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Concentration and penetration depth of H introduced into crystalline Si by hydrogenation methods used to fabricate solar cells

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The hydrogenation of crystalline Si by methods used to passivate defects in Si solar cells has been studied by infrared spectroscopy. For these experiments, floating-zone Si that contained Pt impurities that act as traps for H was used as a model system in which H could be directly detected. In this model system, the concentration and indiffusion depth of H were determined for different hydrogenation treatments so that their effectiveness could be compared. The postdeposition annealing of a hydrogen-rich SiN_x surface layer was found to introduce H into the Si bulk with a concentration of $\sim 10^{15}$ cm^{-3} under the best conditions investigated here. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2363684]

I. INTRODUCTION

Hydrogen is commonly introduced into Si solar cells to reduce the deleterious effects of defects and to increase cell efficiency.[1–8] A popular, low-cost method to introduce H is by the postdeposition annealing of a H-rich SiN_x layer that is deposited for use as an antireflection coating. The effect that the postdeposition annealing of a SiN_x layer has on solar-cell performance has been widely studied.[4–26] Nonetheless, important questions about the hydrogen that is introduced during processing and its subsequent interactions with defects have remained unanswered because the direct detection of H by methods such as secondary ion mass spectrometry (SIMS) is not typically possible; even when D is used instead of H to improve the detection limit, because of hydrogen's small concentration.[27,28] Therefore, the concentration of H that is introduced into the Si bulk by methods used to fabricate solar cells is not known. Furthermore, the indiffusion of H into Si is often limited by trapping,[29] making direct measurements of the appropriate diffusion constant to describe the penetration depth of H desirable. These uncertainties about the concentration and depth of H that has been introduced make explanations of how different processing strategies affect solar-cell efficiency difficult to test and verify. That is, it remains ambiguous whether improved bulk hydrogenation is always the cause of an increase in solar-cell efficiency in situations where this explanation is invoked. Furthermore, any enhancement in the concentration of H introduced into the Si bulk that might occur remains unquantified.

We have recently developed a model system that can be used to study the introduction of H into Si by processes typically used to fabricate solar cells.[30] This model system consists of floating-zone Si that contains Pt impurities. The combination of infrared (IR) spectroscopy with impurities that trap H is used in our experiments to determine the concentration and penetration depth of H in the Si host. Pt impurities are used as traps for H in these experiments because the PtH complexes in Si have been well studied,[31–37] do not dissociate up to an annealing temperature of 650 °C, and have H vibrational lines that have been identified.[33] The intensities of the PtH IR lines have also been calibrated so that the concentration of H in the Si samples can be estimated.[37] This strategy for the direct detection of a hydrogenated impurity in Si was used previously to confirm that H is introduced deeply into the Si bulk by the postdeposition annealing of a SiN_x antireflection coating.[30]

The present paper compares the introduction of hydrogen into Si by the postdeposition annealing of SiN_x layers deposited and processed by different methods. We find that different processing strategies result in H concentrations that can differ by factors greater than 100. The hydrogenation of Si from a microwave-induced remote hydrogen plasma[38] has also been investigated. It has been proposed that the Si vacancy might play a role during hydrogenation processes.[3,39] Vacancy-H complexes have been studied previously by IR spectroscopy,[40,41] which has made it possible for us to detect the presence of vacancies that have been introduced into Si samples during hydrogenation treatments.

II. EXPERIMENTAL PROCEDURE

For our experiments, Pt impurities, to be used as traps for H, were diffused into Si samples grown by the floating-

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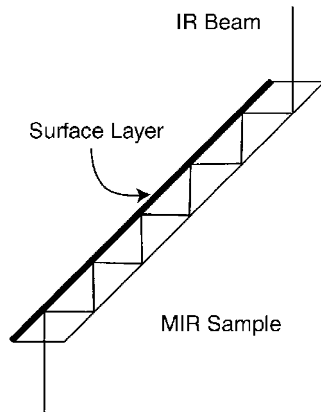

FIG. 1. Multiple internal reflection geometry used for IR measurements.

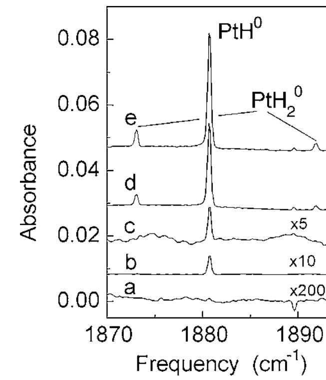

FIG. 2. IR spectra (4.2 K) for Si:Pt samples hydrogenated from a H-rich SiN_x layer. The intensity of the IR line at 1880 cm^{-1} permits the concentration of H bound to defects in the bulk of the Si sample to be determined. Spectra (a) and (c) are for SiN_x layers deposited with a 13.6 MHz reactor, and (b), (d), and (e) are for SiN_x layers deposited at 50 kHz. Samples (a) and (b) were furnace annealed (600 °C, 10 min), and (c)–(e) received a rapid thermal anneal (750 °C, 1 min). Samples (d) and (e) were with and without an Al back-surface layer, respectively.

zone method at a temperature of 1050 °C for an indiffusion time of 72 h. The resulting Pt concentration is estimated to be $\sim 2\times 10^{16}$ cm^{-3} from solubility data in the literature.[42] SiN_x layers were deposited onto several Si samples by plasma-enhanced chemical vapor deposition (PECVD) using 50 kHz and 13.6 MHz reactors. The substrate temperatures for the depositions were 425 and 300 °C for the 50 kHz and 13.6 MHz reactors, respectively, and the nitride layer thicknesses were ~80 nm. Postdeposition anneals to introduce H were performed in a conventional tube furnace or by rapid thermal processing (RTP). Al films, approximately 2 μm in thickness, were evaporated onto the back sides of a few samples to investigate whether cofiring an Al back contact improves the effectiveness of the hydrogenation as has been previously suggested.[6,15] A few samples were also hydrogenated with a microwave-induced remote hydrogen plasma.[38] In this case, a flow of H_2 was passed through a cavity, and a microwave generator (2.45 GHz, 75 W) was used to excite the plasma. Samples were placed downstream where they were not exposed to the UV light from the plasma. In this case, H was introduced at sample temperatures of 350 and 500 °C for exposure times up to 10 h.

