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Migration of the H_2^* complex and its relation to H^- in n-type silicon

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Much, often most, of the hydrogen that is introduced into n-type silicon at moderate temperatures (e.g., 150 °C) forms complexes that have been labeled "H_2^*" to distinguish them from the stable and much less mobile complex "H_2" that forms in p-type silicon. This paper reports measurements by secondary-ion mass spectrometry of the thermally induced depth redistribution of deuterium present mostly as $^2H_2^*$. The activation energy for migration is 0.81 ± 0.06 eV, but the data do not determine whether the migration involves dissociation. Both migration kinetics and direct measurements on reverse-bias-annealed Schottky diodes show that for annealing times up to 25 h at temperatures near 60 °C there is no detectable redistribution or dissociation of $^2H_2^*$, contradicting a currently ambiguous claim that such annealing produces a large redistribution due to dissociations yielding H^-. The effect of the presence of H_2^* on the evolution of the neutralized-donor profiles at such temperatures is negligible.

When the near-surface region of moderately doped n-type silicon is hydrogenated, for example, by exposure to plasma-produced monatomic hydrogen, most of the dissolved hydrogen is present in the form of a charge-neutral species that is unrelated to the donor-H complex and that cannot be ascribed to interstitial monatomic hydrogen because of the absence of an electron paramagnetic resonance signal.[1,2] The penetration of this species and its subsequent redistribution on vacuum annealing are easily measurable at temperatures near 150 °C, so it must be different from the rather stable and much less mobile complex, ascribed to diatomic "H_2," which forms in p-type silicon[1–3] by a process involving interstitial H^+. It has been suggested[1,2] that the mobile entity in n-type material is a metastable diatomic complex, designated as "H_2^*." Some speculations have been offered[4] on its possible atomic nature. This paper describes a systematic study of the thermal redistribution of $^2H_2^*$.

Studying the migration of H_2^* is important not only for its own sake, but also in connection with the issue of the existence and migration of the negative monoatomic species H^- in silicon. Two independent experimental studies of this issue have recently been published.[5,6] Both utilized capacitance-voltage (C-V) techniques to monitor the redistribution of near-surface donor-H complexes[7] when plasma-hydrogenated silicon was made into Schottky diodes and annealed under reverse bias. In both studies the redistribution was found to be such as would be produced by drift of H^- in the high electric field of the diode depletion layer. However, not only are there a number of significant differences between the experimental conditions in Refs. 5 and 6; Ref. 5 also supplemented the C-V measurements of the depth distribution of donor-bound hydrogen with measurements of the depth distribution of total hydrogen from secondary-ion mass spectrometry (SIMS), whereas Ref. 6 omitted discussion of the SIMS measurements that had in fact been made on its samples because it was believed that most of the nondonor-bound hydrogen (H_2^*) was stable and immobile under the annealing conditions used. As originally published, Ref. 5 appeared to strongly contradict this belief, and to show that H_2^*, present at a concentration an order of magnitude higher than that of the donors, could dissociate appreciably at 60 °C to yield H^- species that would drift markedly in an electric field. We therefore felt it important to check this behavior. Our results, reported below, confirm the stability and immobility of H_2^* at 70 °C. The clear contradiction with the original data in Ref. 5 has since been resolved by publication of an erratum[8] which allows the interpretation that the observed migration in the SIMS data of Ref. 5 can be attributed to donor-bound hydrogen and not to H_2^*. Though Ref. 8 implies that several textual statements in Ref. 5 are to be corrected, its brevity may allow this fact to be overlooked.

To study the migration kinetics of H_2^*, two different specifications of n-type single-crystal silicon were used: (1) phosphorus concentration $[P] = 1 \times 10^{17}$ cm^{-3}, Czochralski grown, and (2) $[P] = 8 \times 10^{17}$ cm^{-3}, float-zone grown; both sets were of (100) orientation and uniformly doped. The specimens were first deuterated by exposure to monatomic deuterium (150 °C, 30 min) in a remote hydrogen plasma system[9] and then individually vacuum annealed at temperatures in the range of 125–200 °C; the specimens were held in the dark during both processing steps.

