LONG RANGE COULOMB EFFECTS ON HYDROGEN DEBONDING
FROM BORON ACCEPTORS IN SILICON*

R. A. ANDERSON AND C. H. SEAGER
Sandia National Laboratories, Albuquerque, NM 87185

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ABSTRACT

Previous work has demonstrated that B•H pairs in silicon thermally dissociate obeying simple first order kinetics if they are located in a region depleted of majority carriers. B•H debonding in equilibrium, however, is a slower, more complex process. We have investigated the dissociation of B•H pairs under a variety of equilibrium and non-equilibrium conditions and have demonstrated that the dissociation process is strongly influenced by the local concentration of majority and minority carriers. In particular, we show that injection of minority carriers can markedly accelerate the dissociation process. A model is proposed which suggests that hydrogen released from an acceptor, while initially positive, must always be neutralized before escape is possible. This picture correctly describes the time dependence of debonding in equilibrium, and it predicts the enhanced debonding in forward biased diodes provided the characteristic time for H charge conversion is long.

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INTRODUCTION

A positive charge state for hydrogen in silicon is well established experimentally¹⁻³, but recent data^{2,4-6} have given strong evidence that neutral, mobile, H interstitials are also prevalent. The energy level of the H^0/H^+ transition is not really known nor are the lattice sites for H in either charge state. While bond-centered (b.c.) H is unequivocally favored as the minimum energy site by various theoretical calculations⁷⁻¹², the large lattice distortions associated with this configuration suggest that there may be a substantial activation barrier for forming b.c. hydrogen, leaving open the possibility that the high mobility paths for H diffusion proceed through tetrahedral sites.

The structural model for H-acceptor pairs first suggested by Pankove et al.¹³ seems well established by infrared spectroscopy¹⁴ and channelling measurements^{15,16}. In this picture the hydrogen is located at a bond centered position next to the acceptor. However, there exists some uncertainty about the kinetics of H-acceptor dissociation. Zundel et al.^{3,17} have shown that reverse-bias-annealed hydrogenated Schottky diodes doped with B, Al, Ga, and In display a simple first order kinetic behavior consistent with:

$$\frac{\partial(A \cdot H)}{\partial t} = -k(A \cdot H) , \quad (1)$$

where $(A \cdot H)$ is the concentration of acceptor/hydrogen pairs. The dissociation rate, k , is thermally activated with 1.3 to 1.4 eV, rather independent of the acceptor atom. These same authors also demonstrated that hydrogen was field driven to deeper depths after dissociation consistent with a positive charge state of H, and that virtually all debonded hydrogen became bonded to acceptors deeper in their diodes^{3,17}.

Annealing experiments carried out on unbiased diodes¹⁸ have yielded a much different, slower, kinetic behavior than given by Eq. (1). Zundel et al.¹⁸ attributed this to the effects of H recapture at unpassivated acceptors and to the formation of H_2 . In this letter we re-examine the debonding of H from boron acceptors, under equilibrium and non-equilibrium conditions. We demonstrate that forward bias injection of minority carriers (electrons) speeds up the thermal debonding process markedly. This acceleration apparently is due to the capture of an electron by H^+ , allowing it to diffuse away from a B^- without having to overcome a long range coulomb attractive potential. We also demonstrate that the anomalous equilibrium debonding kinetics observed by Zundel et al.¹⁸ can be explained if debonding is always preceded by this minority carrier capture event ($H^+ \rightarrow H^0$ conversion).

EXPERIMENTAL

Samples for the present study were fabricated from <100>, CZ silicon, B doped in the range 1.6 to $7.5 \times 10^{15} \text{ cm}^{-3}$. A thin oxide (20 to 25Å) was grown in air at 500°C before 400 Å Al diode gate evaporation. Back contacts were sintered Al and had low enough resistance to allow accurate charge density profiling via 1 MHz capacitance techniques; in these measurements the measured negative depletion layer charge density was equated with the free (unpassivated) acceptor density. Extensive discussion of the caveats of this technique has been presented elsewhere^{2,6}. Hydrogenation of our diodes was accomplished by subjecting the diodes to a 1200 eV beam of H ions from a Varian sputter gun. Most of the ions which penetrate the Al gate have a remaining energy which is insufficient to displace a silicon atom from its lattice site; studies employing this technique have suggested that damage effects are minimal in this ion energy range^{6,19}. The resulting starting profiles of B·H pairs (see Figure 1) can be reproduced, even after dozens of implantation and annealing cycles. This particular H loading technique is therefore invaluable for carefully categorizing the effect of different annealing conditions.

