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H Diffusion for Impurity and Defect Passivation: A Physical Model for Solar Cell Processing

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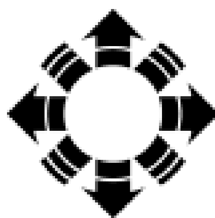

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H DIFFUSION FOR IMPURITY AND DEFECT PASSIVATION: A PHYSICAL MODEL FOR SOLAR CELL PROCESSING

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ABSTRACT

We propose a physical model for diffusion of H in Si containing impurities and defects. The diffusion occurs via several parallel mechanisms, involving complex formation (trapping) and dissociation (detrapping) at impurities and defects, hopping in lattice interstitial sites, and charge-state conversion. The role of bulk and process-induced traps is considered to explain observations from plasma, ion implantation, and PECVD-nitridation processes.

INTRODUCTION

Fabrication of efficient solar cells on commercial Si substrates involves gettering and passivation to mitigate deleterious effects of impurities and defects. Impurity gettering is extensively used through optimization of P-diffusion and Al-alloying needed for junction- and contact-formation, respectively. Even after the gettering processes are applied, significant concentrations of impurities and defects remain electrically active in the cell. Therefore, most commercial Si solar cell manufacturers apply hydrogenation as a technique to passivate residual impurities and defects. Over last two decades, a number of hydrogenation methods have been empirically optimized for solar cell passivation. These include ion implantation, plasma processing, forming gas anneal, and PECVD nitridation. Despite its success, the fundamental understanding of H passivation is still scarce. Concomitantly, it is difficult to design a hydrogenation process for maximum passivation.

In this paper, we address a fundamental problem that has restricted comprehensive understanding of hydrogenation processes—diffusion of H in Si. We elucidate various diffusion mechanisms in impure Si and present a mathematical model including these mechanisms. This model is applied to experimental data from a number of sources to develop a systematic understanding of the modifications of the diffusion behavior of H in Si by impurities and defects.

DIFFUSION OF H IN Si SOLAR CELL MATERIALS

Design of an efficient hydrogenation process must address two issues: (i) how to rapidly diffuse H deep into the bulk of the material, and (ii) how to facilitate a preferential interaction of the diffused H with “bad” impurities. These questions implicitly assume that we know “how much H is needed to do the passivation.” Some detailed answers to these questions will be published in forthcoming papers. Here we will primarily address the H diffusion issue.

Hydrogen diffusion into Si appears to be a mundane issue because it is often believed that diffusivity of H in Si is very high. This perception may be attributed to excellent work published by Van Weirengen and Warmoltz, who measured diffusivity (D_H) at high temperatures and expressed it as [1]:

$$D_H = 9.4 \times 10\text{-}3 \exp\{- 0.48 \text{ eV/kT}\} \text{ cm}^2\text{/s} \qquad (1)$$

When this expression is extrapolated to lower temperature range in which typical hydrogenation is done, it yields diffusivity of about 17^{-7} cm^2/s. This high value of D_H implies that a typical hydrogenation process at 400°C should require only a few minutes for H to diffuse through the entire thickness of a Si solar cell. However, in practice, the optimum time for hydrogenation by plasma processing ranges from 30 to 60 min, indicating significantly lower diffusivities. Lower values of D_H are also borne by measured diffusion profiles of H (or D) in wafers produced by plasma or ion implantation processes. The diffusivities determined from such data are several orders of magnitude lower than those of high-temperature extrapolated data.

Experimental observations have also revealed other interesting properties of H diffusion:

- D_H is different for different Si materials.
- D_H depends on impurities like C and O.
- Concentrations of H introduced by typical hydrogenation methods can far exceed the solubility of H in the Si lattice. Figure 1 shows a plot of solubility as a function of temperature calculated from the expression given in reference 1. The solubility at 400°C is only about 10^8 cm^{-3} and is lower at room temperature. However, as seen later in this paper, the H concentrations in excess of 10^{20} cm^{-3} are measured in hydrogenated samples. It is interesting to note that if the H concentration in Si was solely determined by the lattice solubility (from Fig. 1), low-temperature hydrogenation processes would not introduce sufficient H to passivate solar cells (which contain impurities in excess of 10^{13} cm^{-3}).
- Diffusion profiles are strongly controlled by the diffusion technique.

