

# Feature Article

## A Cross-Discipline Article on Photovoltaic Measurements — HORIBA Scientific instrumentation for the photovoltaic market —

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HORIBA Scientific manufactures several pieces of equipment that perfectly fit into the area of material research applied to photovoltaic technologies, with capabilities that extend from the lab into the fab, to serve the needs of the research community and industry alike. A review of the status of different solar cell technologies is presented here, as well as an overview of our Scientific division technologies of interest to provides background information about applicable techniques. Several typical current applications are then presented, and future potential areas of interest are identified.

### Introduction

The photovoltaic industry has grown steadily in the past decade to become a noticeable source of energy, and a promising source of renewable energy. However popular the technology is today, performances are still far from the theoretical limits of solar-energy conversion, which is why solar energy brings great hopes of becoming a cost-effective alternative to fossil fuels. First-generation cells are now mass-produced by the hundreds or thousands of megawatts to reduce cost, while much research efforts are put into improving second-generation and developing third-generation cells.

### Solar-cell technologies and materials

The primary material used in the solar industry, especially in first generation cells, is the well-known silicon (Si), easily extracted and purified from sand, and therefore theoretically available in quasi-unlimited quantities. Crystalline silicon (c-Si) yields the best performances, yet it is more expensive to produce, and multi-crystalline Si, amorphous, poly-crystalline, and mixtures of those, tend to be more cost-effective; these therefore have dominated the market in terms of volume produced, despite the larger surface area needed per watt. Surface area is typically not the limiting factor for large commercial projects or solar farms. On the other end of the spectrum, solar-concentrator cells pack very high efficiency into small cells typically made of III-V semiconductor

materials such as gallium arsenide (GaAs), indium gallium arsenide (InGaAs) and/or indium gallium phosphide (InGaP). In these smaller cells optical elements (concentrators) are used to focus light from a larger area onto the small cell. Those types of cells usually require solar-tracking systems. Comparatively the cost of materials becomes negligible; it is in reducing the cost of optics and mechanical parts that savings can occur, as well as in improved efficiency.

In between, we find a variety of technologies, all of which offer different trade-offs: thin-film silicon cells became extremely popular in the past few years as the cost of silicon increased, and reducing cost of materials became a main priority. Depositing thin films on top of a glass substrate was more cost-effective than plain silicon wafers, while it also offered new possibilities for much larger cells, and even flexible substrates. Unfortunately the thin-film silicon revolution was short-lived as prices of bulk silicon dropped, thanks to the push of the major producers to increase production and lower costs.

The thin-film effort, however, was not in vain, for many of the latest technologies involve thin-film coatings.

Cadmium telluride (CdTe) has become one of the most popular materials thanks to the ability of FirstSolar to mass-produce this type of thin-film cells at a lower cost per watt than that of silicon based cells. This results, however, at the expense of toxicity, cadmium being a

