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Trap-limited hydrogen diffusion in doped silicon

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Hydrogen depth profiles in highly doped p-type silicon are obtained from the analysis of infrared reflectance spectra of H-passivated samples. From these profiles, H-diffusion coefficients are calculated for different temperatures and dopant concentrations. The results are explained with the assumption that hydrogen diffusion is limited by trapping at the acceptor sites. A binding energy of 0.6 eV is found for B-H complexes, in agreement with previous *ab initio* calculations.

I. INTRODUCTION

It is well known that substitutional acceptors and donors in crystalline silicon can be passivated by atomic hydrogen in a reversible way. In particular, the passivation of acceptors, mainly in the case of boron-doped silicon, has been extensively analyzed in the last few years by means of different experimental and theoretical methods (see Ref. 1 for a review on hydrogen in crystalline semiconductors). From a microscopic point of view, the structure of the acceptor-hydrogen complexes has been studied in detail by different groups. It is now almost generally accepted that, at least in the case of B-H pairs, hydrogen is located near a bond-centered (BC) position between the acceptor and one of its Si neighbors.[1,2,3]

On the other hand, from the point of view of the hydrogen dynamics and diffusion in the Si lattice, until now there has been no general agreement either about the diffusion path or about the electric charge of the interstitial H atoms, in spite of the rather large number of studies related to this topic.[1] From recent calculations,[4,5] it seems that the most stable site for atomic hydrogen in c-Si is a bond-centered position between two silicon atoms, although certain deviations from the exact BC site have been proposed.[6] Van de Walle *et al.*[5] have found that the charge state of the migrating hydrogen may depend on the Fermi level in the material, and thus may be different for n-type, p-type, or intrinsic silicon. This is in agreement with an earlier suggestion by Pantelides[7] that hydrogen has a deep donor level in the silicon gap. In support of the evolving theoretical picture, a number of experimental investigations have provided evidence for an influence of doping on the diffusion coefficient of hydrogen, notably in p-type silicon.[8–10] As it stands, this may be either due to a Fermi-level effect or to the formation of bound complexes between hydrogen and dopants. The first possibility has been discussed by Cappizi and Mitiga,[11] who propose that hydrogen in B-doped silicon is present in two charge states (H^0 and H^+) with quite different diffusion coefficients. The second possibility, namely the effect of complex formation on the diffusivity of hydrogen in boron-doped Si, is investigated in the present paper.

In order to do this, we have used B-doped Si samples with dopant concentrations larger than 10^{19} cm^{-3}. These high dopant concentrations allow us to clearly observe and analyze the effect of B-H complex formation on the H diffusivity, as described below. Diffusion studies performed at lower dopant concentrations generally suffer from the fact that for typical H-diffusion temperatures of 200 °C or more, thermally excited carriers may cause a strong shift of the thermal equilibrium Fermi level towards midgap, depending on the dopant density. Thus, for "low" dopant concentrations ($<10^{18}$ cm^{-3}), the effective charge of the diffusing hydrogen actually may depend quite strongly on temperature if, as predicted, the diffusing H species has a level in the gap. Therefore, an understanding of the trap-limited diffusion of hydrogen in highly doped silicon (where the Fermi-level position depends only weakly on temperature) is a prerequisite for a more accurate description of hydrogen diffusion in general.

II. EXPERIMENTAL PROCEDURE

Samples used in this work were bulk doped with boron concentrations between 1×10^{19} and 1.2×10^{20} cm^{-3}, and were passivated via a remote H_2 glow-discharge plasma at temperatures in the range of 90–210 °C and at a constant gas pressure of 1.5 mbar. The infrared reflectance of the doped and hydrogenated samples was measured at room temperature in the spectral region of the free-carrier plasma edge, which appears at a frequency ω_p given by $\omega_p^2=4\pi ne^2/\epsilon_0 m^*$, where n is the free hole density, ϵ_0 is the static dielectric constant of the material, and m^* the hole effective mass. After passivation, a shift of the plasma edge to lower wave numbers is observed, corresponding to a decrease of the free hole concentration. We also observe in the infrared spectra of the hydrogenated samples an interference pattern [Fig. 1(a)], due to the reflections from the sample surface and from the passivation front inside the sample, which allows us to calculate the thickness of the passivated region. Moreover, the damping of the interference fringes is directly related to the steepness of the B–H-complex profile in

