Hydrogenation of Dislocation-Limited Heteroepitaxial Silicon Solar Cells

Preprint

Michael L. Bolen, Sachit Grover,
Charles W. Teplin, Howard M. Branz,
and Paul Stradins
National Renewable Energy Laboratory

David Bobela
Ampulse Corporation

Hydrogenation of Dislocation-Limited Heteroepitaxial Silicon Solar Cells

Michael L. Bolen[1], Sachit Grover[1], Charles W. Teplin[1], David Bobela[2], Howard M. Branz[1], and Paul Stradins[1]

[1] National Renewable Energy Laboratory, Golden, CO

[2] Ampulse Corporation, Golden, CO

Abstract — **Post-deposition hydrogenation by remote plasma significantly improves performance of heteroepitaxial silicon (Si) solar cells. Heteroepitaxial deposition of thin crystal Si on sapphire for photovoltaics (PV) is an excellent model system for developing the PV technology platform of film c-Si on inexpensive Al_2O_3-coated (100) biaxially-textured metal foils. Without hydrogenation PV conversion efficiencies are less than 1% in our model system, due to carrier recombination at electrically-active dislocations and other growth defects. Hydrogenation dramatically improves performance, with low-temperature hydrogenation at 350ºC being more effective than hydrogenation at 610°C. Spectral quantum efficiency, secondary ion mass spectrometry (SIMS), and vibrational $Si-H_x$ Raman spectroscopy measurements elucidate the effects of hydrogenation on the materials and devices. Quantum efficiency increases at wavelengths >400 nm, indicating hydrogenation is mostly affecting the bulk of the cells. SIMS detects nearly 100 times more hydrogen atoms in our cells than available dangling bonds along all dislocations. Yet, Raman spectroscopy indicates that only low temperature hydrogenation creates $Si-H_x$ bonds; trapped hydrogen does not stably passivate dangling-bond recombination sites at high temperatures.**

I. INTRODUCTION

Heteroepitaxial growth of silicon (Si) on sapphire substrates serves as a model for PV technology we are developing using Al_2O_3 layers on inexpensive, flexible (100) biaxially-textured metal foils. We have recently demonstrated [1] epitaxial crystalline Si grown on a Al_2O_3/buffer layer/NiW-foil stack, resulting in a 1.1% efficient solar cell. [2] Passivation of the numerous growth defects with atomic hydrogen is critical to achieve our goal of ~15% efficient heteroepitaxial Si solar cells on these inexpensive metal foils. The lattice mismatch between the two crystalline materials creates strain, which leads to dislocation nucleation. Device efficiency is severely degraded through carrier recombination at electrically-active sites, such as threading dislocations and point defects. We address this through two complementary approaches: (i) improved growth techniques to prevent defect formation or propagation into the absorber layer and (ii) passivation of the defects. In this paper, we show that hydrogenation is an effective means to passivate the dislocations in our absorber layer, and has improved our cell efficiency by several absolute percent. Thus, hydrogenation treatments improve dislocation-limited cells similarly to hydrogenation of grain boundaries in polycrystalline Si. [3]-[6] In this work, we discuss optimum hydrogenation conditions in these heteroepitaxial Si cells and relate them to hydrogen diffusion and bonding.

II. EXPERIMENTAL DETAILS

Growth of thin heteroepitaxial crystal Si on the r-plane surface of sapphire is performed by hot-wire chemical vapor deposition from pure silane. The substrate temperature is maintained at ~850ºC while the hot tungsten wire decomposes precursors at ~2100ºC. The growth chamber is maintained at 10 mTorr with a 20 sccm flow of silane and calibrated phosphine flow is added for n-type doping. The first layer deposited on the sapphire is a 2 μm n+ Si back surface contact, followed by a ~1 μm thick n- Si absorber layer. One of the two matched sample pieces is processed into a solar cell for electrical characterization and the other is used for material characterization. The same growth recipe is used for every sample in this work. After epi-Si deposition, each pair of samples is hydrogenated using a remote H_2/Ar plasma. The hydrogenation temperature is a variable under study, with experiments at 350ºC or 610ºC now completed. The other hydrogenation parameters are kept constant: time of hydrogenation 4 hours, chamber pressure 100 mTorr with 80 sccm flow of H_2 and 4 sccm of Ar, and the power output to the plasma RF coil 20 W. Subsequently, solar cells are fabricated by deposition of a hydrogenated amorphous Si heterojunction, followed by top ITO. [1]

