Anomalous expansion of tungsten-carbon multilayers used in x-ray optics

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Using microcleavage transmission electron microscopy and x-ray diffraction, we have studied the anomalous expansion observed in tungsten-carbon multilayers. Our results show that the expansion is mostly due to an agglomeration of the tungsten and the effect is larger for samples that have a thinner tungsten layer. Implications for soft x-ray optics are discussed.

Tungsten-carbon (W/C) multilayers are extensively used as elements for soft x-ray optics and their properties in this wavelength range have been studied by a variety of groups.[1,2] We have recently shown that the W/C multilayer structure is destroyed by an abrupt crystallization of the W at 750 °C.[3] Some earlier studies [4,5] have noticed an anomalously large, irreversible expansion of the layers which is unrelated to the simple thermal expansion of the constituents. We have undertaken the present studies in order to elucidate the origin of this anomalous expansion. We find that the expansion occurs for samples that have a very thin ($\sim$10–20 Å) W constituent, and it is due to W agglomeration which separates the rigid C layers and thereby increases the modulation wavelength as measured by small angle x-ray scattering.

W/C multilayers on Si(111) substrates were prepared in multisource diode or triode sputtering systems, with a base pressure of $\sim 5\times 10^{-7}$ Torr and Ar sputtering pressure of 10^{-3} Torr. X-ray diffraction measurements were performed in a Rigaku DMaxII diffractometer using CuK_α radiation and electron microscopy measurements were performed on a JEOL 100 CX electron microscope, both equipped with high-temperature capabilities. A microcleavage technique described earlier was used to prepare the samples for the microscopy measurements.[6]

Several research papers have reported the observation of an anomalous change in the small angle x-ray peaks as a function of temperature.[4,5] In all cases, the small angle peaks move to lower angles which was interpreted as due to an irreversible expansion of the layers. Expansions as large as 5% of the multilayer period have been observed after the samples were annealed at 400 °C.[4,5] We have also observed similar large expansions on a variety of multilayers.

To check whether this effect could possibly be due to an expansion of the constituents, we prepared on the *same* sample a multilayer and a thick W or C layer in a Fabry–Perot configuration. Figure 1 shows such a structure (a) before and (b) after heating to 500 °C during one hour. The dark fringes are due to W, the light fringes and the central thick layer (also labeled "spacer") are from the C. It is clear that the central C layer does not expand but that the multilayer does. A similar result was obtained with W as the central layer. These measurements show unambiguously that *thin layers* are necessary for the expansion; questions relating absolute measurements with an electron microscope do not affect these conclusions since in the composite sample all constituents are affected the same way.

To check if the expansion was due to the C or W we prepared a composite sample made of two superimposed multilayers with the C layer thickness almost constant and 16 layers of 10-Å tungsten on the bottom and seven layers of 65-Å tungsten on the top. A microcleavage TEM (MTEM) image of this sample is shown in Fig. 2. The sample consists of 16 periods of 81 Å (d_1) next to the substrate and seven periods of 125 Å (d_2) on top ($d_2 \simeq \frac{3}{2} d_1$). Figure 3 shows the small angle x-ray diffraction of the composite sample at room temperature and after annealing at 380, 520, and 640 °C. The various orders of reflection for the two multilayers are labeled in the figure and agree to 5% with preparation parameters and MTEM results. A computer simulation using the Fresnel formalism [7] reproduces the x-ray diffraction results quite well (Fig. 4). It is quite remarkable that the

