NISTIR 4860

Metrologic Support for the DARPA/NRL - XRL Mask Program: Ellipsometric Analyses of SiC Thin Films on Si

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Final Technical Report
Period covered: August 1991 - March 1992

Prepared for:
Defense Advanced Research Projects Agency
Arlington, VA 22209

NIST

United States Department of Commerce
Technology Administration
National Institute of Standards and Technology

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January 1993

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Prepared for:
Defense Advanced Research Projects Agency

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TECHNOLOGY ADMINISTRATION, Robert M. White, Under Secretary for Technology
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METROLOGIC SUPPORT FOR THE DARPA/NRL - XRL MASK PROGRAM: ELLIPSOMETRIC ANALYSES OF SiC THIN FILMS ON Si

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ABSTRACT

Ellipsometric analyses were performed on a number of amorphous SiC films grown on Si which are currently being considered for X-ray lithography (XRL) mask membranes. The analyses and conclusions presented here increase the accuracy with which the layer thicknesses can be determined. In addition, materials-related information such as the presence of surface roughness, Si and graphite phases, as well as densification can be discerned from the data. The sensitivity of ellipsometry to very small changes in the phase of light ($\leq 2 \times 10^{-3}$ deg) makes it an extremely accurate optical tool capable of detecting small changes in thickness or optical properties. Samples were measured by single-frequency and spectroscopic ellipsometry. The measurements were analyzed by using a number of models. Three models with increasing degree of complexity and sophistication for the amorphous SiC film are compared: an isotropic one-layer model, an isotropic two-layer model that accommodates a surface layer/region, and a uniaxial one-layer model to account for possible built-in strain in the film. The two-layer model was found to give the most consistent fit to the experimental data. Here, the second layer is believed to be a top layer of different composition about 4 to 5 nm thick that accounts for the surface roughness. The omission of this second layer can adversely affect the determination of the sample optical parameters, including accurate thickness measurements.

Key Words: amorphous SiC; coating thickness; ellipsometry; model; photomasks; refractive index; surface roughness; X-ray lithography

1. Introduction

This report covers the ellipsometric study done at NIST using ellipsometry in support of the SiC material characterization part of the SILICON CARBIDE X-RAY LITHOGRAPHY MASK TECHNOLOGY program under the Naval Research Laboratory contract number N00014-89-C-2241. Amorphous SiC appears well suited to be an important material for XRL mask membranes. Because the material properties can be strongly affected by variations in the processing conditions of film growth, various methods of film characterization are being used to observe these films. Ellipsometry is a nondestructive optical technique particularly sensitive to variations in the microstructure of the films.

2. Technical Report Summary

2.1 Objectives

The objectives of this work were twofold: 1) To provide an understanding of the proper optical model for analysis of single-frequency ellipsometric data for the purpose of obtaining accurate SiC coating thickness measurements and (2) to use these results and spectroscopic ellipsometry (SE) data to study the material properties of the SiC coating.

Ellipsometry is an important measurement technique that is useful for determining the optical properties of the SiC coatings that will be used as photomasks. The output of a single wavelength ellipsometric measurement would be an accurate value of coating thickness and refractive index. However, departures of the sample coatings from an ideal isotropic one-layer configuration can deleteriously affect the measurement output results. SE, where one performs ellipsometric measurements over a large range of wavelengths, is a much more powerful technique to determine the structure and the material properties. However, it is necessary to first find the most appropriate model that describes the sample structure. Only then can these determinations result in accurate values of the thickness and a better understanding of the materials behavior.

The silicon carbide coatings were supplied by Horizon Technology Group, Inc., Arlington, Va., under contract no. NRL N00014-89-C-2241. These coatings were deposited by an ECR-CVD technique by Applied Science and Technology, Inc., Woburn, Mass., in which the substrate is held at a low enough temperature to form amorphous coatings.* Nanostructures, Inc., Mountain View, Calif., is working on process development. It is known that these coatings can have one of various forms of microstructure [1], deviations in stochiometry, phase separation, strain, surface roughness, and spatial variations resulting in nonuniform optical properties. With good processing control, the spatial variations should be minimal. However, there still are noticeable variations of thickness, which one observes

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* Disclaimer: Certain commercial equipment, instruments, or materials are identified in this paper in order to specify the experimental procedure adequately. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

as color variations, across the sample. This is assumed to be caused mainly by the gradient of temperature across the substrate during growth.

