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Negative-charge state of hydrogen in silicon

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It is demonstrated that hydrogen can migrate in silicon as a *negatively charged* species (H^-). The evidence is the combined observation of a strong electric-field dependence in the rate of removal of PH complexes during bias-temperature stress of hydrogenated Schottky-barrier diodes and the resulting spatial redistribution of neutralized donors. The detection of H^- establishes that, in addition to the previously determined deep-donor level, there also exists an acceptor level for hydrogen in the silicon band gap. The PH dissociation kinetics yield an activation energy of 1.18 eV, from which we estimate a binding energy in the range of 0.35 to 0.65 eV.

Because dissolved hydrogen, which may be either deliberately or unintentionally introduced, has important effects on the electrical properties of semiconductors, its behavior in these materials has been the subject of a rapidly expanding literature in recent years.[1,2] One of the most fundmental requirements for an understanding of its crystal chemistry is a knowledge of the possible charge states of isolated monatomic hydrogen in the crystalline environment, that is, of the existence and positions of donor and/or acceptor levels. While it is now generally accepted that hydrogen in silicon has a deep-donor level somewhere near midgap,[3-5] experimental evidence on the existence of a negatively charged species has been limited. The strongest evidence to date has been obtained from an n-type epilayer atop an n^+ substrate that was plasma hydrogenated at 300 °C.[6] The observed increase of hydrogen uptake with depth across the two layers requires dominance of an H^- species if donor-H complexes are nearly completely dissociated at 300 °C. However, fulfillment of this proviso is not necessarily guaranteed by the observation[7] that hydrogen bound to donors can be freed at temperatures well below 300 °C.[8] First-principles theoretical calculations[9] predict that H^+ and H^0 prefer a bond-center site, with a donor level near midgap, while H^- prefers a tetrahedral interstitial site, with an acceptor level also near midgap, possibly even below the donor level, in which case hydrogen would be a "negative-U" impurity.[10] However, because of the large lattice relaxations and the neglect of zero-point energies, the uncertainty in these predictions is considerable. This paper reports a study[11] of the electric-field-induced migration of hydrogen that is thermally released from PH complexes. The results establish that the preferred dissociation reaction for the PH complex is $PH \rightarrow P^+ + H^-$, and thus provide an unambiguous demonstration of the existence of the H^- species.

Donor impurity profiles were measured on Schottky-barrier diodes by the capacitance-voltage (C-V) technique. The diodes were fabricated from Czochralski-grown (100)-oriented silicon wafers that were uniformly doped with phosphorus. The silicon was exposed to monatomic hydrogen at a substrate temperature of 130 °C for 60 min in a remote hydrogen plasma system. Specimens were then wet-chemically etched to remove ~100 nm of the surface which is known[12] to contain a high concentration of hydrogen-stabilized platelets, thus eliminating a possible uncontrolled source of hydrogen for the study of PH dissociation kinetics. The diodes were completed by vacuum evaporation of Pd through a shadow mask to provide current-rectifying contacts. Hydrogenated diodes were bias-temperature stressed by vacuum annealing at moderate temperatures either with or without an applied reverse bias V_R. The C-V measurements were performed at room temperature by recording the diode capacitance (at 1 MHz) as a function of V_R over the range from 0 to 4 V, and the analysis utilized the depletion approximation.

An applied electric field strongly affects the rate of removal of PH complexes in silicon. This is illustrated in Fig. 1 with depth profiles of the donor concentration. Hydrogen neutralization of donor dopants[13] near the exposed

