Thin Film Photovoltaics by Spectroscopic Ellipsometry

What do we mean by photovoltaics? First used in about 1890, the word has two parts: photo, derived from the Greek word for light, and volt, relating to electricity pioneer Alessandro Volta. So, photovoltaics could literally be translated as light-electricity. And that's what photovoltaic (PV) materials and devices do - they convert light energy into electrical energy (Photoelectric Effect), as French physicist Edmond Becquerel discovered as early as 1839.

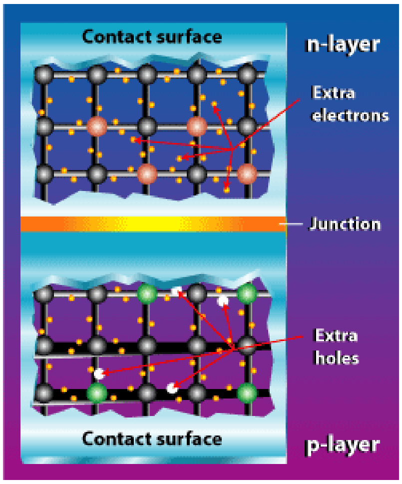
Commonly known as solar cells, individual PV cells are electricity-producing devices made of semiconductor materials. PV cells come in many sizes and shapes - from smaller than a postage stamp to several inches across. They are often connected together to form PV modules that may be up to several feet long and a few feet wide. Modules, in turn, can be combined and connected to form PV arrays.

Did you know that PV systems are already an important part of our lives? Simple PV systems provide power for many small consumer items, such as calculators and wristwatches. More complicated systems provide power for communications satellites, water pumps, and the lights, appliances, and machines in some people's homes and workplaces. Many road and traffic signs along highways are now powered by PV. In many cases, PV power is the least expensive form of electricity for performing these tasks.

The Photoelectric Effect

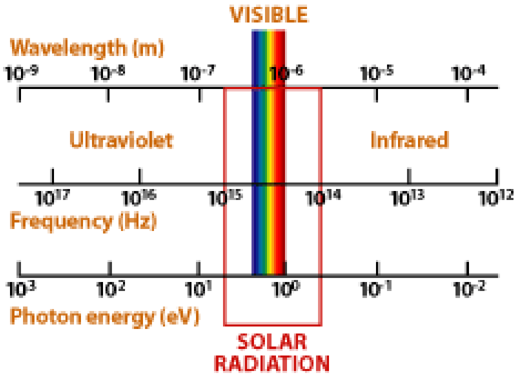
The photoelectric effect is the basic physical process by which a PV cell converts sunlight into electricity. When light shines on a PV cell, it may be reflected, absorbed, or pass right through. But only the absorbed light generates electricity.

The energy of the absorbed light is transferred to electrons in the atoms of the PV cell. With their newfound energy, these electrons escape from their normal positions in the atoms of the semiconductor PV material and become part of the electrical flow, or current, in an electrical circuit.



To induce the built-in electric field within a PV cell, two layers of somewhat differing semiconductor materials are placed in contact with one another. One layer is an «n-type» semiconductor with an abundance of electrons, which have a negative electrical charge. The other layer is a «p-type» semiconductor with an abundance of «holes», which have a positive electrical charge. Sandwiching these together creates a p/n junction at their interface, thereby creating an electric field.

Light and the PV Cell



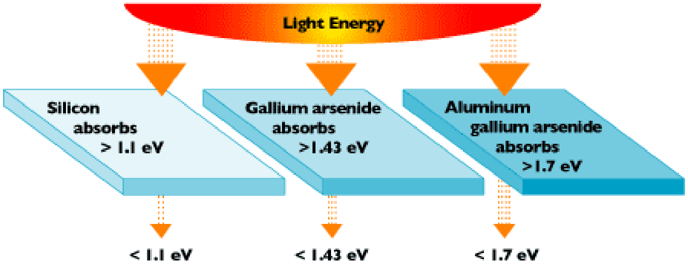
The sun emits almost all of its energy in a range of wavelengths from about $2x10^{-7}$ to $4x10^{-6}$ meters. Most of this energy is in the visible light region. Solar cells respond differently to the different wavelengths of light. In summary, light that is too high or low in energy is not usable by a cell to produce electricity. Rather, it is transformed into heat.