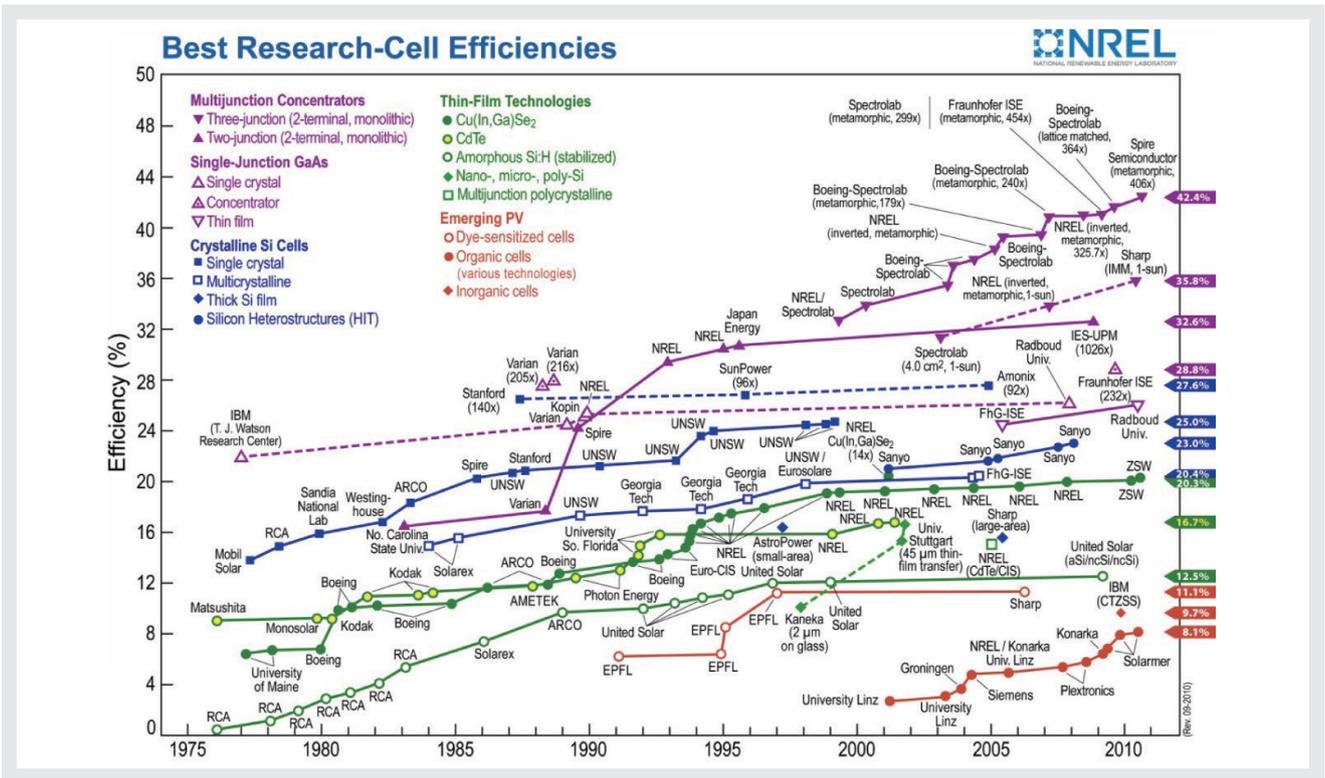


Figure 1 Include a caption for the figure, in the following format: Figure 1. Growth of cell efficiency with time. Refer to Figure 1 in the text. I am not sure where you actually discuss this graph directly in the text, however. If you don't, please add a sentence or two in the text itself with a reference to this graph.

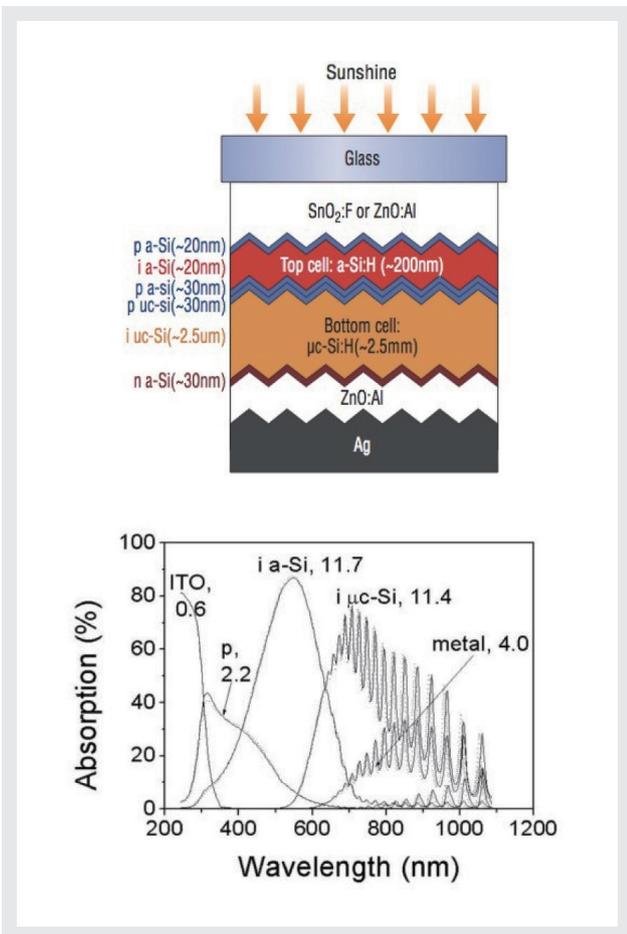


Figure 2 Up: Structure of a multi-junction cell. Down: Absorption of a multi-junction cell vs. wavelength.

well-known health hazard, which implies producing with recycling in mind.

