APPLICATION NOTE

UV/Vis/NIR Spectroscopy

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The Use of UV/Vis/NIR Spectroscopy in the Development of Photovoltaic Cells

UV/Vis/NIR spectroscopy is used to study the optical properties of photovoltaic cells. The various phenomena involved (reflectance, transmittance, absorbance) are considered along with the equipment required to measure them. The study is based on a silicon cell and involves calculations to determine its selective reflectivity.

Introduction

Over recent years, the need to find solutions to the environmental problems currently faced by our planet has become a major issue. Given that fossil fuel resources are becoming rapidly depleted and in view of the considerable environmental damage they cause, the time has come to develop alternative methods of energy production.

The sun is an abundant source of clean energy. The development of the aerospace industry in the middle of the 20th century saw an increase in the number of studies on photovoltaic (PV) conversion. In the meantime, progress towards making this type of energy accessible to the general public has been made on a number of fronts.

Having said this, a considerable amount of research work is still being undertaken. The development and improvement of these technologies involve characterizing the various stages of the process (in chemical, electrical, mechanical and optical terms). UV/Vis/NIR spectroscopy is used to study optical properties.

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UV/Vis/NIR spectroscopy

What is being measured?

Using a clear liquid sample, a standard spectroscope measures direct transmittance as a percentage (%T); this represents the percentage of the incident beam of light transmitted by the sample. This value is then used to calculate absorbance:

Abs=log(1/T)

T=Transmittance=%T/100

Absorbance is widely used to measure concentration in liquid solutions in accordance with the Beer-Lambert law.

A number of things happen when a beam of light comes into contact with a solid. The beam may be reflected, transmitted, diffused, absorbed, refracted or polarized (Figure 1). The respective likelihood of these outcomes depends on the incident beam's angle of incidence in relation to the solid.

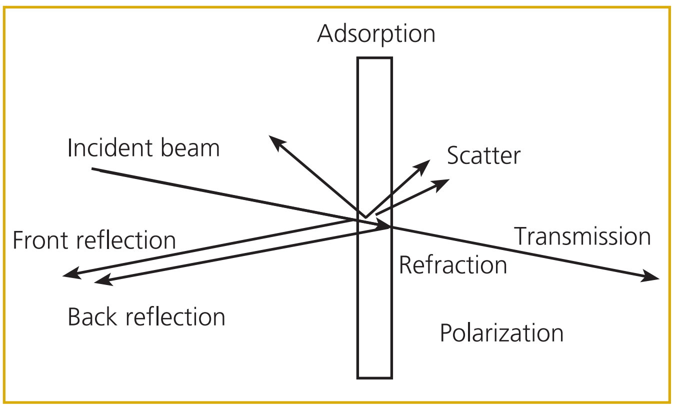

Figure 1. Interactions of light with a solid.

With the right kind of equipment, UV/Vis/NIR spectroscopy makes it possible to measure the different percentages of light reflected, transmitted or absorbed by the sample, whilst taking into account the various phenomena capable of producing misleading measurements (diffusion, refraction, polarization). The maximum spectral range covered is between 175 nm and 3300 nm.

Measuring transmittance for a solid sample

In order to obtain a correct transmittance measurement for a solid, the possibility of the transmitted beam deviating in relation to the incident beam must be taken into account. There are a number of possible reasons for this deviation: refraction, uneven surface of sample, convex/concave surfaces. If the transmitted beam deviates considerably, there is a danger that part of it will not be fully picked up by the detectors. This will result in a reduced signal. The beam could also be diffused in all directions by the sample, producing the same kind of measurement error. Overall transmittance, i.e. direct transmittance plus diffuse transmittance (including any deviation of the beam), can only be measured using a specific item of equipment known as an integrating sphere. Alternatively, direct transmittance and diffuse transmittance can be measured separately.

Measuring reflectance for a solid sample

There are two kinds of reflectance, specular and diffuse. Specular reflectance refers to the part of the incident beam reflected at the same angle as the angle of incidence; mirrors typically produce specular reflectance when used as samples. Diffuse reflectance refers to the part of the incident beam reflected in all directions; powders produce diffuse reflectance when used as samples. Most samples produce a combination of specular and diffuse reflectance.