Bandgap Energies of Semiconductors and Light

Only photons with a certain level of energy can free electrons in the semiconductor material from their atomic bonds to produce an electric current. This level of energy is known as the «bandgap energy,». To free an electron, the energy of a photon must be at least as great as the bandgap energy. However, photons with more energy than the bandgap energy will expend that extra amount as heat when freeing electrons. So, it's important for a PV cell to be «tuned»-through slight modifications to the silicon's molecular structure-to optimize the photon energy. A key to obtaining an efficient PV cell is to convert as much sunlight as possible into electricity.

Crystalline silicon has a bandgap energy of 1.1 electron-volts (eV). (An electron-volt is equal to the energy gained by an electron when it passes through a potential of 1 volt in a vacuum.) The bandgap energies of other effective PV semiconductors range from 1.0 to 1.6 eV. In this range, electrons can be freed without creating extra heat.

The photon energy of light varies according to the different wavelengths of the light. The entire spectrum of sunlight, from infrared to ultraviolet, covers a range of about 0.5 eV to about 2.9 eV. For example, red light has an energy of about 1.7 eV, and blue light has an energy of about 2.7 eV. Most PV cells cannot use about 55% of the energy of sunlight, because this energy is either below the bandgap of the material or carries excess energy.



Different PV materials have different energy band gaps. Photons with energy equal to the band gap energy are absorbed to create free electrons. Photons with less energy than the band gap energy pass through the material.

Thin Film Solar Cells

Thin film solar cells can be made from:

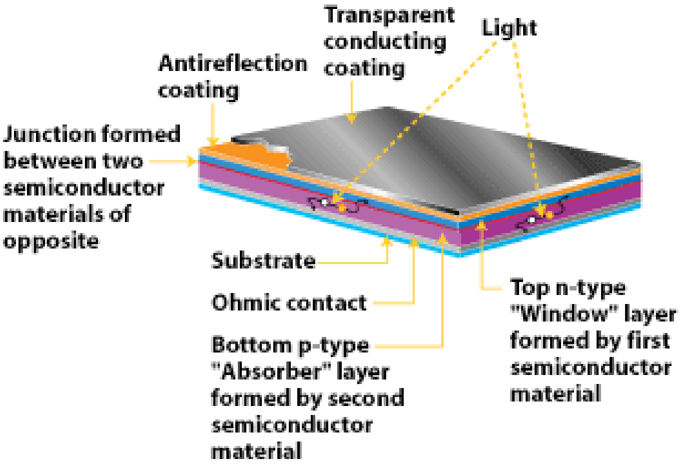
- Polycrystalline thin films-including copper indium diselenide (CIS), cadmium telluride (CdTe), and thin-film silicon
- Single-crystalline thin films-including high-efficiency material such as gallium arsenide (GaAs)

Polycrystalline Thin Film

Thin film cells use much less material: the cell's active area is usually only 1 to 10 micrometers thick, whereas thick films typically are 100 to 300 micrometers thick. Also, thin-film cells can usually be manufactured in a large-area process, which can be an automated, continuous production process. Finally, they can be deposited on flexible substrate materials.

Unlike most single-crystal cells, a typical thin-film device doesn't have a metal grid for the top electrical contact. Instead, it uses a thin layer of a transparent conducting oxide, such as tin oxide. These oxides are highly transparent and conduct electricity very well. A separate antireflection coating might top off the device, unless the transparent conducting oxide serves that function.

The typical polycrystalline thin film cell has a very thin (less than 0.1 micron) layer on top called the «window» layer. The window layer's role is to absorb light energy from only the high-energy end of the spectrum. It must be thin enough and have a wide enough bandgap (2.8 eV or more) to let all available light through the interface (heterojunction) to the absorbing layer. The absorbing layer under the window, usually doped p-type, must have a high absorptivity (ability to absorb photons) for high current and a suitable band gap to provide a good voltage. Still, it is typically just 1 to 2 microns thick.



Polycrystalline thin-film cells have a heterojunction structure, in which the top layer is made of a different semiconductor material than the bottom semiconductor layer. The top layer, usually n-type, is a window that allows almost all the light through to the absorbing layer, usually p-type. An «ohmic contact» is often used to provide a good electrical connection to the substrate.

