Spectroscopic Ellipsometry Methods for Thin Absorbing Coatings

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ABSTRACT

Thin absorbing films are becoming common in optical coating applications. Spectroscopic ellipsometry characterization of such films requires proper techniques to insure unique results for both thickness and optical constants.

This paper provides a review of ellipsometry methods to characterize thin absorbing layers. All methods benefit from either reducing unknown sample properties or increasing measurement information. While both thickness and optical constants for thin absorbing layers can be determined, measurement sensitivity depends on method and implementation. The advantages and limitations of each method are described, along with examples from the optical coatings field.

INTRODUCTION

Spectroscopic Ellipsometry (SE) is routinely used to measure thickness and refractive index of transparent thin films. Absorbing films are more difficult to characterize because the optical constants (*n* and *k*) are often correlated with film thickness. This calls into question the uniqueness of the results. When properly implemented, SE measurements can simultaneously and uniquely determine thin absorbing layer thickness and optical constants.

Optical measurements of absorbing films are increasingly common for two reasons. First, many applications now include thin absorbing coatings as a critical element of the optical design. For example, a thin Ag layer is added for low-emissivity (low-e) coatings. In electrochromic layers, the exchange of ions can vary the absorption within a layer, changing the optical constants with applied voltage.

Second, many coatings are transparent at their design wavelengths, but absorbing in other spectral regions. It may be beneficial to measure the coating at absorbing wavelengths to better understand material properties or monitor coating quality and performance. For example, transparent conductive oxides are intentionally transparent at visible wavelengths, but absorb longer infrared light. The optical response at infrared wavelengths is a measure of the film conductivity. Figure 1 shows the variation in extinction coefficient for an indium tin oxide (ITO) coating at various stages of processing. The increase in near infrared absorption (larger extinction coefficient) indicates improved conductivity.

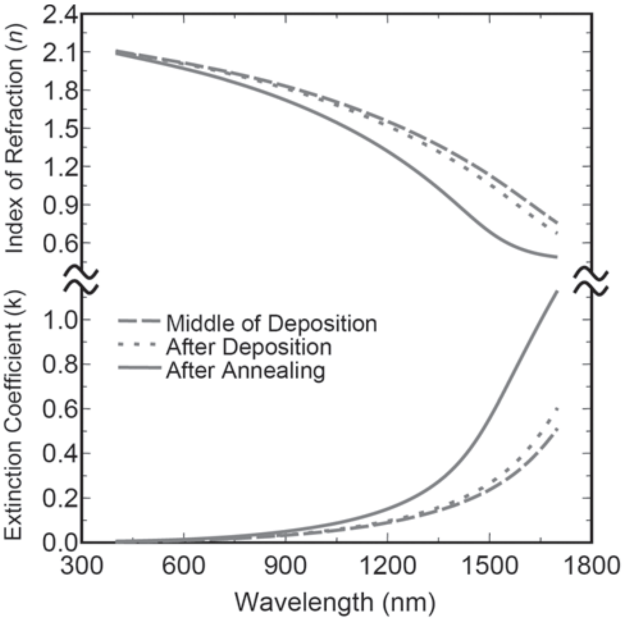

Figure 1: ITO optical constants measured during processing. Increased absorption at long wavelengths is due to free-carriers, indicating improved conductivity from the annealing step.

SPECTROSCOPIC ELLIPSOMETRY

Spectroscopic Ellipsometry (SE) is an optical measurement technique used to characterize film properties based on a change in polarization as light interacts with layered materials. SE theory is discussed elsewhere [1,2], but a few points are worth consideration in the context of this work.

Ellipsometry measures the change in polarization caused by interaction with thin coatings and substrates. This measurement is recorded as two values related to the reflectance ratio of *p*- and *s*- polarized light, given as an amplitude ratio, tan(Ψ) and phase difference, Δ:

$$\rho = \tan(\Psi)e^{i\Delta} = \frac{R_p}{R_s} \tag{1}$$

The polarization change caused by the sample is not of primary interest. Rather, coating properties such as film thickness and optical constants are desired. These properties cause the resulting polarization change measured by SE. Thus, ellipsometry is subject to the “inverse” problem. The “result” is measured but the “cause” must be determined. This is also true of other optical measurements. In this case, the “cause” is the thickness and optical constants of each layer in the optical coating stack, which is described by a model to allow calculation of the optical response. Through regression analysis, the unknown coating properties are found that best generate a theoretical response to match the experimental curves. This process is shown in Figure 2 and is referred to as “fitting” the data.

