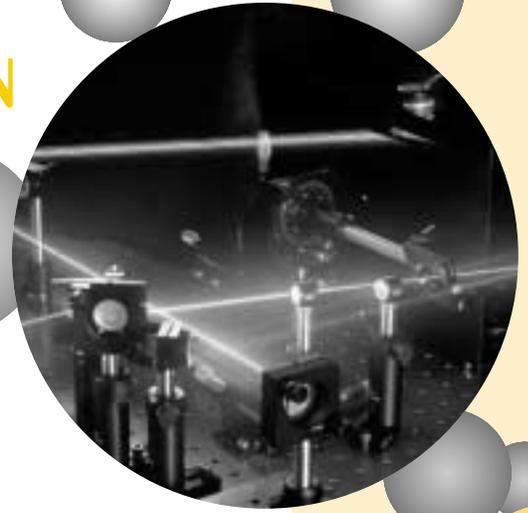
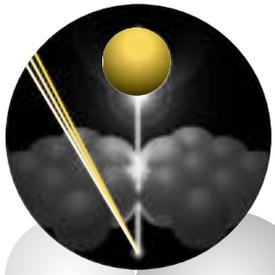


ELECTRO-Optical CHARACTERIZATION



We use various electrical and optical experimental techniques to examine many fundamental properties of materials. The types of information obtained by these techniques range from small-scale atomic-bonding information to large-scale macroscopic quantities such as optical constants and electron-transport properties. Used together, these diverse capabilities can aid in developing and understanding a wide range of material systems. Our primary techniques and capabilities include:

- Photoluminescence spectroscopy — probes the electronic structure of materials, providing information on bandgaps, defect identification, and material quality.
- Minority-carrier lifetime spectroscopy — provides a time-resolved measure of the photo-excited carrier population, allowing for detailed studies of the recombination process.
- Fourier-transform infrared and Raman spectroscopy — probes vibrational modes of atoms in a solid, providing data on composition, concentration, and local environment.
- Spectroscopic ellipsometry — a nondestructive optical probe that measures optical constants, thin-film thickness, and interface roughness.
- Capacitance techniques — measure the flow of electrons within a material in response to changes in applied bias, to determine free-carrier concentration and defect-state parameters.
- Scanning defect mapping — uses a scanning laser and an integrating sphere to provide detailed maps of grain boundaries and dislocations of silicon wafers and cells.
- Technique development — applies existing knowledge and expertise to the creation of new experimental techniques.

The femtosecond laser is used to characterize fundamental properties of solid-state materials such as electron relaxation states and interactions between electrons and atoms of a crystal. (Jim Yost Photography/PIX01435.)

Photoluminescence Spectroscopy

Photoluminescence spectroscopy is a contactless, nondestructive method of probing the electronic structure of materials. Light is directed onto a sample, where it is absorbed and imparts excess energy into the material in a process called "photo-excitation." One way this excess energy can be dissipated by the sample is through the emission of light, or luminescence. In the case of photo-excitation, this luminescence is called "photoluminescence." The intensity and spectral content of this photoluminescence is a direct measure of various important material properties.

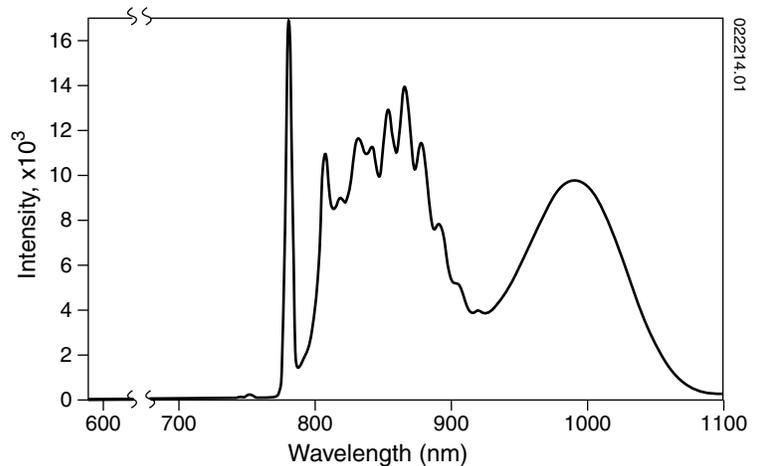
Specifically, photo-excitation causes electrons within the material to move into permissible excited states. When these electrons return to their equilibrium states, the excess energy is released and may include the emission of light (a radiative process) or may not (a nonradiative process). The energy of the emitted light — or photoluminescence — is related to the difference in energy levels between the two electron states involved in the transition — that is, between the excited state and the equilibrium state. The quantity of the emitted light is related to the relative contribution of the radiative process.