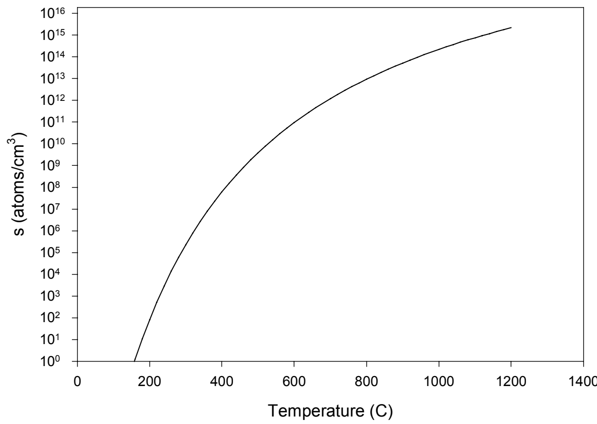

Fig. 1. Calculated solubility of H in Si Lattice as a function of temperature.

Thus, there appear to be many anomalies in the diffusion behavior of H in Si. Some of these have been attributed to trapping of H [2-7]. However, a coherent model for the trapping mechanisms is lacking. Here we briefly present a systematic diffusion model involving trapping mechanisms and effects of the hydrogenation technique. Because of the limited space, we will present only some selected examples to illustrate the significance of these mechanisms.

NATURE OF TRAPS

Hydrogen is electronically very active – it interacts with nearly all impurities and defects in Si to form complexes. Examples of complex formation include saturation of dangling bonds, dopant deactivation, and enhancement of oxygen donor formation [8]. In addition to its interactions with other impurities/defects in Si, H itself can form defects such as dimmers (H_2 and H_2*), platelets, and pile-up as an H-bubble at a relaxed lattice. These complexes are generally localized in the lattice (therefore referred to "stationary traps"). Formation of these complexes has a profound influence on the flow of H during its diffusion. In essence, these processes cause depletion of H from the diffusing flux by trapping or stagnation. The capture rates of H in formation of these complexes are much higher than the release rates. Thus, once formed at the processing temperatures, they are fairly stable with a low probability of dissociation (detrapping) and generally require higher temperatures to dissociate.

Because many trapping/detrapping processes can participate at a given temperature, they provide a number of parallel paths for flow of H. Each of these paths may have different temperature dependence. It is important to note that although many impurities and defects will interact with H, passivation of only some of them (minority-carrier lifetime killing) will have a positive impact on the solar cell performance. Indeed, some may even have a negative effect on the cell performance. For example, deactivation of dopants is not desirable because it alters the resistivity of the substrate. Other interactions, such as formation of H-vacancy complexes and formation of platelets, may also be harmful to the device performance. Hence, it is imperative that a hydrogenation process should promote association of H with only those impurities that have negative influence on the solar cell performance.

Figure 2 illustrates various bulk diffusion processes of H in Si. This figure depicts three types of diffusion mechanisms in the bulk of the material: the basic interstitial BC-to-BC diffusion (identified as the fastest path), trapping and detrapping at stationary traps, and diffusion via "mobile traps." Here, we propose the concept of "mobile traps" to account for formation of complexes such as a H-V (V = vacancy) pair that can readily diffuse and transport H [9,10]. This mechanism was proposed earlier to explain material-to-material variation in D_H.

The above discussion alludes to the bulk traps in the as-grown material caused by the growth process. To explain the variations in the diffusion profiles by different hydrogenation processes, we invoke a mechanism in which traps are generated by the hydrogenation process itself (we have called them process-induced traps or PITs). Typical examples of PITs are defects produced by ion implantation or by a plasma process. In some cases, the PITs can be "mobile" traps.

