

# Mechanism(s) of Hydrogen Diffusion in Silicon Solar Cells during Forming Gas Anneal

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# MECHANISM(S) OF HYDROGEN DIFFUSION IN SILICON SOLAR CELLS DURING FORMING GAS ANNEAL

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## ABSTRACT

Surface damage in a silicon wafer, produced by mechanical polishing or ion implantation, is shown to mediate diffusion of hydrogen from a molecular ambient such as a forming gas. Experimental results show that the formation of a  $N^+$  region of a solar cell can produce significant surface stress similar to mechanical polishing. Results of hydrogen diffusion produced by forming gas annealing of various commercial photovoltaic silicon substrates and cells are discussed.

## BACKGROUND

Recently, several researchers have reported that the performance of some low-cost silicon solar cells improves upon annealing in a forming gas (FG) atmosphere [1-3]. Preliminary work has shown that this improvement is caused by an increase in the red response of the cell and that hydrogen is indeed responsible for the improvement because annealing without hydrogen does not produce the same effect. Thus, it is tempting to attribute the improvement in the cell performance to passivation of impurities and defects by hydrogen diffusing as a molecular species ( $H_2$ ). But, it is difficult to reconcile with this explanation because: (1) the diffusivity of molecular hydrogen in silicon is extremely small, (2) even if molecular hydrogen did diffuse in, it must dissociate before it can couple with impurities and defects in configurations that can passivate them, and (3) there is evidence that  $H_2$  may even be detrimental to the cell performance.

To circumvent the difficulties in invoking molecular diffusion, two arguments were vaguely suggested. First, the presence of Al may generate atomic hydrogen in a manner similar to that used to explain improvement in the quality of oxide in MOS devices. However, this argument is quite weak and suggests that absence of Al can abate the passivation effect. Second, the bulk defects may somehow be responsible for converting molecular hydrogen into atomic hydrogen.

There are also reports of improvement in the minority-carrier diffusion length in as-grown wafers of Polyx and Wacker without a junction. However, this process required extended annealing times and that improvements

on substrates having no N/P junctions were only modest [2]. Another partial explanation has been that hydrogen can be adsorbed at the surface of a wafer if the surface of the wafer has microcracks[4]. It has been speculated that grain boundaries and dislocations have microcracks at the surface sites where they terminate, that can lead to local adsorption.

Recently, we proposed that the surface damage, such as that introduced by phosphorus diffusion, may be responsible for the dissociation of the molecular hydrogen[3]. This paper describes experimental verification of damage-mediated diffusion of hydrogen in silicon from a molecular gas. We show that a small degree of surface damage can act as a catalyst to facilitate deep diffusion of hydrogen. An explanation of this mechanism is given. We show that the degree of damage similar to that introduced by a phosphorous diffusion, e.g., performed at 850°C, is indeed responsible for mediating diffusion of hydrogen from a molecular ambient.

## EXPERIMENTAL DETAILS

We performed experiments in which FG anneals were done on silicon samples with and without surface damage. A variety of P-type samples from different vendors were used. They consist of CZ, FZ, EFG ribbons, and laser recrystallized ribbons (LRR). The annealing was done in two types of forming gas:  $N_2 + H_2$ , (FGH) or  $N_2 + D_2$  (FGD); the latter is more sensitive to SIMS profiling. The damage was produced in two different ways. (1) Mechanical polishing was used with different sizes of alumina grit. The samples were first polished by chemical-mechanical polishing to produce a damage-free flat surface. Next, the samples were mechanically polished with alumina powder of various grit sizes, in the range of 0.01  $\mu m$  to 10  $\mu m$ , using very little pressure. Mechanical polishing was done either by hand on a Suba IV pad, on a pad with bonded grit, or on an automatic polishing machine with minimum pressure. (2) We also used a low-energy H implant and partially removed the implanted hydrogen by annealing the samples in an argon ambient at 500°C for 60 min. Although this process did not completely diffuse the hydrogen out of the samples, this approach is useful in evaluating the effect of uniform damage. The samples with a controlled surface damage were annealed in FG at

400°C for 1 h, followed by a rapid cool down. Samples with N<sup>+</sup>/P (P- diffused) were also included for FG anneal — in this case no mechanical polishing was applied.