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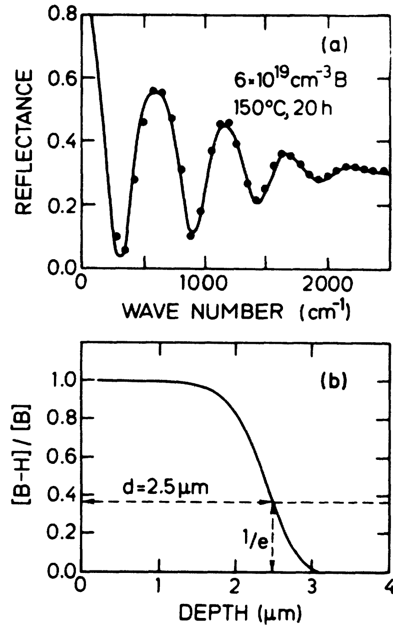

FIG. 1. (a) Experimental (points) and calculated (solid line) infrared reflectance spectra of hydrogenated B-doped silicon. (b) Boron–hydrogen-complex depth profile used to obtain the calculated spectrum in (a).

the passivated samples (the smaller the damping, the more abrupt is the transition between the passivated layer and the unpassivated bulk crystal). Thus, these three variables (hole concentration at the surface, depth of the passivated region, and steepness of the H profile) an be deduced from a fit to the experimental reflectance spectra. This technique has been shown to be a direct, nondestructive and sensitive way to obtain depth profiles of hydrogen in semiconductors.[12,13,14] In particular, the hydrogen depth profiles deduced from infrared reflectance spectra show good agreement with those obtained from secondary-ion mass spectroscopy (SIMS) analysis.[15]

For the simulation of the infrared spectra, the hydrogenated region of a sample is partitioned into approximately 100 layers each being 0.05 μm wide. The optical constants in each layer are calculated as a function of the local hole concentrations. To convert into a boron–hydrogen-complex profile, we use the equation

$$[h^+]=[\mathrm{B}]-[\mathrm{B\text{-}H}] , \qquad (1)$$

i.e., the concentration of free holes is equal to the density of unpassivated boron. A typical spectrum together with a calculated fitting is presented in Fig. 1(a). Figure 1(b) shows the B–H-complex profile used to simulate this reflectance spectrum. The sensitivity of the method to determine the three parameters mentioned above has already been discussed in Ref. 13. However, since the diffusion depth d is the variable of importance for the following determination of the diffusion coefficients, it should be emphasized that this parameter d can be determined in all cases considered here with a relative error smaller than 5%. Moreover, this diffusion depth d is experimentally well defined, as the B–H-complex profiles are rather steep in all cases (see Fig. 1)

Due to the low energy of the hydrogen atoms entering into our samples (≤ 50 eV), the density of defects created by hydrogenation is very low in comparison to the concentration of dopants. Thus, possible variations of the dielectric constant and the hole mobility due to passivation-induced defects, which occur in the case of high-energy atom implantations,[13] are negligible.

III. RESULTS AND DISCUSSION

Hydrogen profiles calculated from our infrared spectra agree well with those obtained for deuterium-passivated samples by means of SIMS.[16] In fact, a plateau close to the dopant concentration followed by a rapid drop of the H concentration is obtained from both techniques. The main difference between infrared and SIMS results is a cusp that appears near the surface in the SIMS profiles, which is most probably due to hydrogen not taking part in the passivation process, i.e., H atoms present in the material at Si—H bonds[17] at extended defects or as molecular H_2.[5] However, in the highly doped samples used for this study, we know from Raman spectroscopy that the concentration of Si—H bonds is at least 2 orders of magnitude smaller than that of B-H complexes.[18]

For a fixed dopant concentration and a given hydrogenation temperature, the penetration depth of hydrogen increases as the square root of the exposure time, as expected for a diffusion limited process. Using the expression $d=\sqrt{D_{\mathrm{eff}}t}$, ($t$: hydrogenation time), we obtain from the calculated B–H-complex profiles an effective diffusion coefficient D_{eff} for H under various conditions.

To the extent that B acceptors act as hydrogen traps, one should expect a dependence of the diffusivity on the boron concentration. In Fig. 2 we show the B–H-complex profiles corresponding to highly doped samples with different B concentrations, hydrogenated under the same conditions. It is clear that the H-penetration depth increases for decreasing dopant concentration, as expected for a diffusion process limited by trapping at the dopant sites. Moreover, we observe that the integrated number of hydrogen atoms increases with B concentration, which shows that the profiles are not limited by the external plasma conditions, but rather by the solubility of H in the doped crystal at the relative low diffusion temperatures ($[\mathrm{H}]_{\mathrm{max}}\simeq[\mathrm{B}]$).

