

7

VISIBLE / UV EMISSION, REFLECTION, AND ABSORPTION

- 7.1 Photoluminescence, PL 373
- 7.2 Modulation Spectroscopy 385
- 7.3 Variable Angle Spectroscopic Ellipsometry, VASE 401

7.0 INTRODUCTION

In this chapter, three techniques using visible (and UV) light to probe the near surface regions of solids are described. In two of them, Photoluminescence, PL, and Modulation Spectroscopy, electronic transitions between valence and conduction bands excited by the incident light are used. Modulation Spectroscopy is simply a specialized way of recording the *absorption spectrum* as the wavelength of the incident light is scanned. The derivative spectrum is recorded by phase-sensitive detection as the temperature, electric field, or stress of the sample is modulated, improving sensitivity to small spectral changes. PL, on the other hand, looks at the *emission spectrum* as the excited electronic states induced by the incident light decay back to lower states. The third technique, Variable Angle Spectroscopic Ellipsometry, VASE, involves measuring changes in intensity of *polarized light* reflected from interfaces as a function of incident wavelength and angle.

All three techniques probe 500 Å to 1 μm or so in depth for opaque materials, depending on the penetration depth of the incident light. For transparent materials, essentially bulk properties are measured by PL and Modulation Spectroscopy. All three techniques can be performed in ambient atmosphere, since visible light is used both as incident probe and signal.

In Modulation Spectroscopy, which is mostly used to characterize semiconductor materials, the peak positions, intensities and widths of features in the absorption spectrum are monitored. The positions, particularly the band edge (which defines the band gap), are the most useful, allowing determination of alloy concentration,

strain, and damage, and identification of impurities. Absolute sensitivities are good enough to detect monolayer concentrations. Lateral resolution down to 100 μm can be achieved with suitable optics. Modulation Spectroscopy can sometimes be used as a screening method for device performance when there are features in the spectrum (positions, widths, or intensities) that correlate with performance. It can also be used as an *in situ* monitor of structural perfection while growing epitaxial material.

PL is currently more widely used than Modulation Spectroscopy in semiconductor and insulator characterization though it basically accesses some of the same information. It is also widely used outside the realm of semiconductor materials science, for example in pharmaceuticals, biochemistry, and medicine, where it is known under the general name of fluorometry. In PL of semiconductors, one monitors emission from the bottom of the conduction band to the top of the valence band. All the properties that can be determined from band-edge movement in Modulation Spectroscopy can also be determined by PL—for example, strain, damage, alloy composition, and the perfection of growing surfaces. Impurities or dopants can be detected with high sensitivity when there are transitions to impurity levels within the band gap. To sharpen transitions, and therefore improve resolution and sensitivity, PL is usually performed at cryogenic (liquid helium) temperatures. Under these conditions PL can detect species down to 10^{10} – 10^{14} cm^{-3} , depending on the particular species. Spatial resolution down to 1 μm can be obtained for fixed-wavelength laser incident PL. Instrumentation for PL and Modulation Spectroscopy is quite similar, often being constructed so that both can be performed. There is no complete “commercial system.” One usually builds up a system using commercial components (light source, monochromator, detector, etc.). Costs vary from a minimum of \$10,000 for primitive detection of PL to \$250,000 for a system that can do everything. PL has the same physical basis as Cathodoluminescence (CL) discussed in Chapter 3. The practical differences caused by the use of an electron beam are: probing depths can be shorter (down to 100 \AA); spatial resolution is better (down to 1000 \AA); beam damage may occur, and a high-vacuum system is necessary.

VASE monitors the intensity of polarized light after it has been transmitted through a thin film to an interface, reflected, and transmitted back through the film. The film thickness (in the 1 nm to 1 μm range), the optical constants, and the interface roughness (if less than 100 nm) can all be extracted if enough measurements at different angles of incidence are made. However, these parameters are derived from a fit to an assumed model (thickness and optical constants), which is not a unique procedure, leaving room for gross error in the wrong hands. Planar interfaces are needed over the lateral area probed, which is usually 1 mm^2 but which can be as small as 100 μm^2 . VASE is used primarily for surface coatings on semiconductors and dielectrics, optical coatings, and multilayer thin-film structures.

7.1 PL

Photoluminescence

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Contents

- Introduction
- Basic Principles
- Common Modes of Analysis and Examples
- Sample Requirements
- Quantitative Abilities
- Instrumentation
- Conclusions

Introduction

Luminescence refers to the emission of light by a material through any process other than blackbody radiation. The term *Photoluminescence* (PL) narrows this down to any emission of light that results from optical stimulation. Photoluminescence is apparent in everyday life, for example, in the brightness of white paper or shirts (often treated with fluorescent whiteners to make them literally glow) or in the light from the coating on a fluorescent lamp. The detection and analysis of this emission is widely used as an analytical tool due to its sensitivity, simplicity, and low cost. Sensitivity is one of the strengths of the PL technique, allowing very small quantities (nanograms) or low concentrations (parts-per-trillion) of material to be analyzed. Precise quantitative concentration determinations are difficult unless conditions can be carefully controlled, and many applications of PL are primarily qualitative.

PL is often referred to as fluorescence spectrometry or fluorometry, especially when applied to molecular systems. Uses for PL are found in many fields, including

environmental research, pharmaceutical and food analysis, forensics, pesticide studies, medicine, biochemistry, and semiconductors and materials research. PL can be used as a tool for quantification, particularly for organic materials, wherein the compound of interest can be dissolved in an appropriate solvent and examined either as a liquid in a cuvette or deposited onto a solid surface like silica gel, alumina, or filter paper. Qualitative analysis of emission spectra is used to detect the presence of trace contaminants or to monitor the progress of reactions. Molecular applications include thin-layer chromatography (TLC) spot analysis, the detection of aromatic compounds, and studies of protein structure and membranes. Polymers are studied with regard to intramolecular energy transfer processes, conformation, configuration, stabilization, and radiation damage.

Many inorganic solids lend themselves to study by PL, to probe their intrinsic properties and to look at impurities and defects. Such materials include alkali-halides, semiconductors, crystalline ceramics, and glasses. In opaque materials PL is particularly surface sensitive, being restricted by the optical penetration depth and carrier diffusion length to a region of 0.05 to several μm beneath the surface.

Emission spectra of impurity levels are used to monitor dopants in III-V, II-VI, and group IV compounds, as well as in dilute magnetic and other chalcogenide semiconductors. PL efficiency can be used to provide a measure of surface damage due to sputtering, polishing, or ion bombardment, and it is strongly affected by structural imperfections arising during the growth of films like SiC and diamond. Coupled with models of crystalline band structure, PL is a powerful tool for monitoring the dimensions and other properties of semiconductor superlattices and quantum wells (man-made layered structures with angstrom-scale dimensions). The ability to work with low light levels makes it well suited to measurements on thin epitaxial layers.

Basic Principles

In PL, a material gains energy by absorbing light at some wavelength by promoting an electron from a low to a higher energy level. This may be described as making a transition from the ground state to an excited state of an atom or molecule, or from the valence band to the conduction band of a semiconductor crystal (electron-hole pair creation). The system then undergoes a nonradiative internal relaxation involving interaction with crystalline or molecular vibrational and rotational modes, and the excited electron moves to a more stable excited level, such as the bottom of the conduction band or the lowest vibrational molecular state. (See Figure 1.)

If the cross-coupling is strong enough this may include a transition to a lower electronic level, such as an excited triplet state, a lower energy indirect conduction band, or a localized impurity level. A common occurrence in insulators and semiconductors is the formation of a bound state between an electron and a hole (called

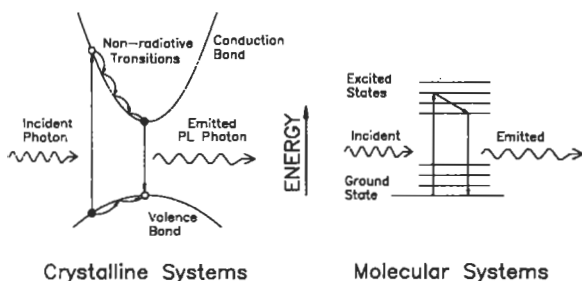


Figure 1 Schematic of PL from the standpoint of semiconductor or crystalline systems (left) and molecular systems (right).

an exciton) or involving a defect or impurity (electron bound to acceptor, exciton bound to vacancy, etc.).

After a system-dependent characteristic lifetime in the excited state, which may last from picoseconds to many seconds, the electronic system will return to the ground state. In luminescent materials some or all of the energy released during this final transition is in the form of light, in which case the relaxation is said to be radiative. The wavelength of this emission is longer than that of the incident light. This emitted light is detected as photoluminescence, and the spectral dependence of its intensity is analyzed to provide information about the properties of the material. The time dependence of the emission can also be measured to provide information about energy level coupling and lifetimes. In molecular systems, we use different terminology to distinguish between certain PL processes that tend to be fast (sub-microsecond), whose emission we call fluorescence, and other, slower ones (10^{-4} s to 10 s) which are said to generate phosphorescence.

The light involved in PL excitation and emission usually falls in the range 0.6–6 eV (roughly 200–2000 nm). Many electronic transitions of interest lie in this range, and efficient sources and detectors for these wavelengths are available. To probe higher energy transitions, UPS, XPS, and Auger techniques become useful. X-ray fluorescence is technically a high-energy form of PL involving X rays and core electrons instead of visible photons and valence electrons. Although lower energy intraband, vibrational, and molecular rotational processes may participate in PL, they are studied more effectively by Raman scattering and IR absorption.

Since the excited electronic distribution approaches thermal equilibrium with the lattice before recombining, only features within an energy range of $\sim kT$ of the lowest excited level (the band edge in semiconductors) are seen in a typical PL *emission* spectrum. It is possible, however, to monitor the intensity of the PL as a function of the wavelength of the *incident* light. In this way the emission is used as a probe of the absorption, showing additional energy levels above the band gap. Examples are given below.

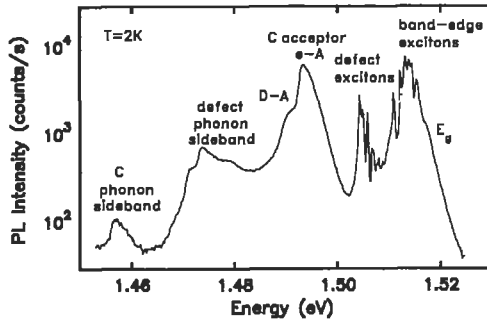


Figure 2 PL spectra of MBE grown GaAs at 2 K near the fundamental gap, showing C-acceptor peak on a semilog scale.