Depth profiles of ^2H from SIMS are illustrated in Fig. 1 for the first set of wafer specifications. For these, and also for the more highly doped samples, both the profile produced by the initial hydrogenation and those remaining after each of the anneals can be well fitted for depths greater than ~ 0.1 μm by distributions calculated from simple diffusion theory with the boundary conditions of a constant surface concentration during hydrogenation and zero surface concentration during annealing. This behavior, similar to that found in our previous work,[1] is a little surprising, since it would be quite possible for the effective diffusion coefficient to be concentration dependent, or even for the locality of the diffusion equation to fail, and since the rapid buildup of platelets[9,10] in the first 0.1 μm of silicon might well result in a time-dependent boundary

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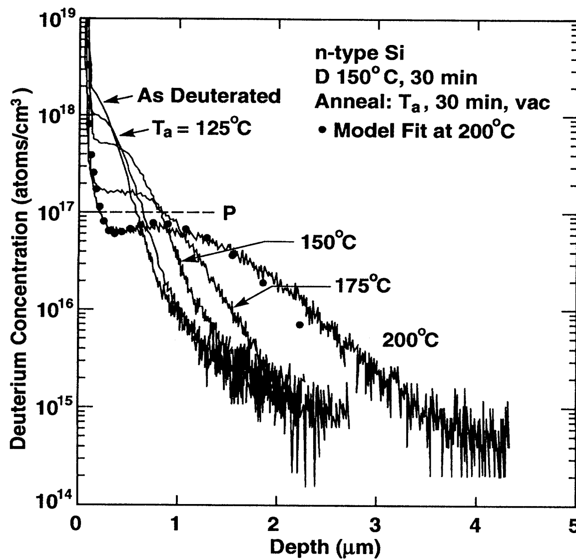

FIG. 1. Depth profiles of deuterium in *n*-type (1×10^{17} P cm^{-3}) silicon after deuteration at 150 °C for 30 min and subsequent vacuum anneals at the specified temperatures (for 30 min). Also shown are results from the diffusion analysis (based on the depth-integrated density) for the deuterium distribution after the 200 °C vacuum anneal; the calculated points include a fit to the near-surface platelet distribution and have been adjusted for the ^{2}H background in the SIMS measurement.

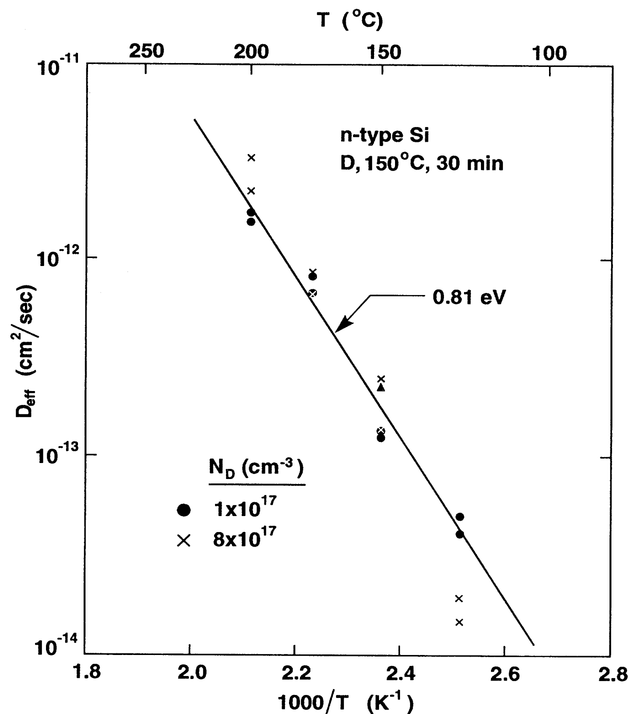

FIG. 2. Arrhenius analysis for the thermally induced redistribution of $^2H_2^*$ in *n*-type silicon after deuteration at 150 °C (30 min). Data are shown for two sets of (100) silicon specimens: (1) [P]$=1\times10^{17}$ cm^{-3}, Czochralski grown, and (2) [P] $=8\times10^{17}$ cm^{-3}, float-zone grown. The line is the least-squares fit to the first set of data (i.e., 1×10^{17} P cm^{-3}). The triangle shows the D_{eff} obtained at 150 °C from the in-diffusion profile.

