

# Silicon Heterojunction Solar Cell Characterization and Optimization Using *In Situ* and *Ex Situ* Spectroscopic Ellipsometry

## Preprint

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# SILICON HETEROJUNCTION SOLAR CELL CHARACTERIZATION AND OPTIMIZATION USING *IN SITU* AND *EX SITU* SPECTROSCOPIC ELLIPSOMETRY\*

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## ABSTRACT

We use *in-situ* and *ex-situ* spectroscopic ellipsometry to characterize the optical, electronic, and structural properties of individual layers and completed silicon heterojunction devices. The combination of *in-situ* measurements during thin film deposition with *ex-situ* measurements of completed devices allows us to understand both the growth dynamics of the materials and the effects of each processing step on material properties. *In-situ* ellipsometry measurements enable us to map out how the optical properties change with deposition conditions, pointing the way towards reducing the absorption loss and increasing device efficiency. We use the measured optical properties and thickness of the i-, n-, and p-layers in optical device modeling to determine how the material properties affect device performance. Our best solar energy conversion efficiencies are 16.9% for a non-textured, single-sided device with an aluminum back surface field contact on a p-type float zone silicon wafer, and 17.8% for a textured double-sided device on a p-type float zone silicon wafer.

## INTRODUCTION

Silicon heterojunction solar cells (SHJ), also known as HIT™ cells (heterojunction with intrinsic thin layer), are a promising new hybrid amorphous silicon – crystal silicon technology that enables high efficiency with relatively simple, low temperature device processing [1]. Extremely thin layers of intrinsic and doped amorphous hydrogenated silicon (a-Si:H) are deposited onto a crystal silicon (c-Si) wafer to passivate the wafer surfaces while also creating an electric field for carrier collection. These devices present unique challenges for characterization and optimization because of the extremely thin layers used in their fabrication. The SHJ devices under development at NREL use 40Å intrinsic layers and 60Å doped layers deposited by hot wire chemical vapor deposition (HWCVD). Effective device optimization requires a method for accurately determining the layer thickness and material properties in a timely manner. Characterization is particularly challenging because it is difficult to measure the properties of such thin layers, and the material properties of a-Si:H change significantly with increasing film thickness and the type of substrate they are grown on. Hence it is not possible to accurately determine the properties of thin a-Si:H layers in the actual devices by growing thicker layers on transparent or other

test substrates. The only accurate method is to measure the material properties and film thickness in the actual device structures.

Spectroscopic ellipsometry (SE) is a powerful method for characterizing the thickness and optical properties of thin films. Because it is an optical technique it can be applied *in-situ* to measure the film thickness and material properties of real SHJ devices during film deposition. Because it is a rapid, non-contact technique, it can be applied to characterize the device at each processing step, providing insight into how each step affects all of the layers in the device. We have made extensive use of both real-time *in-situ* and variable angle *ex-situ* SE (RTSE and VASE) for characterization and optimization of SHJ devices. Extensive details on film deposition conditions and ellipsometry data acquisition and analysis are available in the following reference [2].

## SHJ DEVICE CHARACTERIZATION

A prime example of the value of SE for device optimization is illustrated in figures 1 through 4. Figure 1 shows a comparison of the internal quantum efficiency (IQE) for a standard, diffused junction c-Si solar cell with the IQE for a SHJ cell. Both cells were fabricated on equivalent p-type float zone c-Si wafers with an alloyed aluminum back surface field (BSF) back contact. The only difference between the two devices is the method used for

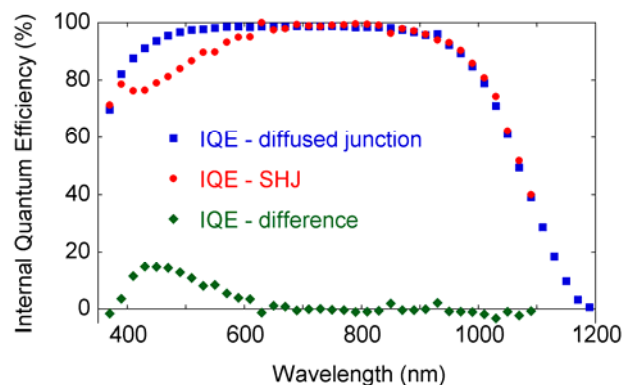


Figure 1. Comparison of the internal quantum efficiency (IQE) for a standard, diffused junction crystal silicon solar cell with the IQE for a silicon heterojunction cell. The diamonds indicate the difference in IQE between the two devices.