Copper indium gallium di-selenide (CuInGaSe<sub>2</sub> or CIGS) seems to have now proven as efficient, if not more efficient, than multi-crystalline silicon, and enormous efforts are made by large photovoltaic manufacturers to bring this technology to mass-production.

Some other exotic materials are also in use, but most research efforts are directed at improving efficiency of the current materials named above, to build cells that are capable of taking advantage of a broader spectral range. This is the reason for multi-junction cells. Also called tandem junction, or tandem cells, they are mostly produced using thin-film deposition methods to make the second- and third-generation photovoltaic cells—by stacking multiple cells that absorb light in overlapping spectral ranges—The final cell absorption spectrum is increased, therefore improving energy-conversion efficiency.

Finally, efforts based on organic materials are still in the research stage, with few commercial products available. These cells are typically of very low efficiency, and lifetime is a problem. However when they can be formulated for stability, this type of cell could bring the lowest manufacturing cost of all technologies, along with

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very low installation costs (such as with adhesive rolls that could be applied to any surface).

### Instrumentation from HORIBA Scientific in use in photovoltaic research and process control.

HORIBA Scientific offers a wide variety of instruments for material characterization, from elemental analysis to molecular analysis, to thin-film thickness, composition and interface characterization, as well as defect, purity and stress measurement. The basics of each technique are described below:

#### Ellipsometry

Ellipsometry is probably the most commonly used piece of instrumentation of all in the field of photovoltaic research and development. Ellipsometry is a light-based technique based on observing the change in polarization of a light beam as it is reflected at interfaces or refracted through a stack of films. The technique typically monitors phase and amplitude of the reflected beam, which translates into the parameters  $n$ , index of refraction, and  $k$ , dielectric constant. These parameters in turn, after fitting a model of the film stack, can provide information about the thickness of each film in the stack.

Spectroscopic ellipsometry uses a broad-band excitation source, as opposed to a single wavelength, so that more information can be extracted from the measured data, such as variation in composition, surface roughness or stress.

HORIBA Scientific's Spectroscopic Ellipsometers (SE) use a unique design (see Figure 3) based on an electro-optical element called a photoelastic modulator (PEM), which allows ultra fast data-acquisition rates with no moving parts, resulting in averaging of many more data points, low noise and the best detection limit on the market.

Ellipsometry is best suited for thin films ranging from a few Angstroms to a few microns thick.

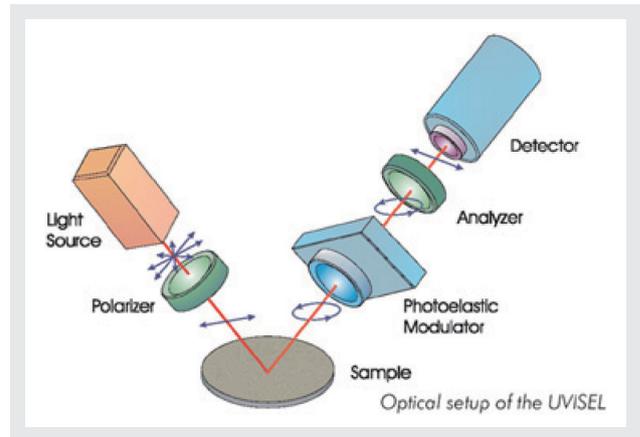


Figure 3 Schematic of a HORIBA Scientific spectroscopic ellipsometer.

#### Glow Discharge

Glow Discharge is a plasma-based elemental analysis technique consisting in sputtering a piece of material to eject one atomic layer at a time, which, when ejected, gets excited in the plasma to emit photons at wavelengths specific to each atom. The emitted light is collected and sent to a polychromator, which disperses the different wavelength towards discrete high-speed photomultiplier (PMT) detectors. This technique is destructive, for the atoms are extracted from the sample; however, it only requires local vacuum and no special sample-preparation, which is much more convenient than similar techniques like Secondary Ion Mass Spectroscopy (SIMS) and comes at a much lower cost.

