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Final Report

SYNTHESIS AND PROPERTIES OF LAYERED SYNTHETIC
MICROSTRUCTURE (LSM) DISPERSION ELEMENTS FOR
62 eV (200Å) to 1.24 keV (10Å) RADIATION
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This report is the final report of a research program entitled "Synthesis and Properties of Layered Synthetic Microstructure (LSM) Dispersion Elements for 62 eV (200Å) to 1.24 keV (10Å) Radiation," performed at Stanford University under the sponsorship of the Department of Energy through Lawrence Livermore National Laboratory and the Regents of the University of California (subcontract No. 5303809). The term of the contract was twelve months starting May 18, 1979 with a no-cost extension through August 1, 1980.

The thrust of this research was to perform experiments designed to explore the x-ray dispersion behavior of LSM structures so that the synthesis process limitations could be determined and the dispersion behavior characterized. The results of these experiments, performed at several laboratories, are included in a paper entitled "Sputtered Layered Synthetic Microstructure (LSM) Dispersion Elements," by Troy W. Barbee, Jr., and included as the body of this report. This paper was presented at the "Topical Conference on Low Energy X-Ray Diagnostics," Monterey, California, July 8-10, 1981, and will be published by the American Institute of Physics as part of the Proceedings of this conference.

In addition to the work reported in the above paper, several LSM elements were delivered to LLNL for characterization and application in laser fusion diagnostics. These were characterized at B. L. Henke's laboratory and applied as part of a fixed angle multi-channel spectrograph for the spectral range 100 eV to 1000 eV by Dr. G. Stradling. Also, preliminary explorations of synthesis of LSM structures on figured surfaces were performed with semi-quantitative characterization. It appears that high quality structures can be deposited onto mechanically prepared surfaces.

This work is being continued under support by LLNL under subcontract LLL #269-5501. Dr. D. T. Atwood is the technical monitor.

Sputtered Layered Synthetic Microstructure (LSM) Dispersion Elements

by

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ABSTRACT

The opportunities offered by engineered synthetic multilayer dispersion elements for x-rays have been recognized since the earliest days of x-ray diffraction analysis. In this paper, application of sputter deposition technology to the synthesis of Layered Synthetic Microstructure (LSMs) of sufficient quality for use as x-ray dispersion elements is discussed. It will be shown that high efficiency, controllable bandwidth dispersion elements, with d spacings varying from 15 Å to 180 Å, may be synthesized onto both mechanically stiff and flexible substrates. Multilayer component materials include tungsten, niobium, molybdenum, titanium, vanadium, and silicon layers separated by carbon layers.

Experimental observations of peak reflectivity in first order, integrated reflectivity in first order, and diffraction performance at selected photon energies in the range, 100 to 15000 eV, will be reported and compared to theory. Emphasis is placed on results giving information concerning limiting structural characteristics of these LSMs. It will be shown that the observed behavior is in accord with theory, both kinematic and dynamic regimes being clearly observed. In addition, the mosaic spread of these LSMs is not detectable, indicating that they are perfect structures. A consistent explanation of these experimental results indicates that roughness at the interfaces between constituent layers is the structural characteristic currently limiting diffracting behavior.

1. Introduction

Early in the development of the field of x-ray diffraction, it was proposed that synthetic man-made materials consisting of alternating layers of high atomic number and low atomic number elements would be useful as dispersion elements for x-rays. Such structures, termed layered synthetic microstructures (LSM) in this paper, were the subject of several investigations. The primary difficulties encountered in this early work were technological, being associated with the synthesis process and materials selection. In this section, a short summary of these efforts will be presented with emphasis on delineation of generic limitations and the structure of this paper outlined.

Earliest efforts (1,2) to form synthetic structures were unsuccessful, the first successful work being that of Dumond and Youtz (3) who vacuum deposited copper/gold LSMs with a characteristic period of approximately 100 Å. Strong dispersing power for Mo K α radiation was observed but decayed, due to the interdiffusion of the components, in approximately one week. More recently, Dinklage and Frericks (4) and Dinklage (5) prepared layer structures of lead/magnesium, gold/magnesium, and iron/magnesium. The lead, gold/magnesium systems exhibited instability due to reaction or diffusion in a manner similar to copper/gold. Iron/magnesium, on the other hand, exhibited stability projected to be longer than one year. In addition, the Fe/Mg-LSM showed many orders of reflection in diffraction scans and exhibited diffracting behavior comparable to ADP and lead stearate.

Since then, a substantial effort to synthesize normal incidence mirrors for soft x-rays has been undertaken by Spiller (6-12) and his associates. Their work has been primarily with radiation having wavelengths longer than 100 Å, though characterization has been made using Cu K α (1.5418 Å) radiation. Analytical procedures have also been developed that are based on optical dispersion theory that allow description of the expected behavior of LSMs. Semiquantitative comparison has been made with results obtained using Cu K α radiation and reasonable agreement attained. Particular emphasis in this work has revolved about improving the interface roughness between constituent layers of the LSMs. It has been demonstrated that inclusion of a correction factor

for such roughness significantly improves the agreement between calculations and experiment.

The synthesis procedure initially used by Spiller was thermal evaporation controlled by quartz crystal oscillators. Difficulties with layer thickness control were encountered due to thermal drift of the oscillators caused by radiation heating from the electron-beam thermal sources. This has been corrected by using an x-ray interference monitoring technique, allowing continuous determination of the individual layer thicknesses during deposition and considerable improvement has been achieved with this process control modification. In addition, the effect of substrate character has been explored with inherently smooth substrates being demonstrated as clearly optimum.

Work at Stanford by the author (13-15) initiated in early 1976 (under NSF/MRL sponsorship through its Center for Materials Research) was on the development of a technique for the synthesis of LSM materials using sputtering technology. In the fall of 1978, it was clear that high efficiency x-ray dispersion elements for Cu K_{α} radiation has been synthesized with a period of ~ 20 Å. These samples were characterized by Mr. L. Kappel of Lawrence Livermore National Laboratory (LLNL) over the energy range 4.5 to 11.5 keV using standard powder diffractometry and a high-resolution of Si (Li) energy dispersive detector. This result represented an existence experiment and indicated that substantial research into the reproducibility and general breadth of periods and constituent materials should be undertaken.

In addition to work specifically oriented toward LSM dispersion elements for x-rays, other investigators have been pursuing the application of such materials as neutron dispersion elements. Saxena and Schoenborn (16), have investigated manganese/germanium structures. Synthesis process control difficulties resulted in substantial imperfection in their materials, though high reflectivities were achieved. These investigators also developed an analytical approach based on scattering theory allowing closed-form description of the intensities diffracted in both the kinematic and dynamic regimes, ignoring absorption effects. In summary, the work on neutron dispersion elements has been consistent with the experience of others and yielded devices of interest to this community.

It is also important to mention the ongoing research on semiconducting materials and on metal/metal LSMs. Molecular beam epitaxy (MBE) (17-21) is the term usually used to describe these processes which are being utilized in many laboratories in the world. Highly perfect LSMs have unique properties and possible significant applications. In metal/metal systems, the results are somewhat less well defined (21-25) as the field is significantly less mature and the variation in material properties definitely much broader than exhibited by semiconductor materials. Again, many of the problems already described in the discussion of dispersion element work have been encountered in this work and engineering solutions achieved. At this time, significant advances in this field will be forthcoming as a better understanding of material effects is gained.

In summary, significant effort in a limited number of laboratories has been placed on the synthesis of LSMs with characterization by a variety of means implemented. Primary difficulties have been encountered with respect to process control, substrate character, and choice of constituent materials. These problems are now under serious investigation and will be considered more fully in the following presentation.

In the following, a short review of the theory of the diffracting behavior of LSM dispersion elements pertinent to this paper will be presented first. The sputter deposition synthesis process will then be reviewed. Experimental results obtained using tungsten/carbon (W/C), vanadium/carbon (V/C) and titanium/carbon (Ti/C) LSM's are then considered. Two applications of these LSM dispersion elements as spectroscopic devices are then presented. The paper is then summarized and recommendations as to further research discussed.

II. Modeling and Theory

Modeling of the diffracting behavior of LSMs takes many approaches all of which are discussed in other papers in this Conference proceedings. The discussion included here is specific to the data presented in the following sections and is not intended to be more than a summary.

The x-ray dispersion behavior of LSMs can be modeled from two viewpoints. One corresponds to the approach taken in the analysis of

x-ray diffraction from crystal-scattering theory. The other follows directly from optical dispersion theory as applied to various types of interference structures. In this section, these two treatments are separately considered with reference to the work of Saxena and Schoenborn (15) and of Spiller (12) (optical dispersion theory), and of Underwood and Barbee (26, 27).