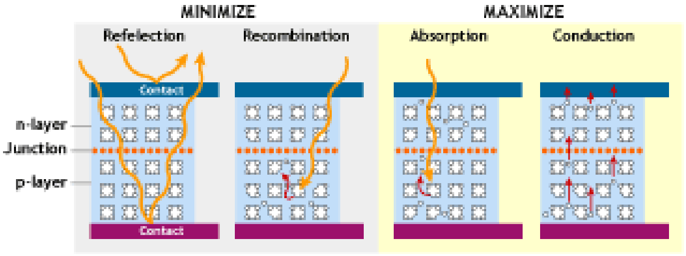
Thin film PV structures characterized by spectroscopic ellipsometry

Proper understanding of thin film materials and thin film stack, tailoring numerous properties of thin films required for an efficient solar cell demands a range of characterization techniques.

Spectroscopic ellipsometry is an optical technique used for the measurement of thin film thickness and optical constants. The technique provides the advantages to be non-destructive, fast, precise to the Angstrom level, and the capability to measure multi-layer stacks.

1 Characterization of anti-reflective coatings

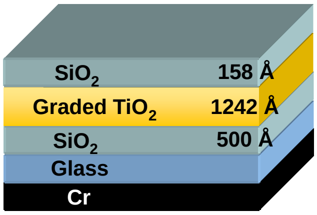
Silicon is a shiny gray material and can act as a mirror, reflecting more than 30% of the light that shines on it. To improve the conversion efficiency of a solar cell, antireflection (AR) coating is applied to the top layer of the cell helping to optimize light absorption. Single AR layer or multiple AR layers basically use SiO_x and TiO_x materials. Another way to reduce reflection is to texture the top surface of the cell, which causes reflected light to strike a second surface before it can escape, thus increasing the probability of absorption.



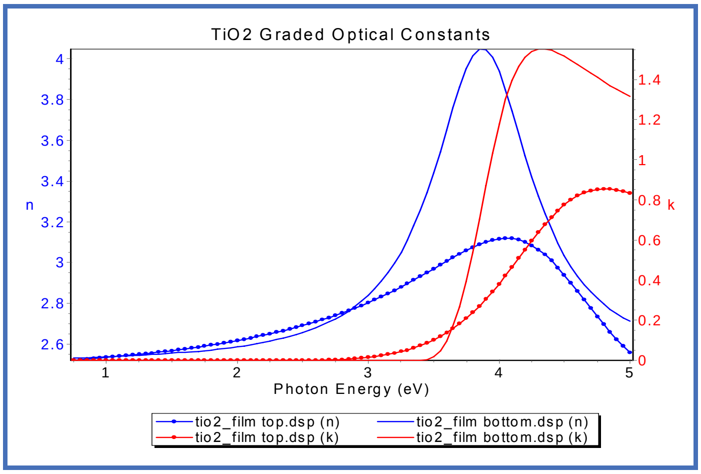
To make an efficient solar cell, we try to maximize absorption, minimize reflection and recombination, and thus maximize conduction.

Experimental Conditions

- Spectroscopic Ellipsometer: UVISEL
- Spectral range: 0.75 - 5.0 eV ⇔ 248 - 1653 nm



Full structure characterization
- ✓ Thicknesses
- ✓ TiO_2 Graded optical constants

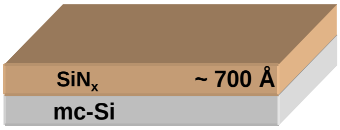


One can notice that the bottom of the TiO_2 film exhibits a higher refractive index than the top of the film.

