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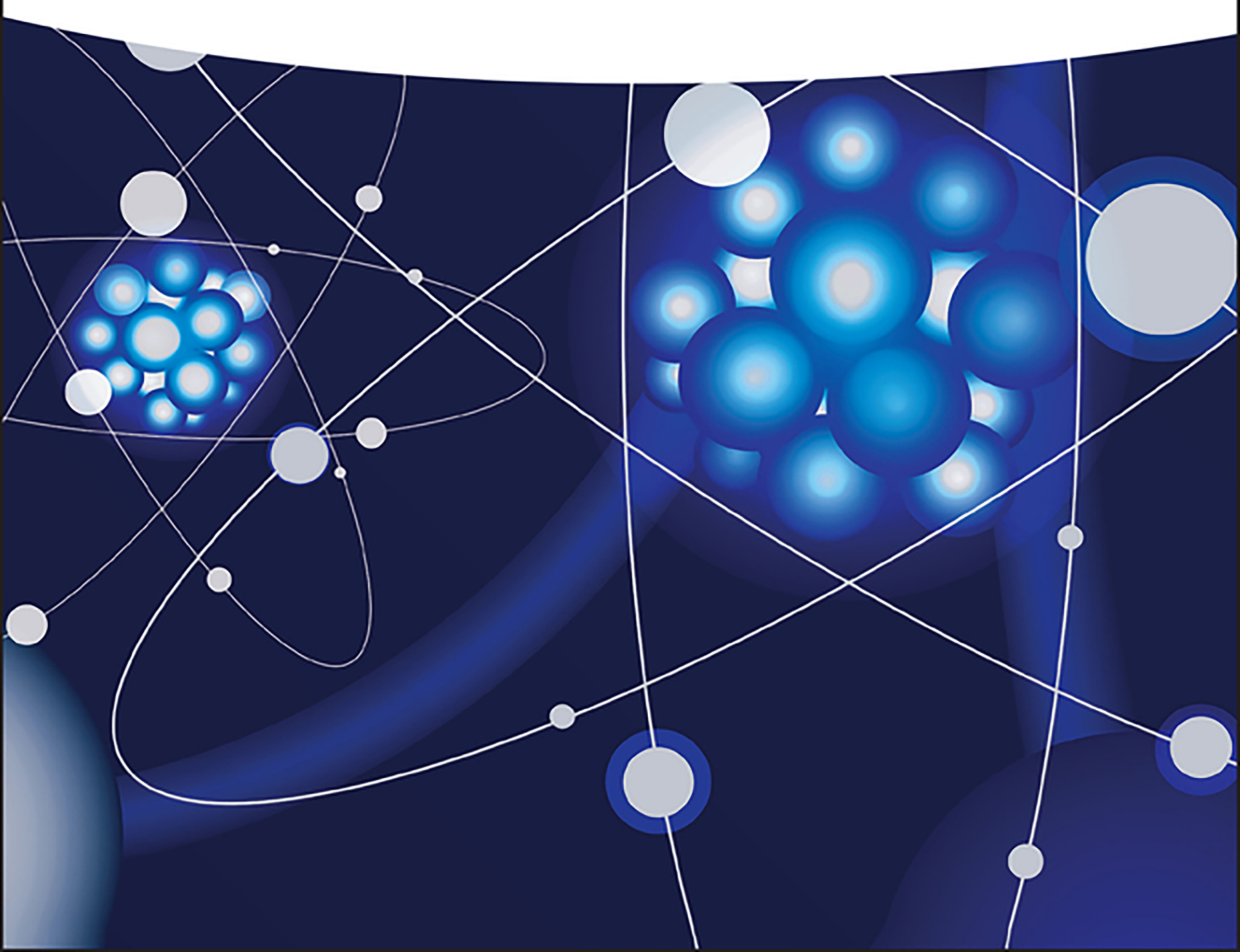

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Contents

Preface

Ellipsometry is an experimental technique that boasts of a developmental history spanning more than a century. Initially proposed by Paul Drude in 1887, its first documented use was in 1945. Even though it was then regarded as an unproductive experimental technique, ellipsometry gained traction in the 1990s with advances in computer technology and data processing, necessary for the efficient automation of ellipsometric instrumentation and data analyses. Since then, spectroscopic ellipsometry has established itself as an ultra-sensitive, high-precision optical characterization technique useful in a diverse range of disciplines ranging from semiconductor physics to microelectronics and from biochemistry to real-time characterization of film growth.