The samples were analyzed by a number of techniques for the surface damage and surface roughness, hydrogen and deuterium diffusion profiles, and for the minority carrier lifetime. These include: SEM, TEM, XRD, Quasi-Steady state PCD, and Fourier Transform Spectroscopy. SIMS measurements were taken in a CAMECA machine. A Cs beam was used for H and D profiling. In some cases, a high etch rate was used to improve the background detection limit.

## RESULTS

It is important to point out that polishing produces two effects: a roughness of the surface, and a lattice damage or distortion (a stress). The surface roughness is a function of a variety of polishing parameters including the size and hardness of the grit, pressure, and qualities of the pad. The maximum surface roughness produced by various grit sizes is shown in Figure 1. These measurements were made by an SEM and a surface profilometer such as Dektak. However, the average roughness is much smaller than the maximum value, but it is difficult to quantify. The degree of lattice distortion is rather complicated. We are in the process of quantifying the “damage” by techniques such as RBS, X-ray analysis, and surface recombination velocity; some results of XRD are given later in the paper. The surface damage produced by grit polishing is typically not uniform. Figure 2 is an SEM photograph of a FZ sample polished with a 0.3 μm grit for 20 minutes. The polishing has produced a series of submicron, localized scratches. A much higher uniform damage is produced by ion beam implantation.

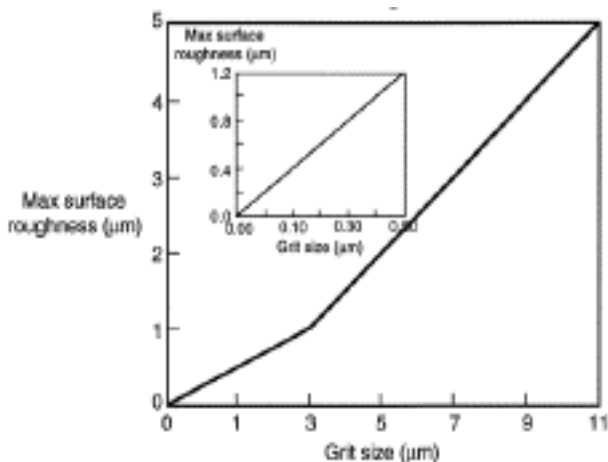


Figure 1. Graph of the **maximum** surface roughness as a function of the grit size. It is important to point out that the average roughness is much smaller than the maximum value.

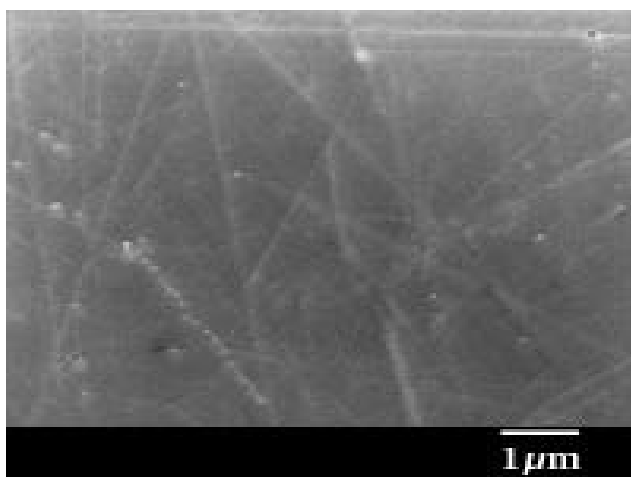


Figure 2. SEM photograph of a FZ sample with a 0.3 μm grit.