Applications

- **Bandgap determination.** The most common radiative transition in semiconductors is between states in the conduction and valence bands, with the energy difference being known as the bandgap. Bandgap determination is particularly useful when working with new compound semiconductors.
- **Impurity levels and defect detection.** Radiative transitions in semiconductors involve localized defect levels. The photoluminescence energy associated with these levels can be used to identify specific defects, and the amount of photoluminescence can be used to determine their concentration.
- **Recombination mechanisms.** As discussed above, the return to equilibrium, also known as "recombination," can involve both radiative and nonradiative processes. The amount of photoluminescence and its dependence on the level of photo-excitation and temperature are directly related to the dominant recombination

process. Analysis of photoluminescence helps to understand the underlying physics of the recombination mechanism.

- **Material quality.** In general, nonradiative processes are associated with localized defect levels, whose presence is detrimental to material quality and subsequent device performance. Thus, material quality can be measured by quantifying the amount of radiative recombination.



Photoluminescence data can reveal a multitude of structure related to electronic states in the semiconductor.

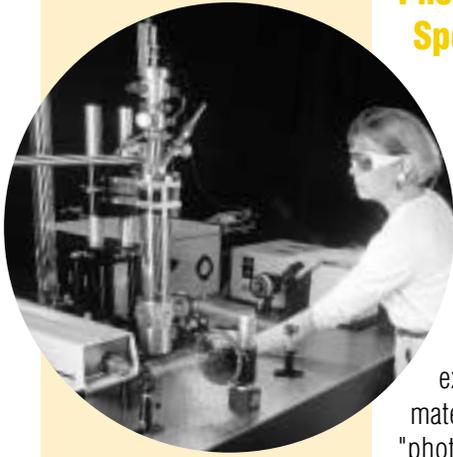
Special Features

- Various excitation wavelengths allow for varying penetration depths into the material, and thus, varying levels of volume excitation.
- Detection of photoluminescence from 0.4 to 2.8 μm using diffraction and Fourier-transform-based systems.
- Mapping capabilities with 1-mm spatial resolution on the Fourier-transform-based system.
- Sample temperatures of 4 to 300 K.
- Sensitivity down to the level of parts per thousand, depending on impurity species and host.

Minority-Carrier Lifetime Spectroscopy

Minority-carrier lifetime spectroscopy is a contactless, nondestructive method of studying the recombination processes of materials. As with photoluminescence spectroscopy, photo-excitation is used to impart excess energy into the material. In this case, though, short pulses of light are used to create an initial non-equilibrium distribution of photo-excited "carriers," or electrons and holes. The return of these excess carriers back to equilibrium is measured — either optically or electrically — as a function of time.

The rate at which the photo-excited carriers return to equilibrium is typically described in terms of an average lifetime that a photo-excited carrier exists. For solar cells, the excitation conditions are such



The energy-resolved photoluminescence system is used to determine bandgaps of solid-state materials and devices, identify defects and impurities, and analyze recombination mechanisms. (Jim Yost Photography/PIX07100.)

that the rate-limiting process is typically determined by the population of minority-carriers; thus, the lifetime is referred to as a "minority-carrier lifetime." We currently use three unique experimental techniques to resolve the time it takes to return to equilibrium during recombination. These techniques are:

- Time-Correlated Single-Photon Counting or Time-Resolved Photoluminescence — measures or correlates the time between individual excitation pulses and the detection of a single emitted photon. By repeating this numerous ($>10^8$) times, this sampling technique creates a histogram that represents the transient process that occurs after a single excitation.
- Pump-Probe and Up-Conversion Femtosecond Spectroscopy — provide unique, high time resolution by probing with a short-duration laser pulse (100 fs, or 100×10^{-15} s) as a probe. The attribute being probed is either the absorption coefficient (pump-probe) or the photoluminescence (up-conversion). Varying the arrival time of the probe beam allows for a complete scan of the transient process.
- Ultra-High-Frequency Photoconductive Decay — a unique, NREL-invented capability for tracking the time-dependent, photo-excited carrier population by monitoring the corresponding change in conductivity. The time-dependent conductivity is measured in real time by a high-frequency circuit and oscilloscope.

