

# Lawrence Berkeley National Laboratory

## LBL Publications

### Title

Fast, Self-Nulling Spectroscopic Ellipsometer: Instrumentation and Application

### Permalink

<https://escholarship.org/uc/item/2ps1212w>

### Authors

Muller, R H

Farmer, J C

### Publication Date

1983-05-01



# Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

LAWRENCE  
BERKELEY LABORATORY

AUG 10 1983

## Materials & Molecular Research Division

LIBRARY AND  
DOCUMENTS SECTION

Presented at the Conference on Ellipsometry and  
Other Optical Methods for Surface and Thin Film  
Analysis, Paris, France, June 7-10, 1983; and  
published in Les Editions de Physique

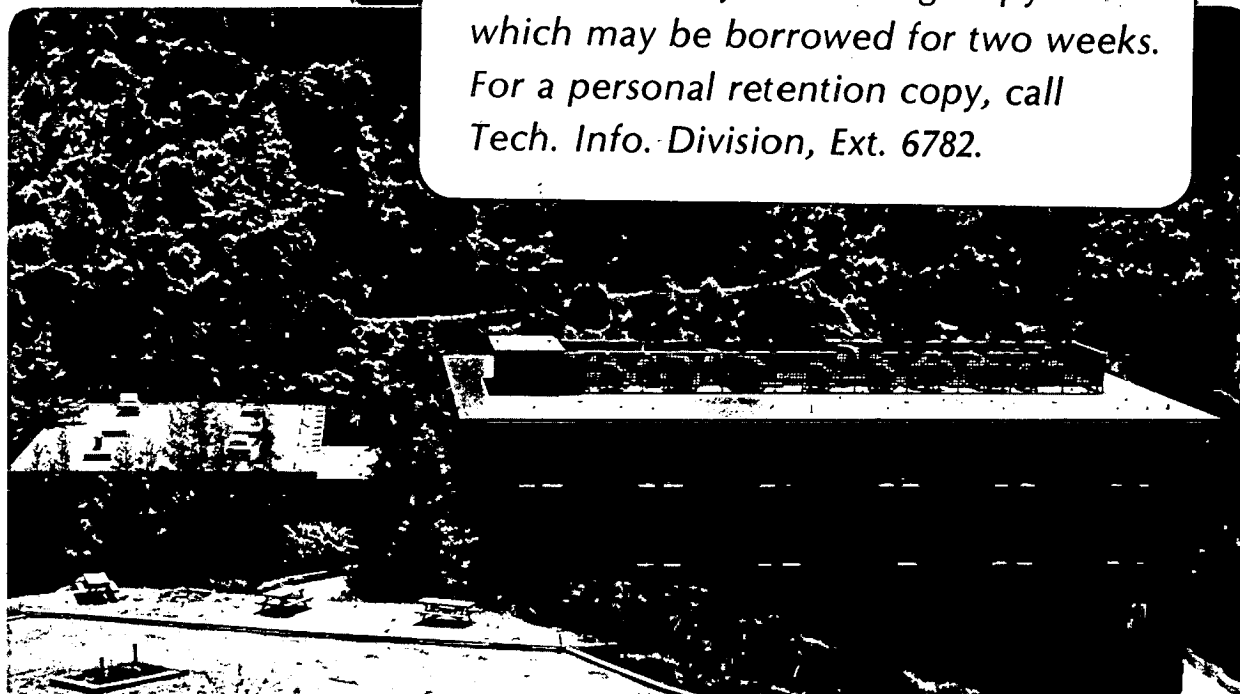
FAST, SELF-NULLING SPECTROSCOPIC ELLIPSOMETER:  
INSTRUMENTATION AND APPLICATION

R.H. Muller and J.C. Farmer

May 1983

### TWO-WEEK LOAN COPY

*This is a Library Circulating Copy  
which may be borrowed for two weeks.  
For a personal retention copy, call  
Tech. Info. Division, Ext. 6782.*



## **DISCLAIMER**

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

FAST, SELF-NULLING SPECTROSCOPIC ELLIPSOMETER:  
INSTRUMENTATION AND APPLICATION

Rolf H. Muller and Joseph C. Farmer

Lawrence Berkeley Laboratory  
Materials and Molecular Research Division  
and  
Department of Chemical Engineering  
University of California, Berkeley  
Berkeley, California 94720