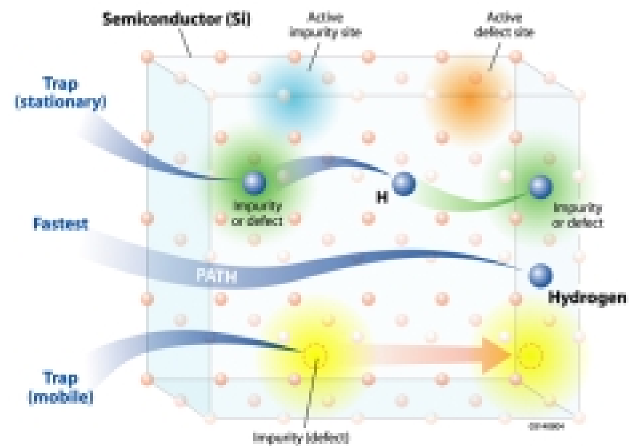

Fig. 2. A schematic illustrating various trapping processes for H in Si. The fastest path corresponds to hopping from BC sites.

From this model, the diffusivity of H in Si is expected to be controlled strongly by the impurities and defects in the lattice rather than the lattice diffusion itself [8]. It is clear that trapping behavior of material from different vendors will be different because they have different concentrations of impurities and defects. Furthermore, trapping (particularly near the surface) is greatly influenced by the hydrogenation process. Because H can associate itself with impurities and defects in Si, its effective "solubility" is much higher than in the perfect Si lattice. This is how we can explain high concentrations of H in the SIMS profiles (as seen later in this paper).

Although H will try to form complexes with nearly all impurities and defects, a passivation process must invoke

conditions that lead to preferential interaction of H with minority-carrier lifetime-killing impurities. An important property of traps is that their trapping and detrapping rates are temperature dependent. In particular, detrapping rate can increase at higher temperatures releasing free H to diffuse rapidly. This can be a valuable means of overcoming diffusivity limitation in which traps can be used as H storage devices.

THEORY

Mathematically, we can include trapping in the diffusion equations and write them as:

$$\frac{\partial[H_{untrapped}]}{\partial t} = D_H \frac{\partial^2 [H_{untrapped}]}{\partial x^2} - \frac{\partial[H_{trapped}]}{\partial t} \quad (2)$$

$$\frac{\partial[H_{trapped}]}{\partial t} = k[H_{untrapped}][T_{unoccupied}] - k'[H_{trapped}] \quad (3)$$

And, the following constraining conditions have to be satisfied:

$$[H_{tot}] = [H_{untrapped}] + [H_{trapped}] \quad (4)$$

$$[T_{unoccupied}] + [H_{trapped}] = [T_{tot}] \quad (5)$$

where $[H_{untrapped}]$ and $[H_{trapped}]$ are the concentrations of mobile and trapped H, $[H_{tot}]$ is the total H concentration, and $[T_{tot}]$ is the total trap density. This model goes beyond a simple fixed-trap model (developed earlier by several other groups) and takes into account mobile trapping, detrapping, charge state conversion, and PITs [11,12]. It invokes parameters corresponding to the following mechanisms: [a] trapping and detrapping processes are characterized by association rate (k) and dissociation frequency (k\`), [b] the association rate is expressed in terms of effective capture cross section, R_c as: $k = 4\pi R_c D_H$, where D_H is the diffusivity of untrapped H, and [c] C_s – concentration of untrapped H or D at the surface is determined by the hydrogenation process.

The boundary conditions, imposed by the hydrogenation process, are depicted below.

For plasma processes:

$$[H_{untrapped}]\Big|_{x=0} = C_s$$

For Implantation: (6)

$$-D_H \frac{\partial[H_{untrapped}]}{\partial x}\Big|_{x=0} = J_s$$

Usually, the sample is thicker than the penetration depth of H. The following boundary at $x = x_c$ was adopted, where x_c, the cutoff depth, is greater than the penetration depth of the H diffusion:

$$\frac{\partial[H_{untrapped}]}{\partial x}\Big|_{x=x_c} = 0 \quad (7)$$

We will use this theory to fit our experimental data as well as that published by others. The major objective is to apply this model to explain contributions to the H diffusion for different materials (different bulk properties) and for different process conditions (different PIT distributions).

