

Hydrogenation of Si from $\text{SiN}_x(\text{H})$ films: Characterization of H introduced into the Si

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A promising method to introduce H into multicrystalline Si solar cells in order to passivate bulk defects is by the postdeposition annealing of a H-rich, SiN_x surface layer. It has previously been difficult to characterize the small concentration of H that is introduced by this method. Infrared spectroscopy has been used together with marker impurities in the Si to determine the concentration and depth of H introduced into Si from an annealed SiN_x film. © 2003 American Institute of Physics. [DOI: 10.1063/1.1598643]

Hydrogen is commonly introduced into multicrystalline Si solar cells to reduce the deleterious effects of defects and increase the minority carrier lifetime.^{1–8} A promising method to introduce H is from a hydrogen-rich (~20 at. %) layer of SiN_x that is deposited onto the Si to act as an antireflection coating.^{4–8} A postdeposition anneal is used to diffuse H from the SiN_x layer into the Si in order to hydrogenate defects in the bulk Si. Unfortunately, it has been difficult to detect directly the H that is introduced because of its small concentration. Therefore, the effectiveness of the hydrogenation that results from the postdeposition annealing of SiN_x layers has remained controversial. For example, there are model calculations that suggest that H concentrations near $5 \times 10^{16} \text{ cm}^{-3}$ can be introduced into bulk Si from a SiN_x layer,⁹ while other recent studies question whether bulk hydrogenation from SiN_x occurs at all.¹⁰ Furthermore, the indiffusion of H into Si is often limited by trapping,¹¹ making the appropriate effective diffusion constant to describe the penetration depth of H uncertain.

In the present letter, a method that combines IR spectroscopy with marker impurities that can trap H in Si is used to determine the concentration and depth of H that is introduced into Si from a SiN_x layer. Pt impurities are used as model traps for H because the Pt–H complexes in Si are thermally stable (up to 650 °C) and their H vibrational absorption lines have been identified.¹² Furthermore, the intensities of the Pt–H IR lines have been calibrated so that the concentration of H in the Si sample can be estimated.¹³

To increase the sensitivity of vibrational spectroscopy for the detection of small concentrations of H-containing defects, IR absorption measurements have been made for samples in a multiple-internal-reflection (MIR) geometry. Samples with dimensions $15 \times 18 \times 1.5 \text{ mm}^3$ were made from lightly doped Si grown by the floating-zone method. The

ends of the samples were beveled at 45°. The probing light was introduced through one of the beveled ends so as to be multiply reflected many times from the internal surfaces as it passes through the sample (Fig. 1).

Pt impurities, to be used as traps for H, were diffused into the Si samples at a temperature of 1225 °C. The resulting Pt concentration is estimated to be $\sim 10^{17} \text{ cm}^{-3}$ from solubility data in the literature.¹⁴ SiN_x layers were deposited onto the Si samples either by plasma-enhanced chemical vapor deposition (PECVD)⁷ or by hot-wire chemical vapor deposition (HWCVD).¹⁵ The substrate temperature for the depositions was $\sim 300 \text{ °C}$ and the nitride layer thicknesses were $\sim 80\text{--}100 \text{ nm}$. Samples were annealed in a tube furnace in an ambient of flowing N_2 . IR absorption measurements were made with a Bomem DA3 Fourier-transform infrared spectrometer equipped with a KBr beamsplitter and an InSb detector. Samples were cooled for IR measurements to near 4.2 K with a Helitran, continuous-flow cryostat.

IR spectra are shown in Fig. 2 for a Si:Pt sample onto which a SiN_x layer had been deposited by HWCVD. The broad band centered at 2160 cm^{-1} is due to Si–H bonds in the H-rich SiN_x layer.¹⁶ For anneals performed at succes-

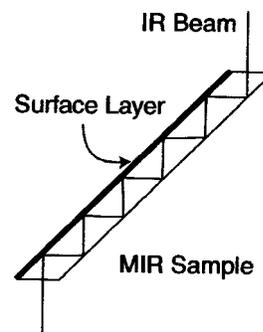


FIG. 1. Multiple-internal-reflection geometry used for IR measurements of Si samples hydrogenated from a SiN_x surface layer.