Figure 3 shows deuterium profiles of two adjacent samples from an EFG ribbon—one without surface damage and the other with a surface damage produced by a 10-μm grit size. This figure clearly shows a deep diffusion of hydrogen in the damaged sample (Note: the average value of surface roughness due to our 10-μm grit-polishing was estimated to be < 2 μm). A further

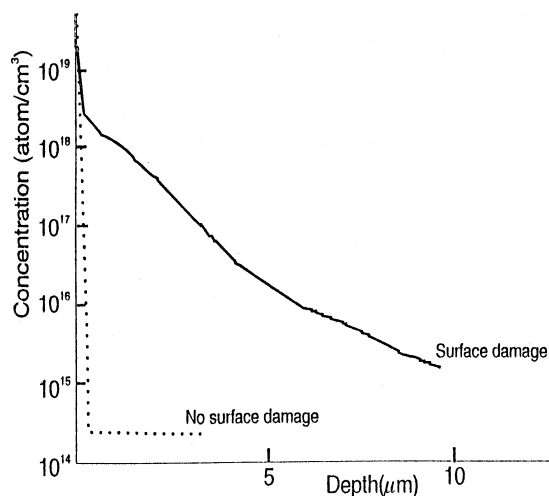


Figure 3. Comparison of SIMS deuterium profiles in an EFG ribbon by a FG(D) anneal with and without surface damage. The surface treatment was introduced by a 10μm Al<sub>2</sub>O<sub>3</sub> grit that produced an average surface roughness < 2 μm. Lack of surface damage produced little deuterium diffusion.

verification of hydrogen diffusion was made by performing FTIR measurements. Figure 4 shows the FTIR spectrum of a surface-damaged EFG sample after hydrogenation by annealing in a FG(H) ambient at 400°C for one hour. The important point is that the hydrogen diffusion takes place

far beyond the roughness of the surface. Figure 5 compares D profiles in four LRR samples in which the surface damage was introduced by different grit sizes. The surface damage in these samples was produced by 0.015- $\mu\text{m}$ , 0.05- $\mu\text{m}$ , 0.1- $\mu\text{m}$ , and 0.3- $\mu\text{m}$  grit sizes. As expected, it is seen that an increase in the surface damage increases the depth of diffusion as well as the solubility of D (i.e., surface concentration) at the surface. Somewhat surprisingly, the diffusivity of D increases with the damage. This feature is, however, in agreement with our diffusion model that includes hydrogen diffusion via a {H-V} mechanism.

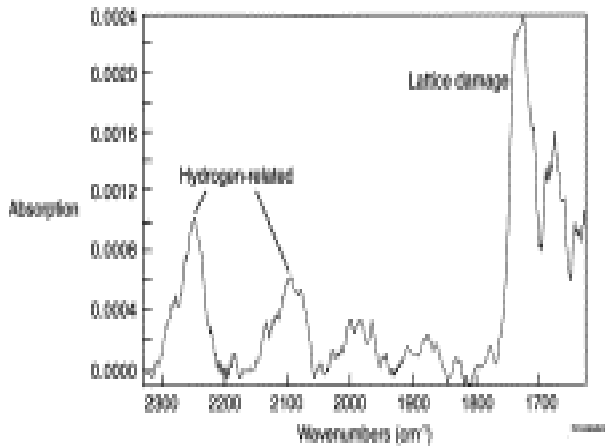


Figure 4. FTIR spectrum of a surface damaged EFG sample after a hydrogen anneal by FG( $\text{H}_2$ ). The hydrogen absorption bands are seen at  $2100\text{ cm}^{-1}$  and  $2250\text{ cm}^{-1}$ . Additional lattice damage is also observed.

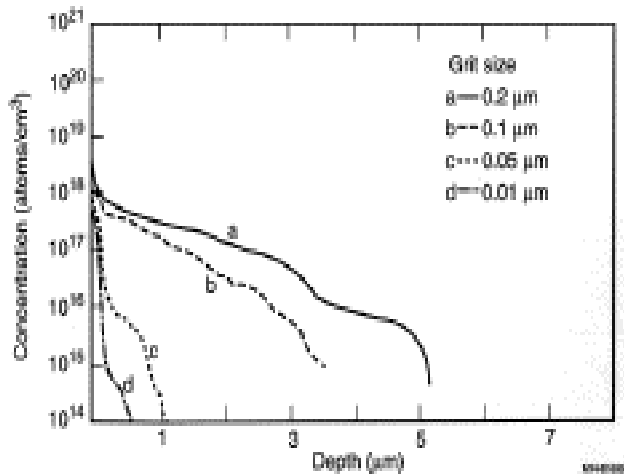


Figure 5. SIMS deuterium profiles of LRR ribbons polished with different size grits.

