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TUNGSTEN-CARBON MULTILAYER SYSTEM STUDIED WITH X-RAY SCATTERING

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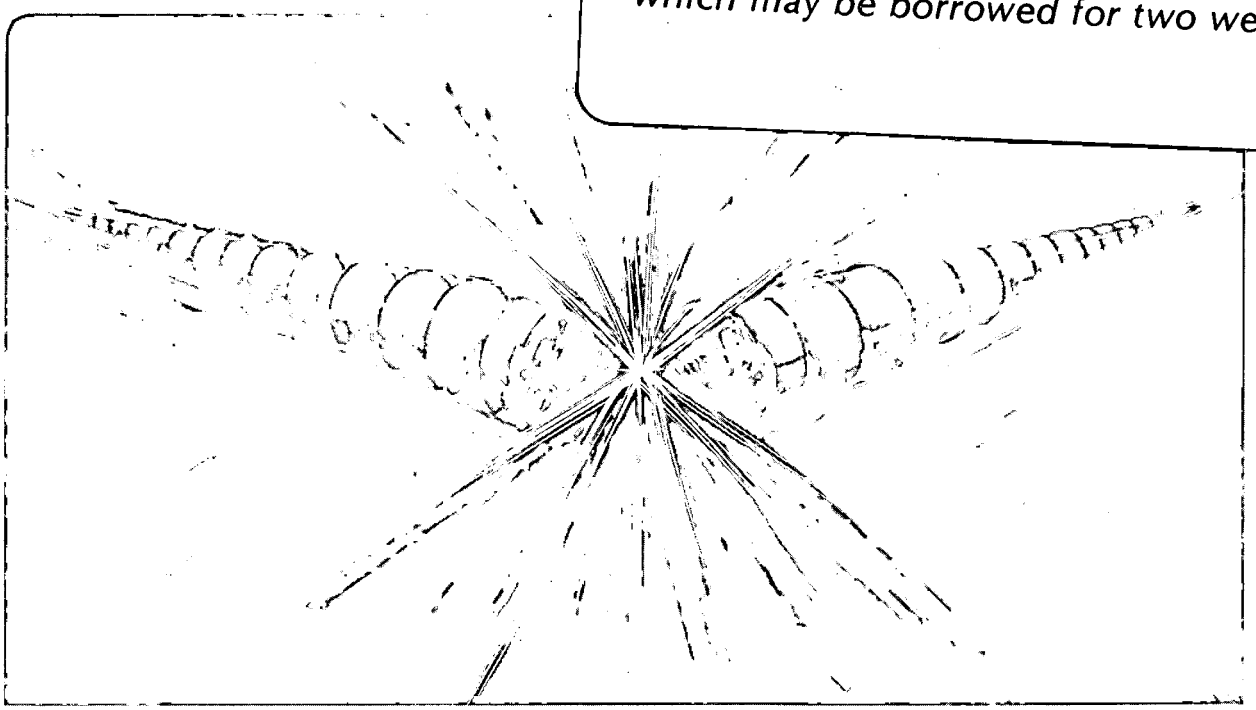

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DISCLAIMER

TUNGSTEN-CARBON MULTILAYER SYSTEM STUDIED WITH X-RAY SCATTERING

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ABSTRACT

The tungsten-carbon multilayer system has been studied using x-ray scattering techniques as a function of multilayer period and annealing. Grazing incidence x-ray scattering shows that interatomic arrangements in the W-rich layers depend strongly on their proximity to the interface with the C-rich layers. Amorphous interface layers are stabilized by intermixing of W and C during deposition into local structures similar to those in the tungsten carbides. Further intermixing and structural relaxation in the amorphous state occurs on annealing these structures. This interatomic structural interpretation is consistent with trends in the observed x-ray optical properties.

INTRODUCTION

The tungsten-carbon multilayer system was one of the first to demonstrate utility as a robust Bragg reflector of x-rays [1], and continues to find new and varied applications as an x-ray optical element. This utility results from the ability to form extremely thin layers of these constituent materials with significant uniformity and stability. Detailed knowledge of the interatomic arrangements of these ultra-thin layered systems, and thermal stability of these interatomic arrangements, has been lacking.