Applications

- Minority-carrier lifetimes for direct- and indirect-bandgap materials. The strong sensitivity of the minority-carrier lifetime to the presence of defects detrimental to device performance makes it a particularly sensitive measure of material quality.

- Recombination processes in direct- and indirect-bandgap materials. The dependence of the lifetime on the level of photo-excitation and temperature is used to determine the underlying physics of the recombination process.

- Surface/interface recombination velocity. The dependence of the lifetime on the geometry of the device under test can be used to distinguish between recombination processes occurring in the bulk of the device and those occurring at interfaces or boundaries.

- Ultrafast dynamics of photo-excited carriers. Using the pump-probe and up-conversion techniques, we obtain relevant information about dynamic processes in the giga-hertz (10^9) and tera-hertz (10^{12}) frequency ranges.



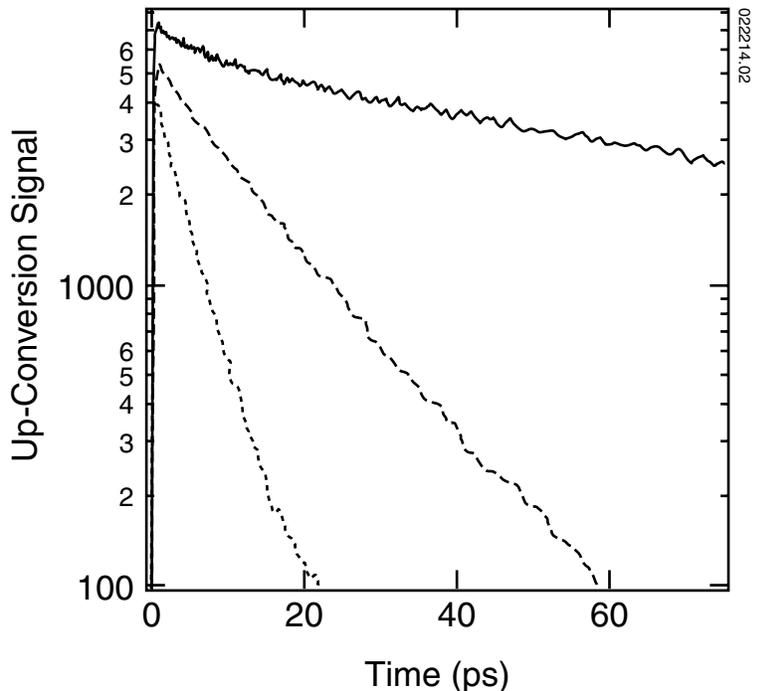
Special Features

- Various excitation wavelengths allow for varying penetration depths into the material, and thus, varying levels of volume excitation.
- Optical detection from 0.4 to 1.0 μm , with 20-ps (2×10^{-11} s) resolution.
- Optical detection from 0.5 to greater than 2 mm, with 100-fs (10^{-13} s) resolution.
- Contactless photoconductive decay, with 1-ns (10^{-9} s) resolution.
- Sample temperatures of 4 to 300 K.

The NREL-developed ultra-high-frequency photoconductive decay system measures minority-carrier lifetimes for any semiconductor material over a wide range of sample sizes and shapes — from thin films to ingots. It is a quick, contactless technique that can be used in research or on an assembly line to assess the quality of wafers prior to fabrication into devices. (Jim Yost Photography/PIX07103.)



Time-resolved photoluminescence is one of three major techniques used by the team to determine minority-carrier lifetimes. This technique samples single photon emissions to create a histogram representing the transient process. (Jim Yost Photography/PIX07101.)



Femtosecond spectroscopy provides unparalleled time resolution, essential for monitoring fast, efficient recombination mechanisms.



The FTIR microscope, one of several instruments used in Fourier transform infrared spectroscopy, allows researchers to map chemical bonding in small areas of a sample. (Lester Lefkowitz/PIX04822.)