2 Thickness mapping of SiN_x thin film

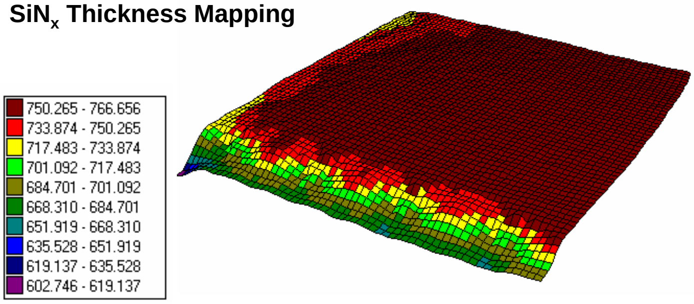
Experimental Conditions

- Spectroscopic Ellipsometer: UVISEL
- Spectral range: 0.6 - 6.5 eV ⇔ 190 - 2100 nm

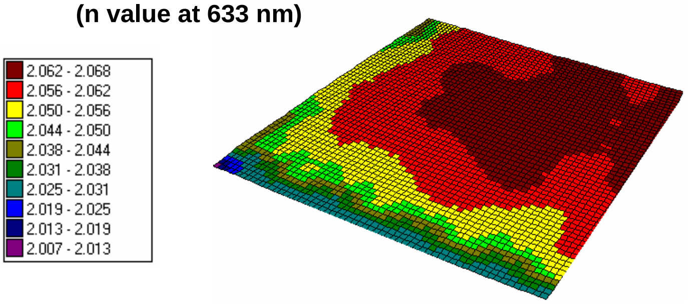


- ✓ Film thickness uniformity
- ✓ Optical constants uniformity

SiN_x Thickness Mapping



SiN_x Refractive Index Mapping (n value at 633 nm)



3 Characterization of TCO electrodes film

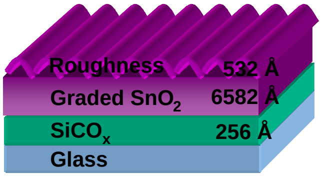
The properties of the contacts and windows layers are critical to device performance.

At least one contact must be electrically conducting and transparent to photons in the spectral range where the absorber creates carriers. Transparent conducting oxides are the material of choice for this purpose (ZnO, ITO, TiO_2, SnO_2).

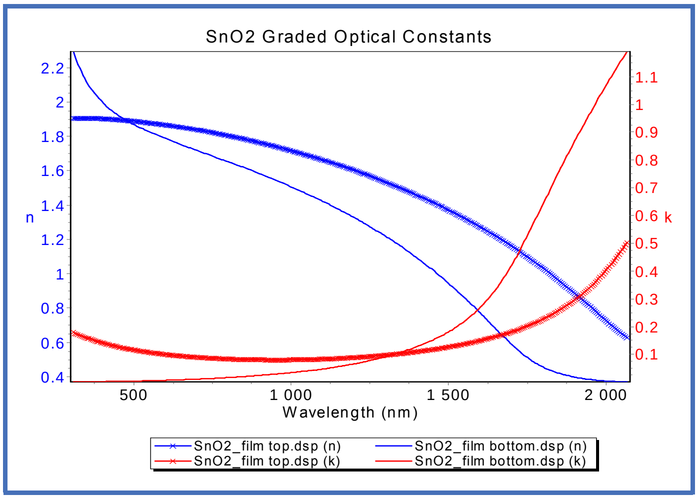
The highest efficiency devices rely on diffusion to transport carriers to the junction of collection.

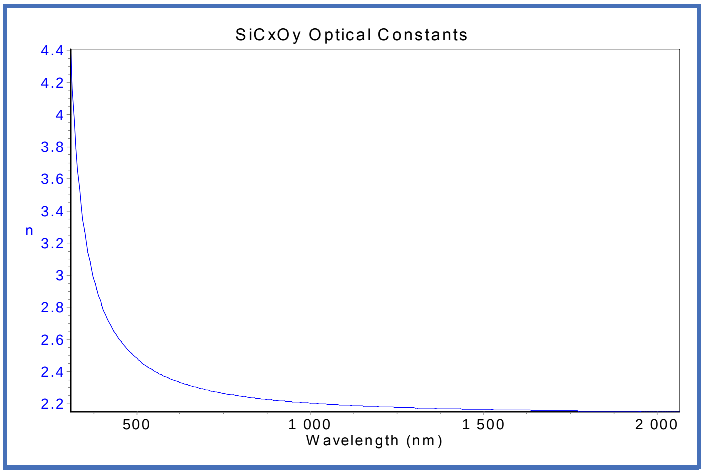
Experimental Conditions

- Spectroscopic Ellipsometer: UVISEL
- Spectral range: 0.6 - 4.0 eV ⇔ 306 - 2066 nm



