HYDROGENATION OF Si FROM SiN$_x$:H FILMS: HOW MUCH HYDROGEN IS REALLY IN THE Si?

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ABSTRACT

A promising method to introduce H into Si solar cells in order to passivate bulk defects is by the post-deposition annealing of an H-rich, SiN$_x$ surface layer. It previously has been difficult to characterize the small concentration of H that is introduced by this method. IR 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.

1. INTRODUCTION

Hydrogen is commonly introduced into Si solar cells to reduce the deleterious effects of defects and increase the minority carrier lifetime [1-7]. 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 [5-7]. A post-deposition 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 x 10^{16} cm^{-3} can be introduced into bulk Si from a SiN$_x$ layer [8], while other recent studies question whether bulk hydrogenation from SiN$_x$ occurs at all [9]. Furthermore, the indiffusion of H into Si is often limited by trapping [10], making the appropriate effective diffusion constant to describe the penetration depth of H uncertain.

In the present paper, a novel 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 [11]. Furthermore, the intensities of the PtH IR lines have been calibrated so that the concentration of H in the Si sample can be estimated [12].

2. EXPERIMENT

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 x 18 mm^2 and a thickness of 1.5 mm were made from lightly doped Si grown by the floating-zone method. The ends of the samples were beveled at 45º. 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 ~10^{17} 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) [6] or by hot-wire chemical vapor deposition (HWCVD) [14]. The substrate temperature for the depositions was ~300°C and the nitride layer thicknesses were ~80 to 100 nm. Samples were annealed in a tube furnace in an ambient of flowing N$_2$. IR absorption measurements were made with a Bomem DA3 FTIR spectrometer equipped with a KBr beamsplitter and an InSb detector. Samples were cooled for IR measurements to near 4.2K with a Helitran, continuous-flow cryostat.

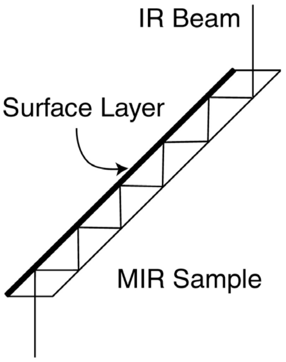

Figure 1. Multiple-internal-reflection geometry used for IR measurements of Si samples hydrogenated from a SiN$_x$ surface layer.

3. EXPERIMENTAL RESULTS

IR spectra are shown in Fig. 2 for a Si:Pt sample onto which a SiN$_x$ layer had been deposited by HWCVD. The

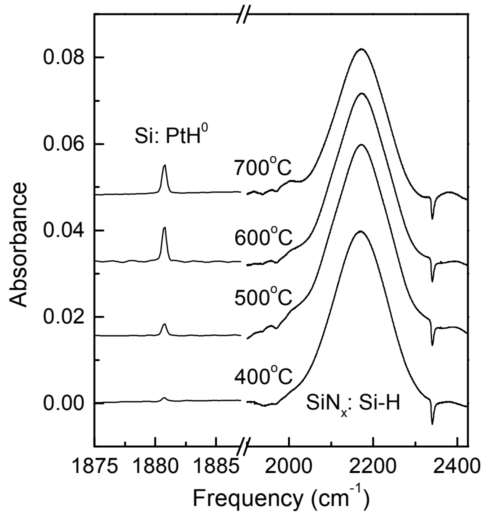

Figure 2. IR spectra for a bulk Si:Pt sample with a SiN$_x$ layer deposited on its surface by hot-wire CVD. The sample was annealed (10 min.) at the indicated temperatures to introduce H into the Si. Vibrational lines assigned to Si-H bonds in the SiN$_x$ layer and to PtH complexes in the Si are shown.

broad band centered at 2160 cm^{-1} is due to Si-H bonds in the H-rich SiN$_x$ layer [15]. For anneals performed at successively 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 PtH complex in Si [8], 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 post-deposition 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. (12), the concentration of PtH complexes is related to the area of the 1880 cm^{-1} absorbance line by,

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

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,

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

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 mm, w = 1.5 mm, and θ = 45°, 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 [16].

Fig. 3(a) shows the PtH IR line for a sample that had been hydrogenated by a post-deposition anneal (5 min. at 600ºC) 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 ~50 to 100 μm were removed from the surface onto which the SiN$_x$ had been deposited. Figs. 3(a) and (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 μm 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 1×10^{13} cm^{-3}. The sample whose spectra are shown in Fig. 2 was thinned and studied similarly by IR spectroscopy (following the anneal at 700ºC, 10 min). In this case, the penetration depth of H was estimated to be 1×10^{3} μm and the concentration of PtH complexes was determined to be 5×10^{13} 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 Pt-H complexes because the concentration of Pt (~10^{17} cm^{-3}) is much greater than the concentration of H [12]. Therefore, the concentration of PtH complexes reflects the total concentration of H introduced into the Si from the SiN$_x$ layer [17].