Depending on the equipment used, it is possible to take separate measurements for specular reflectance, diffuse reflectance or overall reflectance.

As with transmittance, an integrating sphere is needed to measure overall or diffuse reflectance.

Specular reflectance is measured using other types of equipment specially designed for this purpose. Specular reflectance is particularly used when studying thin layer deposits.

Measuring absorbance for a solid sample

The absorbance percentage is the same as the percentage of the incident beam absorbed by the sample, i.e. that part of the beam which is neither reflected nor transmitted.

100%=%R+%T+%Absorbance

Absorbance can be calculated from the measurements taken for reflectance and transmittance.

%Absorbance=100%-%R-%T

Measurement tools: Integrating spheres

A LAMBDA™ 1050+ spectrophotometer with an integrating sphere of 150 mm is used to measure overall transmittance and reflectance over a range of 200-2500 nm.

The sphere is used instead of the standard detection module. The sample is placed against the sphere and the beam transmitted or reflected by the sample is reflected onto the internal reflective surface of the sphere before reaching the detectors inside the sphere (Figure 2). The sample is placed in front of the sphere if transmittance is being measured and behind it if reflectance is being measured.

The sphere's internal surface is made of a high performance polymer, which offers levels of diffuse reflectance approaching 100%. This use of this high performance material restricts the spectral range to 2500 nm.

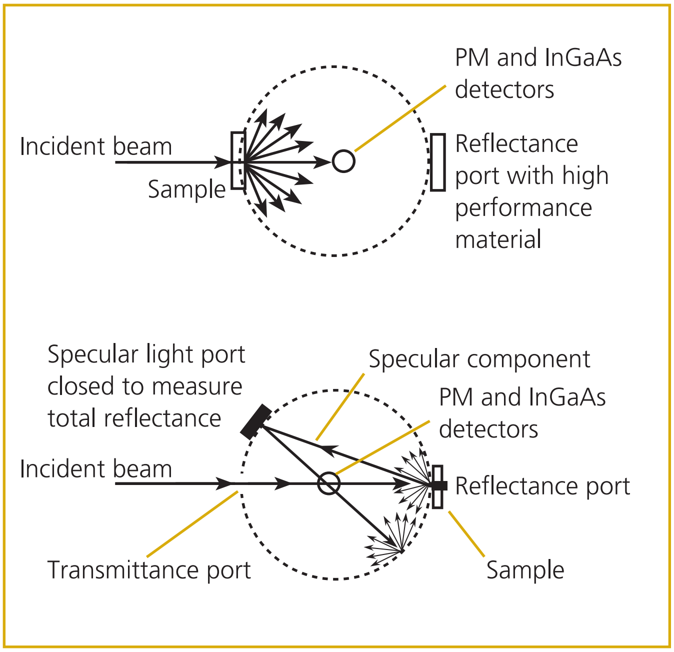

Figure 2. Measurements with a integrating sphere :reflexion (lower) ;transmission (higher).

The most suitable sphere for a spectrophotometer is a double-beam sphere made of high performance material with a diameter of 150 mm. This diameter means the surface area of the ports will equate to around 2.5% of the internal reflective surface. The lower the percentage, the greater the precision. A 60 mm sphere gives a figure of around 7%. The detectors inside the sphere (a photomultiplier for the visible range and an InGaAs for the NIR) are protected against direct reflectance by baffles. These baffles are essential for ensuring the accuracy of the measurements. A disadvantage of the 150 mm sphere compared with the 60 mm version is the greater loss of energy, with the signal to noise ratio being reduced accordingly. It is now possible to address this disadvantage by using an InGaAs detector instead of a Pbs detector for the near infrared region; this detector is 50 times more sensitive. When measuring reflectance, a specular flap can be used to exclude specular reflectance so that only diffuse reflectance is measured. When measuring transmittance, direct transmittance can be excluded by removing the standard fitting from the port facing the incident beam so that only diffuse transmittance is measured.

It is also possible to measure absorbance directly. Depending on its size, the sample can be positioned in the center of the sphere using an item of equipment known as the "center mount". With this configuration, the signal measured is a direct representation of reflectance and transmittance combined (Figure 3). This configuration has the advantage of allowing measurements to be taken at different angles of incidence by pivoting the sample in relation to the incident beam.