A LSM is made up of two materials, A and B, arranged alternately in layers of thickness d_A and d_B , respectively. The structure is thus periodic in the direction perpendicular to the planes, with a period $d = d_A + d_B$. x-rays of wavelength λ , incident at a glancing angle θ on the planes, will be scattered by each layer of atoms. At the Bragg angles θ_n , given by the relation

$$n\lambda = 2d \sin \theta_n \quad (1)$$

the scattered waves will add in phase and the total scattered amplitude will reach a maximum. The positive integer n represents the order of the Bragg "reflection."

Computation of the intensities of the Bragg reflections for an LSM requires the solution of Maxwell's equations in a material having a periodically varying dielectric constant. The problem is exactly analogous to the computation of Bragg reflection intensities from natural crystals, and either of two theoretical approaches may be adopted. In the kinematical theory, the scattering from each volume element is treated as being independent of that from the other volume elements. This theory neglects the details of the wave interactions within the structure, in particular the progressive reduction in amplitude of the forward wave as it travels into the structure and is partially reflected by successive planes (extinction). In the dynamical theory, all wave interactions are taken into account. The dynamical theory is customarily used in the study of the x-ray diffraction from large perfect crystals, while the kinematical theory is more appropriate to the study of thin crystals or "mosaic" crystals which can be thought of as being composed of large numbers of small crystallites whose orientations differ slightly, in a random fashion, from the mean of the crystalline planes examined.

The LSMs are essentially "perfect" from a crystallographic point of view. Although the fabrication process may introduce variation in layer thickness, these errors are not equivalent to the mosaicity of a natural crystal. It is, therefore, more appropriate to use a dynamical theory to compute their properties, although a kinematical approximation suffices if an LSM is of low diffracting power.

A. Scattering Theory

It has been shown by Saxena and Schoenborn (16) that the diffracting power of an LSM, from scattering theory, with $d_A = d_B$ and sharp interfaces between layers is given by:

$$\frac{I}{I_0} = \frac{4}{\pi^2} \frac{N^2 d^4}{n^4} (f_A - f_B)^2 \quad (2)$$

in the kinematic approximation where N is the number of planes, d the period, n the order of the Bragg reflection, and f_A and f_B the atomic form factors for the layers A and B. In the dynamic range this becomes:

$$\frac{I}{I_0} = \tanh^2 \Lambda \quad (3)$$

where $\Lambda = \frac{2}{\pi} \frac{Nd^2}{n^2} (f_A - f_B)$. Note that the diffracted intensity is proportional to $N^2 d^4$ in the kinematic range.

Also, in the kinematic regime the peak width of the Bragg peaks is defined by the number of reflecting planes in a manner directly analogous to the line width dependence on the number of grooves in an optical grating. Analyses of this diffraction effect for structures such as represented by LSMs (28) yields the relationship (Scherrer equation) between full width at half maximum for a Bragg peak, $\Delta 2\theta_{1/2}$, and the crystal thickness $D = Nd$ given as

$$\Delta 2\theta_{1/2} = \frac{0.898\lambda}{Nd \cos \theta_n} \quad (4)$$

where θ_n is the Bragg angle of the n^{th} order reflection. Note that dynamic calculations yield $\Delta 2\theta_{1/2}$ value in agreement with this relationship in the kinematic regime.

B. Dynamical Optical Dispersion Theory Including Absorption (DODT).

When the incoherent absorption in the layer material is taken into account, the dynamic theory becomes difficult to treat analytically. It is therefore better to adopt a computational approach. The approach adopted is analogous to those used in the computation of properties of multilayer dielectric filters for the optical region of the spectrum. The layer material is characterized by a complex index of refraction

$$\mu = 1 - \delta - i\beta. \quad (5)$$

δ , the real part of the refractive index, μ , is related to f

$$\delta = \frac{\lambda^2}{2\pi} N [(f_0 + \Delta f')^2 + \Delta f''^2]^{1/2} r_e \quad (6)$$

where N is the atomic concentration, r_e the classical radius of electron, f_0 the atomic form factor and $\Delta f'$, $\Delta f''$ the anomalous dispersion coefficients while β is related to the linear absorption coefficient μ_a of the material by

$$\beta = \frac{\lambda}{4\pi} \mu_a \quad (7)$$

The method used is based on a treatment of x-ray interference by a few contaminant layers on the surface of a glancing incidence x-ray mirror. However, approximations made by considering δ , $\Delta f'$, and $\Delta f''$ to be small and, furthermore, considering only the σ component of polarization limit this theory and modifications are required to treat more general cases. The theory, together with the required modifications, is given in the article in this volume by Underwood and Barbee (27, 28).

C. Interfacial Roughness

In the calculations described thus far it has been assumed that the interfaces between layers are ideal, smooth and fully specularly reflecting. If the surface is not smooth a fraction of the radiation is not specularly reflected and the diffraction efficiency of the LSMs is reduced. Simple theory (29, 30, 31) gives the reduction in reflectivity

for a single film as a function θ , the angle of incidence, of the x-rays as:

$$I/I_0 = I/I_0|_{\text{Ideal}} \exp\left[-\left[4\pi \frac{\sin\theta}{\lambda} \Delta z\right]^2\right] \quad (8)$$

where $I/I_0|_{\text{Ideal}}$ is the reflectivity calculated for ideal interfaces, λ the wavelength and Δz a surface roughness parameter. Rearrangement of eq. (1) and substitution in eq. (8) yields:

$$\frac{I}{I_0} = \frac{I}{I_0}|_{\text{Ideal}} \exp\left[-\left(2\pi n \frac{\Delta z}{d}\right)^2\right] \quad (9)$$

where n is the order of Bragg reflection and d the period of the LSM. This approach allows analysis for the surface roughness parameter, Δz , if the diffraction efficiency of many orders of Bragg reflections are known and can be compared to model calculations. All calculations against which direct comparisons are made in this paper used the Dynamic Optical Dispersion Theory (DOET) approach, except where noted. Also, except where noted, all calculations are for unpolarized incident radiation. A computational program developed by J. Underwood (27, 28) was used with values of δ and β taken from the literature or provided by Ping Lee and B. Henke (32). The value of δ and β from the literature have given the largest uncertainty in the modeling efforts, particularly for photon energies lower than approximately 1.5 keV.

D. Refractive Index Correction

The Bragg relationship presented in equation (1) ignored the effects of refraction on the position of the Bragg reflections. This refraction shift can be sizable and represents a method for determining the optical constants as a function of photon energy. These data can then both be compared with literature values for δ and β and used in modeling calculations.

A straight forward analysis (33) yields a relationship between observed Bragg angle θ , refractive index μ , and the d spacing and is given as:

$$n\lambda = 2d\sin\theta \left[1 + \frac{(\mu-1)(\mu-1)}{\sin^2\theta}\right]^{-1/2}. \quad (10)$$

δ for photon energies greater than 1000 eV is typically less than 10^{-4} . For small δ , equation (8) can be approximated as:

$$n\lambda = 2d\sin\theta\left[1 - \frac{\delta}{\sin^2\theta}\right] \quad (11)$$

which can be used at the higher photon energies. The value of δ for a given material is determined from the measured Bragg angle and the true period of the material, d .

It is important to note that the Bragg angle used in these calculations of δ is not that corresponding to the peak diffracted intensity. This results from the effect of absorption on the diffracted intensity on the high angle side of the Bragg peak. The intensity in this region is markedly attenuated with the result that the Bragg peak is asymmetric. The position of the maximum in diffracted intensity falls at a slightly smaller value of θ than the maximum intensity when absorption is ignored. An excellent approximation to the position of the Bragg peak is given by the center angle at half height diffracted intensity. This value of θ is the one used in calculating the values of δ from the position of the Bragg peaks in this work.

It will be seen later that the composite refractive indices for the V/C-LSM determined by this method are in good accord with the predictions of Ping Lee and Henke (32). It is also demonstrated that these samples allow the refractive indices to be determined over a wide range of wave lengths using the same samples.

III. LSM Synthesis

The LSM preparation technique used in this work was previously developed under the sponsorship of the NSF-MRL program as part of the activities of the Center for Materials Research at Stanford University by Dr. T. W. Barbee, Jr. This process, as will be seen, represents a step on the developing path whose end can be termed molecular or atomic engineering. It has been applied to a wide variety of combinations of elements, many of which are specific to x-ray dispersion element devices.

In contrast to the majority of work reported, this process uses fixed magnetron sputtering sources and moving substrates; other processes have used fixed thermal sources and fixed substrates with moving shutters. The system is shown schematically in Fig. 1. Note that all sources (A,B,C) are mounted on the same radius and that the substrate table (below the sources) rotates about the center of this mounting circle. Sources are excited using either dc or rf power and substrates are allowed to thermally float, reaching temperatures of approximately 50°C during a long (>2 hr) deposition run. In the following a more detailed description of this process is given.

Sputter deposition is a complex process into which many parameters intrinsic to vapor deposition enter. In addition, there are many extrinsic parameters associated with the particular apparatus and system geometry which must be considered. These are listed in Table 1. The effects of these parameters are considered in a general manner elsewhere (34-38) and the reader is referred there for a more complete discussion. Items 3, 4, (5, & 7), 8, and 9 are briefly considered in the following.