IR absorption measurements have been made for samples in a multiple-internal-reflection (MIR) geometry in order to increase the sensitivity of vibrational spectroscopy for the detection of small concentrations of H-containing defects. Samples with dimensions of $15\times 18\times 1.5$ mm^3 were made from p-type Si into which Pt had been diffused. 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 passed through the sample (Fig. 1). IR absorption measurements were made with a Bomem DA3 Fourier transform IR (FTIR) 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. (The PtH IR lines are narrow at low temperature, improving the detection limit of the IR measurements.) It was found that the presence of an Al back-contact layer that was present for some of our experiments greatly reduced the transmission of the Si samples. After samples were annealed to introduce H, the Al layer was removed by lapping and polishing prior to subsequent IR measurements.

III. EXPERIMENTAL RESULTS

IR spectra are shown in Fig. 2 for Si:Pt samples onto which SiN_x layers had been deposited by PECVD, followed by postdeposition annealing. After each of these samples received a postdeposition anneal, a sharp IR line at 1880 cm^{-1} that is due to PtH^0 defects in the Si bulk grew in strength, with a resulting intensity that depended strongly on how the sample was processed. (The PtH complex has several charge states. The neutral complex is formed in p-type samples.[33,37])

The intensity of the PtH^0 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^0 line reported in Ref. 37, the concentration of PtH^0 complexes is related to the area of the 1880 cm^{-1} absorbance line by

$$[\mathrm{PtH}^0](\mathrm{cm}^{-3}) = 2.6\times 10^{16}\ \mathrm{cm}^{-1}\left(\int A\,d\bar{\nu}\right)/d_{\mathrm{eff}}. \quad (1)$$

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 $A=\alpha d_{\mathrm{eff}}\log_{10} e$). 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

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

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 typical dimensions of L=18 mm, w=1.5 mm, and θ=45°, the MIR geometry, when compared with a single pass at normal incidence, 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.[43]

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 com-

TABLE I. Results for the introduction of H into Si from an annealed SiN_x layer. Deposition method, sample characteristics, annealing treatment, and the areal density of PtH^0 complexes as determined from the area of the 1880 cm^{-1} vibrational line are shown.

Sample	Treatment	PtH^0 areal density (cm^{-2})
SiN_x (13.6 MHz)/Si:Pt	Furnace 600 °C (10 min)	$<5\times10^9$
SiN_x (50 kHz)/Si:Pt	Furnace 600 °C (10 min)	4×10^{11}
SiN_x (13.6 MHz)/Si:Pt	RTP 750 °C (1 min)	1.1×10^{12}
SiN_x (50 kHz)/Si:Pt	RTP 750 °C (1 min)	2.2×10^{13}
SiN_x (50 kHz)/Si:Pt+Al	RTP 750 °C (1 min)	1.9×10^{13}

plexes when the concentration of Pt is much greater than the concentration of H.[37] We have found this to be the situation when hydrogen is introduced by the postdeposition annealing of a SiN_x layer.[30] This conclusion is also consistent with the results of SIMS studies which found D to be below the detection limit for samples deuterated from SiN_x layers.[27] [Deuterated materials were used in the studies by Dekkers *et al.* to improve the detection limit ($\sim1\times10^{15}$ cm^{-3}) of SIMS.[27]] Therefore, under the present experimental circumstances, the concentration of PtH complexes reflects the total concentration of H introduced into the Si from the SiN_x layer. (In any event, the concentration of PtH centers places a lower limit on the concentration of H introduced into the sample.)

A. Introduction of H by the postdeposition annealing of a SiN_x layer

Several processing strategies have been used to improve the introduction of H into Si solar cells and to increase the minority carrier lifetime and cell efficiency. Improvements have been reported for SiN_x layers deposited at low frequency (50 kHz vs 13.6 MHz),[21] for annealing by RTP (Refs. 17, 18, 20, and 24) and for cofiring the SiN_x antireflection coating along with an Al back-contact layer.[6,7,15,24] In the present experiments, we have examined these strategies to test how they affect the concentration of H that is introduced into the Si bulk. A collection of spectra measured for samples processed in different ways is shown in Fig. 2. The areal density of PtH^0 complexes in each sample was determined from the area of the 1880 cm^{-1} absorption line and Eqs. (1) and (2) to yield the results shown in Table I. These experimental results lead to the following conclusions:

(i) SiN_x layers deposited with a 50 kHz reactor were found to introduce a greater concentration of H than SiN_x layers deposited with a 13.6 MHz reactor. For hydrogenation by the furnace annealing (600 °C, 10 min) of a SiN_x layer deposited with a 13.6 MHz reactor, spectrum (a) in Fig. 2 gives an areal density below 5×10^9 cm^{-2} for H bound to Pt impurities in the Si bulk (near the sensitivity limit of this technique).[44] For a furnace annealed sample with a SiN_x layer deposited with a 50 kHz reactor, spectrum (b) gives a PtH^0 areal density of 4×10^{11} cm^{-2}, an increase by a factor of ~100. Similarly, for samples annealed by RTP (750 °C, 1 min), the SiN_x layer deposited with the 50 kHz reactor introduced a much greater amount of H than the nitride layer deposited at 13.6 MHz, in this case with an increase of a factor of ~50. (The annealing times and temperatures used here were selected to permit a stable, reproducible annealing temperature to be achieved and to introduce H throughout a Si layer roughly 500 μm thick. Furthermore, longer anneals did not result in a substantial increase in the intensity of the 1880 cm^{-1} line used here to determine the areal density of H introduced into the Si bulk.)

(ii) Annealing by RTP, as opposed to furnace annealing, led to a greater concentration of hydrogenated defects for samples with SiN_x layers deposited at 50 kHz or 13.6 MHz. For SiN_x layers deposited with the 50 kHz reactor, RTP increased the intensity of the PtH^0 IR line by a factor of ~50 to give an areal density of hydrogenated impurities near 2×10^{13} cm^{-2}. (This value is comparable to a recent estimate of the H areal density made for Czochralski-grown Si containing O precipitates that had been hydrogenated by the postdeposition annealing of a SiN_x layer.[28]) The increased concentration of hydrogenated impurities produced by RTP annealing in these experiments is consistent with the improved efficiencies seen for Si solar cells processed with RTP anneals.[20,24]

(iii) Cofiring the SiN_x layer along with an Al back-contact layer did not increase the concentration of hydrogenated defects in our experiments. These results were for SiN_x layers deposited at 50 kHz on Si samples with and without an evaporated Al back-surface layer. This result supports the conclusion that the improvement in the minority carrier lifetime that arises from cofiring the SiN_x layer with an Al back-contact layer is not due to improved hydrogenation but may instead be due to a gettering effect.[25] We caution, however, that our samples are thicker than typical solar cells, so our experiments do not provide a definitive answer to this question.

The concentration of PtH^0 complexes can be determined from their areal density if the thickness of the hydrogenated layer is known.[43] To determine the depth of H penetration, hydrogenated samples were mechanically thinned in successive steps in which layers of Si ~50–100 μm thick were removed from the surface onto which the SiN_x had been deposited. Figure 3(a) shows the PtH^0 IR line at 1880 cm^{-1} for the sample in Fig. 2 [spectrum (e)] that had been hydrogenated by a postdeposition anneal (RTP, 750 °C for 1 min) of a SiN_x layer deposited by PECVD (50 kHz). [This spectrum also shows vibrational lines associated with a small concentration of PtH_2^0 complexes[33,37] whose presence is consistent with the higher concentration of H present in this sample and also in the sample for spectrum (d)]. Figures 3(a) and 3(b) show that the areal density of PtH^0 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^0 centers for these annealing conditions is approximately constant up to a maximum penetration depth of 640 μm into the sample [determined by extrapolating the line shown in Fig. 3(b) to the horizontal axis]. Several

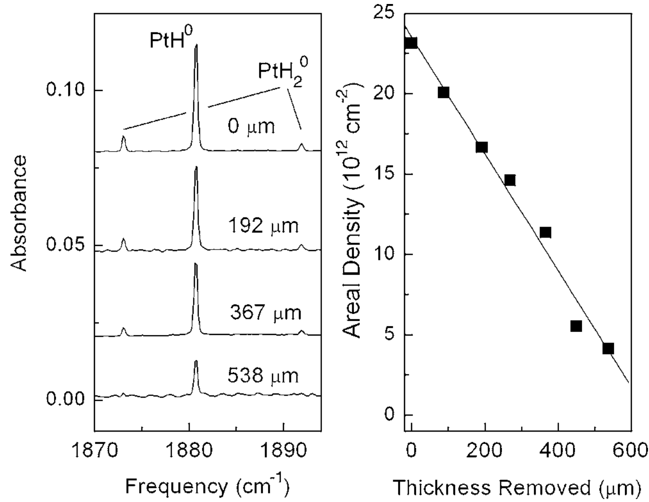

FIG. 3. (a) IR spectra (4.2 K) showing the vibrational lines of the PtH^0 complex in a Si:Pt sample hydrogenated by the postdeposition annealing of a SiN_x layer deposited by PECVD. Spectra were measured after surface layers of the indicated thicknesses had been removed from the sample. (b) The areal density of PtH^0 complexes remaining in the sample vs the thickness of the layer removed from the surface, derived from the data shown in (a).

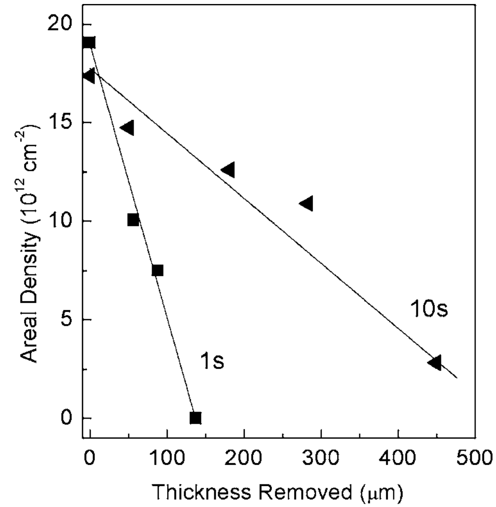

FIG. 4. The areal density of PtH^0 complexes present in Si:Pt samples hydrogenated by the postdeposition annealing of SiN_x layers deposited by PECVD (50 kHz). Samples were annealed by RTP for the times indicated. Samples were thinned successively to determine the penetration depth of H by IR measurements made at normal incidence.

samples that had been hydrogenated by a furnace anneal or RTP were analyzed in this way to determine the penetration depth of H.[30,45] The concentration of PtH^0 complexes for the sample whose spectra are shown in Fig. 3 is 3.4×10^{14} cm^{-3}. A concentration of hydrogenated defects of this magnitude was typical of samples hydrogenated from SiN_x films deposited by PECVD in the 50 kHz reactor and annealed by (RTP, 750 °C for 1 min).