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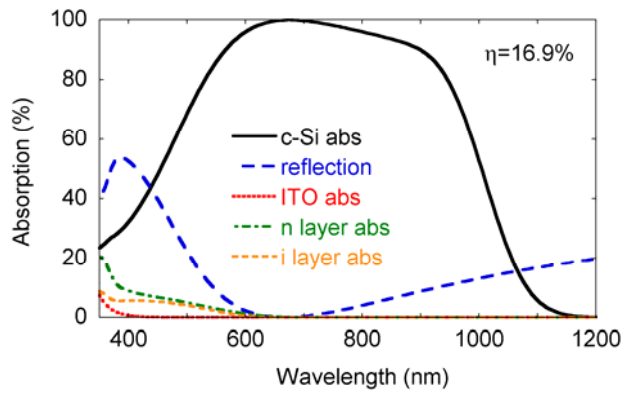


Figure 2. Absorption and reflection components for a 16.9% efficient p-i-n single-sided SHJ device. Values are calculated from optical constants and layer thickness determined from a VASE measurement on the device.

front junction formation. As shown by the diamonds in the figure, the SHJ device suffers a loss in IQE between 400 - 600 nm relative to the diffused junction cell. In order to maximize the current and efficiency in the SHJ device, we would like to determine the origin of this drop in IQE. To investigate this drop, we have measured *ex situ* variable angle spectroscopic ellipsometry, or VASE, on the completed SHJ device. The results of a VASE measurement consist of optical constants and layer thickness for each layer in the device. Using this accurate knowledge of the layer thickness and optical constants we are able to calculate the spectral dependence of the reflection, transmission, and absorption for the various layers that make up the SHJ device. Figure 2 shows the spectral dependence of absorption and reflection as calculated from the optical model of the SHJ device. The solid line is the percent of incident light that is transmitted through the indium-tin-oxide (ITO) and i- and n-layers and absorbed in the c-Si wafer. The dashed line is the total normal-incidence reflection from the device, the dotted line is the absorption in the ITO layer, the dot-dash line is the absorption in the n layer, and the short-dash line is the absorption in the i layer. We note that in comparison to the IQE data in figure 1, the c-Si absorption in figure 2 will correspond more closely to the *external* quantum efficiency rather than the IQE.

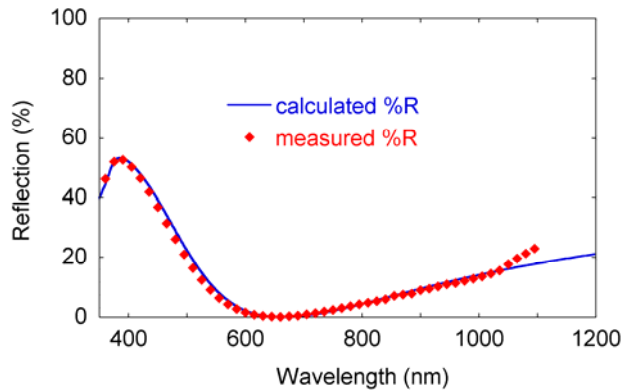


Figure 3. Comparison of calculated normal-incidence reflection from device of figure 2 with measured normal-incidence reflection.

To verify the accuracy of the optical model we have measured normal incidence reflectivity for the complete SHJ device and compared this to the calculated reflectivity based on the VASE measurement. Note that although ellipsometry is a reflection measurement, it measures the phase and amplitude ratio for parallel and perpendicular polarization components at an oblique angle of incidence rather than the normal-incidence reflection amplitude. Hence, the information obtained in an ellipsometry measurement is quite distinct from that obtained in a normal-incidence measure of the reflectivity. Figure 3 shows the normal-incidence reflection data as squares, and the calculated reflectivity as a solid line. Clearly the correspondence is excellent, except at wavelengths greater than 1000 nm. We believe this long-wavelength disparity is due to reflection from the BSF contact at wavelengths beyond the c-Si bandgap, which we have not included in our optical calculation. Based on the excellent correspondence between calculated and measured reflectivity above the c-Si bandgap we have confidence that the calculated values of absorption in the individual layers are also accurate.

This leads to a valuable insight into the nature of the drop in IQE for the SHJ device relative to the diffused junction device. Figure 4 compares the difference in IQE from figure 1 with the sum of the absorption in the i- and n-layers calculated from the ellipsometry results. Although the values diverge at the shortest wavelengths, the agreement is very good. We conclude that in our present device configuration there is almost no collection of carriers photoexcited within the a-Si:H emitter. We are currently working on strategies to reduce the absorption in these layers through increased bandgap or decreased thickness, or to find a way to collect carriers that are photoexcited within these layers.