Also, of importance is the type of sputter source used in the deposition apparatus. Several types are currently available that can be broadly classified as standard and enhanced and are listed in Table 1 along with a simple set of comments on their specific characteristics. The most important information in the table is that it is possible, using magnetron sources, to decouple the sputter plasma from the sample minimizing the effects of high energy ion bombardment and secondary electron effects. Also, the large deposition rates available using magnetron sources, generally an order of magnitude higher than those characteristic of standard diodes, facilitate the synthesis of high quality LSMs.

Fig. 1. Schematic diagram of a triangular array of magnetron sputter deposition sources. When the deposition profiles overlap alloy films may be formed. When the sources are sufficiently separated, the deposition profiles not overlapping, layered structures can be formed on moving substrates.

Fig. 2. X-ray dispersion response of a tungsten/carbon LSM ($d = 22.6 \text{ \AA}$, $n_w = 11.3$, $n_c = 6.2$, C-Top) deposited on (100) orientation single crystal silicon is shown as a function of the energy of the diffracted radiation.

Table 1. Important Parameters in Sputter Source
Vapor Deposition

1. The large atomic quench rate characteristic of vapor deposition.
2. Both surface and bulk atomic motion kinetics - primarily controlled by substrate temperature.
3. The energy distribution of the incident adatoms.
4. The substrate surface morphology.
5. The effects of deposition surface (substrate or deposited film)-adatom atomic interactions.
6. The ambient atmosphere in the experimental apparatus.
7. The effects of the adatom condensation energy.
8. Vapor source-deposition surface interactions.
9. The geometry of the vapor source-substrate configuration.

Table 2. Sputter Sources Characteristics

- I. Standard diodes (R. F., D.C.)
 - A. Rate Low
 - B. Large fraction of power deposited into substrates
 - C. Radiation damage high
- II. Enhanced sources
 - A. Magnetron (R.F., D.C.)
 1. Rate large
 2. Source isolated from substrate. Minimum plasma energy deposited in sample.
 3. Radiation damage minimized
 4. Can be scaled up
 - B. Triode supported (R.F., D.C.)
 1. Rate large
 2. Plasma interaction with substrate large
 3. Radiation damage large
 4. Can be scaled up?

In the apparatus used in this work magnetron sources (A, B, C of Fig. 1) are arranged so that their deposition profiles do not overlap. Deposition onto uniformly moving substrates mounted on a table beneath the substrates at a working distance of 7.5 cm results in the synthesis of layered structures in which both composition and structure can be systematically varied normal to the deposition surface.

of layered structures in which both composition and structure can be systematically varied normal to the deposition surface.

The magnetron sources used are 3"-diameter planar circular configurations. The characteristics of magnetron sources are well documented in the literature, and only those factors important to this application are considered here. Magnetron sources have a magnet structure behind the sputter source plate supporting a fringing field that produces a trap for the secondary electrons important in the argon sputter gas ionization. These electrons are trapped at the target surface, thereby trapping the plasma and increasing the plasma density at the target surface. This trapping mechanism is important as it minimizes the interaction of the deposition surface with the sputtering plasma as well as increasing the deposition rates by approximately an order of magnitude.

The increased sputtering rate results in synthesis of multilayer structures in short times of an engineering scale. A typical run will take no longer than 2 hr. Therefore, control requirements are for stability for a limited time, making synthesis an easier proposition. More importantly, the decoupling of the sputtering plasma from the deposition surface increases the ability to form continuous well-defined layers on the Angstrom scale. In standard sputtering diodes, strong coupling of the plasma to the deposition surface results in an ion bombardment mixing of the constituents that can extend several nanometers into the sample. This degrades the sharpness of the interfaces between layers and, if the layers are thin enough, decreases the composition fluctuation. Such characteristics may be advantageous at large layer thicknesses where interface width will strongly damp the intensities of higher-order Bragg reflections, though for thin layers, this phenomena destroys the layers and results in a homogeneous sample when the layers are sufficiently thin. The nature of the deposits is additionally affected by the sputtered adatom energy, though this is not well documented. The adatoms or depositing atoms have a mean kinetic energy of approximately 8 eV and a tail extending to 80 eV. This can cause interfacial broadening as well as reactions at interfaces where it would not normally be expected.

In addition, substrate rotation results in moving the substrates beneath the sources so that adatom deposition occurs at many angles of incidence. This minimizes the effects of substrate roughness as shadowing is minimized. The basic gain is that substrate quality does not deteriorate and that layering quality is maintained or improved through hundreds of layers.

Many different types of substrates have been investigated, with the most consistent results achieved on single crystal silicon (100) and (111) orientation wafers. Preparation of these materials is done using the technology typical of integrated circuit laboratories. I note here that cleaved mica is also an excellent substrate material yielding results as good as the best silicon substrates. In addition, float glass can be used with success if the quality is high. In some cases very high quality results are obtained with plastic film substrates. In addition, preliminary observations from LSMs deposited in mechanically prepared glass surfaces indicate very high reflectivities. In all cases the area of the sample which is usable is a 2 cm x 7.5 cm rectangular area.

IV. X-Ray Dispersion Behavior of LSMs

Three specific material combinations will be considered in this section, tungsten/carbon, vanadium/carbon and titanium/carbon. The data discussed in the following was gathered in many laboratories by several investigators. These include L. Kappel (L.L.N.L.), G. Stradling (L.L.N.L.), B. Henke and his collaborators (U. of Hawaii), J. Gilfrich and D. Nagel (NRL), T. Barbee (Stanford University), and W. Warburton and T. Barbee, et al. (SSRL).

The techniques used were those typical of x-ray diffraction analysis using standard diffractometry. In some cases white radiation was incident on the sample which was used as a spectroscopic element, the diffracted radiation being analyzed using energy dispersive techniques. In other cases characteristic x-ray emission lines were used with standard detectors, including flow proportional and scintillation counters. At SSRL an apparatus designed to do glancing angle diffraction by W. Warburton was used and allowed data to be collected from Bragg angles of approximately 5×10^{-3} radians.

A. Tungsten/Carbon (W/C)-LSM

The tungsten/carbon system has been extensively studied due to the high electron density fluctuation inherent to this material combination and, hence, the high scattering power per tungsten/carbon layer pair. In addition, this system is stable due to the refractory character of the components and the equilibrium phase diagram which shows that the stable equilibrium is between tungsten carbide (WC) and carbon at temperatures up to $\sim 2800^\circ\text{C}$. In this section the results of a series of experiments designed to provide information concerning parameters important to the performance of LSM as dispersion elements are presented.

Diffraction spectra from a W/C-LSM (78-204; $t_w = t_c = 11.3 \text{ \AA}$; $N_w = 62$) deposited on (100) orientation single crystal silicon are shown in Figure 2. These spectra were taken using the Bremstrahlung radiation from Al or Ti anodes using the LSM as a spectrographic element. The energy of the diffracted radiation varied as the Bragg angle was varied. Peak reflectivity and energy resolution for 9690 eV photons observed are 46% and 295 volts respectively. The drop in reflectivity above 10000 eV is the result of the absorption jump at the tungsten L_{III} edge ($\sim 10300 \text{ eV}$). The fractional change in reflectivity at this edge is in agreement with calculation. These reflectivities are approximately 65% of those predicted by model calculations. This is believed to be the result of interfacial roughness between the constituent layers as will be demonstrated later.

The energy resolutions ($E/\delta E$) shown in Figure 2 are all of the order of 35. These are somewhat less than expected from theory and from examination of the diffracting behavior using $\text{Cu } K_\alpha$ ($\lambda = 1.5418 \text{ \AA}$) radiation. This discrepancy is believed to be the result of the convolution of incident spectrum with the diffracting characteristics of the LSM.

This sample (78-204) is part of a set of samples in which the period of the LSMs was held constant at approximately $21 \text{ \AA}$ and the number of diffracting planes varied so as to explore the transition from the kinematic to dynamic regimes of diffraction response. These samples are described in Table 3 (78-206, 78-204, 78-207, 78-208, 78-209). Peak intensities in first order for $\text{Cu } K_\alpha$ radiation were measured using a

Fig. 3. Calculated and experimentally observed reflectivity in first order for Cu K_{α} radiation for W/C-LSM having $20.3 \text{ \AA} < d < 21.0 \text{ \AA}$ and $N_w = 6, 11, 31, 62, 106$ are plotted as a function of $N^2 d^4$, a parameter for which a linear relationship is expected in the kinematic diffraction regime (see eq. 2).

standard powder diffractometer equipped with a diffracted beam monochromator. These observed peak reflectivities are plotted along with calculated values in Figure 3 as a function of N^2d^4 where N is the number of diffracting planes and d the period of the LSM. It is clear that at small values of N^2d^4 the reflectivities are directly proportional to N^2d^4 in agreement with kinematic theory (Eq. 2). For $N^2d^4 > 10^{-24}$ the reflectivities saturate projecting asymptotically to a value less than 1. This is in accord with theory as shown by the two curves with the experimental values being 50 to 60% of that calculated using the DODT.