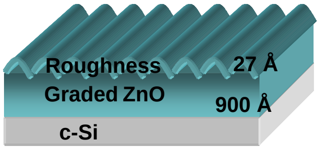
Full structure characterization
- ✓ Thicknesses
- ✓ $SiCO_x$ optical constants
- ✓ SnO_2 Graded optical constants
- ✓ Surface roughness



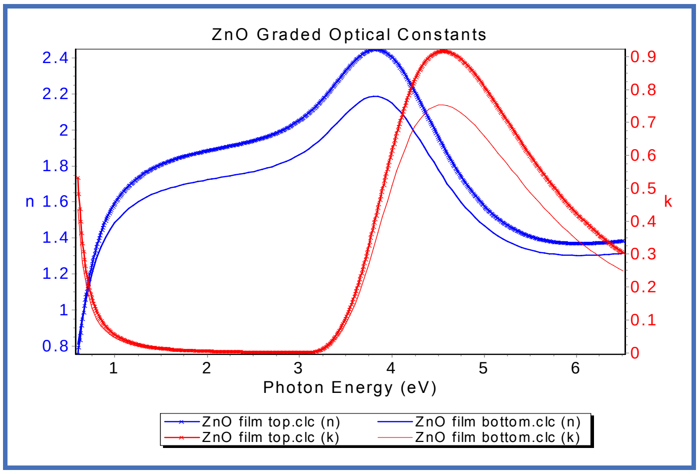


Experimental Conditions

- Spectroscopic Ellipsometer: UVISEL
- Spectral range: 0.6 - 6.5 eV ⇔ 190 - 2100 nm



Full structure characterization
- ✓ Thicknesses
- ✓ Graded ZnO optical constants
- ✓ Surface roughness



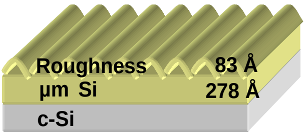
4 Characterization of Micro crystalline & Amorphous Silicon thin films

Microstructure of silicon films can be varied from one extreme of amorphous/nanocrystalline to highly oriented and/or epitaxial growth.

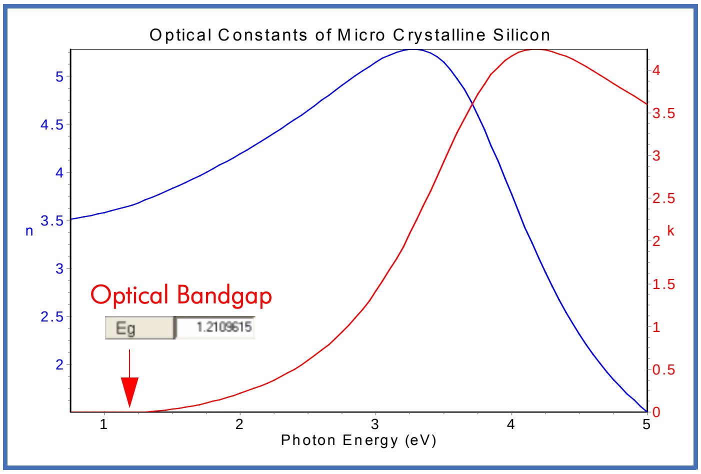
The characterization of silicon thin films by spectroscopic ellipsometry provides a wealth of information such as:
- Optical bandgap
- Inhomogeneities of silicon films (gradient)
- The shape of optical constants is directly linked to the microstructure of silicon materials

Experimental Conditions

- Spectroscopic Ellipsometer: UVISEL
- Spectral range: 0.75 - 5.0 eV ⇔ 248 - 1653 nm