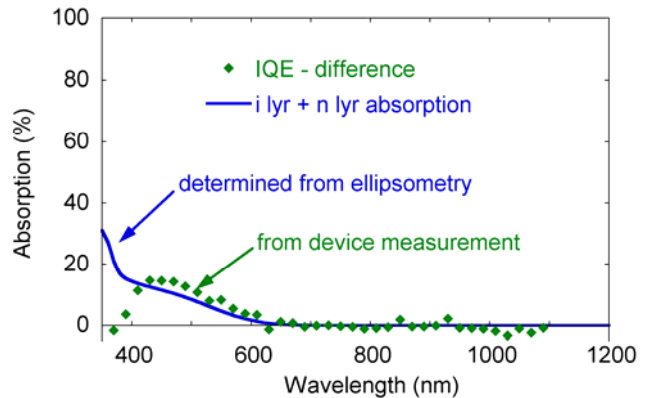


Figure 4. Difference in IQE between the SHJ device and an otherwise identical diffused junction device, compared with the calculated absorption in the i- and n-layers.

### IN SITU CHARACTERIZATION OF MATERIAL PROPERTIES

In addition to VASE measurements, we have also used *in-situ* RTSE measurements to study how changes in deposition parameters affect material properties in SHJ devices. *In situ* measurements are particularly valuable for the very thin (40 - 60Å) layers used in SHJ devices because we are able to obtain a series of ellipsometry



spectra that are constrained to have a linear increase in film thickness while maintaining the same optical properties. This is important because obtaining optical properties from layers less than 200Å thick is pushing the limits of ellipsometry. The additional information and thickness constraints of RTSE data enable accurate determination of the layer optical properties.

During the HWCVD deposition process the substrate temperature  $T_s$  can have a significant and systematic impact on the properties of the deposited film. Optical properties are affected by the structural and electronic properties of the material; hence the optical properties provide a sensitive measure of how the electronic and structural properties are changing. The optical properties of a material can be expressed in terms of the dielectric function  $\epsilon$ , where  $\epsilon$  has both real and imaginary parts,  $\epsilon_1$  and  $\epsilon_2$ , respectively.  $\epsilon_1$  and  $\epsilon_2$  are related by the Kramers-Kronig relation, hence knowing the  $\epsilon_2$  spectrum provides  $\epsilon_1$  as well [3].  $\epsilon_2$  is proportional to the joint density of states for optical transitions between occupied states in the valence band and unoccupied states in the conduction band. As such it is directly related to both the electronic structure and optical properties of the material and we will focus on  $\epsilon_2$  for our discussion of the properties of the thin a-Si:H layers used in SHJ devices.

Figure 5 shows  $\epsilon_2$  for a series of i-layers grown on HF-etched <100> c-Si substrates over a range of  $T_s$  from 90°C to 160°C. The four lowest-temperature films exhibit the broad featureless  $\epsilon_2$  spectrum characteristic of a-Si:H. There is a monotonic increase in amplitude and decrease in center energy with increasing  $T_s$ . These changes in  $\epsilon_2$  indicate a decrease in hydrogen content in the film as  $T_s$  increases [4]. The films deposited at 145°C and 160°C exhibit qualitative differences in their  $\epsilon_2$  spectra relative to the lower-temperature films. The 145°C film appears to be nanocrystalline silicon (nc-Si), while the 160°C film exhibits the dielectric spectrum of crystal silicon, indicating epitaxial deposition. As we have shown previously, high efficiency SHJ PV devices depend on the highly effective passivation of the c-Si surface provided by a-Si:H deposited directly on a clean c-Si surface [5]. Hence it is imperative that i-layer deposition temperatures be kept below 145°C.

Quantitative analysis of the optical properties provides further insight into how the i-layers change with  $T_s$ . Figure

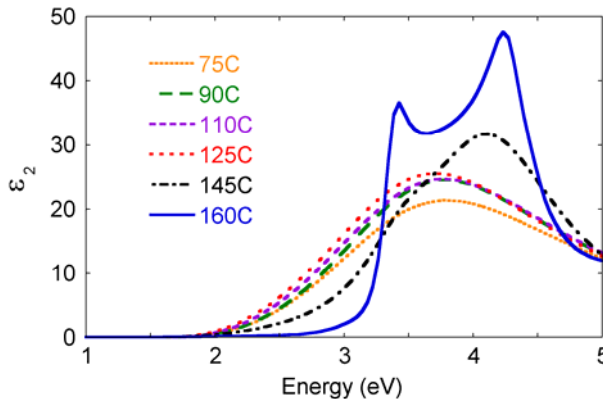


Figure 5.  $\epsilon_2$  spectra for a series of i-layers grown on HF-etched <100> c-Si substrates over a range of  $T_s$  from 75°C to 160°C.