condition for the bulk region. Nonetheless, fits of the observed profiles to the predictions of simple diffusion theory provide values for an effective diffusion coefficient D_{eff} for the total hydrogen at each temperature.

Two simple methods were used to determined D_{eff} for a given profile, and the degree of agreement between them provides a measure of the applicability of the simple theory, which is not expected to be more than an approximation, for the reasons mentioned above. One way was to find the D_{eff} that would make the computed value of the depth-integrated fraction of the hydrogen remaining in the crystal agree with that obtained by numerical integration of the measured profiles, after subtraction of the background and an allowance for stable platelet-related hydrogen[9,10] in the first $\sim$0.1 μm; an example of such a fit is shown in Fig. 1. The other was to make the theoretical profile match the peak density after annealing, expressed as a fraction of the extrapolated preanneal density at the surface. Figure 2 shows, on an Arrhenius plot, the values of D_{eff} obtained in these two ways. The triangle shows for comparison the D_{eff} obtained at 150 °C from the in-diffusion profile. For the more lightly doped sample, the two D_{eff}'s at each temperature agree to within $\leq 25\%$; for the higher doped specimens, D_{eff} from the integrated hydrogen is 30%–80% larger than that based on the maximum concentration. However, the general magnitude of D_{eff} does not seem to change significantly with doping except at the lowest temperature (125 °C), where the higher doping level (8×10^7 P cm^{-3}) reduces it almost threefold below the value at the lower doping. This could perhaps be due to the known tendency for PH complexes to form at this temperature.[6,9] The activation slope of the line, 0.81 ± 0.06 eV, may represent either the migration energy of H_2^* diffusing as a unit, or, if the diffusion occurs by a dissociation-recombination mechanism, the sum of the migration energy of the monatomic species and half of the dissociation energy. Crude estimates of D_{eff} from earlier studies[1,2] are reasonably consistent with the present data.

Does H_2^* play any role in the experiments[5,6] on the field-induced redistribution of donor-H complexes? One might plausibly expect that any such role would be minor, despite the high H_2^* concentrations referred to above, since extrapolation of data like Figs. 1 and 2 to the 50–70 °C range would give very stable distributions on the scale of the annealing times (up to a few hours in Ref. 6), and since direct dissociation of H_2^* would probably yield neutral H^0, which would have a small capture radius on P^+. However, details of the redistribution of PH or SbH complexes on annealing could conceivably be influenced if there were an appreciable release of H^0 from H_2^*, and major changes in this redistribution might be expected if a large part of the H_2^* were to dissociate with production of H^-. Such dissociation in a depletion layer would seem *a priori* unlikely, since unless monatomic H is a "negative-*U* center,"[11] dissociation into $2H^0$ will be less costly energetically, and since charge changes by carrier emission will favor production of H^+ rather than H^-, as seems indeed to have been observed in other experiments.[3,12,13] However, since the text of Ref. 5 explicitly states that H_2^* disso-

ciates appreciably in a 60 °C anneal with production of H^-, we felt it important to check the correctness of the conclusion. The subsequent announcement[8] of a calibration error in Fig. 3 of Ref. 5 renders the data presented there irrelevant as regards the behavior of H_2^* and leaves our present measurement as the only experimental test of possible field migration of dissociating H_2^* at low annealing temperatures.

