1 Introduction to Spectroscopic Ellipsometry

Because of recent advances in computer technology, the spectroscopic ellipsometry technique has developed rapidly. As a result, the application area of spectroscopic ellipsometry has also expanded drastically. In spectroscopic ellipsometry, process diagnosis including thin-film growth can be performed in real time by employing light as a measurement probe. More recently, 'feedback control,' in which complicated device structure is controlled in real time, has been carried out using spectroscopic ellipsometry. In this chapter, we review the features and applications of spectroscopic ellipsometry. This chapter will provide an overview of measurement techniques and data analysis procedures in spectroscopic ellipsometry.

1.1 FEATURES OF SPECTROSCOPIC ELLIPSOMETRY

Ellipsometry is an optical measurement technique that characterizes light reflection (or transmission) from samples [1–4]. The key feature of ellipsometry is that it measures the change in polarized light upon light reflection on a sample (or light transmission by a sample). The name 'ellipsometry' comes from the fact that polarized light often becomes 'elliptical' upon light reflection. As shown in Table 1.1, ellipsometry measures the two values (ψ, Δ). These represent the amplitude ratio ψ and phase difference Δ between light waves known as p- and s-polarized light waves (see Fig. 4.1). In spectroscopic ellipsometry, (ψ, Δ) spectra are measured by changing the wavelength of light. In general, the spectroscopic ellipsometry measurement is carried out in the ultraviolet/visible region, but measurement in the infrared region has also been performed widely.

The application area of spectroscopic ellipsometry is quite wide (Chapter 7). For real-time monitoring, not only characterization of thin-film growth but also process diagnoses including etching and thermal oxidation can be performed (Chapter 8). In particular, spectroscopic ellipsometry allows characterization of thin films formed in

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Table 1.1 Features of spectroscopic ellipsometry

Measurement probe:	Light
Measurement value:	(ψ, Δ) Amplitude ratio ψ and phase difference Δ between p- and s-polarized light waves
Measurement region:	Mainly in the infrared–visible/ultraviolet region
Application area:	
Semiconductor	Substrates, thin films, gate dielectrics, lithography films
Chemistry	Polymer films, self-assembled monolayers, proteins, DNA
Display	TFT films, transparent conductive oxides, organic LED
Optical coating	High and low dielectrics for anti-reflection coating
Data storage	Phase change media for CD and DVD, magneto-optic layers
Real-time monitoring:	Chemical vapor deposition (CVD), molecular beam epitaxy (MBE), etching, oxidation, thermal annealing, liquid phase processing etc.
General restrictions:	i) Surface roughness of samples has to be small ii) Measurement has to be performed at oblique incidence

solution (Section 7.4), because light is employed as the probe. However, there are two general restrictions on the ellipsometry measurement; specifically: (1) surface roughness of samples has to be rather small, and (2) the measurement must be performed at oblique incidence. When light scattering by surface roughness reduces the reflected light intensity severely, the ellipsometry measurement becomes difficult as ellipsometry determines a polarization state from its light intensity. If the size of surface roughness exceeds $\sim 30\%$ of a measurement wavelength, measurement errors generally increase, although this effect depends completely on the type of instrument (Section 4.4).

In ellipsometry, an incidence angle is chosen so that the sensitivity for the measurement is maximized. The choice of the incidence angle, however, varies according to the optical constants of samples. For semiconductor characterization, the incidence angle is typically 70–80° (Section 2.3.4). It should be noted that, at normal incidence, the ellipsometry measurement becomes impossible, since p- and s-polarizations cannot be distinguished anymore at this angle (Section 2.3.2). One exception is the characterization of in-plane optical anisotropy. In this case, the ellipsometry measurement is often performed at normal incidence to determine the variation of optical constants with the rotation of a sample (Chapter 6).

Table 1.2 summarizes the advantages and disadvantages of the spectroscopic ellipsometry technique. One of the remarkable features of spectroscopic ellipsometry is the high precision of the measurement, and very high thickness sensitivity (~ 0.1 Å) can be obtained even for conventional instruments (Section 4.4.3). As we will see in the next section, spectroscopic ellipsometry allows various characterizations including optical constants and thin-film structures. Moreover, as the ellipsometry measurement takes only a few seconds, real-time observation and feedback control of processing can be performed relatively easily (Chapter 8).