Fourier-Transform Infrared and Raman Spectroscopy

Vibrational motions within chemically bonded constituents of a material have frequencies in the infrared energy range.

These motions or oscillations, which are induced by certain vibrational modes within the material, can interact with a beam of infrared radiation directed onto the material: energy is exchanged between the beam and material when the frequencies are synchronous or "in resonance." With Fourier-transform infrared spectroscopy (FTIR), the intensity of the infrared beam is measured before and after it interacts with

the sample, as a function of the light's frequency. The "infrared spectrum" is the ratio of intensities plotted against frequency. From this plot, we can determine the identities, surrounding environments, and concentrations of the chemical bonds in the sample. This technique considerably improves the sensitivity over scanning or dispersive infrared spectroscopy. The enhanced sensitivity of Fourier transform (FT) and FTIR spectroscopic techniques allows weak signals to be measured with high precision. Examples of such weak signals are from low concentrations of active species in a sample or signals from samples that are poor reflectors or transmitters.

The vibrational spectra of non-polar bonds — such as crystal-lattice vibrations and carbon-carbon bonds that do not interact directly with

infrared radiation — can be measured using Raman spectroscopy. In Raman spectroscopy, a laser beam is directed onto the sample. A small fraction of the laser photons passing through the sample are scattered at frequencies that are characteristic of the Raman-active bonds in the sample. Fourier-transform Raman spectroscopy uses a low-energy infrared laser to excite the sample, which prevents fluorescence from the sample from interfering with the weak Raman signal. Performing both FT-Raman and FTIR spectroscopy on a sample gives a complete picture of its bonding structure. Both of these techniques benefit from high FT sensitivity, and they can be used with database searches of our extensive libraries of FTIR and FT-Raman spectra for chemical identification of samples and sample components. The FT-Raman instrumentation can also be used for FT-photoluminescence (FT-PL) spectroscopy, as described above.

Applications

- Contaminant identification. Can be done over a large area, or in spots as small as 1 mm in diameter on a sample, using either FTIR or FT-Raman microspectroscopy.
- In-situ reaction analysis. Gas-solid reactions, relaxation in liquid crystals, solid-solid phase transformations, and aqueous fermentation reactions are typical of systems that we have studied, on time scales that range from microseconds to days.
- Impurity and doping concentrations. This application is done either at room or cryogenic temperatures using FTIR spectroscopy. We can obtain sensitivities as high as parts per billion.
- Vibrational frequencies of chemical bonds. Samples that have unknown composition can be rapidly identified, especially with spectroscopic database searching.
- Compositional, stress, and structural inhomogeneity. This application is particularly useful at the micrometer scale for thin-film semiconductor samples and uses FTIR, FT-Raman, and FT-PL microspectroscopy.

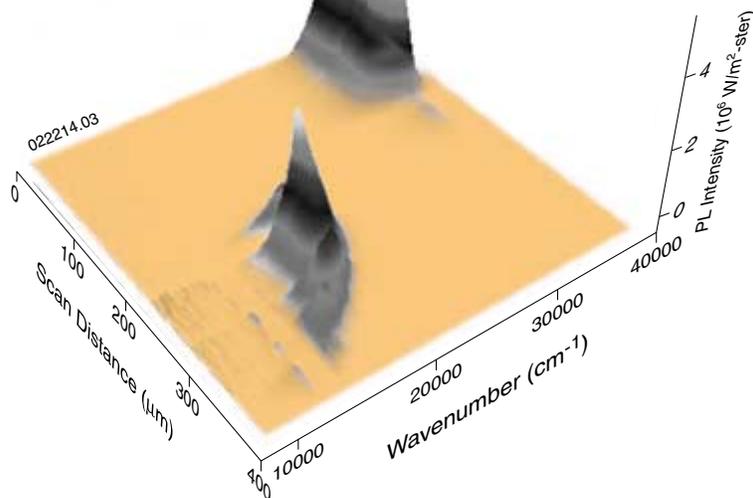
ELECTRO-OPTICAL CHARACTERIZATION TECHNIQUES/CAPABILITIES			
Technique/Capability	Typical Applications	Signal Source	Signal Detected
Photoluminescence spectroscopy	Determine bandgap; identify defects; determine material quality	Continuous-wavelength lasers	Photoluminescence
Minority-carrier lifetime spectroscopy	Measure minority-carrier lifetime and surface recombination; determine dominant recombination mechanisms	Pulsed lasers, LEDs, or flash-lamps	PL or photoconductivity
Fourier-transform infrared and Raman spectroscopy	Identify contaminants; analyze in-situ reactions and concentration of impurities; measure inhomogeneity	Infrared radiation/monochromatic laser	Infrared radiation/light
Spectroscopic ellipsometry	Determine index of refraction (n) and extinction coefficient (k), film thickness, interface roughness, composition of thin surface layers	Laser	Polarized light
Capacitance techniques	Measure carrier concentration profiles, interface state density, and deep-level properties	Voltage	Capacitance
Scanning defect mapping	Map dislocation and grain-boundary distributions in silicon wafers	Two laser beams: 638 and 903 nm	Scattered light
Large-scale laser scanner	Map the electrical performance of PV devices >1 cm ²	Three laser beams: 488, 633, and 1152 nm	Shunt resistance and generated current