Scanning a range of wavelengths gives an emission spectrum that is characterized by the intensity, line shape, line width, number, and energy of the spectral peaks. Depending on the desired information, several spectra may be taken as a function of some external perturbation on the sample, such as temperature, pressure, or doping variation, magnetic or electric field, or polarization and direction of the incident or emitted light relative to the crystal axes.

The features of the spectrum are then converted into sample parameters using an appropriate model of the PL process. A sampling of some of the information derived from spectral features is given in Table 1.

A wide variety of different mechanisms may participate in the PL process and influence the interpretation of a spectrum. At room temperature, PL emission is thermally broadened. As the temperature is lowered, features tend to become sharper, and PL is often stronger due to fewer nonradiative channels. Low temperatures are typically used to study phosphorescence in organic materials or to identify particular impurities in semiconductors.

Figure 2 shows spectra from high-purity epitaxial GaAs ($N_A < 10^{14} \text{ cm}^{-3}$) at liquid helium temperature. The higher energy part of the spectrum is dominated by electron-hole bound pairs. Just below 1.5 eV one sees the transition from the conduction band to an acceptor impurity ($e-A$). The impurity is identified as carbon from its appearance at an energy below the band gap equal to the carbon binding energy. A related transition from the acceptor to an unidentified donor state ($D-A$) and a sideband lower in energy by one LO-phonon are also visible. Electrons bound to sites with deeper levels, such as oxygen in GaAs, tend to recombine non-radiatively and are not easily seen in PL.

PL is generally most useful in semiconductors if their band gap is direct, i.e., if the extrema of the conduction and valence bands have the same crystal momentum, and optical transitions are momentum-allowed. Especially at low temperatures,

Spectral feature	Sample parameter
Peak energy	Compound identification
	Band gap/electronic levels
	Impurity or exciton binding energy
	Quantum well width
	Impurity species
	Alloy composition
	Internal strain
	Fermi energy
Peak width	Structural and chemical "quality"
	Quantum well interface roughness
	Carrier or doping density
Slope of high-energy tail	Electron temperature
Polarization	Rotational relaxation times
	Viscosity
Peak intensity	Relative quantity
	Molecular weight
	Polymer conformation
	Radiative efficiency
	Surface damage
	Excited state lifetime
	Impurity or defect concentration

Table 1 Examples of sample parameters extracted from PL spectral data. Many rely on a model of the electronic levels of the particular system or comparison to standards.

localized bound states and phonon assistance allow certain PL transitions to appear even in materials with an indirect band gap, where luminescence would normally not be expected. For this reason bound exciton PL can be used to identify shallow donors and acceptors in indirect GaP, as well as direct materials such as GaAs and

InP, in the range 10^{13} – 10^{14} cm^{-3} . Boron, phosphorus, and other shallow impurities can be detected in silicon in concentrations¹ approaching 10^{11} cm^{-3} . Copper contamination at Si surfaces has been detected down to 10^{10} cm^{-3} levels.²

Common Modes of Analysis and Examples

Applications of PL are quite varied. They include compositional analysis, trace impurity detection, spatial mapping, structural determination (crystallinity, bonding, layering), and the study of energy-transfer mechanisms. The examples given below emphasize semiconductor and insulator applications, in part because these areas have received the most attention with respect to surface-related properties (i.e., thin films, roughness, surface treatment, interfaces), as opposed to primarily bulk properties. The examples are grouped to illustrate four different modes for collecting and analyzing PL data: spectral emission analysis, excitation spectroscopy, time-resolved analysis, and spatial mapping.

Spectral Emission Analysis

The most common configuration for PL studies is to excite the luminescence with fixed-wavelength light and to measure the intensity of the PL emission at a single wavelength or over a range of wavelengths. The emission characteristics, either spectral features or intensity changes, are then analyzed to provide sample information as described above.

As an example, PL can be used to precisely measure the alloy composition x of a number of direct-gap III-V semiconductor compounds such as $\text{Al}_x\text{Ga}_{1-x}\text{As}$, $\text{In}_x\text{Ga}_{1-x}\text{As}$, and $\text{GaAs}_x\text{P}_{1-x}$, since the band gap is directly related to x . This is possible in extremely thin layers that would be difficult to measure by other techniques. A calibration curve of composition versus band gap is used for quantification. Cooling the sample to cryogenic temperatures can narrow the peaks and enhance the precision. A precision of 1 meV in bandgap peak position corresponds to a value of 0.001 for x in $\text{Al}_x\text{Ga}_{1-x}\text{As}$, which may be useful for comparative purposes even if it exceeds the accuracy of the x -versus-bandgap calibration.

High-purity compounds may be studied at liquid He temperatures to assess the sample's quality, as in Figure 2. Trace impurities give rise to spectral peaks, which can sometimes be identified by their binding energies. The application of a magnetic field for magnetophotoluminescence can aid this identification by introducing extra field-dependent transitions that are characteristic of the specific impurity.³ Examples of identifiable impurities in GaAs, down to around 10^{13} cm^{-3} , are C, Si, Be, Mn, and Zn. Transition-metal impurities give rise to discrete energy transitions within the band gap. Peak shifts and splitting of the acceptor-bound exciton lines can be used to measure strain. In heavily Be-doped GaAs and some quantum two-dimensional (2D) structures, the Fermi edge is apparent in the spectra, and its position can be converted into carrier concentration.

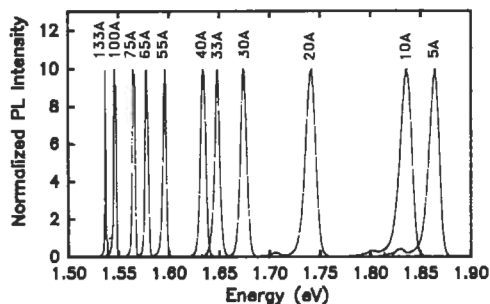


Figure 3 Composite plot of 2 K excitonic spectra from 11 GaAs/ $\text{Al}_{0.3}\text{Ga}_{0.7}\text{As}$ quantum wells with different thicknesses. The well width of each is given next to its emission peak.

A common use of PL peak energies is to monitor the width of quantum well structures. Figure 3 shows a composite plot of GaAs quantum wells surrounded by $\text{Al}_{0.3}\text{Ga}_{0.7}\text{As}$ barriers, with well widths varying from 13 nm to 0.5 nm, the last being only two atomic layers thick. Each of these extremely thin layers gives rise to a narrow PL peak at an energy that depends on its thickness. The well widths can be measured using the peak energy and a simple theoretical model. The peak energy is seen to be very sensitive to well width, and the peak width can give an indication of interface sharpness.

PL can be used as a sensitive probe of oxidative photodegradation in polymers.⁹ After exposure to UV irradiation, materials such as polystyrene, polyethylene, polypropylene, and PTFE exhibit PL emission characteristic of oxidation products in these hosts. The effectiveness of stabilizer additives can be monitored by their effect on PL efficiency.

PL Excitation Spectroscopy

Instead of scanning the emission wavelength, the analyzing monochromator can be fixed and the wavelength of the incident exciting light scanned to give a PL excitation (PLE) spectrum. A tunable dye or Ti:Sapphire laser is typically used for solids, or if the signals are strong a xenon or quartz-halogen lamp in conjunction with a source monochromator is sufficient.

The resulting PL intensity depends on the absorption of the incident light and the mechanism of coupling between the initial excited states and the relaxed excited states that take part in emission. The spectrum is similar to an absorption spectrum and is useful because it includes higher excited levels that normally do not appear in the thermalized PL emission spectra. Some transitions are apparent in PLE spectra from thin layers that would only be seen in absorption data if the sample thickness were orders of magnitude greater.

This technique assists in the identification of compounds by distinguishing between substances that have the same emission energy but different absorption

bands. In semiconductors, it can be valuable for identifying impurity PL peaks, especially donors, by enhancing certain PL transitions through resonant excitation. It is useful for determining the energy levels of thin-film quantum structures, which, when combined with appropriate models, are used to simultaneously determine well widths, interface band offsets, and effective masses. Information about higher energy transitions can also be obtained by Modulation Spectroscopy techniques such as photoreflectance and electroreflectance.

Time-Resolved PL

By monitoring the PL intensity at a chosen wavelength as a function of time delay after an exciting pulse, information can be obtained about the electron relaxation and recombination mechanisms, including nonradiative channels. The time scales involved may vary from two hundred femtoseconds to tens of seconds. A full emission spectrum may be measured also at successive points in time. Spectral analysis then yields, for example, the evolution of a carrier distribution as excitonic states form and as carriers are trapped by impurities. The progress of chemical reactions with time can be followed using time-dependent data. By monitoring the depolarization of luminescence with time of PL from polymer chains, rotational relaxation rates and segmental motion can be measured.

A useful application of time-dependent PL is the assessment of the quality of thin III-V semiconductor alloy layers and interfaces, such as those used in the fabrication of diode lasers. For example, at room temperature, a diode laser made with high-quality materials may show a slow decay of the active region PL over several ns, whereas in low-quality materials nonradiative centers (e.g., oxygen) at the cladding interface can rapidly deplete the free-carrier population, resulting in much shorter decay times. Measurements of lifetime are significantly less dependent on external conditions than is the PL intensity.

PL Mapping

Spatial information about a system can be obtained by analyzing the spatial distribution of PL intensity. Fluorescent tracers may be used to image chemical uptake in biological systems. Luminescence profiles have proven useful in the semiconductor industry for mapping impurity distributions, dislocations, or structural homogeneity in substrate wafers or epilayers. Similar spatial information over small regions is obtained by cathodoluminescence imaging.

For mapping, the sample (or the optical path) is translated, and at each position PL at a single wavelength or over an entire spectrum is measured. The image is formed from variations in intensity, peak energy, or peak line width. Lateral resolution of 1 μm is possible. Figure 4 shows an application of PL to identify imperfections in a 2-in InGaAsP epitaxial wafer.