The one inherent drawback of the ellipsometry technique is the indirect nature of this characterization method. Specifically, ellipsometry data analysis requires an

Table 1.2 Advantages and disadvantages of spectroscopic ellipsometry

Advantages:	High precision (thickness sensitivity: ~0.1 Å)
	Nondestructive measurement
	Fast measurement
	Wide application area
	Various characterizations including optical constants and film thicknesses are possible
	Real-time monitoring (feedback control) is possible
Disadvantages:	Necessity of an optical model in data analysis (indirect characterization)
	Data analysis tends to be complicated
	Low spatial resolution (spot size: several mm)
	Difficulty in the characterization of low absorption coefficients ($\alpha < 100\,\mathrm{cm}^{-1}$)

optical model defined by the optical constants and layer thicknesses of a sample (see Fig. 5.39). In an extreme case, one has to construct an optical model even when the sample structure is not clear at all. In addition, this ellipsometry analysis using an optical model tends to become complicated, which can be considered as another disadvantage of the technique. The spot size of a light beam used for spectroscopic ellipsometry is typically several millimeters, leading to the low spatial resolution of the measurement. However, it is possible to determine the surface area ratio of different materials that cover the sample surface (see Fig. 5.31). Recently, in order to improve spatial resolution, imaging ellipsometry has been developed (Section 4.2.8). As shown in Table 1.2, in ellipsometry, characterization of small absorption coefficients ($\alpha < 100\,\mathrm{cm}^{-1}$) is rather difficult (Section 4.4.3).

1.2 APPLICATIONS OF SPECTROSCOPIC ELLIPSOMETRY

Spectroscopic ellipsometry has been applied to evaluate optical constants and thin-film thicknesses of samples. However, the application area of spectroscopic ellipsometry has been expanded recently, as it allows process diagnosis on the atomic scale from real-time observation. Figure 1.1 shows various physical properties that can be determined from spectroscopic ellipsometry. In particular, this figure summarizes the characterization by *ex situ* measurement. Here, *ex situ* measurement means a measurement performed after finishing sample preparation (processing).

As shown in Fig. 1.1, spectroscopic ellipsometry measures (ψ, Δ) spectra for photon energy $h\nu$ or wavelength λ. In general, the interpretation of measurement results is rather difficult from the absolute values of (ψ, Δ). Thus, construction of an optical model is required for data analysis. From this data analysis, physical properties including the optical constants and film thicknesses of the sample can be extracted. Unlike reflectance/transmittance measurement, ellipsometry allows the direct measurement of the refractive index n and extinction coefficient k, which are also referred to as optical constants. From the two values (n, k), the complex refractive index defined by $N \equiv n - \mathrm{i}k(\mathrm{i} = \sqrt{-1})$ is determined.

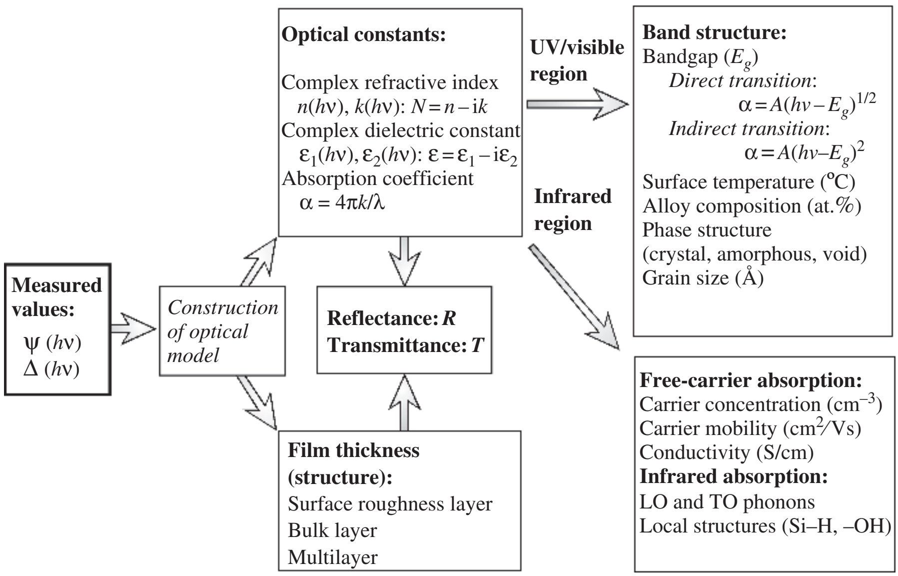

Figure 1.1 Characterization of physical properties by spectroscopic ellipsometry.

