BL-11D/2020G013

Design and preliminary fabrication and evaluation of small incidente angle and high diffraction efficiency laminar-type diffraction grating optimized for the state analysis at the vicinity of Li-*K* emission

Masato KOIKE [1,2], Tadashi HATANO [2*], Alexander S. PIROZHKOV [1],
Nobukazu HAYASHI [3], Tsubasa KAKIO [3], Tetsuya NAGANO [3], and Masami TERAUCHI [2]

[1] Kansai Photon Science Institute, Quantum Beam Sciences Directorate,
National Institutes for Quantum and Radiological Science and Technology
8-1-7 Umemidai, Kizugawa, Kyoto 619-0215, Japan
[2] Institute of Multidisciplinary Research for Advanced Materials, Tohoku University
2-1-1 Katahira, Aoba-ku, Sendai, Miyagi 980-8577, Japan
[3] Device Department, Shimadzu Corporation
1 Nishinokyo-Kuwabaracho, Nakagyo-ku, Kyoto, Kyoto 604-8511, Japan

It has been a common practice to enhance basic performance such as resolution and diffraction efficiency (*DE*) in the widest possible wavelength range in the design of the diffraction grating mounted in the diffraction grating spectrometers for general-purpose soft X-ray emission spectroscopy. However, less consideration was given to the selection of the angle of incidence. We have recently conceived a new evaluation index named "spectral flux (*SF*)" which correlates with the analytical sensitivity of the spectrometer. In this study, we performed the grating design to increase *DE* and *SF*, focusing on Li-*K* emission (54.3 eV, 22.83 nm) by optimizing the parameters of the angle of incidence and coating structure on the surface of the grating by numerical calculation. As the result of the preliminary experimental evaluation of the grating thus designed, the values of *DE* and *SF* at the peaks were > 90% of those obtained by the numerical calculation. However, the peak angle positions deviated up to 5 degrees. This suggests the need to reconsider the material constant of B_4C and its thickness more carefully.

1 Introduction

In the development of secondary batteries, all-solid-state lithium batteries, in which the electrolyte of lithium-ion batteries is replaced with solid electrolytes, is just around the corner. However, it is said that there are many problems to overcome such as optimization of the interface structure between the electrode and the electrolyte [1]. Soft X-ray emission spectroscopy has a potential to measure Li-*K* emission of metallic lithium and lithium in alloys with high energy resolution and high analytical sensitivity [2]. Unfortunately, the lithium oxide used for the positive electrode of a lithium-ion battery cannot be detected because the outermost electrons of lithium are dominated by oxygen and the characteristic X-rays of lithium are not emitted [3]. On the other hand, for sulphur-based lithium compounds used in solid electrolytes in all-solid-state lithium batteries, in an unexposed atmosphere, Li-*K* (54.2 eV, 22.83 nm) along with S-*L* (162 eV, 7.65 nm) can be measured simultaneously [4].

Recently, the soft X-ray diffraction grating emission spectroscope (SXES) combined with an electron microscope has the advantage of being able to perform state analysis because of its excellent resolution. Furthermore, it is also used for measurement of emission spectrum mapping from a local region [5]. However, when it comes to Li-*K* emission measurement, the emission wavelength is near the long wavelength edge of the wavelength range that can be measured by a general soft X-ray grazing incident grating spectroscope, and the design of diffraction grating and its spectroscope was not optimized for the marginal wavelength region. Therefore, if a diffraction grating and spectroscope optimized for this wavelength region are newly designed, it may be possible to improve the analysis sensitivity and shorten the measurement time.

In the previous study, for B-*K* emission (184 eV, 6.76 nm), the authors demonstrated that the diffraction efficiency (*DE*), and spectral flux (*SF*) which is defined as the product of the numerical aperture and the diffraction efficiency and correlates with the analytical sensitivity, can be improved by the optimization of the groove shape and the thickness of supplemental coating, e.g., diamond-like carbon or lanthanum, on the metal surface of the grating, and incidence angle [6]. The purpose of this report is to describe on the similar enhancement of *DE* and *SF* in the vicinity of Li-*K* emission. The numerical calculation showed that it can be obtained by the optimization of the thickness of supplemental coating, B_4C, on a Au coated laminar-type grating and incidence angle. Also the preliminary experimental results are also described.