- Reflectance spectroscopy. Useful in analyzing infrared optical filters and reflectors.

Special Features

- Mid- and far-infrared range (1.3-100 μm).
- Infrared reflection and microscope accessories.
- Sample temperatures of 8 to 900 K.
- Detection limits from 10^{21} to $<10^{13}$ bonds/ cm^3 .

NREL researchers developed a new FTIR technique — scanning Fourier transform photoluminescence microspectroscopy — that produces three-dimensional maps to determine the composition and quality of grown absorber materials. Here, the technique is used to analyze a thermophotovoltaic device that uses a layer of constant composition GaInAs and ten graded layers of InAsP.



Spectroscopic Ellipsometry

Spectroscopic ellipsometry is a non-invasive optical technique for determining the optical constants n and k (index of refraction and extinction coefficient, respectively), film thickness, interface roughness, and composition of thin surface layers and multilayer structures. The method measures the change in the state of polarization of light upon reflection from the sample surface to determine the ellipsometry parameters Δ and Ψ . These parameters completely determine the values of n and k for the measured wavelength.

Measurement of Δ and Ψ is repeated for each wavelength across the spectral range of interest, thus determining n and k as a function of wavelength. These optical parameters are then matched to computer models to determine the structure and composition of the sample.



Applications

- Optical parameters. Measuring the index of refraction (n) and the extinction coefficient (k) for a single layer permits one to determine the material composition, electronic structure, and modeling of optical performance.
- Thickness of thin films and multilayer structures. If the optical constants are approxi-

Spectroscopic ellipsometry is used for determining the index of refraction, extinction coefficient, film thickness, interface roughness, and composition of thin surface layers. (Jim Yost Photography/PIX07105.)

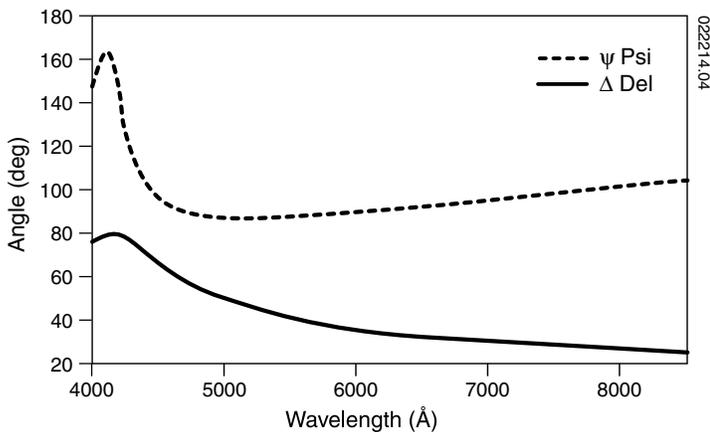
Detection Range	Temperature Range	Non-destructive?	Contact-less?	Imaging Mapping?	Maximum Scan Area	Unique Features
0.4 to 2.8 μm	4 to 300 K	Yes	Yes	Yes	—	Various excitation wavelengths; 1- μm spatial resolution mapping
0.4 to 1 μm with 2×10^{-11} s resolution 0.4 to 2 μm with 1×10^{-13} s resolution Any value with 1×10^{-9} s resolution	4 to 300 K	Yes	Yes	Yes	—	Various excitation wavelengths; noteworthy time resolution; depth lifetime resolution
1.3 to 100 μm	8 to 900 K	Yes	Yes	Yes	—	1- μm spatial resolution; mapping for inhomogeneity
0.3 to 1.7 μm	Room-temperature	Yes	Yes	—	—	Operation in any transparent ambient
Quasi-static to 100 MHz frequencies	77 to 360 K	Yes	No	—	—	Optical DLTS
—	Room-temperature	Yes	Yes	Yes	4 cm x 4 cm	Unique instrument; proprietary etches; integrating sphere
—	Ambient temperature	Yes	Yes	Yes	> 1 m x 1 m	Unique instrument; computer controlled and automated