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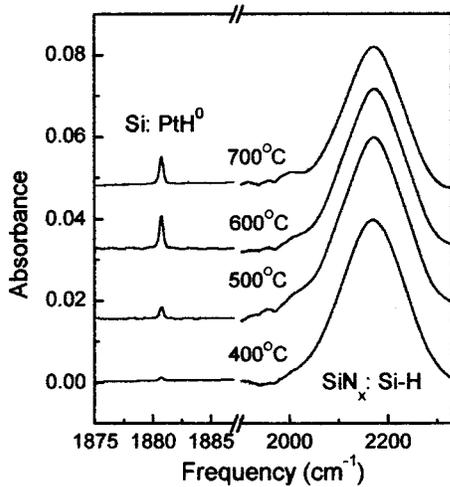


FIG. 2. IR spectra for a bulk Si:Pt sample with a SiN_x layer deposited on its surface by hot-wire CVD. The sample was annealed (10 min) at the indicated temperatures to introduce H into the Si. Vibrational lines assigned to Si-H bonds in the SiN_x layer and to PtH complexes in the Si are shown.

sively higher temperatures, the Si-H band from the SiN_x decreases in intensity and a H vibrational line at 1880 cm^{-1} , assigned previously to the neutral charge state of the PtH complex in Si,¹³ grows in intensity. No other IR lines due to H-containing defects in the Si bulk were detected in our experiments. These results show unambiguously that H from the SiN_x surface layer diffuses into the Si substrate during a postdeposition anneal and that this H forms complexes with defects in the bulk.

The intensity of the PtH IR line at 1880 cm^{-1} provides quantitative information about the concentration of H in the Si sample. From the calibration of the intensity of the PtH line reported in Ref. 13, the concentration of PtH complexes is related to the area of the 1880 cm^{-1} absorbance line by

$$[\text{PtH}](\text{cm}^{-3}) = 2.6 \times 10^{16} \text{ cm}^{-1} \left(\int A d\bar{\nu} \right) / d_{\text{eff}}. \quad (1)$$

Here, $\bar{\nu}$ is the frequency of the light in wave numbers (cm^{-1}), and A is the absorbance (which is related to the absorption coefficient by $A = \alpha d_{\text{eff}} \log_{10} e$). For the MIR geometry shown in Fig. 1, the optical path length, d_{eff} , for the probing light is proportional to the thickness d of the hydrogenated layer and is given by

$$d_{\text{eff}} = Nd \sec \theta = (L \cot \theta / w) d \sec \theta. \quad (2)$$

Here, L is the length of the MIR sample, w is its thickness, θ is the bevel angle, and N is the number of passes the light makes through the absorbing layer. For our samples, with $L = 18\text{ mm}$, $w = 1.5\text{ mm}$, and $\theta = 45^\circ$, the MIR geometry, when compared with a single pass at normal incidence, typically increases the optical path length by a factor of $N \sec \theta \approx 17$. Initially, the thickness d of the absorbing layer is unknown. In this case, the product of the defect concentration times the layer thickness, or the areal density, can be determined from the area of the absorbance line.¹⁷

Figure 3(a) shows the PtH IR line for a sample that had been hydrogenated by a postdeposition anneal (5 min at 600°C) of a SiN_x layer deposited by PECVD. To determine the depth of H penetration, hydrogenated samples were mechanically thinned in successive steps in which $\sim 50\text{--}100$