Numerous publications have dealt with the fundamentals and analytical techniques of spectroscopic ellipsometry. This book serves as a brief introduction to the ellipsometric technique, and greater emphasis will be devoted to its applications in interfacial properties, electronic structures, and quasiparticle properties of different classes of thin-film materials. This book will focus on two-dimensional transition metal dichalcogenides (2D-TMDs), magnetic oxides such as manganite materials and unconventional superconductors in the form of copper oxide (cuprate) systems. In-depth discussions will be provided on how spectroscopic ellipsometry is utilized to characterize the electronic structures, interfacial properties, and quasiparticle dynamics in novel quantum materials.

Through the in-depth and comprehensive coverage of these materials systems, we demonstrate that spectroscopic ellipsometry remains relevant, and its capabilities continue to advance to cater to the rapidly evolving research landscape. Spectroscopic ellipsometry is therefore a versatile experimental technique for measuring these unique novel properties. We hope that researchers and graduate students in the field of condensed matter physics and materials science will find this book a useful resource.

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1

Spectroscopic Ellipsometry: Basic Principles

1.1 Spectroscopic Ellipsometry

Spectroscopic ellipsometry measures the change of light polarization upon its reflection from the sample. A schematic diagram of the experimental setup is displayed in Figure 1.1. The detector of spectroscopic ellipsometry measures the quantities Ψ and Δ at each corresponding wavelength/photon energy. Parameter Ψ denotes the ratio of the amplitude of p- to s-polarized reflected light, while Δ their phase difference. Specifically, p-polarized light has the electric field vector parallel to the plane of incidence, while s-polarized light consists of the electric field vector perpendicular to the incident plane (Figure 1.2).

Typically, the energy range that is commonly used for spectroscopic ellipsometry measurement is the ultraviolet–visible (UV–vis) regime (~0.5–6 eV). In this range, sample properties such as the optical band structures and bandgaps can be investigated. Nevertheless, other regions of the electromagnetic spectrum have also been used in spectroscopic ellipsometry measurements. For instance, the use of mid-to-near-infrared range spectroscopic ellipsometry in the study of low-energy structures in 1T′-phase two-dimensional transition metal dichalcogenides (2D-TMDs), such as their fundamental gap and the anisotropic plasmons, will be discussed in Section 3.4 of Chapter 3.

While spectroscopic ellipsometry is a fast, nondestructive, and surface-sensitive (down to a few angstroms) optical characterization technique, the mathematical analysis involved in extracting the optical parameters from the raw (Ψ, Δ) data is not a straightforward process (see Section 1.5 and Figure 1.7). Generally, to analytically elucidate the optical parameters from the raw (Ψ, Δ) data, the sample in consideration must be homogenous, isotropic, and of sufficient thickness. In more general cases, complications will arise and optical models with associated numerical approximation techniques are required for the proper elucidation of meaningful optical results.

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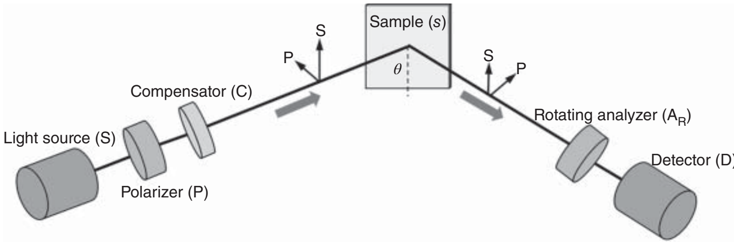

Figure 1.1 Schematic diagram of spectroscopic ellipsometry with the rotating-analyzer configuration.

