

# **H-Diffusion Mechanism(s) in PECVD Nitride Passivation of Si Solar Cells**

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# H-Diffusion Mechanism(s) in PECVD Nitride Passivation of Si Solar Cells

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## ABSTRACT

We have modeled diffusion of H in a two-step Si<sub>3</sub>N<sub>4</sub> passivation process invoking the concept of “storage” of H. The H stored during nitridation is redistributed during a subsequent anneal. The modeling results agree with this hypothesis, and the conclusions also appear to concur with the observations

## Introduction

Hydrogen passivation is now used extensively in commercial Si solar cell fabrication. Until recently, hydrogenation of solar cells was done as a separate solar cell fabrication step using either low-energy ion implantation or plasma processing. Plasma-enhanced chemical vapor deposition (PECVD) nitridation has enabled simultaneous deposition of Si<sub>3</sub>N<sub>4</sub> (as an antireflection coating) and hydrogenation of the solar cell. However, a detailed understanding of the mechanisms involved in such a process is lacking. Concomitantly, each vendor optimizes the hydrogenation process empirically.

Recently, it was suggested that hydrogenation occurs during rapid thermal processing (RTP) when H released from Si<sub>3</sub>N<sub>4</sub> diffuses into Si. This explanation does not consider H diffusion into Si during the nitridation itself. Here we show, through quantitative modeling, that H can be introduced into traps near the surface of Si solar cells during nitridation. This “stored” H is de-trapped and redistributed during subsequent RTP anneal. This mechanism explains most observations related to solar cell passivation.

## Hydrogen diffusion issues and modeling

A good passivation process demands that H diffuse deep into the material so that the entire cell is passivated. However, it is a common experience that process temperature and time, required for optimizing H passivation, are much higher than expected on the basis of diffusivity of H in Si. It is now known that this behavior is a direct result of H trapping by dopants, crystal defects, dangling bonds, point defects, and process-induced traps (PITs). Thus, in a low-temperature plasma process, traps can serve as “storage” sites for H. These traps form complexes with H that are stable at low temperatures. However, at higher temperatures, these traps can dissociate, releasing H that can diffuse rapidly in the Si lattice [1]. We use this concept to explain the diffusion of H accompanying nitridation and RTP anneal. Now, we show some results of modeling that suggest that plasma deposition of a Si<sub>3</sub>N<sub>4</sub> film, typically about 900 Å, can introduce ample H near the surface of the

solar cell which, upon diffusion during a subsequent high-temperature (~800 °C) anneal, can provide passivation of defects and impurities.

## Passivation by nitridation

H is introduced into Si<sub>3</sub>N<sub>4</sub> from deposition reactants such as NH<sub>3</sub>, SiH<sub>4</sub>, and SiH<sub>2</sub>Cl<sub>2</sub>, and is chemically bonded to Si and N. A typical nitridation process uses an RF plasma, a Si-bearing gas like trichlorosilane, and ammonia as a carrier gas. The deposition is typically done at about 300°-400°C for about 10 minutes. After the deposition, the cell is heated in an RTP-like process that is part of the contact formation step.

We envisage the following processes to occur in this two-step method: during Si<sub>3</sub>N<sub>4</sub> deposition, H is “stored” near the surface by the traps present in the material. We assume a PECVD process results in PITs that are primarily confined near the surface. A typical total trap density may be described by the following expression:

$$[T_{tot}] = T_0 \exp\left[-\frac{x}{a+bt}\right] + T_b,$$

where the first time-dependent term is due to process damage and T<sub>b</sub> is a constant bulk trap level. We should emphasize that there is a diffusion of H, but because of the traps, the H is primarily confined in the vicinity of the surface.

The second step of the process is to perform a higher temperature diffusion. In this step, a part of the “stored” H is rendered free and diffuses deep into the bulk of the cell or wafer. It is important to recognize that the bulk traps can exercise a high degree of influence on this diffusion. But, because the higher temperature is associated with a higher de-trapping rate and (perhaps) a lower trapping rate, the diffusion can exhibit properties that are close to that of perfect Si.

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

$$\frac{\partial[H_{untrapped}]}{\partial t} = D_H \frac{\partial^2[H_{untrapped}]}{\partial x^2} - \frac{\partial[H_{trapped}]}{\partial t}$$
$$\frac{\partial[H_{trapped}]}{\partial t} = k[H_{untrapped}][T_{unoccupied}] - k'[H_{trapped}]$$

We can impose the following conditions describing the interaction of H and traps:

$$[H_{tot}] = [H_{untrapped}] + [H_{trapped}]$$

$$[T_{unoccupied}] + [H_{trapped}] = [T_{tot}],$$

where  $[H_{untrapped}]$  = concentration of mobile H,  $[H_{trapped}]$  = concentration of trapped H,  $[H_{tot}]$  = total H concentration, and  $[T_{tot}]$  = total trap density.

Here,  $k'$  is the dissociation frequency and  $k$  is the association rate. In our calculations, we will assume a reasonable value of dissociation frequency (see results and discussion section). The association rate can be expressed in terms of the effective capture cross-section (radius),  $R_c$ , as  $k = 4\pi R_c D_H$ . These equations can be solved under the appropriate boundary conditions discussed in reference 2.