ABSTRACT

The advantages of rapid spectral scanning have been combined with the inherent accuracy of a compensating ellipsometer operated in the polarizer-compensator-sample-analyzer configuration. Wavelength is varied over the visible-UV (370-720 nm) at a maximum rate of 114 nm/s by rotating a continuously-variable interference filter. A three-reflection Fresnel rhomb serves as the achromatic quarter-wave compensator. A microcomputer is used to collect spectroscopic measurements, perform instrument calibrations, digital filtering and interpret data. Wavelength-independent parameters of multiple-film optical models have been determined by treating measurements of delta and psi at different wavelengths as independent measurements. Experimental and predicted ellipsometer measurements are compared by use of statistical techniques for the determination of optimum values and confidence limits of model parameters.

## Optical Components

Extensive modification of a self-compensating ellipsometer built previously (1) has made it possible to combine rapid spectral scanning with the inherent accuracy (2) of compensating measurements. The ellipsometer employs the polarizer-compensator-sample-analyzer configuration. Faraday cells produce a magneto-optic rotation of the plane of polarization which is additive to the mechanical rotation of polarizer and analyzer prisms and is electronically controlled.

Spectral scanning is achieved by rotating a continuously-variable interference filter, positioned between a white light-source (75 W, current stabilized high-pressure Xe arc) and the collimating telescope of the polarizer. The maximum scan rate was 114 nm per second (1 pass through the spectral range every 3 seconds); lower noise levels can be achieved by use of a lower scan rate (23 nm per second or 1 pass through the spectral range every 15 seconds). As the filter revolves, the wavelength passed varies linearly from approximately 370 to 720 nm during the first half turn of rotation, and then decreases to 370 nm during the second half turn of rotation. A digital incremental encoder is used to measure angular position and, thus, wavelength.

The dependence of the specific rotation (effective Verdet coefficient, rotation per unit solenoid current) of the Faraday cells on wavelength has been determined experimentally. Rotation of the analyzer and polarizer azimuths is linearly proportional to solenoid current over the entire dynamic range of the Faraday cells, which is  $\pm 18^\circ$  at 700 nm and  $\pm 70^\circ$  at 400 nm for the SF-6 glass cores.

A three-reflection Fresnel rhomb with extremely low axial skew ( $<0.01$  deg., Continental Optical Co.) has been used as the achromatic quarter-wave compensator.

#### Computer System

The high rate at which ellipsometer data are generated during rapid spectral scanning requires the use of a digital data acquisition system. (Digital LSI-11/2) The current passed through the polarizer and analyzer Faraday cell solenoids to produce nulling are monitored by the computer, converted to analyzer and polarizer azimuths (and, thus, ellipsometer parameters delta and psi) under consideration of the wavelength-dependence of the effective Verdet coefficients. Wavelength is determined from the angular position of the filter. Digital filtering is done by averaging data collected over a 1.7 nm spectral range. Further noise reduction is possible by averaging several scans.

#### Electrochemical Film Deposition

Thin films of lead on copper substrates were prepared by potentiostatic deposition ( $-600$  mV vs. Ag/AgCl) from an electrolyte consisting of 5 mM  $\text{Pb}(\text{NO}_3)_2$  and 1 M  $\text{NaClO}_4$  at a pH of 3. Details of the electrochemical cell are given elsewhere (3,4). Electrochemical film formation has the advantage that the amount of material deposited can be determined independently from the charge passed.

Based upon charge passed, the film thicknesses would have been 31, 60 and 110 nm if the deposit had formed uniformly and had been compact. However, it was found that the deposit was not homogeneous and compact, and multilayer optical models had to be used to explain the spectroscopic ellipsometer measurements.

### Optical Film Models

Predictions based upon three optical models for single layer films (Fig. 1 a-c) were found not to agree with experimental ellipsometer measurements over the entire spectral range, although interpretations at selected wavelengths often appeared possible.