It has been reported recently that reduced annealing times, as short as 1 s, lead to increased minority carrier lifetimes in Si solar cells hydrogenated by the postdeposition annealing of SiN_x.[20,24] Furthermore, an anneal of a few seconds at temperatures near 800 °C is consistent with typical belt furnace anneals used by industry.[46] Here, we have examined SiN_x/Si:Pt samples annealed for 1 and 10 s.[47] Figure 4 shows that the areal density of H introduced by these brief anneals is comparable to that shown in Fig. 3 for a 1 min anneal. (The 1880 cm^{-1} line was sufficiently intense for the samples annealed by RTP to make IR measurements at normal incidence possible, providing a cross-check of the results of MIR measurements described above for similarly prepared samples.) The penetration depth of H is, however, reduced for the shorter anneals. This leads to a greater concentration of H in a thinner hydrogenated layer. For the sample receiving a RTP of 1 s, the thickness of the hydrogenated layer was found to be 140 μm, leading to a hydrogenated defect concentration of 1.4×10^{15} cm^{-3}, the greatest we have detected in these experiments. These results confirm the importance of tuning the annealing time and temperature to optimize both the concentration and penetration depth of H introduced to hydrogenate bulk defects. The increased concentration of hydrogenated defects found here is consistent with the improved efficiencies found for Si solar cells processed with a RTP anneal of 1 s.[24]

B. Introduction of H from a microwave-induced remote hydrogen plasma

Hydrogen-plasma exposure has also been used to passivate bulk defects in Si solar cells.[38] A few samples were hydrogenated for our experiments by exposure to a hydrogen plasma. Spectra for a Si:Pt sample hydrogenated by plasma exposure for 10 h at 500 °C are shown in Fig. 5(a). Exposure of Si:Pt samples to the remote hydrogen plasma produced the 1880 cm^{-1} vibrational line arising from the PtH^0 complex. The intensity of the 1880 cm^{-1} line gives an areal density of 1.7×10^{12} cm^{-2} for the PtH^0 defect. Figures 5(a) and 5(b) show that the areal density of PtH^0 centers was reduced as layers were removed successively from the sample. The penetration depth of H into the sample was found to be 620 μm, leading to a concentration of PtH^0 com-

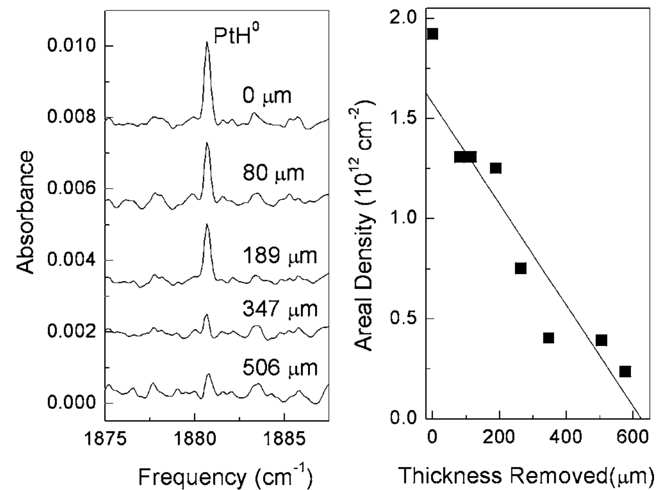

FIG. 5. (a) IR spectra (4.2 K) showing the vibrational lines of the PtH^0 complex in a Si:Pt sample hydrogenated by exposure to a hydrogen plasma (500 °C, 10 h). Spectra were measured after surface layers of the indicated thicknesses had been removed from the sample. (b) The areal density of PtH^0 complexes remaining in the sample vs the thickness of the layer removed from the surface, derived from the data shown in (a).

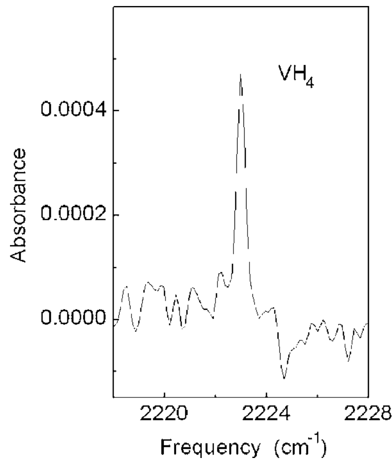

FIG. 6. IR spectrum (4.2 K) of the vacancy-H_4 complex observed in a Si sample that was hydrogenated by the postdeposition annealing (RTP, 750 °C, 60 s) of a SiN_x layer deposited in a 50 kHz reactor.

