Imaging Ellipsometry Study Of Multi-Layer Microflakes

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Ellipsometers are commonly used for characterizing thin film coatings. Although they continue to be useful for many applications, the size of the samples has to be restricted to be no less than a few millimeters. In this paper we report on using an imaging ellipsometer to study the characteristics of an SiO_2 coating on aluminum microflakes. This novel approach overcomes the lateral resolution limit of conventional ellipsometers, providing access to samples with very small dimensions. A comparison was also made between the coating thickness obtained from imaging ellipsometry and electron microscopy.

INTRODUCTION

The coating of thin layers of materials onto microflakes has been routinely done by pigment manufacturers to improve weatherability, photochemical resistance, or conductivity of pigments. The thickness of these coatings range from a few nanometers to micrometers depending on the particular applications. Traditionally, the methods for determining the coating thickness have been cross-sectional scanning electron microscopy (SEM) or transmission electron microscopy (TEM). One of the major drawbacks of using these methods for measuring coatings on microflakes is the time consuming cross-sectional sample preparation process. The other disadvantage is that no information related to the optical characteristics of the coatings can be gained. The optical constants and coating thickness are important parameters in manufacturing optically variable pigments.

Optically variable pigments are multi-layer metal-dielectric microflakes that shift color with changes in the viewing angle.[1] Optical variable pigments, under the tradename ChromaFlair®, are currently being manufactured by Flex Products Inc. as decorative pigments for applications in paints, plastics, textiles, and graphics. The color (hue) and the saturation (chroma) of the pigments are directly related to the optical constants and coating layer thickness on the microflakes.[2] Prior to the development of the imaging ellipsometer, it was nearly impossible to accurately determine the coating thickness and optical constants simultaneously on microflakes of size less than 100 μm.

Ellipsometry is a well-known non-destructive optical method for determining film thickness and optical properties.[3,4] It measures the change in the state of polarization of the light reflected off the film's surface. Fast ellipsometry methods, single or multi-wavelength, have been adopted for monitoring film growth in situ, allowing for the precise control of film deposition processes.[5] The advancement of spectroscopic ellipsometers has extended the analytical power of ellipsometry to complex multilayer coatings, where several optical parameters (n, k of the substrate, n_i, k_i, d_i of the layers, roughness, anisotropy, etc.) can be determined simultaneously.

Ellipsometry had remained a macroanalysis technique, i.e., the sample size had been limited to no less than a few millimeters. The recent development of imaging ellipsometry, which combines the power of ellipsometry with microscopy, has overcome this limitation. The enhanced spatial resolution of imaging ellipsometers will potentially expand ellipsometry into new areas of microanalysis, microelectronics, and bioanalytics. In this paper, we summarize our investigation of the coating characteristics of multilayer metal-dielectric microflakes by using imaging ellipsometry.

EXPERIMENTAL

Samples of metal-dielectric microflakes were prepared on a roll of polyester foil by depositing multi-layer thin films in a vacuum roll coater. The coating was then removed from the polyester foil and ground into

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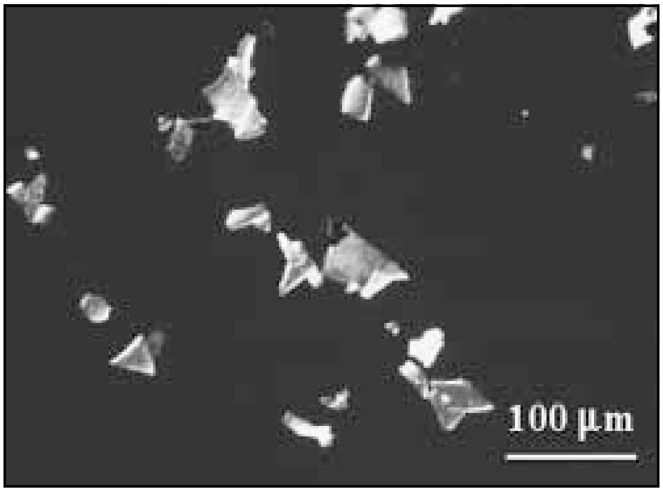

Figure 1—Optical micrograph of multilayered microflakes.