It is beneficial to use ellipsometry to obtain the optical properties of these coatings because one can then determine the optical transmission, coating thicknesses, surface roughness, strain, and some aspects of the microstructure, all of which can be important in the mask performance. As a first step, it is necessary to observe whether an isotropic one-layer or an isotropic two-layer or an anisotropic one-layer model is better able to fit the observed ellipsometric data. The use of inappropriate models can give inaccurate values of the above parameters. A single-wavelength ellipsometer measures two angular parameters, Δ and ψ, and yields precise solutions of coating thickness and refractive index, but these values can be inaccurate if the model is wrong, e.g., if coating absorption or surface roughness is ignored.

2.2 Procedure

Single-wavelength ellipsometric measurements at 632.8 nm have been conducted on a set of SiC samples of various thicknesses at angles of incidence selected for the highest sensitivity to model parameters. The results of using various models to fit the data were then observed. Only the one-layer nonabsorbing model can be solved analytically for the index and thickness of the film for different samples. Then trends in the behavior of the index helped determine the best model.

SE measurements were conducted from 1.5 to 4.5 eV (827 nm to 276 nm) in order to determine the SiC optical constants (the dielectric function and the refractive index) and model any surface roughess, overlayers, and strain that exists. Here, SE is particularly model sensitive to calculations that involve the determination of the dielectric function of thick samples.

2.3 Results

The first task of the effort was to determine the appropriate model to describe the SiC layer. Layer-to-layer consistency and well-known bounds on the properties of the films (e.g., built-in strain) clearly pointed to choosing the two-layer model. The one-layer model with or without film absorption failed to yield a refractive index of SiC that was invariant with coating thickness. The one-layer anisotropic model was also inappropriate, with too large a strain necessary to account for the apparent variations in refractive index with thickness. However, the initial set of samples could not be used to define the nature of the two-layer model adequately because they had such a large variation of thickness across the sample, and because the thermal history of the thick and thin film samples was different, leading to some depth-dependent or sample dependent optical properties.

A new set of samples, where the SiC coating was grown by using the inverted chamber with radiative heating of the substrate, was used in the second part of the study. In addition, SE data were used to determine better the nature of the two-layer model. Measurement data were taken from a photon energy range of 1.5 to 4.5 eV where the higher energy part of the spectrum, 4.0 to 4.5 eV, is particularly sensitive to any overlayers on the SiC coating and is not affected by the lower silicon/SiC interface. The second layer, modeled as a rough surface, was necessary to invert the ellipsometric data properly to obtain the dielectric function of SiC.

The result of the analysis strongly suggests that a rough surface, consisting of a 50/50% volume fraction of voids and SiC and having a thickness of about 5 nm, has to be included in the model. The resultant dielectric function of the SiC films can then be examined to obtain additional material-related information. At present, it can be compared to various models of amorphous silicon carbide, some of which have various degrees of chemical ordering in the tetrahedral bonds of the Si and C [1], with and without phase separation, and for cases where the mole fraction is not 50%.

One major consequence of not using the correct model (two-layer that includes a surface roughness layer) is seen in the thickness calculation from the 632.8-nm data. For example, from a 10% variation in refractive index *n* with SiC coating thickness found from the one-layer model (no absorption), there corresponds a 10% variation in the values of the calculated coating thicknesses. This represents a large uncertainty for these films and can alter the interpretation of measurement results such as the spatial contour mapping of the SiC coating thickness by ellipsometry. Besides, such a large variation in *n* seems unreasonable. Inclusion of a rough surface layer leads to much less variation of the calculated *n* from film to film, strongly supporting the validity of this model and an eventual overall accuracy of the measurement thickness.

2.4 Department of Defense Implications

The Department of Defense is currently producing amorphous SiC X-ray lithography (XRL) masks. Criteria are needed for determining the suitability of various membrane materials for use as masks. The measurements NIST is performing provide models and optical parameters that mask designers can use to determine optical performance of candidate membrane materials.

