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## LETTER TO THE EDITOR

## High thermal stability of amorphous CoMoN/CN compound soft-x-ray multilayers fabricated by dual-facing-target sputtering

H L Bai<sup>1</sup>, Z J He, W B Mi and E Y Jiang

Department of Applied Physics, Faculty of Science, Tianjin University, Tianjin 300072, People's Republic of China

E-mail: baihaili@public.tpt.tj.cn

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### Abstract

The thermal stability of CoMoN/CN compound soft-x-ray multilayers has been investigated by monitoring the structural evolutions of CoMoN and CN sublayers at annealing temperatures up to 800 °C, and the interfacial diffusion at annealing temperatures below 300 °C. It is shown that the thermal stability of CoN/CN multilayers can be improved significantly by enhancing the incorporation of nitrogen in the CoN sublayers through doping with Mo. Both thermodynamic calculations and x-ray photoelectron spectroscopy analyses give information on the charge transfer from the valence band of Mo to the unfilled valence band of Co and a remarkable chemical shift of the N atoms. The strong chemical bonding between the N and Co atoms and the Mo nitride aggregation in the grain boundary of the cobalt are thought to be the main mechanisms producing the high thermal stability of the CoMoN sublayers. The period expansion at annealing temperatures below 600 °C, which is mainly a result of the density reduction of CN sublayers, was suppressed effectively by improving the incorporation of nitrogen in the CN sublayers. The small negative interdiffusivity measured by x-ray diffraction reveals stable interfaces of CoMoN/CN multilayers. These results illustrate that incorporation of refractory metal and establishing strong chemical bonds are quite effective in obtaining high thermally stable CoMoN/CN compound soft-x-ray optical multilayers.

The appearance and wide applications of synchronous radiation have stimulated great interest in x-ray optics, especially in the soft-x-ray band. The research and development of soft-x-ray-imaging instruments are important areas in the current research in x-ray optics. With the

<sup>1</sup> Author to whom any correspondence should be addressed.

**Table 1.** Relative atomic fractions determined by XPS.

Elements	Atomic fraction (at.%)			
	CoMoN	CN of CoMoN/CN	CoN	CN of CoN/CN
C	—	65	—	79
N	25.6	35	17.4	21
Co	68.2	—	82.6	—
Mo	6.2	—	—	—

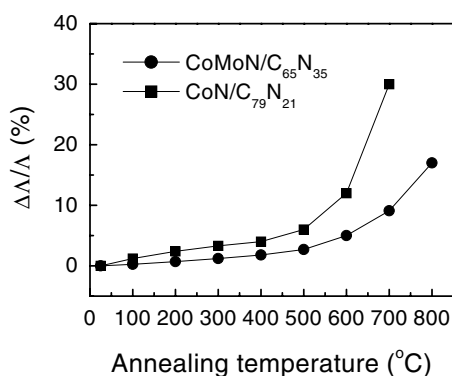
development of materials micro-manufacture technology, it is possible now to manufacture optical devices on the atomic scale. The soft-x-ray multilayer mirror is one such nanometric device, consisting of alternating layers of materials with low and high electron densities, generally referred to as the spacer (C, B<sub>4</sub>C and Si etc) and absorber (Fe, Co, Ni, Cr, W and Mo etc), respectively [1–3].

The thermal stability of soft-x-ray optical multilayer mirrors is related, at high temperatures, to the structural changes of the mirrors, such as sublayer structural revolution, interfacial diffusion and reaction. This is especially important for the soft-x-ray optical multilayer mirrors used under synchronous radiation, as the mirror is usually heated up to several hundred degrees centigrade [4]. Unfortunately, most soft-x-ray optical multilayer systems are destroyed either due to the recrystallization of the amorphous sublayers or due to the interfacial reaction and interdiffusion. We thus need to develop a new generation of soft-x-ray multilayers that can work under a high-power beam without undergoing radiation damage. Compound soft-x-ray multilayers are considered to be good candidates for consideration, because both the absorber and the spacer can be made of relatively inert and stable compounds, so that the tendency to interdiffusion and reaction at the interface is minimized. Another advantage is that compounds are generally deposited in the amorphous condition and their composition can be tuned to get a relatively high glass transition temperature. In this letter, we present an observation of significantly improved thermal stability of CoMoN/CN compound soft-x-ray multilayer mirrors fabricated by facing-target sputtering.