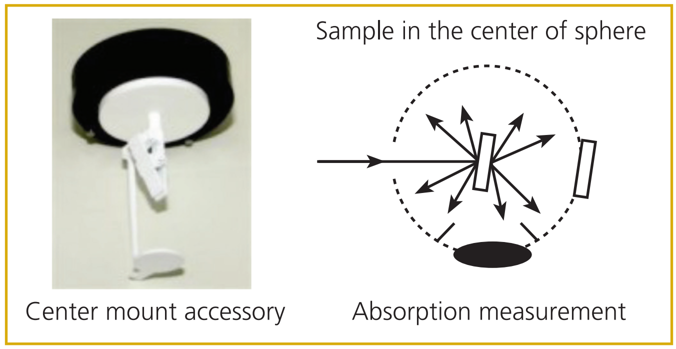

Figure 3. Center mount accessory; measurement of absorption with a sphere.

Measurements for photovoltaic cells

A photovoltaic cell is a semiconductor for converting luminous energy into electrical energy. This requires electrons on the valence band to move to the conduction band. Electron transfer is possible if the energy received as light is greater than or equal to the width of the forbidden band separating the valence and conduction bands (band gap).

The first phase of photovoltaic conversion is the absorbance of light received in the useful spectral range. Reflected light cannot be used for photovoltaic conversion. There are various treatments for increasing absorbance. Texturing (chemical, mechanical, laser, etc.) produces pyramidal indentations on the cell's surface. This process increases the contact surface with the beam and reduces reflectance. Reflected incident beams can be reabsorbed by surrounding indentations. Losses through reflectance are also minimized by covering the surface with an antireflective coating. If an aluminium coating is added on the back of the cell, transmitted photons may be reflected back into the area where they can be absorbed.

The effectiveness of different treatments can be assessed by measuring reflectance, transmittance and absorbance for photovoltaic cells. The picture in Figure 4 gives an idea of the various stages involved in the preparation of a silicon photovoltaic cell.

The items shown are a wafer of untreated silicon, a wafer of textured silicon, a wafer of silicon after doping/treatment with an antireflective coating and a finished photovoltaic cell with its screen-printed conductive grid.

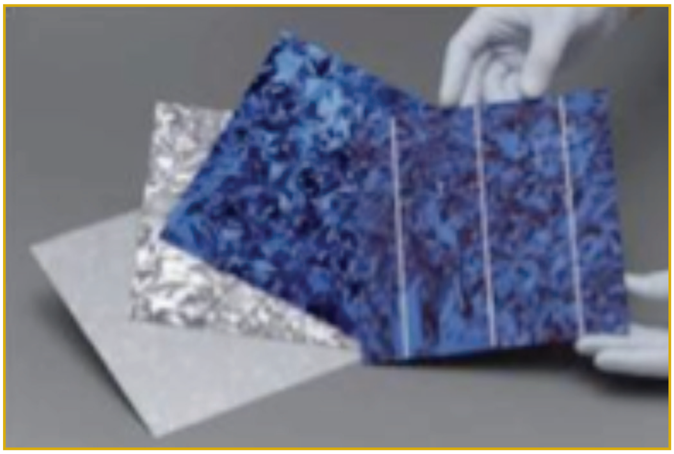

Figure 4. Wafer of untreated silicon, wafer of textured silicon, wafer of silicon after doping/treatment with an antireflective coating , finished photovoltaic cell.

Measurements for silicon cells

We measured transmittance and reflectance for a wafer of untreated silicon and a wafer of textured silicon after doping and treatment with an antireflective coating (Figures 5 and 6).