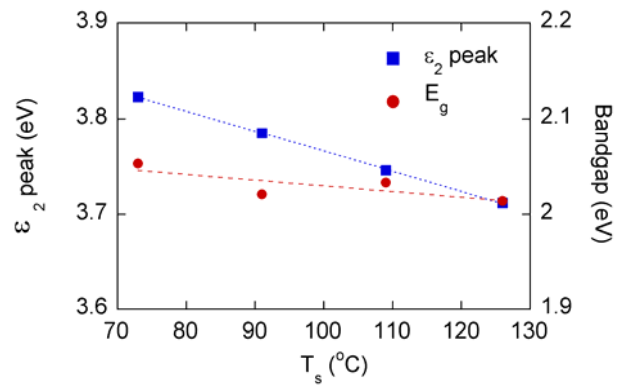


Figure 6. Dependence of i-layer  $\epsilon_2$  peak energy and Tauc's bandgap on substrate temperature for i-layers grown on HF-etched <100> c-Si substrates.

6 shows the  $T_s$  dependence of the  $\epsilon_2$  peak energy and the Tauc's bandgap for the i-layers. Tauc's bandgap is a standard means for expressing the band gap of a-Si:H and is determined by calculating the zero intercept of the tangent to the linear portion of  $\sqrt{\alpha E}$ , where  $\alpha$  is the absorption coefficient and  $E$  is the photon energy [6]. The range of  $T_s$  in the figure is limited to the range where the i-layers are amorphous. The linear fit to the  $\epsilon_2$  peak indicates a drop of 210 meV for each 100°C increase in  $T_s$ . From reference [4] we know that the peak in  $\epsilon_2$  drops 17 meV for each 1% decrease in the hydrogen concentration of the film, hence the hydrogen content in the i-layers likely decreases by 6% over the 50°C range in  $T_s$  depicted in figure 6. The linear fit to the bandgap indicates a decrease of 30 meV over the 50°C range in  $T_s$ .

Figure 7 shows how the  $\epsilon_2$  spectra evolve with  $T_s$  for n-layers deposited on 40Å thick i-layers. Although the graph covers a much larger temperature range of 90-270°C, the  $\epsilon_2$  spectra change much less than the i-layer spectra do over a much smaller range. This is because the n-layers are deposited on an a-Si:H i-layer, hence the onset of nc-Si deposition occurs at much higher temperatures for the n-layer and n-layer optical properties are much less sensitive to substrate temperature.

Figure 8 presents the quantitative analysis of the n-layer dielectric function. Here the linear fit to the  $\epsilon_2$  peak vs.  $T_s$  has a slope of  $-120 \text{ meV} / 100^\circ\text{C}$  and the fit to  $E_g$

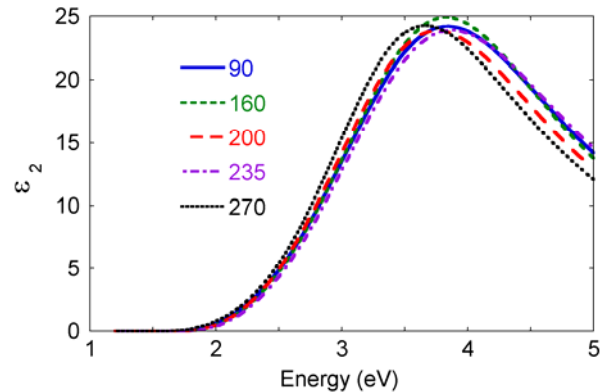


Figure 7.  $\epsilon_2$  spectra for a series of n-layers grown on 40Å thick amorphous i-layers over a range of  $T_s$  from 90°C to 270°C.