It is clear from these results that the experimental diffracted intensity is in general accord with theory though systematically lower. Comparison of full width at half maximum ($\Delta 2\theta_{1/2}$) with calculation also yields information on the structure of these LSMs. Experimentally observed values are listed in Table 3 with values calculated using the DODT and the Scherrer equation (Eq. 4) and the tabulated values of d and N_w , the number of tungsten layers. Note that the number of diffracting planes of eq. (4), N , is given by:

$$N = N_w - 1$$

It is clear from Table 3 that the agreement between the DODT calculations and experiment is excellent. In addition, in the kinematic domain, agreement between experiment and the values of $\Delta 2\theta_{1/2}$ calculated using the Scherrer equation is also good. These results indicate that the LSM structures are highly perfect with angular resolutions $\Delta 2\theta_{1/2}$ in agreement with theory.

The conclusions to be drawn from this data are that the resolutions are in accord with theory demonstrating that the theoretically predicted number of planes are active in the diffraction process. Also, the peak reflectivity in first order is substantially less (~0.6) than that predicted by theory. These are exactly the characteristics attributable to interfacial roughness which is considered in more detail later in this paper.

Table 3. Full width at half maximum ($\Delta 2\theta_{1/2}$) of first order reflections of Cu K α ($\lambda = 1.5418 \text{ \AA}$) radiation from W/C-LSMs calculated using DODT- $\Delta 2\theta_{1/2}(T)$, the Scherrer equation- $\Delta 2\theta_{1/2}(S)$, and experimentally observed $\Delta 2\theta_{1/2}(E)$ are compared.

Sample	N _w	d(Å)	t _w (Å)	Experiment	DODT		Scherrer	
				$\Delta 2\theta_{1/2}(E)$	$\Delta 2\theta_{1/2}(T)$	$\Delta 2\theta_{1/2}(E)/\Delta 2\theta_{1/2}(T)$	$\Delta 2\theta_{1/2}(S)$	$\Delta 2\theta_{1/2}(E)/\Delta 2\theta_{1/2}(S)$
78-206	102	20.3	10.15	0.075	0.76	0.99	0.038	1.96
78-204	62	22.6	11.3	0.085	0.086	0.99	0.057	1.49
78-207	31	20.3	10.15	0.133	0.137	0.97	0.129	1.03
78-208	11	20.3	10.14	0.355	0.356	0.997	0.380	0.95
78-209	6	21.0	10.15	0.69	0.630	1.095	0.74	0.96
78-211	11	24.7	10.0	0.305	--	--	0.318	0.99
78-212	11	33.8	10.0	0.23	--	--	0.232	0.99
78-213	11	59.9	10.0	0.135	--	--	0.131	1.03

Fig. 4. Peak reflectivity in first order for W/C-LSM 78-204, $D = 22.6 \text{ Å}$, $N_w = 62$; 79-086, $D = 52 \text{ Å}$, $N_w = 31$, and 79-091, $D = 58 \text{ Å}$, $N_w = 31$ are presented for photon energies of 277 eV to 15000 eV. These data were collected by B. L. Henke and his students at the University of Hawaii, L. Kappel at L.L.N.L., Jim Underwood at Stanford University, and Troy W. Barbee Jr. at Stanford University and are considered minimum values.

Fig. 5. Observed (39) integrated reflectivity, R , for W/C-LSMs having periods, d , of 21 Å ($2d = 42 \text{ Å}$), 30.5 Å ($2d = 61 \text{ Å}$) and 60 Å ($2d = 120 \text{ Å}$) is shown as a function of the wavelength of the incident radiation. The reflectivities are approximately half that predicted using DDT.

The data presented thus far are limited in that only one photon energy has been used. In Figure 4 peak reflectivity in first order is plotted as a function of photon energy over the energy range (277 eV to 15000 eV) for W/C-LSMs (78-204, $d=22.6$ Å; 79-086, $d=52$ Å; 79-091, $d=58$ Å). The reflectivities observed for the larger d spacing LSMs (79-086, 79-091) are close to values calculated using the DODT both in peak reflectivity and in angular resolution. I note that Ping Lee has calculated the reflectivity in first order (~13%) for W/C-LSMs, $2d=100$ Å for C-K ($E=277$ eV). His results are in good accord with the reflectivity (~12%) shown in this figure for similar samples. Also calculations indicate that the reflectivities over the full spectral range for samples 79-086 and 79-091 are very close to theoretical values. The smaller period sample (78-204) is, as already discussed, somewhat less than theory in reflectivity. It is also important to note that the jumps in reflectivity at the W_M and W_{LIII} edges are in agreement with theory. These values of reflectivity can be easily converted to integrated reflectivity as the observed angular widths of the Bragg diffraction peaks are in excellent agreement with theory though the peak reflectivities are somewhat less than expected.

Integrated reflectivities (39) for a series of W/C-LSMs having periods of 21 Å ($2d=42$ Å) 30.5 Å ($2d=61$ Å) and ~60 Å, ($2d=120$ Å) are shown in Figure 5 for radiation in the wave length range 7 to 13 Å. These samples were synthesized so that the maximum diffracting power was expected. It is important to note that these results semiquantitatively agree with theory.

The comparison of experiment to theory shown thus far has only been parametric consisting of peak reflectivities and peak widths ($\Delta 2\theta_{1/2}$). A comparison between the observed diffraction spectrum using $Cu K_\alpha$ radiation over the angular range $0 < 2\theta < 3.0$ degrees and calculations using DODT is shown in Figure 6 for sample 80-037, a W/C-LSM. The calculation was based on design values for the sample period and the relative thicknesses of the carbon and tungsten component layers. The difference in peak positions is due to the fact that the sample period was 53 Å while the design period was 52 Å. Excellent agreement with the theory is shown, for the critical angle and the secondary Fresnel maxima. Note the experimentally observed peak reflectivity is 55 to 60% while the calculated value is 66%.

Fig. 6. Experimental and theoretical diffraction curves of Cu K_{α} from sample 80-037 ($d = 52.0 \text{ \AA}$, $\tau_w = 17.34 \text{ \AA}$, $n_w = 11$, w-Top) are shown and compared. The data were taken using a standard powder diffractometer equipped with a diffracted beam monochromator.

Fig. 7. Observed peak reflectivity in first order is plotted as a function of $d(\text{\AA})$ for W/C-LSM designed to have constant reflectivity in first order and compared to the predictions of theory in which the effect of a surface roughness ($\Delta Z = 3.15 \text{ \AA}$) is included.

TABLE 4. Peak reflectivity in first order, experimental $\Lambda 2\theta_{1/2}$ and theoretical $\Lambda 2\theta_{1/2}$, for W/C-LSM of varying d designed to have constant reflectivity for Cu K_α .

	$d(\text{\AA})$	N_w	$I/I_0(\%)$	$\Lambda 2\theta_{1/2}(E)$ (degrees)	$\Lambda 2\theta_{1/2}(T)$ (degrees)
80-037	53.0	11	55 to 60	0.20	0.19
80-038	30.9	30	44 to 48	0.125	0.126
80-034	20.3	69	35 to 45	0.079	0.078
80-040	15.4	123	9 to 11	0.0625	0.06
80-041	10.0	274	0.1	0.05	0.04
80-042	(5)	1094	0	--	--

The W/C-LSM 80-037 is one of a series of six samples designed to investigate the effects of interfacial roughness, the characteristics of which are given in Table 4. The samples were all designed to have reflectivities in first order of 65 to 68% for periods of 53 $\text{\AA}$, 30.9 $\text{\AA}$, 20.3 $\text{\AA}$, 15.4 $\text{\AA}$, 10 $\text{\AA}$ and 5 $\text{\AA}$ by increasing the number of diffracting planes as the period decreased, as shown in Table 4. Again note that the $\Lambda 2\theta_{1/2}$ experimentally observed is in excellent agreement with values calculated using DDDT.

The observed values of peak reflectivity are plotted as a function sample period in Figure 7 with the solid line approximating the observed behavior. The circles in Figure 3 are points calculated using eq. (9) with the experimentally determined values of d , and the peak reflectivities predicted using DDDT assuming an interfacial roughness Δz , of 3.15 $\text{\AA}$. The agreement is semiquantitative, with the dependence of peak reflection on the period d being clearly reproduced. This is taken as clear evidence that the interfacial roughness between constituent layers is the characteristic of these LSMs which is limiting the diffracting behavior. Values of approximately 3 $\text{\AA}$ have been reported by Spiller (12) for tungsten-rhenium/carbon LSM structures.