plexes of 2.7×10^{13} cm^{-3}. In these experiments, the concentration of PtH^0 complexes produced in the Si bulk by plasma exposure at 500 °C was roughly a factor of 10 smaller than that produced by the postdeposition annealing of a SiN_x layer under optimal conditions (RTP of SiN_x deposited at 50 kHz). This result is consistent with recent experiments that find the postdeposition annealing of a SiN_x layer to be a more effective lifetime-improvement process than H-plasma exposure for Si solar cells made from edge-defined, film-fed growth (EFG) Si wafers.[26]

A sample was also hydrogenated by exposure to a hydrogen plasma for 10 h at 350 °C.[45] The intensity of the 1880 cm^{-1} IR lines gave an areal density for PtH^0 centers of 2.3×10^{12} cm^{-3}. However, in this case, the indiffusion of H was greatly limited by trapping, presumably by the Pt impurities present in the sample, and the PtH complexes were present only in a thin layer ~35 μm thick at the sample surface. These results give a local concentration of PtH^0 complexes of ~8×10^{14} cm^{-3}. In addition to the PtH^0 complexes, a substantial concentration of $PtH_2{}^0$ defects were also formed, consistent with the greater local hydrogen concentration introduced into the thin layer at the sample surface. These results suggest that the Pt impurities being used here to trap H are not benign probes and have a strong effect on the local concentration of H and its penetration depth when hydrogen is introduced at relatively low temperatures from a hydrogen-plasma source.

C. Vacancy-hydrogen complexes

It has been proposed that Si vacancies might interact with H to play a role in hydrogenation processes.[3,39] In our experiments, we have directly observed the presence of vacancy-H complexes in our samples by IR spectroscopy. Figure 6 shows a vibrational line at 2223 cm^{-1} that is due to the vacancy-H_4 complex in Si (Refs. 40 and 41) that was observed for the same Si sample whose PtH^0 IR spectrum (e) is shown in Fig. 2. While this line is very weak, it provides an unambiguous identification of vacancies in the Si bulk following hydrogenation by the postdeposition annealing of a SiN_x layer.

The hydrogen-plasma exposure of a Si:Pt sample for 10 h at 350 °C also produced a substantial concentration of vacancy-hydrogen complexes, giving rise to characteristic vibrational lines that have been studied previously (VH_4 at 2223 cm^{-1} and V_2H_6 at 2166 and 2191 cm^{-1}).[40,41] The absorbances of these VH_n lines were comparable to those of PtH^0 centers present in the same sample.[45] These results show that IR spectroscopy of the vacancy-H complexes provides a strategy to directly detect vacancies in Si that have been introduced by hydrogenation processes. We note that samples with the largest concentration of vacancy-related defects did not show an increased H penetration depth. Therefore, there is no evidence in these experiments that the presence of vacancies has enhanced the indiffusion of H as has been suggested elsewhere.[3,39]

IV. DIFFUSIVITY OF H DURING HYDROGENATION TREATMENTS

The diffusivity of H in Si was measured at high temperature (near 1400 K) in an early study by Van Wieringen and Warmoltz[48] and gave the following expression for the diffusion constant:

$$D_H = 9.4\times10^{-3}\exp(-0.48\ \mathrm{eV/kT})\mathrm{cm}^2/\mathrm{s}. \qquad (3)$$

Subsequent studies have found that the D_H given by Eq. (3) is valid for the diffusion of H^+, the dominant charge state of H in Si at elevated temperature, for situations where H does not interact with other defects and where relatively immobile H_2 molecules are not formed.[29,49] Other determinations of the diffusivity of isolated H, one near room temperature[50] and another near 130 K,[29,49,51] are also consistent with the diffusivity given by Eq. (3) and support the long extrapolation that is often made of the results of Van Wieringen and Warmoltz to dramatically lower temperatures. In many experimental situations, the diffusion of H is limited by trapping, and an effective diffusion constant is found that is typically from two to three orders of magnitude smaller than Eq. (3) would predict.[29,52] Therefore, it becomes important to obtain data for the indiffusion depth of H that are valid for specific hydrogenation conditions. To help put the values for the diffusivity obtained in the present study in context, experimental results obtained for the diffusivity of H are summarized in Fig. 7. The data points near 1400 K are the results of Van Wieringen and Warmoltz, and the straight line shows the diffusivity given by Eq. (3). Data points from a selection of other experimental studies,[53–60] where the diffusivity of H is believed to be limited by trapping, lie 2–3 decades below the line given by Eq. (3).

Previous results for the hydrogenation of Si from SiN_x layers annealed at 600 and 700 °C (873 and 973 K) were consistent, to within a factor near 2, with the diffusivity given by Eq. (3).[30] Similarly, the results obtained in the present experiments for samples hydrogenated from SiN_x layers are consistent with the rapid indiffusion of H predicted by Eq. (3). For example, the diffusivity given by Eq. (3) at 750 °C is $D_H(750\ °C)=4.1\times10^{-5}$ cm^2/s. For a 1 min anneal at 750 °C, this value predicts a $\sqrt{Dt}$ diffusion length of 500 μm which is close to the penetration depth of H found in experiments reported here [~640 μm from the data shown