III. RESULTS AND DISCUSSION

Figure 1 demonstrates significant improvement in cell performance for two hydrogenation temperatures. Three solar cells are shown: unhydrogenated; hydrogenated at 350ºC; and hydrogenated at 610ºC. Multiple cells are fabricated onto each of the three samples, with similar results, but Fig. 1 shows the highest efficiency device
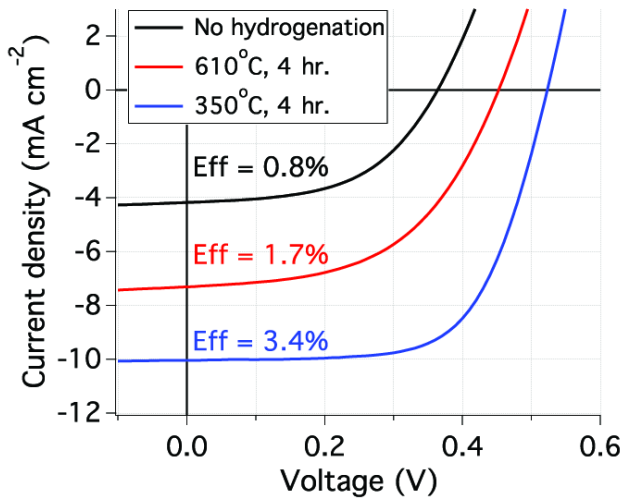
Fig. 1. J-V plot demonstrating efficiency improvement by hydrogenation at two different temperatures for the same time of 4 hours.

Fig. 2. EQE plot showing efficiency increase in wavelengths >400 nm for hydrogenated versus unhydrogenated samples.

from each sample. Without hydrogenation, the best efficiency is 0.8%. With hydrogenation, the efficiency increases significantly for both temperatures. Notably, low-temperature (350°C) treatment, resulting in a 3.4% cell, is superior to that of high-temperature (610°C), yielding a 1.7% cell.

External quantum efficiency (EQE) measurements were performed to identify the spatial regions within the depth of the device that contributed to the increased efficiency by hydrogenation. Figure 2 shows EQE data from the three devices of Fig. 1.

Nearly identical response in the blue region (<400 nm) suggests that near surface junction collection is the same for all of the devices tested, including the unhydrogenated one. Improvement by hydrogenation becomes apparent starting at 400-nm wavelength and continuing into the near infrared portion of the spectrum. Both hydrogenated samples have increased collection efficiency in the bulk of the material, suggesting that hydrogenation has a bulk rather than a surface passivation effect. The long-wavelength EQE improvement is more pronounced for the 350°C sample, in agreement with Fig. 1.

The device results suggest that the efficiency increase is due mainly to improvement in the bulk of the device. We use SIMS and Raman spectroscopy to correlate the results from electrical measurements with materials measurements and gain a deeper understanding of hydrogenation.

SIMS was used to measure the hydrogen concentration profile in the depth of the Si epitaxial layer. Figure 3 shows the hydrogen concentration profiles from the same three devices used in the electrical measurements of Figs. 1 and 2.
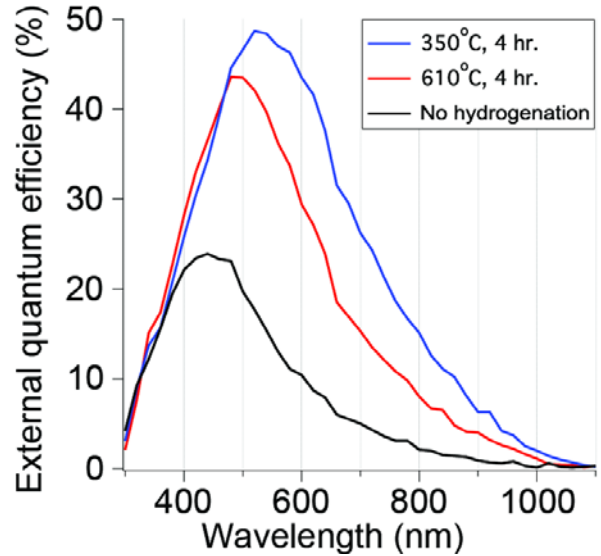
The unhydrogenated sample has a bulk hydrogen concentration value of low-10^{17} cm^{-3} that is nearly two orders of magnitude lower than either of the hydrogenated samples. T he profiles of both hydrogenated samples are qualitatively similar: there is a hydrogen-rich region within the first few hundreds of nm, followed by an almost flat profile deeper in the film. Moreover, the hydrogen concentrations in the flat region are in the same range, between high-10^{18} cm^{-3} to low-10^{19} cm^{-3}, for both hydrogenated samples. Integrating across the Si film, the total amount of hydrogen in both hydrogenated samples is approximately the same: 3.0×10^{15} cm^{-2} in the 350°C sample and 2.6×10^{15} cm^{-2} in the 610°C sample. As a reference, a surface monolayer of hydrogen has approximately 2×10^{15} cm^{-2}, the same order of magnitude as the hydrogen within our whole film.