EXPERIMENTAL

We have performed experiments on Si wafers obtained from different vendors to study the diffusion of H or deuterium under various process conditions. These include plasma, ion implantation, and PECVD nitridation. In some cases, the samples were annealed in multiple steps to examine the changes in the H or D profile and relate them to PITs. The specific results will be discussed in the next section.

A variety of measurements were performed on the hydrogenated samples including SIMS profiling, positron annihilation measurements, FTIR, and TEM analyses. The data are fitted with theoretical modeling and to obtain the parameter values that describe the theory. Interactions of theory and experiment, allowed us to develop a physical insight into our diffusion model.

SYNERGISM OF THEORY AND EXPERIMENT

We will apply this model to learn how a diffusion profile is influenced by various trapping mechanisms. We have previously shown that trapping causes the diffusion profile to deviate from a erfc profile. Furthermore, fitting a diffusion profile with erfc can yield unrealistically low values of D_H and high values of surface concentration [8].

First we apply our model to fit experimental data for a plasma process. Figure 3 shows D-profiles from reference [13], obtained on B-doped, FZ samples that were plasma hydrogenated at 200°C. The dotted lines correspond to data for samples hydrogenated for different durations – 5, 10, and 15 min. To fit these data, we assume PIT distribution for plasma processing to be exponential with a time-independent surface concentration. The total trap density has the following time dependence:

$$[T_{tot}] = T_0 e^{-\frac{x}{a+bt}} + T_b \,, \quad (8)$$

where the first time-dependent term is due to process damage and T_b is a constant bulk trap level. The best fits are obtained with $T_0 = 10^{21}$ cm^{-3}, a = 0.1 µm, b = 0.108 µm, and T_b = 1.3 x 10^{18} cm^{-3}. These results of fitting are shown in Figure 3 by the solid lines. The best fits are obtained if we assume the dissociation frequency, k' = 0.2. It should be noted that same parameters give excellent fit for experimental profiles for different times. To help understand the role of detrapping, Figure 3 also shows calculated results if no detrapping is assumed (k' = 0).

The next example we consider case of low-energy implanted sample. Figure 4 shows a measured deuterium profile (thick, dotted line) of a FZ sample, implanted at 250°C, at approximately 1.5 keV, for 30 min [12]. In this case we assume a PIT distribution function of:

$$[T_{tot}] = [T_0] \cdot \frac{t}{T} \cdot \exp\left(- \frac{(x - x_p)^2}{2\Delta x_p^2} \right) + [T_b] \quad (9)$$

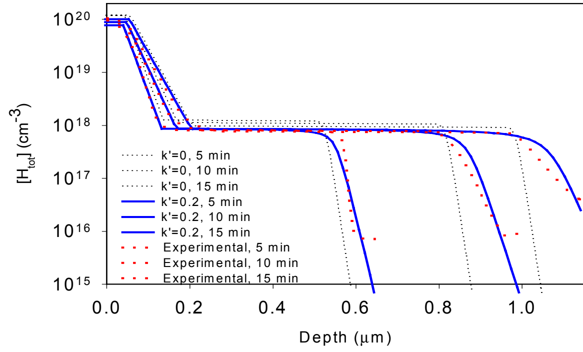

Fig. 3. Experimental data (dotted lines) and fitted with R_c = 10 A, C_s = 2.75 x 10^{14} cm^{-3}.

where, $[T_0]$ = 4.454 x 10^{20} cm^{-3}, T = 1800 s, x_p = 0.0367 μm, Δx_p = 0.028 μm, $[T_b]$ = 1.2 x 10^{17} cm^{-3}. These calculations are performed for different values of deuterium flux – ranging from 1.1 x 10^{12} to 1.11 x 10^{15} cm^{-2}/s. As expected, the near-surface distribution of D does not change with flux. But, there is a strong dependence of bulk distribution on the flux density. The best fit to the distribution in the bulk occurs for a flux density of 1.1 x 10^{13} cm^{-2}/s. However, there is a spreading of the diffusion profile at the knee of the curve. A good fit to the near-surface profile cannot be obtained unless one includes mobile traps.

