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Evaluation of a Procedure for the Measurement of Thin Film Thickness by X-ray Reflectivity

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ABSTRACT

While the theoretical bases for x-ray reflectivity (XRR) have been known for decades, it has been only in the last 5 years that their application to the measurement of roughness, density, and thickness of thin films (~10-1000 angstroms) has started to gain momentum. This is due to recent improvements in x-ray diffraction (XRD) instrumentation and to the increasing use of thin films in many technological fields. While publications related to XRR have been increasing considerably, the need for the development and evaluation of a simple experimental procedure has not been addressed. This paper describes an XRR procedure for the measurement of the thickness of thin films which was developed using a conventional x-ray powder diffractometer with a solid state detector and the same deconvolution programs used for powder XRD. The standards used in the development and the determination of the precision and reproducibility of the method consisted of three SiO_2 standard thin films (200-500 angstroms). The thickness of two of the films were measured by Rutherford backscattering spectroscopy (RBS), variable angle spectroscopic ellipsometry (VASE), and by transmission electron microscopy (TEM). The third standard was analyzed by VASE and conventional ellipsometry. The measurements using other techniques were made in order to compare and obtain an estimate of the accuracy. The results showed that the method is very precise (0.5% standard error), and good accuracy is indicated by the closeness of the values for the thickness as compared to the values obtained by the other techniques. An example of the application of the method would be the calibration of thin film deposition instruments by measuring the thickness of films deposited on witness plates. The advantages and disadvantages of the different techniques as compared to XRR are discussed.

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INTRODUCTION

The study of the scattering of electromagnetic waves such as x-rays is a powerful tool used to obtain information about the structural properties of interfaces. X-ray reflectivity (XRR) and low angle (grazing incidence) x-ray diffraction are especially useful for the study of thin films (<1000 angstroms). The equations to calculate thickness, density, and roughness of a thin film have been established since the 1920s and 1930s (1-3) from the principles of x-ray reflectivity.

The useful information from an x-ray reflectivity experiment is contained in approximately the first six degrees of an angle of incidence vs. intensity pattern. As the incidence angle is increased, diffraction occurs. A conventional x-ray powder diffractometer may be used to obtain diffraction and reflectivity patterns of thin films.

In this study we deal solely with x-ray reflectivity. The equations used to calculate parameters from x-ray reflectivity data are the result of modifications and simplifications based on the original equations describing the theory of x-ray reflectivity. We have used R. Lengeler's simplified equations (4).

When a beam of x-rays hits a surface at an incidence angle close to zero, total reflection occurs because there is no absorption of the x-ray beam by the surface of the film.The angle at which total reflection occurs depends on the density and number of electrons of the atoms involved. After the high intensity total reflection peak is observed, a series of peaks appears, decreasing in intensity as the angle of incidence increases. The peaks are mainly caused by the fact that x-rays reflected from the surface have a shorter path to the detector than those reflected from the interface between the thin film and the substrate (figure 1) and they interfere. Of course the films must be thin enough so the x-rays are reflected from the interfaces and not absorbed by the material. The peaks are, therefore, interference fringes (figure 2). From the angular