### Results and discussion

Figure 1 shows the dynamic H-profiles resulting from a PECVD process performed at 300°C for different times, up to 6 minutes. The wafer is assumed to have a bulk trap density of  $10E17 \text{ cm}^{-3}$ . From this figure, we can see that after 6 minutes H diffuses to a depth of 11  $\mu\text{m}$  with a concentration equal to that of the bulk trap density. Figure 1 includes an inset of a magnified profile above the H concentration of  $1E17 \text{ cm}^{-3}$  to show how the diffusion occurs near the surface. It is seen that near the surface, the H profile is controlled by the PIT density. Our calculations assume that atomic H is continually available at the surface during nitridation to maintain a surface concentration of  $2.75E14 \text{ cm}^{-3}$ . This value has been determined from the best-fit data as discussed in reference [2]. It may be pointed out that this process step is similar to a pre-deposition for a P or B diffusion.

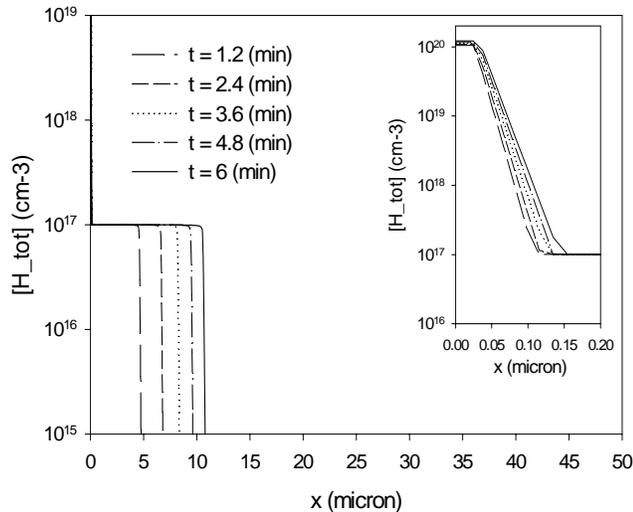


Figure 1. Calculated dynamic profiles of H resulting from the nitridation step.

The diffusion profiles during the second step of the process are shown in Figure 2. Again, these profiles are shown for different times up to 10 s, following the initiation of a rapid thermal anneal. We see that a 10 s anneal at 800°C can diffuse the H as much as 35  $\mu\text{m}$  into the bulk of the wafer. We should point out that our assumption of the absence of H-diffusion across the Si-Si<sub>3</sub>N<sub>4</sub> interface is not a limitation in modeling, but simply the fact that there is no specific information to indicate otherwise.

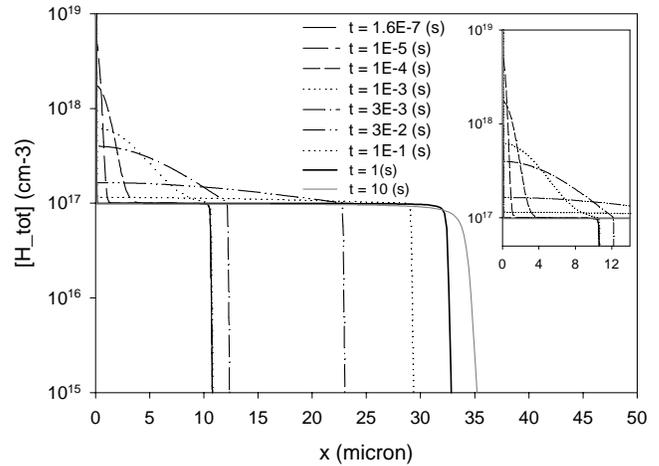


Figure 2. Calculated dynamic profiles of H in an RTP anneal.

We have performed calculations for many cases, from which we can summarize some salient conclusions.

- Si<sub>3</sub>N<sub>4</sub> passivation is a two-step diffusion process. The deposition step is accompanied by a shallow diffusion of H in which H is “stored” near the wafer surface. The profile of the H is controlled by the PIT density, whereas the depth of such diffusion is determined by the bulk trap density.
- In the anneal step, the source of H can be simply the indiffused H. It may be pointed out that while H will be depleted out of Si<sub>3</sub>N<sub>4</sub> film during this step, there is no indication that any H from this film is going into the wafer. A simple redistribution of H is sufficient for effective passivation.
- The diffusion depth of H upon annealing is strongly controlled by the bulk trap density. For example, if the bulk trap density is  $1E16 \text{ cm}^{-3}$ , the H will permeate through the entire wafer in a 1 s anneal at 800°C. This is in agreement with experimental observations [3].
- Because the trap density and distribution play a dominant role in the diffusion of H, it is clear that lower trap density material will require shorter anneal time or lower temperature. Likewise, higher pre-deposition temperatures during deposition can help introduce higher H content necessary to passivate higher trap and impurity concentrations. An interesting effect of the RTP step is that it can anneal out the plasma-process-induced defects, making the H available for passivation.

### REFERENCES

- [1] B. L. Sopori, Y. Zhang, and N. M. Ravindra, “Si device processing in H-ambients :H-diffusion mechanisms and influence on electronic properties,” *J. Elec. Mat.*, to be published
- [2] Y. Zhang, B. L. Sopori, and N. M. Ravindra, “Modeling low-temperature diffusion of H in Si: influence of impurities and defects,” *Procd. 11<sup>th</sup> Workshop on Crystalline Silicon Solar Cell Materials and Processes, Estes Park, CO, Aug. 19-22, 2001*, pp 279-284.
- [3] A. Rohatgi, private communications.