LETTER TO THE EDITOR

Improvement of the thermal stability of Co/C soft x-ray multilayers through doping with nitrogen

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Abstract. The thermal stability of Co/C soft x-ray multilayers is improved by 100–200 centigrade degrees through doping with N. The low-angle x-ray diffraction of CoN/CN soft x-ray multilayers indicates that their period expansion is only 4% at 400 °C, and the interface pattern of the multilayers still exists even if they are annealed at 700 °C. High-angle x-ray diffraction and transmission electron microscopy analyses reveal that this crystalline process is significantly retarded by doping with N atoms, leading to a smaller grain size at higher annealing temperatures. Raman spectroscopy analyses of the multilayers give evidence that the formation of the sp^3 bonding is suppressed effectively by doping with N atoms, and thus the period expansion is decreased considerably. The strong covalent bonding between N atoms and the ionic bonding between Co and N atoms can slow down the structural relaxation. The significant suppression of grain growth is believed to be attributable to the coexistence of hcp and fcc Co structures at annealing temperatures higher than 500 °C.

The thermal stability of soft x-ray multilayers is an important property for many applications, since the multilayer optical elements, usually used as reflecting elements in soft x-ray optics, will be subjected to high-intensity radiation and heated to a few hundred degrees centigrade [1]. Their practical application is thus limited severely by the degradation of their quality in high-temperature environments. The high-temperature stability of soft x-ray multilayers remains an open question. A possible way to avoid such problems is to make compound multilayers instead of elemental multilayers. Both the absorber and the spacer can be made of relatively inert and stable compounds so that the tendency towards interdiffusion and reaction at the interface, and sublayer crystallization can be minimized. Another advantage is that compounds are generally deposited in amorphous conditions. Their composition can be chosen such that they may have a relatively high glass transition temperature. Although such an approach can yield better-quality and more stable multilayers, few reports of such studies can be found in the literature because of the difficulties of depositing thin films of compounds by conventional methods [2–5]. In this letter, we report the first observation of the significant improvement in thermal stability of Co/C soft x-ray multilayers achieved through doping with nitrogen.

The CoN/CN soft x-ray multilayers were prepared by using dual facing-target sputtering (DFTS), and the layer thickness was controlled with a quartz oscillator. Two types of annealing were performed: *in situ* annealing in a transmission electron microscope, and classical thermal annealing in a vacuum furnace. The annealing time at each temperature was 0.5 h. We investigated the thermal stabilities using complementary measurement techniques, such as low-and high-angle x-ray diffraction (LAXD and HAXD, respectively), transmission electron microscopy (TEM), Raman spectroscopy (RS), and x-ray photoelectron spectroscopy (XPS).
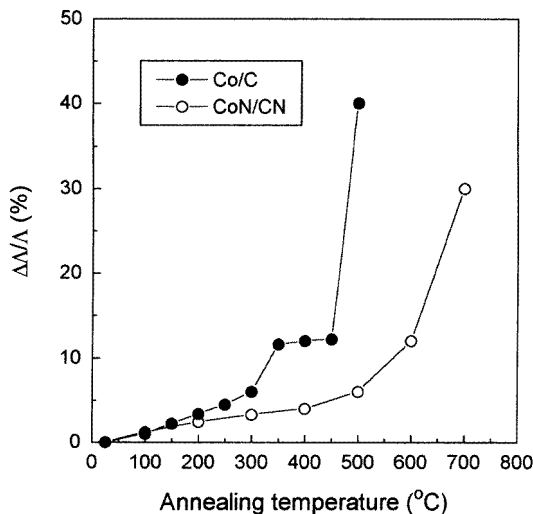
Figure 1. The relative period expansion of the annealed 20-layer-pair Co/C and CoN/CN multilayers.