To examine the characteristics of the process-induced mobile traps, we performed D implantation on different Si wafers at room temperature. The implantation was done at 40 keV. These samples were later annealed to examine the diffusion of the implanted profile. For example, Figure 5a shows D-profiles of as-implanted EFG wafer and after a 15 min. anneal at 300 ºC [14]. It is seen that annealing has produced a diffusion of D toward the surface as well as into the bulk. However, the surface concentration is "pinned" by the surface defects, leading to a "bump" in the annealed profile. Figure 5b shows similar plots for a p-type FZ wafer of the same resistivity as the EFG wafer. Notice that the diffusion causes the surface concentration to grow.

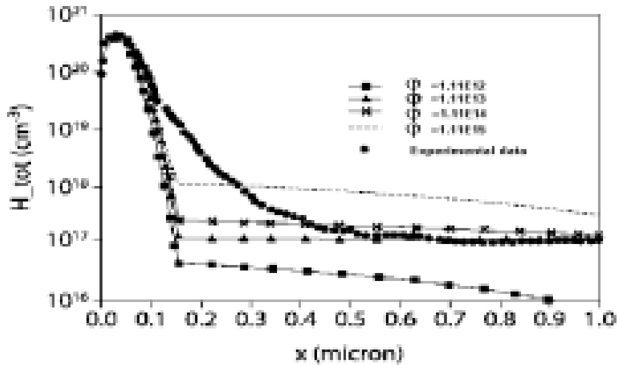

Fig. 4. Measured D-profile of a low-energy implanted Sample and the calculated profiles for different flux densities.

Using the insight from these experiments, we have fitted the experimental data of D-profiles produced by implantation using mobile PITs. Figures 6a and 6b show the experimental and calculated (best fit) profiles for CZ and EFG wafers, respectively. D implantation was done in a Kaufman system, at 1.5KeV and 300°C. The parameter values for flux and the mobility of the traps are shown in the insets. It is seen that the flux values are quite close to each other, whereas the diffusivity of the PITs are higher by an order of magnitude in CZ compared to EFG.

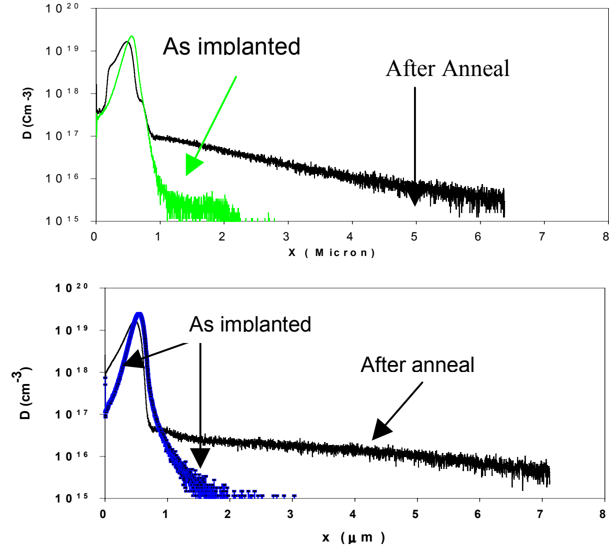

Fig. 5. D-profiles of as-implanted and annealed samples. upper – EFG ribbon, Lower- FZ wafer. Implantation was done at 40 keV, at room temp.