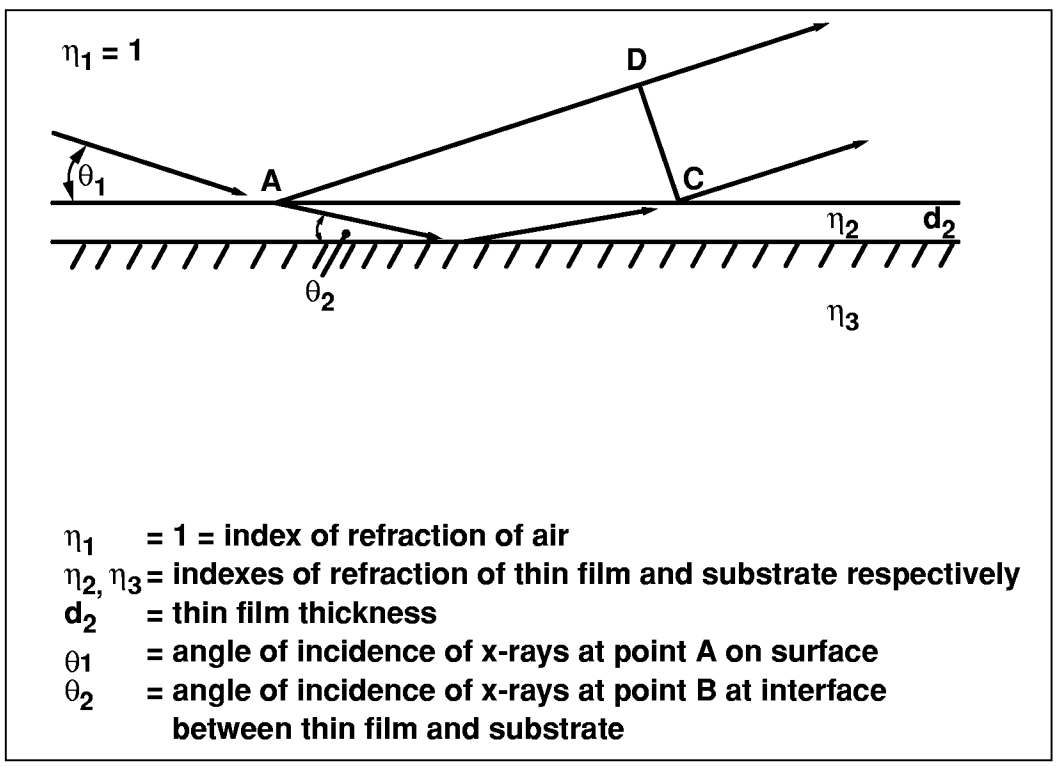

Figure 1. Reflection of X-rays Under Grazing Incidence From a Layer (η_2, d_2) on a Substrate (η_3).