The CoMoN/CN soft-x-ray multilayers were prepared with a dual-facing-target-sputtering (DFTS) system, whose base pressure was better than  $1.33 \times 10^{-4}$  Pa. The layer thickness was controlled with a quartz oscillator, and the  $\Gamma$  ratio of the thickness of the absorber layer (Co layer) to the multilayer period was 0.4. Classical thermal annealing was performed in a vacuum furnace to simulate the real application environment. We investigated the thermal stability using complementary measurement techniques, such as that of low-angle x-ray diffraction (LAXD), transmission electron microscopy (TEM), Raman spectroscopy (RS) and x-ray photoelectron spectroscopy (XPS).

The wavelengths  $\Lambda$  of the multilayers determined from the LAXD pattern are 2.54 nm (for the effective interdiffusivity measurement only) and 5.05 nm. The atomic concentrations of the CoMoN and CN monolayers prepared under conditions the same as those in which the sublayers were deposited are presented in table 1. Also presented in the table are the N concentrations in the CoN and CN sublayers of the CoN/CN multilayer, whose deposition conditions were the same as those for the CoMoN/CN samples except for the different sputtering targets. Obviously, the atomic fraction of N (27.3 at.% without taking Mo into account) from CoMoN films is much higher than that in CoN films, i.e. Mo doping can effectively enhance the incorporation of nitrogen.

Figure 1 shows the relative period expansions ( $\Delta\Lambda/\Lambda$ ) of the annealed CoMoN/C<sub>65</sub>N<sub>35</sub> multilayers. At annealing temperatures below 600 °C, the period expansion is only 5%,



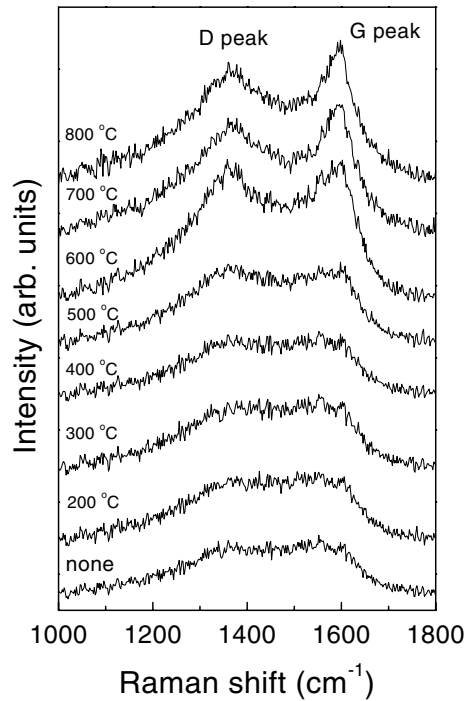
**Figure 1.** The relative period expansion of the annealed CoMoN/CN and CoN/CN soft-x-ray multilayers.

which mainly comes from the structure evolution of CN sublayers, i.e. the bond transformation from  $sp^3$  to  $sp^2$  [5]. At annealing temperatures higher than 600 °C, extra period expansion (4 and 12% at 700 and 800 °C, respectively) due to the recrystallization of the amorphous sublayers (see figure 4) was observed. Comparing with the period expansion of CoN/C<sub>79</sub>N<sub>21</sub> also shown in figure 1, we find that the thermal stability of CoMoN/C<sub>65</sub>N<sub>35</sub> multilayers is much better than that of CoN/C<sub>79</sub>N<sub>21</sub> multilayers.

Figure 2 presents the annealing temperature dependence of the Raman spectra of the CoMoN/C<sub>65</sub>N<sub>35</sub> multilayers. In the range of the Raman shift measurements, the recorded signal is only from the CN sublayers. The fitting results for the diamond-like spectra decomposed by using two Gaussian lines are shown in figure 3. A higher thermal stability of the C<sub>65</sub>N<sub>35</sub> sublayers, reflected by the fact that all the curves for CoMoN/C<sub>65</sub>N<sub>35</sub> multilayers change slowly with the annealing temperature, is visible. As revealed in our previous papers [6, 7], the improved thermal stability originates from a higher fraction of  $sp^2$  bonds in the as-deposited samples caused by the *incorporation annealing effect* of nitrogen. The density reduction of CN sublayers on annealing due to the transformation of  $sp^3$  to  $sp^2$  bonding is therefore attenuated significantly, which accounts for the small period expansion of the CoMoN/C<sub>65</sub>N<sub>35</sub> samples (see figure 1). We can thus suggest that enhanced incorporation of nitrogen in the C sublayers is very important for a higher thermal stability.

