FABRICATION AND MICROSTRUCTURE ANALYSIS OF Pt/C MULTILAYERS FOR HARD X-RAY OPTICS

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Abstract

Pt/C multilayers with periodic length designed for 4, 3, and 2 nm have been fabricated by an ion-beam sputtering process on float-glass or Si wafer substrates. Grazing incidence x-ray reflectivity of the first Bragg peak for the Cu-Kα radiation was significantly reduced with decreasing of the periodic length. Scanning probe microscope analysis and cross-sectional transmission electron microscopy (TEM) studies indicated that the interface roughness of the multilayers increased with decreasing of the periodic length, while density of the Pt layer lowered. Plane-view TEM observations revealed that Pt monolayer films with the thickness corresponding to the periodic length smaller than 4nm have an island structure.

Key Words: Pt/C multilayer mirror, Thin film, X-ray optics, Transmission electron microscopy, Ion beam sputtering

1. Introduction

X-ray multilayer mirror is one of the most important candidates for the optical component applied for x-ray optics such as next generation lithography techniques and x-ray microscopes. Multilayers for x-rays consist of both heavy and light element materials that are alternately deposited with periodic length in the nanometer range. Various combinations of heavy and light elements, and of the periodic length of multilayers, can be chosen depending on the x-ray wavelength and the optics design. Platinum/Carbon (Pt/C) multilayers are advantageous for the applications in a hard x-ray range up to 80 keV with relatively short wavelength, because it has a high contrast of the electron density and no absorption edge in this energy range. Especially, recent development of hard x-ray telescopes successfully demonstrated that the Pt/C multilayers are suitable for focusing optics in astronomical applications [1-3]. The current status of the astronomy regarded with the Pt/C multilayer optics is to observe x-ray with higher energy range above 40 keV. This corresponds to the development of multilayers with the periodic length d=3 – 5 nm or shorter, and improvement of the quality of multilayers in this period range is essential. Since performance of Pt/C multilayers depends heavily on the interface roughness and the errors in the layer thickness, an understanding of microstructures is important to develop multilayers with such extremely small d values. This study aims to investigate interrelations between x-ray reflectivity and microstructures of Pt/C multilayers, and to develop the multilayers with smaller d values for the higher energy x-rays. Transmission electron microscopy techniques are specifically utilized for obtaining atomic details of the microstructural information.

2. Experimental Procedure

Pt/C multilayers with several periodic length were fabricated on float glass or Si(100) wafer substrates by an ion-beam sputtering (IBS) process. Structural parameters of the multilayers were designed as the periodic length d = 2, 3, and 4 nm, the number of layer pairs N = 10, and the thickness ratio of heavy element Γ = 0.4. The IBS system applied for the deposition has a standard arrangement with a 30 mm Kaufman-type DC ion source, a rotative target holder, and a planer substrate holder with rotating and rocking mechanism. The chamber was evacuated to ~5x10⁻⁵ Pa before starting the deposition, and the working pressure during the deposition was ~5x10⁻² Pa. The substrate was kept at room temperature, and the deposition rate was ~5.33 nm/min and ~0.53 nm/min for Pt and C, respectively.

For the evaluation of the reflectivity and microstructure of the fabricated Pt/C multilayers, grazing incidence x-ray reflectivity (GIXR) analyses, scanning probe microscope (SPM) observations, and transmission electron microscope (TEM) observations were employed. The interface roughness σi and surface roughness σs of the multilayer were also evaluated by means of these three analysis methods. The GIXR analyses were made by an x-ray diffractometer (Rigaku, ATX-E) with Cu-Kα line (8.04 keV). The reflectivity profiles were measured for the incident angle range of 0-5 degree. In order to estimate the interface roughness σi and the other structural parameters such as d and Γ, the

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experimental GIXR profiles were compared with calculated profiles using commercial analysis software (Rigaku, GXRR). For the SPM observations, an ordinary atomic force microscope (SII, SPA-400) was used to measure surface roughness $\sigma_s$ of the Pt/C multilayers. TEM observations were performed using three electron microscopes (JEOL, JEM-ARM1250, JEM-4000EX, and JEM-2100F), of which theoretical point resolutions were 0.1 nm, 0.17 nm and 0.19 nm, respectively. A slow-scan CCD camera (Gatan SSC model-694) was utilized to quantitatively measure the electron beam intensity distributions in the TEM image.

3. Results and Discussion

Figure 1 shows a GIXR profile of the Pt/C multilayer with periodic length $d=4$ nm. Solid line is an experimental x-ray intensity, and dotted line indicates a profile calculated to fit to the experimental data. The reflectivity $R$ of the first Bragg peak is 44.4%, and the ratio of the reflectivity $R$ to a theoretical optimum value $R_0$ is 62.7%. This is relatively reasonable performance considering the periodic length of the multilayer. The $R_0$ value was calculated by assuming the interface roughness $\sigma_i$ to zero, while the actual roughness of this specimen was estimated as 0.302 nm rms. Generally, the GIXR intensity is altered by lowering the electron density of the materials, as well as the interface roughness. Although the fitting analysis of the GIXR profile is not yet perfect, it was suggested that the density of the Pt layers of the specimen is lower than the theoretical value for the bulk Pt crystal.