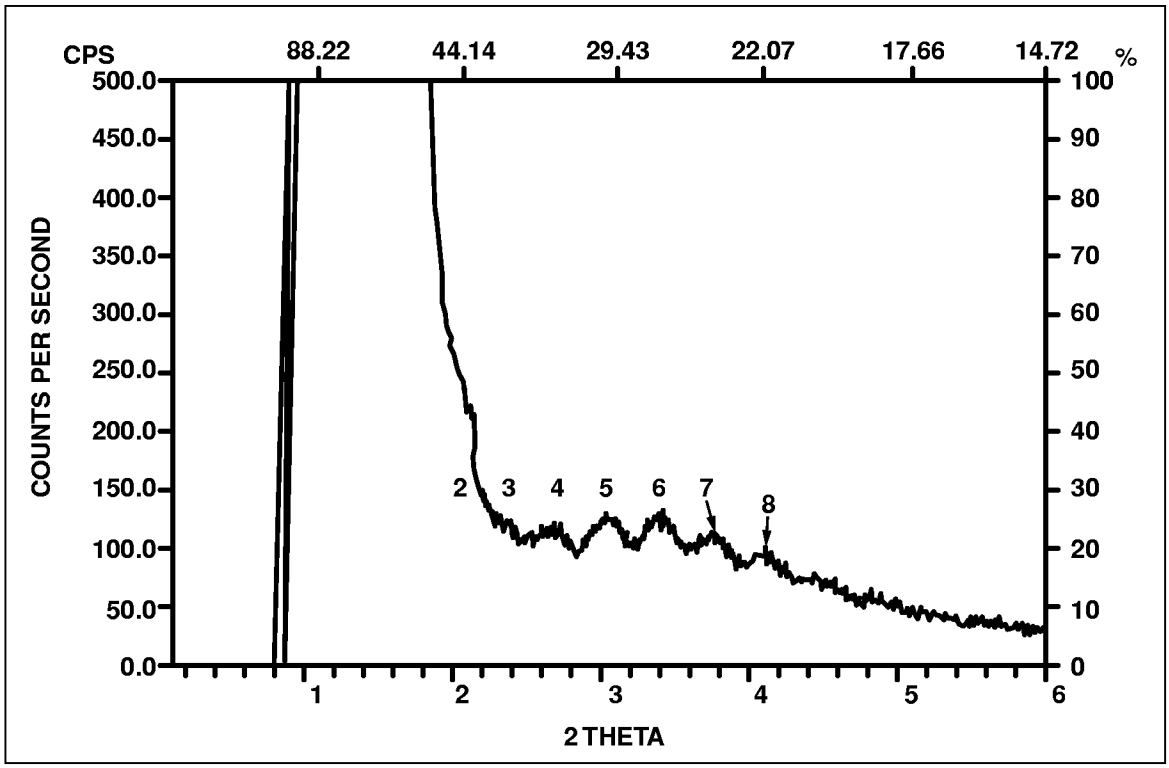

Figure 2. X-Ray Interference Pattern for Standard #1 (2–2).

position of the interference fringes, the thickness of the film can be calculated from equation 1a (4) when the index of refraction of the substrate is higher than that of the thin film, and 1b (4) when it is smaller. See Appendix B for derivation.

$$\theta^2 = \theta_c^{\,2} + (\nu+1/2)^2\, \lambda^2/4d^2 \qquad (1a)$$

$$\theta^2 = \theta_c^{\,2} + \nu^2\lambda^2/4d^2 \qquad (1b)$$

where:

θ = angular position of the maximum of each fringe

θ_c = angle of total reflection

ν = fringe order number

λ = wavelength of the x-rays used (Cu Kα1.54 Å)

d = thickness

From the decrease in the height of consecutive peaks, it is also possible to determine the roughness (5) of a thin film. These calculations are more involved and are usually performed using special software (6). The x-ray reflectivity of a thin film is very sensitive to the roughness, and XRR is a powerful technique to determine surface roughness. As the roughness increases, the intensity of the interference fringes decreases until the higher angle interference peaks start to disappear. There is a point where all interference peaks disappear and therefore, the XRR technique cannot be used. The value of roughness which destroys interference depends on the material and experimental conditions. For example, a simulated XRR pattern using GaAs substrate with a 500 angstroms thin film of Ge and 15 angstroms (6) roughness at the surface produced a reflectivity interference pattern with three peaks after which the interference peaks disappeared. At least two peaks are necessary for measuring the thickness.

Another limitation of XRR in addition to roughness is thickness.

Accurate information can be obtained for films <1000 angstroms thick (sometimes thicker than 1000 angstroms) and as thin as 20 angstroms with the aid of special software.

In addition, it is possible to determine the thickness of interfaces and layers on a multilayered specimen. These calculations also require special software.

A comparison among several techniques used to measure the thickness of thin films is shown in Table 1.

We can observe that x-ray reflectivity is the most versatile technique overall and in addition, has an advantage in that the instrumentation can also be used to determine whether the film is crystalline or amorphous. If crystalline, its chemical structure can be determined by using grazing angle x-ray diffraction (to do this the film must have a thickness of 500Å or higher to produce intense enough x-ray diffraction peaks). All of these measurements can be made without modifying the instrument.

Another important advantage of XRR is that the optical constants are not required to calculate thickness as is the case in the variable angle scanning ellipsometry (VASE) or ellipsometry methods.