This paper reports on a study undertaken to learn details of these interatomic arrangements and their thermal stability, and to correlate these interatomic arrangements with the multilayers' x-ray optical performance. In addition to this structural interest motivated by x-ray optical properties, thin tungsten and carbon films are of interest for protective thin-film coating applications. X-ray scattering techniques formed the basis of this experimental study. Multilayer Bragg scattering was measured as was the in-plane scattering from interatomic correlations in the grazing-incidence scattering geometry.

EXPERIMENTAL

Multilayer samples were prepared by magnetron sputtering onto substrates floating in temperature and rotating in turn over two elemental targets. One multilayer period was deposited during a single rotation of the substrates. Substrates were highly polished optical flats 1 inch in diameter. The samples discussed here were deposited to have different multilayer periods d, with the same nominal relative amounts of W and C, by keeping the W and C sputtering rates fixed and varying only the rotation velocity to change d for the different samples. Based on the sputtering rates of the individual elements, the W layers would make up roughly 0.4 of the period of the various multilayers, a typical relative thickness for x-ray optical applications. The total thickness of multilayer samples ranged from 0.5 to 1.5 μm. One multilayer was annealed at 10^{-6} torr for 18 hours at 420°C.

X-ray measurements were of several types. A two-crystal, Bragg geometry utilizing Cu $K\alpha_1$ radiation was used to measure the absolute reflectivity spectrum of low-angle multilayer Bragg peaks with the multilayer in the position of the second crystal. Large-period samples showed as many as 19 orders of multilayer Bragg scattering. The grazing-incidence scattering (GIS)

geometry was adopted to measure scattering at a larger range of scattering vector, resulting from interatomic correlations. GIS measurements were made at the Stanford Synchrotron Radiation Laboratory on beamline 6 utilizing 1.2398 Å radiation with an incidence angle with respect to the sample surface of about 0.7°, which is slightly above the critical angle for total external reflection. The GIS geometry and these small incidence angles allow for measurement of scattering from the thin films of interest without measuring scattering from the substrate. One sample was studied using the Seeman-Bohlin geometry.

RESULTS AND DISCUSSION

X-ray Optical Performance

By measuring several orders of Bragg reflectivity for each sample, multilayer periods of as-prepared samples were determined as 108.8 Å, 59.4 Å, 37.0 Å, 19.0 Å and 8.3 Å. First order multilayer Bragg peaks for the samples are collectively shown in Figure 1. The incident beam and total reflection regions are shown in addition to the first order peak for the sample with period d = 108.8 Å. Two general trends of W/C multilayer x-ray optical properties are demonstrated by these data.

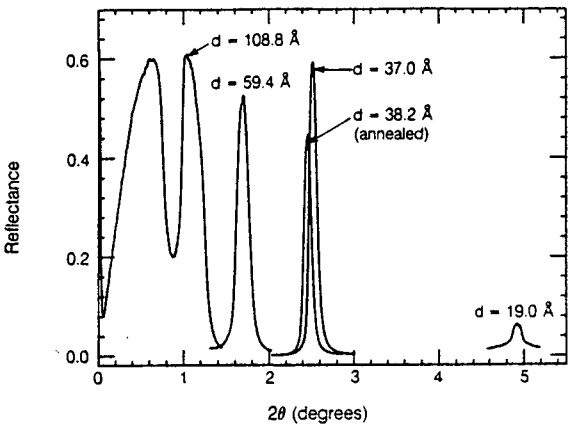

Figure 1. First order Bragg peaks multilayers with different periods.