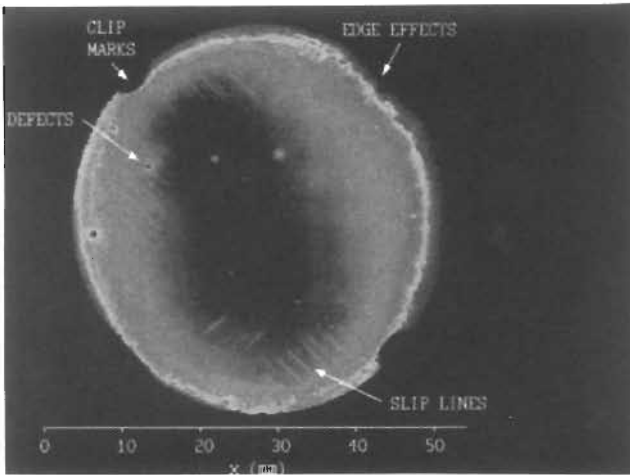


Figure 4 Spatial variation of PL intensity of an InGaAsP epitaxial layer on a 2-in InP substrate shows results of nonoptimal growth conditions. (Data from a Waterloo Scientific SPM-200 PL mapper, courtesy of Bell Northern Research)

Sample Requirements

PL measurements are generally nondestructive, and can be obtained in just about any configuration that allows some optically transparent access within several centimeters of the sample. This makes it adaptable as an *in situ* measurement tool. Little sample preparation is necessary other than to eliminate any contamination that may contribute its own luminescence. The sample may be in air, vacuum, or in any transparent, nonfluorescing medium.

Small probed regions down to 1–2 μm are possible using microscope lenses. Lasers can supply as much pump power as needed to compensate for weaker signals, but a limit is reached when sample heating or nonlinear optically induced processes become significant.

For semiconductor work, either whole wafers or small pieces are used, the latter often being necessary for insertion into a cryostat. Bulk solids may be analyzed in any form, but scattered light may be reduced and the signal increased if the emitting surface is specular.

Quantitative Abilities

Photoluminescence finds its greatest strengths as a qualitative and semiquantitative probe. Quantification based on absolute or relative intensities is difficult, although it is useful in applications where the sample and optical configurations may be carefully controlled. The necessary conditions are most easily met for analytical applica-

tions of molecular fluorescence, where samples may be reproducibly prepared in the form of controlled films or as dilute concentrations of material in a transparent liquid solvent, and where reference standards are available.⁵

PL intensities are strongly influenced by factors like surface conditions, heating, photochemical reactions, oxygen incorporation, and intensity, power density and the wavelength of the exciting light. If these factors are carefully controlled PL intensities can be used to study various aspects of the sample, but such control is not always possible. Other aspects that can cause intensity variations are the focal region of the incident and collection optics, the relationship of the sample's image to the monochromator entrance slit, and the spectral response of the detector and optical path.

Nevertheless, quantification is possible, a good example being the evaluation of the composition of chromatographic separations adsorbed onto glass, alumina, polyethylene, or paper. When compared with known standards, the presence of only a few nanograms of a strong fluorophore may be quantified to better than 10%.

As another example, PL from GaP:N at 77 K is a convenient way to assess nitrogen concentrations in the range 10^{17} – 10^{19} cm⁻³ by observing the ratio of the peak intensity of the nitrogen-bound exciton transition to that of its LO phonon sideband, or to peaks involving nitrogen pairs. Similar ratio analysis allows estimates of EL2 defect concentration in GaAs wafers and has been used to quantify Mn concentrations in GaAs. Under carefully controlled conditions, PL intensity from layered-as-grown device structures can be correlated with device parameters (e.g., lasing threshold and transistor gain) and used to predict final device performance on other similar wafers.

Instrumentation

A variety of commercial instruments are available for PL measurements. These include spectrofluorometers intended primarily for use with liquids in a standard configuration, and simple filter-based systems for monitoring PL at a single wavelength. For use with opaque samples and surfaces, a few complete commercial systems are available or may be appropriately modified with special attachments, but due to the wide range of possible configuration requirements it is common to assemble a custom system from commercial optical components.

Four basic components make up a PL system:

- 1 A source of light for excitation. Surface studies generally require a continuous or pulsed laser. A dye or Ti:sapphire laser is used if tunability is needed.
- 2 A sample holder, including optics for focusing the incident light and collecting the luminescence. Efficient light collection is important, and the sample holder may need to allow for a cryostat, pressure cell, magnet, or electrical contacts.

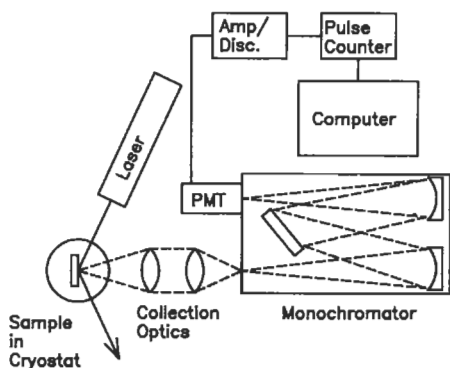


Figure 5 Schematic layout of a high-sensitivity PL system incorporating a laser and photon-counting electronics.

- 3 A dispersive element for spectral analysis of PL. This may be as simple as a filter, but it is usually a scanning grating monochromator. For excitation spectroscopy or in the presence of much scattered light, a double or triple monochromator (as used in Raman scattering) may be required.
- 4 An optical detector with appropriate electronics and readout. Photomultiplier tubes supply good sensitivity for wavelengths in the visible range, and Ge, Si, or other photodiodes can be used in the near infrared range. Multichannel detectors like CCD or photodiode arrays can reduce measurement times, and a streak camera or nonlinear optical techniques can be used to record ps or sub-ps transients.

A schematic of a PL system layout is shown in Figure 5. This optical system is very similar to that required for absorption, reflectance, modulated reflectance, and Raman scattering measurements. Many custom systems are designed to perform several of these techniques, simultaneously or with only small modifications.

Conclusions

Photoluminescence is a well-established and widely practiced tool for materials analysis. In the context of surface and microanalysis, PL is applied mostly qualitatively or semiquantitatively to exploit the correlation between the structure and composition of a material system and its electronic states and their lifetimes, and to identify the presence and type of trace chemicals, impurities, and defects.

Improvements in technology will shape developments in PL in the near future. PL will be essential for demonstrating the achievement of new low-dimensional quantum microstructures. Data collection will become easier and faster with the continuing development of advanced focusing holographic gratings, array and imaging detectors, sensitive near infrared detectors, and tunable laser sources.

Related Articles in the Encyclopedia

CL, Modulation Spectroscopy, Raman Spectroscopy, and FTIR

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7.2 Modulation Spectroscopy

FRED H. POLLAK

Contents

- Introduction
- Basic Principles
- Instrumentation
- Line Shape Considerations
- Applications and Examples
- Conclusions

Introduction

Modulation Spectroscopy is an analog method for taking the derivative of an optical spectrum (reflectance or transmittance) of a material by modifying the measurement conditions in some manner.¹⁻⁶ This procedure results in a series of sharp, derivative-like spectral features in the photon energy region corresponding to electronic transitions between the filled and empty quantum levels of the atoms that constitute the bulk or surface of the material. Using Modulation Spectroscopy it is possible to measure the photon energies of the interband transitions to a high degree of accuracy and precision. In semiconductors these band gap energies are typically 1 eV, and they can be determined to within a few meV, even at room temperature. The energies and line widths of the electronic transitions are characteristic of a particular material or surface. The energies are sensitive to a variety of internal and external parameters, such as chemical composition, temperature, strains, and electric and magnetic fields. The line widths are a function of the quality of the material, i.e., degree of crystallinity or dopant concentration.

The ability to measure the energy of electronic transitions and their line widths accurately, in a convenient manner, is one of the most important aspects of semiconductor characterization. The former can be used to evaluate alloy compositions

(including topographical scans),⁴ near-surface temperatures,⁷ process- or growth-induced strains,⁸ surface or interface electric fields associated with surface or interface states and metallization (Schottky barrier formation),⁸ carrier types,¹⁻⁴ topographical variations in carrier concentrations,⁴ and trap states.⁸ The broadening parameter at a given temperature is a measure of crystal quality and hence can be used to evaluate the influence of various growth, processing and annealing procedures. These include ion implantation, reactive-ion etching, sputtering, and laser or rapid annealing.^{7,8} In real device structures, such as heterojunction bipolar transistors, certain features of the Modulation Spectroscopy spectra have been correlated with actual device performance.⁶ Thus, this method can be employed as an effective screening tool to select materials having the proper device characteristics before undertaking an expensive fabrication process. Various forms of Modulation Spectroscopy can be employed for *in-situ* monitoring of growth by molecular beam epitaxy (MBE), metal-organic chemical vapor deposition (MOCVD), or gas-phase MBE (GPMBE) at elevated temperatures.^{7, 9-11} Modulation Spectroscopy has been used extensively to study semiconductors having diamond (Ge and Si), zincblende (GaAs, GaAlAs, InP, CdTe, and HgCdTe), and wurtzite (CdS) crystal structures. There also has been some work in the area of metals, including alloys.

The characteristic lines observed in the absorption (and emission) spectra of nearly isolated atoms and ions due to transitions between quantum levels are extremely sharp. As a result, their wavelengths (photon energies) can be determined with great accuracy. The lines are characteristic of a particular atom or ion and can be used for identification purposes. Molecular spectra, while usually less sharp than atomic spectra, are also relatively sharp. Positions of spectral lines can be determined with sufficient accuracy to verify the electronic structure of the molecules.

The high particle density of solids, however, makes their optical spectra rather broad, and often uninteresting from an experimental point of view. The large degeneracy of the atomic levels is split by interatomic interactions into quasicontinuous bands (valence and conduction bands). The energy difference between the highest lying valence and lowest lying conduction bands is designated as the fundamental band gap. Penetration depths for electromagnetic radiation are on the order of 500 Å through most of the optical spectrum. Such small penetration depths (except in the immediate vicinity of the fundamental gap), plus other considerations to be discussed later, make the reflection mode more convenient for characterization purposes, relative to absorption measurements.

These aspects of the optical spectra of solids are illustrated in the upper portion of Figure 1, which displays the reflectance curve (R) at room temperature for a typical semiconductor, GaAs. The fundamental absorption edge around 1.4 eV produces only a weak shoulder. Some structure is apparent in the two features around 3 eV and the large, broad peak near 5 eV. However, the dominant aspect of the line shape is the slowly varying background. The derivative nature of Modulation Spectroscopy suppresses the uninteresting background effects in favor of sharp, deriva-

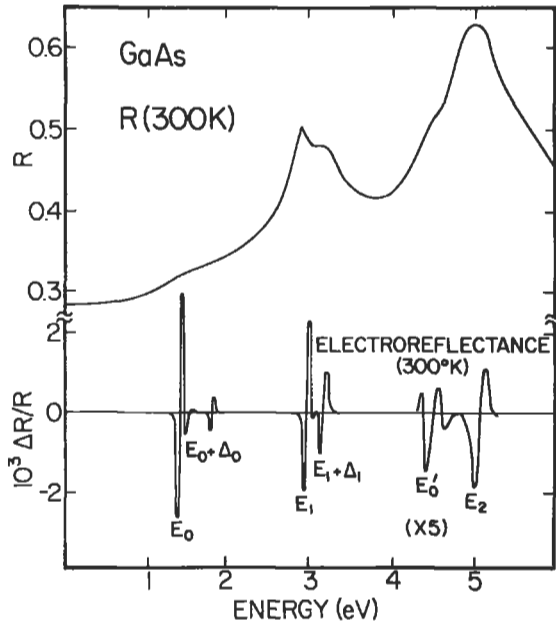


Figure 1 Reflectance (R) and electroreflectance ($\Delta R/R$) spectra of GaAs at 300 K.

tive-like lines corresponding to the shoulders and peaks in Figure 1. Also, weak structures that may go unseen in absolute spectra are enhanced.