In closing this section on W/C-LSMs I will present two recent experimental results obtained at the Stanford Synchrotron Radiation Laboratory. The importance of these results is that they were obtained with tunable, low intrinsic beam divergence radiation using an apparatus that

Fig. 8. The observed first order Bragg reflection for a W/C-LSM (80-038, $d = 30.9 \text{ \AA}$, $\tau_w = 10.3 \text{ \AA}$, $N_w = 30$) for 5478 eV radiation is compared to theory. The experimental data were taken at the Stanford Synchrotron Radiation Laboratory.

Fig. 9. The observed first order Bragg reflection for a W/C-LSM (81-117, $d = 38.5 \text{ \AA}$, $\tau_w = 12.8 \text{ \AA}$, $N_w = 50$) for 10000 eV radiation is compared to theory. The experimental results were taken at the Stanford Synchrotron Radiation Laboratory.

allowed excellent alignment. This apparatus allows data to be taken at angles greater than 0.1° in θ and scans which span the angular range from the region of total specular reflection to higher angles where Bragg reflections are observed. In the following only data from regions about the first order Bragg reflections will be presented and compared to theory.

Results obtained using sample 80-038 (W/C-LSM, see Table 4) and photons of energy 15547 eV are shown in Figure 8 and compared to DODT calculations. $\Lambda 20_{1/2}$ is observed to be in excellent agreement when experiment and calculation are compared. The offset between experiment and DODT calculations is believed to be due to a small error in the period d or uncertainties in the values of δ and β . Also, the predicted peak reflectivity is 62% while the observed value is 54%. This value yields an effective interface roughness Δz of approximately 1.8 Å compared to the 3.15 Å value seen in Figure 7. The implication of this comparison is that the laboratory data (Cu K_α) yields an upper limit to the interface roughness parameter as the reflectivity appears lower; $I/I_0|_E = 44$ to 48%, vs DODT = 67%; for laboratory experiments; $I/I_0|_E = 54\%$ vs DODT = 62% for SSRL experiments. This is supported by results on other samples of Ti/C, Nb/C, V/C-LSMs and indicate that the alignment and low beam divergence possible with synchrotron sources are advantageous in the characterization of LSMs.

The diffraction behavior of sample 81-117, a W/C-LSM, having a period of 38.5 Å ($N_W=50$, $t_W=12.8$ Å, $t_C=25.7$ Å) using 10000 eV radiation is compared to DODT calculations in Figure 9. The offset in the peak reflectivity positions is approximately 0.005° - 0 and is due to an uncertainty with the values of δ and β as well as a possible error in the period. Note that the secondary Fresnel maxima are not clearly defined in the experimental curve due to the inherent beam divergence of $\sim 1 \times 10^{-4}$ radians in this experiment. The experimentally observed peak reflectivity is 73% while DODT predicts 82%. Note that the W-L_{III} edge lies at approximately 10300 eV so that absorption effects are minimized at 10000 eV. Interfacial roughness is calculated to be approximately 1.4 Å for this sample. This indicates that very high quality LSM structures are synthesizable with essentially atomically smooth interfaces between the constituent layers.

In this section it has been demonstrated that high diffraction efficiency W/C-LSM's having periods above 15 Å can be synthesized and have x-ray dispersion characteristics in accord with theory. Interfacial roughness of the order of 1.4 to 3.15 Å is inferred from experiment demonstrating that near atomic level smoothness at these interfaces can be achieved.

Two important comments are made in closing this section. First, these LSM films can be formed on flexible substrates such as mica and polyimide films. Silicon substrates can also be flexed so that an 0.5 meter radii of curvature is achieved over a 7.5 cm distance. Second, these structures are quite stable and samples synthesized in early 1976, though somewhat discolored, still exhibit the x-ray diffraction behavior originally observed. When such samples are heated in inert atmospheres to temperatures of approximately 500°C for 5 to 10 hrs the tungsten layers react with the carbon to form WC which has a density of 15 to 16 gms/cc. The decrease in the carbon layer thickness due to the reaction is not as large as the increase in the thickness of the W(C) layers during the annealing so that the period of the sample increases. There is no apparent degradation in the diffracting efficiency of the samples, an increase in resolution, and possibly an increase in the perfection of the structure, as a result of such annealing.

B. Vanadium-Carbon (V/C)-LSM

The x-ray dispersion behavior of a specific vanadium/carbon LSM is considered in this section. This sample (10-177) consists of twenty-one-45 Å thick vanadium layers separated by 100 Å carbon layers deposited onto (100) orientation Si single crystal substrates. Vanadium was the top layer. This period, ($d = 145$ Å), and the vanadium were chosen so that an efficient diffracting element for very soft x-rays could be constructed with absorption effects minimized.

Diffracting behavior over the photon energy range 100 to 12000 eV is discussed. Direct comparison between experiment and PCOM calculations is made for data taken above and below the V_K edge (18300, 6000 eV), for CuK (8227 eV) and MoK (2039 eV). Estimation of the interfacial roughness are inferred from the higher order Bragg reflections

Fig. 10a. Observed diffracting behavior over the angular range 0 to 6 degrees in 2θ for a V/C-183 (80-177), $d = 143.5 \text{ \AA}$, $t_V = 33.5 \text{ \AA}$, $R_V = 21$ for 5300 eV radiation is shown.

Fig. 10b. Predicted (FOPF) diffracting behavior over the angular range 0 to 6° in 2θ for a V/C-183 (80-177), $d = 143.5 \text{ \AA}$, $t_V = 33.5 \text{ \AA}$, $R_V = 21$ for 5300 eV radiation is shown.

Fig. 11a. Observed diffracting behavior over the angular range 0 to 6° in 2θ for a V/C-18% (80-177; $d = 143.5 \text{ \AA}$, $t_V = 43.5 \text{ \AA}$, $N_V = 21$) for 6000 eV radiation is shown.

Fig. 11b. Predicted (D.C.) diffracting behavior over the angular range 0 to 6° in 2θ for V/C-18% (80-177; $d = 143.5 \text{ \AA}$, $t_V = 43.5 \text{ \AA}$, $N_V = 21$) for 6000 eV radiation is shown.

Fig. 12. The predicted diffracting behavior for a V/C-JSM (80-177, $d = 143.5 \text{ \AA}$, $r_v = 43.5 \text{ f}$, $k_v = 21$) for C-K ($\lambda = 44.7 \text{ \AA}$) radiation is shown for $0 \leq \theta \leq 15$ degrees. Two cases are compared; (1) a case for which the top layer is vanadium, and (2) a case for which the top layer is carbon.

Fig. 13. Experimentally observed diffracting behavior of C-K $_{\alpha}$ ($E = 277 \text{ eV}$, $\lambda = 44.7 \text{ \AA}$) radiation from a V/C-JSM (80-177) is compared to theoretical predictions made using values of δ and β for the vanadium and carbon developed by Ping Lee and Henke (12).

($E=5300, 6000$ eV). Also, it is shown that the positions of the Bragg reflections in first order allow the value of δ , the real part of the refractive index, to be estimated. The measured values are for the composite material and values for the component elements must be unfolded. These composite material values are compared to those derived from classical theory and recent results of Ping Lee and B. Henke (32). DDT calculations exploring the effects of the nature of the top layer and the polarization of the incident light are also presented.

Diffraction scans and DDT calculations for a V/C-LSM (80-177) for radiation of energy 5300 eV and 6000 eV are shown in Figure 10a,b, and 11a,b respectively. The basic agreement is excellent with respect to the predicted critical angles, θ_c , and the peak reflectivities in first order. The predicted values are 93% (5300 eV) and 67% (6000 eV) while experiment yields 88% (5300 eV) and 65% (6000 eV). Observed intensities for 2nd, 3rd, 4th, and 5th order Bragg reflections are all substantially less than predicted.

This disagreement between theory and experiment at the higher orders can be rationalized in terms of an interfacial roughness. In Eq. (3) a relationship between the order of reflection of a sample and the interfacial roughness parameter Δz was given. Values of Δz calculated using this equation are listed for photon energies of 5300 eV and 6000 eV as a function of the order of reflection in Table 5. The apparent interfacial roughness is ~ 7.7 Å which is several vanadium interatomic distances. The values of Δz are in general agreement for all orders of reflection, supporting the analysis, indicating that this simple approach provides a reasonable framework for understanding these results.

Table 5. The interfacial roughness parameter Δz as a function of the order of reflection for $E=5300$ eV, 6000 eV (Sample 80-177)

$E(\text{eV})$	Order of Bragg Reflection				
	$n=1$	$n=2$	$n=3$	$n=4$	$n=5$
5300	--	6.8 Å	8.8 Å	8.4 Å	7.8 Å
6000	--	6.0 Å	7.2 Å	8.7 Å	8.0 Å

Fig. 14. Predicted diffracting behavior for a V/C-LSM (80-177) for 108 eV ($\lambda = 114 \text{ \AA}$) for π and σ polarized radiation are compared. Note the Bragg reflectivity of the σ polarized radiation is significantly larger than the π polarized as the Bragg angle is a large fraction of the Brewster angle.

