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TITLE: AUGER AND DEPTH PROFILE ANALYSIS OF SYNTHETIC CRYSTALS
FOR DISPERSION OF SOFT X-RAYS

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Auger and Depth-Profile Analysis of Synthetic Crystals
for Dispersion of Soft X rays

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Numerous samples have been fabricated and analyzed as part of a program to produce soft X-ray dispersion elements for various laboratory applications. The majority of this work has centered around the carbon/tungsten system, although several other low-Z/high-Z pairs have been investigated. This report describes the development of certain vacuum-deposition technique for fabricating these dispersion elements, based upon results obtained from X-ray reflectivity measurements and Auger depth-profile analysis. The composition of the films is chiefly alternating layers of tungsten carbide and carbon, similar to other recent work [1]. Excess carbon is introduced during the deposition of the tungsten to ensure that the carbide layer is fully stoichiometric. Layer thickness ranged from ~ 5 to $30 \text{ \AA}$ for the carbide and from ~ 15 to $80 \text{ \AA}$ for the carbon. The reflectivity measurements were made using Fe and Al K_{α} at grazing incidence. The emphasis in these studies is on the application of surface-analysis results in suggesting modifications to the

fabrication process and in evaluating the results such modifications have on the layer stoichiometry, continuity, and periodicity of the dispersion elements so produced.

Introduction

Although there exist a number of natural single-crystalline materials (e.g. quartz, NaCl, LiF, etc.) suitable for dispersion of x-rays for laboratory applications (such as crystal monochromators for wavelength-dispersive x-ray spectrometry or x-ray photoelectron spectroscopy, x-ray telescopes and microscopes, etc.), these materials are only suited for use with relatively hard x-rays. According to Bragg's law, for a wavelength of about $1.94 \text{ \AA}$ (Fe K_{α}), a d-spacing of $27.7 \text{ \AA}$ is required to obtain the first order reflection at a grazing angle of 2 degrees. Similarly, for Al K_{α} x-rays ($8.408 \text{ \AA}$), d must equal $120 \text{ \AA}$ for a 2 degree dispersion. Clearly, no natural crystals are available with sufficiently large d-spacing for dispersion of these soft x-rays.

Synthetic microstructures capable of reflecting soft x-rays have been made from many different materials by various investigators[2,3]. Basically, they all involve the separation of layers of a strongly absorbing material with a weakly absorbing material. An excellent summary of the types of structures which have been fabricated, their stability, and modeling of their dispersion behavior is given by T.W. Barbee [1]. The intent of this project is to study different material combinations and various fabrication methods in an attempt to produce such tailor-made dispersion elements. Workers in the field have coined the term "layered synthetic microstructures," or LSM's, to describe these structures.

Tungsten was chosen as the high Z/strongly absorbing material. Several low Z/weak absorber materials were used in initial attempts, but we soon settled on carbon as the separation element between tungsten layers. Although the W-C system has been explored by other workers for LSM's, this is the first report of efforts to employ surface analysis as part of the fabrication process development.

Fabrication

Our LSM's were made using sputtering from a pair of magnetron sources onto a substrate. The substrate-source distance is fixed; however, the substrates rotate about their center in order to enhance step coverage. The power level of the targets is kept constant. Shutters placed in front of the sources are cycled automatically to control the layer thickness. Although the vapor deposition profile from a source will change as the target is eroded, the time needed to deposit a 50 layer pair dispersion element is sufficiently short (approximately 30 minutes) that no significant profile changes occur. The deposition system is illustrated schematically in Figure 1.

The solid solubility of carbon in tungsten is fairly high; however, it is known that carbon is not as soluble in stoichiometric WC. Hence, we attempted to deposit carbon and tungsten from sputter sources of the pure elements in ratios sufficient to produce stoichiometric tungsten carbide layers separated by pure carbon layers. The WC formed thus acts essentially as a diffusion barrier to prevent subsequent "wash out" of the fabricated periodic layers.

LSM samples numbered M-0 through M-40 have been fabricated using various deposition parameters. The main variable was the equivalent thickness of either carbon or tungsten which was deposited onto the substrate. Calibration

or tool factor runs were made on the individual sources to determine their particular deposition rates. Ultimately, LSM's were made with the carbon source running continually while shuttering the W source periodically. Varying the ratio of C to W equivalent thicknesses effectively varied the relative atomic concentrations of these elements, ideally forming layers of nearly stoichiometric WC separated by pure carbon layers. Varying the sum of C and W layer thicknesses provided changes in the synthetic d-spacing of the microstructure. Of course, simply adding more layers also changed the nature of the LSM's, similar to optical design for visible light mirrors.