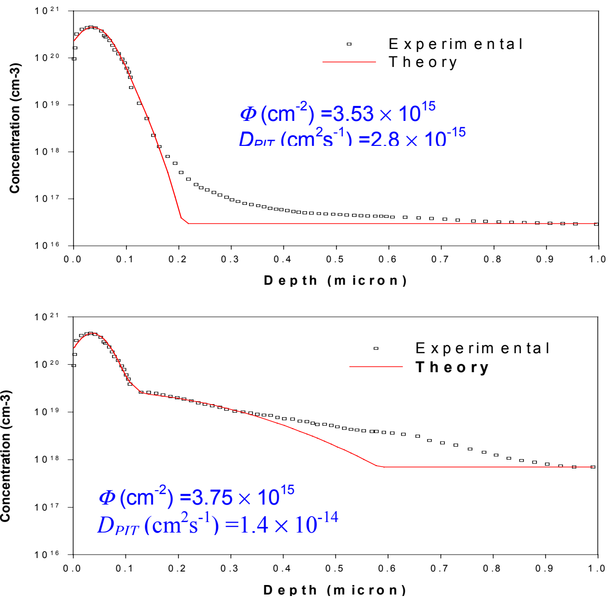

Fig. 6. Experimental and calculated profiles of D in CZ (upper) and EFG (lower) wafers. The best fits include mobile PITs.

We have also used this model to investigate diffusion of H during a PECVD nitridation process. In this process, a Si_3N_4 coating is deposited on a solar cell at a low temperature, typically about 300°C. Next, the cell undergoes a rapid thermal annealing (RTA) for a short time [15]. It is generally thought that H, required for passivation, is released form the nitride coating during RTA step and somehow diffuses into the solar cell. However, our analyses show that H is "stored" in the PITs produced by the plasma process until RTA redistributes the H rapidly within the wafer. Figure 7 shows the dynamic distributions of H during an RTA in which temperature of a nitride coated wafer is raised to 800°C. We assumed a 6-min plasma process for deposition of 780 A of nitride at 300°C. Other parameters are identified in the figure. It is seen that H diffusion is rapid and that in 10 s H has diffused through the entire wafer.

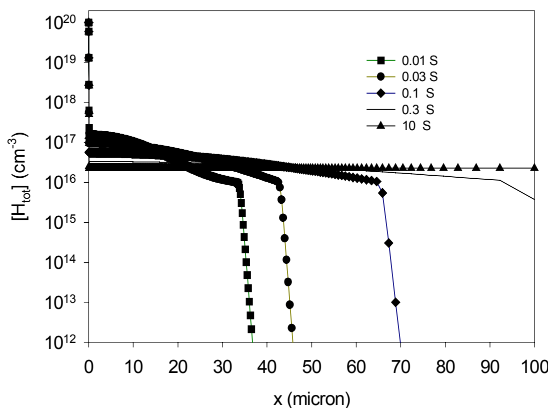

Fig. 7. Dynamic distributions of total H concentration during an 800ºC RTP anneal of a Si_3N_4 film deposited at 300ºC by a PECVD process. The bulk trap density, $N_b = 10^{16}$ cm^{-3}, $J_s = 0$, $R_c = 1$ A, $k' = 40$ s^{-1}.

CONCLUSION

We presented a physical model for trapping of H by impurities and defects in Si. This model explains many apparent anomalies of the behavior of H in Si, and provides insight into hydrogenation processes used for solar cell passivation. The results of theoretical modeling agree well with the experiment. Some of the results important to solar cell processing are:

- Traps retard hydrogen diffusion and can increase the effective solubility of hydrogen in Si. At low temperatures, trapping and detrapping is the dominant H diffusion mechanism in impure Si.
- Process-induced traps were invoked primarily to fit the diffusion profile at surface. However, PITs also play an important role by acting as a storage medium for hydrogen. For example, in a PECVD hydrogenation process, H is stored in the PITs during the initial phase of nitridation. It is then released during an RTA-like, high-temperature step, resulting in a deep passivation.
- An optimum passivation process demands conditions that cause little or no trapping (i.e. a high temperature) to promote a rapid, intrinsic diffusion of H. However, it is important to establish appropriate process conditions in which H will be favor association with only those impurities and defects that have harmful effects on the solar cell performance. Thus, a suitable ramp-down from the high temperature can be crucial in optimizing the passivation.

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