Fig. 15. The predicted behavior (DDDT) for diffraction of unpolarized 108 eV radiation ($\lambda = 114 \text{ \AA}$) from a V/C-LSM (80-177, $d = 143.5 \text{ \AA}$, $L_V = 43.5 \text{ \AA}$, $N_V = 21$) for $0 < \theta < 3.5$ degrees is shown. Two cases are compared; (1) a case in which the top layer is vanadium, and (2) a case in which the top layer is carbon.

The behavior at high photon energies is not as strongly affected by absorption as at low energies, the reflectivity under the least favorable conditions at energies just above the vanadium K edge still being of the order of 65%. At low photon energies absorption dominates and it is necessary to consider the effects of the top layer composition. In addition, due to the long wavelengths, Bragg reflection occurs at high enough angles that the polarization of the incident radiation may be important. These effects are discussed in the following for C-K ($E=277$ eV) and B_e -K ($E=108$ eV) radiation diffracted from this V/C-LSM.

DDOT calculations using values of β and δ provided by Ping Lee and B. Henke for C-K ($E=277$ eV) are shown in Figure 12. One curve is for carbon as the top layer and the other for vanadium as the top layer. The effect of the top carbon layer is important as it provides guidance as to the possible effects of contamination layers which will always be present in such deposited films. Such contamination layers are expected to be both oxides of the vanadium as well as carbon containing organic films.

A comparison between experimental results taken by Tesker and Henke and these DDOT calculations are shown in Figure 13. The predicted reflectivity is approximately 1.5 times the observed value of 30% (above background). In addition the experimental value of $\lambda/20_{1/2}(\text{FWHM})$ is approximately 1.5 times the predicted value. It is likely that the disagreement between the experimental value of peak reflectivity and the predicted value is the result of an underestimate of the β values for the component layers, as well as of the scattering power per layer. This is supported by the fact that the integrated reflectivities compare very well.

Measurements were also made of the diffracting behavior of B_e -K ($E=108$ eV). The diffracting behavior for σ and π polarized 108 eV radiation calculated using DDOT are presented in Figure 14. As the Brewster angle is approached the σ polarization is more strongly diffracted as shown in this figure. There is essentially no difference between the σ and π polarizations in the specular region of the curve. This is included so that the possible effects of incident light polarization are delineated.

Fig. 16. Observed peak reflectivity in first order is compared with theory for 108 eV radiation ($\lambda = 114 \text{ \AA}$) from a V/C-LSM (80-177, $d = 143.5 \text{ \AA}$, $\tau_v = 43.5 \text{ \AA}$, $N_v = 21$). Two theoretical cases are presented (1) a sample with a vanadium top layer and (2) a sample with a carbon top layer.

Fig. 17. Values of apparent d spacing calculated from experimentally observed positions of the Bragg reflections for radiation having energies of 108, 151, 192, 277, 5300, 6000, 10000, and 13000 eV are plotted as a function of the order of reflection. Apparent d spacings calculated from the differences in the angular positions of adjacent orders of Bragg reflections are also plotted, these points lying midway between the respective orders used in the analysis (the d values are all larger than the correct value of d for this sample).

More importantly, the effect of the composition of the top most layer is seen both in the specular reflection regime and at the Bragg peak as shown in Figure 15. The calculations demonstrate that the specular reflection from a LSM having carbon as the top layer is at all angles larger than from a vanadium top layer sample. This is due to the high absorption coefficient for 108 eV radiation of the vanadium which markedly decreases the reflected intensity in the specular regime. Conversely, the vanadium top layer sample exhibits a markedly higher value of peak reflectivity in the first order Bragg peak than the carbon top layer calculation. This is more clearly shown in Figure 16 where experimental data is compared to these calculations. Note that the observed reflectivity lies at an intermediate value between the two calculated curves and that the observed $\Delta\theta_{1/2}$ is again approximately 1.5 times that calculated. The observed peak reflectivity above background is approximately 6.5% and the value calculated for a vanadium top layer structure is approximately 10.5% again a factor of 1.5 larger.

As discussed in the theory section the value of the sample period, d , calculated using the observed Bragg peaks differs from the actual value of d as a result of refractive index effects (eqs. 10 and 11). This can lead to substantial error in the determination of the actual period unless higher order reflections are used as the refractive index effect decreases at higher angles. Values of d calculated from actual peak positions in $Q[d(\theta)]$ for five orders of Bragg reflection are shown in Figure 17 for photons of energy 13000, 10000, 6000 and 5300 eV. Also shown are values calculated from the first order position of the Bragg peaks observed for 277, 192, 151 and 108 eV radiation. These values all lie below the horizontal dotted line in the figure. Apparent values for d [$d(\Delta\theta)$] can also be calculated from the value of $\Delta\theta$, the difference in angular position between adjacent orders of Bragg reflection are also shown and are always larger than the real sample period. They lie above the horizontal dotted line in this figure. These two types of analysis yield curves asymptotic to the actual period of the sample at high angles or at high orders of Bragg reflection. The horizontal line in this figure represents the actual d spacing of this V/C-LSM which, from this analysis is $143.5 \pm 1.0 \text{ \AA}$.

It is also possible once the value of the sample period is well established, to calculate a value of $\bar{\delta}$, the composite value of the real part of the refractive index for a given LSM structure. Values of $\bar{\delta}$ derived from the positions of first order Bragg reflections observed for photon energies of 108 to 13000 eV for V/C-LSM 80-177 are presented in Table 6.

Table 6. The real part of the composite refractive index, $\bar{\delta}$, calculated from the experimental positions of the first order reflections of photons $108 \text{ eV} < E < 13000 \text{ eV}$ from a V/C-LSM ($d = 143.5 \text{ \AA}$, $t_v = 43.5 \text{ \AA}$, $N_v = 21$) are compared to predictions based on simple theory δ_i and values calculated using the results of Ping Lye and B. Henke for the values of δ and β of carbon and vanadium ($928 \text{ eV} > E > 108 \text{ eV}$).

E(eV)	$\lambda(\text{\AA})$	$\bar{\delta}$ (Theory)			$\bar{\delta}_{(\text{exp})}$
		δ_{ideal}	δ_{sum}	δ_{mix}	
13000	0.953	3.64×10^{-6}	3.73×10^{-6}	3.64×10^{-6}	3.29×10^{-6}
10000	1.239	6.15×10^{-6}	6.31×10^{-6}	6.15×10^{-6}	5.98×10^{-6}
6000	2.066	1.71×10^{-5}	1.76×10^{-5}	1.71×10^{-5}	1.53×10^{-5}
5300	2.332	2.19×10^{-5}	2.23×10^{-5}	2.19×10^{-5}	2.27×10^{-5}
928	13.33	7.13×10^{-4}	7.21×10^{-4}	6.83×10^{-4}	7.8×10^{-4}
277	44.7	8.01×10^{-3}	3.18×10^{-3}	3.74×10^{-3}	1.21×10^{-3}
192	64.4	1.66×10^{-2}	9.71×10^{-3}	8.99×10^{-3}	7.83×10^{-3}
151	82.1	2.7×10^{-2}	1.58×10^{-2}	1.42×10^{-2}	1.29×10^{-2}
108	114.0	5.21×10^{-2}	2.94×10^{-2}	2.52×10^{-2}	2.45×10^{-2}

These are compared to predicted values calculated assuming

$$\bar{\delta} = 2.72 \times 10^{-6} \frac{\sum z}{\bar{\rho} \bar{M}} \lambda^2 \quad (12)$$

and

$$\bar{\rho} = \left[\frac{t_v}{d} \rho_v + \frac{t_c}{d} \rho_c \right] \quad (13)$$

where λ is the wavelength, z the atomic number, M the atomic weight, ρ_v the density of vanadium, ρ_c the density of carbon, t_v the thickness of the vanadium layers, t_c the thickness of the carbon layers and d the sample period. The values calculated assuming $Z_v = 23$, $Z_c = 6$, $\rho_v = 5.96 \text{ gms/cc}$, $\rho_c = 2.0 \text{ gms/cc}$, $d = 143.5 \text{ \AA}$ and literature values for the atomic weights for all photon energies are shown in Table 6 as δ_i and

Fig. 18. $\bar{\delta}$, the composite refractive index of the V/C-LSM 80-177 calculated from the angular position of the first order Bragg reflection of radiation $0.953 \text{ \AA} < \lambda < 114 \text{ \AA}$ is plotted as a function of the wavelength of the radiation. These data are compared to a simple theory in which the effective number of electrons for vanadium and carbon are assumed to be 23 and 6 respectively and to predictions made using the values of $\bar{\delta}$ and developed by Ping Lee and Henke (32).

are all larger than experiment with major disagreement shown for the very low energy radiation, as is expected.