Band gaps in semiconductors can be investigated by other optical methods, such as photoluminescence, cathodoluminescence, photoluminescence excitation spectroscopy, absorption, spectral ellipsometry, photocurrent spectroscopy, and resonant Raman spectroscopy. Photoluminescence and cathodoluminescence involve an emission process and hence can be used to evaluate only features near the fundamental band gap. The other methods are related to the absorption process or its derivative (resonant Raman scattering). Most of these methods require cryogenic temperatures.

For applied work, an optical characterization technique should be as simple, rapid, and informative as possible. Other valuable aspects are the ability to perform measurements in a contactless manner at (or even above) room temperature. Modulation Spectroscopy is one of the most useful techniques for studying the optical proponents of the bulk (semiconductors or metals) and surface (semiconductors) of technologically important materials. It is relatively simple, inexpensive, compact, and easy to use. Although photoluminescence is the most widely used technique for characterizing bulk and thin-film semiconductors, Modulation Spectroscopy is gaining in popularity as new applications are found and the database is increased. There are about 100 laboratories (university, industry, and government) around the world that use Modulation Spectroscopy for semiconductor characterization.

Basic Principles

The basic idea of Modulation Spectroscopy is a very general principle of experimental physics. Instead of measuring the optical reflectance (or transmittance) of a material, the derivative with respect to some parameter is evaluated. The spectral response of the material can be modified directly by applying a repetitive perturbation, such as an electric field (electromodulation), a heat pulse (thermomodulation), or stress (piezomodulation). This procedure is termed *external* modulation. The change may also occur in the measuring system itself, e.g., the wavelength or polarization conditions can be modulated or the sample reflectance (transmittance) can be compared to a reference sample. This mode has been labeled *internal* modulation. Because the changes in the optical spectra are typically small, in some cases 1 part in 10^6 , phase-sensitive detection or some other signal-processing procedure is required.

To illustrate the power of Modulation Spectroscopy, displayed in the lower part of Figure 1 is the electromodulated reflectance spectra ($\Delta R/R$) of the semiconductor GaAs at 300 K in the range 0–6 eV. Although the fundamental direct absorption edge (E_0) at about 1.4 eV produces only a weak shoulder in R it is observed as a sharp, well-resolved line in $\Delta R/R$. There are also other spectral features, labeled $E_0 + \Delta_0$, E_1 , $E_1 + \Delta_1$, E_0' , and E_2 , that correspond to transitions between other quantum levels in the semiconductor. In the region of the features at E_0 and $E_0 + \Delta_0$ the penetration depth of the light (the sampling depth) is typically several thousand Å, while for the peaks at E_1 and $E_1 + \Delta_1$ the light samples a depth of only a few hundred Å.

For characterization purposes of bulk or thin-film semiconductors the features at E_0 and E_1 are the most useful. In a number of technologically important semiconductors (e.g., $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$, and $\text{In}_x\text{Ga}_{1-x}\text{As}$) the value of E_0 is so small that it is not in a convenient spectral range for Modulation Spectroscopy, due to the limitations of light sources and detectors. In such cases the peak at E_1 can be used.⁴ The features at E_0' and E_2 are not useful since they occur too far into the near-ultraviolet and are too broad.

Instrumentation

External Modulation

For characterization purposes the most useful form of external modulation is electromodulation, because it provides the sharpest structure (third derivative of R in bulk or thin films) and is sensitive to surface or interface electric fields.^{1–5} The most widely used contactless mode of electromodulation is termed Photoreflectance (PR).^{5, 7, 8}

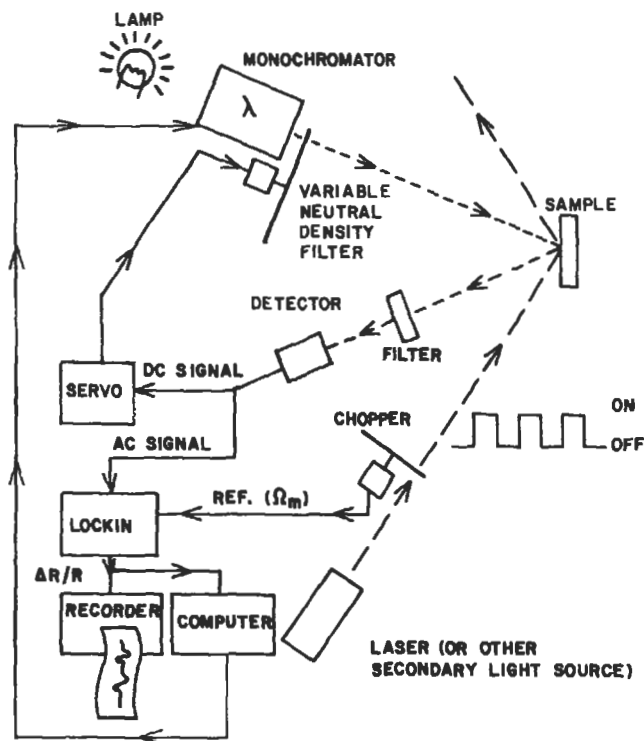


Figure 2 Schematic representation of a photoreflectance apparatus.

A schematic representation of a PR apparatus is shown in Figure 2.⁵ In PR a pump beam (laser or other light source) chopped at frequency Ω_m creates photo-injected electron-hole pairs that modulate the built-in electric field of the semiconductor. The photon energy of the pump beam must be larger than the lowest energy gap of the material. A typical pump beam for measurements at or below room temperature is a 5-mW He-Ne laser. (At elevated temperatures a more powerful pump must be employed.)

Light from an appropriate light source (a xenon arc or a halogen or tungsten lamp) passes through a monochromator (probe monochromator). The exit intensity at wavelength λ , $I_0(\lambda)$, is focused onto the sample by means of a lens (or mirror). The reflected light is collected by a second lens (mirror) and focused onto an appropriate detector (photomultiplier, photodiode, etc.). For simplicity, the two lenses (mirrors) are not shown in Figure 2. For modulated transmission the detector is placed behind the sample.

The light striking the detector contains two signals: the dc (or average value) is given by $I_0(\lambda)R(\lambda)$, where $R(\lambda)$ is the dc reflectance of the material, while the modulated value (at frequency Ω_m) is $I_0(\lambda)\Delta R(\lambda)$, where $\Delta R(\lambda)$ is the change in reflectance produced by the modulation source. The ac signal from the detector, which is

proportional to $I_0\Delta R$, is measured by a lock-in amplifier (or using another signal-averaging procedure). Typically $I_0\Delta R$ is 10^{-4} – 10^{-6} I_0R .

To evaluate the quantity of interest, i.e., the relative change in reflectance, $\Delta R/R$, a normalization procedure must be used to eliminate the uninteresting common feature $I_0(\lambda)$. In Figure 2 the normalization is performed by the variable neutral density filter (VNDF) connected to a servo mechanism. The dc signal from the detector, which is proportional to $I_0(\lambda)R(\lambda)$, is introduced into the servo, which moves the VNDF in such a manner as to keep $I_0(\lambda)R(\lambda)$ constant, i.e., $I_0(\lambda)R(\lambda) = C$. Under these conditions the ac signal $I_0(\lambda)\Delta R(\lambda) = C\Delta R(\lambda)/R(\lambda)$.

Commercial versions of PR are available. Other contactless methods of electro-modulation are Electron-Beam Electro-reflectance (EBER)¹² and Contactless Electroreflectance (CER)¹³. In EBER the pump beam of Figure 2 is replaced by a modulated low-energy electron beam (~ 200 eV) chopped at about 1 kHz. However, the sample and electron gun must be placed in an ultrahigh vacuum chamber. Contactless electroreflectance uses a capacitor-like arrangement.

An example of a contact mode of electromodulation would be the semiconductor–insulator–metal configuration, which consists of a semiconductor, about 200 Å of an insulator like Al_2O_3 , and a semitransparent metal (about 50 Å of Ni or Au). Modulating (ac) and bias (dc) voltages are applied between the front semitransparent metal and a contact on the back of the sample. To employ this mode the sample must be conducting.

In temperature modulation, the sample may be mounted on a small heater attached to a heat sink and the temperature varied cyclically by passing current pulses through the heater.¹ If the sample is properly conducting, the current can be passed through the sample directly. Generally, for this method Ω_m must be kept below 10–20 Hz, and hence there are often problems with the $1/f$ noise of the detector.

In piezoreflectance (PzR), modulation is achieved by mounting the sample on a piezoelectric transducer that varies the lattice constant of the material, producing a band gap modulation.¹⁴ Although PzR is contactless it requires special mounting of the sample, as does thermomodulation.

Internal Modulation

Differential Reflectivity

A commonly used form of internal modulation is differential reflectometry, in which the reflectance of the sample under investigation (or a portion of it) is compared to a standard material. This can be accomplished either by holding the sample stationary and scanning the probe beam between two regions¹⁵ or by holding the light spot fixed and moving the sample.¹⁶

Reflection Difference Spectroscopy

In Reflection Difference Spectroscopy (RDS) the difference between the normal-incidence reflectance R of light polarized parallel and perpendicular to a principal crystallographic axis in the plane of the crystal is measured experimentally as a function of time, photon energy, or surface conditions.^{9–11} Because of the cubic symmetry of zincblende semiconductors, the bulk is nearly isotropic (i.e., there is no distinction between parallel and perpendicular), while regions of lower symmetry, like the surface or interfaces can be anisotropic. In the case of (001) surfaces of zincblende semiconductors, the contribution from the bulk is expected to vanish. Thus, RDS is sensitive to both the chemical and structural state of the surface. Sensitivities to surface species of 0.01 monolayer have been demonstrated, with averaging times of 100 ms. Being an optical probe, RDS is well suited either to the reactive, relatively high-pressure sample environments in MOCVD reactors or to the ultrahigh-vacuum environment of MBE chambers. Moreover, the presence of a film deposited on the viewport can be overcome.

