Influence of process parameter variation on the reflectivity of sputter-deposited W–C multilayer diffraction gratings

B. Sager, P. Benson, K. Jahoda, J. R. Jacobs, J. J. Bloch, W. T. Sanders, and M. G. Lagally
University of Wisconsin, Madison, Wisconsin 53706

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Multilayer W–C diffraction gratings with nominal d spacings of 35 Å have been fabricated by magnetron sputter deposition. The peak and integrated reflectivities of these films have been measured with AlK_α x rays and compared to theoretical values. The rms surface roughness has been evaluated. The influence of several sputtering-system process parameters on the reflectivities has been investigated.

I. INTRODUCTION

Multiple thin-film layers of two or more different materials have a very wide range of applicability and provide unique testing grounds for physical properties of materials in which the ratio of interface area to volume is large. One important use of multilayer structures is in the fabrication of high-quality soft-x-ray mirrors[1] that can be designed either to act as a diffraction grating for one particular wavelength or as a bandpass reflector that scatters a range of wavelengths into a defined solid angle with high efficiency. The former has applications in wavelength-dispersive, soft-x-ray spectrometry, e.g., for space astronomy or light-element detection in scanning electron microscopy, and in soft-x-ray microscopy. The latter has applications in producing focused beams of x rays for x-ray lithography or other techniques where a high flux of x rays in a range of wavelengths is required in a small area. Multilayer structures that are suitable for x-ray mirrors consist of alternate layers of strong and weak scatterers of x rays. A common combination is W–C, although other suitable ones exist.[2] Layered structures are typically made by sputter deposition or evaporation. The clear advantage of producing x-ray diffraction gratings in this manner relative to such alternatives as Langmuir–Blodgett films is the ultimate tunability of the layer spacing. Model calculations indicate that a significant increase in reflectivity may be possible as well.[1,3]

The major considerations in fabricating a soft-x-ray diffraction grating are high peak and integrated reflectivities at the chosen wavelength, uniformity over a reasonably large substrate area, and stability under high radiation loads and over time. The ability of the grating to produce a diffracted beam with a narrow full width at half-maximum may also be important in some applications, e.g., in high-resolution spectroscopy.

The reflectivities depend on a number of parameters, some of which are related to fundamental principles of scattering from materials and others that are related to deviations from an ideal grating. Among the former, which may be considered as design parameters, are layer spacing, number of layer pairs, and ratio of thicknesses of high- and low-reflectivity materials in a layer pair. Among the features that represent deviations from an ideal grating and thus affect the grating quality and efficiency are interfacial roughness between layers; impurities, especially light impurities in the high-reflectivity material; variations in layer thickness, and substrate roughness or other morphological or impurity defects on the substrate.

The influence of some of the design parameters on the reflectivity is illustrated in Figs. 1–3 with model calculations for W–C multilayers. The calculation[4] uses, as inputs, complex optical constants derived from Henke's measurements[5] for W and C at the appropriate wavelengths and angles, W and C layer thicknesses, and the number of layer pairs. Figure 1 shows the reflectivity of a 20-layer-pair W–C grating with $d = 35$ Å for x rays with wavelengths from 8.34 Å (near-grazing incidence and exit angles) to 67.6 Å (near-normal incidence and exit). The increase in reflectivity at low λ's reflects the well-known dependence of the x-ray scattering power of atoms on θ and λ, i.e., an increase in forward directions and for short wavelengths. Although absorption will have the opposite effect, i.e., depress the reflectivity for grazing angles, a 20-layer grating is not opaque for any diffraction condition in Fig. 1 and the scattering-power dependence dominates the absorption. Figure 2 shows the reflectivity of 20-layer-pair W–C gratings with different d spacings for AlK_α x rays ($\lambda = 8.34$ Å). The increased reflectivity for large d spacings now reflects independently the angular dependence of the scattering power, i.e., to satisfy

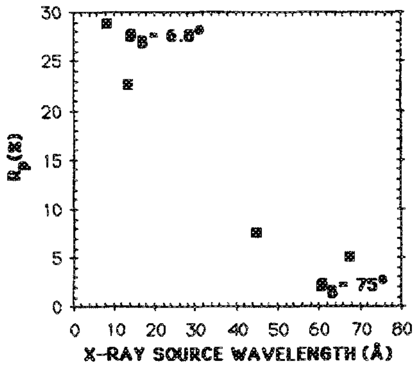

FIG. 1. Dependence of the theoretical peak reflectivity of a 20-layer-pair W–C diffraction grating with $\Gamma = 0.5$ and $d = 35$ Å on x-ray wavelength. The values are given as the percent of incident flux. Bragg angles are shown for AlK_α and BK_α wavelengths.