Table 1. Comparison of XRR With Other Thin Film Analysis Techniques

	XRR	TEM	ELLIP	VASE	RBS	AES	XPS
• Nondestructive	X		X	X	X		
• Use of Index of Refraction			X	X	X		
• Type of Material:							
Amorphous or Crystalline	X	X	X	X	X	X	X
Organic or Inorganic	X	Limited	In.	In.	X	In.	In.
Conductive or Nonconductive	X	Cond.	X	X	X	Cond.	Cond.
Liquid or Solid	X	Sol.	Sol.	Sol.	Sol.	Sol.	Sol.
Transparent or Opaque	X	X	Trans.	Trans.	X	X	X
Note: X means both in the above items.							
• Sensitivity	10Å	10Å	10Å	10Å	2Å	20Å	50Å
• Average Cost of Instrumentation	150K	500K	100K	200K	500K	700K	600K
• Multilayers	X	X	X	X	X	X	X
• Chemical Composition Information	X*				X	X	
• Roughness (quality of the film)	X						
• Density	X**						

*If the films are 500 angstroms or more, x-ray diffraction patterns may be obtained by grazing angle techniques.

**By using equation 1 after plotting equation 2 and obtaining the value of the intercepts.

XRR = X-ray reflectivity
TEM = Transmission electron microscopy
Ellip. = Ellipsometry
VASE = Variable Angle Scanning Ellipsometry
RBS = Rutherford backscattering
AES = Auger electron spectroscopy
XPS = X-ray photoelectron spectroscopy

The sample size requirements for x-ray diffraction (XRD) depends on the size of the sample holder in the instrument (usually about 4 cm^2). In addition, the sample must be flat.

In the past few years, there has been a wide range of publications concerning applications of XRR to study thin films and several of these have been very helpful in this study (7, 8, 9). However, for our applications, a simplified and proven procedure for the measurement of thickness was needed[1].

EXPERIMENT

The x-ray reflectivity measurements were performed using a Scintag[2] PAD V powder Diffractometer with a Scintag Peltier and water cooled detector.

The SiO_2 thin films were prepared under contract with J.A. Woollam Co.,[3] Inc. by thermal oxidation of silicon wafers (6.5 cm in diameter). The analyses by VASE, Rutherford backscattering (RBS), and transmission electron microscopy (TEM) were also included in the contract. The nominal oxide thickness for the standards were 100 and 200 angstroms. The disks were broken in several pieces and these samples were submitted for analysis by the different techniques.

The samples were placed in the sample holder making sure that their surface coincided exactly with the diffraction plane. The standards were relatively thin (~.5 mm) so they were placed on top of a thicker block (1 cm) that fit the holder.

The following conditions (optimal) were used for the scans:

Detector

Slits = scatter .3 mm and receiving .5 mm
Scan range = 1-5 degrees
Scan mode= step scan
Step size = .01 degrees
Preset time = 10 seconds per step (total scan time/sample=67 minutes)

X-ray tube

Target = Copper
Cu Ka radiation wavelength = 1.54 Å
Slits = scatter 1 mm and divergence 2 mm
Power = 40 mA, 45 kV

XRR patterns were obtained at three different areas on each specimen by moving its position in the holder. Under the above conditions, the x-rays can illuminate an area of about 1 cm^2 (maximum) on the specimen. Each specimen was placed in the holder in such a way that the area illuminated by the x-rays was within the total area of the specimen. The areas analyzed overlapped each other since the specimens were not large enough to analyze three independent areas. On each area, 10 different XRR patterns were obtained (without moving the specimen) to determine the instrumental error.

The positions of the fringes were determined using the deconvolution program used for identification of x-ray peaks during a normal x-ray powder diffraction analysis.

The positions of the fringes (θ^2) were plotted vs. $(\nu+1/2)^2$ (figure 3). Our interference patterns have some of the fringes overlapped by the total reflection peak because we used high wattage in the x-ray tube to obtain fringes of low intensity. We assigned the fringe order from the plot of angular position

[1] We do not have the values of density and roughness of our films by other methods, therefore, our evaluation concerns only the measurement of thin film thickness.
[2] Scintag Inc., 707 Kifer Road, Sunnyvale, CA 94086.
[3] J.A. Wollam Co. Inc., 650 J Street, Suite 39, Lincoln, NE 68508.