mately known, then ellipsometry can determine the thickness, interface roughness, and inhomogeneity in multilayer structures with thickness from sub-monolayer to millimeters.

- Thin-film measurements. Ellipsometry can be used to study the formation and properties of thin films on thick substrates, e.g., SiO₂ on silicon.

Special Features

- Spectral range from 0.3 to 1.7 μm. By using either a photomultiplier tube or a germanium detector, samples can be studied over the spectral range from the ultraviolet to the near-infrared.
- Operates in any transparent ambient, including vacuum, gases, liquids, and air. This versatility allows ellipsometry to be applied in-situ to study the deposition and processing of materials.
- Materials must, in general, have parallel interfaces and smooth, specular surfaces.



Plot of the angles psi and del from spectroscopic ellipsometry measurement of Al₂O₃ film on Si substrate.

Capacitance Techniques

These techniques monitor the movement of electronic charge within a semiconductor device. Measurements are taken of the charge storage capacity, or capacitance, across a rectifying junction.

Capacitance-voltage (C-V) measurements use a time-varying voltage of variable frequency to determine the concentration of majority carriers in the bulk of the device, and/or energy levels of interface states that often exist between the surfaces of dissimilar materials.

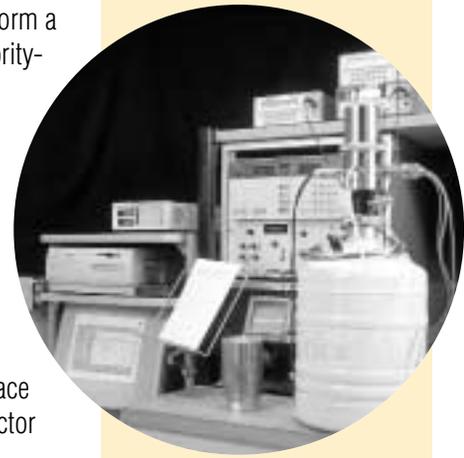
Deep-level transient spectroscopy (DLTS) examines the time-dependent flow of charge into and out of localized energy states associated with defects in the semiconductor. DLTS can thus determine many important defect-related properties.

Applications

- Uniform and non-uniform carrier concentrations. By varying the applied dc voltage bias — and thus, varying the depletion width

— it is possible to perform a depth profile of the majority-carrier concentration.

- Interface-state densities. The frequency dependence of the C-V measurement allows one to determine free and localized charge. The localized charge is often found at the interface between the semiconductor and an oxide overlayer.
- Deep-level properties. With DLTS, we can determine the energy levels, capture/emission rates, and concentration of the various deep states. This is a non-destructive complement to secondary-ion mass spectrometry and Auger electron spectroscopy (see *Surface Analysis* insert).



The DLTS system is used to examine the time-dependent flow of charge into and out of localized energy states associated with defects in a semiconductor. (Jim Yost Photography/PIX07104.)

Special Features

- C-V measurements can be obtained at frequencies ranging from quasi-static to 100 MHz.
- DLTS spectra and transients can be obtained for sample temperatures of 77 to 320 K.