Of note, the zones of highest hydrogen concentration do not correlate with the regions of highest dislocation density in the samples. TEM micrographs (not shown) exhibit a large number of defects, primarily twins and threading dislocations, with a total density of approximately 10^{10} cm^{-2} at the Si/sapphire interface. As the Si film grows these dislocations coalesce and annihilate, and their concentration decreases approximately inversely proportional to film thickness. After 3 μm of growth the dislocation density is ~10^{8} cm^{-2}. However, this inverse proportionality is not seen in the profiles of either of the hydrogenated samples in Fig. 3. If each diffusing hydrogen atom only bonded along dislocations, then there should be two orders of magnitude more hydrogen at the Si/sapphire interface than in the absorber. Instead, the hydrogen concentration
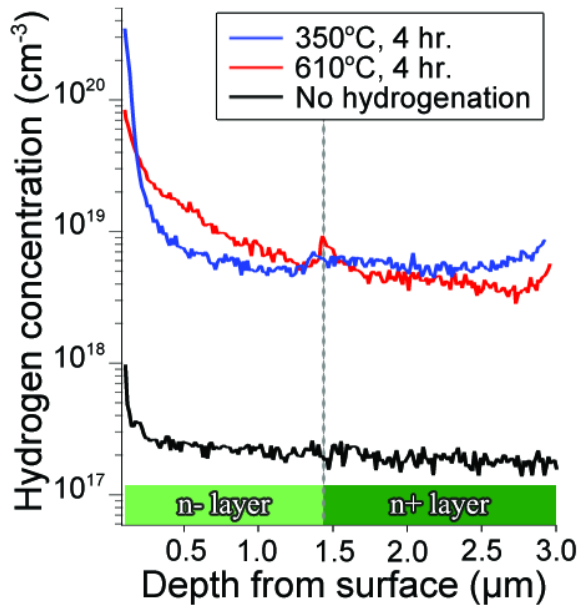
2

Fig. 3. SIMS plot showing increased hydrogen concentration for hydrogenated versus unhydrogenated samples.

Fig. 4. Raman spectra of hydrogenated and unhydrogenated samples with Si-H$_x$ bonds seen only for the low-temperature hydrogenated sample.

differs by less than 3 times throughout the bulk of the hydrogenated films.

Furthermore, let us consider a simplified model: (i) there is an unpassivated dangling bond at each Si atom along a dislocation, and (ii) a dislocation density of $\sim 10^{10}$ cm^{-2} remains constant throughout the crystal Si film (no dislocation annihilation). In this limiting case, the average bulk Si dangling bond density is $\sim 4 \times 10^{17}$ cm^{-3}. From Fig. 3, the unhydrogenated sample already has nearly sufficient bulk hydrogen concentration (from the SiH$_4$ growth precursor) to passivate all dangling bonds. However, the J-V results in Fig. 1 demonstrate poor electrical performance. Moreover, the SIMS hydrogen concentrations of the hydrogenated samples are two orders of magnitude higher than the maximum density of dislocation-related dangling bonds. Orders of magnitude more hydrogen than defects might be a prerequisite for electrical passivation; however, the issue is far from resolved. Nickel *et al* found as little as 3% of hydrogen in their fine-grained polycrystalline Si films passivated dangling bonds. [4]