The Glow Discharge GD Profiler is especially useful for rapid depth-profile analysis of multi-layer multi-element films of variable thicknesses from nanometers to several dozen microns. The very high speed and high dynamic range of the PMT detectors allow measurement of relative composition from 100% down to the parts-per-million (ppm) level.

#### Energy Dispersive X-Ray Fluorescence (ED-XRF)

X-Ray Fluorescence is a non-destructive elemental-analysis technique using a parallel x-ray beam as a source projected onto the material to be analyzed (Figure 4). The x-ray bombardment causes electrons to be ejected from the atoms in the materials, which are quickly replaced by electrons from higher electronic shells, emitting photons in the x-ray spectral region as they

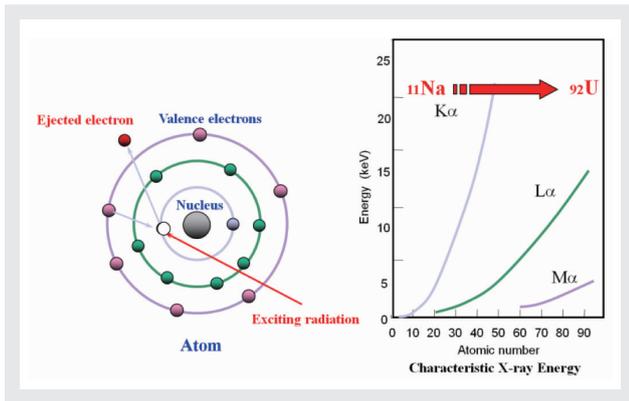


Figure 4 How ED-XRF works. Left: Exciting radiation ejects a K-shell (inner) electron. Right: Shift of inner-shell ejected-electron energies with atomic number.

decay.

A silicon-based energy dispersive detector (EDS) collects the emitted x-ray wavelength.

An EDS detector contains a crystal that absorbs the energy of incoming x-rays by ionization, yielding free electrons in the crystal that become conductive and produce an electrical charge bias. The x-ray absorption thus converts the energy of individual x-rays into electrical voltages of proportional size; the electrical pulses correspond to the characteristic x-rays of the element.

Only local vacuum around the detector is required for most elements, so the technique is very fast and convenient, requiring no sample preparation.

HORIBA’s guide-tube technology used in the XGT system series provides a unique way to concentrate high-energy x-rays into a small spot for high spatial resolution, while keeping a parallel beam, which eliminates the need to focus the beam precisely.

### EMGA Oxygen/Nitrogen analyzer

EMGA is used to determine very low concentrations of oxygen or nitrogen in materials. The sample is placed in a graphite crucible, and the crucible is supported between the upper and the lower electrode of the impulse furnace. A very high current is passed through the crucible to bring the sample to very high temperature. (See Figure 5.)

In the sample, the oxide that reacts with the graphite crucible is extracted as carbon monoxide (CO), and flows through a dust filter to the analyzer with a carrier gas. The oxygen concentration is determined by CO analysis

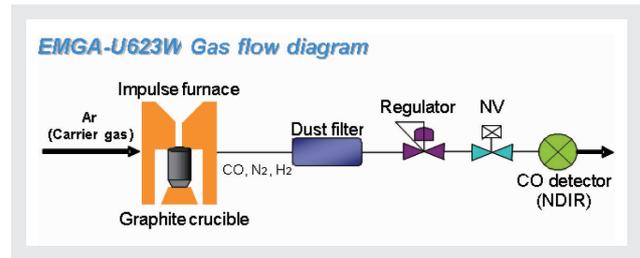


Figure 5 Schematic of an EMGA analyzer. Argon, the carrier gas, carries gaseous analytes from the crucible through filtration to a CO detector.

with a non-dispersive infrared analyser (NDIR).

