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STABILITY OF MULTILAYERS FOR SHORT-WAVELENGTH OPTICS*

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ABSTRACT

A variety of multilayer mirrors with transition metal absorber layers (W-C, WRe-C, Co-C, and Cr-C) have been fabricated and tested up to 1000 C using standard θ - 2θ x-ray diffraction, Debye-Scherrer scattering and microcleavage transmission electron microscopy.

The θ - 2θ x-ray diffraction during annealing shows the Bragg peak position to shift toward lower angles with increasing temperature. This irreversible shift starts at around 300 C and is equivalent to as much as 12% expansion of the multilayer period with a temperature change from ambient to 750 C.

In all cases a crystallization occurs in the metal component between 650-750 C. The different types of crystalline compounds formed have been identified by the Debye-Scherrer technique. As a consequence of this crystallization abrupt changes occur in the multilayer structure. Electron microscopy shows that the surface roughness increases by formation of hillocks and the layered structure is destroyed. Moreover the x-ray reflectivity decreases considerably.

The expansion and crystallization are of great importance in cases where a precise multilayer period is required or in devices intended for high x-ray flux applications.

INTRODUCTION

Metallic multilayers are expected to fill the lack of reflectors between the natural crystals x-rays applications domain and the noble heavy metals U.V. reflecting materials.¹ In addition, to be useful, high thermal or radiation load capabilities are required. This is the case for applications such as synchrotron radiation,² and free electron laser.³

To the best of our knowledge, no high flux-long time experiments have been performed. A short time-high flux experiment (700 MW/cm² in a 20 nsec pulse) reports⁴ that the W-C multilayer reflecting surface placed at 15 cm was destroyed during the reflection of a 1 keV radiation pulse peak. On the other hand, W-C radiation exposure tests⁵ at SSRL for 2.5 months and at ACO for 300

hours showed no change at $\text{CuK}\alpha$ energy (8 keV). Earlier annealing studies⁶ at 400°C for 4 hours in vacuum for ReW/C, Cr/C, V/C, and Ru/C multilayers showed no appreciable changes in X-ray reflectivity, while Ni/C, Co/C and Fe/C multilayers crystallized and lost their reflectivity. A volume expansion of the layers with temperature has been also reported.^{6,7} Expansions as large as 5% have been observed when the samples were heated to 400°C.⁶ This interpretation is based on the observation of a shift of the small angle X-ray peaks to lower angles.

The purpose of this paper is to study the behavior of metallic multilayers under thermal load, which as a first approximation is expected to lead to similar consequences as under radiation load.

MULTILAYER FABRICATION

A variety of multilayers mirrors with transition metal absorber layers (W-C, WRe-C, Cr-C, and Co-C) have been prepared on Si substrates in a multisource evaporation system.^{8,9} Here, two electron beam guns produce evaporation at typical rates of 0.5 Å/sec in a vacuum of $\sim 10^{-6}$ Torr. Some W-C multilayers were also prepared using a multisource triode sputtering system. In this case the substrates rotate on a planetarium and the sputtering targets are alternately commuted.

EXPERIMENTAL SET-UPS

X-ray diffraction measurements on the multilayers were performed with a Rigaku D/max diffractometer at $\text{CuK}\alpha$ line. Each sample, placed inside a controlled atmosphere chamber, was heated by electric resistances surrounding the multilayer and its holder. A temperature controller was able either to maintain a given temperature (between ambient temperature and 1000°C) or to perform a given heat-cool thermal cycle. A large Al foil angular window and the possibility of sample alignment allowed in-situ X-ray reflectometry measurements. Transmission Electron Microscopy (TEM) and electron diffraction using a microcleavage preparation technique described earlier¹⁰ were made on a Jeol 100 CX microscope using a hot stage grid holder. Debye-Scherrer scattering was also performed on these multilayers before and after annealing.