2.5 Implications for Further Research

Further work on process control by ellipsometry is possible. Ex-situ measurements can be made for accurate contour mapping of coating thickness, surface roughness, and possibly the stoichiometry of the SiC coatings. The photon energy range necessary for these modeling studies will need to be extended to at least 6.0 eV from the present 4.5 eV because the sensitivity to changes in the stochiometry with these additional data above 4.5 eV will be higher. The viability of an in-situ ellipsometry process control monitor is promising.

The measurements indicate systematic variations in the refractive index from batch to batch. This may originate in differences in the sample growth history, particularly with thermal treatments. This materials-related property should be investigated more thoroughly. SE can also be used as a sensitive probe of modifications of the material properties with radiation dosage, a good understanding of which is critical for successful use of SiC XRL masks.

3. Technical Report Details

3.1 Introduction

Spectroscopic Ellipsometry is a nondestructive optical technique used to determine the optical dielectric function of a material medium, and thereby study the composition and quality of a material sample. Ellipsometry involves shining monochromatic polarized light onto a flat surface of a material at an oblique angle of incidence and measuring the relative magnitude and phase changes that occur between the two normal components in the specularly reflected light. The magnitude and phase change are sensitive to material composition, crystalline quality, surface and interface roughness, and film thicknesses in fabricated material structures. Since ellipsometry is capable of measuring phase changes as small as $2\pi/2000$, extremely small changes in optical constants ($\sim 10^{-3}$) and/or optical thickness (~0.3 nm) can be observed. However, to identify the quality, composition, roughness, and film thicknesses of a sample, it is necessary to model the spatial distribution and the dispersion relationship of the optical dielectric function of the sample, calculate the model phase shifts, and compare them to the measurement data.

In this report, the results are presented of performing ellipsometry on several samples of SiC coatings. First, ellipsometric measurment data were taken and then they were fitted to an appropriate model for these samples. The parameters of the model can then be used to assess the quality of the coatings.

3.2 Apparatus

The NIST-SED SE uses a rotating analyzer design and measures the ellipsometric angles, Δ and ψ, as a function of both the angle of incidence and the frequency of light. The ellipsometric angles, Δ and ψ, correspond to the relative phase and amplitude shifts of the polarized light that take place upon reflection of the light off the sample's surface. The schematic diagram of the apparatus is shown in figure 1. The spectral range of frequencies corresponds to a range of energies from 1.5 to 4.5 eV. A HeNe laser is used at 632.8 nm (1.96 eV) for precision measurements at that wavelength. The uncertainty in the measured ellipsometric angles is less than 0.05 degrees and the precision of the measurements is of the order of a few millidegrees. This high level of accuracy in the measurements provides a sensitive probe of the material characteristics of a fabricated sample.

3.3 Data and Analyses

The following lists the samples that were received along with a select set of typical raw ellipsometric data for both single and spectroscopic measurements. Then some of the artifacts of the modeling effort are shown and discussed that lead to the choosing of the two-layer model.

A listing of the samples is given in table 1. There are four groups of samples; each group of samples was used to study various aspects of the processing and material characteristics. Group 1, composed of five different sample thicknesses, were grown to aid in the initial modeling effort by incorporating various parameters common to each sample, i.e., the SiC refractive index. Group 2, composed of three samples, were provided to study the effects of densification by using a flashlamp annealing process. Group 3 had one older sample on which Rutherford Backscattering (RBS) data had been taken. Group 4 had two samples, one sample having been left in the processing chamber at the processing temperature for an hour before being removed. This latter sample is called the annealed sample.

Table 2 summarizes the measurements and analyses completed on the total set of samples. Data analyses begin with the modeling procedure [2-4] in which one uses the simplest model, a one-layer model to see how adequately the data can fit the model. Table 3 shows the one-layer modeling results, in which the single wavelength ellipsometric measurement data are used to obtain the thickness t and refractive index, n of the silicon carbide film. The optical properties of the silicon substrate are known from handbook values. The values of n for the thin samples from the first and second group of samples are shown in figure 2. The plot is of refractive index versus coating thickness. One can see that this apparent refractive index can vary by ~3% between samples grown under similar conditions. This is most likely not a physical solution for the index of the SiC film, but is a cyclical phenomenon often seen with other structures as a result of a poor model [5].