### Raman Spectroscopy

Raman spectroscopy is a vibrational spectroscopy technique that provides information on molecular bonds and their local environment, which helps determine chemical composition and properties. It typically consists of using a continuous-wave single-wavelength laser to excite the chemical bonds within a sample. Starting from a ground state, a bond can be brought to a virtual vibrational state, and either return to the ground state or be excited up to a higher real vibrational state. When returning to the ground state, there is no energy change, and the scattered light is the same wavelength as the laser. This is called Rayleigh scattering, and is the most common phenomenon. However, if the bond drops down to a different vibrational state, it will have absorbed some energy from the excitation laser beam, and scatter light at a different wavelength, offset from the laser by a value specific to the molecular bond. This effect is called Raman scattering. (See Figure 6.)

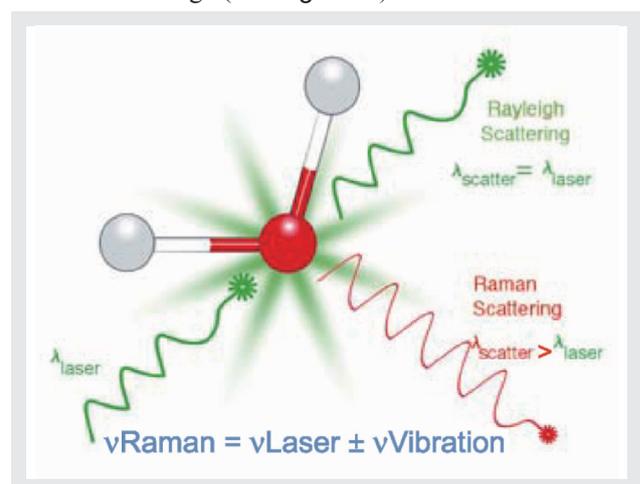


Figure 6 How Raman spectroscopy works. The source wavelength (green) excites a molecule, causing Rayleigh and Raman scattering (see text for details).

Because each possible molecular-bond vibration (also called mode) has a specific energy shift, Raman scattering provides a “fingerprint” of the bonds present in the

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molecule, and allows identification of complex molecules as well as differentiation of closely-related polymorphs, of phases of the same material, or stress and defects in ordered structures.

Because it is a light-based technique, it is non-contact, non-destructive, and is the ideal technique for process control or quality control.

### Photoluminescence spectroscopy

Photoluminescence is a type of fluorescence (which is a process in which a substance absorbs photons and then re-radiates photons). This can be described as an excitation to a higher energy state and then a return to a lower energy state accompanied by the emission of a photon. The period between absorption and emission is typically extremely short, in the order of 10 nanoseconds. Under special circumstances, however, this period can be extended into minutes or hours. Ultimately, available energy states and allowed transitions between states (and therefore wavelengths of light preferentially absorbed and emitted) are determined by the rules of quantum mechanics. Photoluminescence is usually observed using a single wavelength for excitation, so it is very similar to the Raman hardware configuration, which makes it possible to do with the same equipment.

Photoluminescence provides information on possible electronic transitions, which is directly related to the ability to convert energy from electron to photons, and back.

### Applications

In order to improve cell efficiency, the photovoltaic research community needs tools to analyze characteristics of the materials developed, and understand the mechanisms involved in producing a successful prototype. For the industry, the challenge is to find ways to mass-produce cells with characteristics as close to the prototype as possible, using cheap manufacturing techniques. Since producing a cell requires many steps, from substrate to absorbing layer to contacts layer and protective layers, and it is critical to minimize costs, unsatisfactory products need to be rejected as early as possible. Process monitoring and quality-control tools are important to insure high yields.

Some common applications of HORIBA Scientific

instruments are presented below, which are not only popular but more and more critical to successful development and manufacturing of efficient cells.

### Thin film thickness-measurement and depth-profiling (SE, GD-OES)

Layer-thickness measurement is one of the most common applications in the thin-film type of cells (Figure 7), because of specific cell-stack requirements for efficiency, or more often for material cost-savings.