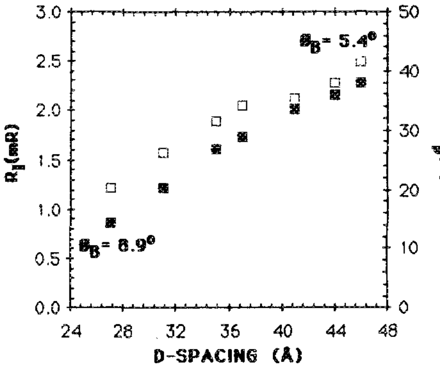

FIG. 2. Theoretical reflectivities for AlK_α x rays of 20-layer-pair W–C gratings with different d spacings. □: integrated reflectivity R_I; ▨: peak reflectivity R_p. Integrated reflectivities are given in milliradians (percentage x angle). Bragg angles are shown for the end points.

the Bragg condition for a given λ, more grazing incidence is required for larger d spacings. Again, the scattering power dependence dominates the absorption, because the multilayer film is not opaque. In both figures, a particular ratio of W to C layer thicknesses, $d_{\rm W}$ and $d_{\rm C}$, was assumed. This ratio is commonly quoted as $\Gamma = d_{\rm W}/d_{\rm W} + d_{\rm C}$. The variation of reflectivity with Γ is shown in Fig. 3, which is plotted for scattering of AlK_α x rays off a 20-layer-pair, $d = 35$ Å grating. It is evident that the reflectivity is highest in the range where the W layer is between 1/3 and 2/3 of the total layer thickness. For thinner W layers there are increasingly few atoms to scatter the x rays. For thicker W layers, the grating definition decreases, and no distinct beams form. The resolution $\lambda/\Delta\lambda$ is also dependent on Γ, a higher resolution resulting for smaller Γ. This effect becomes more pronounced for gratings with many layers. For opaque gratings (>150 layers) the range of Γ's for highest peak reflectivity shifts downward to $1/4 < \Gamma < 1/2$. For such gratings the maximum number of strong scatterers is in any case participating; it is better to have them distributed into more layers rather than fewer. An additional consequence is increased resolution.

Most thin-film multilayer structures have been fabricated by magnetron sputter deposition.[1] A variety of process parameters affect the physical parameters mentioned above. These include, e.g., substrate cleaning, system pressure at the deposition conditions, base pressure of the deposition system, deposition rate, substrate cooling, substrate bias, source anode bias, distance between source and substrate, and rate of rotation of substrates over the source. In this paper we present results of measurements of the influence of some of these parameters on the reflectivity of W–C multilayer films with a nominal 35 Å layer spacing and 20 layer pairs.

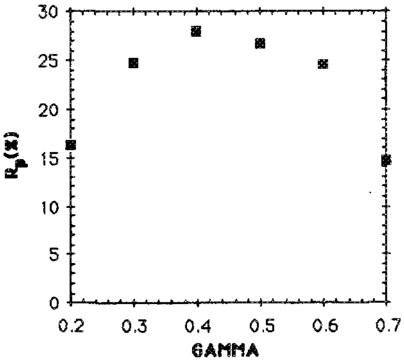

FIG. 3. Dependence of the theoretical peak reflectivity for AlK_α x rays of a 20-layer-pair W–C grating on the value of the ratio Γ of W layer to total layer thickness. The layer spacing is 35 Å.