The complex dielectric constant ε and absorption coefficient α can also be obtained from the simple relations expressed by $\varepsilon = N^2$ and $\alpha = 4\pi k/\lambda$, respectively (Chapter 2). Moreover, from optical constants and film thicknesses obtained, the reflectance R and transmittance T at a different angle of incidence can be calculated.

From the measurements in the ultraviolet/visible region, interband transitions (band structures) are characterized. In particular, the bandgap E_g can be deduced from the variation of α with $h\nu$ (Section 7.2.1). Since band structure generally varies according to surface temperature, alloy composition, phase structure, and crystal grain size, these properties can also be determined from the spectral analysis of optical constants (Section 7.2.4). In the infrared region, on the other hand, there exists free carrier absorption induced by free electrons (or holes) in solids. When carrier concentration is high enough ($>10^{18}\,\mathrm{cm}^{-3}$), electrical properties including carrier mobility, carrier concentration, and conductivity can be obtained (Section 7.3.2). Moreover, in the infrared region, lattice vibration modes (LO and TO phonons) as well as local atomic structures, such as Si–H and –OH, can also be studied (Sections 7.5.1 and 7.4).

In real-time spectroscopic ellipsometry, (ψ, Δ) spectra are measured continuously during processing. This technique further allows a number of characterizations illustrated in Fig. 1.2 (Chapter 8). From real-time monitoring, for example, initial growth processes or interface structures can be studied in detail (Section 8.2). In a compositionally modulated layer in which alloy composition varies continuously in the growth direction, the alloy compositions of each layer are determined. In particular, the real-time measurement enables us to characterize reaction rate during

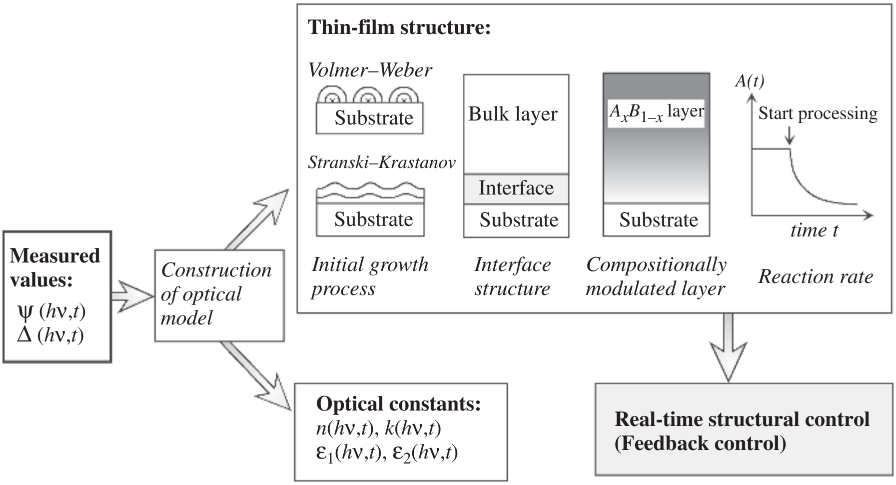

Figure 1.2 Characterization of thin film structures by real-time spectroscopic ellipsometry.

processing. Real-time spectroscopic ellipsometry can be applied further to perform process control. From real-time observation, the feedback control of semiconductor alloy composition has already been performed (Section 8.3.3). Accordingly, the ability of spectroscopic ellipsometry has opened up a new way for more advanced process control.

1.3 DATA ANALYSIS

Figure 1.3 shows (a) optical model consisting of an air/thin film/substrate structure and (b) (ψ, Δ) spectra obtained from a hydrogenated amorphous silicon (a-Si:H) thin film formed on a crystalline Si (c-Si) substrate. As mentioned earlier, an optical model is represented by the complex refractive index and layer thickness of each layer. In Fig. 1.3(a), N_0, N_1 and N_2 denote the complex refractive indices of air, thin film, and substrate, respectively. The transmission angles (θ_1 and θ_2) can be calculated from the angle of incidence θ_0 by applying Snell's law (Section 2.3.1). As shown in Fig. 1.3(a), when light absorption in a thin film is small, optical interference occurs by multiple light reflections within the thin film. In particular, this figure illustrates the optical interference in which each optical wave is superimposed destructively. Of course, the total intensity of the reflected light becomes smaller in this case.