To test for the occurrence of field-induced migration of hydrogen from H_2^*, Czochralski-grown (100) Si wafers with $[P]=1\times10^{16}$ cm^{-3} were deuterated by a 4-h exposure at 130 °C in a remote hydrogen plasma reactor, metallized with Pd to form Schottky diodes, and then vacuum annealed at 70 °C for 25 h both with and without an applied reverse bias of 25 V; the diodes displayed negligible leakage currents. The resulting D distributions are shown in Fig. 3; they are clearly identical to within the accuracy of the SIMS measurement, and also coincide equally well with the profile (not shown) of an unannealed, as-deuterated specimen. (These profiles were designed to simulate roughly the unannealed profile of Fig. 3 of Ref. 5, as originally calibrated. The time, voltage, and donor density were also the same, except for the use of P instead of Sb. Note that the expected rearrangement of donor-bound hydrogen, as observed, for example, for similarly doped material in Fig. 2 of Ref. 5, should cause the two curves of our Fig. 3 to differ from each other by an amount merely of the order of the noise in the curves.) A similar experiment, conducted using parameters similar to those of Ref. 6 (1×10^{17} P/cm^3, deuterated at 130 °C for 1 h) also showed no detectable difference in

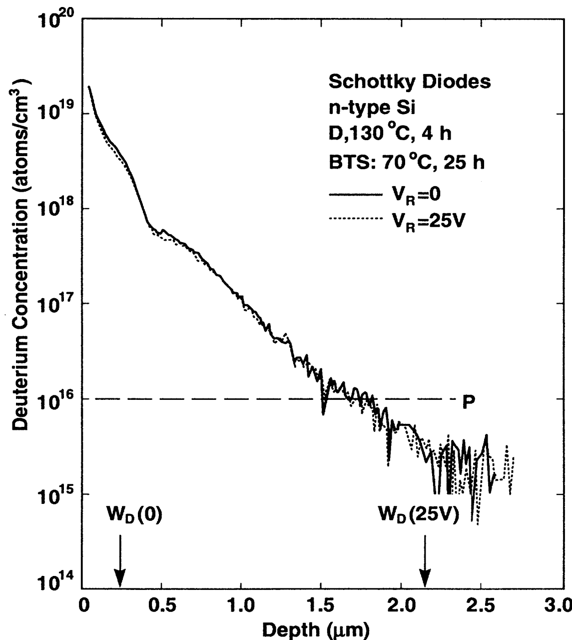

FIG. 3. Depth profiles of deuterium in n-type Schottky diodes after a postdeuteration anneal at 70 °C for 25 h under zero bias and with a reverse bias of 25 V. The silicon was deuterated at 130 °C for 4 h prior to diode fabrication. Also shown are the uniform phosphorus concentration and the depletion widths W_D at the two biases.

the depth profiles for specimens unannealed and annealed at 85 °C for 1 h with or without a 4-V reverse bias. (In this second experiment, even though there is a larger amount of donor-bound hydrogen available for rearrangement, its contribution to the depth profile within the reverse-biased depletion layer is still negligible because the higher doping concentration restricts the depletion layer to the region where the density of H_2^* is highest and completely dwarfs that of the donor-bound hydrogen.) We conclude that in the bias-annealing experiments of Refs. 5 and 6, migration of H_2^*, and in particular of any possible H^- resulting from dissociation of H_2^*, did not play a significant role.