First, significant peak reflectance values drop sharply as multilayer periods decrease below roughly 20-25 Å. Reflectance values in excess of 0.5 are typically observed for samples with periods larger than these values. The peak reflectance for the 19.0 Å period multilayer in this case is roughly 0.06 [2]. Not shown in Fig. 1 is the first order peak from a sample with period 8.3 Å. For this sample the first order peak reflectivity was of order 10^{-5}. For practical purposes, composition modulation in this sample is negligible. Calculations of multilayer first order of peak reflectance, assuming ideal models with layers consisting of homogeneous, elemental materials with compositionally sharp and smooth interfaces, predict that first order reflectance values remain high with decreasing period. The results presented below are consistent with the hypothesis that decreasing reflectivity with period is associated with intermixing of discrete atoms at the interfaces.

Another trend demonstrated in Fig. 1 is the observation that the period of W/C multilayers expands on annealing. This phenomenon appears to be a general feature in this system [3,4]. In the present case, the sample with period 37.0 Å expanded during annealing to d = 38.2 Å, causing the first order peak to shift by a significant fraction of its width. In this case the multilayer peak reflectivity shows a decrease of 23 percent on annealing. Decreasing peak reflectances are not always observed on annealing this multilayer system under similar conditions; sometimes peak reflectivity remains essentially unchanged or even increases [3,5]. Annealing temperatures of roughly 600°C must be reached before peak reflectances of W/C multilayer systems show catastrophic decreases, signalling gross departures from the layered microstructure of the as-deposited samples.

Grazing-incidence Scattering

Grazing-incidence x-ray scattering was used to study the same multilayer samples to understand interatomic arrangements in these systems and to relate this understanding with trends in multilayer optical performance with period and annealing. In this geometry [6], the scattering vector is predominantly in the plane of the multilayer thin film, so that scattering from in-plane interatomic correlations is measured. The atomic scattering factor describing the scattering amplitude is roughly an order of magnitude greater for W than for C atoms. Thus, W-W correlations scatter with roughly an order of magnitude greater intensity than W-C correlations, which in turn scatter with greater intensity than C-C correlations. Radial distributions obtained from the measured intensity thus have contributions primarily from correlations involving W, and we learn primarily of the W environment in the W-rich layers of these samples with this technique.

Figure 2a shows the GIS intensity for this set of multilayers. These scattering patterns show that for samples with $d \leq 60$ Å, interatomic arrangements appear to be entirely amorphous. The sample with $d = 108.8$ Å shows polycrystalline diffraction peaks resulting from W in its equilibrium, body-centered cubic phase. The observed polycrystalline peaks, together with Seeman-Bohlin geometry diffraction results from this sample, indicate that the bcc W is not highly textured. Utilizing the Scherrer equation for particle-size broadening [7], an estimate of the grain size of the bcc W in the plane of the W-rich layers of 170 Å is obtained from the GIS data. Broadening of these peaks in the Seeman-Bohlin geometry, where the scattering vector is directed more along the sample normal than in the GIS geometry, results in an estimate of the grain size normal to the layers in rough agreement with the nominal thickness of the W-rich layers in this sample. The absence of crystalline peaks associated with C suggests that the C-rich layers of all