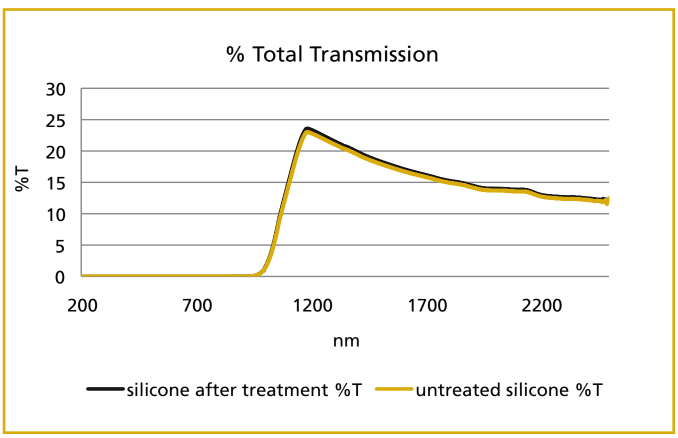

Figure 5. % Transmission of silicon (untreated and after treatment).

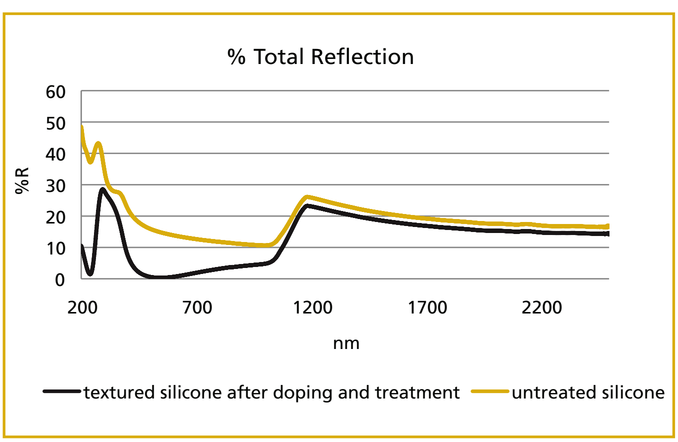

Figure 6. % Reflexion of silicon (untreated and after treatment).

A value for the gap can be calculated from the transmittance spectrum. This is 1.12 eV for silicon. The relationship between the light wavelength and the corresponding energy is expressed as follows:

$E = (h*c)/\lambda$ E= energy in joules

h= Planck constant (6.63 10-34 joules/sec.)

λ= wavelength

c= speed of light in a vacuum ($\approx 3\times10^8$ m/s)

Energy of 1.12 eV corresponds to a wavelength of 1240 nm. This means the useful spectrum for the purpose of conversion is less than 1240 nm. With longer wavelengths, the energy involved is inadequate. With shorter wavelengths, energy in excess of the band gap is lost as heat. Cells have been developed to provide a range of band gaps so that the solar spectrum's energy can be exploited to the full.

Transmittance values for wavelengths shorter than 1240 nm are very low (Table 1), with both untreated and treated silicon behaving the same as far as transmittance is concerned. In terms of reflectance, the solar component has been optimized for the visible part of the solar spectrum. Below the band gap, reflectance is considerably reduced for treated silicon (Table 1). The minimum value is around 500nm, which is the maximum for solar irradiance.

Sample	%T 500nm	%T 250nm	%R 500nm	%R 250nm
Untreated silicon	0.000011	0.0004	5.93	8.58
Treated silicon	0.000014	0.00037	0.611	0.73

Calculating selective solar reflectivity

In order to evaluate photovoltaic cells and compare them with each other, solar reflectance must be calculated in percentage terms. This means the percentage of solar radiation received and then reflected by the cell. A spectrum has been defined for solar irradiance received at sea level.

Solar radiation emitted by the sun is absorbed by the atmosphere to some extent. Absorbance levels depend on wavelength (ozone absorbs at wavelengths below 350 nm, water vapor and carbon dioxide absorb at wavelengths above 2500 nm), cloud cover, pollution and atmospheric particles. These various factors determine the spectrum which reaches the ground. The spectrum also depends on the thickness of the atmosphere it has to cross. Definitions have been drawn up for standard atmospheres under the name AM (Air Mass). AM 1 refers to the thickness of a standardized atmosphere crossed when the sun is at its zenith.

The field of photovoltaics uses the Air Mass 1.5 solar irradiance spectrum. This is the energy spectrum received at sea level when the sun is at a zenith angle of 48.18° and so corresponds to an atmospheric thickness 1.5 times that of AM1. The ASTM® E173 standard contains standard tables for the Air Mass 1.5 spectrum and replaces previous standards (E891, E892).