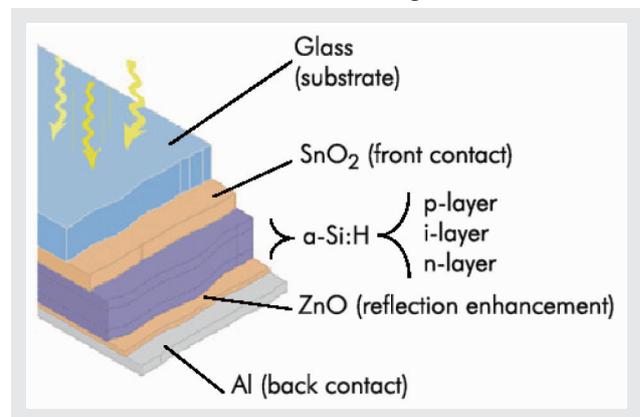


Figure 7 Multiple layers in a thin-film cell, all of which need to be characterized.

Spectroscopic Ellipsometry (SE) is particularly effective on very thin layers, and is the only technique for monitoring layers in the Angstrom-to-nanometer thickness range, as well as for monitoring complex stacks in one measurement. Because it is a non-contact and non-destructive method, it is well suited for quality control, either inline or at-line, or even in-situ within a process chamber, for real-time monitoring of layer deposition.

This monitoring method applies to silicon thin films, as well as CdTe, CIS and CIGS materials, which are all thin-film technologies, although they require different detection ranges. It also applies to the other layers such as TCO (transparent conductive oxides) used as electrodes, and polymer-based thin films.

Sometimes, however, layers are too thick to be easily analyzed by ellipsometry, which can then only characterize the top of the stack. Other techniques are required to generate a profile of the whole stack.

Glow Discharge Optical Emission Spectroscopy (GD-OES) has proven an efficient technique much cheaper and

faster than SIMS or other methods, to probe a full stack of films, obtain layer thickness down to a few nanometers, as well as provide elemental composition of each layer, with an accurate representation of the depth location of each element in the stack, which also provides information about how certain layers may diffuse into others as the materials are deposited.

Unfortunately, GD-OES is a destructive technique and only allows monitoring on sample test-cells, or on a test pad on the cell, which becomes inactive after measurement; yet it is still a very important technique with no equal on the market.

### CIGS Bulk Composition measurement (XRF, GD-OES)

While ideally one would want to know thickness, composition, and phase of each layer in a film stack, it was explained above that this is not possible with a single technique. Spectroscopic ellipsometry provides thickness measurements down to a certain depth, but requires a model that assumes composition is known. GD-OES profiling provides elemental composition across the depth of the whole film stack, but is a destructive method not well-suited for online monitoring. GD-OES can also be used as a bulk analysis tool to provide very accurate elemental analysis, most useful for development and process development, but again not well-suited for process control.

X-ray fluorescence is another elemental-analysis technique which, as opposed to GD-OES, is non-contact and non-destructive, and does not require any sample preparation. X-ray fluorescence can provide bulk elemental analysis, which gives a good indication of the layers' composition, an important parameter to track.

Bulk-composition monitoring with XRF provides qualitative information as well as the relative composition of the film stack. Looking at the film of interest, relative elemental concentration can give an idea of the phase as well, although it cannot confirm this information, and values may be the result of the observation of different phases, which average out to the observed value over the probed area. In the case of CIGS films (copper indium gallium di-selenide), the phase of selenide is critical to the efficiency of the cell. Raman spectroscopy is a better way to observe and confirm phase.

### Crystallinity, phase and surface-composition measurement (Raman)

As stated above, it is critical to control the phase of the diselenide in CIGS thin-film solar cells. Raman spectroscopy is the ideal tool for this application, with one main drawback: the shallow penetration-depth of most laser wavelengths into the CIGS material. Nevertheless, Raman spectroscopy is often used for process development as well as process monitoring in CIGS solar fabs but limited to surface-composition measurement.

By monitoring the position of the  $A_1$  peak of  $\text{CuInSe}_2$ , it is possible to get the stoichiometry ratio of Ga/GaIn, while any change in the spectrum shape and relative peak-intensity is an indication of the change of phase of indium or selenide. (See Figure 8.)