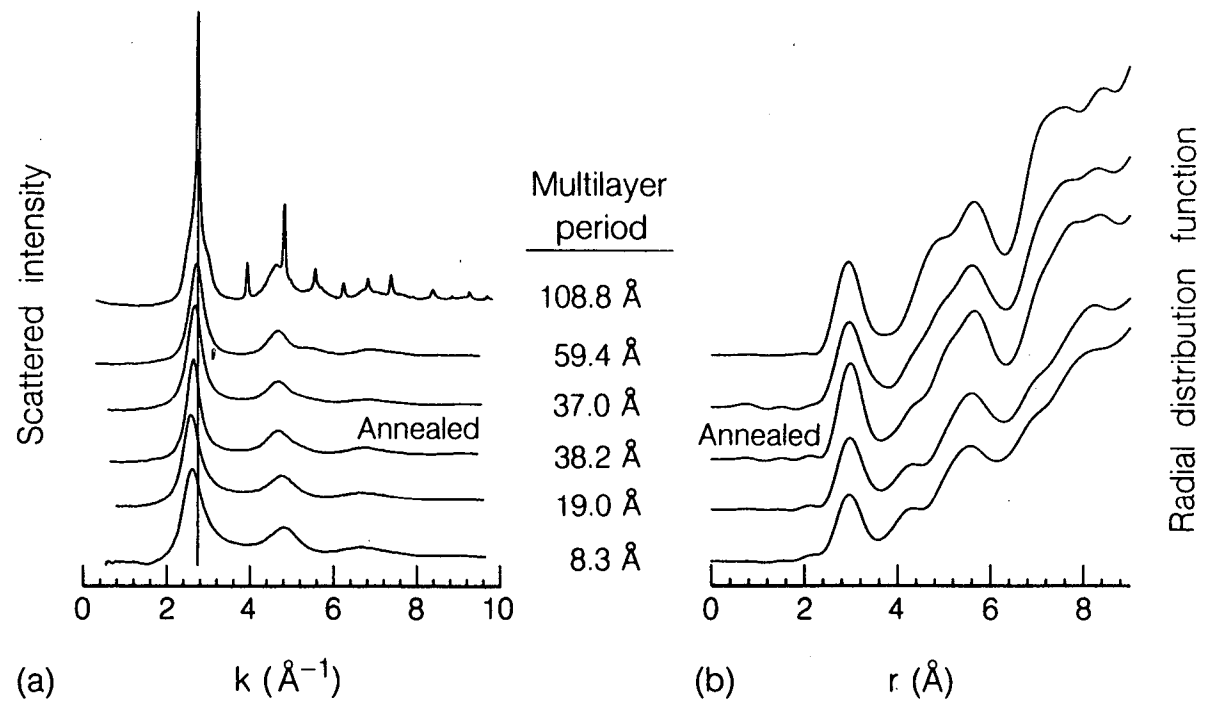

Figure 2. Grazing-incidence scattered intensity from in-plane interatomic correlations in multilayers with different periods is shown in (a). The vertical line at $k = 2.8$ Å^{-1} is positioned at the bcc W 110 peak as a guide to the eye. Radial distribution functions for multilayers with amorphous interatomic arrangements and different periods are shown in (b).

samples are amorphous.

Several inferences about the nature of the interfaces between W- and C-rich layers in this multilayer system can be drawn by observing the trends in the scattering patterns in Fig. 2a with period. In addition to the polycrystalline bcc W in the W-rich layers, a diffuse amorphous scattering pattern makes a significant contribution to the scattered intensity in the 108.8 Å period sample. Considering that the W-rich layers of smaller period samples appear entirely amorphous while the 108.8 Å period sample exhibits both amorphous and polycrystalline components, we conclude that the polycrystalline bcc W exists at the center of the thin W-rich layers and that the interface regions between W- and C-rich layers exhibits the amorphous scattering pattern. Evidently, amorphous interatomic arrangements are stabilized at the sputter-deposited interfaces between W and C, and bcc W does not form until some critical thickness is exceeded. Given that bcc W appears at a period between 59.4 and 108.8 Å, and that the W-rich layers are nominally 0.4 of the period, this critical thickness for bcc W formation must be at least 10-15 Å. The interfaces thus strongly influence local atomic arrangements over significant distances in the W/C multilayer system. Possible differences in W-on-C and C-on-W interfaces cannot be distinguished from these data, though could be significant.

Subtle changes are seen in the amorphous scattering patterns for samples with varying period in Fig. 2a. The amorphous interface regions of the W-rich layers of the d = 108.8 Å sample have an amorphous scattering profile most closely matching the d = 59.4 Å sample. Samples with decreasing periods show systematic changes in peak positions and shapes. Interpretation of these subtle differences is more easily accomplished by studying the radial distribution functions obtained by Fourier transformation of the normalized and background-corrected scattered intensity patterns.