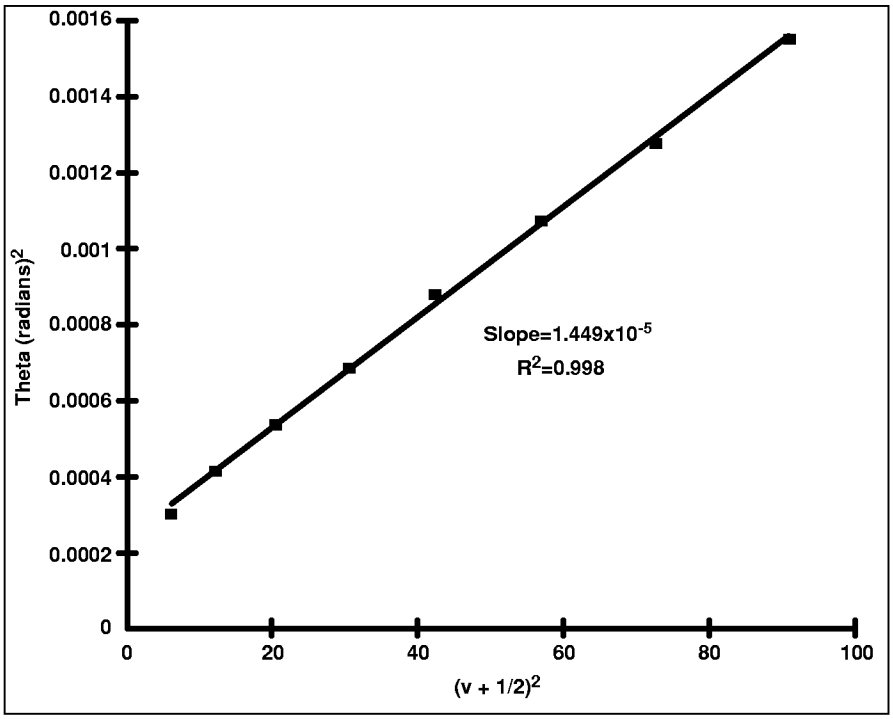

Figure 3. Theta vs. Fringe Order for Standard #1 (2–2).

vs. the fringe order that gave us the straightest line. In the majority of our cases, the best line was obtained by assigning the number seven to the first fringe that we were able to observe. The slopes and standard deviation from the best-fit line were obtained using Microsoft Excel spreadsheet software. The thickness (d) was calculated from the slope (m) since $m=\lambda^2/4d^2$ (see Appendix B).

RESULTS

The values of thickness measured by XRR are shown in Table 2.

There are two sources of variation in the measurements, one is because of instrumental factors and the other is because of the sample itself.

Table 2. Measured Thickness by XRR (angstroms +/- Standard Deviation)

FILM #	AREA 1	AREA 2	AREA 3	AREA 4	AVERAGE
1	207+/- 1	204+/- 1	203+/- 1		205+/- 2
2	470+/- 2	472+/- 2	476+/- 2	479+/- 2	474+/- 3
3	380+/- 1				

Note: 10 XRR measurements were made per area.

In order to determine the instrumental error, 10 measurements were performed on 3 to 4 areas. These measurements were performed without moving the sample or changing any of the experimental conditions. The instrumental error can be determined from each of the 10 reflectivity patterns and from the variation among them. The instrumental error present in each individual measurement is given by the correlation coefficient of the best fit lines obtained. Figure 3 is an example of one of these lines for the second measurement on area 2 of film #1 (see Table 2). These coefficients were very consistent and reproducible with an average values of 0.997 +/- 0.002. The other part of the instrumental error is determined from the variations among the slopes of the reflectivity curves for a given area on a specimen. This variation was always less than 0.5%.

The variation mainly caused by the sample characteristics was determined by moving the sample and obtaining reflectivity patterns of a different area. The variation observed was about 1%. This small value suggests that the specimens used for the XRR analysis are fairly uniform in thickness.