A quartz lamp on a rotatable shutter was added to the system after M-20 for pre-deposition heat cleaning of the substrates. Normally, the depositions were run with the substrate at ambient temperature, about 100°C. However, a few depositions were started before the substrates had cooled to room temperature following heat cleaning. These may have been as high as about 250°C for much of the deposition run. The consequences of these elevated temperature depositions is discussed below.

Yet another important variable was the smoothness of the substrate. As in all optical coatings, the surface roughness of the initial substrate has a direct relationship to the quality of the final material; but when dealing with x-ray wavelengths, this parameter is even more crucial. Although one can argue that, as a result of the sputter deposition process, the surface grows ever-smoother, we chose to minimize this substrate effect by selecting good quality substrates at the start. Originally our LSM's were deposited on commercial electronic grade silicon with a mean roughness value of approximately $40\text{\AA}$ rms. Notice that this value is large compared to the wavelengths of x-rays being dispersed. For this concern we later used very smooth glass or highly polished silicon wafers ($\sim 8\text{\AA}$ rms) as substrates.

Examination of this substrate roughness effect on LSM quality has shown negligible differences thus far in Auger depth profile analysis. Careful quantitative reflectivity studies of these materials is pending.

Analysis

A. Auger and Depth Profile Analysis

Surface analysis data were obtained on a Physical Electronics Model 548 Scanning Auger Microprobe system. Base pressure in the system was typically 3×10^{-8} Pa. Depth profiling was accomplished using a Model 04-303 differential ion gun, mostly without differential pumping. With the ionizer running at 25mA electron emission and approximately 15mPa argon pressure, the main chamber remained below 4×10^{-5} Pa throughout the analysis. Very recently we have operated the gun with differential pumping, allowing the main chamber to remain below 3×10^{-6} Pa. Initial attempts to depth profile LSM's with approximately 40Å layer spacings were done using a 1kV argon beam of 200nA beam current rastered over roughly a 3mm x 3mm area. No periodicity was ever observed using these beam conditions due to the rapid etch rate and mixing at this current density. However, we found that using a 500eV argon ion beam of ~50nA beam current rastered over the same (or slightly less) area, periodicity of the W and C Auger peak-to-peak amplitudes was observed in LSM's. These latter beam conditions were used throughout most of this investigation.

Auger spectra were taken in the derivative mode using a 5keV electron beam of 0.5µA. For depth profiles, we monitored the carbon KLL peak at 272eV and the tungsten Coster-Kronig transition at 179eV. Early profiles also

included the tungsten MNN transition at 1710eV. However, this peak was not preferred, since the large escape depth of such energetic electrons exceeds the layer spacing of the LSM's. Nonetheless, profiles using the W MNN peak still show periodicity, albeit less dramatically. Even the relatively short escape depth of the 179eV W Auger electrons leads to noticeable distortion of the depth profiles of such thin layers. Very recently we have used the "pre-C" peak, the positive excursion of the carbon KLL, characteristic of graphite vs. carbide carbon. This proved to be very illustrative of the chemical behavior of the carbon throughout the alternating layers.

Wide scan Auger spectra were initially taken on all samples to identify possible contaminants and calculate relative atomic concentrations of C and W to determine stoichiometry. It was found that atomic concentrations calculated directly from the depth profiles (considering the gain) were sufficient for determining C and W ratios important in characterizing the LSM's. Therefore, later analyses only included wide scans when looking for impurities.

A. X-Ray Reflectivity

The ultimate quality of the LSM's are, of course, related to how well they disperse soft x-rays. This data is obtained on two separate systems. Crude qualitative screening measurements are made using a standard Philips x-ray diffractometer system using Fe K_α radiation of $1.94 \text{ \AA}$ wavelength. Sweeping the goniometer from 2 to 5 degrees gives a spectrum of the $n=1$ reflectivity for the most of the d spacings made to date. A typical spectrum is given under Results. More quantitative measurements are desired in order to evaluate the LSM's. This data is obtained in a vacuum-mounted

diffractometer system using Al K_{α} radiation ($8.408 \text{ \AA}$ wavelength). With this system we are able to determine the percent of incident radiation reflected from the LSM's. To date, the highest reflectivities measured have been approximately 10%.