Figure 2b shows radial distribution functions (RDFs) obtained from the amorphous scattering patterns in Fig. 2a. Trends in peak shape and position are observed with period and annealing, especially in the intermediate-range order between roughly 4 and 6 Å. Interpretation of the changing interatomic

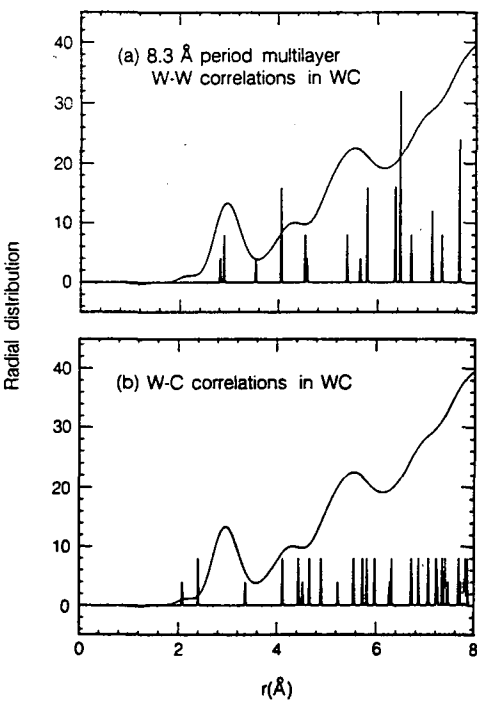

Figure 3. Comparison of RDF for d = 8.3 Å sample with radial correlations in the compound WC.

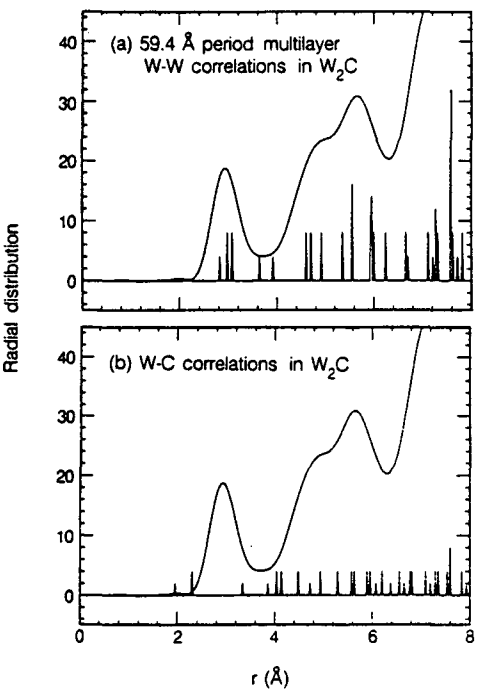

Figure 4. Comparison of RDF for d = 59.4 Å sample with radial correlations in the compound W_2C.

arrangements for samples with d ≤ 60 Å is aided by comparison with radial distributions of W-W and W-C correlations in the tungsten carbides W_2C and WC. These comparisons are, in part, made in Figures 3 and 4, where the RDFs of the d = 8.3 Å and d = 59.4 Å samples are compared with the carbides WC and W_2C respectively. In each figure, (a) shows the radial distribution of W-W correlations and (b) shows that of W-C correlations in the carbides compared to the RDF of the multilayer sample. In these comparisons, the W-W and W-C correlations for the carbides give the number of atoms at a given distance. In the RDFs, W-W correlations are weighted more heavily than W-C correlations, as previously discussed.

Figure 3 shows the RDF for the 8.3 Å period sample compared to the stronger scattering correlations in WC. A small shoulder in the RDF at 2.2 Å coincides with the short W-C first neighbor distances in WC. The peak in the RDF at 4.2 Å corresponds closely to a strong second neighbor W-W feature in WC. Because of the coincidence of these and other features for both the amorphous sample and the compound WC, and because there is closer similarity of these features to correlations in WC than in W_2C, we conclude that the short-range interatomic arrangements in the 8.3 Å period sample are, on average, similar to those in WC. This is consistent with the known small composition modulation of this sample, and is direct evidence for significant intermixing between W and C.

Figure 4 shows the RDF for the 59.4 Å period sample compared to the correlations in W_2C. The features in the RDF are similar to those of typical transition metal-metalloid amorphous alloys, and are better described by the correlations in W_2C than those in WC. Note in particular the close similarity of the first distances and the shape of second neighbor distribution. The close match of the RDF and the correlations in W_2C suggests that intermixing of W and C into local structures as in this carbide provides a reasonable first order description of the W-rich layers in this sample.