A three-layer model, illustrated in Fig. 1d, provided very good agreement between predictions and measurements. The first layer was assumed to be an isotropic film representing the underpotential deposit. Optical properties of this layer were determined in a separate study (5). The second layer was assumed to be a granular, porous deposit with optical constants computed from the properties of Pb and electrolyte, by use of the Bruggeman theory for a binary mixture. Incorporation of this layer into the optical model was motivated by light scattering measurements (3). The third layer represented dendritic Pb islands, visible in scanning electron micrographs, and was modeled by an island film and coherent superposition of polarization states for reflection from adjacent surface elements with and without island coverage. Use of coherent superposition implies that the diameter of islands is smaller than the spacial coherence of the illuminating light. The total amount of Pb contained in the three layers was chosen to agree with the coulometric measurements. For the spectroscopic ellipsometer, the longitudinal coherence ranges from 16 microns at 400 nm to 49 microns at 700 nm (6); the transverse (lateral) coherence ranges from 10 microns at 400 nm to 17 microns at 700 nm (7). These estimates assume (conservatively) a bandwidth twice that of the monochromatore (20 nm). Since complementary SEM studies of the films investigated here have shown the dimensions of dendritic islands to be less than 15 microns, the coherent superposition model is

justified for the present experiments.

Computations have shown that the optical effect of the third (dendritic island) layer is often negligible, because the surface coverage by islands is small (5-10%). A simplified two-layer model was therefore used for interpretations. Only 3 unknown parameters have to be determined with this model (thickness of the first, compact layer, thickness and porosity of the second, porous layer) as opposed to six parameters required for the three-layer model. Despite the insignificant optical effect of the dendritic island layer, it usually contained about 2/3 of the Pb deposit known to be present from coulometric measurement. All optical constants were determined experimentally from independent measurements and were not treated as adjustable parameters.

#### Optimization of the Two-Layer Model

By minimizing the sum-of-squares error (8) between the model predictions and measured values of  $\delta$  and  $\psi$  over the entire spectral range, one determines the optimum values of the wavelength-independent adjustable parameters, thickness and porosity of the second layer, and thickness of the first compact layer (the underpotential deposit (3,5). Optimization of the wavelength-independent parameters required to specify only the first two layers resulted in smaller parameter variances than if all three layers were included.

Results of the optimization are shown in Fig. 2 for the ellipsometer parameter  $\delta$  (results for  $\psi$  were similar). The solid lines represent experimental measurements and the circles represent points calculated by a multidimensional optimization routine. Very good agreement was obtained by optimization of the thickness and porosity of the second layer, which are wavelength-independent adjustable parameters. Table I summarizes the results of the optimization.



Parameter confidence intervals are calculated from the variance and the student t-statistic at a 95% confidence level for "2N-P" degrees of freedom, where "N" is the number of delta-psi measurements over the spectral range (from a single spectroscopic scan) and "P" is the number of adjustable parameters (3,5). Wavelengths of individual measurements are spaced at intervals greater than the source bandwidth; measurements at 10 different wavelengths have been treated as independent observations of the same surface. The variance for any parameter and, therefore, the confidence interval increases dramatically as the total number of model parameters P approaches the number of data points (2N) used in the optimization. The high uncertainty in the thickness of the 110 nm layer reflects the diminishing sensitivity of the ellipsometer as the penetration depth of the light is approached by the thickness of the layer.

### Conclusions

A novel fast spectral-scanning self-nulling magneto-optic ellipsometer, based on an earlier design has been built. The instrument is fully computerized.

Spectroscopic ellipsometry allows one to calculate confidence intervals of wavelength-independent parameters for micromorphological optical models and to justify the use of more sophisticated optical models on the basis of the greater degrees-of-freedom.

For three electrolytically formed Pb deposits (compact thickness 31 nm, 60 nm, and 110 nm) the best agreement between measurements and model predictions was obtained for a three-layer model or a two-layer simplification of it. The distribution of deposited material between compact, porous (granular) and dendritic island layers could be determined.