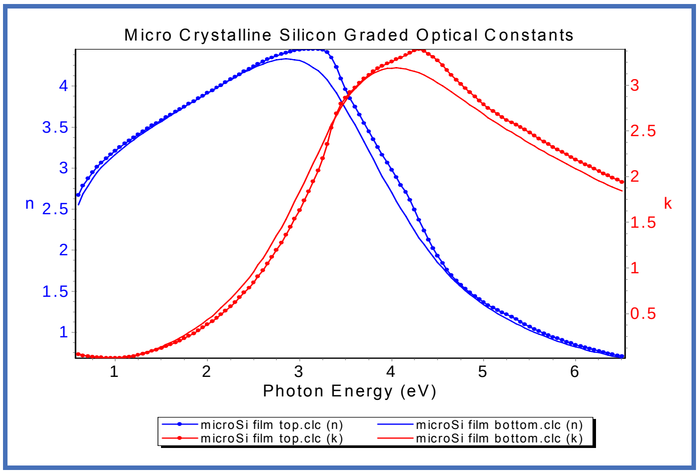
- ✓ Thicknesses
- ✓ Micro crystalline Si optical constants
- ✓ Surface roughness



Experimental Conditions

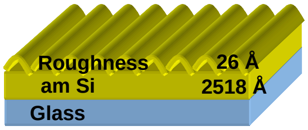
- Spectroscopic Ellipsometer: UVISEL
- Spectral range: 0.6 - 6.5 eV ⇔ 190 - 2100 nm

- ✓ Thickness
- ✓ Graded Micro crystalline Si optical constants

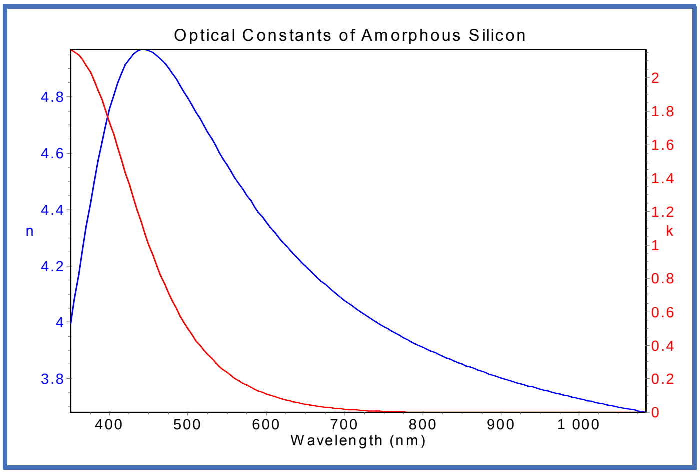


Experimental Conditions

- Spectroscopic Ellipsometer: UVISEL
- Spectral range: 1.14 - 3.54 eV ⇔ 350 - 1088 nm



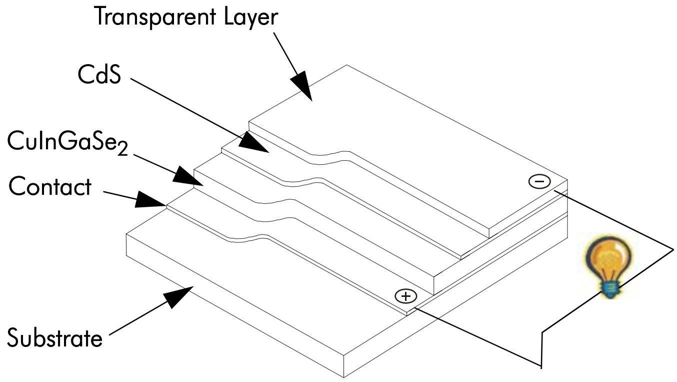
- ✓ Thicknesses
- ✓ Amorphous Si optical constants
- ✓ Surface roughness



5 CIGS PV Cell

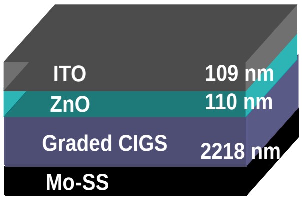
Copper Indium Selenide ($CuInSe_2$) have extremely high optical absorption coefficients that allow nearly all of the available light within the terrestrial spectrum to be absorbed in the first micrometer of the material. Therefore, the total thickness of the active layers is in the order of 2 micrometers, resulting in efficient use of materials without negatively impacting the conversion efficiency.
The addition of controlled amounts of gallium and/or sulfur into the $CuInSe_2$ absorber layer allows to adjust its energy gap to provide device with higher voltage, better carrier collection and higher conversion efficiency.