Results and Discussion

As expected, our first LSM's were not "show quality." The surface analysis capability proved invaluable in ferreting out particular fabrication problems. The characteristics which were studied in order to optimize the LSM fabrication process were:

- a. layer continuity;
- b. contamination;
- c. stoichiometry/atomic concentrations;
- d. periodicity or variation of atomic concentrations, Y axis;
- e. layer spacing or variation in layer thickness, X axis.

Overcoming problems as identified by these characteristics led to an improved fabrication process. A summary of all our depth profile results to date is given in Table 1. Details of investigating the problems above are given in the following paragraphs.

A. On several occasions (M-1, M-2, etc.) an excess amount of N was detected during the profiling of the LSM's. This was traced to minor air leaks on the sputter deposition system. Subsequent runs were checked carefully to insure that the N sources had been eliminated. Another set of samples (M-16 and M-20) showed large concentrations of Al. This was determined to be from the

secondary sputtering of the Al plate used to support the substrates during the deposition. Switching to a glass plate eliminated this problem, as glass is known to have a lower sputter rate than Al. Although these contaminants were certainly undesirable in the fabrication process, their presence would probably not cause deleterious effects in the LSM's

B. One critical aspect of the sputter deposition process was the ability to form continuous layers of carbon and tungsten. This was checked out early in the process development by depositing thin (approximately 5 to 40 $\text{\AA}$) layers of C and W onto silicon wafers. Using the different escape depths for the Si KLL and LMM Auger transitions (16 and 4 $\text{\AA}$, respectively) we calculated the apparent thickness of the films. For thicker films, Auger spectra were taken while rastering the electron beam over a fairly large area to sample for the Si KLL peak. Hence, if the deposit agglomerated into patches or islands (a problem often encountered with very thin films), either of the above techniques would detect such poor continuity. Numerous samples were prepared employing modifications to the deposition process (such as rotation of the substrates) to enhance the coverage.

C. Another concern for these LSM's was the formation of fully stoichiometric tungsten carbide layers to inhibit diffusion of C layers. Again, samples were prepared and subsequently analyzed to determine atomic concentrations of W and C and to observe the carbon KLL lineshape characteristic of carbides. Deposition conditions were adjusted accordingly to provide a near 1:1 ratio of W to C for the carbide layers.

D. The next requirement for useable LSM fabrication is the assembly of alternating layers of C and WC, or periodic variation of atomic concentrations with depth. In the fabrication process this was accomplished by shuttering the C and W sources. A later modification was the automatic control of these shutters to improve repeatability. For post-fabrication analysis, Auger depth profiling was employed. Since the layers being examined were between 5 and 80 Å, it was very important to use an ion beam of sufficiently low energy and current density to permit Auger analysis of individual layers as they were eroded from the sample. Initial attempts using argon ion beams of 1 and 2 keV at a few hundred nanoamperes gave profiles which showed no periodicity and quickly penetrated to the silicon substrate. Subsequent experimentation determined that a beam of 500 eV at approximately 50nA (~1.5mm diameter spot size) rastered over an area of between 4 and 16mm² provided a low enough sputter removal rate to resolve the individual layers in these LSM's.

Separate Auger wide scans were taken at the peaks and valleys of the depth profiles to calculate approximate atomic concentration. Subsequently, C and W peak-to-peak amplitudes taken directly from the Auger depth profiles were used in calculating atomic concentrations, and these agreed within a few atomic percent to the other method. From these data we were able to characterize our LSM's according to the C:W ratios observed through the material. An excess of either C or W in the layers resulted in a "washing out" of the periodicity. In this regard, Auger depth profile analysis was a very useful tool for identifying deposition problems and their causes.

E. Although we were concerned that atomic mixing and knock-on effects of the argon ion beam would distort the profile, these turned out to be relatively minor problems, provided that the beam conditions were carefully controlled.

The latter effect was investigated in a separate experiment [Ref. 4] and determined to be minimal. Although a few profiles "washed out" after a few layers, most showed very good periodicity through as many as 43 separate layers of C and WC (M-20). However, residual C and O-bearing gases in the chamber while profiling in the non-differential mode may have been responsible for minor knock-on and mixing of the C and WC layers. A very recent improvement was obtained in this depth profiling technique by differential pumping of the ion gun and switching to xenon as the sputter gas. By calculating the sputter rate from known reference samples we were later able to determine layer spacings in our LSM's.