It is known that a two-layer model can be used successfully to yield a constant index for occurences of an apparent index that varies periodically with the the film-phase thickness (as the phase change of the light cycles through increments of 2π: see [5] again). In addition, since it is known that the films possess a rough top surface and that ellipsometric measurments are sensitive to it, a two-layer model with a rough surface of 2.0 nm, consisting of a composition having a 50/50 mixture of SiC and air, was added. The dielectric function of the rough layer was modeled by using a well-established procedure that uses the Brugemann effective medium approach [6]. The results obtained with this improvement are shown in table 3 and in figure 2. Note that the apparent variation in n is reduced from ~3% to <1%, with proportional improvements in the measured thickness values. This procedure emphasizes the importance of including the effect of roughness in single frequency ellipsometric analysis. It was found that the testing of an anisotropic one-layer model involved too high values of strain in order to have effects anywhere near those of the two-layer model and hence was rejected.

The addition of the rough surface layer or other corrections such as accounting for absorption in the film could not account for the large differences between the refractive indices of the thin (620-n24, 625-z11, and 621-n22) and some of the thick (622-n24 and 623-n24) samples. It is strongly suspected that the large differences in the thermal history may have led to differences in the materials properties such as an in-situ annealing-induced densification. Further careful work is required before this issue can be settled.

The next step in the effort was to employ SE to test the two-layer model as well as to obtain the dielectric function $\epsilon(\omega)$ [7,8], and hence materials-related information. Figure 3 shows the values for ϵ calculated from the measurement data of sample 712, group 4, with a one-layer model. Here, we see oscillations with photon energy in the values of ϵ_1 and ϵ_2, the real and imaginary parts of ϵ, respectively, indicative of a poor model. However, the figure also shows a similar calculation except that a second (top) layer of roughness is added to the model. Now the spectrum of SiC is much smoother, as it should be in this photon energy region, showing the need for a top layer of surface roughness. Initially, a top surface of oxide was tried and also gave similarly good fits. This surface was subsequently treated with an etchant to remove oxide, and the measurement was repeated with similar results, indicating that an oxide was not present. This again points to the importance of accounting for the rough surface.

The next step in the study is to understand the implications of the calculated $\epsilon(\omega)$ on materials-related issues. One simple procedure is to compare the empirical $\epsilon(\omega)$ to previously reported data and attempt to express $\epsilon(\omega)$ as resulting from a reasonable combination of constituent phases. The geometrically averaged SiC model for $\epsilon(\omega)$ along with small combinations from microcrystalline Si and graphite was used as a starting point, and the measured Δ and ψ values were computer fit to the modeled values. This analysis was performed on sample 38-T31 on which RBS studies had been conducted. The results of the analysis are provided in figure 4. The presence of the oxide overlayer on this sample is known from RBS. The fit to the measured Δ and ψ is surprisingly good.

This part of the effort is meant to demonstrate the level of sophistication of the ellipsometric analysis. Independent information from chemical techniques will be required to provide a good starting point. Once a reasonable starting point is available, SE can yield a wealth of very useful information. Such a detailed study on every sample is beyond the scope of this effort.

3.4 Conclusions

It is the extreme sensitivity of the ellipsometric measurement to such sample imperfections as overlayers and surface roughness that necessitates the fitting of the data to a more complex model than the one-layer model, i.e., the two-layer model. From modeling a few representative samples of SiC coatings that were measured by ellipsometry, there is a significant misfit to the one-layer model. The two-layer model which includes a top overlayer or surface roughness can give good fits to the data taken on representative samples that were grown in the new chamber. Surface profilometry showed roughness existing on a macroscopic level ($\sim$2 nm), indicating that the surface is not smooth. In order to proceed with ellipsometry, whether single-wavelength or spectroscopic, knowing what model is most representative of the sample is fundamental to the optical characterization procedure.

The information obtained in this initial study help in interpreting the widely used HeNe ellipsometric analysis. Thickness measurements can be made with greater accuracy than before. However, materials-related issues have to be better understood and optical parameters catalogued for further metrological improvements.

Acknowledgments

We thank Alex Shimkunas of Nanostructures, Inc. for technical discussions about the properties of the SiC coatings. J.J. Kopanski, for electrical measurements, and T.V. Vorburger, for profilometry measurements, are also acknowledged. We thank Robert McIntosh of Horizon Technology and Jerry Lowney of NIST for helping to administrate these experiments. Also without the cooperation of Michael Cresswell and Loren Linholm, this project would not have been possible.

