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Development of Multilayer-Coated Grating for Tender X-Ray Emission Spectroscopy Toward Application of Operando Analysis

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1 Introduction

To understand the functionality and deterioration mechanisms in thin-film devices, it is effective to analyze the electronic states of the material responsible for the functionality with keeping the thin-film device structures, that is, under actual operating conditions (operando measurement). X-rays in the range of 1 to 4 keV, which are recently called “tender X-rays”, have large probing depths of several micrometers, and therefore it can be expected that X-ray emission spectroscopy with tender X-rays are effective for operando electronic states analysis.

A soft X-ray flat-field spectrometer equipped with a varied-line-spacing (VLS) spherical grating typically covers energy ranges of a few hundreds to one thousand electron-volts at a constant angle of incidence, i.e., without wavelength sweep. In general, such gratings are coated with gold-thin film and the use of which is available below the energy of approximately 2 keV. Alternative to gold coating, multilayer one is effective for enhancement of the reflectivity in the higher energy range. However, such the multilayer with a sole period length has strong wavelength dependence of the reflectivity at a constant angle of incidence, resulting in that multilayer-coated diffraction gratings have been mainly used for synchrotron radiation monochromators requiring for wavelength sweep rather than flat-field spectrometers.

We previously developed a flat-field spectrometer equipped with an aperiodic Ni/C multilayer-coated VLS spherical grating and demonstrated to be able to detect simultaneously the 1–3.5 keV X-ray emissions from the absorber and electrode layers in a thin-film solar cell, leading to the conclusion that the previous spectrometer shows enough performance for qualitative analysis but insufficient energy resolution to electronic states analysis. [1]

In this study, we aimed to develop a Monk-Gillieson spectrometer for operando electronic states analysis using tender X-rays. For this purpose, we proposed aperiodic Ni/C multilayer coatings for a VLS plane grating and a pre-focusing mirror to enable simultaneous measurement of the 1–4 keV X-ray emissions at high resolution without wavelength sweep. Here we report reflectivity measurement results of an aperiodic Ni/C multilayer-coated plane mirror evaluated at the BL-11B beamline of the Photon Factory.

2 Spectrometer design and multilayer fabrication

We designed a Monk-Gillieson spectrometer consisting of a toroidal mirror, M, and a laminar-type VLS plane grating, having a 1200 lines/mm groove density, a 4.6 nm groove depth, and a 0.5 duty ratio, so as to expand a detection energy range up to 4 keV and to improve resolving power up to 3.3 times higher than that of the former spectrometer, where the angles of incidence are at 88.80 degrees for M and 89.04 degrees for G. To accomplish this goal, it is necessary to develop a high reflective mirror coating coverage over the entire energy range 1–4 keV at a constant angle of incidence. We employed aperiodic Ni/C multilayer coatings enabling to enhance the reflectivity uniformly over a wide energy range, while reducing the strong wavelength selectivity in the reflectance profile of a periodic multilayer mirror. [1]

Figure 1 shows a schematic of the layer structure of an aperiodic Ni/C multilayer. The aperiodicity origins from the continuous carbon layer just under the topmost nickel layer, which is formed by the N_1-th carbon of the ordinal periodic Ni/C multilayer and the carbon of the bilayer. Layer parameters of aperiodic Ni/C multilayer coatings optimized for M and G are listed in Table 1. The number of layers N_1 was actually set to 40 for this feasibility study, instead of 80.

We prototyped several multilayer mirrors based on the layer parameters for M shown in the above table. The multilayer coatings were deposited on plane glass substrates with a 25 mm-diameter and a 6 mm-thickness by an ion beam sputtering deposition method. The layer structures were evaluated by reflection measurement using the Cu-Kα_1 radiation, and therefore confirmed that the multilayer sample was fabricated as designed.