Figure 2 shows part of the Auger depth profile of sample M-18. Although prior samples had shown periodicity, this LSM showed good quality throughout the entire microstructure. Notice especially that the C valleys are relatively flat. This we believe is due to the diffusion of sufficient carbon into the tungsten layer to form a fully stoichiometric carbide, resulting in a fairly constant distribution of carbon through this region. Conversely, the W peaks are rather sharp, probably due to the fairly narrow regions containing W, convoluted with the exponential escape depth function. The sample was fabricated using 7 layers of W $15 \text{ \AA}$ thick, separated by 6 layers of C $45 \text{ \AA}$ thick. Thus, the d-spacing was $60 \text{ \AA}$. All 6.5 layers were clearly resolved in the depth profile. Tungsten atomic concentrations varied from approximately 22 to 35 percent.

Figure 3 shows part of the depth profile for M-20. This sample was fabricated with 50.5 layers, i.e., 50 layers of C and 5' layers of W. In this profile one can see 12 very clearly resolved layers of W signal, while the C signal is somewhat less distinct. A total of 25 layers of each material were

easily distinguished in this series of depth profiles, at which point depth profiling was halted without seeing any evidence of "wash out."

Figure 4 shows an absorbed current image of M-15 following depth profiling. The alternating layers of C and W are conspicuous in the concentric "zebra rings" formed by the ion beam etch. A scanning Auger map of the W signal appears in Figures 4b and 4c. A similar attempt to image the C signal was less successful, probably due to the fact that carbon appears in the WC layers also. This same fact explains the poor peak-to-valley contrast observed in most of the depth profiles.

Most of the samples from M-0 through M-40 are included in Table 1. Those which are not included are samples which failed the qualitative diffractometry screening. Several others were run more than once to verify the reproducibility of our analytical technique, which usually proved to be quite good (e.g., M-5 and M-14).

Notice that several of the samples showed no detectable periodicity (e.g., M-0 and M-26). M-0, for instance, exhibited a very high W concentration which resulted in a relatively constant distribution throughout the LSM. At the other extreme, M-26 showed a constant low W concentration which was due to migration during the deposition which was begun before the substrate had cooled sufficiently from the outgassing step.

Very good correlation was obtained between reflectivity measurements and Auger depth profiles. Those LSM's having high reflectivities showed large differences in valley-to-peak W concentrations and in the number of individual layers clearly resolved in the depth profiles (e.g., M-14, M-15, M-18, and M-20). In some cases, depth profiling was continued until the silicon substrate was observed and nearly all the layers were resolved (e.g., M-14, M-15 and M-39).

M-18* was annealed after fabrication to check the diffusion of the species in the LSM. It is thought that this annealing step may enhance reflectivity by sharpening the layer boundaries. No noticeable differences were observed in the depth profiles of this sample, but further investigation of annealing LSM's is planned.

Figure 5 shows our first profile obtained using xenon gas, also in the differential pumping mode. In addition to the usual C and W signals, we followed the "pre-C" region, i.e. the low energy side of the C KLL transition, that positive excursion which typically distinguishes graphitic from carbidic species. As expected, this additional signal follows the normal C signal in peak-to-peak amplitude. However, one will notice that in the C valleys the "pre-C" signal goes through a secondary peak. Apparently this signal is predominately similar to the normal C signal amplitude except that in regions of high WC concentrations the additional sharp excursions of the "pre-C" peak provide extra peak-to-peak height to the total signal, resulting in the secondary hump in the WC-rich regions.

Figure 6 shows a typical diffractometer trace for qualitative reflectivity screening of the LSM's. This scan is for M-39 which had a designed d-spacing of $30\text{\AA}$. This measurement peaks at 4 degrees, corresponding to a $28\text{\AA}$ d-spacing. The error is thought to be due to poor alignment of the diffractometer and is of little concern since this is merely a crude measurement for screening samples for further analysis. The high angle shoulder is due to unfiltered Fe K_β x-rays.

It has been shown mathematically[5] that the reflectivity is a maximum for an absorber layer thickness to layer spacing ratio of 0.4. Figure 7 illustrates the change in reflectivity as a function of the absorber layer (WC) thickness for M-38, M-39, and M-40. For our case it is optimum near a

ratio of 0.33. This may be due to interfacial roughness of interfacial diffusion causing the layers to spread out slightly.