Line Shape Considerations

One of the great advantages of Modulation Spectroscopy is its ability to fit the line shapes of sharp, localized structures, as illustrated in the lower part of Figure 1. These fits yield important relevant parameters, such as the value of the energy gap and the broadening parameter.

Electromodulation

The most complicated form of Modulation Spectroscopy is electromodulation, since in certain cases it can accelerate the electron-hole pairs created by the light. If the electric field is not too large the quantity $\Delta R/R$ can be written as:^{1–4}

$$\frac{\Delta R}{R} = \text{Re} \left[A e^{i\phi} (E - E_g + i\Gamma)^{-m} \right] \quad (1)$$

where A is the amplitude of the signal, ϕ is phase angle that mixes together the real and imaginary parts of dielectric function, E is the photon energy, E_g is the energy gap and Γ is a parameter that describes the broadening of the spectral line. The parameter $m = 2.5$ or 3.0 for the E_0 and E_1 optical features, respectively. Equation (1) is related to the third derivative of R .

At low temperatures the electron and hole created by the probe light beam can form a bound state (called an *exciton*) because of the Coulomb interaction between them. In this case the exponent m in Equation (1) becomes 2 and the line shape is only a first derivative.^{1–5}

For sufficiently high built-in electric fields the electromodulation spectrum can

display an oscillatory behavior above the band gap; these are called Franz-Keldysh oscillations (FK oscillations). In the presence of the field F the energy bands are tilted by an amount eFz , where e is the electronic charge and z is in the direction of F . Resonances appear whenever an integral number of de Broglie wavelengths fit into the triangular well formed by the electric field. The de Broglie wavelength is equal to $4\pi^2/hp$, where h is Planck's constant and p is the momentum of the electron (hole). The energy of the m th resonance E_m is proportional to $F^{2/3}$. Thus the periods of these resonances, or FK oscillations, are a direct measure of the built-in electric field.^{3,5}

Piezo- and Thermomodulation

These modulation methods do not accelerate the electron-hole pairs and hence produce only a first-derivative Modulation Spectroscopy. Their line shapes are given by Equation (1), with $m = 2$.

Applications and Examples

Alloy composition

Among the most important parameters for materials characterization are the compositions of binary $A_{1-x}B_x$ (e.g., $Ge_{1-x}Si_x$) alloys, ternary $A_{1-x}B_xC$ (e.g., $Ga_{1-x}Al_xAs$, $Hg_{1-x}Cd_xTe$) alloys, and quaternary $A_{1-x}B_xC_yD_{1-y}$ (e.g., $In_{1-x}Ga_xAs_yP_{1-y}$) alloys. The spectral features in Figure 1, e.g., E_0 and E_1 vary with alloy composition. Modulation Spectroscopy thus can be employed conveniently for this purpose even at 300 K.

Shown in Figure 3 is the variation of the fundamental direct band gap (E_0) of $Ga_{1-x}Al_xAs$ as a function of Al composition (x). These results were obtained at 300 K using electromodulation. Thus it would be possible to evaluate the Al composition of this alloy from the position of E_0 .

The case of $Ga_{1-x}Al_xAs$ alloy determination is an example of the importance of the reflectance mode in relation to transmittance. In almost all cases the $Ga_{1-x}Al_xAs$ material is an epitaxial film (0.1–1 μ m) grown on a GaAs substrate (~0.5 mm thick). Since the band gap of GaAs is smaller than that of $Ga_{1-x}Al_xAs$, the reflectance mode must be used.

Some materials, such as $Hg_{1-x}Cd_xTe$, have a value of E_0 in certain composition regions that is too far into the infrared to be conveniently observed using Modulation Spectroscopy. In such circumstances other higher lying features, such as the peaks at E_1 , can be used more readily.

The compositional variation of E_0 or higher lying features has been reported for a large number of alloys, including GeSi, GaAlAs, GaAlSb, GaAlP, InGaAs, InAsSb, InAsP, GaInSb, HgCdTe, HgMnTe, CdMnTe, CdZnTe, ZnMnTe, CdMnSe, InGaAsP lattice-matched to InP, GaAlInAs lattice-matched to InP, and

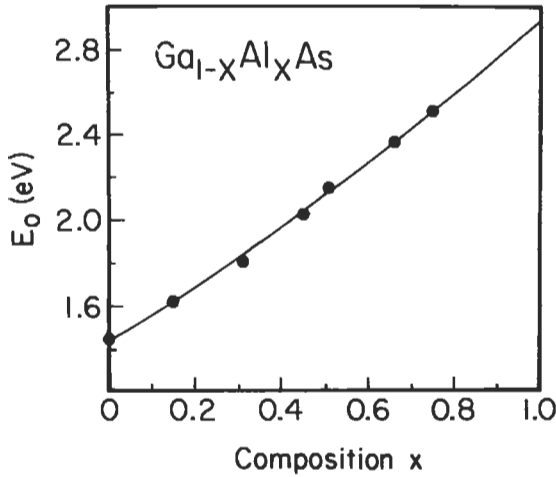


Figure 3 Aluminum composition dependence of E_0 of $\text{Ga}_{1-x}\text{Al}_x\text{As}$ at 300 K (solid line).

GaAlInPAs lattice-matched to GaAs. The alloy composition x can be evaluated with a precision of $\Delta x = \pm 0.005$. By using a high-quality lens to focus the light from the probe monochromator onto the sample (see Figure 2) a spot size of about $100 \mu\text{m}$ can be achieved. By mounting the sample on an x - y stage it is possible to perform topographical scans with a spatial resolution of $100 \mu\text{m}$.

Growth or Process-Induced Strain or Damage

Modulation Spectroscopy can be very useful in evaluating strains induced by growth (lattice-mismatched systems) or processing procedures, such as reactive-ion etching or oxide formation. The size and magnitude of the strain can be evaluated from the shifts and splittings of various spectral lines, such as E_0 or E_1 .⁶⁻⁸

Device Structures

Certain features in the PR spectra at 300 K from GaAs/ $\text{Ga}_{1-x}\text{Al}_x\text{As}$ heterojunction bipolar transistor structures have been correlated with actual device performance; thus PR can be used as an effective screening tool.⁶ From the observed FK oscillations it has been possible to evaluate the built-in dc electric fields F_{dc} in the $\text{Ga}_{1-x}\text{Al}_x\text{As}$ emitter, as well as in the n-GaAs collector region. The behavior of F_{dc} (GaAlAs) has been found to have a direct relation to actual device performance, i.e., dc current gain. Shown in Figures 4a and 4b are the PR spectrum at 300 K for MBE and MOCVD fabricated samples, respectively. There are a number of FK oscillations in the vicinity of both the GaAs (-1.42 eV) and $\text{Ga}_{1-x}\text{Al}_x\text{As}$

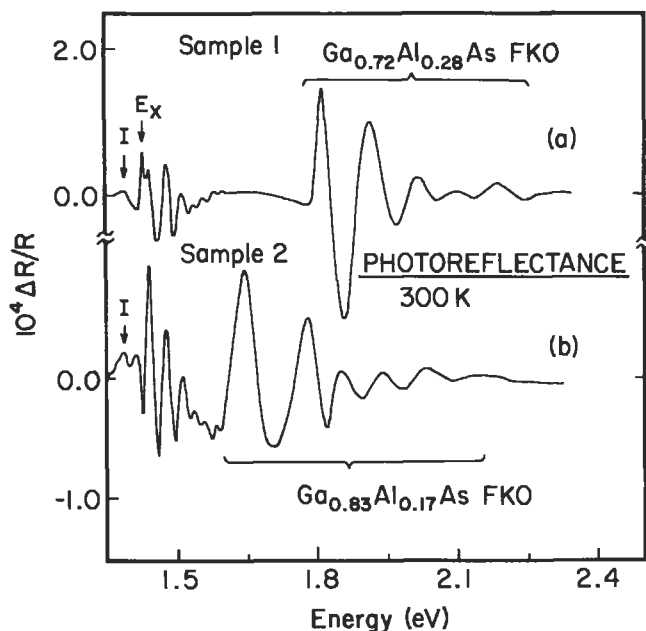


Figure 4 Photoreflectance spectra for two GaAs/Ga_{1-x}Al_xAs heterojunction bipolar transistor structures fabricated by MBE and MOCVD, respectively, at 300 K.

band gaps. The Ga_{1-x}Al_xAs portions of the two samples are 1.830 eV and 1.670 eV, which corresponds to $x = 0.28$ and 0.17 , respectively, as shown in Figure 3. The most important aspects of Figure 4 are the FK oscillations associated with the Ga_{1-x}Al_xAs band gap. From these features it is possible to evaluate F_{dc} in the emitter-base p-n junction. The electric fields, as deduced from the GaAlAs FK oscillations (F_{dc} , GaAlAs), were compared with fabricated heterojunction bipolar transistor MBE samples. Below electric field values of about 2×10^5 V/cm high current gains were obtained. Shown in Figure 5 is F_{dc} (in GaAlAs) as a function of dc current gain at 1 mA. Note that there is a sudden drop when F_{dc} (in GaAlAs) $> 2 \times 10^5$ V/cm. The explanation of this effect is the redistribution of the Be dopant in the p-region in these MBE samples. When the redistribution moves the p-n junction into the emitter, there is an increase in the electric field in this region; i.e., the value of F_{dc} becomes greater. The movement of the Be has been verified by Secondary Ion Mass Spectroscopy (SIMS). When the p-n junction and the GaAs/GaAlAs heterojunction are not coincident, carrier recombination occurs, reducing the current and the performance of fabricated heterojunction bipolar transistors.

These observations have made it possible to use PR as a contactless screening technique to eliminate wafers with unwanted characteristics before the costly fabrication step.

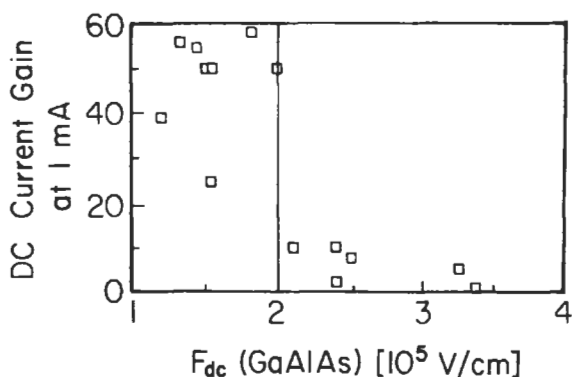


Figure 5 Electric field F_{dc} (GaAlAs) in the p-n junction as evaluated from the GaAlAs FK oscillations as a function of the dc current gain of a fabricated heterojunction bipolar transistor.