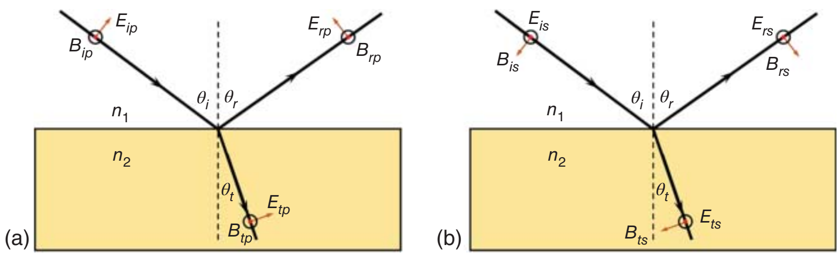

Figure 1.2 Electric and magnetic fields for (a) p-polarized and (b) s-polarized waves [1].

1.1.1 p- and s-Polarized Lights and Fresnel Coefficients

The electromagnetic wave features of light can be expressed in terms of its electric, E, and magnetic field, B, components [1]:

$$\vec{E}(\vec{r}, t) = \vec{E}_0 \exp[i(\vec{k} \cdot \vec{r} - \omega t + \delta)] \tag{1.1}$$

$$\vec{B}(\vec{r}, t) = \vec{B}_0 \exp[i(\vec{k} \cdot \vec{r} - \omega t + \delta)] \tag{1.2}$$

where $\vec{k}$ denotes the wave vector, ω denotes the angular frequency, and δ denotes the initial phase.

When light is reflected or transmitted through a sample/medium via an oblique angle, the electromagnetic wave can be resolved into two components – p-polarized (in-plane incidence) and s-polarized (perpendicular to incident plane) E-field components, respectively.

For a medium with refractive index n, based on Maxwell's equations and boundary conditions, the amplitude of the reflection coefficient for the p-polarized light is expressed as

$$r_p \equiv \frac{E_{rp}}{E_{ip}} = \frac{n_{\{t\}} \cos\theta_i - n_i \cos\theta_t}{n_t \cos\theta_i + n_i \cos\theta_t} \tag{1.3}$$

Likewise, the amplitude of the transmission coefficient for the p-polarized light can be expressed as

$$t_p \equiv \frac{E_{tp}}{E_{ip}} = \frac{2n_i \cos\theta_i}{n_t \cos\theta_i + n_i \cos\theta_t} \tag{1.4}$$

whereas the s-polarized counterparts are expressed as

$$r_s \equiv \frac{E_{rs}}{E_{is}} = \frac{(n_i \cos\theta_i - n_t \cos\theta_t)}{(n_i \cos\theta_i + n_t \cos\theta_t)} \tag{1.5a}$$

$$r_p \equiv \frac{E_{ts}}{E_{is}} = \frac{2n_i \cos\theta_i}{n_i \cos\theta_i + n_t \cos\theta_t} \tag{1.5b}$$

These equations are known as the Fresnel equations. When the refractive indices are complex, $\widetilde{n}$, the Fresnel equations still hold. The complex dielectric function can be obtained via the expression

$$\widetilde{n}^2 \equiv \varepsilon \tag{1.6}$$

Based on Snell's law, the Fresnel equations for reflection can be further generalized as

$$r_\mathrm{p} = \frac{\widetilde{n}_{ti}^2 \cos\theta_i - \left(\widetilde{n}_{ti}^2 - \sin^2\theta_i\right)^{\frac{1}{2}}}{\widetilde{n}_{ti}^2 \cos\theta_i + \left(\widetilde{n}_{ti}^2 - \sin^2\theta_i\right)^{\frac{1}{2}}} \tag{1.7a}$$

$$r_\mathrm{s} = \frac{\cos\theta_i - \left(\widetilde{n}_{ti}^2 - \sin^2\theta_i\right)^{\frac{1}{2}}}{\cos\theta_i + \left(\widetilde{n}_{ti}^2 - \sin^2\theta_i\right)^{\frac{1}{2}}} \tag{1.7b}$$

