BL-11B & 11D/2014G531

Heat load testing of wideband multilayer gratings in the multi-keV region

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A wideband multilayer-coated replica grating showing uniformly high diffraction efficiency in a range of 2–4 keV at a constant angle of incidence has been developed. However its applications have been limited to spectrometers operating without baking which gives heat stress to the grating. To overcome this difficulty and explore the possibilities to improve heat resistance of the grating, we fabricated an Au-coated replica grating by use of an epoxy resin having a relatively higher glass transition temperature than conventional ones and then coated with a W/B_4C multilayer. X-ray reflectivity (XRR) and X-ray diffraction efficiency (XDE) measurements were performed at the conditions of both as-deposited and after a heat treatment at about 90°C for 60 hours in vacuum. The obtained XRR curve of the heated multilayer grating showed the well maintained multilayer structure, and moreover the peak position and peak value of the XDE profile coincided well with those of the as-deposited one. All of these results certifies the high heat load resistance of newly developed multilayer replica grating.

1. Introduction

Spectral analysis of X-ray emissions generated from the materials irradiated by electron beam gives information on the electronic structure related to the material properties. Electron microscopes (EMs) are powerful tools for structural and compositional characterization of materials at nanometer scales. We have developed soft X-ray gratings installed in a flat-field spectrometer optimized for EMs applications [1-3]. They were designed so as to cover the soft X-ray energy range from 50 eV to 4 keV by using four varied-line-spacing gratings interchangeably in the spectrometer. The commercial version spectrometer covering the low energy range of 50–210 eV using two gratings of the four ones has been already on the market [4].

On the other hand, the grating for the highest energy range of 2–4 keV has been fabricated by the deposition of an aperiodic W/B_4C multilayer on a gold-coated grating to enhance the diffraction efficiency uniformly in the whole energy range at a constant angle of incidence [5–7]. A combination of an EM and soft X-ray spectrometer equipped with the multilayer grating have opened the door to high resolution soft X-ray emission spectroscopy in laboratory base. For example, using a TEM equipped with the soft X-ray spectrometer, the emission spectra of In-$L_{\beta 1}$ (3487 eV) and Sn-L_{α} (3444 eV) from indium tin oxide (ITO), which is well-known as transparent conducting oxides, were clearly separated and detected in spite of the small energy difference of 43 eV between two emission lines. [8]

A spectrometer chamber is often baked out prior to TEM observation to get rid of residual gas. However, despite of low-temperature baking even at about 80°C, we experienced a critical issue that the surface of the multilayer grating was damaged seriously. It is considered that this phenomenon is resulted from the heat stress between multilayer coating and base grating because it has been not seen in other replica diffraction gratings coated with Au single-layer. The result of the cross-sectional observation of the layer structure by TEM showed that the multilayer structure was maintained well, but the groove structure formed with conventional epoxy resin was crucially deflected. It indicates that we need to circumvent this problem due to the interface between multilayer coating and epoxy material caused by baking.

Almost of catalogue products of soft X-ray gratings commercially available are generally replica gratings, which are fabricated out of holographic [9] or mechanically ruled [10] master gratings. It is because replica gratings have high productivity in geometrical progression and result in good quality, uniformity and cost performance. Therefore, it is quite important to improve the heat load resistance of replica gratings which are used as the substrates to realize practical wideband multilayer gratings in the multi-keV range.

For the purpose of improving the heat load resistance of the W/B_4C multilayer-coated replica gratings for the soft X-ray spectrometer to be installed in EMs, we fabricated a prototype grating having a periodic W/B_4C multilayer with an epoxy resin having higher glass transition temperature (T_g) than the conventional ones.

This report describes the detail specification of prepared sample gratings and heat load test. Also description is extended to the experimental results of X-ray reflectivity (XRR) measurements of the multilayer-coated replica gratings before and after a heat treatment in addition to X-ray diffraction efficiency (XDE) measurements at the BL-11B are presented.

2. Sample preparation

Two laminar-type replica gratings, having a radius curvature of 11,200 mm, grating constant of 1/2400 mm, groove depth of 2.8 nm, and duty ratio of 0.5, were fabricated by a new replica technique using high T_g epoxy material. The detail information of the new technique will be seen elsewhere. The surface of the replica gratings was coated with a gold film of 50 nm thickness by a vacuum deposition method. A periodic W/B_4C multilayer of period of 5.6 nm; W-layer thickness/period of 0.5; the number of layers of 41; and topmost layer of W, was deposited on the Au-coated replica gratings by an ion beam sputtering method. The reason to employ a period multilayer structure at this time is for the sake of simplicity to evaluate the results of XRR and XDE measurements.