In-Situ Monitoring of Growth

RDS and PR are proving to be very useful methods for *in-situ* characterization of semiconductor thin-film growth by MBE, MOCVD, and GPMBE. RDS was first applied to study GaAs growth in an MBE environment. Results showed that the maximum surface anisotropy between (2×4) As-terminated and (4×2) Ga- and Al-terminated surfaces of GaAs and AlAs occur in the photon energy region between 2.0–2.5 eV and 3.5 eV, respectively. The strong dependence of this anisotropy on photon energy makes it possible to spectrally distinguish between Al–Al and Ga–Ga surface dimer bonds. The time dependence of RDS and simultaneously measured reflection high-energy electron diffraction (RHEED) signals for changes in surface conditions revealed that the RDS measurements follow surface structure. The RDS–RHEED correlation gives a valuable reference when RDS is applied to nonultrahigh-vacuum techniques, such as MOCVD, where RHEED cannot be used. A commercial model of an RDS system is available.

MBE Growth Studied by RDS

Figure 6 shows typical RDS (bottom) and RHEED (top) responses for an As-to-Ga-to-As surface stabilization sequence—from As-stabilized (2×4) to Ga-stabilized (4×2) (001) surface reconstructions and return—generated by interrupting and resuming the As flux at times $t = 1$ s and 10 s, respectively, during otherwise normal growth of GaAs at a rate of 1 GaAs monolayer per 4.6 s.^{9, 10} The As growth-surface pressure of 6×10^{-6} torr provided 2.6 times the amount needed to consume the arriving Ga. The differences between the RDS data on the left and those on the right are due to the differences in energy of the photons used to obtain them. The differences in the RHEED data are due to small angle-of-incidence drifts of the electron beam in the time interval between the recording of successive sets of data.

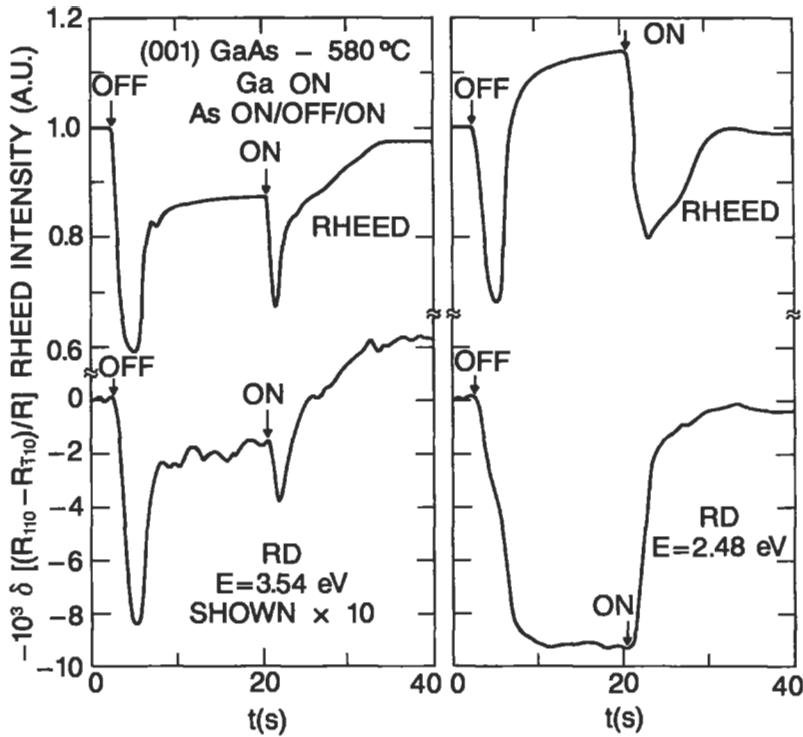


Figure 6 RHEED (upper) and reflection anisotropy (lower) transients obtained by interrupting and resuming As flux during otherwise normal growth (001) GaAs at 1 semiconductor ML per 4.6 s. Data are shown for photon energies near the Ga RD peak at 2.5 eV (right) and minimum at 3.5 eV (left).

The maximum change of the 2.48-eV RDS signal is nearly 1%, with R_{110} increasing relative to R_{T10} as the surface becomes increasingly covered with Ga.

As soon as the As flux is terminated, the RDS signal begins to change nearly linearly in time, and saturates near $t = 5$ s; i.e., it tracks the amount of excess Ga accumulating on the surface up to one monolayer. Since RDS responds only to surface species that are in registry with the crystallographic axes of the substrate (i.e., have already reacted with it), and since it is insensitive to the presence of randomly oriented species, this time dependence implies that the excess Ga atoms are forming Ga-Ga dimer bonds instantly on arrival, with respect to laboratory time scales, and that the 2.48-eV RDS signal directly follows the chemistry of the (001) GaAs growth surface. It also implies that Ga diffusion lengths under Ga-stabilized surface conditions are large, in particular, hundreds of times greater than under As-stabilized conditions.

The 3.54-eV RDS response is completely different, exhibiting a striking similarity to the RHEED signal shown above it. Clearly, at this photon energy the RDS signal, as RHEED, is determined by surface structure. Thus RDS data either can complement or supplement RHEED data, depending on the measurement wavelength. As the saturation RDS signal at 3.54 eV is about an order of magnitude smaller than that at 2.48 eV, it follows that the small inflection in the otherwise linear initial 2.48-eV RD transient is due to the contribution of the structure-sensitive component, which is relatively minor at the lower photon energy.

Substrate Temperature and Alloy Composition by PR

It has been demonstrated that PR can be used to measure E_0 of technologically important materials, such as GaAs, InP, $\text{Ga}_{0.82}\text{Al}_{0.18}\text{As}$, and $\text{In}_x\text{Ga}_{1-x}\text{As}$ ($x = 0.06$ and 0.15), to over 600°C .^{6,7} Such temperatures correspond to growth conditions for thin-film methods like MBE, MOCVD, and gas-phase MBE. The value of E_0 can be evaluated to ± 5 meV at these elevated temperatures. Thus, the temperature of GaAs and InP substrates can be evaluated to $\pm 10^\circ\text{C}$ to within a depth of only several thousand Å from the growth surface. In addition, the alloy composition of epilayers of $\text{Ga}_{1-x}\text{Al}_x\text{As}$ and $\text{In}_x\text{Ga}_{1-x}\text{As}$ can be determined during actual growth. Measurements have been performed under actual growth conditions, including the case of a rotating substrate. Topographical scans can be performed to evaluate temperature or compositional homogeneity.

Figure 7 shows E_0 for GaAs and $\text{Ga}_{0.82}\text{Al}_{0.18}\text{As}$ as a function of temperature T to about 900 K. Additional measurements on samples having differing Al contents would generate a family of curves. The solid line is a least-squares fit to a semi-empirical relation that describes the temperature variation of semiconductor energy gaps:

$$E(T) = E(0) - \frac{\alpha T^2}{\beta + T} \quad (2)$$

In Equation (2) $E(0)$ is the energy gap at $T = 0$, while α and β are materials parameters to be evaluated from experiment. Once the GaAs substrate temperature is measured from the position of $E_0(\text{GaAs})$, the Al composition of an epilayer can be determined readily from the position of $E_0(\text{GaAlAs})$ at that temperature.

Conclusions

Modulation Spectroscopy has proven to be an important characterization method for semiconductors and semiconductor microstructures. The rich spectra contain a wealth of information about relevant materials, surfaces and interfaces, as well as device characteristics. In general, the apparatus is relatively simple, compact (except EBER), inexpensive (except EBER), and easy to use. One of the main advantages of Modulation Spectroscopy is its ability to perform relevant measurements at room

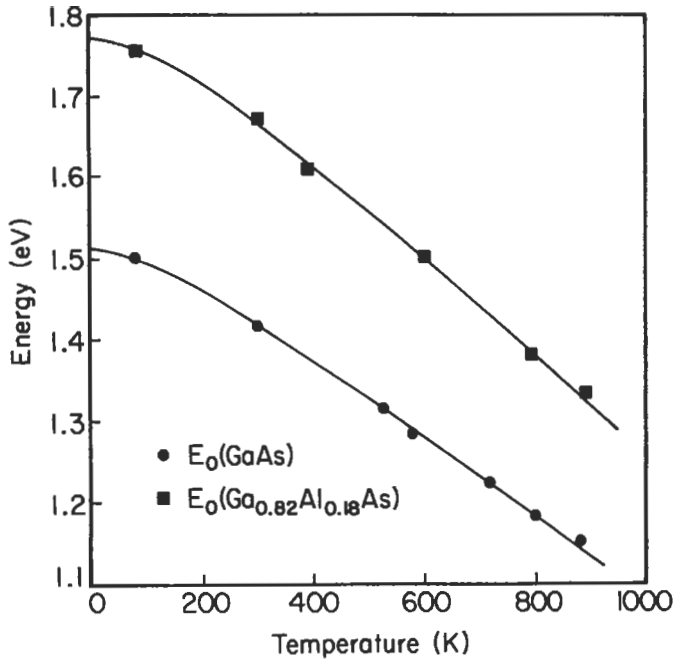


Figure 7 Temperature dependence of E_0 of GaAs (circles) and $\text{Ga}_{0.82}\text{Al}_{0.18}\text{As}$ (squares). The solid lines are least-squares fits to Equation (2).

temperature (or even above). Several modulation techniques, such as PR and RDS, not only are contactless but also require no special mounting of the sample and can be performed in any transparent ambient.

In bulk or thin films, material properties like the alloy composition (including topographical variations), the near-surface temperature, growth- or process-induced strain or damage, the influence of annealing procedures, surface or interface electric fields associated with Fermi level pinning, carrier types, topographical variations in carrier concentrations, and trap states, can be determined. Various contactless modulation methods, such as PR and RDS, can produce valuable information about surface and interface phenomena, including crystal growth at elevated temperatures.

In real device structures like heterojunction bipolar transistors, certain features in the PR spectrum can be correlated with actual device performance. Thus PR has been employed as an effective contactless screening technique to eliminate structures that have unwanted properties.

A major thrust in the future will be the use of contactless modulation methods like PR or RDS (together with scanning ellipsometry) for the *in-situ* monitoring and control of growth and processing, including real-time measurements. These methods can be used not only during actual growth at elevated temperatures but also for *in-situ* post growth or processing at room temperature before the sample is removed from the chamber. Such procedures should improve a material's quality and specifications, and also should serve to reduce the turn-around time for adjusting growth or processing parameters. The success of PR as a contactless screening tool for an industrial process, i.e., heterojunction bipolar transistor structures, certainly will lead to more work on real device configurations.