where $\widetilde{n}$ denotes the complex refractive index and

$$\widetilde{n}_{ti} = \frac{\widetilde{n}_t}{\widetilde{n}_i} \tag{1.8}$$

The reflectances of the p- and s-polarized lights are expressed by

$$R_\mathrm{p} \equiv \frac{I_{rp}}{I_{ip}} = \left|\frac{E_{rp}}{E_{ip}}\right|^2 = |r_\mathrm{p}^2| \tag{1.9a}$$

$$R_\mathrm{s} \equiv \frac{I_{rs}}{I_{is}} = \left|\frac{E_{rs}}{E_{is}}\right|^2 = |r_\mathrm{s}^2| \tag{1.9b}$$

where the light intensity $I = n|E|^2$. Since the difference between r_p and r_s is maximized at the Brewster angle [2], ellipsometric measurements are usually performed at incident angles, θ_i, typically in the range of 70–80° for the optical characterization of semiconducting systems [3].

In multilayered systems, the resultant amplitude of the reflection coefficients is expressed as the sum of individual components of the reflection and transmission coefficients at each interface. The phase differences of each wave are considered in the analysis.

1.1.2 Representation of Polarized Lights

Electromagnetic waves traversing along the z-direction can be expressed by superimposing two waves that are oscillating parallel to the x- and y-axes. The vector sum of the respective E-fields, E_x and E_y, is given by

$$
\begin{aligned}
E(z,t) &= E_x(z,t) + E_y(z,t) \\
&= E_{x_0} \exp i(\omega t - kz + \delta_x)\hat{x} + E_{y_0} \exp i(\omega t - kz + \delta_y)\hat{y}
\end{aligned} \tag{1.10}
$$

where $\hat{x}$ and $\hat{y}$ denote the unit vectors along the respective axes. Ultimately, the phase difference, $\delta_y - \delta_x$, is the most important quantity that determines the state of the polarization of the resultant wave.

To mathematically represent the polarization states and analyze the effects of the optical components in a neat and elegant manner, they are expressed in the form of *Jones vectors* and *Jones matrices* [4].

A complete representation of the polarization of a wave can be expressed in the form of the Jones vector as

$$
E(z,t) = \begin{bmatrix} E_{x_0} \exp i\delta_x \\ E_{y_0} \exp\ i\delta_y \end{bmatrix} \tag{1.11}
$$

which can be further simplified as

$$
E(z,t) = \begin{bmatrix} E_x \\ E_y \end{bmatrix} \tag{1.12}
$$

where $E_x = E_{x_0} \exp i\delta_x$ and $E_y = E_{y_0} \exp i\delta_y$.

Relative changes to the amplitude and phase are important in spectroscopic ellipsometry. Jones vectors are therefore expressed in terms of normalized intensities. Linearly polarized waves along the x- and y-axes are expressed, respectively, as

$$
E_{\text{lin},x} = \begin{bmatrix} 1 \\ 0 \end{bmatrix} \qquad E_{\text{lin},y} = \begin{bmatrix} 0 \\ 1 \end{bmatrix} \tag{1.13}
$$

When light is linearly polarized at an orientation of 45°,

$$
E_{+45^\circ} = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 \\ 1 \end{bmatrix} \tag{1.14}
$$

In the formalism where optical components are expressed in the form of 2×2 matrices, they are known as *Jones matrices*. Based on this formalism, the operation performed on the light by each component in spectroscopic ellipsometry, such as the polarizer, analyzer, and compensator, can be represented as a 2×2 matrix operator.

For instance, in the case of a linear polarizer with the azimuthal angle, α, relative to the x–y coordinates of a linearly polarized light, E_i, the process of linear polarization can be expressed as

$$
E_{\text{f}} = \begin{bmatrix} \cos\alpha & 0 \\ 0 & \sin\alpha \end{bmatrix} \tag{1.15}
$$

Transformations by a series of optical components can be represented by the corresponding series of matrix operations.

While the Jones vector is a concise way for describing polarized light, it is unable to express unpolarized light and light that is partially polarized. Therefore, the *Stokes parameters* (vectors) are used for the description of lights with different polarization [4].