The multilayers used in this study had a period Λ of 4.94 nm, determined on the basis of the Bragg equation, modified for refraction [6]. The Γ ratio of the thickness of the absorber layer (Co layer) to the multilayer period is 0.4. XPS analyses indicate that the N concentrations in the CoN and CN monolayers prepared under the same conditions as for deposition of the sublayers are 17.3 at.% and 20.6 at.%, respectively. We can thus assume that the sublayers have the same N concentrations. Figure 1 shows the relative period expansion ($\Delta\Lambda/\Lambda$) of the annealed Co/C and CoN/CN multilayers. It is found that, for Co/C multilayers, the period expansion increases continuously with increasing annealing temperature below 350 °C, and reaches a value of nearly 12% in the annealing temperature range 350–450 °C. At a higher annealing temperature, 500 °C, 40% period expansion is observed. Annealing at about 600 °C completely destroys the interface pattern of Co/C multilayers. For the CoN/CN multilayers, as shown in the figure, although the period expansion increases with the increase of the annealing temperature, presenting a similar tendency to Co/C multilayers, it is much smaller than that of Co/C multilayers annealed at the same temperatures, and an enormous period expansion larger than 12% is observed at annealing temperatures higher than 700 °C. Furthermore, the destructive temperature for CoN/CN multilayers is 800 °C, which is much higher than that for Co/C multilayers, indicating that the thermal stability of CoN/CN multilayers is much better than that of Co/C multilayers.

Presented in figure 2 are the HAXD patterns of the Co/C and CoN/CN multilayers annealed at different temperatures. It is apparent from the figure that the annealed CoN/CN multilayers have a grain size much smaller than that of Co/C multilayers; furthermore, the hcp (which is stable at temperatures below 420 °C) and fcc structures coexist in the annealed CoN/CN multilayers even if the annealing temperatures are much higher than the phase transformation temperature, while the Co/C multilayers are solely fcc controlled above 600 °C.

Shown in figure 3 are selected-area electron diffraction (SAED) patterns and bright-field micrographs of both Co/C and CoN/CN multilayers annealed at different temperatures. A
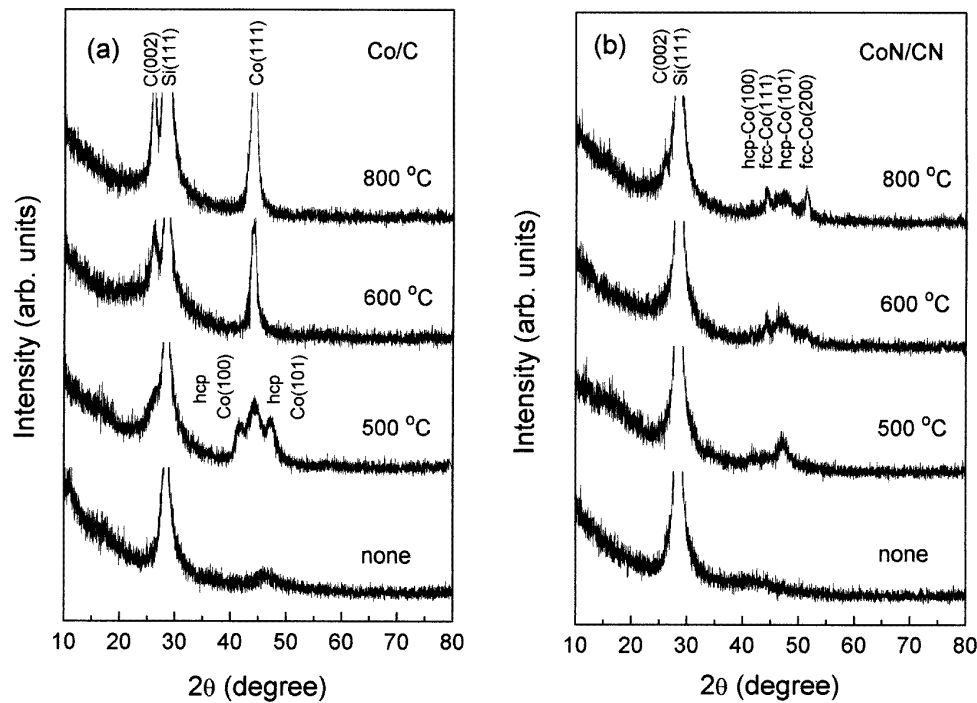
Figure 2. The high-angle x-ray diffraction spectra of 20-layer-pair Co/C (a) and CoN/CN (b) multilayers annealed at different temperatures.

significant reduction in particle size on doping with N can be observed directly and clearly. This result further confirms that the CoN/CN multilayers have a better structural stability than Co/C multilayers. From the SAED patterns (figures 3(c) and 3(d)), we can also observe the coexistence of hcp and fcc structures, which is consistent with the XRD results.