Figure 6 compares diffusion profiles of D in FZ and CZ samples (nominal  $= 5\text{ cm}$ ); both these samples had damage introduced with 0.3- $\mu\text{m}$  grit size. This figure

displays two important features: (a) small damage produced by a 0.3  $\mu\text{m}$  grit polish provides a means for H diffusion, and (b) as shown previously, the effective diffusivity of H in FZ material is higher than in the CZ material. From TEM cross-sectional analyses, we found that polishing with a grit size of 0.2 - 0.3  $\mu\text{m}$  produces damage very close to that of the P diffusion. These

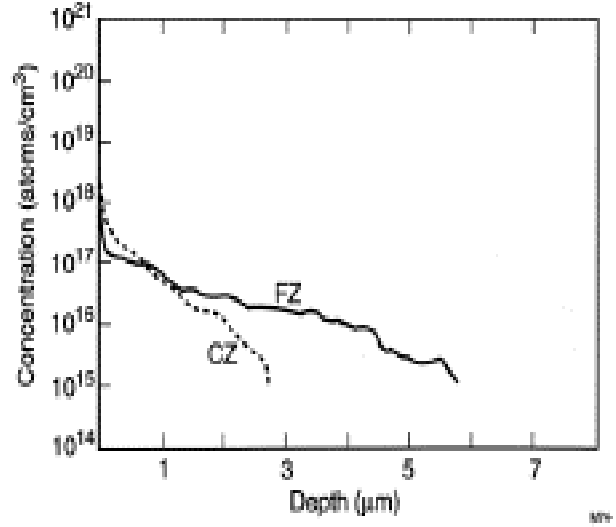


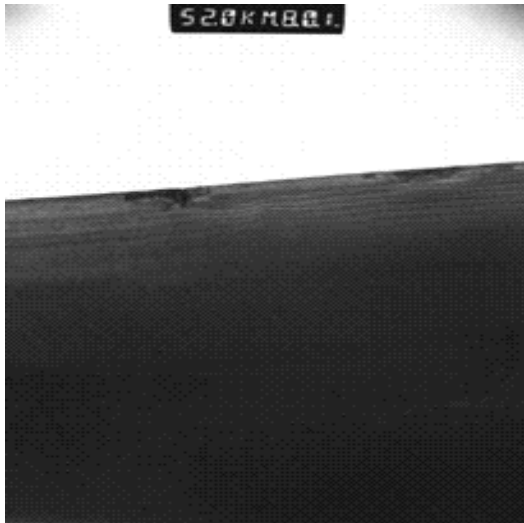
Figure 6. SIMS deuterium profiles of 0.3  $\mu\text{m}$  grit damaged FZ and CZ samples.

results can be seen from Figures 7a and 7b, which show XTEM photographs of one sample with an  $\text{N}^+$  diffusion and the other with a 0.3- $\mu\text{m}$  grit size polish followed by a FG anneal. The photo in Fig. 7a shows formation of an extrinsic stacking fault and stress arising from a precipitate. A similar localized stress is also seen in Fig. 7b arising from mechanical polishing.

A similar observation can be made from the XRD results. Figure 8 shows the results of XRD using a grazing angle incidence for three ASE samples - (a) as-grown substrate, (b) with a 0.3- $\mu\text{m}$  polish, and (c)  $\text{N}^+$  surface after a phosphorus diffusion. The grains were selected to have the same orientation, and the diffraction corresponds to the family of (100) planes. This figure qualitatively demonstrates the degree of average surface damage in terms of a shift in the peak position. The average strain associated with the  $\text{N}^+$  region appears to be significantly large compared to that produced by the mechanical polishing with a 0.3- $\mu\text{m}$  grit.



a)



b)

Figure 7. XTEM showing stress from a) precipitate b)mechanical polish

As may be expected, the degree of damage caused by polishing with a given grit size can vary with the method of polishing, producing a profound effect on the diffusion profile of H(or D). Figure 9. compares the diffusion profiles corresponding to two different ways of polishing with a grit size of  $0.3\mu\text{m}$  - hand polishing for two minutes (referred to as light polish) and machine polishing for 20 minutes (referred to as heavy polish). The samples consisted of CZ wafers and ASE ribbons. A significantly deeper diffusion resulting from a heavy polishing is evident in the figure. A deep diffusion of H also occurs if the damage is produced by implantation.