There also will be improvements in instrumentation and software to decrease data acquisition time. Changes can be made to improve lateral spatial resolution. For example, if the probe monochromator is replaced by a tunable dye laser spatial resolutions down to about 10 μm can be achieved.

Related Articles in the Encyclopedia

RHEED, VASE

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7.3 VASE

Variable Angle Spectroscopic Ellipsometry

JOHN A. WOOLLAM AND PAUL G. SNYDER

Contents

- Introduction
- Basic Principles
- Applications
- Conclusions

Introduction

The technique of ellipsometry was introduced in the 1800s, but until computers became available, it was painfully slow to perform.¹ Rapid advances in small computer technology have made ellipsometric data acquisition rapid and accurate. Most important, fast personal computers make possible quick and convenient analysis of data from complex material structures.

Early work in ellipsometry focused on improving the technique, whereas attention now emphasizes applications to materials analysis. New uses continue to be found; however, ellipsometry traditionally has been used to determine film thicknesses (in the range 1–1000 nm), as well as optical constants.^{1–6} Common systems are oxide and nitride films on silicon wafers, dielectric films deposited on optical surfaces, and multilayer semiconductor structures.

In ellipsometry a collimated polarized light beam is directed at the material under study, and the polarization state of the reflected light is determined using a second polarizer. To maximize sensitivity and accuracy, the angle that the light makes to the sample normal (the angle of incidence) and the wavelength are controlled.^{4–6} The geometry of a typical ellipsometry set up is shown in Figure 1.

Ellipsometry is a very powerful, simple, and totally nondestructive technique for determining optical constants, film thicknesses in multilayered systems, surface and

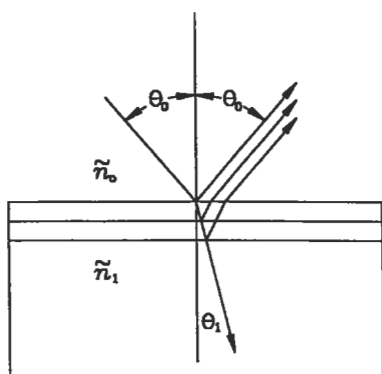


Figure 1 Planar structure assumed for ellipsometric analysis: n_0 is the complex index of refraction for the ambient medium; n_1 is the complex index for the substrate medium; θ_0 is the value of the angles of incidence and reflection, which define the plane of incidence.

interfacial roughness, and material microstructures. (An electron microscope may alter surfaces, as may Rutherford backscattering.) In contrast to a large class of surface techniques such as ESCA and AUGER, no vacuum chamber is necessary in ellipsometry. Measurements can be made in vacuum, air, or hostile environments like acids. The ability to study surfaces at the interface with liquids is a distinct advantage for many disciplines, including surface chemistry, biology and medicine, and corrosion engineering.

Ellipsometry can be sensitive to layers of matter only one atom thick. For example, oxidation of freshly cleaved single-crystal graphite can be monitored from the first monolayer and up. The best thicknesses for the ellipsometric study of thin films are between about 1 nm and 1000 nm. Although the spectra become complicated, films thicker than even 1 μm can be studied. Flat planar materials are optimum, but surface and interfacial roughness can be quantitatively determined if the roughness scale is smaller than about 100 nm. Thus ellipsometry is ideal for the investigation of interfacial surfaces in optical coatings and semiconductor structures.^{2, 4, 7}

In some applications lateral homogeneity of a sample over large areas needs to be determined, and systems with stepper driven sample positioners have been built. Use of focused ellipsometer beams is then highly desirable. As normally practiced, the lateral resolution of ellipsometry is on the order of millimeters. However, the light beam can be focused to $\sim 100 \mu\text{m}$ if the angle of incidence variation is not critical. For smaller focusing the beam contains components having a range of angles of incidence that may alter the validity of the data analysis.

Depth resolution depends on the (spectrally dependent) optical absorption coefficient of the material. Near-surface analysis (first 50 nm) frequently can be per-

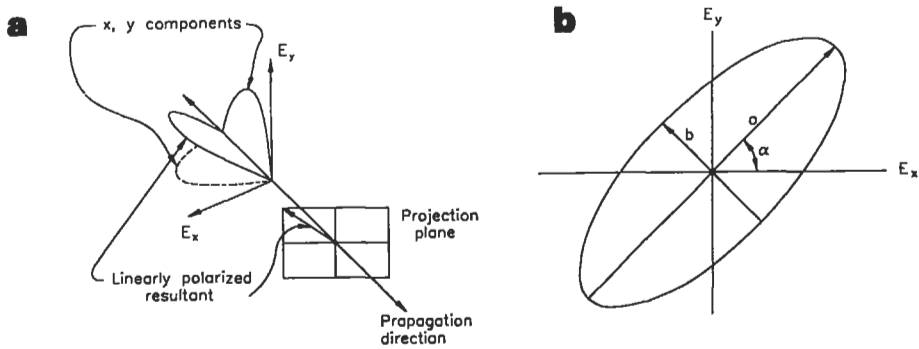


Figure 2 (a) Representation of a linearly polarized beam in its x - and y - or (p - and s -) orthogonal component vectors. The projection plane is perpendicular to the propagation direction; (b) locus of projection of electric vector of light wave on the projection plane for elliptically polarized light— a and b are the major and minor axes of the ellipse, respectively, and α is the azimuthal angle relative to the x -axis.

formed using short wavelength light (~ 300 nm) where absorption is strongest, and infrared radiation probes deeply (many μm) into many materials, including semiconductors.

Basic Principles

Light Waves and Polarization

Light is an electromagnetic wave with a wavelength ranging from 350 nm (blue) to 750 nm (red) for visible radiation.⁸ These waves have associated electric (E) and magnetic (H) components that are related mathematically to each other, and thus the E component is normally treated alone. Figure 2a shows the electric field associated with linearly polarized light as it propagates in space and time, separated into its x - and y -vector components. In the figure the x - and y -components are exactly in phase with each other thus the electric vector oscillates in one plane, and a projection onto a plane perpendicular to the beam propagation direction traces out a straight line, as shown in Figure 2a.

When the vector components are not in phase with each other, the projection of the tip of the electric vector onto a plane perpendicular to the beam propagation direction traces out an ellipse, as shown in Figure 2b.

A complete description of the polarization state includes:¹

- 1 The azimuthal angle of the electric field vector along the major axis of the ellipse (recall the angle α in Figure 2b) relative to a plane of reference

- 2 The ellipticity, which is defined by $e = b/a$
- 3 The handedness (righthanded rotation of the electric vector describes clockwise rotation when looking into the beam)
- 4 The amplitude, which is defined by $A = (a^2 + b^2)^{2/3}$
- 5 The absolute phase of the vector components of the electric field.

In ellipsometry only quantities 1 and 2 (and sometimes 3) are determined. The absolute intensity or phase of the light doesn't need to be measured, which simplifies the instrumentation enormously. The handedness information is normally not critical.

All electromagnetic phenomena are governed by Maxwell's equations, and one of the consequences is that certain mathematical relationships can be determined when light encounters boundaries between media.^{1, 8} Three important conclusions that result for ellipsometry are:

- 1 The angle of incidence equals the angle of reflectance θ_0 (see Figure 1).
- 2 Snell's Law holds: $n_1 \sin \theta_1 = n_0 \sin \theta_0$ (Snell's Law), where n_1 and n_0 are the complex indexes of refraction in media 1 and media 0, and the angles θ_1 and θ_0 are shown in Figure 1.
- 3 The Fresnel reflection coefficients are:

$$r_p = \frac{E_{op}^r}{E_{op}^i} = \frac{n_1 \cos \theta_0 - n_0 \cos \theta_1}{n_1 \cos \theta_0 + n_0 \cos \theta_1} \quad (1a)$$

$$r_s = \frac{E_{op}^r}{E_{op}^i} = \frac{n_1 \cos \theta_0 - n_0 \cos \theta_1}{n_1 \cos \theta_0 + n_0 \cos \theta_1} \quad (1b)$$

where s refers to the light vector component perpendicular to the plane of incidence, p refers to the component parallel to the plane of incidence, and r and i refer to reflected and incoming light. The plane of incidence is defined by the incoming and outgoing beams and the normal to the sample. The complex indices of refraction for media 0 and 1 are given by n_0 and n_1 . The relations r_s and r_p are the complex Fresnel reflection coefficients. Their ratio is measured in ellipsometry:

$$\rho = \frac{r_p}{r_s} = (\tan \Psi) e^{j\Delta} \quad (2)$$

Since ρ is a complex number, it may be expressed in terms of the amplitude factor $\tan \Psi$, and the phase factor $\exp j\Delta$ or, more commonly, in terms of just Ψ and Δ . Thus measurements of Ψ and Δ are related to the properties of matter via Fresnel coefficients derived from the boundary conditions of electromagnetic theory.^{1, 8}

There are several techniques for measuring Ψ and Δ , and a common one is discussed below.

Equations 1a and 1b are for a simple two-phase system such as the air–bulk solid interface. Real materials aren't so simple. They have natural oxides and surface roughness, and consist of deposited or grown multilayered structures in many cases. In these cases each layer and interface can be represented by a 2×2 matrix (for isotropic materials), and the overall reflection properties can be calculated by matrix multiplication.¹ The resulting algebraic equations are too complex to invert, and a major consequence is that regression analysis must be used to determine the system's physical parameters.^{1, 2, 5, 9}

In a regression analysis Ψ_i^c and Δ_i^c are calculated from an assumed model for the structure using the Fresnel equations, where Ψ and Δ in Equation 2 are now indexed by c , to indicate that they are calculated, and by i , for each combination of wavelength and angle of incidence.

The unknown parameters of the model, such as film thicknesses, optical constants, or constituent material fractions, are varied until a best fit between the measured Ψ_i^m and Δ_i^m and the calculated Ψ_i^c and Δ_i^c is found, where m signifies a quantity that is measured. A mathematical function called the *mean squared error* (MSE) is used as a measure of the goodness of the fit:

$$\text{MSE} = \frac{1}{N} \sum_{i=1}^N (\Psi_i^c - \Psi_i^m)^2 + (\Delta_i^c - \Delta_i^m)^2 \quad (3)$$

where N is the number of wavelength and angle of incidence combinations used. The MSE is low if the user's guess at the physical model for the system was correct and if starting parameters were reasonably close to correct values.

The model-dependent aspect of ellipsometric analysis makes it a difficult technique. Several different models fit to one set of data may produce equivalently low MSEs. The user must integrate and evaluate all available information about the sample to develop a physically realistic model. Another problem in applying ellipsometry is determining when the parameters of the model are mathematically correlated; for example, a thicker film but lower index of refraction might give the same MSE as some other combinations of index and thickness. That is, the answer is not always unique.