One of the two multilayer gratings, named A, was kept as-deposited. The other grating, named B, was heat treated at 90°C for 60 hours under vacuum below 10 Pa in the furnace. The surface temperature of B had been continuously monitored by a thermocouple probe during the test. Figure 1 shows a plot of the surface temperature vs. heating time. The average temperature between 60 hours was estimated to be 94.7°C which was slightly higher than the preset temperature of 90°C. In visual inspection the sample surface was confirmed to be still kept specular.

3. <u>XRR measurements</u>

Figure 2 shows the XRR curves of the sample B obtained before and after heat treatment measured at Cu-K_α wavelength. We found that the reflectivities at the Bragg peaks were reduced slightly but the multilayer period almost has remained unchanged. Considering these results, a minimal diffusion phenomenon would be occurred at the interfaces between the multilayer pair but the multilayer structure is maintained well. It is expected that the deterioration of diffraction efficiency remains small. The results of XRR measurements regarding the heat load test are summarized in Table 1.

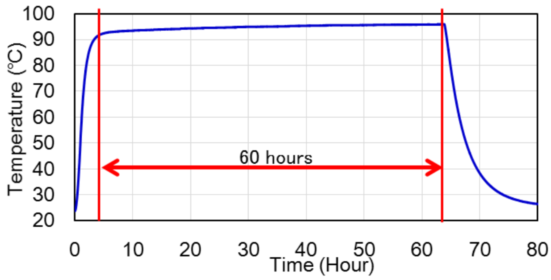

Fig. 1: Plot of surface temperature of the multilayer grating, B, vs. heating time. It took about 4 hours to reach the preset temperature of 90 °C. After heating for 60 hours the grating was cooled down to the room temperature, RT, in the furnace.

In our previous study, it has been known that the groove structure of a conventional replica grating coated with multilayer is crucially damaged even by a short heating above about 60°C. From the above results, it is expected that the multilayer grating fabricated based on the new replication processing using high T_g epoxy resin demonstrates excellent heat resistance performance overcoming ones made by use of conventional resins.

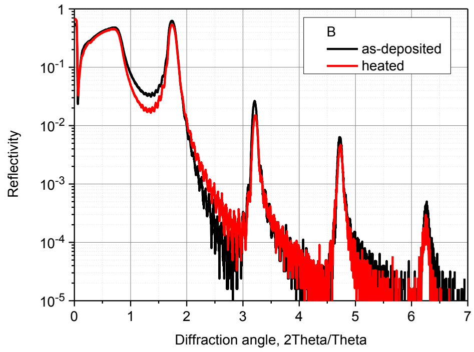

Fig. 2: XRR curves of the multilayer grating, B, before and after heat treatment.

Table 1: Preset temperatures, the first Bragg peaks, and multilayer periods of the two multilayer gratings, A and B, obtained by XRR. RT means room temperature, i.e., as-deposited. Sample B was actually heated at about 94.7°C on an average during 60 hours.

Sample name	A	B	
Preset temperature (°C)	RT	RT	90
1st Bragg peak	0.627	0.621	0.540
Multilayer period (nm)	5.648	5.660	5.652

4. <u>XDE measurements</u>

XDE measurements of multilayer gratings were performed using our carry-on reflectometer installed at the end of the BL-11B beamline [11]. A double-crystal monochromator with Si(111) was chosen to use the energy range of 2.8–4.2 keV. The beam size was limited to 0.3 (V) × 2.0 (H) mm^2 by a four-quadrant slit installed in front of our apparatus and consequently it was estimated to be about 0.6 (V) × 4 (H) mm^2 at the center of sample stage, assuming normal incidence. The use was made of an X-ray photodiode detector coated with Si/Zr (AXUV100 Si/Zr, IRD Inc.) as a detector. An acceptance area of the detector was restricted to 2 (V) × 8 (H) mm^2 from 10 × 10 mm^2 by a variable slit just before the detector. The incident angle was set to be at 88.65° throughout the measurement. The diffraction efficiency of the light of various diffraction orders was measured in an energy range of 2.8–4.2 keV.

Figures 3(a) and 3(b) show the measured diffraction efficiencies of the zeroth and first orders of two multilayer gratings, as-deposited (A) and heated (B). The zeroth order diffraction efficiencies as well as the first ones of the two gratings are in good agreement above 3.5 keV. On the contrary, in the lower energy region discrepancies between the both curves of the zeroth and first orders are observed. Unfortunately we cannot determine from this phenomenon caused by whether heating effect or individual specificity between two samples. However, paying attention to the peak positions and values of the first diffracted lights, they agree well with each other. Therefore, it is not possible to find a crucial degradation on both grating grooves and multilayer structures occurred by the heat treatment (at 94.7°C for 60 hours) in sample B, Thus we can safely conclude that the new replication process using the high T_g epoxy resin makes it possible to improve the performance of heat resistance to 90°C which is about 30°C higher than the conventional process.