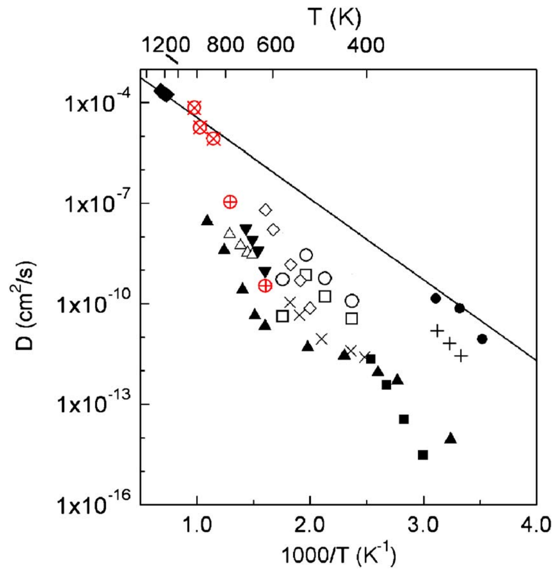

FIG. 7. (Color online) Diffusion constant for H in Si. The straight line corresponds to the diffusion constant given in Eq. (3), determined near 1400 K by Van Wieringen and Warmoltz (♦) (Ref. 48). Values of D_{eff} determined in the present studies are shown by crossed circles (⊗) at 600, 700, and 750 °C, and (⊕) at 500 and 350 °C. Data from Seager *et al.* (●) (Ref. 50) and Gorelkinskii and Nevinnyi (Ref. 51, not shown) are consistent with Eq. (3) and have been attributed to the diffusivity of isolated H^+ (Refs. 29 and 49). Values for D_{eff} determined in several other studies are also shown. These values have been attributed to an effective diffusivity for H that is limited by trapping (Ref. 29). See Ichimiya and Furuichi (△) (Ref. 53), Pearton (▲) (Ref. 54), Mogro-Campero *et al.* (×) (Ref. 55), Newman *et al.* (◇) (Ref. 56), Zundel and Weber (■) (Ref. 57), Johnson and Herring (+) (Ref. 58), Huang *et al.* (▼) (Ref. 59), Sopori *et al.* for floating-zone Si (○) (Ref. 60), and Sopori *et al.* for Czochralski Si (□) (Ref. 60).

in Fig. 3(b)]. The values for the diffusivity of H estimated from the penetration depth of H introduced by the postdeposition annealing of a SiN_x layer are shown by the symbol ⊗ in Fig. 7.

Hydrogenation from a hydrogen plasma for long exposure times (10 h) at lower temperatures gave H penetration depths in these experiments that are consistent with a reduced effective diffusivity D_{eff} that is typical of trap-limited diffusion. The penetration depths given in Sec. III B, 620 and 35 μm for plasma exposures at 500 and 350 °C, correspond to diffusivities of $D_{\mathrm{eff}}=1\times10^{-7}$ and 3×10^{-10} $\mathrm{cm^2/s}$, respectively (symbol ⊕ in Fig. 7). These results suggest that the Pt impurities being used here as traps for H lead to trap-limited diffusion under these experimental conditions and show that the indiffusion depth of H introduced at reduced temperature from a plasma source can be sensitive to the defect and impurity content of the Si sample being treated.

V. CONCLUSION

Spectroscopic studies of the hydrogenation of floating-zone Si that contained Pt impurities (which act as traps for H) provide quantitative information about the concentration and penetration depth of H introduced by processes commonly used to passivate bulk defects in Si solar cells. Several strategies used recently for introducing H were examined to provide quantitative information about how effectively impurities are hydrogenated in the Si bulk. In our experiments, the rapid thermal annealing of a SiN_x antireflection coating deposited with a 50 kHz reactor was found to result in a greatly increased concentration of hydrogenated impurities in the Si bulk compared to SiN_x layers that were furnace annealed or prepared by deposition in a 13.6 MHz reactor. Under the best conditions achieved here, the concentration of hydrogenated defects was $\sim10^{15}$ $\mathrm{cm^{-3}}$. This concentration is more than an order of magnitude larger than was found in our previous study[30] and is consistent with SIMS experiments reported in the literature[27] which find that the concentration of H lies below the detection limit, even when deuterated materials are used. This concentration of H, while modest, is sufficient to passivate lifetime killing defects in Si solar cells.

The direct detection of H in our experiments allowed the penetration depth of H to be estimated. Hydrogenation by the postdeposition annealing of a SiN_x layer leads to a H penetration depth that is consistent with the rapid indiffusion of H estimated from the diffusivity determined by Van Wieringen and Warmoltz[48] both for samples that were furnace annealed at 600 °C and for samples that were rapid thermally annealed at 750 °C. The hydrogenation of Si:Pt samples by hydrogen-plasma exposure at lower temperatures was consistent with the reduced effective diffusivity of H that is typical of trap-limited diffusion.

The different values observed for the penetration depth of H for hydrogenation treatments conducted near 750 °C from a SiN_x layer and near 500 °C from a hydrogen plasma demonstrate an important difference between these hydrogenation methods. The rapid thermal annealing of a SiN_x layer results in a depth profile for hydrogenated impurities that is consistent with the rapid diffusion typical of isolated H whereas a long plasma exposure at lower temperature results in trap-limited diffusion. We note that the values of the H penetration depth and the corresponding D_{eff} obtained in our experiments depend on the concentration and stability of hydrogen traps in the sample and that our results which are valid for the model system we have chosen [floating-zone Si:Pt] may not necessarily apply in other situations. Nonetheless, this model system provides unique, quantitative information about hydrogenation processes used to fabricate solar cells. The ability of hydrogenation treatments performed by the spike annealing of SiN_x layers to rapidly and effectively hydrogenate defects deep into the Si bulk is especially well matched to the requirements of solar-cell passivation processes.