Access to the correlation matrix generated during the regression analysis is thus important^{1, 9} to determine which, and to what degree, variables are correlated. It is common for the user of an ellipsometer mistakenly to make five wrong (correlated) measurements of an index of refraction and film thickness at, say, 632.8 nm and then to average these meaningless numbers. In reality all five measurements gave nonunique values, and averaging is not a valid procedure—the average of five bad numbers does not yield a correct number! The solution to the correlation problem

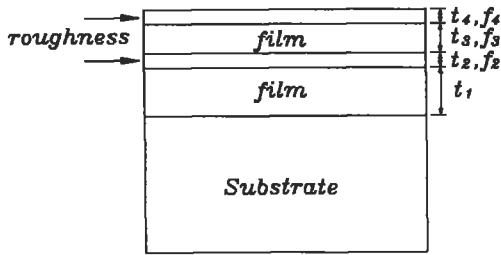


Figure 3 Common structure assumed for ellipsometric data analysis: t_1 and t_3 are the thicknesses of the two deposited films, for example; t_2 and t_4 are interfacial and surface roughness regions; f_2 is the fraction of film t_1 mixed with film t_3 in an effective medium theory analysis of roughness—film f_3 could have void (with fraction $1-f_3$) dispersed throughout; and f_4 is the fraction of t_4 mixed with the ambient medium to simulate surface roughness.

is to make many measurements at optimum wavelength and angle combinations, and to keep the assumed model simple yet realistic. Even then, it is sometimes inherently not possible to avoid correlation. In this case especially it is important to know the degree of correlation. Predictive modeling can be performed prior to making any measurements to determine the optimum wavelength and angle combinations to use, and to determine when there are likely to be correlated variables and thus nonunique answers.^{5, 6}

A typical structure capable of being analyzed is shown in Figure 3, consisting of a substrate, two films (thicknesses t_1 and t_3), two roughness regions (one is an interfacial region of thickness t_2 , and the other is a surface region of thickness t_4). One of the films t_1 or t_3 may consist of microscopic (less than 100 nm size) mixtures of two materials, such as SiO_2 and Si_3N_4 . The volume ratios of these two constituents can be determined by ellipsometry using effective medium theory.¹⁰ This theory solves the electromagnetic equations for mixtures of constituent materials using simplifying approximations, resulting in the ability of the user to determine the fraction of any particular species in a mixed material. Likewise the roughness layers are modeled as mixtures of the neighboring media (air with medium 3 for the surface roughness, and medium 1 with medium 3 for interfacial roughness, as seen in Figure 3).

The example in Figure 3 is as complex as is usually possible to analyze. There are seven unknowns, if no indices of refraction are being solved for in the regression analysis. If correlation is a problem, then a less complex model must be assumed. For example, the assumption that f_2 and f_4 are each fixed at a value of 0.5 might reduce correlation. The five remaining unknowns in the regression analysis would then be $t_1, t_2, t_3, t_4,$ and f_3 . In practice one first assumes the simplest possible model, then makes it more complex until correlation sets in, or until the mean squared error fails to decrease significantly.

Polarization Measurement

Manual null ellipsometry is accurate but infrequently done, due to the length of time needed to acquire sufficient data for any meaningful materials analysis. Automated null ellipsometers are used, for example, in the infrared, but are still slow. Numerous versions of fast automated ellipsometers have been built.¹⁻³ Examples are:

- 1 Polarization modulation
- 2 Rotating analyzer
- 3 Rotating polarizer.

The most common versions are 2 and 3, and the rotating analyzer system will be briefly described here.¹¹ Such a system consists of a light source, monochromator, collimating optics, and polarizer preceding the sample of Figure 1, and a rotating polarizer (called the analyzer) and detector following the sample. The intensity of the light measured at the detector oscillates sinusoidally according to the relation

$$I = 1 + \alpha \cos 2A + \beta \sin 2A$$

where α and β are the Fourier coefficients, and A is the azimuthal angle between the analyzer "fast axis" and the plane of incidence. There is a direct mathematical relationship between the Fourier coefficients and the Ψ and Δ ellipsometric parameters. The actual experiment involves recording the relative light intensity versus A in a computer. The coefficients α and β , and thus Ψ and Δ , can then be determined. By changing the angle of incidence and wavelength, the user can determine N sets of Ψ_i and Δ_i values for the regression analysis used to derive the unknown physical properties of the sample.

The polarizer and analyzer azimuthal angles relative to the plane of incidence must be calibrated. A procedure for doing this is based on the minimum of signal that is observed when the fast axes of two polarizers are perpendicular to each other. For details the reader can consult the literature.¹¹

Applications

In this section we will give some representative examples. Figure 4 shows the regression procedure for $\tan \Psi$ for the glass/TiO₂/Ag/TiO₂ system. The unknowns of the fit were the three thicknesses: TiO₂, Ag, and the top TiO₂. Initial guesses at the thicknesses were reasonable but not exact. The final thicknesses were 33.3 nm, 11.3 nm, and 26.9 nm, and the fits between measured Ψ_i^m and Δ_i^m and calculated (from Fresnel equations) Ψ_i^c and Δ_i^c were excellent. This means that the assumed optical constants and structure for the material were reasonable.

Because Ψ and Δ can be calculated for *any* structure (no matter how complex, as long as planar parallel interfaces are present), then the user can do predictive modeling. Figure 5 shows the expected Δ versus wavelength and angle of incidence for a

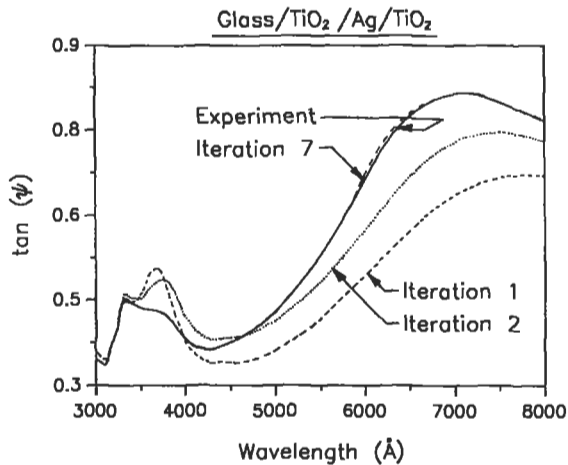


Figure 4 Data plus iterations 1, 2, and 7 in regression analysis (data fit) for the optical coating glass/TiO₂/Ag/TiO₂.

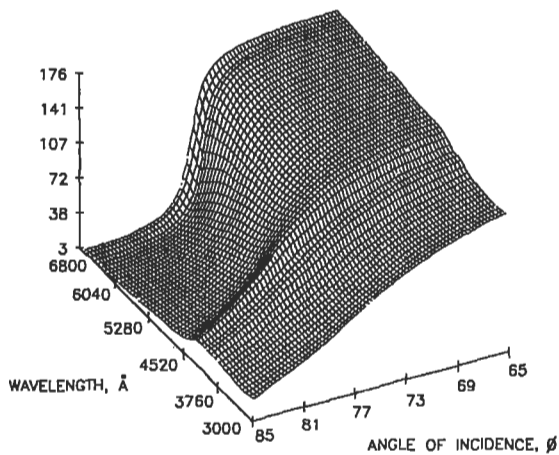


Figure 5 Three-dimensional plot of predicted ellipsometric parameter data versus angle of incidence and wavelength.

structure with a GaAs substrate/50 nm of Al_{0.3}Ga_{0.7}As/30 nm of GaAs/3 nm of oxide.⁵ The best data are taken when Δ is near 90° , and generated surfaces such as Figure 5 help enormously in finding the proper wavelength and angle regions to take data.⁴⁻⁶ Equally useful are contour plots made from the surfaces of Figure 5 which show quantitatively where the $90^\circ \pm 20^\circ$ regions of Δ will be found.^{4, 6, 12}

Many materials have been studied; examples include:

- 1 Dielectrics and optical coatings: Si_3N_4 , SiO_2 , SiO_xN_y , Al_2O_3 , a-C:H, ZnO, TiO_2 , ZnO/Ag/ZnO, $\text{TiO}_2/\text{Ag}/\text{TiO}_2$, AgO, $\text{In}(\text{Sn})_2\text{O}_3$, and organic dyes.
- 2 Semiconductors and heterostructures: Si, poly-Si, amorphous Si, GaAs, $\text{Al}_x\text{G}_{1-x}\text{As}$, $\text{In}_x\text{Ga}_{1-x}\text{As}$, and numerous II-VI and III-V category compound semiconductors; ion implanted compound heterostructures, superlattices, and heterostructures exhibiting Franz-Keldysh oscillations. Work has been done on these materials at room temperature, as well as from cryogenic (4 K) to crystal growth temperatures (900 K).
- 3 Surface modifications and surface roughness: Cu, Mo, and Be laser mirrors; atomic oxygen modified (corroded) surfaces and films, and chemically etched surfaces.
- 4 Magneto-optic and magnetic disc materials: DyCo, TbFeCo, garnets, sputtered magnetic media (CoNiCr alloys and their carbon overcoats).
- 5 Electrochemical and biological and medical systems.
- 6 *In-situ* measurements into vacuum systems: In these experiments the light beams enter and leave via optical ports (usually at a 70° or 75° angle of incidence), and ψ and Δ are monitored in time. Example studies include the measurement of optical constants at high temperatures, surface oxide formation and sublimation, surface roughness, crystal growth, and film deposition. *In-situ* measurements were recently reviewed by Collins.³

Conclusions

Ellipsometry is a powerful technique for surface, thin-film, and interface analysis. It is totally nondestructive and rapid, and has monolayer resolution. It can be performed in any atmosphere including high-vacuum, air, and aqueous environments. Its principal uses are to determine thicknesses of thin films, optical constants of bulk and thin-film materials, constituent fractions (including void fractions) in deposited or grown materials, and surface and interfacial roughness. Recent trends in the relatively small community of scientists using ellipsometry in research have been towards *in-situ* measurements during crystal growth or material deposition or processing. Fast-acquisition automated ellipsometers have not been used widely in medical research, which represents an opportunity. Simple one-wavelength ellipsometers are in common use (and misuse due to correlated variables) in semiconductor processing. Use of a full spectroscopic ellipsometer is strongly advised.

The ellipsometer user will always get data; but unfortunately may not always know when the data or the results of analysis are correct. Improper optical alignment, bad calibration constants, reflection from the back surface of partially trans-

parent materials, as well as correlation of variables are all potential problems to be aware of. Ellipsometry is a powerful technique when used properly.

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