Figure 4 shows the temperature dependence of the Raman spectra of CoN/CN multilayers. It is apparent that the Raman spectra resemble those of diamond-like carbon films. Using a procedure similar to the fitting method used to analyse Co/C multilayers [7], the Raman spectra can be fitted by using two Gaussian lines. From the fitting results, the following important features, different from those of Co/C multilayers [7], are noticeable.

(1) The integral intensity ratio of the D line to the G line increases with annealing temperature, but the peak feature observed at 600 °C for Co/C multilayers no longer exists.

(2) In the temperature range of the annealing, the D-line position shifts from 1352.1 to 1367.7 cm^{-1}, and the G line from 1553.7 to 1594.0 cm^{-1}. The D- and G-line positions of the as-deposited CoN/CN multilayers are much higher than those for Co/C multilayers, and close to that for polycrystalline graphite.

(3) The space between the G line and the D line changes slowly with the annealing temperature, from 201.6 to 224.9 cm^{-1}.

(4) The linewidths of the D and G lines decrease with the increasing annealing temperature, and they are much smaller than those for Co/C multilayers.

Those features, especially the second one, indicate that the primary bonding in the CN sublayers is sp^2, and that it is ordered over a small range (maybe tens of atoms). The disappearance of the peak feature implies that the ordered range of sp^2 is not large enough
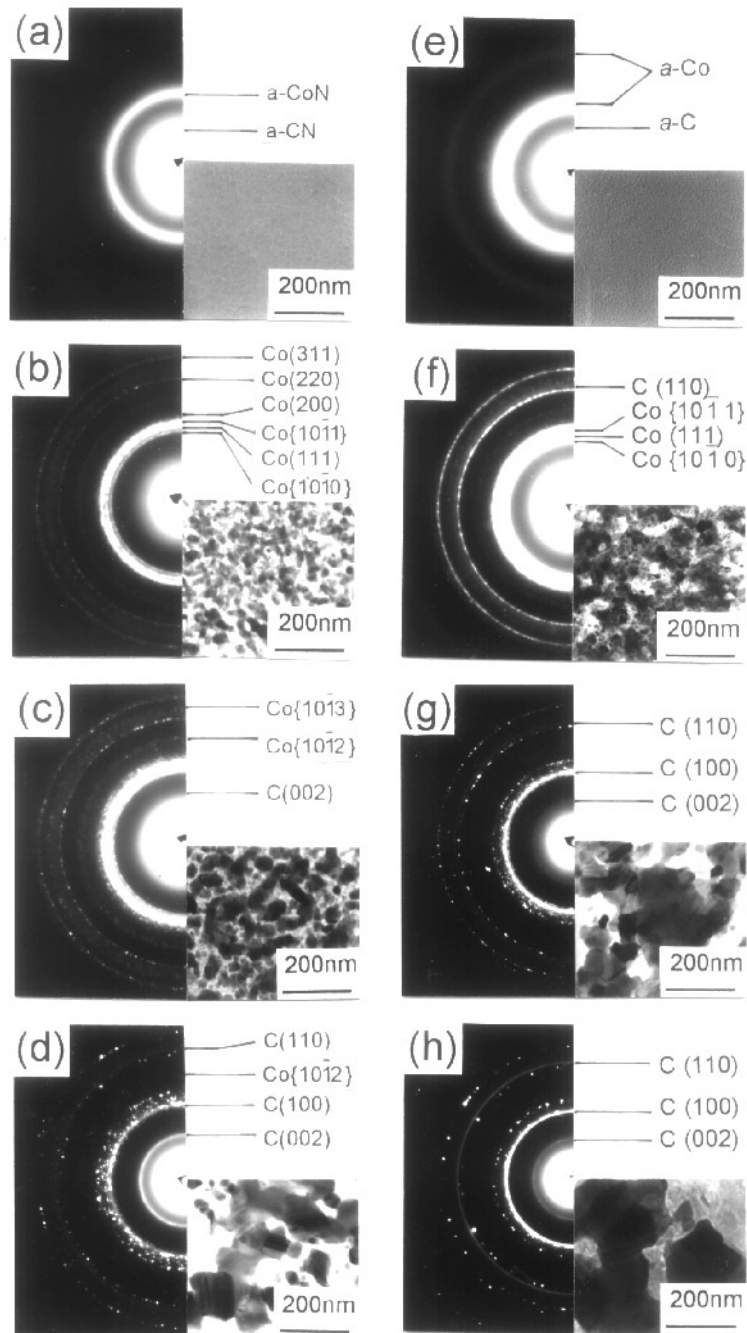
Figure 3. The SAED patterns and the electron microstructures of the 10-layer-pair Co/C and CoN/CN multilayers annealed at different temperatures. CoN/CN multilayers: (a) as-deposited, (b) annealed at 500 °C, (c) annealed at 600 °C, (d) annealed at 800 °C; Co/C multilayers: (e) as-deposited, (f) annealed at 500 °C, (g) annealed at 600 °C, (h) annealed at 800 °C.
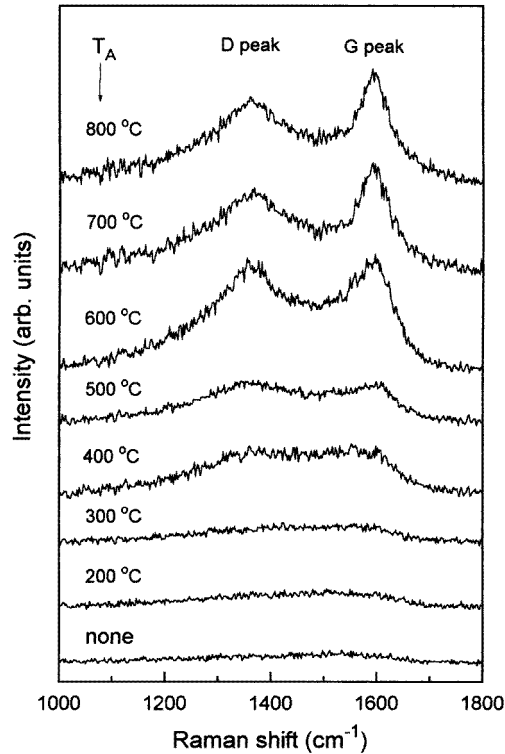
Figure 4. The changes of the Raman spectra of CoN/CN multilayers as a function of the annealing temperature.