II. EXPERIMENTAL

Films were deposited in a cryopumped 22 in. diam sputter deposition system equipped with two 4 in. diam magnetron sources and a rotating hollow table connected to a variable-speed motor. The table can be cooled with water or LN_2 and its height relative to the sources is adjustable. A bias can be applied to the table. The sputter sources have shields, shutters, and independently controlled power sources. During deposition the table rotates continuously and a layer is deposited each time the substrate moves over the source. The base pressure in the system is $\sim 3 \times 10^{-7}$ Torr. Si(111) wafers are used as substrates. They are cleaned using an ultrasonic acetone clean, deionized water rinse, ultrasonic methanol clean, deionized water rinse, HF/HNO_3 etch, deionized water rinse, methanol rinse cycle, and are placed immediately into the vacuum chamber.

The reflectivity of the multilayer film is measured in a soft-x-ray diffractometer with interchangeable sources producing AlK_α, CK_α, CuL_α, and BK_α lines. The measurements reported here were made principally with AlK_α x rays ($\lambda = 8.34$ Å). The resolution of the instrument is approximately 10^{-2} rad. The spot size on the sample at normal incidence is of the order of 4×8 mm. The diffraction measurements at AlK_α wavelengths (where the Bragg angle $\theta_{\rm B}$ is $\sim 7^0$) represent an average over an area of 34×8 mm. The $d_{\rm W}/d_{\rm C}$ ratio is determined from diffraction measurements using multilayers with two different d spacings, fabricated by adjusting the deposition rates so that $d_1 = d_{\rm W} + d_{\rm C}$ and $d_2 = d_{\rm W} + 2d_{\rm C}$. From measurements of d_1 and d_2, one can solve for $d_{\rm W}$ and $d_{\rm C}$, and thus Γ. Auger electron spectroscopy (AES) is used to check the impurity concentration and to verify the W/C ratio. All films show a small concentration ($<2\%$) of O as the only impurity, which may, of course, exist as OH. The depth resolution of AES is not good enough to resolve 15–20 Å layers, and only an average W:C concentration can be determined. By assuming bulk densities, one can determine Γ from the AES measurements. AES and diffraction measurements of Γ agree with each other.

Figure 4 shows a θ–2θ plot for a 20-layer-pair film with $d = 46$ Å and $\Gamma = 0.5$, measured with AlK_α x rays. First- and second-order reflections ($\theta_{\rm B} = 5.2°$ and $10.7°$, respectively) are observed. The corresponding theoretical curve for the first-order peak is shown as the solid line. The experimental peak intensity is about 40% of theoretical. The integrated intensity is ~ 1.3 mrad, about 50% of theoretical. The reflectivity of other multilayers made in this range of d spacings seems generally to have been tested with shorter-wavelength x rays (e.g., CuK_α, $\lambda = 1.54$ Å) for which the scattering angle is of the order of 1° and theoretical values are

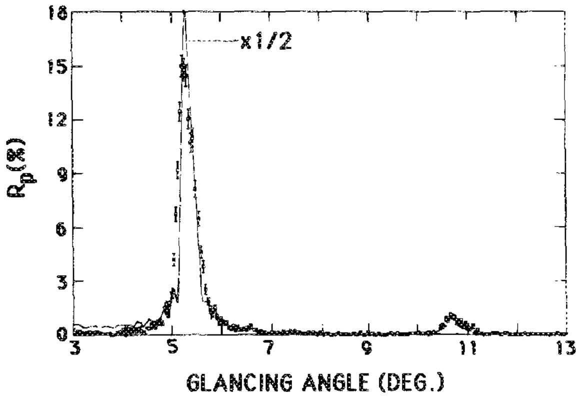

FIG. 4. Diffractometer θ–2θ plot for a 20-layer-pair W–C grating with $d = 46$ Å and $\Gamma = 0.5$ illuminated with AlK_α x rays. The first- and second-order reflections are observed. A calculation of the reflectivity in the first-order reflection for an ideal grating with these parameters is shown as the solid curve; note that the scale is 1/2. The theoretical curve is also slightly narrower.

consequently about a factor of 2 higher.[6] Experimental peaks reflectivities vary from 5% to 90% of theoretical, with most values below 50%. Thus our results are comparable to the current state-of-the-art.

III. INFLUENCE OF PROCESS PARAMETER VARIATION ON REFLECTIVITY

We have investigated the effect of varying several of the sputter deposition process parameters on the x-ray reflectivity of the multilayer structure. One that most transparently shows an influence is substrate cleaning. Figure 5 shows a comparison for a thoroughly cleaned Si(111) substrate and for partially cleaned ones. A factor of 2 improvement is observed for a cleaned substrate relative to situations in which the oxide is not removed or in which hydrocarbon species are left on the substrate.

