silicon remains *n* type everywhere after the boron implantation. In addition, the deuterium profiles in Fig. 3 for heavily P-doped silicon are essentially identical to those obtained from specimens that were not boron implanted. Thus, hydrogen neutralization of shallow-acceptor impurities is suppressed by counterdoping.

The accumulated experimental information on hydrogen compensation of shallow-acceptor impurities in single-crystal silicon may be summarized as follows: (1) exposing *p*-type silicon (doped with B, Al, Ga, or In) to monatomic hydrogen results in acceptor compensation as evidenced by changes in the electrical conductivity [Refs. 1–5 and illustrated in Fig. 1(a)], (2) no conductivity change is observed in silicon doped with shallow-donor impurities,[1,2,4,5] (3) hydrogen diffuses into silicon under the conditions of acceptor passivation, with the hydrogen profile strongly influenced by the acceptor concentration and dropping sharply at the compensation depth (Fig. 1 and Ref. 8), (4) oxygen does not

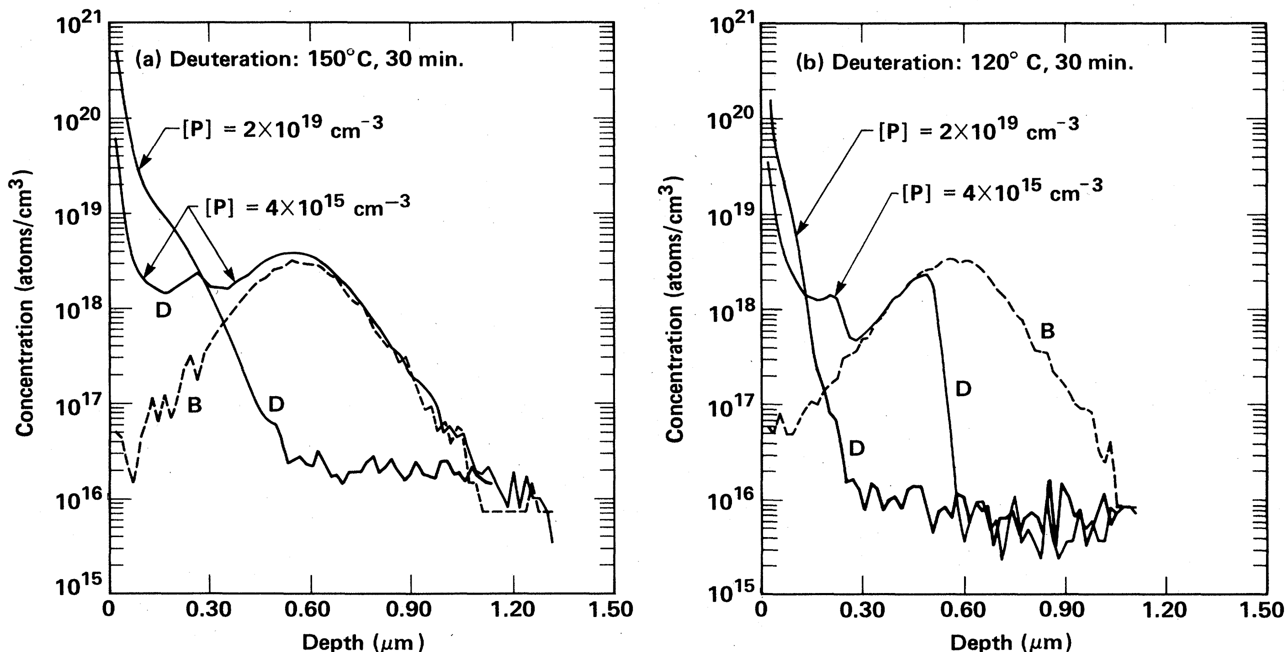


FIG. 3. Effect of dopant compensation on deuterium diffusion in boron-implanted single-crystal silicon: (a) deuteration at 150 °C for 30 min and (b) deuteration at 120 °C for 30 min. In each graph deuterium profiles are shown for low vs high uniform concentrations of phosphorus [P]. The boron distribution was introduced by ion implantation followed by rapid thermal annealing.

diffuse into silicon under these conditions [Fig. 1(b) and Ref. 8], (5) acceptor compensation involves silicon-hydrogen bonding (Fig. 2), and (6) acceptor passivation is suppressed by counter doping to produce *n*-type conductivity (Fig. 3). These observations are fully consistent with the hydrogen-acceptor pair model. The applicability of this model is further established with recent normal-mode calculations[15] which show that the computed vibrational frequencies are in excellent agreement with the measured IR absorption bands of Fig. 2; the calculated frequency for hydrogen-boron pairing is 1880 $cm^{-1}$. The analysis reveals that the shift of the absorption band from the experimentally observed 1985 $cm^{-1}$ for the silicon monohydride to 1870 $cm^{-1}$ for the boron-neutralizing Si–H bond is a consequence of a weak, attractive interaction between the adjacent, but well separated, hydrogen and boron atoms. This tends to decrease the effective spring constant appropriate to the hydrogen coordinate and thereby shifts the absorption band to lower wave numbers. It is therefore concluded that hydrogen-acceptor pairing is responsible for hydrogen neutralization of shallow-acceptor impurities in silicon.

With the sixth of the above experimental observations, the chemical reaction for acceptor neutralization can be identified. In the counter doping experiment (Fig. 3), it should be noted that virtually all of the substitutional boron atoms were in their (negatively charged) ionized state for *both* phosphorus concentrations. (Said another way, each boron atom was ionized nearly all of the time.) Counter doping changed the density of free holes; the density decreased from near degenerate concentrations (e.g., $\sim 3\times 10^{18}$ $cm^{-3}$ at the peak of the boron distribution in the lightly P-doped material) to negligible values as the Fermi level shifted from near the valence-band edge for the *p*-type surface layer to the conduction-band minimum in the heavily phosphorus-doped material. This suggests the direct participation of free holes in the neutralization reaction. In addition, it is generally accepted that the diffusing species in silicon is interstitial monatomic hydrogen.[16,17] Then the following overall chemical reaction is proposed for hydrogen neutralization of shallow-acceptor impurities in *p*-type silicon:

$$A^- + h^+ + H^0 \leftrightarrow (AH)^0 \ , \qquad (1)$$

where $A^-$ represents an ionized acceptor, $h^+$ is a (positively charged) free hole, and $H^0$ is a neutral hydrogen atom. Thus, suppression of acceptor neutralization in *n*-type silicon under the annealing conditions that produced passivation in *p*-type material can be attributed to a decrease of the free-hole density. Equation (1) can be written as the following two-step reaction which emphasizes the intermediate role of neutral acceptors: (1) $A^- + h^+ \leftrightarrow A^0$ and (2) $A^0 + H^0 \leftrightarrow (AH)^0$. This conforms with the theoretical prediction that the hydrogen-acceptor pair will form spontaneously if an interstitial hydrogen atom approaches a neutral substitutional-acceptor impurity.[7] It is suggested that acceptor neutralization could also proceed in *n*-type material if the extra electron at the ionized acceptor site is transferred, by either thermal excitation or photoexcitation, to the conduction band; to illustrate, for steady-state photoexcitation the reaction would be the following: $A^- + H^0 + h\nu \leftrightarrow (AH)^0 + e^-$, where $h\nu$ is the photon energy for a transition from an ionized acceptor to the conduction band and $e^-$ is the photoexcited free electron. In summary, it is concluded that hydrogen-acceptor pairing is responsible for hydrogen neutralization of shallow-acceptor impurities in silicon and that the chemical reaction involves free holes or equivalently neutral acceptors.

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