Acknowledgment

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

## References

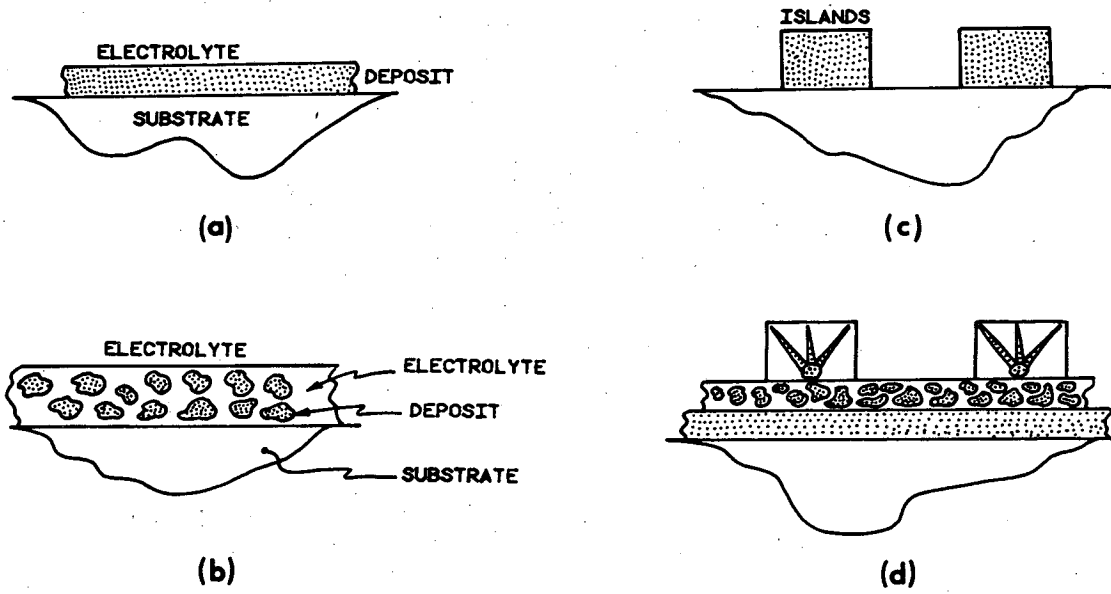
1. H. J. Mathieu, D. E. McClure and R. H. Muller, Fast Self-Compensating Ellipsometer, Rev. Sci. Instrum., 45, 798 (1974).
2. D. E. Aspnes, Precision Bounds in Ellipsometer Systems, Appl. Opt. 14, 1131 (1975).
3. J. C. Farmer and R. H. Muller, Nucleation of Pb Electrodeposits on Ag and Cu, submitted to J. Electrochem. Soc.
4. J. C. Farmer and R. H. Muller, The Effect of Rhodamine-B on Pb Electrodeposition on Ag and Cu, submitted to J. Electrochem. Soc.
5. R. H. Muller and J. C. Farmer, Macroscopic Model for the Ellipsometry of an Underpotential Deposit: Lead on Copper and Silver, submitted to Surf. Sci.
6. G. R. Fowles, INTRODUCTION TO MODERN OPTICS, 2nd ed., Holt, Rinehart, and Winston, New York, 1975, pp. 74-75.
7. M. Born and E. Wolf, PRINCIPLES OF OPTICS, MacMillan, New York, 1964, p. 551.
8. G. E. Box and G. A. Coutie, Application of Digital Computers in the Exploration of Functional Relationships, Proc. Inst. Electr. Engrs., 103 B Suppl. 1, 100 (1956).

Table I. Spectroscopic Ellipsometry of Pb Deposits: Optimization of 2-Layer Model. Confidence Intervals for Model Parameters given for 95% Confidence Limits.

Amount of Deposit	30 nm	60 nm	110 nm
Sum of squares error between measured and calculated $\Delta$ and $\psi$ (deg)	5.359	6.049	6.835
Thickness of compact layer (Å)	$4.8 \pm 1.1$	$4.8 \pm 1.1$	$4.8 \pm 1.1$
Thickness of porous layer (Å)	$310 \pm 41$	$500 \pm 162$	$870 \pm 2664$
Vol. fraction Pb in porous layer	$0.585 \pm 0.139$	$0.775 \pm 0.165$	$0.968 \pm 0.274$