The effect of trapping on the diffusion of interstitial impurity atoms in crystalline solids has been studied in different investigations.[19] In particular, the effective diffusion coefficient D_{eff} in the presence of randomly distributed unsaturated point traps can be obtained from the diffusion coefficient D in the pure crystal by means of the equation[20]

$$D_{\mathrm{eff}}=D\left[1+c\frac{\tau_1}{\tau_0}\right]^{-1} , \qquad (2)$$

where c is the concentration of traps expressed as a lattice site fraction, τ_0 is the mean jump time between lattice sites in a perfect crystal, and τ_1 is the mean time that a

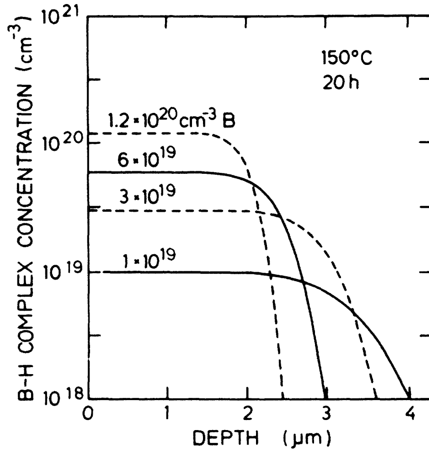

FIG. 2. Depth profiles of boron-hydrogen complexes calculated from the infrared spectra for silicon samples with different bulk acceptor concentrations.

diffusing atom remains trapped at an impurity site. The coefficient D, which denotes the diffusion coefficient in the absence of traps, is supposed to be given, as usual, by an Arrhenius expression

$$D=D_0 \exp(-E_M/kT) , \tag{3}$$

where E_M is an activation energy for hydrogen migration in pure silicon. The ratio τ_1/τ_0 will change as a function of temperature, depending on the binding energy of the B-H complex. Defining this energy (called hereafter E_B) as the energy difference between the energy minima for hydrogen in pure Si and at a trap site (see Fig. 3), one has

$$\frac{\tau_1}{\tau_0}=\frac{\nu_0}{\nu_1}\exp(E_B/kT) , \tag{4}$$

where ν_0 and ν_1 are the attempt-to-jump frequencies for hydrogen in the free and trapped configurations, respectively, and T is the hydrogenation temperature.

In Eq. (4) it is assumed that, at a given time, in each point of the material thermal equilibrium between trapping and detrapping processes is reached. Then, the ratio between the concentrations of hydrogen in trapping sites [B-H] and in nontrapping sites [H] will be given by detailed balance as

$$\frac{[\text{B-H}]}{[\text{H}]}=[\text{B}]\frac{\nu_0}{\nu_1}\exp(E_B/kT) . \tag{5}$$

This equation is an approximation for the case that $[\text{B}] \gg [\text{H}]$, so that the trap density can be considered as constant throughout the sample and independent of time. However, in our case, the effective concentration of traps, which is equal to the density of unpassivated boron, will decrease as a function of time during the acceptor passivation process. This saturation of traps makes Eqs. (2), (4), and (5) no longer valid. In fact, assuming a total concentration of hydrogen $[\text{H}]_T$ at a given point in the sample ($[\text{H}]_T=[\text{B-H}]+[\text{H}]$), the equilibrium between the different species taking part in the passivation reaction $\text{B}_{\text{un}}+\text{H}\rightleftharpoons\text{B-H}$ will be given by the mass-action law

$$\frac{[\text{B-H}]}{[\text{B}_{\text{un}}][\text{H}]}=A\exp(E_B/kT) , \tag{6}$$

where $[\text{B}_{\text{un}}]$ is the concentration of unpassivated boron ($[\text{B}_{\text{un}}]=[\text{B}]-[\text{B-H}]$). The pre-exponential term A is given by $A=Zf$, where Z is the number of equivalent nearest sites for H around B, and f arises from the variation of the vibrational entropy.[21] Now, the ratio [B-H]/[H] between trapped and free hydrogen will depend on the concentration of unpassivated boron (which decreases for increasing exposure time) and on temperature, as expressed by Eq. (6). The total concentration of hydrogen $[\text{H}]_T$ is a variable that depends on the hydrogenation conditions, and is usually not known *a priori*. In any case, if one takes into account the trap saturation during the diffusion, the effective diffusion coefficient of hydrogen will be given by

$$D_{\text{eff}}=D\left[1+r[\text{B}]\exp\left[\frac{E_B}{k_T}\right]\right]^{-1} , \tag{7}$$