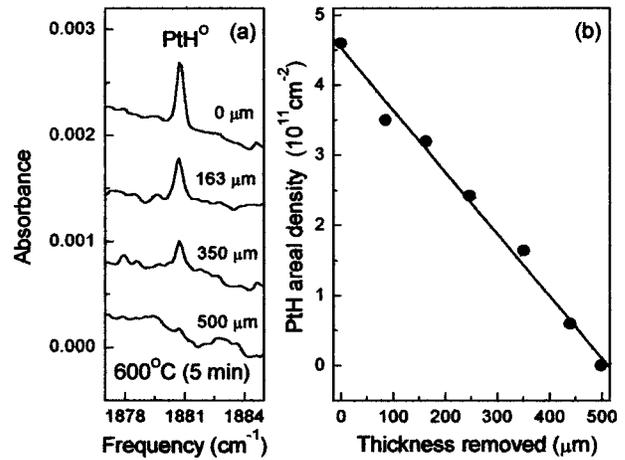


FIG. 3. (a) IR spectra showing the vibrational line of the PtH complex in a Si:Pt sample that was hydrogenated by the postdeposition annealing (5 min at 600°C) of a PECVD SiN_x film. Spectra were measured after a surface layer of the indicated thickness had been removed from the sample. (b) The areal density of PtH complexes remaining in the sample vs the thickness of the layer removed from the surface, derived from the data shown in (a).

μm were removed from the surface onto which the SiN_x had been deposited. Figures 3(a) and 3(b) show that the areal density of PtH centers is reduced as layers are removed successively from the sample. The linear decrease of the IR intensity with the increasing thickness of the removed layer shows that the concentration of PtH centers for these annealing conditions is approximately constant up to a maximum penetration depth of $500\text{ }\mu\text{m}$ into the sample.

The concentration of PtH complexes can be determined from their areal density once the thickness of the hydrogenated layer has been determined. The concentration of PtH complexes for the sample whose spectra are shown in Fig. 3 is $1 \times 10^{13}\text{ cm}^{-3}$. The sample whose spectra are shown in Fig. 2 was thinned and studied similarly by IR spectroscopy (following the anneal at 700°C). In this case, the penetration depth of H was estimated to be $1 \times 10^3\text{ }\mu\text{m}$, and the concentration of PtH complexes was determined to be $5 \times 10^{13}\text{ cm}^{-3}$. Our previous experience with the trapping of H by Pt impurities in Si indicates that the majority of the H introduced into the Si will be trapped by Pt to form PtH complexes because the concentration of Pt ($\sim 10^{17}\text{ cm}^{-3}$) is much greater than the concentration of H.¹³ Therefore, the concentration of PtH complexes reflects the total concentration of H introduced into the Si from the SiN_x layer.¹⁸

The concentration of H introduced into Si from a SiN_x layer has been found to be modest in the experiments performed here, i.e., from near 1 to $5 \times 10^{13}\text{ cm}^{-3}$. The H that diffuses into the Si bulk corresponds to the order of only \sim a tenth of a percent of the total H that is liberated from the SiN_x coating by an anneal at near 600°C . For example, for the data shown in Fig. 2, the 600°C anneal reduces the area of the 2160 cm^{-1} Si-H IR band by 5%. If we estimate that the 80-nm-thick SiN_x layer contains a H concentration of $\sim 1 \times 10^{22}\text{ cm}^{-3}$, this corresponds to an areal density of released H of $\sim 4 \times 10^{15}\text{ cm}^{-2}$.¹⁹ The intensity of the 1880 cm^{-1} PtH line following the anneal at 600°C leads to an areal density of PtH complexes in the Si of $6 \times 10^{12}\text{ cm}^{-2}$, or only 0.15% of the total H released from the SiN_x . While the concentration of H introduced into Si is small, it is, none-

theless, sufficient to affect the electrical activity of dislocations and impurities like the transition metals that are highly effective lifetime killers. Our experiments suggest that hydrogenation of Si from a SiN_x layer yields a H concentration that lies between optimistic estimates of the amount of H that can be introduced into the Si bulk⁹ and the negative viewpoint taken by Boehme and Lucovsky that bulk hydrogenation does not occur.¹⁰