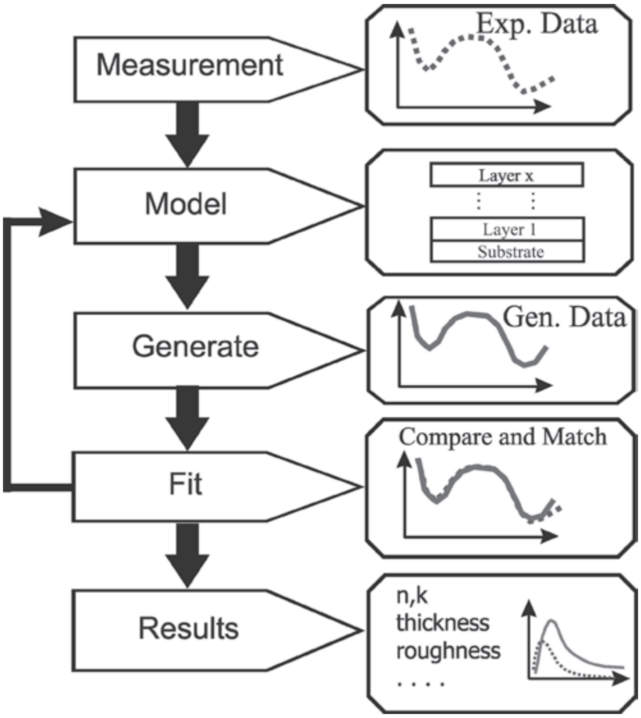

Figure 2: Flow chart for the ellipsometry process. Through regression analysis, a model is adjusted to find the optical constants and layer thicknesses that generate data curves that best match the experimental data curves.

The final model is a layered description that best predicts the measured data. However, the model must be assessed to insure sensitivity and uniqueness.

The Mean Squared Error (MSE) is used to quantify the difference between a given model and the experimental data [3]. A low MSE implies a good match between model and experiment. However, a low MSE can also be obtained if too many sample parameters are fit. This leads to a non-unique result. To ensure the final model is correct, it is important to obtain adequate data content to determine all sample unknowns using a minimum number of free fit parameters.

ABSORBING FILM CHALLENGE

SE measurements of absorbing films are not as common as measurement of transparent films due to the increased complexity of the measurements and models. The optical constants for absorbing layers contain two unknown values per wavelength: index of refraction and extinction coefficient (n and k). The extra level of sample complexity can lead to correlation between parameters. To better understand this situation, first consider the case of a transparent film.

Transparent Films: single-wavelength

Transparent films are commonly measured with spectroscopic ellipsometry to determine film thickness and index. Consider first a single-wavelength ellipsometry measurement. For a transparent coating on known substrate, there are two unknown sample properties: film thickness and index (n). The ellipsometer measures two values, Ψ and Δ. This provides adequate information to solve for both sample properties.

However, the single-wavelength ellipsometric data is a periodic function of film thickness so that different thicknesses cycle through the same Ψ,Δ values. Figure 3a shows the data “cycle” as thickness increases. This leads to uncertainty in the real thickness as any measured point along the circle can correspond to multiple possible thicknesses separated by the “cycle-period”.

Transparent Films: SE

To solve the uncertainty associated with single-wavelength ellipsometry, the measurement is extended to cover multiple angles and/or wavelengths. For example, SE data from a thin transparent coating on known substrate would lead to $\lambda+1$ unknown sample properties (λ index values plus 1 thickness) where λ is the number of measured wavelengths. The number of measured values is 2λ, as Ψ and Δ are determined for each wavelength. Thus, the problem becomes “over-determined” when multiple wavelengths are measured.

The wavelength variation eliminates any misinterpretation from thicknesses possible at different multiples of the periodic cycle. The first three thicknesses from the cycle of Figure 3a are shown versus wavelength in Figure 3b. Although the data are identical at one wavelength, their wavelength dependence is significantly different, ensuring a unique result.

