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LAYER FORMATION IN CuNi/C X-RAY OPTICS

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ABSTRACT

A series of Cu/C and CuNi/C multilayer films are prepared for potential use as normal incidence x-ray reflectors. The use of a metal alloy layer is intended to enhance layer formation without metastable metallic carbide formation. The films are characterized both in composition and structure. Addition of Ni to the Cu-rich layer is seen to markedly improve the formation of continuous metal layers.

INTRODUCTION

Multilayer coatings for x-ray optics are becoming increasingly important in applications as x-ray telescopes and soft x-ray projection lithography [1,2]. A primary goal is to maximize normal incidence reflectivity for these uses. For example, theoretical reflectivities as high as 50% are attainable at a 4.5nm wavelength for several metal/carbon multilayer systems (Fig.1). To achieve such high reflectivities requires that the repeat period be short and that the layers be continuous, smooth and the interfaces be compositionally abrupt. Unfortunately, these requirements are usually incompatible. Metals with limited carbon solubility (e.g. Ni, Cr, Co, Fe) often form metallic carbides. These carbon-metal systems are expected to react at the interfaces. Multilayers then result with both rough interfaces and a broadening of the composition gradient. On the other hand, metals with virtually no carbon solubility (e.g. Cu) will not react. These metals have low wettability on C. Layering is unexpected whereas discontinuous metal clusters in a C matrix are most probable. A modified carbon solubility is therefore preferable for controlled surface wettability, the kinetic suppression of compound formation and consequently the promotion of stable layer formation.

Since the conventional method of multilayer synthesis involves a sputter deposition process, metastable phase formation can occur. The interface roughness found in Ni/C multilayers may consequently be attributable to the tendency for metastable metallic carbide (i.e. Ni₃C) formation. Attempts to avoid metallic carbide formation by alloying the carbon layer directly have been successful, for example through the replacement of carbon with amorphous boron-carbide B₄C [3,4]. However, boron additions are not always desirable since boron may act as an absorber of x rays (as for the 4.5nm wavelength) and therefore greatly reduce reflectivity from the initial design standpoint. It is therefore proposed that simple alloying of the (Ni) metal layer may inhibit interface compound formation with each carbon layer.

The reaction between Cu and C is opposite to that with Ni and C. Nickel will tend to wet C and form a metastable compound whereas Cu will apparently not even wet a carbon surface and thereby cluster. The Cu-Ni system features continuous solid solubility. Addition of Ni to the Cu layers may promote wettability, yet inhibit metastable carbide formation. Therefore, competition between surface energy effects - compound formation versus limited wettability, should ideally lead to a CuNi/C multilayer with morphologically sharp interfaces and smooth layers which are well suited for 4.5nm x ray normal incident reflection.

EXPERIMENTALS

The multilayer coatings are prepared by sputter deposition. A nominal 5 mTorr working gas pressure of argon is used to sputter >0.99994 targets from circumferentially arranged planar magnetrons operated in the dc mode onto rotating silicon substrates situated 20 cm above each collimated target surface [5]. Under these conditions the sputtered neutrals are essentially

Fig.1. The normal incidence reflectivity of Cu/C and Ni/C are plotted as a function of x-ray wavelength for ideal multilayers with 250 layer pairs and a 2.24nm repeat period, in which the metal to layer pair thickness ratio is 0.4.

'thermalized' [6,7] and strike the substrate surface at near normal incidence. Deposition rates ($<0.2\text{nm/s}$) and total accumulation are monitored using 6MHz Au coated quartz crystals. The Cu_xNi_y alloy layer, which constitutes 40% of the layer pair thickness, is formed from codeposition of a 6.35 cm diameter composite target. The design structure for normal incidence reflection of 4.5 nm x rays is a 2.24 nm layer pair with a 0.89 nm thick metal layer (Fig.1).

The layer formation is characterized using grazing incidence x-ray diffraction (XRD), transmission electron microscopy (TEM) and Auger electron spectroscopy (AES) coupled with depth profiling. A standard powder diffractometer is operated in the $\Theta/2\Theta$ mode using a graphite monochromator and 8.0 KeV Cu radiation. The coatings are prepared in cross-section for TEM viewing. Image formation is accomplished using amplitude (and unavoidable phase) contrast. AES atomic concentration profiles of the coatings are measured using characteristic peak (920 eV Cu and 783 eV Ni) intensity data accumulated in the derivative mode.

RESULTS

The first series of structures examined are formed by sequential deposition of pure Cu and C. No layers are evident in these films. Repeat periods as large as 3 nm were attempted in this series. TEM bright field imaging (Fig.2a) reveals the Cu clustering into polycrystalline aggregates as a result of the deposition process. The clustering of Cu also evidences in the AES depth profile (Fig.3a).

The second series of films are formed by placing a 3cm diameter Ni cap within the erosion ring of the Cu sputter target. In this way, a Cu_9Ni_1 composition metal alloy is formed (Fig.3b). No layers are formed in the second films series for attempted repeat periods as large as 3 nm. The Cu no longer clusters, however, but appears uniformly dispersed in a C-matrix (Fig.2b). The Ni has been an effective wetting agent for Cu on C.

The third series of films are made with a Ni target superpositioned on top of a Cu target. The Ni target has 9.5mm holes every 60° in a 3.2 cm diameter circle. This produces a sputtered Cu_7Ni_3 metal alloy (Fig.3c). The increased Ni concentration should further promote, enhanced wetting of the Cu-rich 'layers' on C. Near continuous Cu-Ni layers are found (Fig.2c) sequential to C layers as in a 30 layer pair, 3.43nm repeat period multilayer. Layer formation is enhanced, as found from XRD, for repeat periods greater than 2.5 nm (Fig.4).