EXPERIMENTS

We have measured the first Bragg peak position as a function of temperature for different ReW-C multilayers. Figure 1 shows the relative variation of the $\lambda/\sin\theta$ parameter from the $\lambda/\sin\theta_0$ value at the initial ambient temperature. All the samples exhibit few changes to 300°C followed by a 4% increase of $\lambda/\sin\theta$ to 500°C, and then depending on the sample (period, number of layers, atmosphere) a variation of 5% to 12% between 600 and 750°C. This variation is due to the multilayer period (d) variation ($2d = \lambda/\sin\theta$). In order

to understand the underlying physical mechanism of this expansion, a variety of other studies have been performed.¹¹

The irreversibility of the expansion has been studied by performing a series of cyclic thermal annealing experiments. Figure 2 shows the evolution of the first Bragg peak position (2θ) for a ReW-C stack versus "Temperature Log (time)" as is customary in amorphous glasses which exhibit irreversible behavior.¹² The black symbols in figure 2 show that the peak position decreases with increasing temperature. The white symbols show that the peak position does not return to its initial value with decreasing temperature: i.e. the expansion remains at the last value attained and even continues to increase slightly. Since a heat-cool-heat cycle is not instantaneous after the second heating step the peak position is always lower (black symbol).

Fig. 1 $\lambda/\sin\theta$ relative variation of the first order Bragg peak value versus temperature for ReW-C multilayers. The change from the value at ambient temperature is given in percent.

Fig. 2 Evolution of the first order Bragg peak position (2θ) versus temperature $\times$ log(time) for a 100-layer ReW-C stack (period = 36 Å).

Together with the study of the X-ray peak position (Fig. 1) we have followed the evolution of the first Bragg peak intensity versus temperature (figure 3). Care was taken that the observed effects are not due to temperature induced changes in diffracto-

meter alignment. Moreover, most samples were annealed in an Ar environment in order to avoid oxygen contamination. In this case, a correction was applied to account for changes in the absorption due to the Ar gas. Some samples were also annealed in air (curve xxx Fig. 3) in order to study their behavior in a room environment. Figure 3 shows that the intensity of the first order

Fig. 3 Intensity of the first order Bragg peak as a function of temperature.

Bragg peak in all cases is relatively constant and then precipitously decreases at 600 to 750°C (500°C in air). A top TEM view after this step of a W-C (Fig. 4a) and a Cr-C (Fig. 4b) multilayer clearly shows the formation of large grains. Interestingly the C layers remain almost intact as observed in the upper corner of fig. 4b for Cr-C. Electron Diffraction (Fig. 5) shows crystalline rings which were not present at the initial stage. In order to study the nature of the crystallites we performed Debye-Scherrer diffraction on sample scrapped off the substrate. These studies indicate that the abrupt decrease of the first Bragg peak intensity corresponds to the crystallization of the metallic layer which destroys the layered structure. Table I summarizes the results and shows the crystalline material formed in each case. Notice that i) the Debye-Scherrer diffraction before annealing shows the multilayers to be amorphous or very disordered (Fig. 6a); ii) crystallization of W or Re at ~ 750°C (Fig. 6b) causes the destruction of the layers, iii) this occurs before the formation of carbides at higher temperatures.

Fig. 4 Multilayer top view obtained by Transmission Electron Microscopy a) W-C after annealing at 900°C, b) Cr-C after annealing at 745°C. Notice the C layers remaining almost intact (upper corner).

CONCLUSION

X-ray diffraction measurements of a variety of C containing multilayers show an anomalous layer expansion and the destruction of the layered structure around 700°C. The electron microscopy confirms that the destruction is due to crystallization, and the Debye-Scherrer gives an unambiguous determination of the crystallites formed.

Because this expansion and crystallization seemingly occurs for all metal-carbon multilayers, care must be taken to include these changes in design consideration where a precise multilayer period is assumed. In the case of high X-ray fluxes efficient cooling is necessary to limit the optics temperature. We hope that these type of studies will lead to the development of more stable multilayered structures in the near future.

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Fig. 5 Electron Diffraction of a W-C multilayer after crystallization showing seven distinct tungsten rings.

Fig. 6 a) Debye-Scherrer picture of a ReW-C multilayer after fabrication showing only the presence of silicon substrate.
b) Corresponding Debye-Scherrer picture after annealing at 750°C showing a crystalline Re pattern.

High Z material (d = period)	Number of layers	Gas environment	Crystal formed	Annealing temperature
ReW (d = 77 Å)	34	Ar	hexagonal not indexed	950°C
ReW (d = 36 Å)	110	Ar	Re	750
		Air	WO ₃ + Re	500
			W	770
W (d = 32 Å)	51	Ar		
			WO ₃	630
Co (d = 32 Å)	128	Ar	not indexed	575
Cr (d = 71 Å)	27	Ar	Cr ₂ O ₃	745

Table 1 Summary of the result on multilayer annealing

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