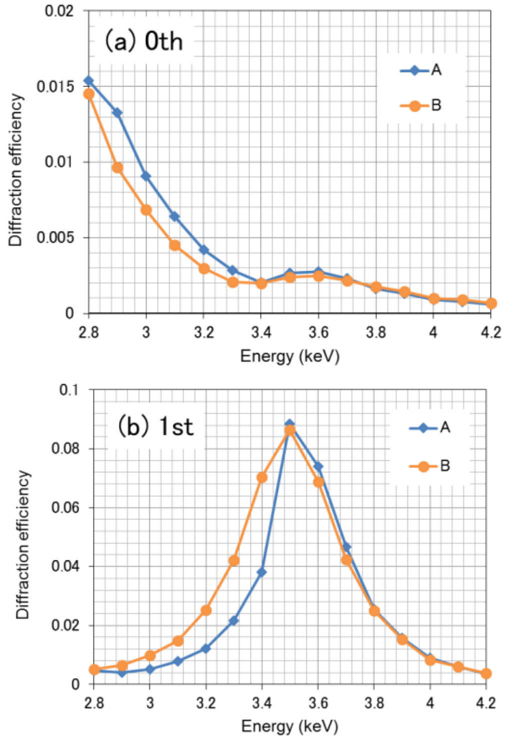

Fig. 3: Diffraction efficiencies of the zeroth (a) and first (b) orders of two multilayer gratings, as-deposited (A) and heated (at 94.7°C for 60 hours) (B).

5. Results and Discussion

In order to improve the heat resistance of wideband multilayer gratings for electron microscopy-based soft X-ray spectroscopy in the multi-keV region, we fabricated multilayer gratings based on the new replication processing using high T_g epoxy. It was found that, for the multilayer grating heated at 94.7°C for 60 hours, the multilayer structure is maintained well from XRR measurements and the peak position and value of the diffraction efficiency are in good agreement with those of as-deposited multilayer grating from the XDE measurements. Considering the fact that the heat resistance of the conventional multilayer-coated replica grating is about 60°C, which is fabricated based on the replication processing using the commonly used standard epoxy resins, our results thus obtained indicate that the prospect of practical use of wideband multilayer gratings with high heat resistance of at least 30°C higher than the current status has been shown.

Unfortunately, it is quite difficult to explain the origin of the discrepancies between the diffraction efficiencies below 3.5 keV. In the near future we have a plan that heat load testing using a same individual sample is performed and the correlation between the surface roughness and diffraction efficiency is clarified as a function of applied temperature so as to develop more practical wideband multilayer gratings with higher heat resistance over 100°C or more.

In addition, efforts to develop practical multilayer gratings in multi-keV region have been extended to those working in the energy range 1–3.5 keV. A wideband Ni/C multilayer having an aperiodic layer structure was deposited on a gold-coated replica grating fabricated by the conventional replication processing. The diffraction efficiency was evaluated by using not only the BL-11B but also a soft X-ray reflectometer installed in the BL-11D beamline. [12] More information of this grating is given another paper [13]. Using the new replication processing, it would be possible to improve the heat resistance of the Ni/C multilayer gratings as well.

Acknowledgement

Diffraction efficiency measurements were conducted under the approval of the Photon Factory Program Advisory Committee (Proposal No.2014G531). This research was carried out as part of the joint research program between the Japan Atomic Energy Agency and Shimadzu Corp. This work was partially supported by Japan Society for the Promotion of Science (JSPS), Grant-in-Aid for Young Scientists (B) (No. 25790060).

References

[1] T. Imazono *et al.*, *Appl. Opt*. **51**, 2351 (2012).
[2] T. Imazono *et al.*, *Proc. of SPIE* **8848**, 884812 (2013).
[3] T. Imazono *et al.*, JP Pat. 5948558, June 17, 2016.
[4] http://www.jeol.co.jp/en/products/detail/SXES.html
[5] T. Imazono *et al.*, *PF Act. Rep 2011 B*, **29** (2012).
[6] T. Imazono *et al.*, *AIP Conf. Proc*. **1437**, 24 (2012).
[7] T. Imazono *et al.*, JP Pat. 5669295, December 26, 2014.
[8] M. Terauchi *et al.*, *Microscopy* **62**, 391 (2013).
[9] http://www.shimadzu.com/opt/products/dif/o-k25cur0000006zd0.html
[10] http://www.hitachi-hightech.com/us/product_detail/?pn=ana-grating
[11] T. Imazono *et al.*, *AIP Conf. Proc.* **1465**, 22 (2012).
[12] T. Hatano and T. Harada, *J. Electron Spectrosc. Relat. Phenom*.**196**, 156 (2014).
[13] T. Imazono, *AIP Conf. Proc.* **1741**, 040044 (2016).

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