Absorbing Films

For an absorbing film, the unknown sample properties increase to $2\lambda+1$: $n(\lambda)$, $k(\lambda)$ and film thickness. Only 2λ data values (Ψ, Δ) are measured from a spectroscopic ellipsometer at one angle. The initial reaction is to simply measure additional data at a second angle of incidence, increasing the number of measured values to 4λ. However, this will only succeed if the second angle provides new information. Unfortunately for many thin absorbing films, multiple angles provide essentially the same information.

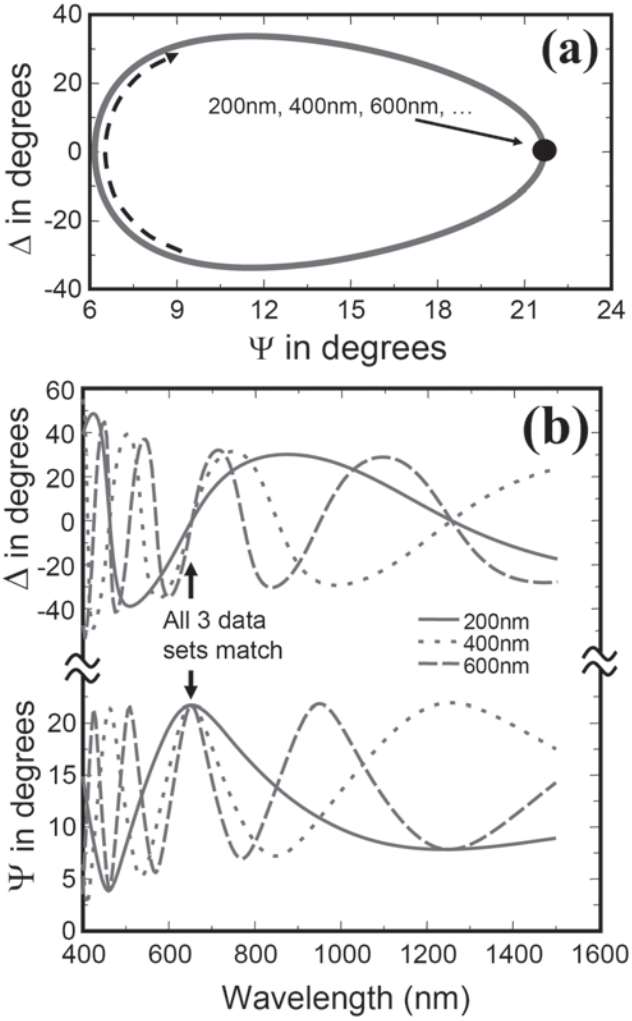

Figure 3: (a) Data cycle versus thickness for a TiO_2 coating on fused silica. The data at a single-wavelength are equivalent for 200nm, 400nm, 600nm etc. (b) Spectroscopic data for the same three coatings at 70° angle show the match for data at 633nm, but have very different spectral responses, which allows SE measurements to uniquely determine between the possible thicknesses from cycle.

Consider a thin TiN film deposited on Si substrate. SE data are collected at 4 angles of incidence, providing 8λ total data points. This should be adequate to solve 2λ+1 unknown sample properties, unless the different angles provide essentially the same information. However, this case remains under-determined, with multiple solution sets of thickness and optical constants that provide the same data fit quality (similar low MSE value). Figure 4 shows the uniqueness test using data from all four angles for the thin TiN layer on Si. There are multiple thicknesses that provide the same MSE – accomplished by fitting different optical constants for each thickness. Which answer is correct? Because all combinations fit the data with similar resulting MSE, a unique result is not obtained, even though plenty of experimental data had apparently been collected. This is the primary problem with absorbing films. How to ensure a unique solution? It is important to consider the information "content" of the data rather than just the amount of measured data.