Presented in figure 4 are the selected-area electron diffraction (SAED) patterns and bright-field images of the CoN/CN and CoMoN/CN multilayers annealed *in situ* at different temperatures. Also presented in the figure is the result for Co/C multilayers for comparison. The as-deposited CoMoN/CN multilayers are amorphous (not shown). For annealed samples, all diffraction rings are from Co–N compounds (below 500 °C), fcc and hcp Co (above 600 °C); no crystalline Mo–Co alloys or Mo–N compounds were detected, indicating that they are amorphous and exist in the grain boundary. The continuous rings in parts (b), (e), (g) and (h) are from graphite. It is also apparent from the images that the annealed CoMoN/CN multilayers have a grain size much smaller than that of the CoN/CN multilayers at equal annealing temperatures. The significant reduction in particle size caused by doping with Mo reflects the better thermal stability of the CoMoN sublayers.

XPS analyses (not shown) give information on the chemical shift on Mo, which is 1.1 eV higher than that for Mo–Mo metallic bonds and assigned as relating to the binding energy of Co–Mo metallic bonds. In the literature [8, 9], the shifts in core-level binding energy were revealed both theoretically and experimentally for bulk and mixed-metal surface systems,

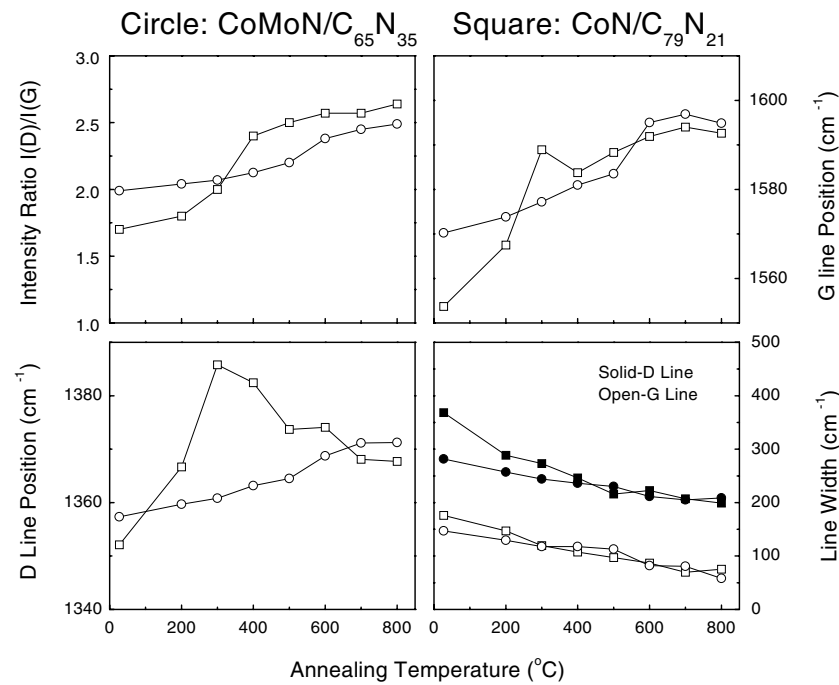


**Figure 2.** Raman spectra of CoMoN/C<sub>65</sub>N<sub>35</sub> soft-x-ray multilayers annealed at different temperatures.

and ascribed to charge transfer, orbital rehybridization and volume renormalization of the atomic energy levels. The shift observed here is believed to be associated with charge transfer from the d band of Mo to an unfilled d band of Co, which has a higher electronegativity. The perturbation of Co atoms caused by low-content Mo atoms is so small that the shift in core-level binding energy associated with charge transfer was not detected. XPS analyses also reveal a multi-peak-structured N<sub>1s</sub> spectrum. The peak energy  $\sim 399.03$  eV, which is slightly higher than that of nitrogen itself,  $\sim 399.0$  eV, is from N $\equiv$ N bonding. The other two peaks, located at 397.25 and 398.17 eV, respectively, are thought to be associated with the Mo–N and Co–N metallic nitrides, because Mo has a stronger affinity with nitrogen as indicated by thermodynamic calculations (not shown) based on the Miedema model [10, 11]. During the deposition, Mo may easily form nitrides because of its strong affinity for nitrogen. This is believed to be the main factor in the significantly enhanced incorporation of nitrogen into Co–N films by Mo addition. On the other hand, when annealed, Mo nitrides may aggregate in the grain boundary of cobalt and inhibit the grain growth during further annealing. A better thermal stability was thus observed.