We have deposited films with the rotating table cooled by water and by LN_2, and have observed no difference in reflectivities. We cannot measure the surface temperature of our films, but estimate that it does not exceed 100 °C during the deposition. Although many films fabricated by others are made with LN_2 cooling, we are not aware of published evidence that this cooling matters for W/C multilayers.

Figure 6 shows peak and integrated reflectivities as a function of layer spacing, measured with AlK_α x rays. As demonstrated in Fig. 2, the reflectivity of x rays with a particular wavelength is expected to decrease for lower d spacings. However, the observed decrease is greater than the model prediction shown in Fig. 2. We believe that this decrease is evidence for the increased influence of surface roughness or layer thickness variation at low d spacings, but have not been able to demonstrate this directly. An estimate of surface roughness, using the standard approach,[7] and attributing all differences between measured and theoretical reflectivities to surface roughness gives rms values of ~7 Å in our films.

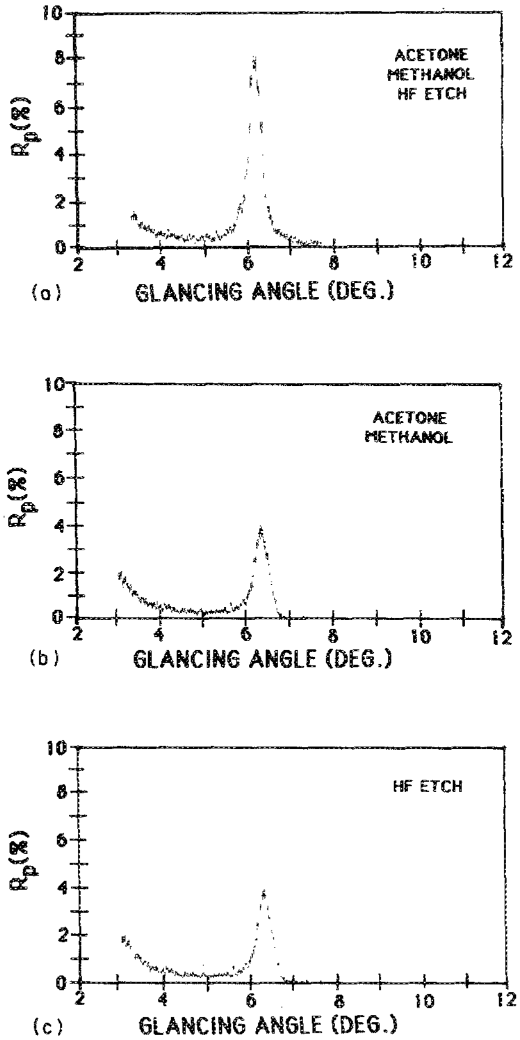

FIG. 5. Diffractometer θ–2θ plot using AlK_α x rays for 20-layer-pair W–C gratings fabricated on substrates subjected to different cleaning procedures. $\Gamma = 0.5$ and $d = 35$ Å.

The dependence of reflectivity on sputter gas pressure is shown in Fig. 7. It is clear that lower pressures produce better gratings. We presume that smoother layers are created at lower pressures. We can think of two reasons. At lower pressures, there will be fewer collisions between sputtered species and the sputtering gas. The average energy of arriving species will thus be higher. This can lead to some atomic mixing in the growing film and also to reduced shadowing effects because of the greater mobility of arriving atoms. Both phenomena can make the film smoother. Second, at lower pres-

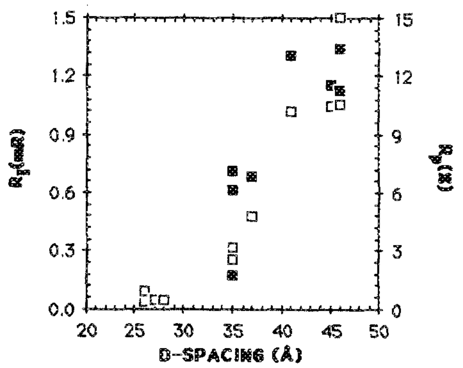

FIG. 6. Dependence of the reflectivity on the d spacing of 20-layer-pair W–C gratings, for AlK_α x rays. ☐: integrated reflectivity R_I; ■: peak reflectivity R_p. $\Gamma = 0.5$.