Fig.2 High resolution electron micrographs of CuNi/C multilayers on (111) Si substrates are viewed in cross-section. Cu clusters (dark regions) in a C-matrix (light region) are found in a) Cu/C whereas the addition of Ni to Cu refines the particle size in b) Cu_{0.9}Ni_{1.1}/C. Layer formation is evident with the further addition of Ni in c) a 3.43nm Cu_{0.7}Ni_{1.3}/C and for d) a 4.33nm Ni/C structure. Bar = 13nm.

Fig.3. Auger electron concentration profiles of the CuNi/C multilayers reveal the average composition of each film over a 25mm² area as a function of sputter time (i.e. depth). In a) the Cu/C 'multilayer', profiling through the Cu clusters (Fig.2a) is evidenced by spikes in the depth profile. In b) the Cu₉Ni₁/C 'multilayer', the addition of Ni to the Cu layer has reduced the size of the metal clusters (Fig.2b) resulting in the disappearance of concentration spikes as evidenced for Cu/C. In c) the Cu₇Ni₃/C multilayer, the further increase in Ni content has resulted in a layered structure (Fig.2c). The last two layer pairs of the film are almost discernable in the first 30 min. of the depth profile.

Fig.4. Intensity of the grazing incidence reflections from CuNi/C multilayers are plotted, as determined from $\Theta/2\Theta$ scans in a powder diffractometer using 8.0 KeV Cu radiation and a graphite monochromator. The onset of layer formation is seen for both Ni/C and Cu₇Ni₃/C as an order of magnitude increase in the reflectivity is measured for layer pairs increasing from <2.6 to >3.3 nm.

The grazing incidence diffraction scans clearly show the intensity of the Cu₇Ni₃/C first order reflection increasing by more than an order of magnitude as the layer pair increases from 2.87 to 3.43 nm.

The fourth series of structures are formed by sequential deposition of pure Ni and C. Layer formation becomes evident, as for Cu₇Ni₃/C, at layer pairs greater than 2.5 nm (Fig.4). The diffraction scan of a 3.27nm Ni/C multilayer is nearly identical to the 3.43nm Cu₇Ni₃/C multilayer with respect to both peak intensity and width. Similar observations of interlayer roughness (Fig.2d) are apparent from TEM, as well.

ANALYSIS

It is interesting to consider the implications of our current findings with respect to the surface energy relationships of the CuNi/C multilayer system. The condition to form a stable layer is the result of the tendency for material X to successfully wet the surface of material Y. A general expression for this condition using the free surface energy ϕ is

$$\phi_X - \phi_Y + \phi_{X/Y} < 0 \quad (1)$$

where ϕ_X and ϕ_Y are the free surface energies of materials X and Y, and ϕ_{XY} is the energy associated with the X-Y interface formation. The calculated surface energies [8] for Cu, Ni and C are $\phi_{Cu} = 1.93 \text{ J/m}^2$, $\phi_{Ni} = 2.36 \text{ J/m}^2$ and $\phi_C = 0.51 \text{ J/m}^2$. (Although different in absolute magnitude, a similar difference between Cu (1.27 J/m²) and Ni (1.73 J/m²) is measured for liquid element, surface tensions [9].)

Since Cu and C are immiscible, we can assume that the Cu on C interface energy $\phi_{Cu/C}$ is negligible (i.e. zero). For Cu on C, we find upon substitution into eqn.(1) that $\phi_{Cu} - \phi_C +$

$\sigma_{\text{Cu/C}}$ equals 1.4 J/m². The predicted increase in surface energy for the Cu on C case shows that layer growth is energetically unfavorable, in agreement with our observations of the Cu/C 'multilayer' structures (Fig.2a). Since layering, however, is indeed observed in Ni/C (Fig.2d), the eqn.(1) inequality must be valid. Therefore, upon eqn.(1) substitution we find $\sigma_{\text{Ni/C}}$ is negative and that $|\sigma_{\text{Ni/C}}| > 1.8 \text{ J/m}^2$. This is not unexpected since Ni and C are soluble suggesting $\sigma_{\text{Ni/C}}$ must be less than zero.

The surface energy of the Cu-Ni alloys, $\sigma_{\text{Cu-Ni}}$, should be between the values of the pure elements. The fact that we have observed improved layer formation upon the addition of Ni to Cu implies that the increase in surface energy is offset by a large (negative) Cu-Ni on C interface energy $\sigma_{\text{Cu-Ni/C}}$. From eqn.(1), we find that

$$\sigma_{\text{Cu-Ni}} + \sigma_{\text{Cu-Ni/C}} < 0.51 \text{ J/m}^2 \quad (2)$$

The observed improvement in layering with increasing Ni content is strong evidence of a concomitant increase in the magnitude of the interface energy $\sigma_{\text{Cu-Ni/C}}$.

SUMMARY

The use of Ni alloying with Cu, by cosputtering, has lead to stable layer formation in the CuNi/C multilayer system. Pure Cu is found to cluster rather than form layers. The use of Ni, in solid solution with Cu, enhances the wettability of Cu on C. Metastable metallic carbide(s) formation is avoided using CuNi rather than pure Ni. This should ultimately result in higher reflectivities for CuNi/C (than for Ni/C) since broadening of the composition gradient is reduced by the suppression of interface compound formation. The procedure of creating stable metal alloy layers, by balancing competing surface energy effects between constituents, is promising for producing short period multilayer x-ray optics.

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