where r is a factor which depends on the external hydrogenation conditions (the higher the hydrogen flux, the lower the value of r) and on the changes of entropy (configurational and vibrational) associated with the trapping of an H atom near an acceptor. This change in configurational entropy will be important close to trap saturation, as was already expressed in a different way by Eq. (6), where $[\text{B}_{\text{un}}]$ appears instead of the total boron concentration [B], which would appear in the absence of saturation. Notice that in the absence of trap saturation, the effective diffusion coefficient D_{eff} is independent of the hydrogen flux, and then one has $r=A$ [cf. Eq. (6)]. In the case close to trap saturation, and if the hydrogen injection is not limited by the external plasma conditions, one expects for the parameter r values much lower than unity, to the extent to which the effective trap concentration will be lower than the boron concentration [B], in the region where hydrogen diffuses. For our purposes, we can assume that the parameter r is independent of temperature and acceptor concentration, and that it plays the

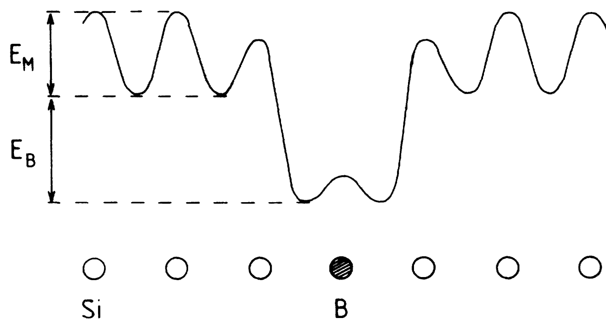

FIG. 3. One-dimensional scheme of the potential energy curve for interstitial hydrogen near a trapping site (B acceptor). E_B: binding energy of the B-H complex; E_M: migration energy of hydrogen in undoped silicon.

role of an effective pre-exponential factor in Eq. (7).

In order to compare our experimental results with Eq. (7), we first note that for a given temperature and constant plasma conditions, the effective diffusion coefficient is only a function of dopant concentration. In Fig. 4(a) we show the obtained diffusion coefficients for different acceptor concentrations at 150° C, along with a fitting to Eq. (7). Our model gives the correct dependence for D_{eff} as a function of boron concentration, and we obtain for H diffusion in pure silicon an extrapolated coefficient $D(150\,^{\circ}\text{C}) = 1.9\times10^{-12}$ $\text{cm}^2\,\text{s}^{-1}$, in good agreement with experimental values obtained by deep-level transient spectroscopy (DLTS) measurements on low-defect-density material at this temperature.[22] However, from the analysis of the B-concentration dependence alone it is not possible to obtain directly the binding energy E_B of B-H complexes, due to the uncertainty in the value of r. This indetermination can be resolved by recalling that, for a given dopant concentration, the effective diffusion coefficient of hydrogen D_{eff} will depend on temperature due to changes in both the coefficient D and the ratio τ_1/τ_0 [cf. Eqs. (3) and (4)]. We have measured this dependence for a B concentration of 1.5×10^{19} cm^{-3}, and the results are shown in Fig. 4(b). It is obvious that the experimental points depart from the usual Arrhenius plot. By means of Eq. (7), instead, we can obtain a good fitting to those points using a value for the binding energy $E_B = 0.6$ eV (with an estimated error of about ±0.1 eV). The corresponding value for the pre-exponential factor is $r = 7\times10^{-5}$. This unusually low value for the pre-exponential constant is largely due to the phenomenon of trap saturation as described above, which we can quantify also after the diffusion in terms of the degree of acceptor passivation (typically $\geq 99\%$ for $[\text{B}] = 1.5\times10^{19}$ cm^{-3}). For high temperatures ($\geq 200\,^{\circ}\text{C}$), the effect of trapping becomes negligible and D_{eff} converges towards the coefficient diffusion D in pure silicon. The extrapolated values for H diffusion in pure crystalline silicon [$E_M = 0.43$ eV, $D_0 = 2.4\times10^{-7}$ $\text{cm}^2\,\text{s}^{-1}$ in Eq. (3)] agree well with those calculated by Mogro-Campero *et al.*[23] from spreading resistance profiles of silicon hydrogenated at temperatures in the range 130–275 °C and under conditions where the trap density is much lower (at least 3 orders of magnitude) than the ones considered here.

