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Nanometer-scale period Sc/Cr multilayer mirrors and their thermal stability

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Abstract

Results of comprehensive characterization of Sc/Cr multilayers for soft X-ray mirrors working in the water window range (2.4–4.4 nm) are presented. Multilayer samples were prepared by ion beam sputtering with up to 250 periods in a range of 1.3–1.75 nm. They were analyzed by transmission electron microscopy (TEM), high resolution TEM, X-ray diffractometry, specular X-ray scattering and diffuse X-ray scattering. The TEM inspection showed good periodicity of the multilayer structure. From simulation studies of the specular reflectivity and a reciprocal space map of the diffuse scattering, it follows that the effective roughness of interfaces is 0.25–0.28 nm, being equal to the geometrical roughness data. Lateral and vertical correlation lengths of the roughness are 7 and 35 nm, respectively. Heat treatment study of the Sc/Cr multilayers revealed a reasonable thermal stability. An increase of the multilayer period of 2.4% was observed after 33 h annealing at 280 °C and a considerable decrease of reflectivity followed above 300 °C annealing for 3 h, which corresponds to the low mutual miscibility between Sc and Cr.

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1. Introduction

Recently, increasing attention has been paid to the interface properties of multilayer structures. In their application of high reflectivity mirrors [1,2], it has been shown that both, the interface roughness resulting from the growth process itself and the interface mixing related to the thermodynamic properties of constituents, affect the quality of a multilayer stack. At present, the most interesting structures are the nanometer-scale period multilayers with a layer thickness below 1 nm. They determine the progress of soft X-ray microscopy of biological objects in the water window between the K absorption edges of C at photon energy of 283 eV and of O at 523 eV [3], which correspond to wavelengths of 4.4 and 2.4 nm, respectively. The effect of the interface roughness σ on the multilayer reflectivity R is well described by a Debye–Waller type term $R/R_o = \exp\{-(2\pi m\sigma/D)^2\}$, where R_o represents the reflectivity of an ideal multilayer with interface roughness $\sigma = 0$, with m and D for the reflection order and the multilayer period, respectively [1]. For a smaller multilayer period, even a small interface roughness produces a large reflectivity reduction. Therefore, the choice of materials for nanometer-scale period multilayers should strictly refer to their characteristics in optical and material sciences.

For the water window, the Sc/Cr multilayer system has been proposed [4–8]. In spite of numerous data reported on the reflectivity of Sc/Cr multilayers, the growth process and interface characteristics are not yet well understood. According to the Miedema calculations [9], ΔH, the heat of formation of a compound of a Sc/Cr pair is +1 kJ/mol. Therefore, a low solubility of a few percents cannot be excluded. Completely immiscible systems such as Ag/Co have a higher ΔH of around +26 kJ/mol.

In this work we present a comprehensive characterization of Sc/Cr multilayers in terms of the intermixing, interface

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morphology, geometrical interface roughness and its replication and crystalline structure of the layers. This characterization relies on a single set of simulation parameters retrieved from the reflectivity and the reciprocal space map of a particular multilayer. First, the basic characteristics of the multilayer stack such as multilayer period, Sc and Cr layer thicknesses and effective interface roughness were derived from the reflectivity scan. Using these values as starting parameters for reciprocal space map simulations, the geometrical interface roughness and its correlation properties were obtained. Finally, the multilayer parameters were refined by the simulation of the soft X-ray reflectivity measured at near normal incidence. We demonstrate that such an approach overcomes ambiguities of the evaluation. The evolution of the multilayer structure with heat treatment is analyzed as well. The study is completed by inspection of the structure inside the layers using the transmission electron microscopy and X-ray diffraction.