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[1]C. H. Seager, D. S. Ginley, and J. D. Zook, Appl. Phys. Lett. **36**, 831 (1980).
[2]J. I. Hanoka, C. H. Seager, D. J. Sharp, and J. K. G. Panitz, Appl. Phys. Lett. **42**, 618 (1983).
[3]B. L. Sopori, X. Den, J. P. Benner, A. Rohatgi, P. Sana, S. K. Estreicher, Y. K. Park, and M. A. Roberson, Sol. Energy Mater. Sol. Cells **41/42**, 159 (1996).
[4]R. Hezel and R. Schörner, J. Appl. Phys. **52**, 3076 (1981).
[5]A. G. Aberle, Sol. Energy Mater. Sol. Cells **65**, 239 (2001). This paper reviews the SiN_x passivation of *c*-Si solar cells and includes a historical overview.
[6]F. Duerinckx and J. Szlufcik, Sol. Energy Mater. Sol. Cells **72**, 231 (2002).
[7]A. Cuevas, M. J. Kerr, and J. Schmidt, *Proceedings of the Third World Conference on Photovoltaic Energy Conversion*, IEEE Catalog No. 03CH37497, Part 1 (Arisumi Printing Inc., Japan, 2003), p. 913.
[8]G. Hahn and A. Schönecker, J. Phys.: Condens. Matter **16**, R1615 (2004).
[9]Z. Chen, A. Rohatgi, R. O. Bell, and J. P. Kalejs, Appl. Phys. Lett. **65**, 2078 (1994).
[10]L. Cai and A. Rohatgi, IEEE Trans. Electron Devices **44**, 97 (1997).
[11]S. Winderbaum, F. Yun, and O. Reinhold, J. Vac. Sci. Technol. A **15**, 1020 (1997).
[12]R. Lüdemann, Mater. Sci. Eng., B **58**, 86 (1999).
[13]A. Ebong, P. Doshi, S. Narasimha, A. Rohatgi, J. Wang, and M. A. El-Sayed, J. Electrochem. Soc. **146**, 1921 (1999).
[14]A. Rohatgi, P. Doshi, J. Moschner, T. Lauinger, A. G. Aberle, and D. S. Ruby, IEEE Trans. Electron Devices **47**, 987 (2000).
[15]V. Yelundur, A. Rohatgi, A. Ebong, A. M. Gabor, J. Hanoka, and R. L. Wallace, J. Electron. Mater. **30**, 526 (2001).
[16]H. Mäckel and R. Lüdemann, J. Appl. Phys. **92**, 2602 (2002).
[17]V. Yelundur, A. Rohatgi, J.-W. Jeong, and J. I. Hanoka, IEEE Trans. Electron Devices **49**, 1405 (2002).
[18]A. Rohatgi and J.-W. Jeong, Appl. Phys. Lett. **82**, 224 (2003).
[19]J. Hong, W. M. M. Kessels, W. J. Soppe, A. W. Weeber, W. M. Arnoldbik, and M. C. M. van de Sanden, J. Vac. Sci. Technol. B **21**, 2123 (2003).
[20]A. Rohatgi, D. S. Kim, K. Nakayashiki, V. Yelundur, and B. Rounsaville, Appl. Phys. Lett. **84**, 145 (2004).
[21]M. M. Hilali, A. Rohatgi, and S. Asher, IEEE Trans. Electron Devices **51**, 948 (2004).
[22]S. De Wolf, G. Agostinelli, G. Beaucarne, and P. Vitanov, J. Appl. Phys. **97**, 063303 (2005).
[23]A. W. Weeber, H. C. Rieffe, I. G. Romijn, W. C. Sinke, and W. J. Soppe, Proceedings of the 31st IEEE Photovoltaic Specialist Conference, IEEE Catalog No. 05CH37608 (IEEE Electron Devices Soc., Piscataway, 2005), p. 1043.
[24]K. Nakayashiki, A. Rohatgi, S. Ostapenko, and I. Tarasov, J. Appl. Phys. **97**, 024504 (2005).
[25]M. Kaes, G. Hahn, and A. Metz, Proceedings of the 31st IEEE Photovoltaic Specialist Conference, IEEE Catalog No. 05CH37608 (IEEE Electron Devices Soc., Piscataway, 2005), p. 923.
[26]M. Kaes, G. Hahn, Th. Pernau, and A. Metz, Proceedings of the 20th European Photovoltaic Solar Energy Conference, Barcelona, 2005 (unpublished), p. 1063.
[27]H. F. W. Dekkers, S. DeWolf, G. Agostinelli, J. Szlufcik, T. Pernau, W. M. Arnoldbik, H. D. Goldbach, and R. E. I. Schropp, Proceedings of the Third World Conference on Photovoltaic Energy Conversion, IEEE Catalog No. 03CH37497, Part 1 (Arisumi Printing Inc., Japan, 2003), p. 983.
[28]Hydrogen could be detected by SIMS in Si samples containing a high concentration of O precipitates. See G. Hahn, D. Karg, A. Schönecker, A. R. Burgers, R. Ginige, and K. Cherkaoui, Proceedings of the 31st IEEE Photovoltaic Specialist Conference, IEEE Catalog No. 05CH37608 (IEEE Electron Devices Soc., Piscataway, 2005), p. 1035; G. Hahn, A. Schönecker, A. R. Burgers, R. Ginige, K. Cherkaoui, and D. Karg, *Proceedings of the 20th European Photovoltaic Solar Energy Conference*, Barcelona, 2005 (unpublished), p. 717.
[29]M. Stavola, in *Properties of Crystalline Si*, edited by R. Hull (INSPEC, London, 1999), p. 511.
[30]F. Jiang, M. Stavola, A. Rohatgi, D. Kim, J. Holt, H. Atwater, and J. Kalejs, Appl. Phys. Lett. **83**, 931 (2003).