The GIXR measurements of the other multilayer samples with different design parameters indicated that the ratio of the reflectivity $R/R_0$ decreases significantly when the periodic length $d$ become shorter. The obtained $R/R_0$ ratio for the $d=3$ nm was 36.5%, and it fell down to 3.61% for the $d=2$ nm sample. The interface roughness $\sigma_i$ of these specimens were estimated as 0.327 nm rms and 0.418 nm rms for $d=3$ nm and $d=2$ nm, respectively. The density of the Pt layers estimated by the GIXR profile of these multilayers also indicated a tendency to become lower for the shorter periodic length. The degrading of the reflectivity ratio can be basically attributed to such changes of roughness and density.

Figure 2 is an SPM image of the $d=4$ nm multilayer sample. It shows a surface morphology of the top Pt layer. The surface rms roughness value $\sigma_s$ as measured for this 500 nm $\times$ 500 nm area was 0.079 nm. Figure 3 shows a relation between the periodic length and the $\sigma_s$ value measured by the SPM. The interface roughness values $\sigma_i$ by the GIXR analyses are also indicated. It should be noted that the interface roughness $\sigma_i$ estimated by the GIXR includes an influence of the interdiffusion of Pt and C, while the SPM measures only a morphological feature of the top surface detected by the probe tip with restricted spatial resolution. Nevertheless, both $\sigma_i$ and $\sigma_s$ values have the same tendency, indicating that the roughness increases for the smaller periodic length.
In order to reveal detailed microstructures as origins of the GIXR and SPM results, atomic resolution TEM observations of cross-sections of the multilayers were performed. Figures 4(a) - (c) are cross-sectional TEM images of Pt/C multilayers with \(d=4\), 3, and 2 nm. Alternating layers of Pt and C are observed as dark and blight stripes. The image contrast exhibits that the Pt layers consist of crystal phase, while the carbon layers are amorphous. Fine fringes with the spacing of about 0.3 nm observed in the Pt layers correspond to the \([111]\) lattice planes \([4]\). For each TEM images with deferent \(d\) value, it seems that the grain size of the Pt crystallites in the direction across the layers is nearly equal to the layer thickness. On the other hand, the lateral size (aspect ratio) of the Pt grains changes depending on the deposition period. The image apparently indicates that the \(d=2\)nm multilayer has Pt grains with smaller aspect ratio, and the contrast at the layer interface is unclear, compared with the specimens with longer \(d\) values.

Figure 5(a) shows a TEM image of a Pt/C multilayer deposited with graded thickness. The thickness of Pt layers was designed as 9.0, 3.0, 1.0, and 0.3 nm. The image was obtained from a relatively thick area of the TEM specimen and recorded with a slow-scan CCD camera. It is to be noted that the darkness of the Pt layers in the image changes depending on the layer thickness. Figure 5(b) is a profile of the image contrast of Figure 5(a) along the direction across the multilayers. In this case, considering the experimental condition, the darkness of image contrast is basically proportional to the packing density of atoms, which is averaged along the incident electron beam. The contrast profile presents that the density of the Pt layer lowers with decreasing of the thickness.

In order to verify the above results obtained by the cross-sectional TEM observations, a plane-view observation of Pt monolayer films was carried out. Figures 6 (a) - (c) are plane-view TEM images of Pt monolayer film deposited by the IBS process on the amorphous carbon film substrate. The thickness values \(t\) of Pt films are 2 nm, 1.5 nm, and 1 nm, which correspond to the periodic length \(d = 4\) nm, 3 nm and 2 nm, respectively. The image shows that, in the case of \(t=2\) nm
specimen, the substrate carbon film is covered nearly 100% by the Pt crystal grains. On the other hand, a number of holes, observed as blighter contrast, exists in the Pt monolayer films with smaller thickness. The coverage of Pt grains on the substrate estimated from the image are approximately 95% and 80% for the t=1.5 nm and 1 nm films, respectively. This indicates that the Pt monolayers with the thickness smaller than 2 nm is in a transition stage during the growth from so called island structure to the continuous film. It is reasonably concluded that the observed characteristics of the roughness and density of the Pt/C multilayers depending on the periodic length primarily originate in the same feature.

4. Conclusions

Pt/C multilayers for the hard x-ray optics applications with periodic length d = 4, 3, and 2 nm were fabricated by an ion beam sputtering process, in order to reveal microstructures and their relations with the reflectivity. The multilayers were characterized by means of grazing incidence x-ray reflectivity (GIXR) measurement with Cu-Kα radiation, scanning probe microscopy (SPM), and transmission electron microscopy (TEM) observations. The GIXR intensity of the first Bragg peak of the d=4 nm multilayer was 62.7% of the theoretical optimum intensity. The GIXR intensity was significantly reduced with decreasing of the periodic length. This can be mainly attributed to an increasing of the interface roughness and a lowering of the Pt layer density, which are observed by the TEM and SPM studies. Plane-view TEM observations revealed that Pt monolayer films with the thickness corresponding to the periodic length smaller than 4 nm have an island structure, which causes relatively large interface roughness and low Pt layer density.

Acknowledgements

Part of this work was supported by the Grants-in-Aid for Scientific Research (B) Nos. 14350077 and 15360075 of the Japan Society for the Promotion of Science, and the "Nanotechnology Support Project" of the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan.

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