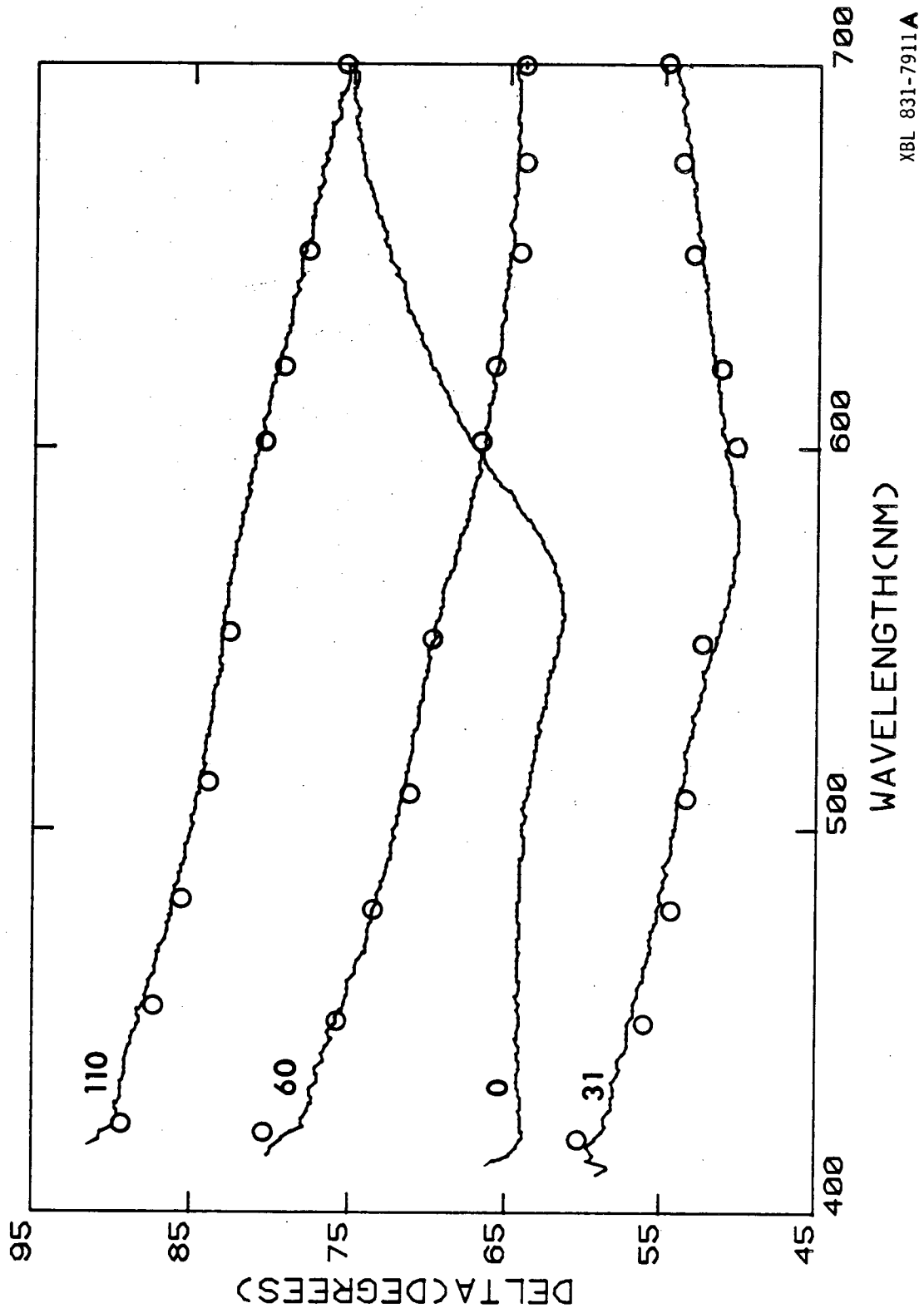
Fig. 1. Schematic of film models investigated for the interpretation of spectroscopic ellipsometer measurements of thin Pb deposits on Cu substrates. Number of adjustable parameters given in parentheses. (a) compact single film (1); (b) porous single film, optical constants of effective medium determined according to Maxwell-Garnett (2) or Bruggeman (2); (c) island single film, reflection coefficient determined by coherent superposition of polarization states, islands compact (2), porous (3) or anisotropic (6); (d) multilayer films, three layers: compact and porous layers, dendritic islands (6) or two layers: compact and porous films (3).

Fig. 2. Spectroscopic simulation for optimum fit of ellipsometer parameter  $\delta$  for a two-layer film model (circles) and measurements (solid lines) for equivalent deposit thicknesses of 0, 31, 60 and 110 nm. Film parameters derived from optimum fit of model predictions to measurements given in Table I.



XBL 829-11873 A

Fig. 1



XBL 831-7911A

Fig. 2

1

This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

2

Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U.S. Department of Energy to the exclusion of others that may be suitable.



TECHNICAL INFORMATION DEPARTMENT  
LAWRENCE BERKELEY LABORATORY  
UNIVERSITY OF CALIFORNIA  
BERKELEY, CALIFORNIA 94720