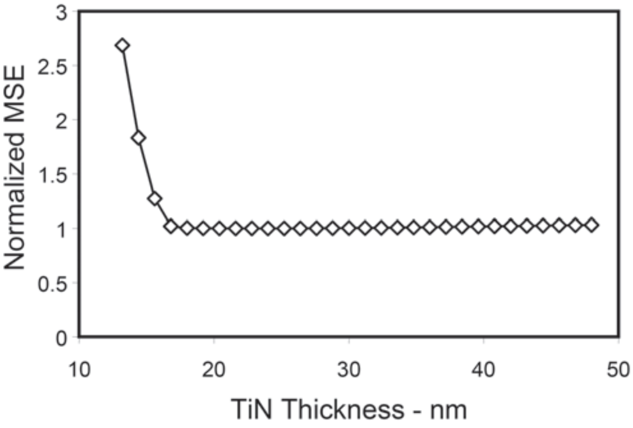

Figure 4: Example of correlation, where multiple sets of thickness and n,k values provide similar quality fit (low MSE). Thus, it is not possible to determine which result is correct. More information is needed.

CHARACTERIZING ABSORBING FILMS: METHOD REVIEW

To insure a unique analysis of absorbing films, it is important to apply special measurement and analysis procedures. These methods have been discussed when applied to Cr metal coatings [4], but are reviewed here with consideration for optical coatings. Each method is described along with its inherent advantages and limitations. All methods either increase the measured data content or reduce the number of unknown sample properties. Choosing the correct method can make the difference between an under-determined, non-unique solution and accurately determining the optical coating properties.

Opaque Coatings

The most common method applied to absorbing films is to deposit a thick, opaque layer of the same material. Because the coating is opaque, no light can penetrate the film and the thickness is no longer a consideration. This reduces the number of unknown sample properties (no thickness to consider) and allows a direct inversion of Ψ(λ) and Δ(λ) to determine the *n*(λ) and *k*(λ) for the film [3]. These optical constants are referred to as "pseudo" values because the direct inversion assumes a sharp interface between the absorbing coating and ambient. Thus, any surface roughness or oxidation is ignored and may affect the accuracy of the measured result.

This opaque film technique can provide a basic description of the optical response from a specific material. However, the resulting optical constants may not represent the values from a thinner layer for two reasons. First, as mentioned – the direct inversion ignores all effects from surface layers (oxides, roughness, etc.) which may change from thin to thick layers. Second, for many materials, the optical properties will vary with film thickness, especially in the sub-100nm regime under consideration. Figure 5 shows optical constants determined from a series of Ag films with varying thickness. Note the changes in optical properties as thickness increases. For this case, the opaque coating does not describe the optical constants of thinner layers.

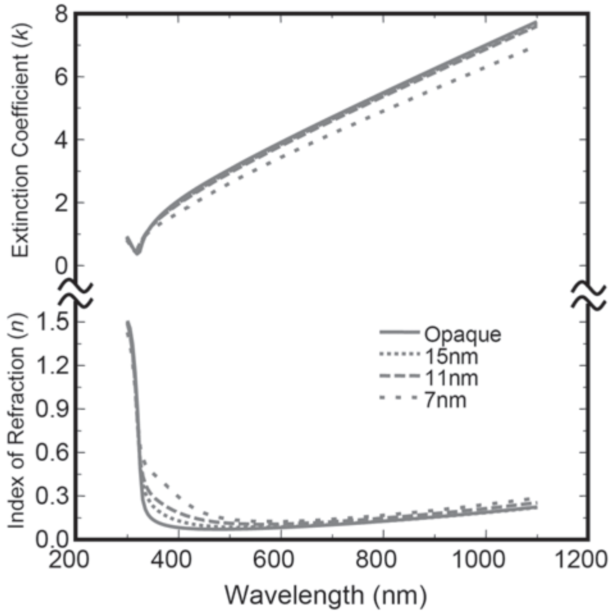

Figure 5: Optical constants for Ag thin films versus thickness.

Transparent Wavelength Region

Many coatings are absorbing at some wavelengths, but transparent at others. While metals generally don't meet this criterion, almost all dielectrics, organics, and semiconductors will. A common and successful approach for these coatings involves two steps. First, the thickness is determined from the transparent region, where only thickness and $n(\lambda)$ are unknown. After the thickness is accurately determined, $n(\lambda)$ and $k(\lambda)$ can be determined in the absorbing spectral region on a wavelength-by-wavelength basis. Here, again the number of unknown sample properties are reduced, as thickness was determined from the transparent region and is fixed.