The thermal stability of multilayer interfaces can be investigated by measuring the interfacial interdiffusivity, which is usually obtained by monitoring the enhancement of the first-order modulation peak on annealing in the low-temperature range, and has been proved to be quite effective [12, 13]. Quantitatively, the interdiffusivity can be calculated according to the following equation:

$$D_{\Lambda} = -\frac{\Lambda^2}{8\pi^2} \frac{d}{dt} \ln[I(t)/I(0)] = D \left( 1 + \frac{8\pi^2 k}{\Lambda^2 f_0''} \right), \quad (1)$$



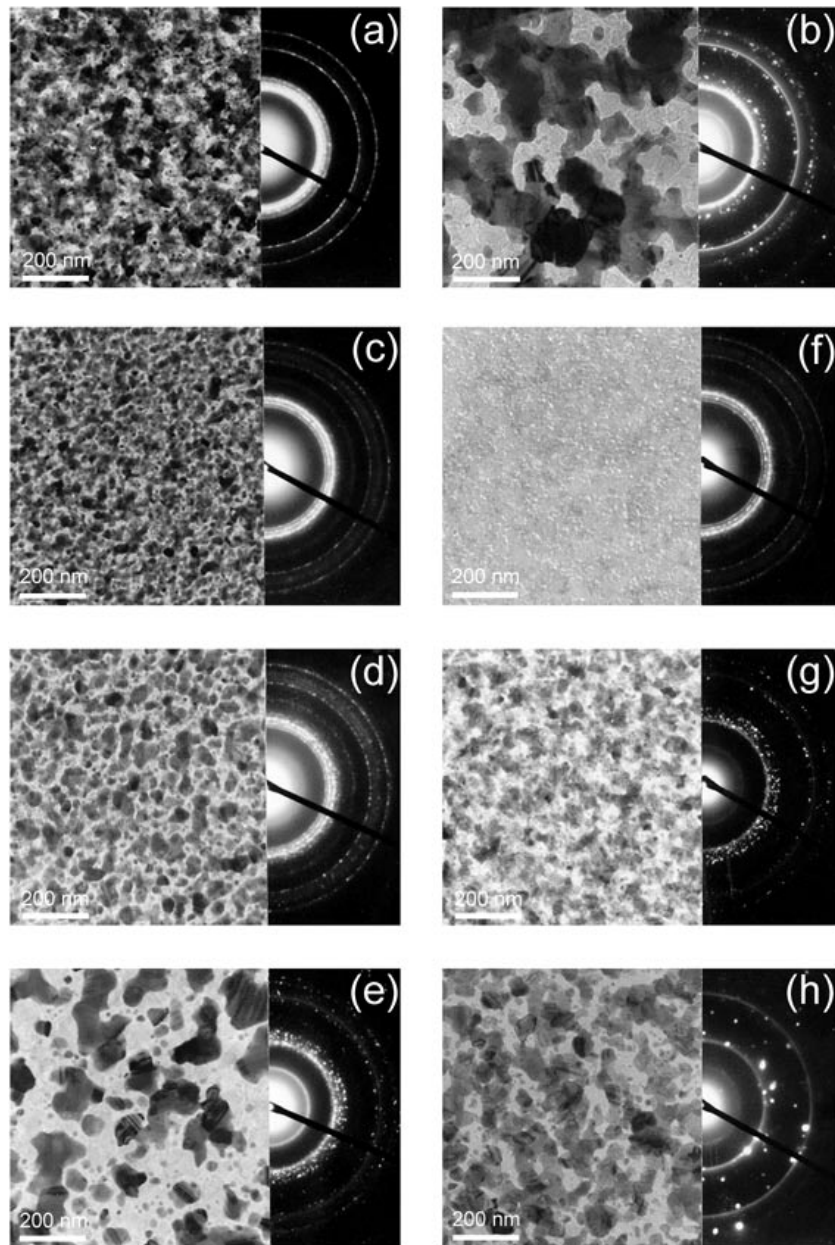
**Figure 3.** Gaussian decomposition of the Raman spectra of the annealed CoMoN/C<sub>65</sub>N<sub>35</sub> and CoN/C<sub>79</sub>N<sub>21</sub> soft-x-ray multilayers.