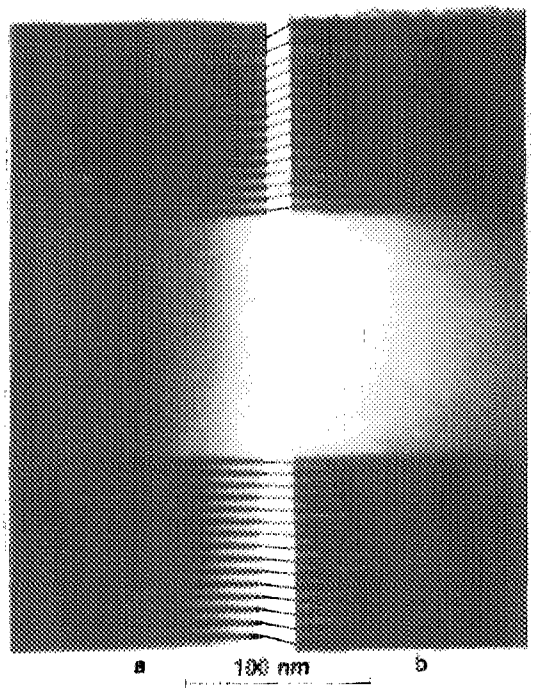

FIG. 1. Microcleavage TEM of a Fabry–Perot structure consisting of a W (dark) /C (light) multilayer on top and bottom and a C spacer; (a) as-prepared sample, at room temperature and (b) after annealing to 500 °C during one hour.

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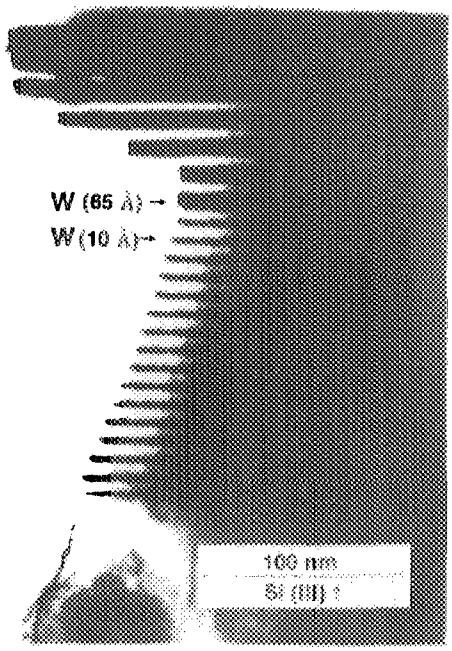

FIG. 2. Microcleavage TEM of a composite sample consisting of 16 periods of (10 Å) W and (71 Å) C (bottom) and of seven layers of (65 Å) W and (60 Å) C (top).

Fresnel formalism works so well for these very thin layers using *only* the thickness of W as an adjustable parameter.[8] Again, as in the case of the Fabry–Perot configuration (Fig. 1), having two multilayers obviates any question relating to absolute measurements with microscopy or experimental difficulties with alignment of the x-ray diffractometer. Figure 3 shows that the sample with the thinner W layer exhibits a larger relative expansion; $d_1 = \frac{2}{3}\, d_2$ before annealing, reaching $d_1' = \frac{3}{4}\, d_2'$ after annealing at 640 °C. A plot of the

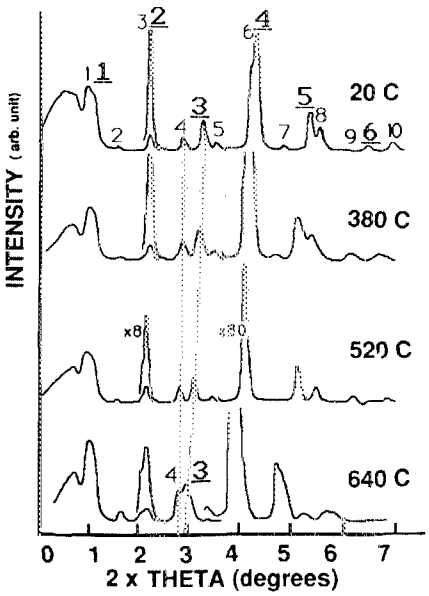

FIG. 3. θ–2θ small angle x-ray diffraction of the composite sample shown in Fig. 2 for various temperatures. The integer numbers indicate the various orders of reflection from the two portions of the sample. The underlined numbers are the orders of reflection for the portion with periodicity d_1. Note that the thinner W sample exhibits a larger shift in the x-ray peaks.