The main limitation of this method is the requirement of film transparency over some spectral range accessible by the measurement tool. As mentioned earlier, metals absorb at all wavelengths. Low bandgap semiconductors absorb light from the ultraviolet to the near infrared and only become transparent at mid-infrared wavelengths. While IR ellipsometers are available, they are less common.

Optical Constant Parameterization

Another common method for absorbing film characterization is the use of a mathematical dispersion equation to describe the optical constants of a material versus wavelength. This significantly reduces the total number of variable "fit" parameters in the model – typically 5 to 25 parameters are varied to match data from hundreds of wavelengths. However, the dispersion equation does not add information content to the experimental data, or significantly reduce the amount of information unknown about the film. The same coating properties (thickness, $n(\lambda)$ and $k(\lambda)$) need to be determined. The dispersion equation only reduces the number of fit parameters and constrains the possible choices that are allowed during the fit. The key advantage of a dispersion equation is that many are developed according to physical descriptions of material properties, relating changes in k to changes in n and vice-versa. As such, many functions have been developed over the years which serve as dispersion equations and enforce Kramers-Kronig consistency. This ensures the resulting optical constants retain a physically reasonable shape that is possible in nature. Thus, dispersion equations can eliminate many of the "unphysical" possibilities of a direct wavelength-by-wavelength fit to optical constants.

One limitation of optical constant parameterization is that the final dispersion equation must match the shape of the material's real optical constants. This can be easy for amorphous semiconductors such as amorphous silicon, which have broad features and can be described with a single Tauc-Lorentz or Cody-Lorentz oscillator [5]. For example, Figure 6 shows the imaginary dielectric function for a series of amorphous, microcrystalline, and polycrystalline silicon films used for photovoltaic applications. A Kramers-Kronig consistent dispersion equation with five to ten free parameters can describe the optical constants over the full spectral range.

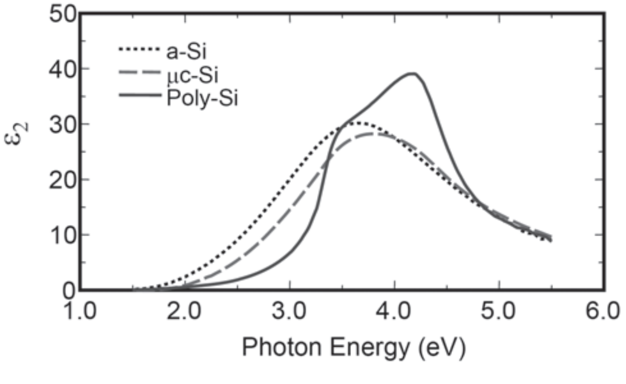

Figure 6: Imaginary dielectric functions developed using dispersion equations for amorphous, micro-crystalline, and poly-crystalline silicon films.

Optical constant parameterization is more difficult for organics, crystalline semiconductors, and metals that exhibit multiple absorption features. Here, a summation of "oscillator" terms are combined to describe the optical constants versus wavelength. As the dispersion equation becomes more complex, it also becomes less effective at reducing correlation. Thus, optical constant parameterization is often best utilized in combination with the other methods described in this review.

Interference Enhancement

While multiple angles do not necessarily provide additional information for all samples, there is a special type of sample structure that benefits from multiple angles. If the absorbing film is deposited over a thick dielectric layer or stack, the interaction between light and the absorbing film is significantly modified by the underlying coating(s). This is referred to as interference enhancement and was first demonstrated by McGahan et al. for amorphous carbon films [6].

To demonstrate interference enhancement, compare the uniqueness tests of two TiN coatings. The first is deposited directly on a Si substrate and is shown in Figure 4. Although SE data are collected at four different angles of incidence, each of the multiple angles provide essentially the same information and there is correlation between thickness and optical constants. A similar TiN film is also deposited over a thick SiO_2 coating on Si. The underlying dielectric enhances the light interaction with the absorbing film at multiple angles. Because there is significant change versus angle, new information is measured at each angle and a unique solution for optical constants and thickness is obtained. In Figure 7 this is shown by a Uniqueness test that only has a single unique result (MSE minimum) for optical constants and thickness.