A comparison of the values of thickness as measured by different techniques is shown in Table 1. The standard experimental errors for each method are approximate.

In the case of VASE, two small spots of 1mm^2 each were analyzed on each standard and the values ranged from 213-293 Å for film #1 and from 430-509 Å for film #2. The value given in Table 3 is an average. The RBS analysis was performed on a single area of approximately 1 mm^2. The area analyzed by XRR is approximately 4 cm^2.

The film labeled #3 is not from the same batch as the others. This film was purchased for calibration of the XPS. For this reason, the film was not analyzed by all techniques only by VASE, by the manufacturer, and ellipsometry in our laboratory. The higher intensity of the fringes and their symmetry for this standard suggested that this film is smoother than the others.

The values for thickness for films #2 and #3 by XRR are in good agreement with the other techniques. According to the VASE results, film # 2 is not uniform over the entire area of the disk but there is a deviation from the average of at least 40 angstroms as indicated. It is important to note that the areas analyzed by VASE are small (1 mm^2) and far apart (approximately 4 cm across the middle).

Table 3. Measured Thickness by Several Techniques

FILM #	XRR	RBS	VASE	TEM	ELLIP.
	(+/- 2)	(+/- 10)	(+/- 40)	(+/- 4)	(+/- 4)
1	205	250	253	180	
2	474	480	470	470	
3	380		400		390

Note: The +/- values indicate averages in the case of XRR and VASE (3 and 5 areas analyzed per film respectively, the instrumental errors for XRR and VASE are +/- 1 and +/- 4 angstroms respectively) and instrumental errors for RBS and ellipsometry (because only one area was analyzed per film by these techniques). The ranges of thickness for VASE are 213–293 and 430–509 angstroms respectively.

The fact that the results for film #2 by all the techniques agree so well may mean that the areas analyzed were close. In the case of film #1 there is also a deviation from the average value of thickness 40 angstroms as in film #2, but it appears that the areas analyzed by XRR, TEM, and the thinner area analyzed by VASE (213 angstroms) were close while the area analyzed by RBS is farther. This would explain why the RBS value of thickness vary considerably from the others for film #1. It is, thus, most likely that the variations found among methods arebecause of variations in the films themselves rather than the small experimental errors associated with each technique.

It is not easy to determine with certainty which technique is the most accurate, however it is important to note that XRR has only a few possible sources of error and these can be easily minimized by using a good software program to determine accurately the angular position of the fringes' maxima and by keeping the diffractometer well aligned.

CONCLUSION

X-ray reflectivity is, in general, a very versatile, accurate, and precise technique to determine the thickness of thin films. The XRR procedure developed and evaluated in this study is relatively simple and fast. There is no special sample preparation required as in TEM. The method is also reproducible and accurate if we consider that the sources of error are only the alignment and the positioning of the fringes which can be easily minimized. In addition, our results are in good agreement with measurements of thickness performed by other techniques when the films are uniform in thickness. The sources of error for methods like ellipsometry and VASE include inaccurate values of indexes of refraction for the material analyzed. Sometimes these values are not available. The main source of error in the RBS is the theoretical calculation of the density of a film. These densities are usually not known, a priori. However, they are required in order to calculate the thickness.

The time necessary for the XRR analysis of one sample is about one hour and about another hour or less to process the data and calculate the thickness. The time required by RBS is similar but TEM, VASE, AES, XPS, and ellipsometry require more time.

We expect that this procedure will be very helpful in studying thin films for space applications including for example, monitoring of thickness in vapor deposition chambers.

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APPENDIX A

From figure 1(4), Lengeler derives formulas 2a and 2b as follows:

When the angle of total reflection for the thin film θ_1 is exceeded, the x-rays penetrate into the film. The x-rays reflected from the surface have a different amplitude than the x-rays reflected from the interface between the thin film and the substrate and can interfere.