Typical GIGS PV Cell

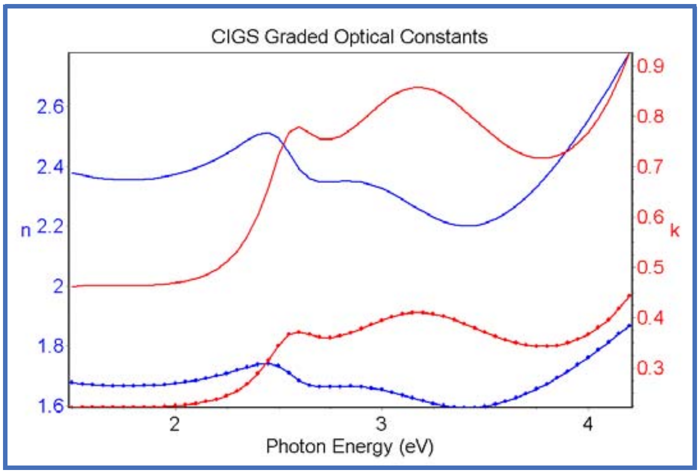


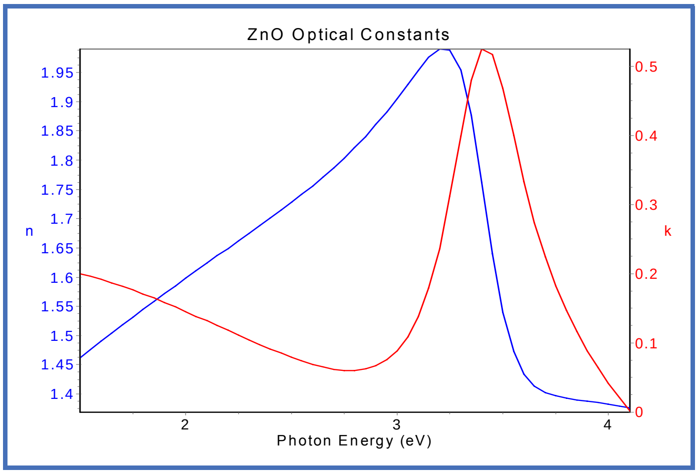
Experimental Conditions

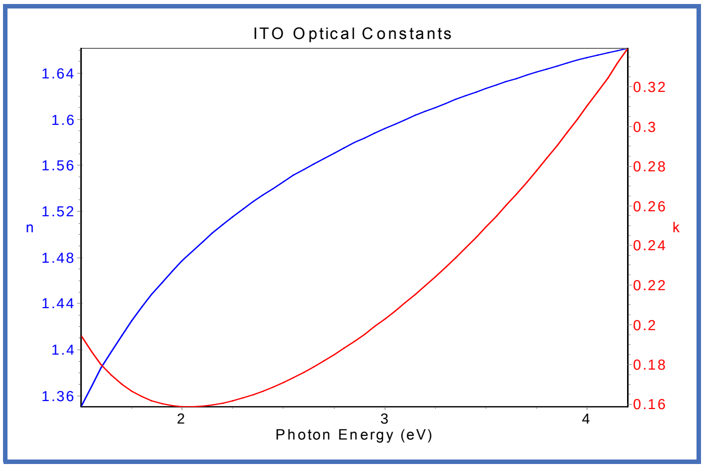
- Spectroscopic Ellipsometer: UVISEL
- Spectral range: 0.6 - 4.2 eV ⇔ 295 - 2066 nm

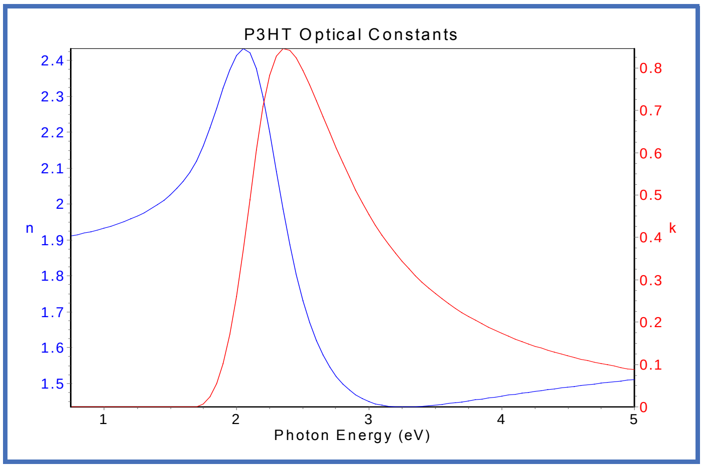


Full CIGS PV Structure Characterization
- ✓ Film Thicknesses
- ✓ CIGS, ITO, ZnO Optical constants
- ✓ CIGS Film gradient