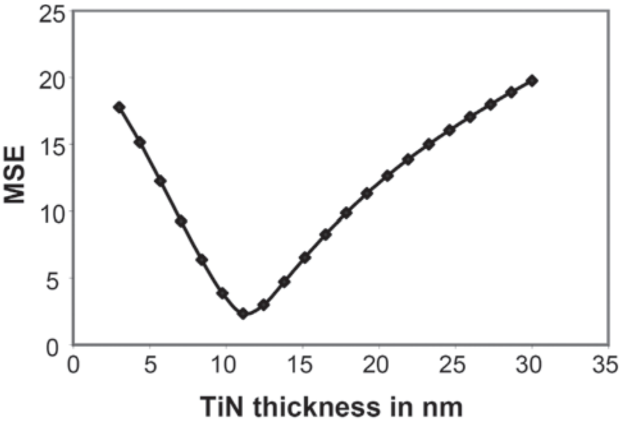

Figure 7: Uniqueness test for a thin absorbing TiN coating deposited on Si substrate with thick SiO_2 dielectric layer. The underlying dielectric enhances the information content available from multiple angle measurements, which provides a unique solution for optical constants and thickness.

Simultaneous SE and Intensity

Another method that increases the measured information content is to combine ellipsometry measurements with intensity reflectance or transmittance measurements from the same coating. The most common implementation involves transmittance, as it is more sensitive to the absorption than reflected measurement techniques. This has been demonstrated as early as 1992 for diamond-like carbon (DLC) films and has been commonly used for absorbing coatings on glass and plastic substrates ever since [7]. The extra intensity measurement helps break the correlation between thickness and optical constants and allows a unique result.

Consider the uniqueness test results shown in Figure 8. When only SE data are considered, the fit result is not unique. Adding transmission intensity to the fit provides the additional information to break correlation between optical constants and thickness and provides a single unique solution (MSE minimum) for the coating optical constants and thickness.

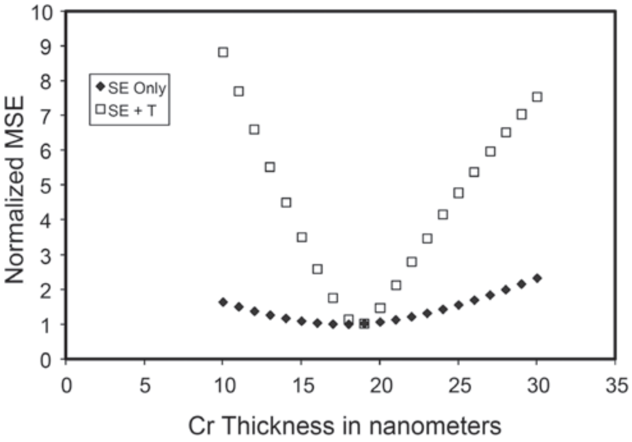

Figure 8: Uniqueness test shown for Cr thin film, comparing results when only SE data are analyzed and when SE and Transmission are simultaneously analyzed.

Multiple Sample Analysis

Another method to increase measured data content is to measure multiple samples of the same coating with different film thickness. The data are fit simultaneously using a common set of optical constants. Consider measurement of three different samples that contain an absorbing coating, but with different film thickness. The unknown sample properties include three thickness values, but only one "set" of optical constants: $n(\lambda)$ and $k(\lambda)$. The measured Ψ,Δ data include 2λ values from each sample, which totals 6λ for three samples. The information content will be different from each sample as long as the light interaction is different (different path length through each film). Thus, there are 6λ values to uniquely determine the $2\lambda+3$ unknown sample properties.

In-Situ Monitoring

In-situ SE measurements collect data during the deposition process. This provides access to the same coating at different points during deposition (different film thickness). This is equivalent to the benefits from multiple sample analysis, but applied to the same coating and often includes tens or hundreds of different thicknesses. As all measurements are from the same coating the optical constants are often more consistent than with the multi-sample approach. This method is the most successful approach of all the methods surveyed. However, it requires integration of the ellipsometer on to the deposition process chamber. As an added benefit of integrating SE tool onto the process chamber, the real-time monitoring of films allows control of the final film thickness [8].