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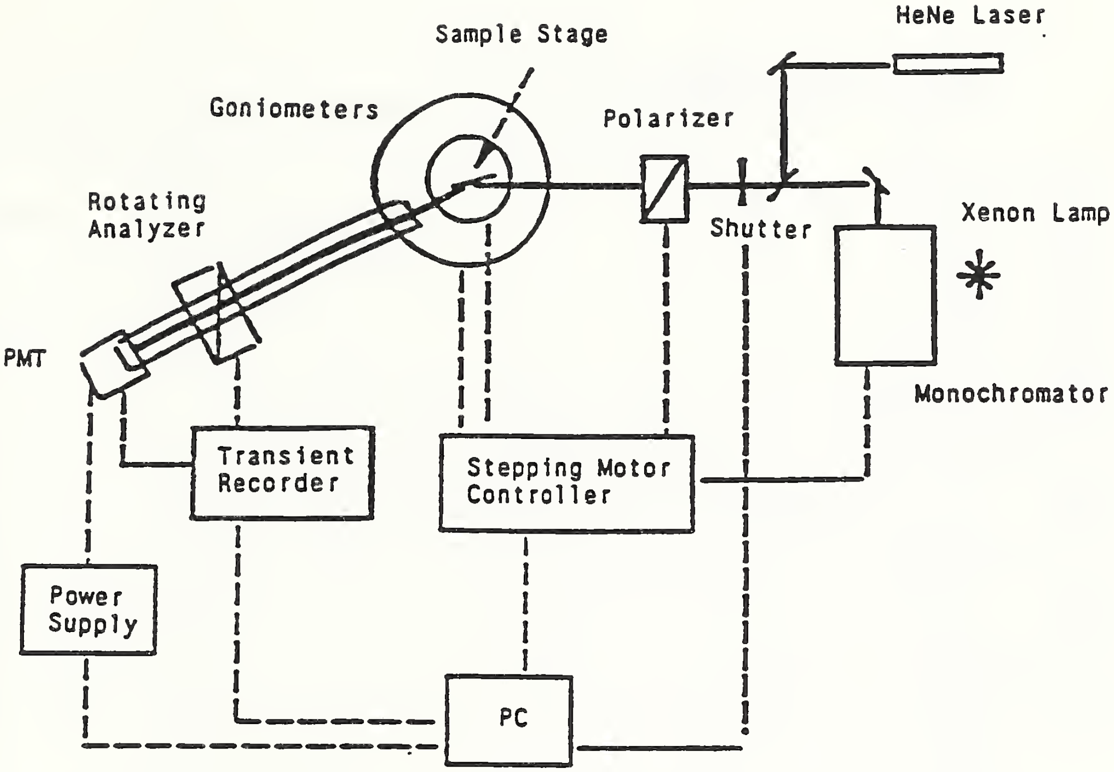

Figure 1. Schematic diagram of ellipsometer.