In Figure 1a, the time dependence of the active acceptor density is shown for a series of equilibrium vacuum anneals (diode bias=0) performed at 145°C. Plots of $\log(B \cdot H)$ versus time are not linear (not shown) but have a much slower time dependence. Figure 2 illustrates this rather peculiar time dependence on a logarithmic plot; similar data have been reported by Zundel et al.^{3,17}. If anneals are carried out with reverse diode bias, B·H pairs dissociate quite rapidly in the depleted regions and hydrogen is driven deeper into the diode where it is bonded to previously unpassivated acceptors. Figure 1b illustrates this behavior; the B·H concentration (for $x=0.75 \text{ } \mu\text{m}$) displays a time dependence consistent with Eq. (1) and the temperature dependence of the debonding rate is displayed in Figure 3 along with similar data obtained by Zundel and Weber^{3,17}. Satisfactory agreement with their results is observed.

DISCUSSION

We now turn to the issue of the equilibrium debonding data. What is the origin of the slow time dependence seen in Figures 1a and 2? Apparently there is some rate limiting step to the dissociation process which is not present in reverse bias; is this just the rebonding of hydrogen with other, unpassivated acceptors? In order to compare the equilibrium debonding data with the first order debonding rates seen in reverse bias, we have plotted the inverse of the time required to debond $(1 - 1/e)$ of the B·H pairs at $V=0$ in Figure 3. This "effective" debonding rate is seen to be decades slower than that observed in reverse bias (Figure 3). A clue to understanding this situation comes from examining the data in Figure 2. Here we demonstrate that forward diode bias greatly accelerates the debonding process, while

leaving the functional form unchanged. Forward bias leaves the majority carrier density unchanged for $x > 0.5 \mu\text{m}$, and does not introduce any electric fields into this region. It does, however, inject excess minority carriers into the debonding region, and some previous studies^{20,21} on p/n and Schottky diodes have shown that this can accelerate BH debonding. Scharfetter has shown that for Schottky barriers, the injected minority carrier density at the depletion edge is given by²²:

$$n = \left(\frac{I_F}{I_R} + 1 \right) n_{eq}, \quad (2)$$

where I_F is the diode forward current, I_R the reverse saturation diode current, and n_{eq} the equilibrium minority carrier density. If the B·H dissociation rate were proportional to the minority carrier density, one might expect the time acceleration factors, f_A , of the curves in Figure 2 to be given by:

$$f_A = \left(\frac{I_F}{I_R} + 1 \right) \quad (3)$$

However, when a thin oxide barrier is present, some of the conditions assumed for the derivation of (2) do not hold; in particular, the concentration of electrons at the Si/SiO₂ interface is not constant, but will increase with forward bias²³. This means f_A will rise faster with I_F than predicted by (3), and for $I_F/I_R \gg 1$ it will be superlinear in I_F , as we observe (note the time shift values listed in the caption of Figure 2).

If we assume, for the moment, that minority carrier capture is a precursor to B·H dissociation in equilibrium, then:

$$k \propto n = \frac{n_i^2}{p} = \frac{n_i^2}{B - (B \cdot H)} \quad (4)$$

where p is the hole density, B is the boron density, and n_i the intrinsic carrier concentration. Thus, as B·H decreases, k will fall and kinetic behavior slower than first order is predicted. We have used a finite element analysis computer code (see ref. 2 for details) to simulate debonding, diffusion, and drift with a rate given by Equation (4). The results, shown as the dashed line in Figure 2, illustrate that the combined effect of a (B·H) dependent k and rebonding of H produce a time dependence for (B·H) which closely mimics the "anomalous" equilibrium and forward bias debonding data.

Assuming the existence of both positive and neutral charge states for H, how can we model the dissociation process? Starting with the ground state, neutral B·H defect, we expect that thermal dissociation of the hydrogen to a nearby tetrahedral, or a second nearest neighbor b.c. site will produce a correlated defect pair:

(5)

Further movement of the H^+ will be impeded by the long range coulomb interaction and rapid recombination is likely; however, if H^+ captures an electron, simple diffusion will allow the pair to become separated. We assume that in depleted regions of the diode almost all of the correlated BH pairs have a net negative charge, so charge capture is not the rate limiting step for dissociation. The activation energy observed for k will then be the sum of the dissociation and motional energies, as proposed by Zundel et al.^{3,17}, and k will have a simple phonon frequency prefactor, as found experimentally^{3,17}.