The modest H concentration introduced by a postdeposition anneal of a SiN_x film is consistent with the sensitivity of the effectiveness of hydrogenation treatments to processing methods.⁵⁻⁹ That is, one is not in the situation where there is an excess of H available to effectively passivate all of the defects that might be present. Therefore, changes in the H concentration that result from differences in processing methods can have a pronounced effect. Experiments are currently underway to investigate the synergistic effect that co-firing the SiN_x antireflection coating and Al backcontact layers has on the improvement of the minority carrier lifetime of solar cells,^{8,20} and whether this processing synergy might result from the introduction of a greater H concentration into the solar cell.

The results presented here provide information about the diffusivity of H during hydrogenation from SiN_x. There has been considerable interest in the penetration depth of H into Si because of its importance in the design of processes that will optimize the hydrogen passivation of solar cells.^{3,21} The diffusivity of H in Si was measured at high temperature in an early study by Van Wieringen and Warmoltz²² and gives the diffusion constant

$$D = 9.4 \times 10^{-3} \exp(-0.48 \text{ eV/kT}) \text{ cm}^2/\text{s}. \quad (3)$$

Subsequent studies have found that the D given by Eq. (3) is valid for the diffusion of H⁺, the dominant charge state of H in Si at elevated temperature,²³ for situations where H does not interact with other defects and where relatively immobile H₂ molecules are not formed.¹¹ In many experimental situations, the diffusion of H is limited by trapping, and an effective diffusion constant is found that is typically two to three orders of magnitude smaller than Eq. (3) would predict.¹¹ Therefore, it becomes important to obtain data on the indiffusion depth of H that are valid for specific hydrogenation conditions. The data in Fig. 3 show that for a 5 min anneal at 600 °C, the thickness of the hydrogenated layer that results is ~500 μm. Equation (3) gives a diffusion constant of $D = 1.6 \times 10^{-5} \text{ cm}^2/\text{s}$ at 600 °C; for a 5 min anneal, this value would give a \sqrt{Dt} diffusion length of 690 μm. This comparison shows that the effective diffusion constant in our experiments is roughly within a factor of 2 of the value extrapolated from the results of Van Wieringen and Warmoltz.²² (A similar conclusion is obtained from the H penetration depth determined for the sample annealed for 10 min at 700 °C.) This is a surprising result, given that one might expect the H penetration depth to be limited by trapping in our experiments and to be greatly reduced from the value predicted from Eq. (3). Nonetheless, the rapid indiffusion observed here is consistent with the effectiveness of typical annealing treatments of a few minutes near 750 °C used to passivate Si solar cells and suggests that such anneals drive H deep into the Si bulk.

Vibrational spectroscopy, coupled with the use of Pt marker impurities in Si, has been used to probe the H that is introduced into Si by the postdeposition annealing of a H-rich SiN_x AR coating. The H concentration has been found to be modest in these experiments, less than $\sim 10^{14} \text{ cm}^{-3}$. The thickness of the hydrogenated layer is consistent with a H diffusion constant that is a factor of only ~ 2 smaller than an extrapolation of the classic results of Van Wieringen and Warmoltz²² would predict.

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¹⁷The integrated absorption coefficient is proportional to the concentration of absorbing centers. However, the absorbance, A , determined by experiment, is proportional to the product of the absorption coefficient times the thickness of the absorbing layer. The integrated absorbance, therefore, is proportional to the concentration of centers times the thickness of the absorbing layer, that is, to the areal density.

¹⁸If H₂ molecules were introduced into the Si, they would not be easily seen by IR spectroscopy because of the weakness of their vibrational absorption. We have annealed a few samples at 200 °C where the H₂ molecule would be dissociated and give rise to impurity-H complexes. No new PtH complexes were found in these test experiments, leading us to conclude that any concentration of H₂ molecules is smaller than the concentration of PtH complexes we have detected.

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