Multiple Ambient Method

The final method to collect additional data from a sample involves varying the ambient surrounding the sample (e.g. air and water). If the ambient index changes, the light interaction with the coating also changes and provides new information. Thus, measurements with multiple ambients should be adequate to solve for thickness and optical constants of an absorbing film. The main limitation to this technique is consideration of how the coating may change in different ambient. Some coatings may absorb some of the ambient, which will modify the coating optical constants. This will increase the complexity of the data analysis and reduce the effectiveness of determining a unique result for absorbing films. However, this is used to an advantage for porous coatings to help study the pore size.

COMBINED METHODS

In practice, the methods described to help measure absorbing films are best used in combination. This provides the benefits from each method and overcomes many of their individual limitations. A perfect example of combined methods is demonstrated by Pribil et al [9]. They combined three of the above methods in their study of thin absorbing metal layers. Both SE and Transmittance were measured *in-situ* during the deposition of the metals. During data analysis, the optical constants were parameterized with a dispersion equation. Thus, three methods were combined to ensure unique results.

SUMMARY

A variety of methods have been presented that allow spectroscopic ellipsometry measurements of thin absorbing films. Each method helps reduce the correlation between thickness and optical constants (n and k) to ensure a unique result. Many methods succeed by reducing the number of free-parameters in the model analysis. These include measurement of an opaque absorbing film, measuring a transparent spectral region to fix the thickness before characterizing the absorbing region, and optical constant parameterization. Other methods rely on collecting additional data from the sample that provides additional information to be used in the fit. These methods include multiple angle measurements that benefit from interference enhancement, combined SE and intensity measurements, multiple sample analysis, *in-situ* monitoring, and multiple ambient measurements. All methods work well on a variety of thin absorbing and semi-absorbing film, but have their own limitations which need to be considered when characterizing such coatings. Best results often result from the combination of multiple available methods.

REFERENCES

1. H.G. Tompkins, E.A. Irene (Eds.), *Handbook of Ellipsometry*, William Andrew Publishing, Norwich NY, 2005.

2. H. Fujiwara, *Spectroscopic Ellipsometry Principles and Applications*, John Wiley & Sons Ltd, West Sussex, England, 2007.

3. J. Hilfiker et al. “Survey of methods to characterize thin absorbing films with Spectroscopic Ellipsometry,” *Thin Solid Films*, 2008, In Press.

4. B. Johs, J.A. Woollam, C.M. Herzinger, J. Hilfiker, R. Synowicki, C. Bungay, in: G.A. Al-Jumaily (Ed.), “Overview of Variable Angle Spectroscopic Ellipsometry Part I,” *Proceedings of SPIE, Denver, U.S.A., July 18-19, 1999, Critical Review of Optical Science And Technology* **CR72** 1999.

5. R.W. Collins and A.S. Ferlauto, in: H.G. Tompkins, E.A. Irene (Eds), *Handbook of Ellipsometry*, William Andrew Publishing, Norwich NY, pp. 93-235, 2005.

6. W.A. McGahan, B. Johs, J.A. Woollam, “Techniques for ellipsometric measurement of the thickness and optical constants of thin absorbing films,” *Thin Solid Films* **234** pp. 443-446, 1993.

7. B. Johs, D. Meyer, J.A.Woollam, J.F. Elman, T.E. Long, R.F. Edgerton, J.T. Koberstein, “Characterization of Inhomogeneous and Absorbing Thin Films by Combined Spectroscopic Ellipsometry, Reflection, and Transmission Measurements,” *Optical Interference Coatings Technical Digest* **15** pp. 443-436, 1992.

8. B. Johs et al. “Recent developments in spectroscopic ellipsometry for *in situ* applications” *SPIE Proc.* **4449** pp. 41-57, 2001.

9. G. Pribil, B. Johs, N.J. Ianno, “Dielectric function of thin metal films by combined *in situ* transmission ellipsometry and intensity measurements” *Thin Solid Films* **455-456** pp. 443-449, 2004.