**Table 2.** Effective interdiffusivities and macroscopic interdiffusion coefficients of the CoMoN/CN multilayers at 523 K.

Interdiffusion coefficient (10 <sup>-24</sup> m <sup>2</sup> s <sup>-1</sup> )	$\Lambda$ (nm)	CoMoN/CN		CoN/CN
$D_{\Lambda}$	2.54	-0.637	-3.079	
	5.05	-1.53	-8.132	
$D$	—	-1.83	-9.798	

where  $D_{\Lambda}$  is the composition- and wavelength-dependent *effective* interdiffusion coefficient (interdiffusivity),  $D$  the macroscopic interdiffusion coefficient,  $f_0''$  the second derivative of the Helmholtz energy and  $k$  the energy gradient coefficient. By applying equation (1) to the linear change of  $\ln[I(t)/I(0)]$  versus annealing time, the effective interdiffusivities and macroscopic interdiffusion coefficients for the CoMoN/CN multilayers at 523 K were obtained and these are listed in table 2. Also given in the table are the data for CoN/CN multilayers [14]. The smaller sizes of the effective interdiffusivities and macroscopic interdiffusion coefficients for CoMoN/CN multilayers are caused by the increased activation energy for Co diffusion [12], which is believed to originate from the strong chemical bonding between Mo and Co and between Co, Mo and N, as indicated above. The results imply that the thermal stability of the interfaces of CoN/CN multilayers is improved by doping with refractory metals such as molybdenum.

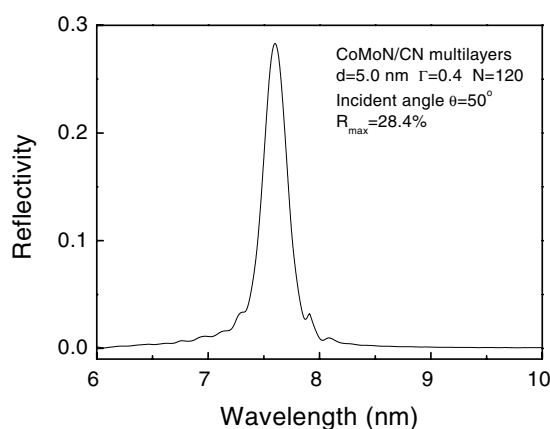
Using dynamic theory [15–17] and the optical indices from Henke tables [18], we have calculated the theoretical reflectivity of ideal CoMoN/CN multilayers. Figure 5 shows the calculated reflectivity curve at an incident angle of 50°. It can be seen that a peak reflectivity



**Figure 4.** SAED patterns and electron microstructures of the Co/C, CoN/CN and CoMoN/CN soft-x-ray multilayers annealed at different temperatures. Co/C multilayers: (a) 500 °C, (b) 800 °C; CoN/CN multilayers: (c) 500 °C, (d) 600 °C, (e) 800 °C; CoMoN/CN multilayers: (f) 500 °C, (g) 600 °C, (h) 800 °C.

of 28.4% can be obtained. The reflectivity of actual multilayers may much smaller than the calculated ideal values due to imperfections such as interfacial roughness and diffusion, and layer fluctuation [12].

In conclusion, the thermal stability of CoN/CN multilayers can be improved through doping with Mo, which can effectively enhance the incorporation of nitrogen in the CoN sublayers.



**Figure 5.** Calculated reflectivity of  $\text{Co}_{68.2}\text{Mo}_{6.2}\text{N}_{25.6}/\text{C}_{65}\text{N}_{35}$  soft-x-ray multilayers ( $d = 5.0$  nm,  $\Gamma = 0.4$ ) containing  $N = 120$  layers at an incident angle of  $50^\circ$ .

XPS analyses detected a charge transfer from the valence band of Mo to the unfilled valence band of Co and a remarkable chemical shift of the N atoms. The thermodynamic calculations performed, based on the Miedema model, agree well with the XPS analyses. Mo nitrides aggregate in the grain boundary and inhibit the grain growth during annealing. Enhancement of the incorporation of nitrogen in the CN sublayers is quite effective in improving the  $\text{sp}^2$  fraction in the as-deposited CN sublayers and thus suppressing the period expansion during annealing. The smaller negative interdiffusivity found by monitoring the changes of the first-order modulation peak on annealing reveals stable interfaces of the CoMoN/CN multilayers. These results suggest that highly thermally stable CoMoN/CN compound soft-x-ray optical multilayers have been formed due to slight doping with refractory metals.

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