It is interesting to note that the relative diffusivity of various samples follows a trend that was previously observed with H implantation, and explained on the basis of H-V diffusion mechanism

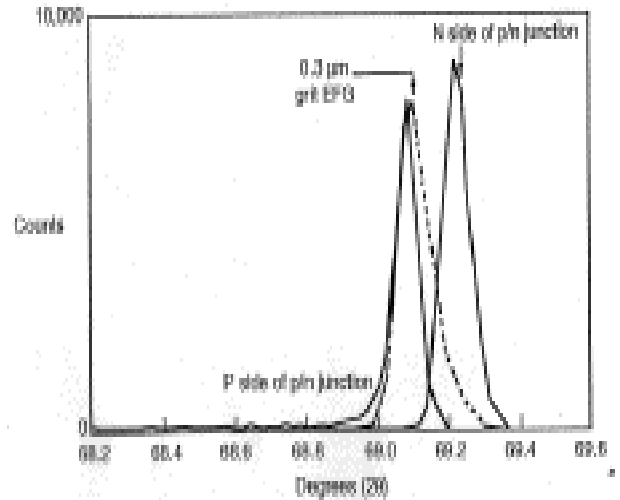


Figure 8. XRD thin film grazing angle incidence of p-side of p/n junction,  $0.3\mu\text{m}$  grit and n-side of p/n junction respectively . A shift and broadening of the 2 peak is observed depending on the treatment.

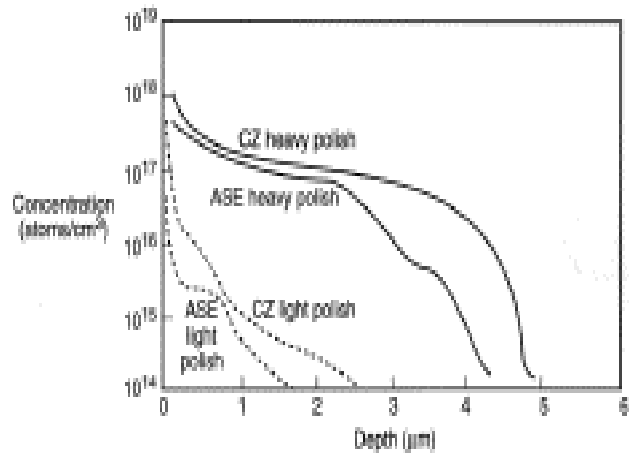


Figure 9. H-profiles of CZ and ASE ribbon with a heavy polish and light polish. A deeper diffusion occurs with the heavy polish for both types of samples.

We have also measured H profiles of a variety of samples consisting of: solar cells fabricated on ASE ribbons which have PECVD nitride with and without an RTP step; and N/P junctions annealed in FG, with and without Al alloying. These results show that hydrogen diffusion deep into the bulk of the cell can occur in some samples. The diffusion depends not only on the material but also on the process parameters used for nitridation, junction formation, and Al alloying. Because of the limitations on the length of this paper, the details of these results cannot be included here but will be given elsewhere[5].

## MECHANISM OF H DISSOCIATION AND DIFFUSION

We believe that surface damage is responsible for the dissociation of molecular hydrogen. Specifically, the surface damage has two contributions to facilitate diffusion of hydrogen: First, it releases vacancies during annealing that can spontaneously dissociate the  $H_2$  molecule. Theoretical calculations, based on *ab initio* considerations, suggest that there is no formation energy involved in such a process[5]. Figure 10 illustrates schematically the lattice configurations where the presence of vacancy (dotted circle) in a strained silicon lattice containing a hydrogen molecule can lead to reconstruction of bonds to produce dissociation of an  $H_2$ , and formation of Si:H bonds. The dissociated hydrogen can also associate with defects and traps. Thus, we hypothesize a reaction that  $H_2 + V \rightarrow \{H-V\} + H$ . Unfortunately, at this time it is not known what the dominant charge states of  $\{H-V\}$  and H are. However, from theoretical considerations, it is known that a neutral  $\{H-V\}$  can diffuse very rapidly in the silicon lattice. We also believe that at lower temperatures  $\{H-V\}$  is the dominant