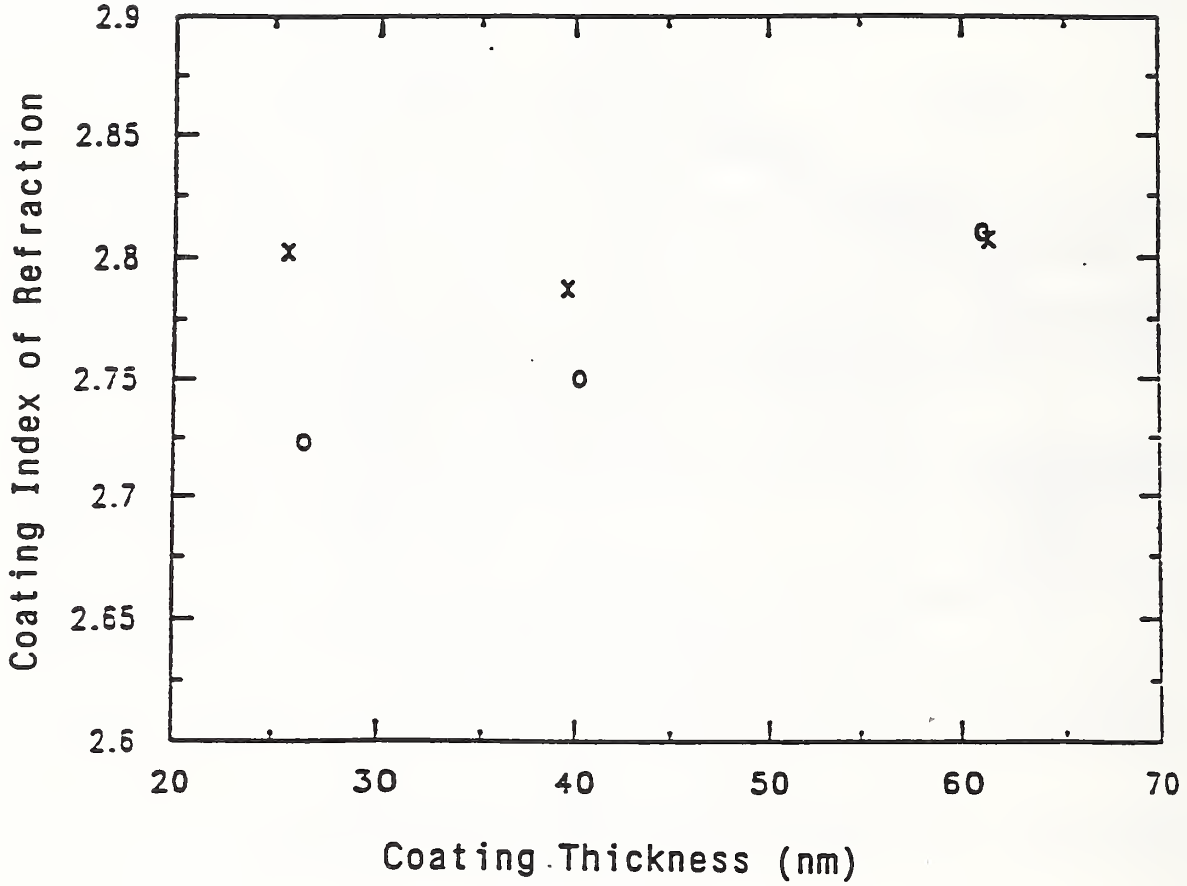

Figure 2. One-layer model (o's) and two-layer model (x's) plot of the apparent index of refraction versus coating thickness.