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 5×10^{13} cm^{-3}. The H that diffuses into the Si bulk corresponds to the order of only ~ 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 ~1×10^{22} cm^{-3}, this corresponds to an areal density of released H of ~4×10^{15} cm^{-2} [18]. 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 6×10^{12} 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, nonetheless, 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 bulk [8] and the negative viewpoint taken by Boehme and Lucovsky that bulk hydrogenation does not occur [9].

The modest H concentration introduced by a post-deposition anneal of a SiN$_x$ film is consistent with the sensitivity of the effectiveness of hydrogenation treatments to processing methods [4-8]. 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

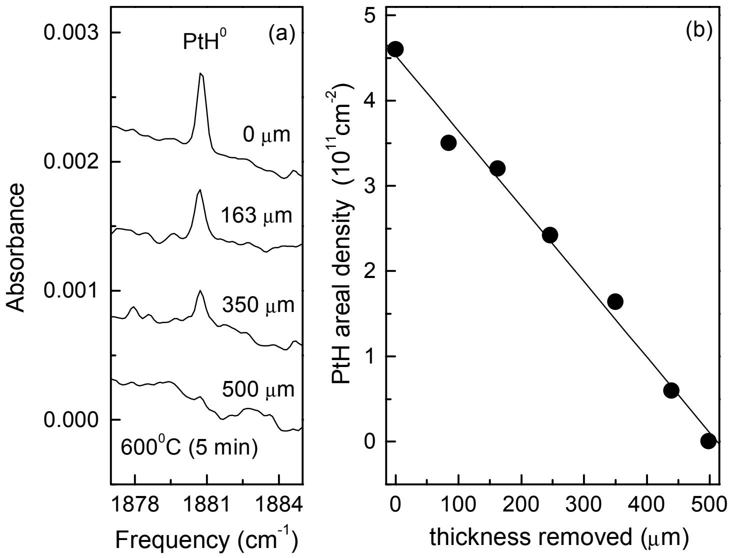

Figure 3. (a) IR spectra showing the vibrational line of the PtH complex in a Si:Pt sample that was hydrogenated by the post-deposition annealing (5 min at 600°C) of a PECVD SiN_x film. Spectra were measured after a surface layer of the indicated thickness had been removed from the sample. (b) The areal 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).

result from differences in processing methods can have a pronounced effect. Experiments are currently underway to investigate the synergistic effect that cofiring the SiN_x AR coating and Al back contact layers has on the improvement of the minority carrier lifetime of solar cells [7,19], 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 [3,20]. The diffusivity of H in Si was measured at high temperature in an early study by Van Wieringen and Warmoltz [21] and gives the diffusion constant,

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

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 [22], for situations where H does not interact with other defects and where relatively immobile H_2 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. A compilation of results for the diffusivity of H in Si is shown in Fig. 4. The data in Fig. 3 show that for a 5 min. anneal at 600ºC, the thickness of the hydrogenated layer that results is ~500 μm. We take this penetration depth to be $\approx \sqrt{D_{eff}\, t}$ to obtain a diffusivity of $D_{eff}(600ºC) = 0.8 \times 10^{-5}$ cm^2/s.

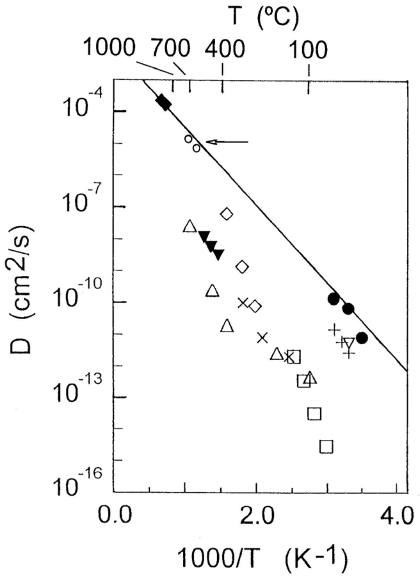

Figure 4. Diffusion constant for H in Si. The straight-line corresponds to the diffusion constant given in Eq. (3), first determined by Van Wieringen and Warmoltz (♦), [21]. Values of D_{eff} determined in the present paper are shown by open circles at 600 and 700°C and are marked by an arrow. Data from Seeger *et al.* (●) [23] and Gorelkinskii and Nevinnyi (not shown) [24] are consistent with Eq. (3) and have been attributed to the diffusivity of isolated H^+ [22]. 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 [10]; see Ichimiya & Furuichi (▼) [25], Pearton (Δ) [26], Mogro-Campero *et al.* (x) [27], Newman *et al.* (◊)[28], Zundel & Weber (□) [29], and Johnson and Herring (+,∇) [30,31].