[31]P. M. Williams, G. D. Watkins, S. Uftring, and M. Stavola, Phys. Rev. Lett. **70**, 3816 (1993).
[32]M. Höhne, U. Juda, Yu. V. Martynov, T. Gregorkiewicz, C. A. J. Ammerlaan, and L. S. Vlasenko, Phys. Rev. B **49**, 13423 (1994).
[33]S. J. Uftring, M. Stavola, P. M. Williams, and G. D. Watkins, Phys. Rev. B **51**, 9612 (1995).
[34]J.-U. Sachse, E. Ö. Sveinbjörnsson, W. Jost, J. Weber, and H. Lemke, Appl. Phys. Lett. **70**, 1584 (1997).
[35]J.-U. Sachse, E. Ö. Sveinbjörnsson, W. Jost, J. Weber, and H. Lemke, Phys. Rev. B **55**, 16176 (1997).
[36]J.-U. Sachse, J. Weber, and E. Ö. Sveinbjörnsson, Phys. Rev. B **60**, 1474 (1999).
[37]M. G. Weinstein, M. Stavola, K. L. Stavola, S. J. Uftring, J. Weber, J.-U. Sachse, and H. Lemke, Phys. Rev. B **65**, 035206 (2002).
[38]M. Spiegel, P. Fath, K. Peter, B. Buck, G. Willeke, and E. Bucher, Proceedings of the 13th European Photovoltaic Solar Energy Conference (H. S. Stephens & Assoc., Bedford, UK, 1995), p. 421.
[39]B. L. Sopori, Y. Zhang, and R. Reedy, Proceedings of the 29th IEEE Photovoltaic Specialists Conference (IEEE, New York, 2002), p. 222.
[40]B. Bech Nielsen, L. Hoffman, M. Budde, R. Jones, J. Goss, and S. Öberg, Mater. Sci. Forum **196–201**, 933 (1995).
[41]B. Bech Nielsen, L. Hoffman, and M. Budde, Mater. Sci. Eng., B **36**, 259 (1996).
[42]*Impurities and Defects in Group IV Elements and III-V Compounds*, Landolt-Bornstein, New Series, Vol. III/22b, edited by O. Madelung and M. Schulz (Springer, Berlin, 1989). In a previous study (Ref. 37), the concentrations determined from solubility data for Pt impurities in Si were found to be consistent with the degree of compensation of shallow dopants in the samples.
[43]The 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.
[44]Hydrogenated layers in our experiments were typically ~500 μm thick, so an areal density of 5×10^9 cm^{-2}, the detection limit for hydrogenated defects in these experiments, corresponds to a defect concentration of 1×10^{11} cm^{-3}.
[45]Additional spectra and results for hydrogenated Si:Pt samples are given in a preliminary report of the work presented here. M. Stavola, W. Tang, F. Jiang, V. Yelundur, A. Rohatgi, G. Hahn, and J. Kalejs, Proceedings of the 14th Workshop on Crystalline Silicon Solar Cells and Modules: Materials and Processes, Winter Park, CO, August 2004, Report No. NREL/BK-520-36622, p. 134.
[46]F. Huster, Proceedings of the 20th European Photovoltaic Solar Energy Conference, Barcelona, 2005 (unpublished), p. 1466.
[47]We recognize that the results for the nominally brief annealing times used here are influenced by the additional time it takes for samples to heat and cool. The cooling rate was measured for these brief anneals with a thermocouple placed in contact with the sample surface. The cooling rate from 750 to 500 °C was near 20 °C/s. Furthermore, rapid cooling can lead to the hydrogenation of defects not thermally stable at the maximum annealing temperature, and this effect can lead to improved defect passivation.
[48]A. Van Wieringen and N. Warmoltz, Physica (Amsterdam) **22**, 849 (1956).
[49]C. Herring, N. M. Johnson, and C. G. Van de Walle, Phys. Rev. B **64**, 125209 (2001).
[50]C. H. Seager, R. A. Anderson, and D. K. Brice, J. Appl. Phys. **68**, 3268 (1990).
[51]Y. V. Gorelkinskii and N. N. Nevinnyi, Mater. Sci. Eng., B **36**, 133 (1996).
[52]S. J. Pearton, J. W. Corbett, and M. Stavola, *Hydrogen in Crystalline Semiconductors* (Springer-Verlag, Heidelburg, 1992).
[53]T. Ichimiya and A. Furuichi, Int. J. Appl. Radiat. Isot. **19**, 573 (1968).
[54]S. J. Pearton, J. Electron. Mater., **14a**, 737 (1985).
[55]A. Mogro-Campero, R. P. Love, and R. Schubert, J. Electrochem. Soc. **132**, 2006 (1985).
[56]R. C. Newman, J. H. Tucker, A. R. Brown, and S. A. McQuaid, J. Appl. Phys. **70**, 3061 (1991).
[57]T. Zundel and J. Weber, Phys. Rev. B **46**, 2071 (1992).
[58]N. M. Johnson and C. Herring, Phys. Rev. B **46**, 15554 (1992).
[59]Y. L. Huang, Y. Ma, R. Job, and A. G. Ulyashin, J. Appl. Phys. **96**, 7080 (2004).
[60]B. L. Sopori, K. Jones, and X. J. Deng, Appl. Phys. Lett. **61**, 2560 (1992).