to make the intensity ratio decrease at higher annealing temperatures. The smaller linewidths give evidence of lower disorder in CN sublayers.

Since nitrogen does not form a solid at room temperature, it must be bonded with carbon in some way. In order to further clarify the C–N bonding, we also measured the Raman spectrum of the CoN/CN multilayers, scanned from 1800 to 2600 cm^{-1} (not shown). The peak detected at 2230 cm^{-1}, characteristic of carbon–nitrogen stretching, indicates that nitrogen is chemically bonded to carbon with sp^2 bonding in the CN sublayers [8].

To summarize, the formation of sp^3 bonding in the CN sublayers can be effectively suppressed by doping with N atoms, and thus the transformation of sp^3 to sp^2 bonding on annealing [7] will be attenuated significantly.

Although not presented here, XPS analyses suggest that strong ionic and covalent chemical bonds exist between Co and N, and C and N atoms, respectively.

Collectively, the high-temperature annealing results reveal that the damage threshold of Co/C multilayers can be improved by 100–200 centigrade degrees through doping with N atoms. The significant improvement of the thermal stability can be interpreted in terms of the results from Raman spectroscopy and x-ray photoelectron spectroscopy analyses.

As mentioned above, the transformation of sp^3 to sp^2 bonding on annealing is attenuated significantly by doping with N. Therefore, the change of density of CN sublayers on annealing is small, which accounts for the period expansion being smaller than for Co/C multilayers (see figure 1).

The x-ray photoelectron spectra give information on the existence of strong covalent bonding between N atoms and ionic bonding between Co and N atoms, which slow down the tendency towards structural relaxation. Due to the large difference in radius between the Co and N atoms, the N atoms will occupy the interstitial sites of Co lattices. The interstitial N atoms increase the moving viscosity of Co atoms, and thus fcc-Co and hcp-Co coexist even though the annealing temperature is much higher than the phase transformation temperature of 420 °C, leading to suppression of the grain growth.

In conclusion, the thermal stability of Co/C multilayers can be improved by 100–200 centigrade degrees through doping with N. Raman spectroscopy analyses give evidence that the formation of sp^3 bonding can be suppressed effectively by doping with N atoms, and thus the period expansion can be decreased considerably. The strong covalent bonding between N atoms and the ionic bonding between Co and N atoms decrease the tendency towards structural relaxation. Interstitial N atoms are believed to be responsible for the coexistence of the hcp and fcc structures, which leads to the suppression of grain growth.

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