Given this interpretation of the 8.3 and 59.4 Å period RDFs, the trends in Fig. 2 are interpreted as resulting from intermixing of W and C in amorphous interface layers with local structures similar to those in the carbides. As the multilayer period decreases, and with annealing, local atomic arrangements in the W-rich layers tend toward those in the more C-rich carbide WC. The similarity of the amorphous part of the d = 108.8 Å scattering pattern with that of the d = 59.4 Å sample suggests that the amorphous interfaces for the large period sample are stabilized by intermixing similar to that in W_2C. The 37.0 Å period sample clearly has features intermediate between those identified for the 59.4 and 8.3 Å period samples. Presumably, more W-rich amorphous arrangements exist in the center of the W-rich layer, with local structures more similar to those in WC in an interface region between the C-rich layers. The d = 19.0 Å RDF is nearly identical to that of the d = 8.3 Å sample, which we take as a model for a nearly homogeneous amorphous mixture of W and C. Thus, significant intermixing in the 19.0 Å period sample is correlated with the decreased x-ray optical performance of this sample.

Annealing causes the 37.0 Å period RDF to change towards that of the 19.0 Å period sample. These structural rearrangements on annealing in the amorphous state thus result in further intermixing of W and C towards local structures like those in WC. The first peak in the RDF of the annealed sample is narrower than that of the unannealed sample, and features at larger r appear more distinct in the annealed sample. This suggests that structural relaxation into more well-ordered local arrangements like those in the carbides is a part of the rearrangements accompanying annealing. The observation of atomic rearrangements on annealing is evidence that the observed intermixing at interfaces of as-deposited samples occurs during the deposition process, rather than after deposition.

CONCLUSIONS

In summary, this atomic-scale structural understanding of the W/C multilayer system helps to explain the changing x-ray optical performance of these structures with period and annealing, and provides insight on the deposition process and stability of this system. GIS techniques have provided direct information about interatomic arrangements in amorphous W-rich layers of W/C multilayer samples of interest as x-ray optical elements. Interatomic arrangements are seen to be highly correlated with the spacing between the interfaces, which is proportional to the multilayer period. Multilayers of large period have polycrystalline bcc W at the center of the W-rich layers and amorphous interfaces with the C-rich layers, while lower period samples have W-rich layers which are entirely amorphous. RDFs suggest that these amorphous arrangements are stabilized by intermixing of W and C during deposition. This intermixing results in local atomic arrangements like those in the tungsten carbides, which may help to account for the room-temperature thermal stability of the ultra-thin metastable layers in these small-period structures. Further intermixing and structural relaxation in an amorphous state are observed on annealing.

ACKNOWLEDGEMENTS

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REFERENCES

1. T.W. Barbee, Jr., in Low Energy X-ray Diagnostics--1981, edited by D.T. Attwood and B.L. Henke (AIP Conf. Proc. 75, AIP New York, 1981), p. 131.

2. The authors have fabricated other W/C multilayers with period roughly 19 Å having first order peak reflectance as great as 0.32. Even so, the general trend of rapidly decreasing reflectivity with period below 20 Å remains.

3. T.W. Barbee, Jr., in X-ray Microscopy, edited by G. Schmahl and D. Rudolph (Springer-Verlag, Berlin, 1984), p. 144.

4. Y. Lepêtre, E. Ziegler, I.K. Schuller and R. Rivoira, J. Appl. Phys. 64, 2301 (1986).

5. E. Ziegler, Y. Lepêtre, I.K. Schuller and E. Spiller, Appl. Phys. Let. 48, 1354 (1986).

6. J.B. Kortright and A. Fischer-Colbrie, J. Appl. Phys. 61, 1130 (1987).

7. B.E. Warren, X-ray Diffraction (Addison-Wesley Publishing Co.. Reading, MA, 1969), p. 251.

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