# Characterization of Microcrystalline and Amorphous Thin Film Silicon Devices with Raman Spectroscopy


J. Hodkiewicz* and M. Wall**

*Thermo Fisher Scientific, 5225 Verona Road
Madison, WI 53711, USA, joe.hodkiewicz@thermofisher.com
**Thermo Fisher Scientific, Madison, WI, USA, mark.wall@thermofisher.com



## ABSTRACT

Silicon deposited on glass or silicon carbide is widely used in manufacturing photovoltaic cells. Both the proportion and distribution of amorphous and crystalline silicon are critical for performance and are therefore important to monitor. Raman spectroscopy is an ideal technique for this application, as the two forms generate readily distinguishable spectra that lend themselves to simple quantification methods using Beer's Law. Mapping generates chemical images with detailed information on the spatial distribution of the crystalline and amorphous forms. Since excess excitation laser power can convert amorphous silicon into crystalline silicon, care must be taken to limit the amount of power used. The Thermo Scientific DXR Raman microscope, which is equipped with a laser power regulator, is ideal for this application, particularly if the method has to be replicated from instrument to instrument at multiple manufacturing plants.



***Keywords***: microcrystalline silicon, raman, silicon fraction


## 1 EXPERIMENTAL

All Raman microscopy characterization was performed with a Thermo Scientific DXR Raman microscope configured with a 532 nm excitation laser. The instrument was operated using the Thermo Scientific OMNIC 8 software suite. OMNIC™ Atlμs™ mapping software was used to collect and analyze mapping data.

## 2 RESULTS AND DISCUSSION

### 2.1 Crystalline Versus Amorphous Silicon

Figure 1 shows typical silicon spectra from samples that range from pure crystalline to those containing significant amounts of amorphous material. The strong band at 521 $cm^{-1}$ of the crystalline sample is clearly distinguishable from the broad band centered at 480 $cm^{-1}$ that is exhibited by the amorphous silicon. These very distinct spectra make it possible to use a simple Beer's law calculation based on the ratio of the peak heights at 521 $cm^{-1}$ and 480 $cm^{-1}$ to estimate the relative amounts of the two forms.

### 2.2 Distribution of Amorphous and Crystalline Silicon

Raman mapping is an excellent way to obtain information about potential variations in crystallinity over areas of deposited silicon. By mounting the sample on a motorized stage and collecting Raman spectra at specified intervals across the sample, it is possible by analyzing the spectra to determine the distribution of the silicon forms. Figure 2 shows a 30 micron line map across a sample of deposited silicon. The strong Raman band at 521 $cm^{-1}$ at about half way across the map shows that there is a small region of crystalline silicon at this location. The remainder of the mapped sample shows the broad Raman band at 480 $cm^{-1}$.

A two-dimensional (x, y) map collected across a boundary region between crystalline and amorphous forms is shown in Figure 3. In this case OMNIC Atlμs software was used to display the spectral data as a chemical image of the distribution of the two forms by calculating the ratio of the peak heights at 521 $cm^{-1}$ and 480 $cm^{-1}$. The map shows the gradient between the two forms and can be used as a quality check during manufacture.

### 2.3 Considerations in Using Raman Spectroscopy for Silicon Analysis

Laser power is the key instrumental parameter that needs to be given careful consideration for this analysis.