Similarly, results for the sample annealed at 700ºC give a diffusivity of $D_{eff}(700ºC) = 1.8 \times 10^{-5}$ cm^2/s. These values are plotted in Fig. 4 and show that the effective diffusion constant in our experiments is roughly within a factor of two of the value extrapolated from the results of Van Wieringen and Warmoltz [21]. 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 750ºC used to passivate Si solar cells and suggests that such anneals drive H deep into the Si bulk.

4. CONCLUSION

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 post-deposition annealing of an H-rich SiN_x AR coating. Our results show unambiguously that H diffuses from the SiN_x layer into the Si where it forms complexes with Pt impurities in the Si bulk. The H concentration has been found to be modest in these first experiments, less than $\sim10^{14}$ cm^{-3}. The thickness of the hydrogenated layer is consistent with an H diffusion constant that is a factor of only ~2 smaller than an extrapolation of the classic results of Van Wieringen and Warmoltz [21] would predict.

5. ACKNOWLEDGMENTS

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REFERENCES

[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, Solar Energy Materials and Solar Cells 41/42, 159 (1996).

[4] R. Lüdemann, Mater. Sci. Eng. B 58, 86 (1999).

[5] A. Rohatgi, P. Doshi, J. Moschner, T. Lauinger, A.G. Aberle, and D.S. Ruby, IEEE Trans. Electron. Dev. 47, 987 (2000).

[6] A. G. Aberle, Sol. Energy Mater. Sol. Cells 65, 239 (2001) reviews the SiN_x passivation of c-Si solar cells and includes a historical overview.

[7] F. Duerinckx and J. Szlufcik, Sol. Energy Mater. Sol. Cells 72, 231 (2002).

[8] B. L. Sopori, Y. Zhang, and R. Reedy, Proc. 29th IEEE-Photovoltaic Specialists Conference, New Orleans, May 2002, edited by R. D. McConnell (Report No. NREL/EL-590-32461).

[9] C. Boehme and G. Lucovsky, J. Appl. Phys. 88, 6055 (2000); J. Vac. Sci. Technol. A 19, 2622 (2001).

[10] M. Stavola, in *Properties of Crystalline Si*, edited by R. Hull (INSPEC, London, 1999), p. 511.

[11] S.J. Uftring, M. Stavola, P.M. Williams, and G.D. Watkins, Phys. Rev. B 51, 9612 (1995)l

[12] 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).

[13] *Impurities and Defects in Group IV Elements and III-V Compounds, Vol. III/22b*, in the Landolt-Bornstein, New Series, edited by O. Madelung and M. Schulz (Springer, Berlin, 1989).

[14] J.K. Holt, D.G. Goodwin, A.M. Gabor, F. Jiang, M. Stavola, and H.A. Atwater, Thin Solid Films, to be published.

[15] A. Fadini and F.-M. Schnepel, *Vibrational Spectroscopy* (Wiley, New York, 1989). p. 41.

[16] 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.

[17] If H_2 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 200ºC where the H_2 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 H_2 molecules is smaller that the concentration of PtH complexes we have detected.

[18] An estimate of the concentration of released H made from the change in the IR intensity of the Si-H absorption intensity for the SiN and the calibration given by, W. A. Lanford and M. J. Rand, J. Appl. Phys. 49, 2473 (1978), yields a similar result.

[19] V. Yelundur, A. Rohatgi, A. Ebong, A.M. Gabor, J. Hanoka, and R.L. Wallace, J. Electron. Mater. 30, 526 (2001).

[20] J. P. Kalejs and S. Rajendran, Appl. Phys. Lett. 55, 2763 (1989).

[21] A. Van Wieringen, and N. Warmoltz, Physica 22, 849 (1956).

[22] C. Herring, N. M. Johnson and C. G. Van de Walle, *Phys. Rev. B* 64, 125209 (2001).

[23] C. H. Seager, R. A. Anderson, and D. K. Brice, J. Appl. Phys. **68**, 3268 (1990).

[24] Y. V. Gorelkinskii, and N. N. Nevinnyi, Mater. Sci. Eng. B **36**, 133 (1996).

[25] T. Ichimiya and A. Furuichi, Int. J. Appl. Radiat. Isotopes **19**, 573 (1968).

[26] S. J. Pearton, J. Electron. Mater. **14a**, 737 (1985).

[27] A. Mogro-Campero, R. P. Love, R. Schubert, J. Electrochem. Soc. **132**, 2006 (1985).

[28] R. C. Newman, J. H. Tucker, A. R. Brown, and S. A. McQuaid, J. Appl. Phys. **70**, 3061 (1991).

[29] T. Zundel and J. Weber, Phys. Rev. B **46**, 2071 (1992).

[30] N. M. Johnson and C. Herring, Phys. Rev. B **46**, 15554 (1992).

[31] N. M. Johnson and C. Herring, Mater. Sci. Forum **143-147**, 867 (1994).