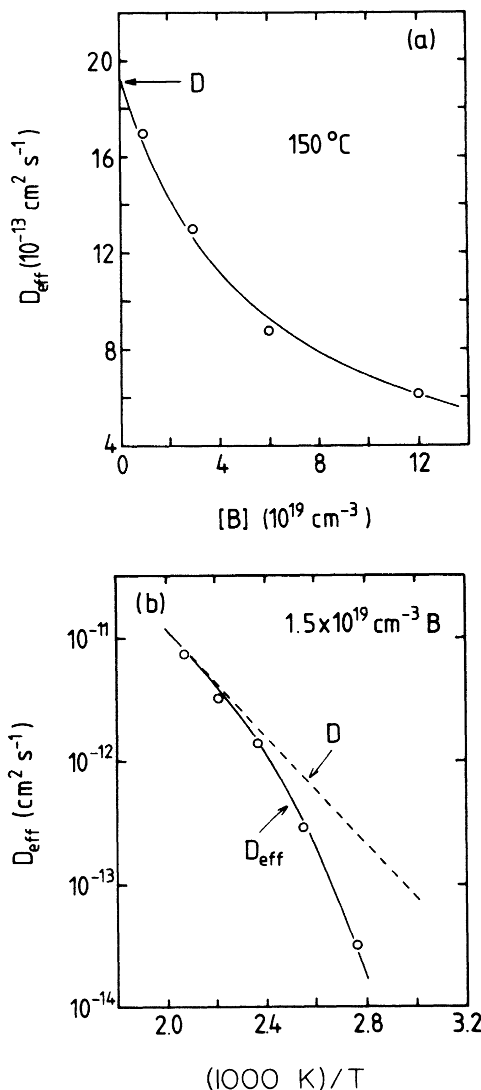

FIG. 4. (a) Boron-concentration dependence of the effective hydrogen diffusion coefficient D_{eff} at 150°C. (b) Temperature dependence of D_{eff} for 1.5×10^{19} boron atoms/cm^3. Solid lines are fittings to Eq. (7) in the text, with $E_B = 0.6$ eV and $r = 7\times10^{-5}$. D is the H-diffusion coefficient in undoped silicon. The dashed line in (b) corresponds to Eq. (3) with $D_0 = 2.4\times10^{-7}$ $\text{cm}^2\,\text{s}^{-1}$, $E_M = 0.43$ eV.

IV. CONCLUDING REMARKS

The value obtained for the binding energy of H at boron sites ($E_B = 0.6$ eV) is in good agreement with the one calculated by Denteneer *et al.*[24] using the first-principles pseudopotential-density-functional method. These authors found that in p-type silicon H acts as a donor, and consequently it should diffuse as H^+. The binding energy calculated by them, which coincides with the one obtained here, is thus the energy difference between the global energy minima for H^+ in pure silicon and H^0 in Si:B.

According to our results, the activation energy for outdiffusion, which is the sum of the binding energy E_B and the migration energy E_M for the diffusing hydrogen, is calculated to be about 1 eV. Using a first-order kinetics model,[1] an activation energy of about 1.5 eV was found from the reactivation temperature for passivated boron ($\geq 160\,^{\circ}\text{C}$). This energy is higher than the one found by us. In fact, this is expected if a simple first-order kinetics model is used to interpret exodiffusion data. The first-order model considers only one detrapping step, and neglects possible retrapping events during the migration of the atoms, which may occur either at other unsaturated traps along its path, or more importantly at the sample/vacuum interface. Thus, first-order models of exodiffusion kinetics can only provide upper bounds for the binding energies of the initial configurations.

Instead, Sah *et al.*[25] obtained for B-H pairs in silicon an activation energy of 1.1 eV from an analysis of

thermal annealing experiments which involves second-order kinetics. This value agrees well with the activation energy obtained here for these complexes ($E_B + E_M \sim 1$ eV). It is also noteworthy that our trap-limited diffusion analysis in the high-boron-concentration regime ([B] $> 10^{19}$ cm^{-3}) is in quantitative agreement (as far as both H-diffusion coefficient D and binding energy E_B are concerned) with results obtained recently by Zundel and Weber[26] for [B]$\simeq 10^{15}$ cm^{-3}, indicating that results obtained in either extreme case can be generalized to other acceptor concentrations.

In summary, we have shown that the H diffusion in p-type silicon at temperatures at which hydrogenation is usually performed is controlled by trapping near the acceptors. More generally, a trap-limited diffusion analysis is imperative for those cases in which the H solubility is similar to the concentration of possible traps. Trap saturation has to be considered in order to give a correct interpretation of the experimental results. In the present case of H diffusion in B-doped silicon we were able to explain the experimental data for different temperatures and acceptor concentrations in a consistent way assuming the diffusion of only one H species. From this diffusion analysis, we find that B-H pairs is passivated crystalline silicon have a binding energy of 0.6 ± 0.1 eV, in agreement with *ab initio* calculations.

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