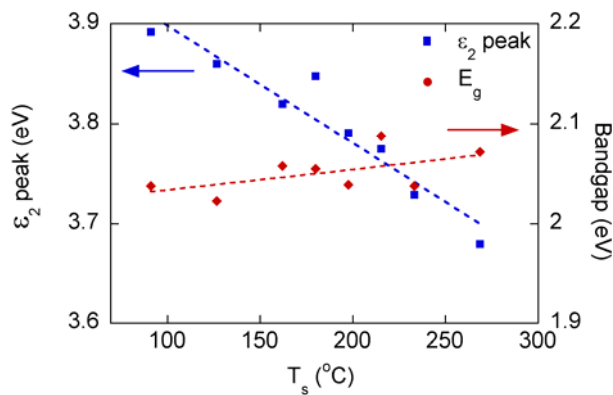


Figure 8. Dependence of n-layer  $\epsilon_2$  peak energy and Tauc's bandgap on substrate temperature for n-layers grown on 40Å thick amorphous i-layers over a range of  $T_s$  from 90°C to 270°C.

vs.  $T_s$  has a slope of +20 meV / 100°C. It is notable that the rate of change of the  $\epsilon_2$  peak is nearly half that of the i-layers, while the rate of change of  $E_g$  has the opposite sign of that for the i-layers. This is likely due to two competing factors in the n-layer properties. Because the n-layers are deposited on amorphous silicon layers, the transition to nc-Si growth occurs at a much higher temperature and short-range order can increase without initiating nc-Si growth. Increasing short-range order tends to increase the bandgap and the  $\epsilon_2$  peak energy. Hence the effects of reduced hydrogen composition and increased short-range order tend to offset each other and reduce the overall changes in the optical properties with substrate temperature.

The discussion up to this point has focused on i- and n-layers used in n-i-p SHJ devices deposited on p-type FZ c-Si wafers. Our research team at NREL has recently transitioned to fabrication of p-i-n SHJ devices deposited on n-type FZ c-Si wafers. This necessitates developing an understanding of the growth dynamics and properties of p-layers as a function of deposition conditions.

The dependence of the  $\epsilon_2$  on substrate temperature for the p-layers is quite similar to the n-layer dependence, although the bandgap tends to slightly decrease with increasing  $T_s$ , as opposed to the n-layers, where it slightly increases. For the p-layers the linear fit to the  $\epsilon_2$  peak vs.  $T_s$  has a slope of -135 meV / 100°C and the fit to  $E_g$  vs.  $T_s$  has a slope of -10 meV / 100°C. The difference in trends is likely due to differences in doping with di-borane as opposed to phosphene used for n-layers.

As efforts proceed to optimize the p-i-n SHJ devices, our research team has initiated a study of the effect of doping in the p-layers through variation of the concentration of  $B_2H_6$  during p-layer deposition. This is accomplished by varying the flow rate of  $B_2H_6$  gas into the HWCVD deposition chamber. Figure 9 shows how the p-layer Tauc's bandgap changes with  $B_2H_6$  flow. For flow rates between 5 and 18 sccm, we find that the bandgap decreases slightly, at a rate of 8.5 meV per 1 sccm of  $B_2H_6$  flow. At the flow rate of 2 sccm we find that the  $\epsilon_2$  spectrum is beginning to show signs of a transition to nc-Si growth. Although the Tauc's gap bandgap analysis is no longer rigorously accurate for this material that is

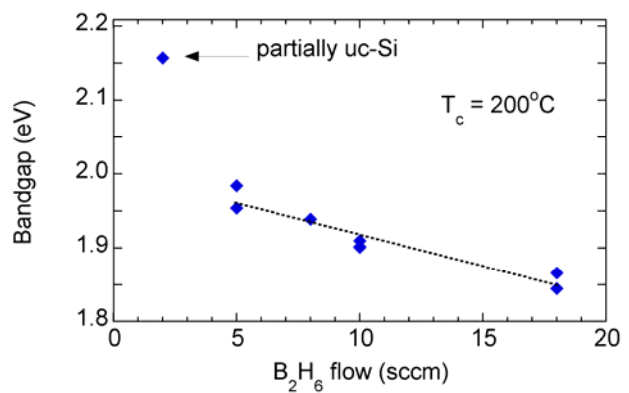


Figure 9. Tauc's bandgap vs.  $B_2H_6$  flow for p-layers deposited on 40Å thick amorphous i-layers at  $T_s$  of 200°C.

beginning to transition to an indirect gap, we include a point on the plot to emphasize the qualitative change that occurs at 2 sccm.

## CONCLUSIONS

The combination of *in situ* and *ex situ* spectroscopic ellipsometry provides unique capabilities in characterizing the properties of very thin layers used in SHJ PV devices. Due to the thinness of these layers and the template effects associated with growing test films on non-device substrates, ellipsometry provides one of the only techniques capable of obtaining information on the material properties of these layers in actual device structures. This knowledge of the i-, n-, and p-layer properties has proven useful in delineating the effects that changes in these layers have on the device function and efficiency, and also provide guidance in optimizing SHJ device function and efficiency.

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