Comparisons of the experimental values and values calculated using the results of Ping Lee and B. Henke (32) for vanadium and carbon for energies of 928 eV or less are also shown. δ_{sum} was calculated on the basis of volume fraction:

$$\bar{\delta}_{\text{sum}}(\lambda) = \frac{t_v}{d} \delta_v(\lambda) + \frac{t_c}{d} \delta_c(\lambda) \quad (14)$$

where $\delta_v(\lambda)$ and $\delta_c(\lambda)$ are the values for the elements at a wavelength λ . $\bar{\delta}_{\text{mix}}$ is calculated using eq. (12) and eq. (13) assuming effective values of Z for vanadium and carbon in accord with the calculation of Ping Lee and Henke (32). In general, the values of $\bar{\delta}_{\text{sum}}$, $\bar{\delta}_{\text{mix}}$ and $\bar{\delta}_{\text{exp}}$ are in reasonable agreement at all energies with surprisingly good agreement found in the low energy region.

These data are plotted in Figure 13 where $\bar{\delta}$ is shown as a function of λ , the radiation wavelength. The solid line represents values calculated using eq. (12) and eq. (13) with $Z_v = 23$ and $Z_c = 6$ at all wavelengths, the open circles the experimental data, and the triangles values calculated on the basis of a mixture using values of Z predicted by Ping Lee and Henke (32). At high energies agreement of experiment with the simple model is acceptable. The largest disagreement is observed for C-K ($\lambda = 44.7 \text{ \AA}$) radiation and remains currently unexplained. Again, acceptable agreement between calculated and experimental values of $\bar{\delta}$ is shown at low photon energies.

The diffracting behavior of V/C-LSM 80-177 has been discussed and compared to calculation over the photon energy range 100 to 13000 eV. Agreement between experiment and theory has been shown to be good for high photon energies (5300 eV, 6000 eV) and less satisfactory at low energies. The disparity at low photon energies is believed to result from surface contamination and from uncertainties in the values of δ and β used in the calculations. In addition it has been shown that these LSM structures allow determination of δ over a broad energy range using a single sample thereby maintaining the material and sample structure effects constant.

FIG. 19. Integrated reflectivities for a Ti/C-LSM (80-073); $d = 56.4 \text{ \AA}$, $t_{\text{Ti}} = 26.0 \text{ \AA}$, $N_{\text{Ti}} = 70$) for radiation in the wavelength range $2.066 \text{ \AA} < \lambda < 13.33 \text{ \AA}$ are shown as a function of radiation wavelength and compared to theory. Data and calculations for RAP are included for comparison. Also, data at the Ti-K edge were taken at SSRL and are in better agreement with theory, as shown in Table 7.

C. Titanium-Carbon (Ti/C)-LSM

The diffracting behavior of a titanium-carbon (Ti/C)-LSM having a period of 56.4 Å consisting of 70 titanium layers 26.0 Å thick separated by carbon layers 30.4 Å thick is summarized in this section. The data discussed were taken (39) at the Naval Research Laboratory and as part of a program at the Stanford Synchrotron Radiation Laboratory. Experimental values of R, the integrated reflectivity, P the peak reflectivity in first order, and angular resolution $2\theta/\Delta 2\theta$ are summarized in Table 7.

Table 7. Experimental (39) integrated reflectivities (R), peak reflectivities in first order (P), and angular resolution ($2\theta/\Delta 2\theta$) for a Ti/C-LSM 80-073 ($d = 56.4$ Å) are tabulated and compared to theoretical predictions (DOBT).

E(eV)	$\lambda(\text{Å})$	Experiment			Theory		
		R(Radians)	P(%)	$\theta/\Delta\theta$	R(Radians)	P(%)	$\theta/\Delta\theta$
277	44.7	1.9×10^{-3}	10.6	37.0	3.1×10^{-3}	35.4	45
930	13.33	2×10^{-4}	--	--	6.7×10^{-4}	14.5	43.0
1040	11.91	3.3×10^{-4}	--	--	6.5×10^{-4}	18.6	44.0
1490	8.34	3.6×10^{-4}	--	--	5.9×10^{-4}	35.2	47.0
1740	7.13	3.7×10^{-4}	--	--	6.5×10^{-4}	43.1	45.0
2620	4.729	3.1×10^{-4}	--	--	6.7×10^{-4}	65.5	45.0
4795	2.585	3.57×10^{-4}	67	45.4	5.1×10^{-4}	82.1	42.5
4980	2.489	6.14×10^{-5}	16	59.3	--	--	--
6000	2.066	2.17×10^{-4}	47	41.8	2.5×10^{-4}	52.0	45.0
13000	0.953	1.50×10^{-4}	60.0	34.6	--	--	--
17000	0.729	1.23×10^{-4}	60.0	31.7	--	--	--

Comparison of calculated (DOBT) values of R and experimental values show that in nearly all cases the experimental values are greater than half that predicted. Calculated and observed angular resolution ($\theta/\Delta\theta$) are also in reasonable agreement with the largest discrepancy observed for the lowest energy radiation C-K (277 eV). In addition the angular resolution, $\theta/\Delta\theta$, increases significantly at 4980 eV while both the peak reflectivity P and integrated reflectivity are markedly reduced. This photon energy lies at the titanium K

Fig. 20. Elevation and plan views of a dual electron spectrometer used to compare the performance of a W/C-LSH and a RAP crystal irradiated by a laser generated plasma from a teflon (CF_2) target are schematically shown

Fig. 21. Optical densitometer traces of film records of laser excited plasma spectra from CF_2 simultaneously obtained using a W/C-LSH and an RAP crystal as dispersion elements mounted in the apparatus shown in Fig. 20 are shown.

Fig. 22. A calculated (POBT) diffractometer profile for a W/C-LSM having 125 tungsten layers $8 \text{ \AA}$ thick separated by $11 \text{ \AA}$ of carbon is shown for incident radiation having a wavelength of $16.807 \text{ \AA}$.

edge, the decrease in reflectivity resulting from the absorption edge jump and the effect of the anomalous dispersion of the titanium on the scattering power per vanadium/carbon layer pair. This decrease in scattering power is reflected in the significant increase in the angular resolution at this energy.

The integrated reflectivity experimentally observed is compared to calculated values over the wavelength range of 7 to 13.1 Å in Fig. 19. R values for RVP are also shown for comparison. The general behavior is clearly in agreement while the actual experimental values are, at all wavelengths, less than the predicted values. Again, it is likely that an uncertainty in the correct values of δ and β contribute to this disparity.

V. Application of LSMs as Dispersion Elements

In this paper the primary purpose has been to present information providing a picture of the current status of the development of LSM x-ray dispersion elements synthesized using sputter deposition technology. The results discussed have demonstrated that the application of such LSM structures as dispersion elements is now possible. Two such applications are briefly discussed in the following.

A series of observations have been made by Loder, Nagel, and Barbee (40) at the Naval Research Laboratory in which a W/C-ISM was used as a spectroscopic element dispersing the emitted radiation from a laser induced plasma generated by irradiation of a Teflon Target using a ruby laser as shown in Figure 20. The arrangement of the W/C-ISM and a rubidium acid phthalate (RVP) analyzing crystal in a dual element spectrograph is also shown in Figure 20. This arrangement allowed direct comparisons of the dispersion characteristics of the two spectroscopic elements. This is shown in Figure 21 which presents microdensitometer traces of the films exposed during the same laser shot. Note the integrated and peak reflectivities of the W/C-ISM are substantially lower than those of the RVP, and the resolution is apparently a factor of 6 smaller. DOP calculations for $\lambda = 16.107$ Å have been made and are shown in Figure 22. The calculations indicate a resolution of approximately 0.21 Å is expected

Fig. 12. A comparison of the diffracted intensity of the (101) quartz peak observed using $\text{Cu K}\alpha$ and a curved focusing graphite crystal and a flat W/C-LSM ($\lambda = 39.2 \text{ \AA}$, $n_w = 50$) as dispersion elements in a diffracted beam monochromator is shown. The signal to noise ratio was observed to be 1.65 times larger with the W/C-LSM dispersion element relative to the graphite crystal.

compared to an observed value of approximately $0.25 \text{ \AA}$. Also, the ratio of the predicted value of integrated reflectivity for $\lambda = 16.807 \text{ \AA}$ to that of R₀P is ~ 14.3 ignoring the effects of interfacial roughness on peak reflectivity. The experimentally observed value is 11.3. If the effects of interfacial roughness on the diffracting behavior of this LSM are included the agreement is considerably improved. Exact agreement is found for $\Delta Z = 1.6 \text{ \AA}$, a value similar to that observed for other W/C-LSMs discussed earlier in this paper.

These results demonstrate that W/C-LSMs provide a spectroscopic element having higher energy throughput than standard acid phthalate crystals in the X-UV range and resolution sufficient for analysis of prominent emission lines.