To better understand the chemical bonds being formed by the hydrogen, we use Raman spectroscopy with an exciting wavelength of 532 nm to probe ~ 0.5 µm into the epitaxial layer. Two wavenumber ranges were explored for this work: molecular H$_2$ vibrations at ~ 4158 cm^{-1} and the Si-H$_x$ (x=1,2,3) stretching modes around ~ 2100 cm^{-1}. [7][8] No molecular H$_2$ peak was found in any of the measured samples, indicating either a lack of formation or
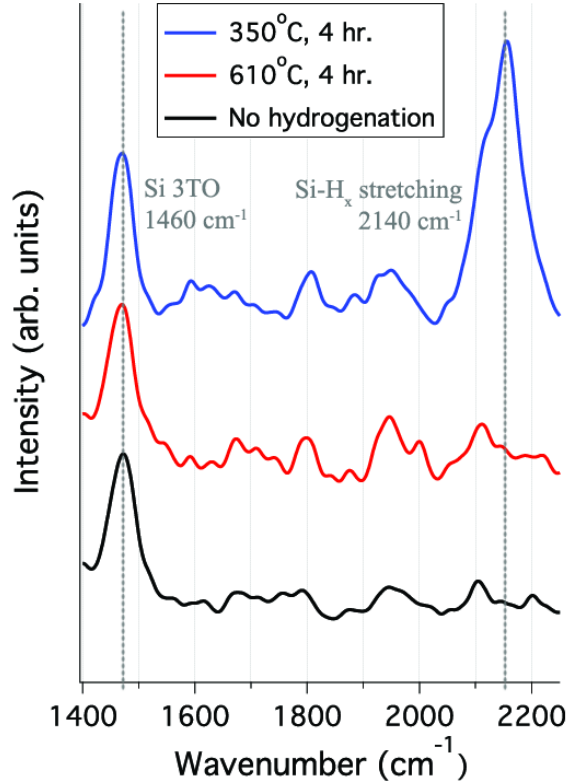
quantities below the detectable limit. Figure 4 shows the Raman spectral range from 1400 to 2250 cm^{-1} for the one unhydrogenated and two hydrogenated samples of Fig. 1. All three samples have a peak around 1460 cm^{-1}, corresponding to the third-order TO phonon peak in c-Si. [9] Only the low-temperature hydrogenated sample shows a Raman signature of Si-H$_x$ bonding. This agrees with low-temperature hydrogenation being more effective than high-temperature (Fig.1). At high-temperatures, hydrogenation is not able to stably form the Si-H$_x$ bonds for dislocation passivation. The Raman signal of Si-H$_x$ formation at low-temperature appears correlated to improved device performance, suggesting that low-temperature hydrogenation is more effective for dislocation passivation. However, the formation of Si-H$_x$ bonds cannot be the sole cause of electrical passivation, since even the high-temperature hydrogenation condition showed increased efficiency. Low-temperature Si-H$_x$ vibrations have been also linked to hydrogen-induced extended defects (i.e. platelets) forming in c-Si, which are not related to dislocation passivation. These defects are circumstantially believed to create midgap traps as found

3

by deep-level transient spectroscopy measurements and correlated to TEM micrographs. [10] However, no platelets have been observed in any TEM micrographs of our material, leading us to conclude that the Si-H$_x$ bonding in our Raman spectra is not due to platelets.

Both electrical- and materials-based characterizations can be explained by the thermal re-emission of hydrogen from Si-H$_x$ trapped states. As the hydrogen diffuses into the Si, it proceeds along a migration energy level. The hydrogen diffuses spatially into the material and is trapped into states at varying energy depths, including deep energy traps around dangling Si bonds. [11] It is energetically favorable for hydrogen to bond at these traps, but if there is enough thermal energy, the hydrogen has a probability of being re-emitted to the migration level. [12] The probability of re-emission falls exponentially with energy depth. At 350°C, if hydrogen falls into a deep trap, there may be a lack of thermal energy to escape the trap state, forming thermally stable Si-H$_x$ vibrational modes that are detected by Raman spectroscopy. Conversely, at 610°C, there is likely enough thermal energy for re-emission from deep Si-H$_x$ traps and the hydrogen does *not* stably fill these trap states; it does not passivate them as effectively. Assuming an energy difference of 1.4 eV between the Si-H bond strength and hydrogen migration energy level [13], it is ~2000 times more likely for the Si-H bond to be broken at 610°C than 350°C. Furthermore, using an attempt frequency of 10^{13} Hz, the Si-H trap will be stable for ~2×10^{-2} s at 350°C versus ~1×10^{-5} s at 610°C. Refilling an empty, unstable dangling bond relies on hydrogen diffusion, and the diffusion energy of atomic hydrogen through c-Si is ~0.5 eV [14], ~1 eV less than the Si-H bond strength. With increasing passivation temperature, the fraction of empty Si-H traps increases, despite increased atomic hydrogen diffusivity through the material. Thus, hydrogenation is less effective at 610°C than 350°C, which is reflected in the electrical results.