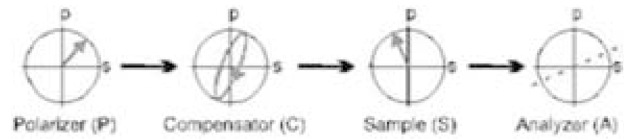

Figure 3—PCSA configuration that generates a null condition.

microflakes as shown in *Figure* 1. The microflakes are symmetrically structured, i.e., an aluminum layer sandwiched between two SiO_2 layers. The manufacturing process of making optical variable pigments has been previously published.[6] As shown in *Figure* 1, nearly all of the microflakes are less than 100 µm in size.

A commercial imaging ellipsometer (I-Elli2000, Nanofilm Technologie GmbH) was used for this study. The imaging ellipsometer was operated on the principles of classical null ellipsometry and real-time ellipsometric contrast imaging. The light source of the imaging ellipsometer was a 532-nm laser. The laser beam became elliptically polarized after it passed through a linear polarizer (P) and a quarter-wave plate (C). The elliptically polarized light was then reflected off the sample (S) onto an analyzer (A) and imaged onto a CCD camera through a long working distance objective with numerical aperture of 0.21 or 0.35 (*Figure* 2). In this PCSA configuration, the orientation of the angles of P and C were chosen in such a way that the elliptically polarized light was completely linear polarized after it was reflected off the sample. As shown in *Figure* 3, the ellipsometric null condition was satisfied when A was "crossed" with respect to the polarization axis, i.e., the state at which the absolute minimum of light flux was detected at the CCD camera. The angles of P, C, and A that satisfied the null condition were related to the optical properties of the sample. Reduction of the measured data with computerized optical modeling led to a deduction of film thickness and the complex refractive indexes.

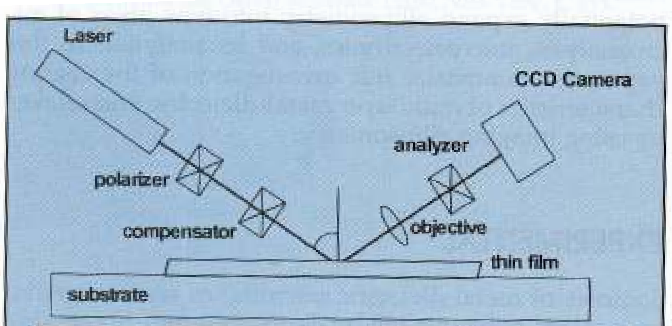

Figure 2—Schematic and photograph of an imaging ellipsometer.

Prior to the imaging ellipsometric analysis, the microflakes were dispersed onto a silicon wafer that was held by a specimen holder horizontally. The microflakes were generally not lying flat on the wafer. Flexure or tilt caused a portion of the flakes to be out of focus, therefore inducing brightness differences and interference fringes along the edges. Such effects could easily be viewed through the objective of the imaging ellipsometer as shown in *Figure* 4. Since the horizontal orientation was crucial for accurate measurement, only the microflakes that did not exhibit brightness gradients or interference fringes were selected for the measurement. A distinct advantage of this approach was that it eliminated the need for assuming flat flakes.

Cross-sectional microscopy was performed to independently verify the SiO_2 layer thickness measured with imaging ellipsometry. A JEOL 6330 field emission scanning electron microscope was used and the cross-sectional image of a microflake at 100,000X is shown in *Figure* 5.

RESULTS AND DISCUSSION

The images of the microflakes were captured and only the area where the flakes actually laid flat was analyzed.

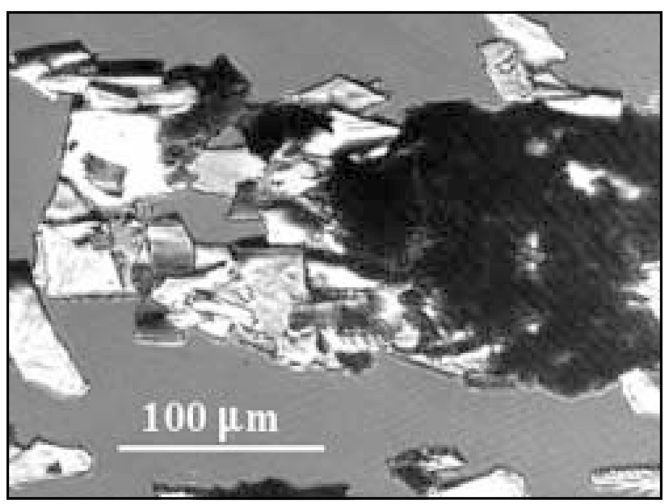

Figure 4—A typical ellipsometric image of aggregated microflakes.