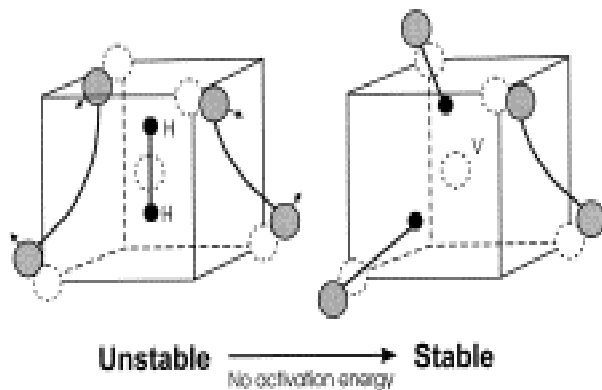


Figure 10. Illustrates how to produce dissociation of an  $H_2$  and formation of Si:H bond. The presence of a vacancy is noted by the dotted circle.

diffusion mechanism that leads to higher diffusivity of hydrogen in materials with high non-equilibrium concentration of vacancy-related defects. The second role of surface damage is to increase the solubility of hydrogen at the surface, producing a hydrogen-rich layer that acts as the source of hydrogen. Because the solubility of hydrogen will increase with increased damage, the net hydrogen flux diffusing into the wafer will also increase with damage. Because the molecular hydrogen is dissociated into  $\{H-V\}$  and H species, and both of these can independently diffuse into the Si lattice, it is likely that the damage-induced diffusivity can be higher than that observed in the case of hydrogen diffusion by other techniques. This is supported by the experimental observation of varying diffusivities of H or D by numerous researchers.

## DISCUSSION

Surface damage appears to be responsible for dissociation of molecular hydrogen during a forming gas anneal of solar cells at low temperatures. The dissociated hydrogen may diffuse via a  $\{H-V\}$  or interstitial mechanisms. The  $\{H-V\}$  mechanism favors higher diffusivity in vacancy-rich materials such as rapidly-grown ribbons, and materials containing low concentration of oxygen and high concentrations of carbon. Because the degree of the damage in a phosphorous diffused junction depends on the surface concentration of P, the junctions fabricated at higher temperatures may favor deeper hydrogen diffusion during a FG anneal. Surface damage may also be involved in PECVD passivation process [6].

Clearly, a process such as forming gas anneal for passivation has a lot of commercial importance. It can be a low-cost process compared to any other hydrogenation technique such as implantation, plasma processes, and PECVD. However, it is important to understand how such a process works before it can be fully exploited. We have verified that hydrogen diffusion is mediated by surface damage. The passivation properties were also verified; the lifetimes ( $\tau$ ) of samples before and after FG anneals, and with and without surface damage, were measured using the PCD technique. These results showed that FG anneal led to a large increase in  $\tau$  in the samples with surface damage, whereas no improvement was seen in undamaged samples. Our results suggest that in the absence of a junction, a FG anneal will not improve the minority-carrier lifetime of a wafer. This is indeed the observation made by researchers who found that FG anneals can improve  $\tau$  only when the samples have an  $N^+$  junction. They speculated that a field-aided diffusion could be responsible; however, this argument may have validity only for H or D that is already in the lattice.

It is important to point out that in a process where Al alloying and FG treatments are made in one step, Al can favor diffusion of hydrogen through an increased population of  $\{H-V\}$  species. This increased formation is expected to be due to injection of vacancies from the Si-Al interface during an alloying process. Our model also predicts that FG anneal will not produce the same degree of passivation in all materials. This is because diffusivity of these materials is different and depends on factors such as concentrations of oxygen and carbon, and the concentration of vacancy-related defects.

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