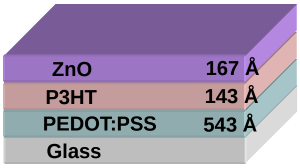


6 Polymer solar cells

Organic solar cells and polymer solar cells are built from thin films (typically 100 nm) of organic semiconductors such as polymers and small-molecule compounds like polyphenylene vinylene, copper phthalocyanine and carbon fullerenes.
Energy conversion efficiencies achieved to date using conductive polymers are low at 6% efficiency. However, these cells could be beneficial for some applications where mechanical flexibility and disposability are important.

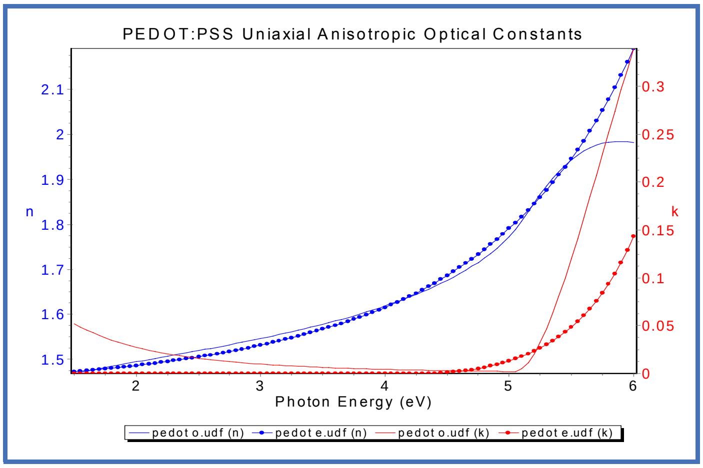
Experimental Conditions

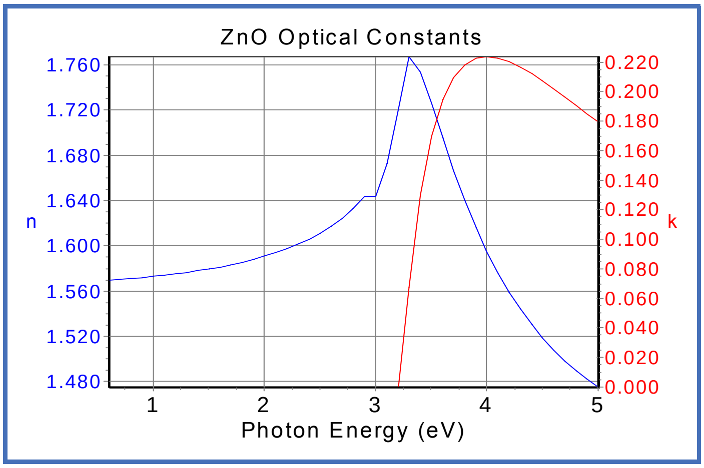
- Spectroscopic Ellipsometer: UVISEL
- Spectral range: 0.6 - 5.0 eV ⇔ 248 - 2066 nm



Organic PV Structure Characterization

✓ Film thicknesses
✓ PEDOT: PSS, P3HT, ZnO Optical constants (n,k)





Conclusion

Spectroscopic ellipsometry is an ideal technique to characterize film thicknesses and optical constants and optical bandgap for photovoltaic applications. Spectroscopic ellipsometers are also sensitive to the presence of rough overlayer and graded optical constants.
The technique provides the advantage to be fast, simple to operate and non-destructive for the characterization of the samples.

Sources and Acknowledgements

- http://www1.eere.energy.gov/solar/tf_polycrystalline.html
- Céline Eypert, Li Yan, Michel Stchakovsky, Marzouk Kloul, Assia Shagaleeva, Roland Seitz, application engineers - HORIBA Jobin Yvon ellipsometry.