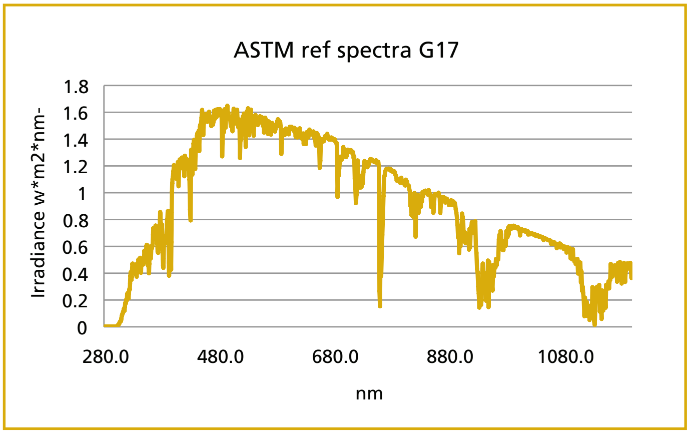

Figure 7. Solar irradiance spectrum

Effective reflectivity is calculated using the reflectivity integral once the relevant weighting has been applied by the AM1.5G solar spectrum.

$$\mathrm{Re}\,ff = \frac{\sum_{\lambda=0}^{\infty} S_\lambda \cdot R(\lambda)\cdot\Delta\lambda}{\sum_{\lambda=0}^{\infty} S_\lambda \cdot \Delta\lambda}$$

$R(\lambda)$ %R measured

S_λ Solar irradiance spectrum (expressed as photon flow)

Effective reflectivity can be measured at any point during the process and the value thus obtained can be used to compare different samples on the basis of an index.

The surface of finished cells is covered by a screen-printed conductive grid. It is important that the beam does not come into contact with this grid when measuring reflectance. In view of this, we use a device to reduce the size of the beam and focus it between the bars of the grid. This ensures that only the reflectance generated by the surface involved in photovoltaic conversion is measured. This "small spot size" device consists of a diaphragm and a wheel with 3 lenses for focusing on the transmittance or reflectance positions or on the center of the sphere.

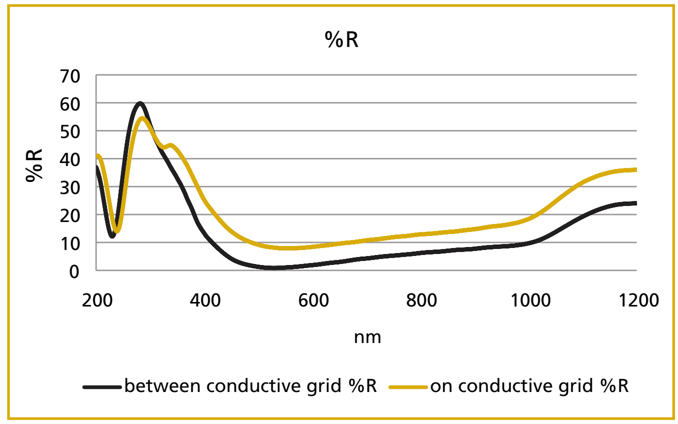

Figure 8. Reflexion of finished cell ,with and without the small spot size kit.

The cell's effective reflectivity was calculated using the black spectrum in Figure 8; this was obtained by avoiding the bars. The yellow spectrum was obtained by the beam coming into contact with the metal grid. The difference between the two highlights the importance of a carefully aimed beam when taking measurements.

The value calculated for effective reflectivity is 14.7.

Conclusion

As detectors, integrating spheres play an essential role in measuring overall transmittance and reflectance in solar applications. The development of new types of photovoltaic cell also calls for other forms of measurement. For example, using special equipment to measure specular reflectance is common practice when implementing quality assurance measures for the thin layer deposits found in thin film cells. Measurements need to be performed on ever larger samples, with whole modules (as opposed to cells) now undergoing tests.

Investigations are focusing on the importance of the angle of incidence, with a growing emphasis on the need to measure transmittance and reflectance at precisely the same part of the sample. New types of equipment are also being developed. These are transforming standard UV/Vis/NIR spectrophotometers into specialized devices for performing measurements on photovoltaic cells.

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