Another possible spectroscopic application (41) is use of these LSMs as dispersing elements in a standard powder diffraction apparatus. An example of this is shown in Figure 23 where scans of the (101) peak from polycrystalline quartz with Cu K $_{\alpha}$ ($\lambda = 1.5418 \text{ \AA}$) using a curved focussing graphite crystal and a flat W/C-LSM ($d = 39.2 \text{ \AA}$ and $N_w = 50$) as dispersion elements in a diffracted beam monochromator are compared. Excitation of the source was the same for both scans. The peak intensity observed with the W/C-LSM was 1.85 times larger than with the graphite crystal and the signal to noise ratio 1.6 times larger. This comparison, though simple gives an indication of the utility of these LSM structures even though near grazing incidence geometries are needed.

VI. Summary

It has been demonstrated in this paper that synthetic crystals, termed layered synthetic microstructures (LSM) here, can be synthesized using sputter deposition processes with x-ray dispersion characteristics that are in accord with theory. Such structures can be synthesized with useful properties from a wide variety of materials allowing control of band width and, in special instances, the dispersion response as a function of wavelength. The periods accessible at this time have a lower limit of $15 \text{ \AA}$ though layering is evidenced for periods greater than $8 \text{ \AA}$.

These LSM have been deposited onto a variety of substrates, the results reported here being only for materials deposited onto single crystal silicon substrates. Results on these other substrates are also in accord with theory and comparable to those obtained from LSMs deposited on single crystal silicon substrates. Many of these materials are very flexible (mica, plastic films) and allow curved surfaces to be developed. Preliminary observations of LSM behavior when deposited onto mechanically prepared figured surfaces indicate that high performance elements with periods of approximately 40 Å can be synthesized.

It has also been shown that a systematic explanation for the disagreement between experiment and model calculations can be based on the effects of the interfacial roughness between constituent layers on the angular distribution of scattered x-rays. Surface roughness, ΔZ , for the W/C-LSMs was inferred to be in the range 1.4 to 3.15 Å with the most likely value in the range 1.4 to 1.8 Å. A somewhat larger value, $\Delta Z = 7.7$ Å, was inferred from experimental results obtained from a V/C-LSM in which the vanadium layer was 43.5 Å thick. These results demonstrate that the character of the interface is an important parameter, and at this time, apparently the controlling factor determining the behavior of LSM dispersion elements.

Extension of this work will include investigation of new materials as components for the individual layers of an LSM. This will result in the development of understanding necessary for engineering of such LSMs for particular applications. Each new material will have characteristic interfacial effects and will require significant experimentation for development. Investigation of such interfacial effects will constitute a major part of the materials research in this field. It is likely that significant understanding of the surfaces between materials will be generated by such efforts.

In addition, actual development of optical devices for x-ray manipulation will be pursued. This will entail both model calculations and specific, designed LSM configurations which will undoubtedly extend the current synthesis process technology. A simple extension of current technology will allow synthesis of samples

having multiple periods or graded periods through thickness. In addition, samples having periods varying along the substrate can also be synthesized. These now become elements for specific spectroscopic applications. The conclusion is that the variety of structures which can be envisioned is only limited by experience and imagination at this time.

A final statement concerning the sputter deposition, synthesis process used here must be made. At this time usable sample areas are rectangular (2 cm x 7.5 cm). This is determined by the source geometry and by the particular system design used in this process. It is clearly possible to scale up the system so that large area substrates may be coated with high quality LSM films. In addition it is likely that highly figured surfaces may be uniformly coated with appropriate source design and substrate motion.

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REFERENCES

1. H. Koeppel, Dissertation Giessen (1929). Quoted by Deubner.
2. W. Deubner, Ann. der Phys. 5, 261 (1930).
3. J. DuMond, and J. P. Youtz, J. Appl. Phys., 11, 357 (1940).
4. J. Dinklage, and R. Frerichs, J. Appl. Phys. 34, 2633 (1963).
5. J. Dinklage, J. Appl. Phys. 38, 3781 (1967).
6. E. Spiller, Appl. Opt. 15, 2333 (1976).
7. E. Spiller, Appl. Phys. Lett. 20, 365, (1972)
8. E. Spiller, "Handbook on Synchrotron Radiation," Vol. 1. (Ed. by E. E. Koch, D. E. Eastman and Y. Farge), North Holland, Amsterdam (1980).
9. R.-P. Haelbich, A. Segmüller and E. Spiller, Appl Phys. Lett. 34, 184 (1979).
10. E. Spiller in Proc. of ICO-IX, Santa Monica, Calif. (NAS-NRC, Wash. D.C., 1974), p. 525.
11. R.-P. Haelbich and C. Kunz, Opt. Commun. 17, 287 (1976).
12. E. Spiller, "Evaporated Multilayer Dispersion Elements," this conference.
13. T. W. Barbee Jr. and D. L. Keith, "Workshop on Instrumentation for Synchrotron Radiation Research," Ed. by H. Winick and G. Brown, Stanford SSRL Report No. 7804 (1978), III-26.
14. T. W. Barbee, Jr. and D. L. Keith, "Lithography/Microscopy Beam Line Design Workshop," Ed. by C. R. Dannemiller, Stanford SSRL Report No. 79/02 (1979), 185.
15. T. W. Barbee Jr., in "National Science Foundation - Twenty Sixth Annual Report for Fiscal Year 1976," U.S. Gov. Printing Office - Stock No. 038-000-00313-5, pg. 19.
16. A. M. Saxena, and B. P. Schoenborn, Acta Cryst. A33, 805 (1977).
17. L. L. Chang, L. Esaki, W. Howard, and R. Ludeke, Proc., 11th International Conf. on the Physics of Semiconductors, Polish Academy of Science, PWN-Polish Scientific Publishers (1972), 431.
18. L. L. Chang, L. Esaki, W. Howard, R. Ludeke and G. Schul, J. Vac. Sci. Technol. 10, 655 (1973).
19. L. Esaki, Jap. J. Appl. Phys. Suppl. 2, Part 1, 821 (1974).

20. A. C. Gossard, P. M. Petroff, W. Weigmann, R. Dingle and A. Savage, Appl. Phys. Lett. 29, 323 (1976).
21. R. M. Fleming, D. B. McWhan, A. C. Gossard, W. Weigmann, and R. A. Logan, J. Appl. Phys., 51, 357 (1980).
22. E. M. Philofsky and J. E. Hilliard, J. Appl. Phys., 40, 2198 (1969).
23. J. E. Hilliard in "Modulated Structures -1979" (Ed by J. M. Cowley, J. B. Cohen, M. B. Salamon, and B. J. Wuensch) A.I.P. Conf. Proc. No. 153 (1979).
24. I. K. Schuller, Phys. Rev. Lett. 44, 1597 (1980).
25. W. P. Lowe, T. W. Barbee Jr., T. H. Geballe, and D. B. McWhan "X-ray Scattering from Multilayers of Nb Cu" (submitted for publication).
26. J. H. Underwood and T. W. Barbee Jr., "Layered Synthetic Microstructures as Bragg Diffractors for X-rays Extreme Ultraviolet: Theory and Performance," Accepted for publication in Appl. Opt.
27. J. H. Underwood and T. W. Barbee, Jr., "Synthetic Multilayers as Bragg Diffractors for X-rays and Extreme Ultraviolet: Calculations of Performance," this conference.
28. A. Guinier, "X-ray Diffraction," W. H. Freeman, London, England, 1963, pg. 121.
29. H. E. Bennett and J. H. Bennett in "Physics of Thin films," Vol. 4, Ed. by G. Hass and R. E. Thun, Academic Press, 1969, pg. 1.
30. P. Beckmann, "The Scattering of Electromagnetic Waves by Rough Surfaces," Pergamon Press, New York, 1963, Part 1.
31. J. M. Elson and J. M. Bennett, Opt. Engineering, 18, 116 (1979).
32. Ping Lee and B. Henke, Private communication.
33. L. V. Azároff, "Elements of X-ray Crystallography," McGraw-Hill, New York (1968), 130.
34. T. W. Barbee Jr. and D. L. Keith, "Synthesis of Metastable Materials by Sputter Deposition Techniques, to be published, TMS-AIME Conf. on Metastable Materials, Nov. 1979.
35. L. J. Maissel and R. Glang, Eds., "Handbook of Thin Film Technology," McGraw-Hill, New York (1970).
36. K. L. Chopra, "Thin Film Phenomena," McGraw-Hill, New York (1969).

37. J. L. Vossen and W. Kern, Eds., "Thin Film Processes," Academic Press, New York (1978).
38. S. Schiller, U. Heisig and K. Goedicke, Thin Solid Films, 40, 1977.
39. J. V. Gilfrich, D. J. Nagel and T. W. Barbee Jr., Unpublished work.
40. H. G. Loter, D. J. Nagel and T. W. Barbee Jr., unpublished work.
41. T. W. Barbee Jr., unpublished work.