The components of the Stokes vector are

$$\mathbf{S}_0 = I_x + I_y = E_x E_x^* + E_y E_y^* \tag{1.16a}$$

$$\mathbf{S}_1 = I_x - I_y = E_x E_x^* - E_y E_y^* \tag{1.16b}$$

$$\mathbf{S}_2 = I_{+45^\circ} + I_{-45^\circ} = 2E_{x_0} E_{y_0} \cos\Delta \tag{1.16c}$$

$$\mathbf{S}_3 = I_\mathrm{R} - I_\mathrm{L} = -2E_{x_0} E_{y_0} \sin\Delta \tag{1.16d}$$

where I_x and I_y denote the intensities of the linearly polarization light along the x- and y-axes, respectively. Likewise, $I_{\pm 45^\circ}$ represents light polarization ±45° to the x-axis, while $I_\mathrm{L}/I_\mathrm{R}$ represent intensities of left-/right-circularly polarized light. Finally, $\Delta = \delta_x - \delta_y$.

The Stokes vector can also be expressed as

$$\mathbf{S} = \begin{bmatrix} \mathbf{S}_0 \\ \mathbf{S}_1 \\ \mathbf{S}_2 \\ \mathbf{S}_3 \end{bmatrix} \tag{1.17}$$

Transformation of a Stokes vector can be expressed via a 4×4 matrix representation, also known as a *Mueller matrix*. The calculation is performed in a fashion similar to the Jones matrix. For instance, when linear polarization oriented at 45° passes a polarizer with transmission axis along the x-direction, the resultant light that emerges from the polarizer is transformed via the following:

$$\frac{1}{2}\begin{pmatrix} 1 & 1 & 0 & 0 \\ 1 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} 1 \\ 0 \\ 1 \\ 0 \end{pmatrix} = \begin{pmatrix} 1/2 \\ 1/2 \\ 0 \\ 0 \end{pmatrix} \tag{1.18}$$

1.2 Principles of Ellipsometric Measurements

When light is reflected/transmitted from a sample, the p- and s-polarized components of the incident light undergo changes to their amplitude and phase. Hence, spectroscopic ellipsometry is a technique that capitalizes on these changes where the essential optical parameters are derived. As mentioned, the raw quantities measured using ellipsometry are Ψ and Δ, representing the amplitude ratio and phase difference between reflected or transmitted p- and s-polarized waves, respectively. These two quantities are related complex reflection coefficients via the expression

$$\rho \equiv \tan\Psi \exp i\Delta = \frac{r_\mathrm{p}}{r_\mathrm{s}} \tag{1.19}$$

with r_p and r_s defined as ratios of the light reflected to the incident E-fields.

Equation (1.19) can be further expressed as

$$\tan\Psi \exp i\Delta = \frac{r_\mathrm{p}}{r_\mathrm{s}} = \frac{E_{rp}/E_{ip}}{E_{rs}/E_{is}} = E_{rp}/E_{rs} \tag{1.20}$$

where the final step of simplification can be performed since $E_\mathrm{ip} = E_\mathrm{is}$.

Different spectroscopic ellipsometry setups are available, of which the raw Ψ and Δ are measured by different means. Generally, the systems are classified into two main categories – spectroscopic ellipsometers with rotating optical elements and those with photoelastic modulators. In our study, focus will be on the system with rotating optical elements (i.e. rotating analyzer with compensator). The working principle of such spectroscopic ellipsometers will be described briefly in Section 1.2.1.

1.2.1 Rotating-Analyzer Ellipsometer

A rotating-analyzer spectroscopic ellipsometer (Figure 1.1) is one of the few ellipsometric setups that is widely used. The changes made to an incident light wave when passing through a rotating-analyzer spectroscopic ellipsometer can be represented as a series of matrix operations $\mathrm{PSA_R}$, where P, S, and $\mathrm{A_R}$ denote the polarizer, the sample, and the rotating analyzer, respectively. In spectroscopic ellipsometry, the wavelength of the incident photon is typically changed using a monochromator. However, this slows down the operational speed of the system. Hence, in many spectroscopic ellipsometry systems, especially those for real-time monitoring, a grating spectrometer is typically used in the detector probe, while white light is used as the incident source.