In ellipsometry, the two ellipsometry parameters (ψ, Δ) are defined by $\rho \equiv \tan\psi \exp(i\Delta)$ (Section 4.1.1). In the optical model shown in Fig. 1.3(a), ρ is expressed by the following equation (Section 5.1):

$$\tan\psi \exp(i\Delta) = \rho(N_0, N_1, N_2, d, \theta_0) \qquad (1.1)$$

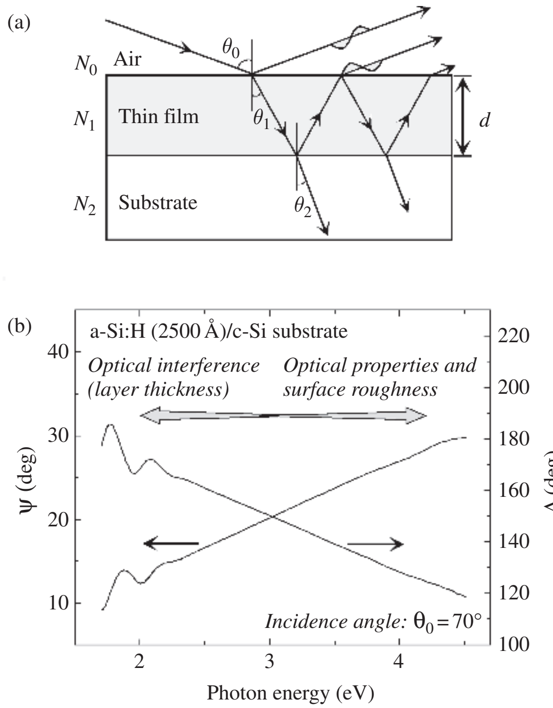

Figure 1.3 (a) Optical model consisting of an air/thin film/substrate structure and (b) (ψ, Δ) spectra obtained from an a-Si:H thin film (2500 Å) formed on a c-Si substrate.

Notice that the above equation shows only variables used in the calculation. The complex refractive index of air is given by $N_0 = 1$, and the values of N_2 and θ_0 are usually known in advance. In the (ψ, Δ) spectra shown in Fig. 1.3(b), the optical interference effect appears in the energy region where optical light absorption is relatively small (<2.5 eV). From the analysis of this interference pattern, the thin-film thickness d can be estimated. If d is determined from this analysis, the unknown parameters in Eq. (1.1) are only $N_1 = n_1 - ik_1$. In this condition, these two values (n_1, k_1) can be obtained directly from the two measured values (ψ, Δ) (Section 5.5.3). In spectroscopic ellipsometry, the optical constants and thickness of the thin film are determined in this manner. In the high-energy region, on the other hand, light absorption in samples generally increases and penetration depth of light becomes smaller. Thus, optical interference is negligible in this region. From the analysis of this energy region, band structure and effect of surface roughness can be studied. In spectroscopic ellipsometry, therefore, from (ψ, Δ) spectra measured in a wide energy range, characterization of various physical properties becomes possible.

Figure 1.4 shows the data analysis example of a multilayer structure by spectroscopic ellipsometry [5]. In this figure, (a) the cross-sectional image obtained