Conclusions

The requirements for fabricating and analyzing layered synthetic microstructures for dispersion of soft x-rays have been investigated. We have obtained dispersion elements with reflectivities up to about 10% for Al K α radiation. Surface analysis has played a major role in the fabrication process development. We have determined argon and xenon ion beam conditions which provide etch rates delicate enough to dynamically sputter very thin (5 to 80 Å) layers of C and WC up to 43 layers each while maintaining very good resolution of these layers. Although we have only been in the field of LSM's for a few months, we feel that the development of successful fabrication techniques has been expedited by the proper application of surface analysis tools. Future efforts will focus on further optimization of fabrication parameters to provide higher reflectivities approaching the theoretical limit.

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TABLE 1

Sample	%W,v/p	t,W-W	J,nA	#C/#W	$\frac{\text{\AA} \text{ W}}{\text{\AA} \text{ C}}$	d	# Layers
M-0	66	---	45/9	--/--	--/--	--	---
M-1	59/62	13	40/2X	7+/8+	23/46	69	10.5
M-2	14/28	38	40/2X	6+/5+	20/80	100	10.5
M-5	41/54	23	32/9	4+/4+	15/60	75	10.5
M-6	53/57	35	44/9	2+/3+	30/45	75	10.5
M-8	77	---	45/9	--/--	30/45	75	10.5
M-8	56/58	40	45/9	3+/3+	30/45	75	10.5
M-9	36/43	25	45/9	2+/2+	10/60	70	7.5
M-14	15/33	55	47/9	2+/2+	15/45	60	6.5
M-14	16/31	54	47/4	6/7	15/45	60	6.5
M-15	23/35	39-44	47/4	6/7	15/45	60	6.5
M-16	19/33	46	47/16	5+/6+	10/30	40	6.5
M-17	23/34	26	47/16	7/7	5/15	20	7.5
M-18	23/35	40	45/16	5+/6+	10/30	40	10.5
M-18*	22/35	27	45/9	12+/12+	10/30	40	10.5
M-20	25/40	15	47/4	24+/25+	10/30	40	50.5
M-20	26/39	26	56/9	43/43?	10/30	40	50.5
M-22	22/40	38	43/9	4+/4+?	10/30	40	50.5
M-22	23/33	38	43/9	5+/5+	10/30	40	50.5
M-26	27	--	42/4	- /--	7/21	28	76.5
M-27	38/41	7	45/4	4+/4+?	7/28	35	50.5
M-28	39/40	9?	45/9	2+/2+?	7/21	28	100.5
M-30	34/38	11	43/9	3+/3+?	7/21	28	50.5
M-38	22/24	30	34/9	4+/5+?	7.5/22.5	30	50.5
M-39	24/36	20	34/9	9+/14+	10/20	30	50.5
M-39	24/27	9	45/9@	50/50	10/20	30	50.5
M-40	25/31	13	45/9@	9+/18+	12/18	30	50.5

%W,v/p - Tungsten atomic concentration, valley/peak; single entry indicates that no periodicity was observed.

t,W-W - Average sputter time between tungsten peaks, in minutes.

J,nA - Sputter ion beam current in nanoamperes over the raster area; 2X denotes use of Model 04-191 sputter ion gun.

#C/#W - Number of C layers and W layers resolved in depth profiling; + denotes further peaks beyond end of profile; ? denotes poor layer resolution or "wash-out"; solid numbers represent all layers resolved by end of profile.

$\frac{\text{\AA} \text{ W}}{\text{\AA} \text{ C}}$ - As-deposited equivalent thicknesses of W and C, from fabrication data.

d - Sum of $\frac{\text{\AA} \text{ W}}{\text{\AA} \text{ C}}$ and $\frac{\text{\AA} \text{ C}}{\text{\AA} \text{ W}}$.

Layers - Total number of layer pair deposited.

M-18* received an annealing step after fabrication

@ - Profiled with 1KeV instead of 500eV ion beam

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Figure 1. Sputter deposition system schematic .

Figure 2. Auger depth profile of sample M-18 using 500 eV argon ion etch. Note flat "valleys" in the carbon signal.

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(b) Scanning Auger micrograph of the tungsten signal, 100x.
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Figure 5. Auger depth profile of sample M-20 using 500eV xenon ion etch, showing (a) the carbon KLL and tungsten Coster-Kronig transitions and (b) the "pre-carbon" signal. Note secondary peaks in the "pre-carbon" signal, probably due to carbide lineshape.

Figure 6. X-ray diffractometer scan of M-39 using iron x-rays.

Figure 7. Plot of peak reflectivity versus tungsten layer thickness for a series of LSM's.

LSM M-18

LSM M-20

LSM M-20

LSM M-20

REFLECTIVITY VS ABSORBER THICKNESS

(a.)

(b.)

(c.)