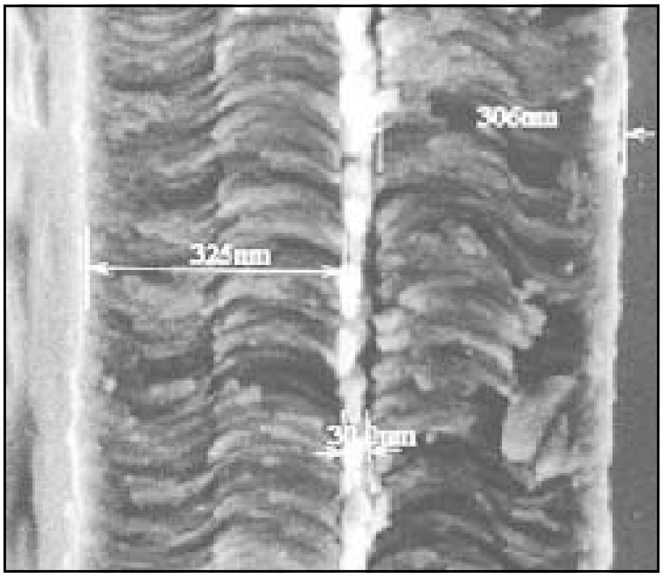

Figure 5—The cross-sectional image of a microflake at 100,000X.

The region in an image appeared dark when it was in a null state, while bright in an off-null state. These two states were each related to a unique set of angles of P, C, and A. The nulling method of constant ellipsometric contrast allowed the samples to be viewed at the video rate with an extremely high image contrast. The area of interest in the sample was individually selected for analysis using the sequence of component rotations (fixed compensator nulling scheme) and signal minimization algorithms.

The null and off-null ellipsometric contrast images were taken from a single microflake at two different sets of P, C, and A angles. *Figure* 6a shows the bright off-null state and *Figure* 6b is the dark null state. The absence of any detectable brightness gradient in the images indicated the entire flake was laying flat on the specimen holder. The ellipsometric analysis was performed within the area of the rectangle cursor marked over the flake. The signal was extracted from the video images with a digital image processing system.

Ellipsometry measures the ratio (ρ) of the complex Fresnel reflection coefficients for light polarized parallel (r_p) and perpendicular (r_s) to the plane of incidence. The mathematical expression for this ratio is:

$$r = \tan Y \cdot \exp(i\Delta) \tag{1}$$

where

$$\tan\Psi \frac{|r_p|}{|r_s|} \tag{2}$$

and,

$$\Delta = \delta_p - \delta_s \tag{3}$$

δ_p and δ_s are the phase factors of the complex Fresnel reflection coefficients r_p and r_s, respectively.

With the exception of the most simple case of a single interface where the indexes of refraction can be obtained from the measured reflectance coefficient, r, and from the angle of incidence by inverting the Fresnel equa-