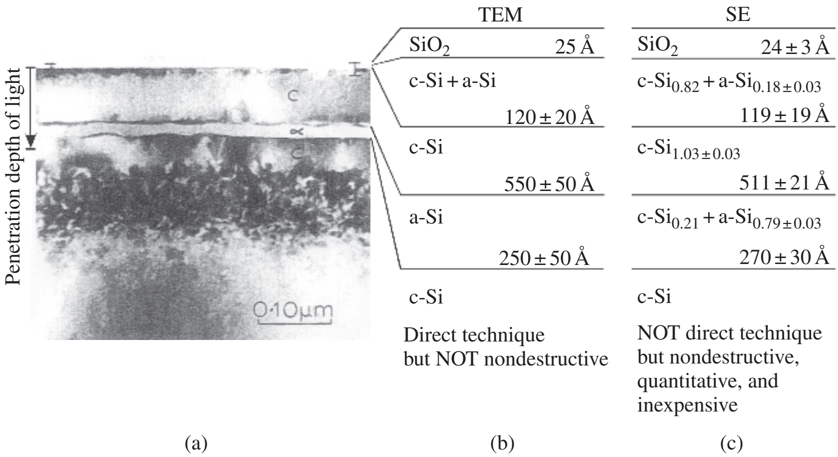

Figure 1.4 (a) Cross-sectional TEM image of a Si(100) wafer implanted with Si ions, (b) structure obtained from TEM, and (c) structure estimated from spectroscopic ellipsometry (SE). Reprinted from *Thin Solid Films*, **313–314**, K. Vedam, Spectroscopic ellipsometry: a historical overview, 1–9. Copyright (1998), with permission from Elsevier.

from transmission electron microscope (TEM), (b) the structure obtained from TEM, and (c) the structure estimated from spectroscopic ellipsometry (SE) are shown. The sample is a Si(100) wafer implanted with Si ions and, by this Si ion implantation, a partial phase change from c-Si to a-Si occurs. As confirmed from Fig. 1.4, the results obtained from TEM and spectroscopic ellipsometry show excellent agreement. Nevertheless, spectroscopic ellipsometry further allows the characterization of the volume fractions for the c-Si and a-Si components. As shown in Fig. 1.4(a), structural characterization by TEM is very reliable since TEM is a direct measurement technique. In TEM, however, difficulties in sample preparation as well as measurement itself generally limit the number of samples for the measurement. In contrast, although spectroscopic ellipsometry is an indirect measurement technique, highly quantitative results can be obtained. Moreover, spectroscopic ellipsometry provides fast and easy measurement, which permits characterization of many samples. Accordingly, for samples that allow proper data analysis (see Fig. 5.32), spectroscopic ellipsometry is a quite effective characterization tool.

1.4 HISTORY OF DEVELOPMENT

Table 1.3 summarizes the history of development for ellipsometry instruments (ellipsometers) [5]. As shown in Table 1.3, ellipsometry was developed first by Drude in 1887. He also derived the equations of ellipsometry, which are used even today. Drude is well known from 'the Drude model' which expresses the optical properties of metals

Table 1.3 History of ellipsometry development

Year	Technique[a]	Parameters determined[b]	Number of data	Time taken (s)	Precision (deg)	Author and reference
1887	E	Δ, ψ	2	Theory and first experiment		Drude [6]
1945	E	Δ, ψ	2	3600	$\Delta = 0.02$ $\psi = 0.01$	Rothen [7]
1971	E	Δ, ψ, R	3	3600	$\Delta = 0.02$ $\psi = 0.01$	Paik, Bockris [8]
1975	SE	$(\Delta, \psi)\lambda$	200	3600	$\Delta = 0.001$ $\psi = 0.0005$	Aspnes, Studna [9]
1984	RTSE	$\{(\Delta, \psi)\lambda\}t$	80 000	3–600	$\Delta = 0.02$ $\psi = 0.01$	Muller, Farmer [10]
1990	RTSE (PDA)[c]	$\{(\Delta, \psi)\lambda\}t$	2×10^5[d]	0.8–600	$\Delta = 0.02$ $\psi = 0.01$	Kim, Collins, Vedam [11]
1994	RTSE (PDA)[c]	$\{(\Delta, \psi, R)\lambda\}t$	3×10^5[d]	0.8–600	$\Delta = 0.007$ $\psi = 0.003$	An, Collins *et al.*[12]

[a] ellipsometry (E), spectroscopic ellipsometry (SE), real-time spectroscopic ellipsometry (RTSE)
[b] reflectance (R), wavelength (λ), time (t)
[c] photodiode array (PDA),
[d] maximum capacity. Reprinted from *Thin Solid Films*, **313–314**, K. Vedam, Spectroscopic ellipsometry: a historical overview, 1–9. Copyright (1998), with permission from Elsevier.