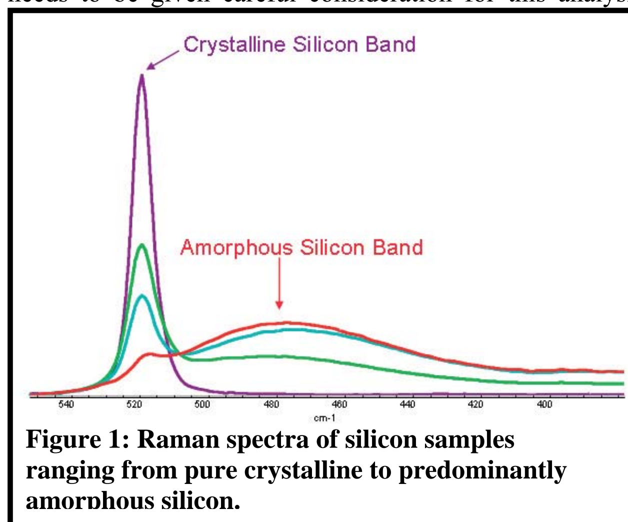


**Figure 1: Raman spectra of silicon samples ranging from pure crystalline to predominantly amorphous silicon.**

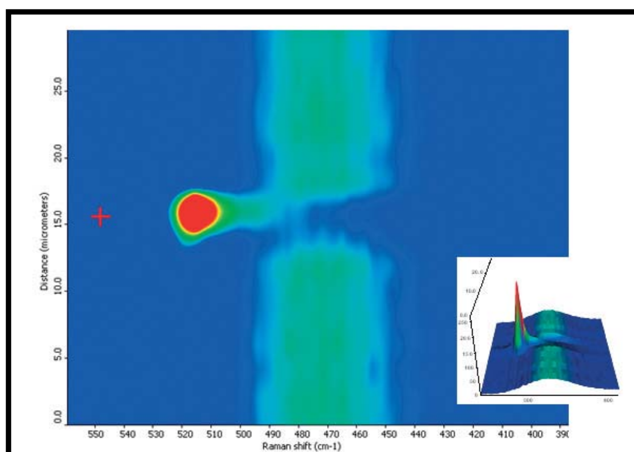


**Figure 2: A 30 micron line map across a sample of deposited silicon. Raman intensity is indicated by color (high intensity is red; low intensity is blue).**

The results in Figure 4 show that as the power of the excitation laser is increased above a threshold, amorphous silicon is converted to the crystalline form. The DXR Raman microscope used in these experiments features a laser power regulator which uses a feedback mechanism to control closely the amount of laser power delivered to the sample. This is important, as laser power output can vary quite markedly from one laser to another, even when the lasers are nominally rated to be equivalent. When using instruments without a laser power regulator, users need to exercise care, particularly when transferring methods from one instrument to another. Using the DXR Raman microscope configured with a high brightness 532 nm laser, we saw no evidence of conversion of amorphous to crystalline silicon at power levels lower than 4 mW. In developing analytical methods for this application, we recommend starting at low excitation laser power levels to ensure that no conversion of amorphous to crystalline silicon takes place.

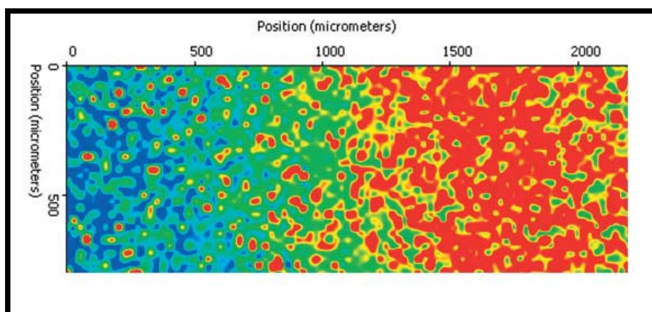


**Figure 3: A 750 x 2,250 micron, two-dimensional map of a sample of silicon deposited on glass. The chemical image was generated by calculating the ratios of the peak heights at 521 and 480 cm-1 at each point on the map. Crystalline areas are shown in red and amorphous in blue.**

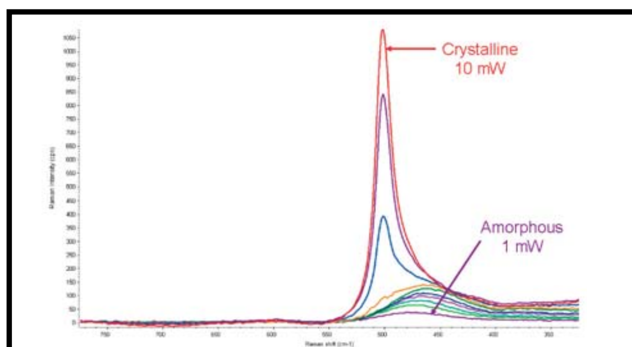


**Figure 4: The effect of excitation laser power on amorphous silicon. The 532 nm excitation laser power at the sample was controlled by the DXR Raman microscope laser power regulator and was increased in 1 mW steps from 1 to 10 mW. Results show little effect on the amorphous silicon at power levels up to 4 mW. Higher laser power progressively converts the amorphous silicon to the crystalline form.**

## 3 SUMMARY

Raman is a very powerful and valuable technique that can be of great benefit to characterization of silicon crystalline fraction. This application note demonstrates that Raman spectroscopy is an excellent technique for monitoring deposited silicon used for photovoltaic applications. The technique readily permits quantification of amorphous and crystalline forms. Raman mapping provides detailed information about spatial distribution. Every lab that is characterizing silicon photovoltaics will benefit from having access to Raman instrumentation.