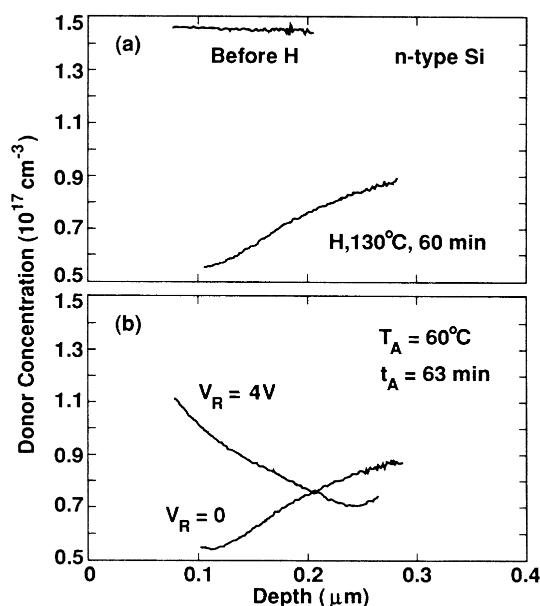

FIG. 1. Depth profiles of the donor concentration in n-type Schottky diodes: (a) before and after hydrogenation (130 °C, 60 min) and (b) after a post-hydrogenation anneal at 60 °C with and without a reverse bias of 4 V.

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surface is shown in Fig. 1(a). The effect of a reverse bias applied during a subsequent vacuum anneal is displayed in Fig. 1(b). While the donor profile for the zero-biased diode is only slightly changed by the anneal, the profile for the reverse-biased diode is substantially altered. The effect is further illustrated in Fig. 2 with donor profiles that were recorded after isothermal anneals with $V_R=4$ V. The maximum recorded depth in each profile corresponds to $V_R=4$ V and closely approximates the edge of the depletion layer during the biased anneal. The profiles reveal that during the anneal the removal of PH complexes is accelerated in the region of the space-charge layer nearest the surface while the concentration of neutralized donors actually increases in the region of the space-charge layer nearest the depletion edge as well as (by extrapolation) in the region immediately beyond the depletion layer. Figures 1 and 2 are strikingly similar to profiles previously reported[3,4] for thermal dissociation of acceptor-H complexes in p-type silicon diodes.

The obvious interpretation of the profiles in Figs. 1 and 2 is that the monatomic hydrogen released by the thermal dissociation of PH complexes during the anneal undergoes little net drift in the absence of a bias voltage, but drifts markedly away from the surface in the presence of a reverse bias, because it is negatively charged. To establish that this is indeed the case, we first show that mere migration of an H^0 species cannot account for the observed evolution of the profiles. Figure 2 clearly reveals that thermal dissociation, which naturally occurs everywhere, is being accompanied by substantial recombination, and the recombination rate must increase considerably with depth over the range 0.08–0.24 μm. While a postulated recombination reaction $H^0+P^++e^-\rightarrow PH$ might be much slower in the depletion region than in the undepleted bulk, because of the scarcity of electrons, it hardly seems possible to obtain from this a recombination rate that is both sizable and increasing with depth over the interval 0.08–0.18 μm, since here the electron concentration remains nearly constant and strongly depleted, while the concentrations of H^0 and P^+ during most of the anneal

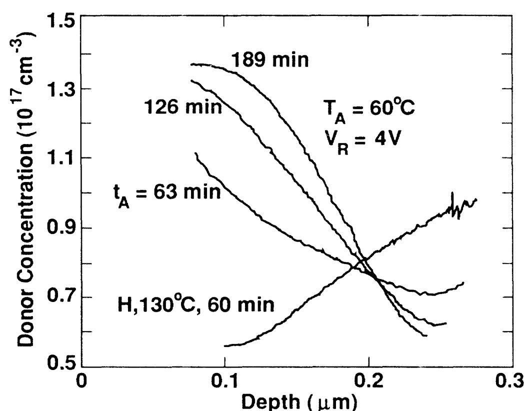

FIG. 2. Depth profiles of the donor concentration in an n-type Schottky diode after a series of post-hydrogenation anneals at 60 °C with a reverse bias of 4 V. The silicon was hydrogenated at 130 °C for 60 min.

decrease with depth. We can exclude the possibility that a significant amount of H^0 survives the anneal and recombines only after removal of the bias, since profiles measured with and without intermediate interruption of the bias are indistinguishable. More exotic recombination processes, involving hole emission or possible formation of $(PH)^+$, also seem incapable of accounting for the observed bias and depth dependences, and besides are energetically implausible.