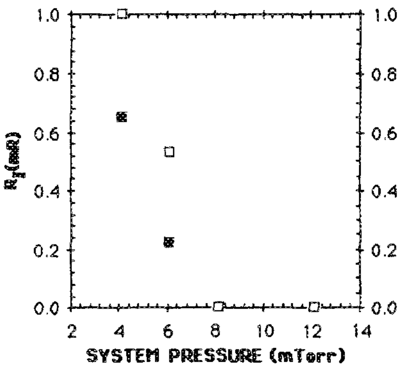

FIG. 7. Dependence of the reflectivity of 20-layer-pair W–C gratings on sputter gas pressure. ☐: integrated reflectivity R_I; ▩: peak reflectivity R_p. $\Gamma = 0.5$, $d = 35$ Å, measured with CK_α x rays. Note the much lower reflectivity values, indicative of strong absorption for CK_α x rays.

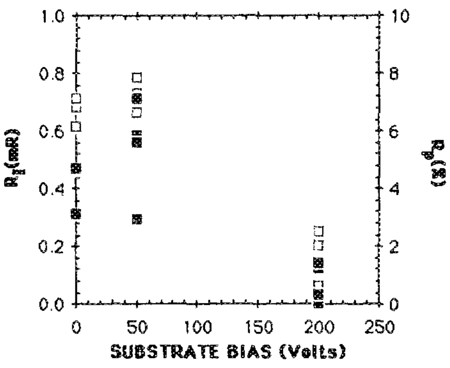

FIG. 8. Dependence of the reflectivity of a 20-layer-pair W–C grating on substrate bias during deposition, measured with AlK_α x rays. $\Gamma = 0.5$ and $d = 35$ Å. ☐: integrated reflectivity R_I; ▩: peak reflectivity R_p.

sures the gas flow through the source will likely be more uniform, causing less variability in sputter rate and thus in layer thickness. There could also be less Ar gas inclusion in the layers at lower pressures.

Some, albeit weak, supporting evidence that slight mixing at the growing film is beneficial comes from substrate bias variation measurements. Figure 8 shows reflectivities for films made with different biases applied to the substrate. It is clear that a large (e.g., 200 V) bias produces poorer films. However, a 50 V bias appears to improve the reflectivities slightly compared to no bias.

Finally, the use of anode rings at the magnetron sources to collect electrons appears to have little influence on the reflectivity of films produced in our system. This result is consistent with the earlier conclusion that substrate cooling has no influence. The elimination of electrons that might otherwise strike the growing film may cause a somewhat lower surface temperature, but the temperature is apparently already low enough to avoid significant diffusion. In fact, an interesting question is whether some surface diffusion may actually be beneficial for smooth morphology. To test this hypothesis would require making films at several substrate temperatures above the ambient (< 100 °C) film temperature. Films annealed after deposition show strong morphological changes above several hundred °C.[8]

IV. CONCLUSIONS

We have fabricated W–C multilayer films using sputter deposition. Reflectivities at the wavelengths that we have used for testing are comparable to those reported in the recent literature. We have evaluated the influence of several process parameters on the reflectivities. We have found that, at least for Si substrates, thorough cleaning is essential; that sputter gas pressure markedly affects the quality of the grating; that high substrate bias leads to a degradation in properties, whereas a low bias may be beneficial; that collection of electrons with anode rings appears to have little effect on grating quality; and that the quality of gratings with small *d* spacings is, as usually found,[1] worse than that for gratings with larger spacings, reflecting the influence of surface roughness and layer thickness variation. The effect of some of these parameters separately has been known; however, the synergism between them may be of considerable importance in determining grating quality. This work is an initial attempt at exploring such possibilities.

ACKNOWLEDGMENTS

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[1] For recent progress in this area, see papers in Proc. S.P.I.E. **563** (1985).

[2] See, for example, R.-P. Haelbich, A. Segmuller, and E. Spiller, Appl. Phys. Lett. **34**, 184 (1979).

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