By applying the Jones vectors and Mueller matrices, the output of the $\mathrm{PSA_R}$ ellipsometric configuration can be expressed as

$$L_\mathrm{out} = \mathrm{AR}(A)R(-P)PL_\mathrm{in} \tag{1.21}$$

where the Jones vector of the light wave at the detector can be expressed as $L_\mathrm{out} = \begin{bmatrix} E_A \\ 0 \end{bmatrix}$. $L_\mathrm{in} = \begin{bmatrix} 1 \\ 0 \end{bmatrix}$ denotes the input Jones vector of the incident light source. $R(A)$ represents the rotation matrix with a rotation angle of the analyzer at A. P denotes the rotation angle of the polarizer and S represents the Jones matrix corresponding to the reflected light off the sample.

Hence, Eq. (1.21) is expressed in the matrix form as

$$\begin{bmatrix} E_A \\ 0 \end{bmatrix} = \begin{bmatrix} 1 & 0 \\ 0 & 0 \end{bmatrix} \begin{bmatrix} \cos A & \sin A \\ -\sin A & \cos A \end{bmatrix} \begin{bmatrix} \sin\Psi \exp i\Delta & 0 \\ 0 & \cos\Psi \end{bmatrix} \begin{bmatrix} \cos P & -\sin P \\ \sin P & \cos P \end{bmatrix} \begin{bmatrix} 1 & 0 \\ 0 & 0 \end{bmatrix} \begin{bmatrix} 1 \\ 0 \end{bmatrix}$$

If polarization angle $P = 45°$, it will then take the form

$$\begin{bmatrix} E_A \\ 0 \end{bmatrix} = \begin{bmatrix} 1 & 0 \\ 0 & 0 \end{bmatrix} \begin{bmatrix} \cos A & \sin A \\ -\sin A & \cos A \end{bmatrix} \begin{bmatrix} \sin\Psi \exp i\Delta \\ \cos\Psi \end{bmatrix} \tag{1.22}$$

which ultimately leads to the solution

$$E_A = \cos A \sin\Psi \exp i\Delta + \sin A \cos\Psi \tag{1.23}$$

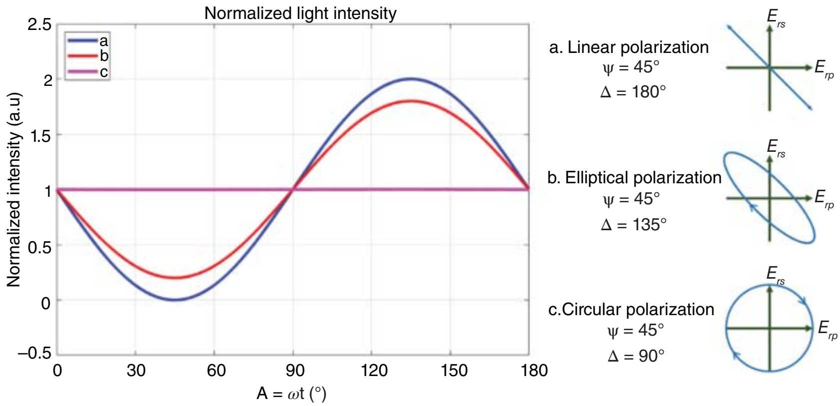

Figure 1.3 Normalized intensity of linearly, elliptical, and circularly polarized light based on the rotating-analyzer configuration.

The light intensity registered at the detector can then be expressed as the modulus square of E_A:

$$\begin{aligned} I &= |E_A|^2 \\ &= I_0(1 - \cos 2\Psi \cos 2A + \sin 2\Psi \cos \Delta \sin 2A) \\ &= I_0(1 + S_1 \cos 2A + S_2 \sin 2A) \end{aligned} \tag{1.24}$$

where I_0 represents the proportionality constant of the reflected light. The period of the intensity variation is π radians (180°). Generally, the Stokes parameters, S_1 and S_2, in a rotating-analyzer ellipsometer (RAE) are measured as Fourier coefficients of cos 2A and sin 2A, respectively. When the analyzer rotates at an angular frequency of ω, the general expression of the detector intensity is expressed as

$$I(t) = I_0(1 + \alpha \cos 2\omega t + \beta \sin 2\omega t) \tag{1.25}$$

where the normalized intensity registered at the detector based on Eq. (1.25) is plotted in Figure 1.3.