In contrast, migration of the dissociated hydrogen as H^- accounts very simply for the observed recombination behavior. The rate of the process $P^++H^-\rightarrow PH$ should be high because of the large Coulomb capture radius, and it should increase with depth x in the depletion region because the drift flux of H^- must increase with x due to the predominance of dissociation over recombination (e.g., for $x<0.2$ μm), while the drift velocity, proportional to the electric-field intensity, decreases with x. While some H^- is probably lost in the depletion region due to charge-state conversion into H^0 and H^+, such loss seems to be modest at the doping levels and field intensities used here. (This loss plus that due to formation of neutral all-hydrogen complexes, can be roughly estimated by extrapolating the data in Fig. 2 and integrating over depth. The resulting overall loss rate for PH is of the same order as the net transfer rate of PH across the plane at the depth of 0.19 μm.)

To analyze the data in Fig. 2 we adopt a simple model of the PH dissociation kinetics that is applicable in the high-field region of the space-charge layer. The PH complexes predominantly dissociate through the reaction $PH\rightarrow P^++H^-$. Within the space-charge layer of a reverse-biased diode, H^- drifts in the applied electric field toward the edge of the depletion layer, beyond which migration is primarily by diffusion. Immediately adjacent to the metal-silicon junction the magnitude of the electric field is greatest and there is no source of H^- to replenish that which has drifted toward the substrate after release from P^+. In this region, the rate of removal of PH complexes depends only on the rate of dissociation so that their concentration decreases exponentially with a characteristic dissociation time τ_d which is thermally activated.

The applicability of the above model depends on two characteristic distances in the PH dissociation kinetics. The first is the mean drift distance λ_r of H^- before recapture by P^+, a quantity expressible[8] in terms of the electric field, the donor density n_D, and the Coulomb capture radius. The second is the mean drift distance λ_0 of H^- in the electron-depleted region before its loss of charge via $H^-\rightarrow H^0+e^-$, a distance that depends[8] on two as yet unknown quantities: the cross section σ_{0e} for electron capture by H^0 and the hydrogen acceptor level ϵ_A. However, λ_{-0} is independent of n_D, while λ_r varies as $1/n_D$. Thus we may expect that for sufficiently large n_D, $\lambda_r<\lambda_{-0}$. The large amount of recapture shown by Fig. 2 implies that $\lambda_r\le\lambda_{-0}$ for net donor concentrations as large as those represented by the curves (i.e., for $n_D>5\times10^{16}$ cm^{-3}) and appears to be consistent with reasonable combinations of values for ϵ_A and σ_{0e}. Since for the high-field, near-surface region in Fig. 2 the value of λ_r is a few tenths of a μm, H^- can be expected to drift

out of this region before being recaptured or changing charge state, which supports the application of the above simple model to the high-field region of the space-charge layer for the analysis of the PH dissociation kinetics.

Dopant profiles for isothermal anneals (e.g., Fig. 2) were recorded over a range of anneal temperatures with $V_R = 4$ V. At each temperature the time dependence of the donor concentration was determined at the shallowest depth that was common to the entire set of profiles, in order to most closely approximate the conditions of the simple model described above. In each case the data fit an exponential time decay with a time constant that is an upper limit to τ_d, the underestimation ratio (< 1.5) being nearly independent of temperature. The Arrhenius analysis of this approximate τ_d is shown in Fig. 3 and yields a dissociation energy of 1.18 ± 0.01 eV.