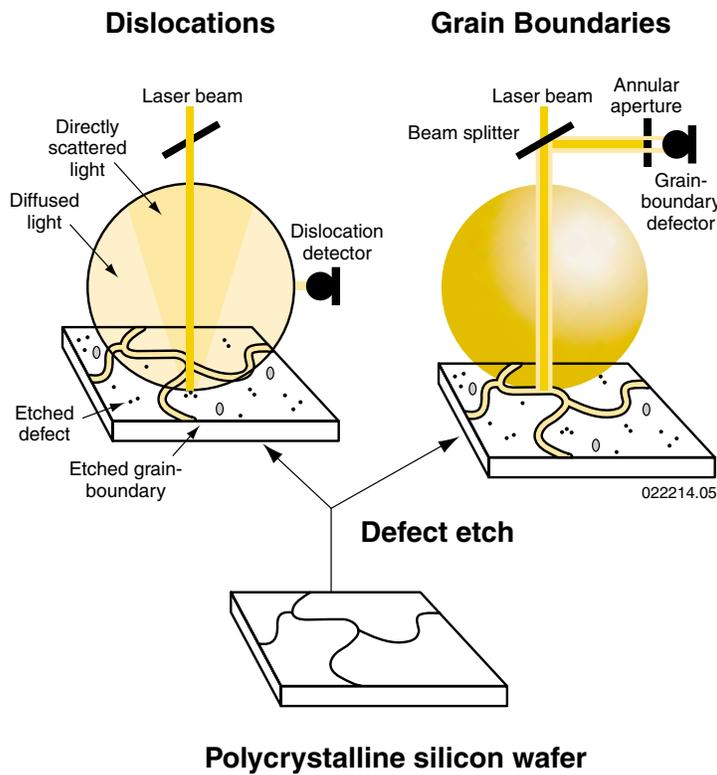
Scanning Defect Mapping System (SDMS)

Defect mapping uses optical scattering to quickly and accurately map defect distributions in silicon semiconductor wafers. To map defects, a wafer is first treated with a NREL-developed etch of hydrofluoric, acetic, and nitric acids to enhance the light scattered by the defects. The etch produces V-shaped grooves at grain boundaries and circular or elliptical pits at dislocations. The grooves produced at the grain boundaries scatter light in a streak-like shape perpendicular to the length of the grain boundary. The etch pits produced at dislocations scatter light primarily in a well-defined cone.

The SDMS moves the treated wafer across a stationary laser beam and maps the defects for each location on the wafer. An integrating sphere collects the diffuse light scattered by the etch pits and directs it to a detector. The amount of light reflected from an area is proportional to the dislocation density for that area and provides a direct statistical count of the number of dislocations. Part of the streaks from the grain-boundary grooves that reflect close to the direction of the incoming light passes through an opening in the integrating sphere to a separate detector that maps the grain boundaries.

Applications

- Dislocation mapping. Quickly and accurately maps dislocation defects in silicon wafers.
- Grain-boundary mapping. Quickly and accurately maps grain boundaries in silicon wafers.
- Photovoltaic response mapping. By using amplifiers to measure the laser-beam-induced current (LBIC) generated by each spot as it is illuminated, the SDMS produces photocurrent maps of completed cells. The photocurrent maps may be compared with the dislocation and grain-boundary maps to show the effect of defects and crystalline discontinuities on photovoltaic response.
- Reflectance mapping. The SDMS can also map the reflectance of a completed cell (i.e., the amount of light that does not penetrate the cell). The current produced by laser scanning is the "external" photoresponse. By mapping reflectance, the SDMS can calculate a cell's performance based on the light that is actually absorbed by the cell, which is a better measure of the effectiveness of the cell material.
- Minority-carrier diffusion length. The SDMS can measure the minority-carrier diffusion length (the average distance traveled by light-generated electrical carriers) in a completed solar cell. It can do this because the beam from its 903-nm laser penetrates the cell to produce carriers, and because the local internal response of the cell is proportional to the diffusion length.



The SDMS uses differentially reflected light to distinguish between defect types. After treatment with a special etch, dislocations scatter the laser beam in a cone-shaped pattern that is captured by an integrating sphere. The V-shaped grooves marked by grain boundaries are redirected to a separate detector.