2. Experimental details

Sc/Cr multilayers of up to 250 periods were deposited by ion-beam sputtering of an electron cyclotron resonance type operating at the lowest Ar gas pressure of 10^{-3} Pa. The fabrication conditions are: Ar pressure 4.3×10^{-3} Pa, Ar flow rate 0.5 sccm, the acceleration voltage 1.0 kV, Ar ion beam current density 0.8 mA/cm^2 and microwave power 80 W. Other details of the deposition process are published elsewhere [10]. Samples with periods of 1.30–1.75 nm were prepared and analyzed. The regularity of the multilayer stack was checked by X-ray reflectivity. For the sample with a period of 1.75 nm the detailed analysis of the multilayer stack and interface morphology were performed using high-resolution transmission electron microscopy (HR TEM), TEM, electron diffraction (ED) and X-ray scattering methods. Microscopic samples were prepared with cross sectional geometry. After the standard thinning process with 5 keV Ar ions a low energy (300 eV) Ar ion thinning as finishing step was also used to reduce the thickness of damaged layer on the surface of the TEM specimen used for high resolution. A JEOL 200 CX microscope (200 keV, with a point-to-point resolution of 0.34 nm) and a JEOL 3010 electron microscope (working at 300 keV, with a point-to-point resolution of 0.17 nm) was used for conventional and high resolution transmission electron microscopic studies, respectively. X-ray scattering experiments were performed with the CuK$_\alpha$ radiation. The specular and diffuse scattering spectra were measured using a STOE high resolution diffractometer equipped with a GaAs double crystal monochromator. The reciprocal space map was measured by a home-built diffractometer, in which the size of the resolution element in the reciprocal space is $2.10^{-4} \times 2.10^{-4}$ nm^{-2}. The structure of individual layers was checked by a powder X-ray diffractometer equipped with a focusing graphite monochromator located in the diffracted beam path. To study the temperature evolution of the multilayer structure, the samples were heat treated up to 650 °C in a vacuum of 10^{-4} Pa.

3. Results and discussion

TEM inspection of the Sc/Cr multilayer stack showed a periodic multilayer structure. A part of the multilayer stack is shown in Fig. 1 Both periodicity and homogeneity of the multilayer is clearly visible and they illustrate the precise control of the deposition conditions. The stability of the sputtering rate was better than 0.5% during the deposition [10]. High-resolution TEM images of the bottom (near the substrate) and top parts of the multilayer along with the corresponding ED micrographs are shown in Figs. 2 and 3. For all TEM images the Cr layers are dark and Sc layers are bright since the atomic number of Cr is higher than that of Sc. In Fig. 2 (a) the crystalline structure of the Si wafer provides a length scale to estimate the Sc and Cr layer thicknesses. From the TEM pictures it is not possible to decide whether the Sc and/or Cr layers are partially crystalline or amorphous. Although the X-ray diffraction spectra showed no crystalline phase in the multilayer, an ordering tendency within the Sc or Cr layers cannot be excluded since the Sc and Cr layer thicknesses are around 1 nm. The rings in area-selected ED micrographs (Figs. 2b, 3b) are smeared only partly suggesting poorly developed nanograins (1–2 nm in size) in one or both of Cr and Sc layers. As mentioned above, Sc and Cr show low mutual solubility. From the high-resolution TEM images, no intermixing at Sc/Cr interfaces was detected.

In order to determine the parameters of the multilayer stack and to characterize multilayer interfaces both the specular reflectivity and a reciprocal space map by scanning the diffusely scattered intensity were measured. In Fig. 4, the specular reflectivity scan is presented along with its simulation. Clearly distinguished Bragg maxima indicate a stable periodic structure of the multilayer stack, which is also confirmed by TEM. For the reflectivity simulation, the Fresnel optical computation code was used [11]. In the region of the scattering vector $Q_z \geq 0.6$ A^{-1}, the measured intensity decreased until it reached the background level ($\sim 10^{-6}$). The bump around $Q_z \geq 0.2$ A^{-1} is because of the presence of surface oxide layer that was also detected by TEM. The reflectivity simulation provides the layer thickness, its variation across the multilayer stack, and the effective interface roughness.

Generally, the effective interface roughness is related to the interface width combining the effects of the geometrical roughness σ_r resulting from the growth process and interdiffu-

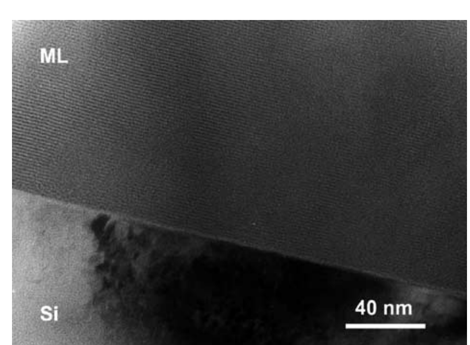

Fig. 1. TEM of the Sc/Cr multilayer with a period of 1.75 nm.