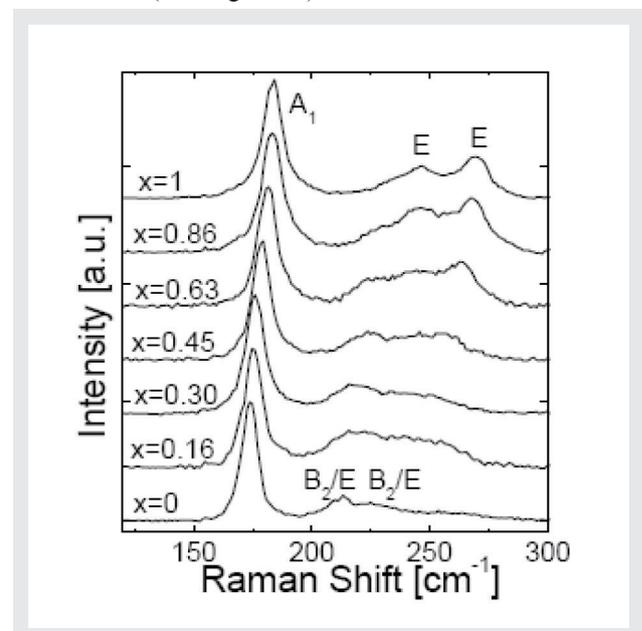


Figure 8 Example of Raman-peak shift with depth of analyte in a thin-film Cell.

Tracking the peak position requires fairly high resolution, which is one of the strong products of HORIBA Scientific instruments.

Raman spectroscopy is also a useful technique for silicon-based thin-film solar cells. Silicon is one of the most studied materials via Raman spectroscopy, and there is a tremendous amount of literature about silicon's different forms. Raman spectroscopy can easily determine crystalline phase as well as determine the stoichiometry of mixtures, as is the case in silicon thin films that typically incorporate crystalline silicon, micro-crystalline silicon, poly-crystalline silicon, and/or amorphous silicon (Figure 9).

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Raman spectroscopy can probe up to a few microns deep, which is generally enough for most thin-film stacks that are more likely to be on the order of a few hundred nanometers thick.

### Bandgap and defects (SE, PL)

One other important parameter that solar-cell researchers and manufacturers alike want to monitor is the bandgap, which gives a good indication of the material's ability to convert photon energy into electrons. Photoluminescence is the most common way to measure bandgap, and it is a very simple measurement, only made more difficult due to the fact that the emission is typically in the lower IR range (950-1600 nm) which requires an IR detector as opposed to a CCD detector.

The measurement is, however, feasible on the same platform used for Raman.

Photoluminescence is also an excellent tool to examine defects across a wafer, because defects reduce recombination, causing a sharp drop in the photoluminescence signal intensity. Wafer photoluminescence-mapping provides both the bandgap and defect information.

Bandgap can also be derived from the fitted model when using spectroscopic ellipsometry, for it is closely linked to the  $n$  and  $k$  coefficients, and can be determined by scanning across a large range of wavelengths.

### Future materials, future applications, and conclusion

The advancement of tandem structures and multi-junction cells, as well as new techniques such as surface texturing, bring new challenges for metrology, but HORIBA Scientific instruments, of course, are applicable to those new challenges.

### Tandem/multi-junction cells

Tandem or multi-junction cells consist of different materials, or different forms of the same materials (in the case of Si) in order to promote absorption of photons from a large wavelength range, so as to cover a larger portion of the visible spectrum. That implies more layers and

thicker cells, which make modeling more complex for spectroscopic ellipsometry, yet this is where the best detection limit on the market becomes indispensable.

### Absorption enhancement surface coatings

Texturing has been researched and integrated into the regular silicon solar-cell processes in order to enhance absorption. This type of coating brings thin-film technology to the standard bulk silicon wafer manufacturers, and is a new opportunity for thin-film metrology tools.

### Organic materials and particle-embedded polymers

Finally, much has to be developed in order to produce cost-effective polymer-based photovoltaic cells. New research involving nanoparticle doping also brings new challenges, and may require technologies such as Raman spectroscopy to further investigate the possibilities these materials can offer.

In conclusion, the number of photovoltaic research facilities and the number of researchers getting involved in this field is constantly growing, while the need for quality control and process-monitoring equipment increases with the requirement to produce efficient cells and consistent quality, so that there are still many opportunities to come for HORIBA Scientific products in this field.

One of the keys to success, though, consists of the ability to support customers as the technology and the associated metrology requirements move from the lab to the fab.



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