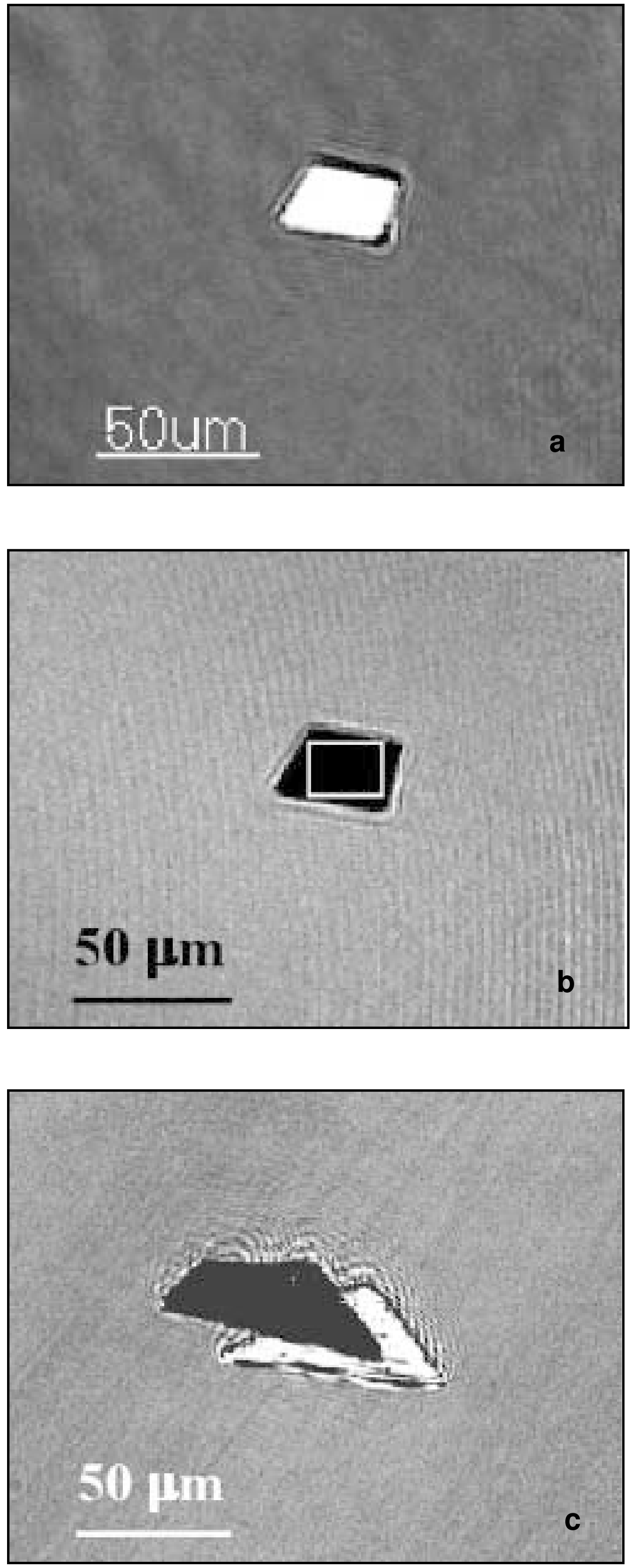

Figure 6—Ellipsometric contrast images: (a) The bright off-null state; (b) The dark null state. The rectangle cursor encompasses the area being analyzed; and (c) Two flakes of opposite orientation.

tions, the analytical solution for calculating the indexes of refraction of a multilayer system is algebraically too complex for practical applications. Because of the difficulty in inverting the Fresnel equations for multilayer systems, a modeling based ellipsometric analysis is necessary for materials analysis. In this approach, Ψ and Δ are measured and compared to those calculated for an assumed model.

In the present study, the Al layer in the microflakes was about 30 nm thick as revealed from SEM cross-sectional micrograph in *Figure* 5. At this thickness, Al is opaque to the light that was used in the imaging ellipsometer, thus enabling us to reduce the complexity of our optical model from the multi-layer $SiO_2/Al/SiO_2$ stack to a single layer SiO_2 film on Al substrate. The handbook values of the optical constants are n_{SiO2}=1.4608 for SiO_2, and n_{Al}=0.8850, and k_{Al}=6.5500 at λ= 532 nm for Al.[7] By constraining optical constants and solving for thickness, we found the SiO_2 layer thickness to be a bimodal distribution centered about 315 ± 3 nm and 340 ± 10 nm. Since the ellipsometric angle Δ was highly sensitive to the thickness of the SiO_2 layer, microflakes that had different orientations were observed to have a distinct image contrast. *Figure* 6c shows two stacked flakes of reverse orientation. The slight thickness asymmetry corresponded to variation in the microflakes' manufacturing process.

The thickness range derived from imaging ellipsometry was in good agreement with that of the cross-sectional analysis, 320 ± 20 nm, measured by electron microscopy. The enhanced magnification feature of the imaging ellipsometer allowed us to analyze microscopic samples in less time than the time required for cross-sectional electron microscopy. This work is the first application of imaging ellipsometry to measure coating thickness on microscopic flakes. The independent SEM cross-sectional measurement verified the reliability of the imaging ellipsometry result.

CONCLUSION

We have successfully applied imaging ellipsometry to characterize coatings on microflakes. This approach has overcome the lateral resolution limit of conventional ellipsometers, as we have shown that imaging ellipsometry is a powerful technique for characterizing microscopic layered structures. The coating thickness obtained from the imaging ellipsometer was found to be in good agreement with the measurement acquired from a field emission scanning electron microscope. While ellipsometry has been widely used for measuring optical constants and film thickness, our present work has expanded the application of this technique to a new area of microanalysis.

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