(Section 5.2.5). Until the early 1970s, most ellipsometers were operated manually and the ellipsometry measurement was very time consuming. In 1975, however, Aspnes *et al.* realized the complete automation of spectroscopic ellipsometry measurements [9] (Section 4.2). As shown in Table 1.3, the development of this instrument improved not only the measurement time but also the measurement precision significantly. A spectroscopic ellipsometry instrument for real-time monitoring was reported first by Muller and Farmer in 1984 [10], and this instrument increased the number of measurement data drastically. In 1990, a group from the Pennsylvania State University developed a real-time instrument that has been used widely up to now [11]. In particular, this instrument unitizes a photodiode array (PDA) detector that allows the simultaneous measurement of light intensities at multiwavelengths (Section 4.2). Figure 1.5 shows real-time spectra obtained from this instrument [13]. In this figure, $\langle\varepsilon_1\rangle$ and $\langle\varepsilon_2\rangle$ represent pseudo-dielectric function that can be calculated from (ψ, Δ) spectra (Section 5.4.2). In this measurement, the total of 250 spectra were measured in 16 seconds with a repetition time of 64 ms during the a-Si:H growth on a c-Si substrate. From analysis of the real-time data set, the initial growth process of the thin film can be characterized on the atomic scale (Section 8.2).

Up to now, spectroscopic ellipsometry instruments have been improved continuously and four different types of instruments are mainly used. Nevertheless, ranges and errors for the (ψ, Δ) measurement vary significantly depending on the type of instrument (see Tables 4.2 and 4.3). In order to perform accurate data analysis, therefore, understanding of the ellipsometry measurement is necessary.

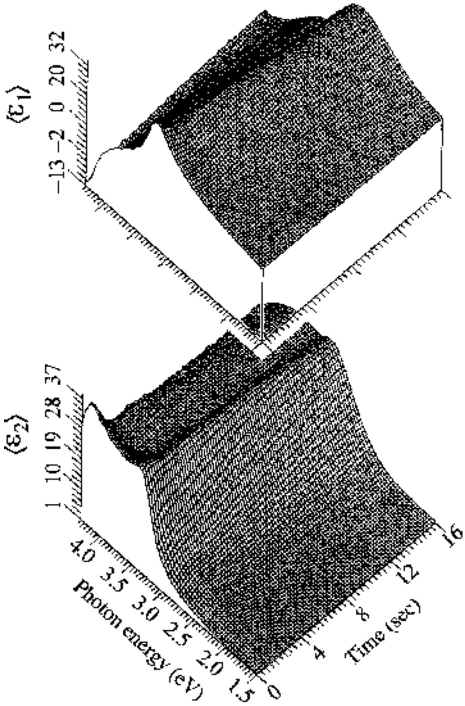

Figure 1.5 Real-time spectra obtained from the spectroscopic ellipsometry measurement performed during the a-Si:H growth. Reprinted with permission from *Review of Scientific Instruments*, **63**, I. An, Y. M. Li, H. V. Nguyen, and R. W. Collins, Spectroscopic ellipsometry on the millisecond time scale for real-time investigations of thin-film and surface phenomena, 3842–3848 (1992). Copyright 1992, American Institute of Physics.

1.5 FUTURE PROSPECTS

Recently, optically anisotropic materials have been studied extensively by applying Mueller matrix ellipsometry that allows the complete characterization of optical behavior in anisotropic materials (Section 4.2.7). For the characterization of conventional isotropic samples, current spectroscopic ellipsometry instruments are highly satisfactory. Thus, most of recent ellipsometry studies have been made on material characterization, rather than the development of ellipsometry instruments.

Figure 1.6 shows the number of papers published each year with 'ellipsometry' in the title [14]. The two large peaks at 1993 and 1997 are due to publications of the ellipsometry conference proceedings [15–17]. Since the early 1990s, research that applies spectroscopic ellipsometry has increased drastically due to the commercialization of spectroscopic ellipsometry instruments. During the 1990s, spectroscopic ellipsometry was mainly employed to characterize semiconductor materials. Now, from advances in instruments as well as data analysis methods,

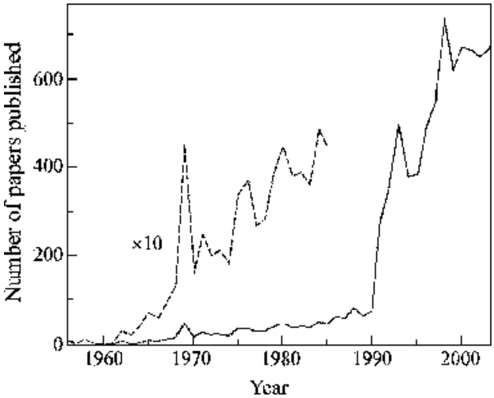

Figure 1.6 Number of papers published with 'ellipsometry' in the title versus year. Reprinted from *Thin Solid Films*, **455–456**, D. E. Aspnes, Expanding horizons: new developments in ellipsometry and polarimetry, 3–13. Copyright (2004), with permission from Elsevier.