In equilibrium or forward bias, however, the hole population is large, and only a few correlated BH pairs will be in the negative state. However, if the energy required to put an electron on the neutral pair is less than the long range Coulomb barrier for separating the pair, charge conversion to $B^- H^0$ will represent the rate limiting step in the dissociation process. A crucial issue in modelling this separation process is whether steady state occupation of the H charge state is achieved on a time scale short compared with the time necessary for an H^0 to diffuse outside the coulomb capture radius of an ionized acceptor.

Using a Shockley, Read, Hall (SRH) analysis²⁴ for the occupation of H^0 and H^+ , we have previously shown that²⁵, in equilibrium, the fraction of neutral H sitting near to a B^- is:

$$\frac{B^- H^0}{B^- H} = \frac{n}{N_C} \exp\{-(E_C - E_{0/+})/kT\} \quad (6)$$

where N_C is the conduction band effective state density, and $E_{0/+}$ is the energy required to place an electron on an H^+ (sitting near a B^-). If dissociation only occurs when H^0 can diffuse away from B^- , this argument shows that the fraction of BH pairs which dissociate is inversely proportional to p ; this proportionality is precisely the one necessary to explain the data in equilibrium (figures 1a and 2).

The analogous SRH arguments for forward bias (where p is fixed but n increases) predict that $(B^- H^0)/BH$ will change with injection²⁵, but only under restricted circumstances. Either $E_{0/+}$ must lie within ~ 0.3 eV of E_C if the attempt frequency for hole emission is assumed to be the usual lattice frequency (10^{13} to 10^{14} sec⁻¹), or the attempt frequency must be considerably lower. This latter circumstance might hold if H charge change requires a large Si lattice relaxation, or perhaps even a site change. Both imply long H^0/H^+ equilibration times; at present we know of little experimental information which addresses this issue. A second approach to modelling our data would be to assume that dissociation always occurs whenever a $B \cdot H$ captures an electron. While this picture successfully describes the zero and forward bias data, it cannot explain the rapid debonding seen in reverse bias, since the electron concentration in depletion is lower than in the bulk

SUMMARY

In summary, it is clear that the local electronic equilibrium strongly influences the dissociation of boron-hydrogen pairs. The data is consistent with the assumption that hydrogen must be in the neutral state before full separation of the BH pair can be achieved, and this appears to explain the "anomalous" annealing kinetics seen by us and by Zundel et al.. More precise modelling of the dissociation process would be aided by a better understanding of the equilibrium lattice positions for neutral and positive hydrogen.

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FIGURE CAPTIONS

Figure 1. Negative charge density versus depth for a boron doped capacitor vacuum annealed at 145°C at zero diode bias (A) and at 115°C with -5 V diode bias (B). Total annealing time in minutes is shown next to each curve. The "virgin" state was achieved with a 200°C, 10 min. anneal. The sample was then hydrogenated by irradiating the front aluminum metallization at 297 K with 1200 eV H ions for 8 minutes at a system pressure of 3×10^{-5} Torr.

Figure 2. The fraction of boron acceptors which are H passivated versus annealing time for zero bias and forward bias vacuum anneals at 125°C. Forward currents were: $\circ$ 0, $\triangle$ 6 mA, $\diamond$ 12.2 mA, $\square$ 22 mA. The filled symbols are the forward bias data time-shifted by factors of 2.65, 14.5 and 36.5, respectively. The dashed line is a finite element analysis computer code fit using a debonding rate having the functional form given by equation (4) and a capture radius of 40 Å for recapture of debonded hydrogen.

Figure 3. Hydrogen debonding rates measured after reverse bias anneals (open squares) and the "effective", $(1-1/e)$, debonding rates measured after zero bias anneals (open circles). The dashed line is the reverse bias data of Zundel and Weber (references 3 and 17).

A. $T=145\text{ C}$

$V=0$

B. $T=115\text{ C}$

$V=-5\text{ V}$

DEPTH (μm)

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