1.3 Experimental Setup

The spot size of the beam is in the range of 3–5 mm with additional detachable microfocus, which can be used to focus the spot size to an even smaller dimension of about 200 μm. Such a small beam spot is suitable for the optical characterization of smaller samples to reduce the instances of back reflection and scattering in transparent samples.

The input unit consists of a lens mount, a polarizer stage, and an alignment detector socket. Polarization state of the light beam is detected before its incidence on the sample, which is mounted on the sample stage. After reflecting off the sample surface, the detector unit converts the reflected beam into a voltage and measures

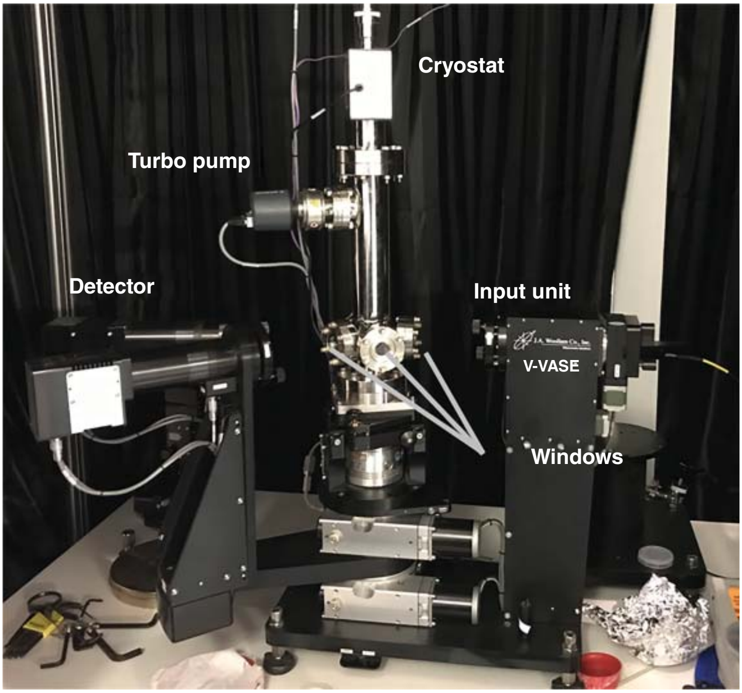

Figure 1.4 Woollam VASE spectroscopic ellipsometer.

its polarization state. The software (WVASE32) is then used to analyze the raw data from which the optical parameters of the sample are derived.

1.3.1 VASE Spectroscopic Ellipsometer

The setup of the Variable-Angle Spectroscopic Ellipsometer (VASE) by J. A. Woollam Co., Inc. is displayed in Figure 1.4. The arc lamp provides a broadband light source for the HS-190 monochromator (Czerny–Turner Scanning Monochromator), which the software uses to supply a selected wavelength/photon energy of light for the system. This spectroscopic ellipsometer provides both high accuracy and precision along with a wide spectral range of ~190–2500 nm (~0.5–6.5 eV), covering the near-IR, visible, and near-UV regimes. With this broad spectral range, this system is suitable for characterizing optical bandgaps and electronic transitions for semiconducting and Mott-insulating systems (Figure 1.5).

RAE of the VASE spectroscopic ellipsometer helps to maximize data accuracy near the "Brewster" angle [1], where the raw Ψ and Δ data are content-rich. The autoretarder is a computer-controlled waveplate that modifies the beam polarization (from linear to circular polarization or vice versa) before reaching the sample. This process provides greater accuracy for the measurement of the Δ parameter even when the phase difference is close to the extremum angles of 0° and 180°. This process produces optimum measurement conditions for the sample.