The difference in optical path is:

$$J = (AB + BC)\,\eta_2 - AD = 2d_2\theta_2 \sim 2d_2\sqrt{\theta_1 - \theta_{1c}}$$

The reflectivity shows maxima and minima as a function of θ_1. The maxima are at:

$$\nu\lambda = 2d_2\sqrt{\theta_1^2 - \theta_{1c}^2} \qquad \text{for } \eta_2 < \eta_3$$

$$(\nu+1/2)\lambda = 2d_2\sqrt{\theta_1^2 - \theta_{1c}^2} \qquad \text{for } \eta_2 < \eta_3$$

From here equations 2a and 2b are obtained by rearranging the terms.

APPENDIX B

Calculation of Film Thickness

The angular maxima of the fringes shown in figure 2 were determined using a Pearson VII algorithm from the Scintag XRD software package. This algorithm tries to fit the shape of the fringe to a Pearson VII equation, and after several iterations to reduce the error, the maxima (2θ) is calculated. For film #1 (2-2) the following angles were obtained:

ν	θ^0	θ^2 **(radians)**
1	1.0022	.000306
2	1.1686	.000416
3	1.3289	.000538
4	1.5008	.000686
5	1.6957	.000876
6	1.8729	.001069
7	2.0401	.001268
8	2.2482	.001540

The first and second fringes were partially hidden by the total reflection peak (figure 2). The computer program was, however, able to locate maxima. These values were considered acceptable because we obtained a very good straight line (R^2 >0.99) when we used these values. Sometimes the low angle fringes are not visible at all and we do not know if the first peak observed is actually fringe 1. In this case, it is recommended to plot the values of angles assuming different fringe numbers until a straight line is obtained. For example, above, we assigned first angular value to fringes 1, 2, and 3. The line where the first angular position was assigned to fringe 1 had the higher value of R^2 and these R^2 values decreased with increasing fringe number.

The slope of the plot of θ^2 (radians) vs. $(n+1/2)^2$ (figure 3) is 1.449×10^{-5} radians.

This slope is equal to $\lambda^2/4d^2$ (2a) or $d=\lambda/2\sqrt{m}$, where λ=1.5406 Å and $2\sqrt{m}$= 7.6×10^{-3} (value rounded according to a 0.2% error).

The calculated thickness is 1.5406 (+/- 0.0001)Å/ 7.6×10^{-3} (+/- 0.0005) =202.6 (+/- 0.2)Å.

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13. ABSTRACT *(Maximum 200 words)*
While the theoretical bases for x-ray reflectivity (XRR) have been known for decades, it has been only in the last five years that their application to the measurement of roughness, density, and thickness of thin films (~10-1000 angstroms) has started to gain momentum. This is due to recent improvements in x-ray diffraction (XRD) instrumentation and to the increasing use of thin films in many technological fields. While publications related to XRR have been increasing considerably, the need for the development and evaluation of a simple experimental procedure has not been addressed. This paper describes an XRR procedure for the measurement of the thickness of thin films which was developed using a conventional x-ray powder diffractometer with a solid state detector and the same deconvolution programs used for powder XRD. The standards used in the development and the determination of the precision and reproducibility of the method consisted of three SiO_2 standard thin films (200-500 angstroms). The thickness of two of the films were measured by Rutherford backscattering spectroscopy (RBS), variable angle spectroscopic ellipsometry (VASE) and by transmission electron microscopy (TEM). The third standard was analyzed by VASE and conventional ellipsometry. The measurements using other techniques were made in order to compare and obtain an estimate of the accuracy. The results showed that the method is very precise (0.5% standard error), and good accuracy is indicated by the closeness of the values for the thickness as compared to the values obtained by the other techniques. An example of the application of the method would be the calibration of thin film deposition instruments by measuring the thickness of films deposited on witness plates. The advantages and disadvantages of the different techniques as compared to XRR are discussed.

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