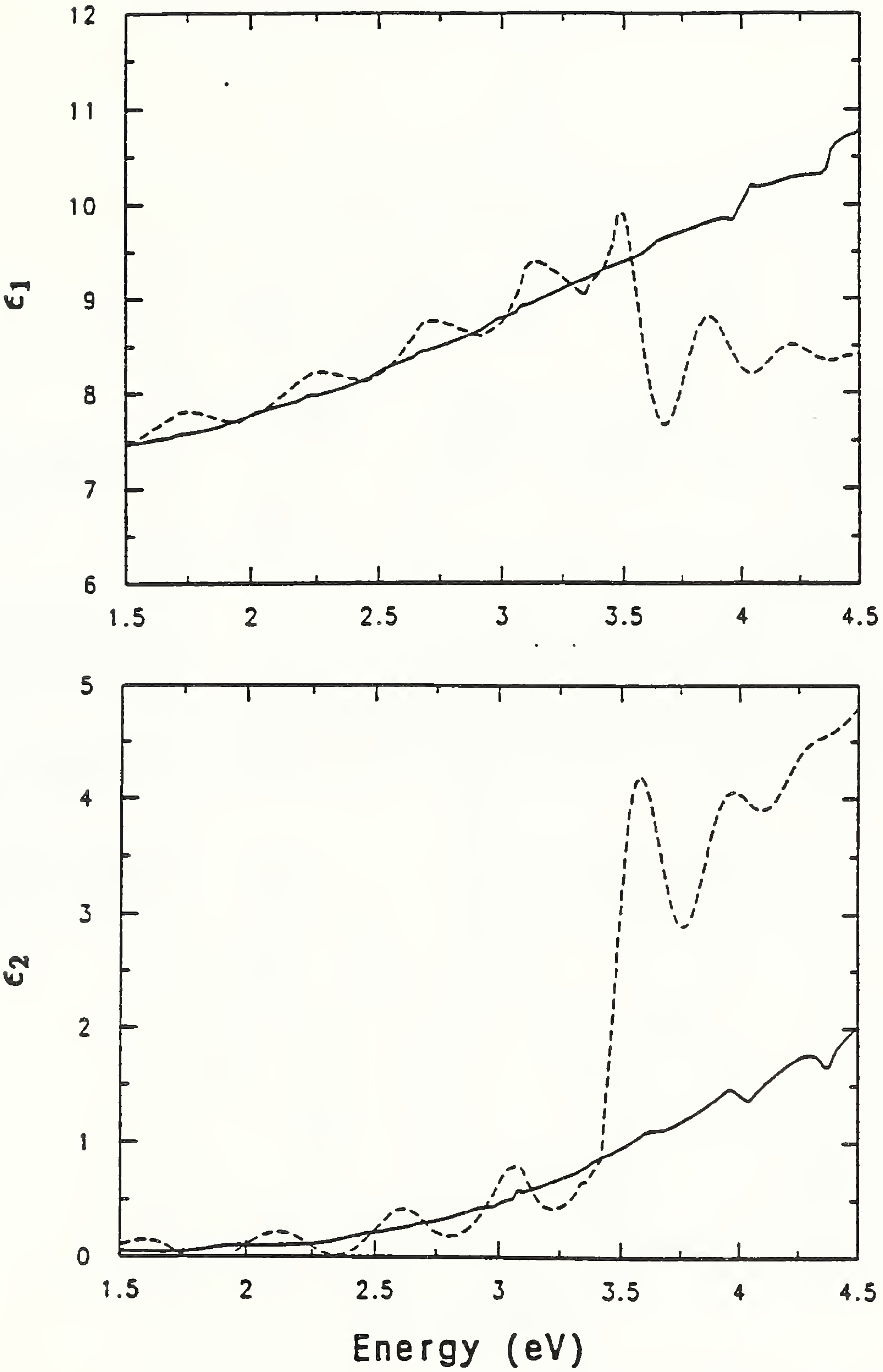

Figure 3. Dielectric function of SiC coating 712 determined with a one-layer model (dashed) and a two-layer model (solid). The top layer is a 5-nm-thick (50% SiC, 50% voids) rough layer.