The escape time shown in Fig. 3 depends on two fundamental quantities, the binding energy ΔE_{PH} of H^- and P^+ and the diffusion coefficient D_- of the H^- species. According to the usual detailed-balance argument from the diffusion theory of reactions,[8,14] the relation is

$$\tau_d = [\Omega_0 f/(4\Pi D_- R_C)]\exp(\Delta E_{\mathrm{PH}}/kT) , \quad (1)$$

where Ω_0 is the primitive-cell volume (two Si atoms), f is a quantity of order unity involving the number of sites per primitive cell for the species P^+, H^-, and PH, and the associated vibrational partition functions, R_C is the Coulomb capture radius (i.e., e^2/KkT, where K is the dielectric constant), k is Boltzmann's constant, and T is the absolute temperature. Equating the Arrhenius slope of Eq. (1) to that of Fig. 3 yields

$$\Delta E_{\mathrm{PH}} + Q_- \approx 1.18\ \mathrm{eV} + kT \approx 1.21\ \mathrm{eV} , \quad (2)$$

where Q_- is the activation energy of D_-. Alternatively, Eq. (1) can be equated to the ordinate in Fig. 3 at a single T, say $\log_{10}\tau_d = 3.40$ at 340 K. With $f \approx 2$, this gives

$$\Delta E_{\mathrm{PH}} = 0.55 + 0.0293 \ln(D_-/10^{-12}\ \mathrm{cm}^2/\mathrm{sec})\ \mathrm{eV} . \quad (3)$$

Unfortunately, little is known about D_- and its temperature dependence. The observed transport rate in Figs. 1 and 2 sets a very small *lower limit* for D_-, of the order of 10^{-15} cm^2/sec. A D_- at 340 K that is anywhere from this lower limit to say 3×10^{-11} cm^2/sec (which is less than the value recently established[15] for H^+) would give ΔE_{PH} in the range of 0.35 to 0.65 eV; this entire range is significantly below the estimated[8] binding energy of 0.87 eV for the BH complex in silicon.

Bergman *et al.*[7] have reported an activation energy of 1.32 eV for the dissociation of PH complexes in silicon. The escape time τ_d of Fig. 3 is related to the annealing time τ_a that they observed for the disappearance of PH complexes from P-implanted layers as detected by IR absorption spectroscopy. However, τ_d and τ_a are not expected to be equal, at a given temperature, because τ_a is determined by many successive dissociations and retrappings and depends on the thickness and P concentration of the implanted layer. In the limit of nearly complete dissociation, τ_a should become the time constant of the lowest diffusional mode of the implanted layer and be proportional to the product of D_- and the fraction of the hydrogen in the layer that is H^- rather than bound in PH, so that the activation energy of 1.32 eV for τ_a should agree with Eq. (2). The slightly higher value reported in Ref. 7 was not obtained, however, by an analysis for this limiting case, and it is, in fact, reasonably consistent with the results presented here.

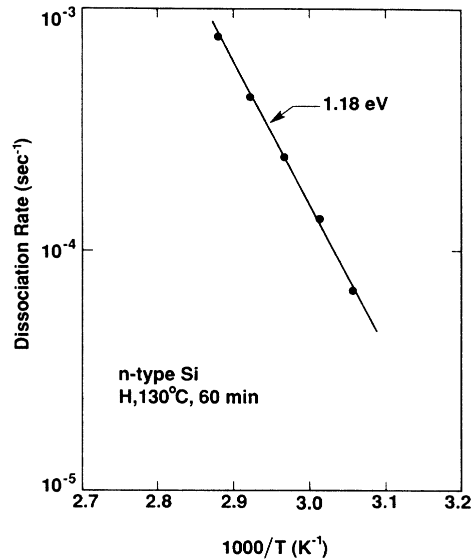

FIG. 3. Arrhenius analysis of the dissociation rate ($1/\tau_d$) of PH complexes in the space-charge layer of hydrogenated Schottky diodes. The diodes were reverse biased at 4 V during the anneals.

As a final note, this paper (and Ref. 13) offers a microscopic model for understanding the observation[16] of a reversible field-induced doping effect in *n*-type hydrogenated amorphous silicon (*a*-Si:H). The dramatic increase in the net shallow donor concentration that results from annealing *n*-type *a*-Si:H with a high-electric field may involve the dissociation of PH complexes and the drift of H^- out of the space-charge layer as described above.

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