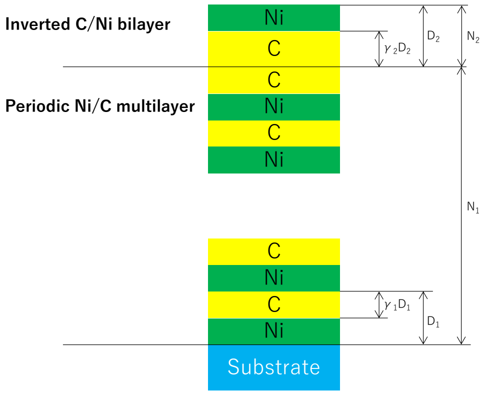

Fig. 1: Schematic of the layer structure of an aperiodic Ni/C multilayer, which consists of an inverted C/Ni bilayer (i = 2) on an ordinal periodic Ni/C multilayer (i = 1), where D_i is the periodic length, γ_i is the carbon thickness ratio to the period D_i, and N_i is the number of layers (i = 1, 2).

Table 1: Layer parameters of aperiodic Ni/C multilayer coatings optimized for M and G. The prototype samples were set to N_1 = 40 in this study.

Parameters	**unit**	**M**	**G**
D_1	nm	9.2	9.2
γ_1	-	0.5	0.5
N_1	-	80	80
D_2	nm	9.2	9.2
γ_2	-	0.2	0.4
N_2	-	2	2

3 Experiment

The experiments were carried out at the BL-11B using an original evaluation apparatus for diffractometry and reflectometry. To provide tender X-rays from 2.1 to 4.0 keV as the incident beams, we employed the Si(111) double-crystal monochromator. The beam size at the sample position in the reflectometer was estimated to be approximately 2 mmH×0.5 mmV. An X-ray photodiode detector coated with a Si/Zr thin-film filter (AXUV100, OptDiode) was employed in the reflectometer.

4 Results and Discussion

Figure 2 shows the reflectivities of both the periodic and the aperiodic Ni/C multilayer plane mirrors (pNiC and apNiC, respectively) measured at a constant angle of incidence of 88.80° in the energy region of 2.1–4.0 keV. In contrast with that the pNiC enhances only the reflectivity around 3.7 keV due to the strong wavelength selectivity, the apNiC reduces the peak reflectivity compared to that of pNiC, nevertheless it improves uniformly the reflectivity over a couple of hundred electron-volts around 3 keV, and thus showing the wideband reflectivity over the entire energy range 2.1 to 4 keV. These features are in good agreement with the respective calculation results shown in the figure for the reference. The fringes around 3.5 keV in the calculated curves appear due to the reduction of the number of layers N_1 to 40, nevertheless they disappear with increasing the N_1.

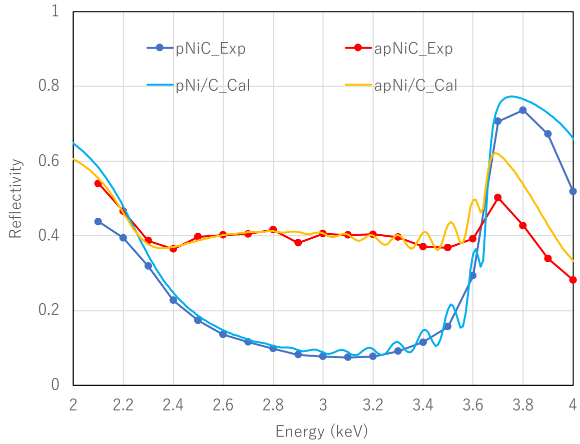

Fig. 2: Plots of reflectivities of the periodic and the aperiodic Ni/C multilayer-coated plane mirrors (pNiC and apNiC, respectively) vs photon energy from 2.1 to 4.0 keV.

Reflectivity measurements below 1.5 keV was planned to be performed with the dedicated soft X-ray reflectometer installed at the BL-11D endstation, but unfortunately, there was no choice to be canceled due to the large earthquake on March 16, 2022, during the beamtime. We consider that the intended aperiodic multilayer coating is a useful scheme to obtain a wide coverage at a fixed angle of incidence, and it has been confirmed that the aperiodic Ni/C multilayer-coated plane mirror, which is a prototype for the pre-focusing mirror M, shows uniformly high reflectivity at least over tender X-ray range of 2.1–4 keV.

In the future, we try to coat the well-optimized aperiodic Ni/C multilayers on a diffraction grating and a pre-focusing mirror, and then confirm their optical performance in the 1–4 keV X-ray range. In addition, we would demonstrate tender X-ray emission spectroscopy in operando using the Monk-Gillieson spectrometer equipped with aperiodic multilayer-coated optical components.

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