the application of the spectroscopic ellipsometry technique has become quite common in wider scientific fields from semiconductors to biomaterials (Chapters 7 and 8). Moreover, some characterizations including the feedback control of alloy composition can be performed only using spectroscopic ellipsometry. Therefore, the application of spectroscopic ellipsometry is expected to expand further in the future. For some materials, however, no optical data is available. Thus, the construction of a larger optical database has been required in this field. As mentioned earlier, ellipsometry data analysis requires the construction of an optical model. In Chapters 5–8, we will see examples that will explain how data analyses are performed using various optical models and when data analyses are difficult.

REFERENCES

[1] R. M. A. Azzam and N. M. Bashara, *Ellipsometry and Polarized Light*, North-Holland, Amsterdam (1977).

[2] H. G. Tompkins and W. A. McGahan, *Spectroscopic Ellipsometry and Reflectometry: A User's Guide*, John Wiley & Sons, Inc., New York (1999).

[3] H. G. Tompkins and E. A. Irene, Eds, *Handbook of Ellipsometry*, William Andrew, New York (2005).

[4] M. Schubert, *Infrared Ellipsometry on Semiconductor Layer Structures: Phonons, Plasmons, and Polaritons*, Springer, Heidelberg (2004).

[5] For a review, see K. Vedam, Spectroscopic ellipsometry: a historical overview, *Thin Solid Films*, **313–314** (1998) 1–9.

[6] P. Drude, *Ann. Phys.*, **32** (1887) 584; *Ann. Phys.*, **34** (1888) 489.

[7] A. Rothen, The ellipsometer, an apparatus to measure thicknesses of thin surface films, *Rev. Sci. Instrum.*, **16** (1945) 26–30.

[8] W. Paik and J. O'M. Bockris, Exact ellipsometric measurement of thickness and optical properties of a thin light-absorbing film without auxiliary measurements, *Surf. Sci.*, **28** (1971) 61–68.

[9] D. E. Aspnes and A. A. Studna, High precision scanning ellipsometer, *Appl. Opt.*, **14** (1975) 220–228.
[10] R. H. Muller and J. C. Farmer, Fast, self-compensating spectral-scanning ellipsometer, *Rev. Sci. Instrum.*, **55** (1984) 371–374.
[11] Y.-T. Kim, R. W. Collins and K. Vedam, Fast scanning spectroelectrochemical ellipsometry: in-situ characterization of gold oxide, *Surf. Sci.*, **233** (1990) 341–350.
[12] I. An, H. V. Nguyen, A. R. Heyd, and R. W. Collins, Simultaneous real-time spectroscopic ellipsometry and reflectance for monitoring thin-film preparation, *Rev. Sci. Instrum.*, **65** (1994) 3489–3500.
[13] I. An, Y. M. Li, H. V. Nguyen, and R. W. Collins, Spectroscopic ellipsometry on the millisecond time scale for real-time investigations of thin-film and surface phenomena, *Rev. Sci. Instrum.*, **63** (1992) 3842–3848.
[14] D. E. Aspnes, Expanding horizons: new developments in ellipsometry and polarimetry, *Thin Solid Films*, **455–456** (2004) 3–13.
[15] A. C. Boccara, C. Pickering, and J. Rivory, Eds, *The Proceedings of the 1st International Conference on Spectroscopic Ellipsometry*; *Thin Solid Films*, **233** (1993) 1–306; *Thin Solid Films*, **234** (1993) 307–572.
[16] R. W. Collins, D. E. Aspnes, and E. A. Irene, Eds, *The Proceedings of the 2nd International Conference on Spectroscopic Ellipsometry*; *Thin Solid Films* **313–314** (1998) 1–835.
[17] For the latest proceedings, see M. Fried, K. Hingerl and J. Humlíček, Eds, *The Proceedings of the 3rd International Conference on Spectroscopic Ellipsometry*; *Thin Solid Films*, **455–456** (2004) 1–836.