To put this conclusion into quantitative terms and to interpret the details of the annealing experiments would require knowing the rate at which monatomic hydrogen is released by thermal dissociation of H_2^*. While further experiments will be needed to determine this quantity, a few plausible assumptions already suffice to extract a rough upper limit, simply from the failure of the annealing schedules used to produce a detectable approach toward a new equilibrium ratio of the concentrations of H_2^* and PH complexes. Specifically, we assume the following: (1) the hydrogenation schedule of Fig. 3 produces, in the depth range below about 0.5–0.8 µm, position-dependent relative concentrations of H_2^* and PH that correspond at least roughly to local thermal equilibrium; (2) for given concentrations of P and total H, the equilibrium ratio of concentrations of these two species is the more favorable to PH the lower the temperature; and (3) in the depth range 0.5–1.0 µm, complexes other than PH and H_2^* do not contribute significantly to the total hydrogen during the anneal. Although there is some empirical evidence (which we shall not discuss here) for the validity of these assumptions, further experimental work will be needed before they can be considered established. Using them as a working hypothesis, we can note that during the 25-h anneal at 70 °C there occur many dissociations and reformings of PH complexes, since the dissociation lifetime of PH at this temperature is only about 0.7 h.[6] If there were also a significant number of dissociations of H_2^* complexes (i.e., if the lifetime of these were ≤ 25 h), there would be a significant redistribution of hydrogen between PH and H_2^* in the direction toward the 70 °C equilibrium ratio, which would involve, by our assumption, an increase in the local concentration of PH. C-V measurements of the PH distribution before and after the 25-h zero-bias annealing revealed essentially no change. Thus, we conclude, subject to verification of the assumptions, that the dissociation lifetime of H_2^* is greater than ~ 25 h at 70 °C.

Is the inference of the existence of an H^- species, advanced in Refs. 5 and 6, dependent on the assumption that any H_2^* present is completely passive at the annealing temperatures used? Without discussing H_2^*, Ref. 6 argued that although the depth distribution of PH could be altered by annealing under a reverse bias even if the only monatomic species present were H^0, the details of the profile changes observed were inconsistent with the absence of H^-. The essence of this argument was that from the sequence of profiles of PH versus depth during

reverse-bias annealing, one can identify a range of depths and times for which (a) the rate of formation of new PH complexes is increasing with depth and (b) the densities of all possible reactants other then H^- that might combine to form new PH are decreasing with depth, or in one case (e^-) small and constant. For the case of Fig. 2 of Ref. 6, a range with these properties occurs around 0.12–0.14 μm, where the bands have been bent by over 0.5 eV above their bulk limit, and for times of the order of 1 h after the start of annealing. Although one aspect of the argument, which is independent of the existence of H_2^*, merits further scrutiny, namely, the neglect of possible induced dissociations of PH by processes $H^0+(PH)^0 \rightarrow P^+ + e^- + H_2$ (or H_2^*), it can be stressed that in the absence of such processes the argument is unaffected by the presence of H_2^* and its possible dissociation or formation.

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[1] N. M. Johnson and C. Herring, in *Shallow Impurities in Semiconductors 1988,* Proceedings of the Third International Conference, edited by B. Monemar, IOP Conf. Proc. No. 95 (Institute of Physics and Physical Society, London, 1989), p. 415.

[2] C. Herring and N. M. Johnson, in *Hydrogen in Semiconductors,* edited by J. I. Pankove and N. M. Johnson, Semiconductors and Semimetals Vol. 34 (Academic, New York, 1991), Chap. 10.

[3] N. M. Johnson and C. Herring, Phys. Rev. B **38**, 1581 (1988).

[4] K. J. Chang and D. J. Chadi, Phys. Rev. Lett. **62**, 937 (1989).

[5] A. J. Tavendale, S. J. Pearton, and A. A. Williams, Appl. Phys. Lett. **56**, 949 (1990).

[6] J. Zhu, N. M. Johnson, and C. Herring, Phys. Rev. B **41**, 12354 (1990).

[7] N. M. Johnson, C. Herring, and D. J. Chadi, Phys. Rev. Lett. **56**, 2224 (1986).

[8] A. J. Tavendale, S. J. Pearton, and A. A. Williams, Appl. Phys. Lett. **57**, 2377(E) (1990).

[9] N. M. Johnson, in *Hydrogen in Semiconductors* (Ref. 2), Chap. 7.

[10] N. M. Johnson, F. A. Ponce, R. A. Street, and R. J. Nemanich, Phys. Rev. B **35**, 4166 (1987).

[11] P. W. Anderson, Phys. Rev. Lett. **34**, 953 (1975).

[12] C. H. Seager and R. A. Anderson, Appl. Phys. Lett. **53**, 1181 (1988).

[13] C. H. Seager and R. A. Anderson, Solid State Commun. **76**, 285 (1990).