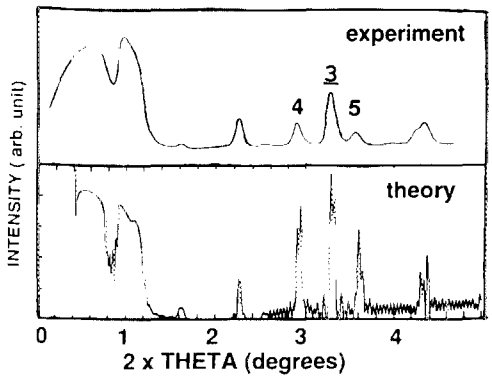

FIG. 4. Small angle x-ray scattering measured at room temperature and calculated using the Fresnel formalism for the sample shown in Fig. 2.

expansion Δd *normalized* to the W thickness d_W is shown in Fig. 5. The expansion occurs in a continuous, irreversible fashion up to the crystallization temperature, where the layered structure disappears, as shown earlier.[3] It is clear from these measurements that the expansion is larger for the *thinner tungsten layers.*

In order to investigate the physical origin of the expansion we annealed *in situ* in the electron microscope a sample that had a gradual variation of W thickness from layer to layer (Fig. 6). These studies show that the thinnest W layers tend to agglomerate with the C layer remaining almost intact. In this fashion, the multilayer period increases. However, it becomes nonuniform in the plane of the film. We should stress that this agglomeration occurs in a monotonic and continuous fashion with temperature.

It is of importance to include these changes in design considerations for x-ray optics using multilayers, especially in the shorter wavelength region (below 10 Å). This type of expansion might introduce serious alignment problems in the optics during use. Perhaps an improvement over existing optics can be obtained by producing crystalline W during the layering process, by introducing an artificial mosaic spread (by slightly roughening the substrate), or by grading the layer thickness.

In summary, we have found the underlying phenomenon for the anomalous expansion observed in W/C multilayers which are used in soft x-ray optics. The expansion is larger in samples with a thinner W constituent and is found to be due to an agglomeration of the W. This phenomenon

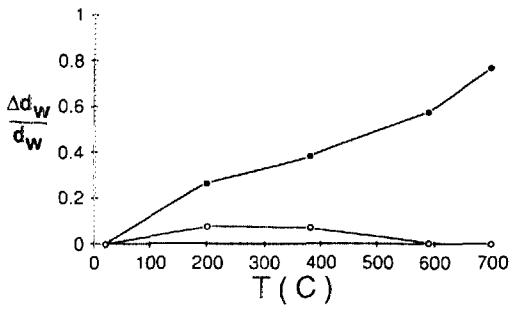

FIG. 5. Relative expansion of the thin (●) and thick (○) W samples shown in Fig. 2.

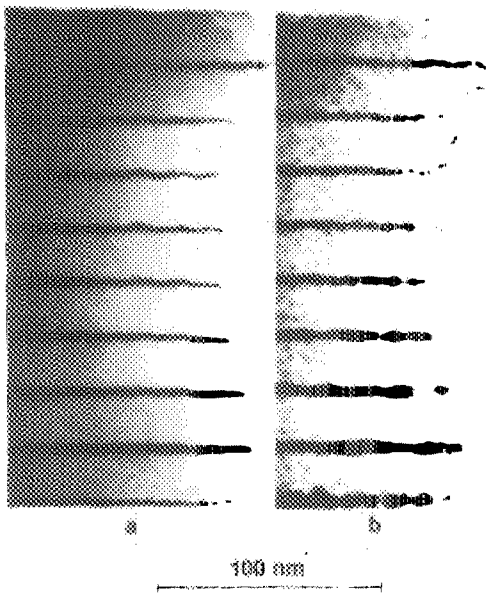

FIG. 6. Microcleavage TEM of a graded W sample (a) as prepared, at room temperature and (b) after annealing to 500 °C during one hour. Note the agglomeration of the W (dark area) in the thinner W samples.

occurs in a monotonic, continuous fashion as a function of temperature reaching 80% relative expansion at 700 °C. Several possible solutions are suggested to improve on materials for x-ray optics designs.

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[8]The periodicity was extracted from the electron microscopy picture shown in Fig. 2. The x-ray refractive indices were obtained from Ref. 7.