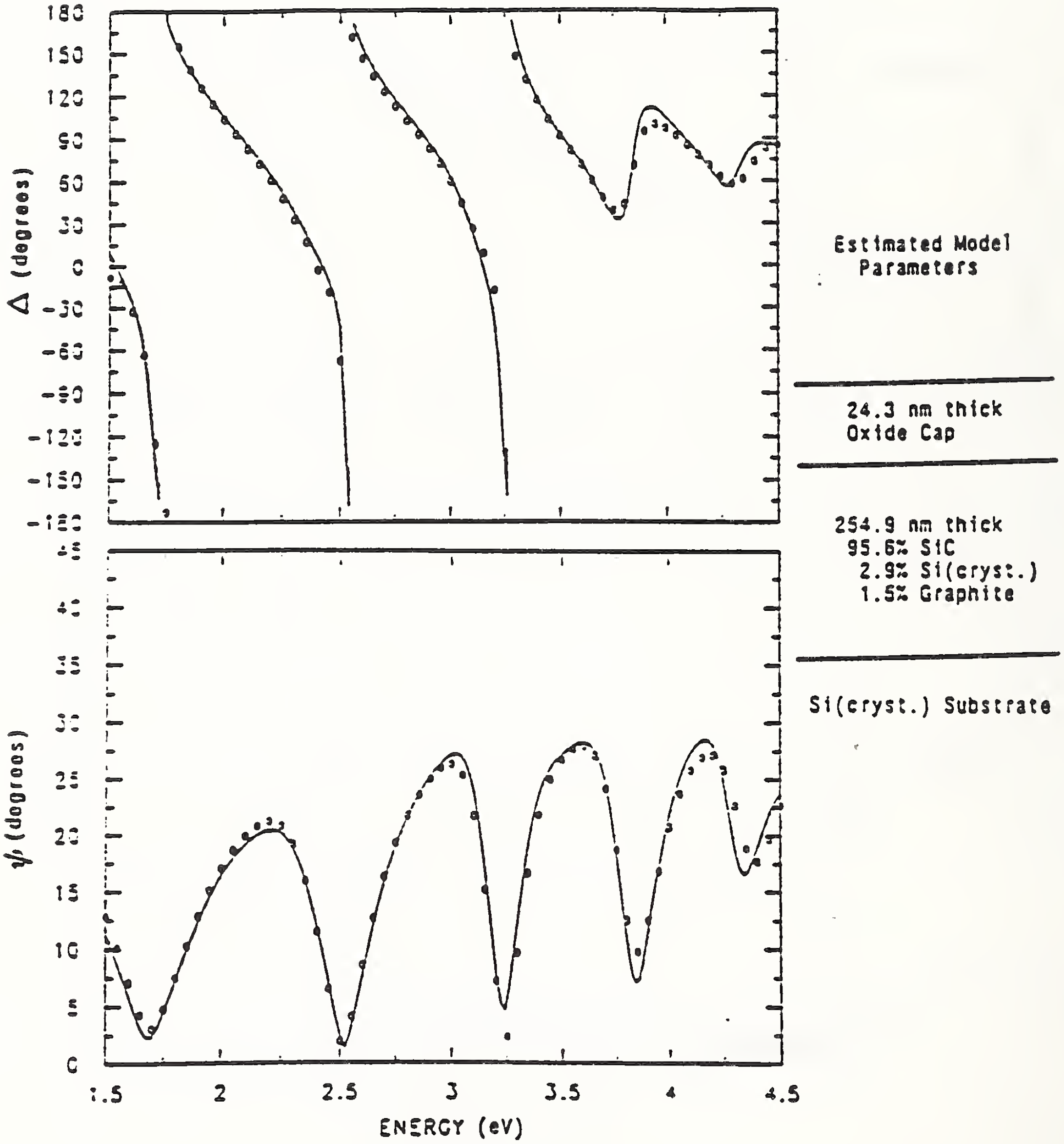

Figure 4. Computer fit (solid curve) to the measurement data (o's) for the RBS sample that had a thick oxide top layer.

TABLE 1

SIC SAMPLES MEASURED BY ELLIPSOMETRY

GROUP	ID	DEL. DATE	NOMINAL THICKNESS (nm)	COMMENTS
1	620-N21	4/18/91	26	SiC Phase III Set 1 coatings
	625-Z11		40	Grown under same deposition parameters
	621-N22		61	
	622-N24		410	
	623-N24		1040	
2	764-N36	9/24/91	34	SiC Phase III Set 4
	765-N37		40	Grown in new chamber
	770-N38		40	770 grown after chamber cleaning
3	38-T31	10/14/91	180	Phase I, one of oldest coatings, RBS data
4	710-N32	10/24/91	408	Sample 712 annealed for 1 hr in-situ
	712-N41		413	Sample 710 had C/Si atomic ratio 1.08

TABLE 2

SiC MEASUREMENTS AND ANALYSES

GROUP	ID	HeNe		SE	
		Measurement	Analysis	Measurement	Analysis
1	620-N21 625-Z11 621-N22 622-N24 623-N24	mult. angle data taken on all these samples	1 layer model showed n varying with thickness 2 layer model consistent within a batch, batch-to batch variation in index	mult. angle 1.5 to 4.5 eV on all these samples	inverted to get e Determined e with 1 and 2 layer models
2	764-N36 765-N37 770-N38	single angle data taken on these samples	index values were consistently lower	single angle 1.5 to 4.5 eV	determined e
3	38-T31	Not measured due to thick oxide overlayer		single angle 1.5 to 4.5 eV	determined e and computer fit
4	710-N32 712-N41	single angle		mult. angle 1.5 to 4.5 eV	determined e with 1 and 2 layer model

TABLE 3

One-Layer Model and Two-Layer Model Results for Refractive Index n and Thickness t (single freqency 632.8 nm and k=0)

ID	One-layer Model		Two-layer Model (with 2 nm roughness)	
	n	t	n	t
620-N21	2.723	26.5	2.802	25.7
625-Z11	2.750	40.2	2.787	39.6
621-N22	2.810	61.0	2.807	61.3
622-N24	2.637	409.5	2.727	394.0
623-N24	2.982	1030.6	3.090	991.2
764-N36	2.638	34.7	2.688	33.9
765-N37	2.635	37.9	2.677	37.1
770-N38	2.676	35.2	2.725	34.4
38-T31	N/A		N/A	
710-n32	2.922	397.5	2.926	397.3
712-n41	2.810	408.5	2.827	405.9