IV. CONCLUSION

We have shown a pronounced passivation effect by hydrogenation on our thin heteroepitaxial crystalline Si films. Without hydrogenation, the solar cells have efficiencies of less than 1%. Hydrogenation at 610°C increases the efficiency to 1.7% and hydrogenation at 350°C increases it to 3.4%. EQE measurements show that bulk defect passivation by hydrogenation is dominant, compared to the near-surface defect passivation, in increasing carrier collection. SIMS shows that the hydrogen profile and concentration is similar after a 4 hr hydrogenation at 350°C and 610°C. Furthermore, the bulk hydrogen concentration is ~100 times greater than the number of dangling bonds within the epitaxial layer. Finally, Raman spectroscopy shows Si-H$_x$ resonance in only the 350°C hydrogenated sample; suggesting that hydrogenation at 610°C might not stably passivate Si dangling bonds.

REFERENCES

[1] C. W. Teplin et al., "Heteroepitaxial film crystal silicon on Al$_2$O$_3$: new route to inexpensive crystal silicon photovoltaics," *Energy & Environmental Science*, vol. 4, no. 9, pp. 3346-3350, 2011.

[2] S. Wee et al., "Heteroepitaxial film silicon solar cell grown on Ni-W foils," *Energy & Environmental Science*, vol. 5, no. 3, p. 6052-6056, 2012.

[3] L. Carnel, I. Gordon, K. Van Nieuwenhuysen, D. Vangestel, G. Beaucarne, and J. Poortmans, "Defect passivation in chemical vapour deposited fine-grained polycrystalline silicon by plasma hydrogenation," *Thin Solid Films*, vol. 487, no. 1, pp. 147-151, Sep. 2005.

[4] N. Nickel, N. Johnson, and W. Jackson, "Hydrogen Passivation of Grain-Boundary Defects in Polycrystalline Silicon Thin-Films," *Applied Physics Letters*, vol. 62, no. 25, pp. 3285-3287, 1993.

[5] M. L. Terry, D. Inns, and A. G. Aberle, "Rapid Thermal Annealing and Hydrogen Passivation of Polycrystalline Silicon Thin-Film Solar Cells on Low-Temperature Glas," *Advances in OptoElectronics*, vol. 2007, pp. 1-11, 2007.

[6] B. Rau et al., "Development of a rapid thermal annealing process for polycrystalline silicon thin-film solar cells on glass," *Materials Science and Engineering B*, vol. 159, pp. 329-332, Mar. 2009.

[7] A. W. R. Leitch, V. Alex, and J. Weber, "Raman Spectroscopy of Hydrogen Molecules in Crystalline Silicon," *Physical Review Letters*, vol. 81, no. 2, pp. 421-424, Jul. 1998.

[8] S. J. Pearton, J. W. Corbett, and M. Stavola, *Hydrogen in crystalline semiconductors*. Springer-Verlag, 1992.

[9] A. Zwick and R. Carles, "Multiple-Order Raman-Scattering in Crystalline and Amorphous-Silicon," *Physical Review B*, vol. 48, no. 9, pp. 6024-6032, 1993.

[10] N. M. Johnson, F. A. Ponce, R. A. Street, R. J. Nemanich, "Defects in single-crystal silicon induced by hydrogenation, " *Physical Review B*, vol. 35, no. 8, pp. 4166-4169, 1987.

[11] N. Nickel, N. Johnson, and C. Van de Walle, "Hydrogen-Induced Metastable Changes in the Electrical-Conductivity of Polycrystalline Silicon," *Physical Review Letters*, vol. 72, no. 21, pp. 3393-3396, 1994.

[12] R. A. Street, *Hydrogenated amorphous silicon*. Cambridge University Press, 1991.

[13] W. Beyer, "Diffusion and evolution of hydrogen in hydrogenated amorphous and microcrystalline silicon," *Solar Energy Materials & Solar Cells*, vol. 78, pp. 235-267, 2003.

[14] A. van Wieringen and N. Warmoltz, "On the permeation of hydrogen and helium in single crystal silicon and germanium at elevated temperatures," *Physica*, vol. 22, pp. 849-865, 1956.