Special Features

- Special etching solution. Hydrofluoric, acetic, and nitric acids in a ratio of 36:15:2 produce the characteristic grooves and pits that enable the quick and easy mapping of dislocations and grain boundaries. The etching solution works at room temperature in 30 seconds (versus several hours for some other etches) and has no metals to contaminate the sample.
- Integrating sphere. This is an optical device that uses the inside surface of a spherical shell to collect diffuse light for detection and integration of dislocation defects.
- Two laser sources (638 nm and 903 nm). The 638-nm laser enables mapping of grain boundaries and dislocations in wafers. Both lasers are used to generate photoresponse maps for completed cells, with the shorter-wavelength laser generating response from the cell surface and the 903-nm laser producing response from the bulk of the cell. The 903-nm laser also enables the mapping of minority-carrier diffusion lengths.



The scanning defect mapping system (left), shown with computer screen displaying a grain-boundary defect map (right). (Jim Yost Photography/PIX03916.)

Technique Development

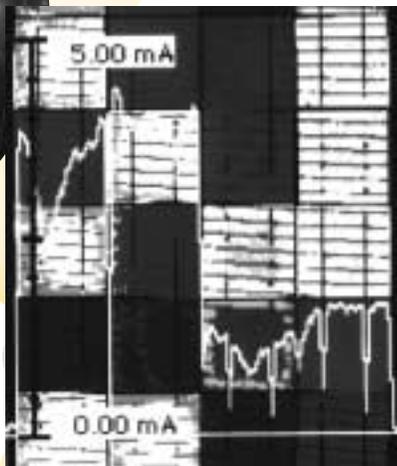
By drawing on the diverse expertise and range of experiences of our team members, we have extended existing techniques and developed completely new ones to address particular issues related to materials or devices.

Four examples of this capability include:

- Enhancing the existing radiofrequency photoconductive decay technique. Currently existing techniques were unable to measure small-scale samples (1 mm) with sufficiently high resolution (10 ns). We responded by extending the current technology to increase both the sensitivity and time resolution. Our patented work ultimately allowed for the required characterization of a novel photovoltaic system, and it is currently used within industry and research environments.
- Developing an optical probe to measure the thickness of a CdS film. We developed this probe to satisfy the need for the fast, reliable, accurate, and nondestructive measurement of the thickness of polycrystalline CdS films. The finished system uses materials with strong absorption of above-bandgap light to allow

for simple, fast measurement of CdS and CdTe film thickness. This design is currently used within industry and research environments.

- Developing an optical probe to screen the quality of polycrystalline thin-film CdTe/CdS after CdCl₂ treatment. Solar Cells Inc. (currently First Solar) discovered an empirical correlation between CdS sub-bandgap photoluminescence (PL) and the efficiency of solar cells made from thin-film CdTe/CdS. After researching the physics of the PL process, we developed a custom, portable instrument that quantitatively measures the sub-bandgap PL from the CdS layer.
- Developing a large-scale laser scanner (LSLS) to identify defects and variations in performance within PV cells, submodules, and modules. This is a computer-controlled system that scans a laser beam across a PV device — of any dimensions — and amplifies and



Laser-beam-induced current (LBIC) maps of a 60-cm x 120-cm polycrystalline silicon module with light bias. The superimposed LBIC line scans (white curve) show the values of the induced current at the position of the scan (white horizontal line). (Although the LBIC maps are shown here in greyscale, the LSLS actually produces them in full color, promoting easy interpretation of results.)

records the resulting laser-beam-induced current (LBIC) as a function of laser position. The results are presented as a line scan, as a Y-modulated map, or as a color-coded LBIC map. The LSLS uses three lasers: a 633-nm-wavelength laser, which is characteristic of the peak of the solar spectrum, and lasers with wavelengths of 488 nm and 1152 nm, which allow one to probe the response of devices to different wavelengths and, therefore, at different depths. We developed this system as a versatile tool for investigating PV cells and module designs during R&D, for quality control in a production setting, and for failure analysis for modules after use. It can be used to identify not only problem cells within a module, but also, problem areas within a cell. Once the LSLS identifies defective areas, NREL's full arsenal of tools — down to the atomic level — can then be used to determine the exact cause of the problem.

The large-scale laser scanner can scan a full-sized encapsulated module in a few minutes or a few seconds (depending on scanning mode) to produce line scans and LBIC maps to detect nonuniformities in current output. (Pat Corkery/PIX01029.)



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