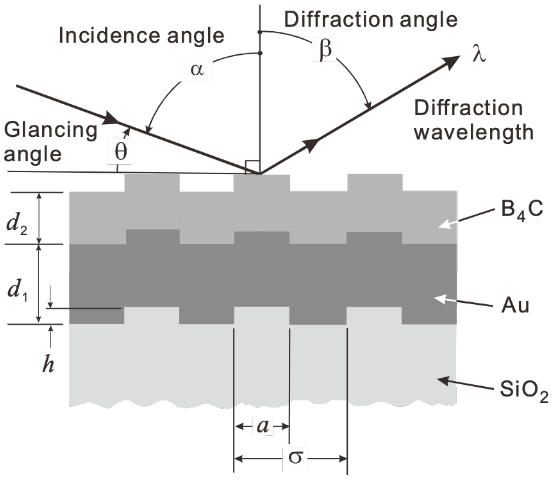

Fig. 1: Schematic diagram of a laminar-type grating having a B_4C overcoating. Wavelength, incidence angle, glazing incident angle, and diffraction angle are denoted as λ, α, θ, and β, respectively. Also, h, a, d_1, d_2 are the groove depth, the width of the crest portion, Au layer thickness, and B_4C layer thickness, respectively.

2 Laminar-type grating

Figure 1 shows a schematic diagram of the cross section of the developed laminar-type diffraction grating having a rectangular groove shape and B_4C overcoating. The material of grating blank is SiO_2 and Au layer is coated on the top of the grating grooves. The detail design parameters of the grating are as follows: grating constant, σ, of 1 / 1200 mm; duty ratio, $D = a/\sigma$, of 0.30; groove depth, h, of 20.0 nm; diffraction order, m, of +1. Also the thickness of Au layer, d_1, is 30 nm. This diffraction grating was developed as JS50XL in a previous project [7] and manufactured by Shimadzu Corporation.

The thickness of B_4C, d_2, and incidence angle, α, were optimized to maximize diffraction (*DE*, Case A) and spectral flux (*SF*, Case B) at 54.3 eV [8]. As the result, two sets of (d_2, α) were determined for the respective cases:

Case A $d_2 = 22$ nm, $\alpha = 78.2°$,
Case B $d_2 = 14$ nm, $\alpha = 74.0°$.

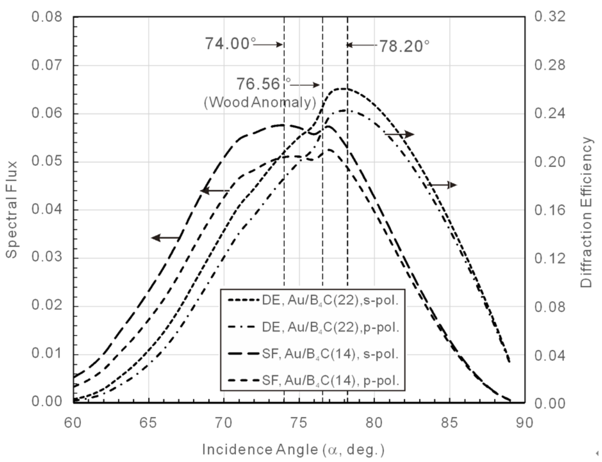

Fig. 2: Diffraction efficiency (*DE*) and spectral flux (*SF*) vs. incident angle of the Au/B_4C coated gratings. For d_2 refer to text [8].

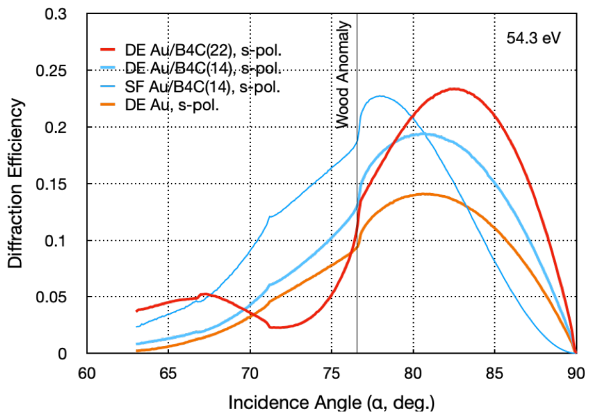

Fig. 3: Measured diffraction efficiencies and sprcral flux of the gratings having B_4C overcoating showing incidence angle dependance at an energy of 54.3 eV. The thickness of B_4C layers is 22 nm (red curve), 14 nm (blue curve) and zero (orange curve), respectively, at 54.3 eV. The thin blue curve is *SF* for the grating having B_4C overcoating at 14 nm scaled to coincide with *DF* at the peak angle.

Figure 2 shows the diffraction efficiency *DE* and spectral flux *SF* vs. incident angle of the Au/B_4C coated gratings thus designed. The B_4C overcoating on the JS50XL grating was performed by the ion beam sputtering method at IMRAM, Tohoku University.

3 Results and Discussion

Measurements of the diffraction efficiency *DE* and spectral flux *SF* of the Au/B_4C coated gratings were performed at BL-11D, the Photon Factory. Figure 3 shows the measured *DE* and *SF* of the gratings showing incidence angle dependance at an energy of 54.3 eV. The thickness of B_4C layers is 22 nm (red curve, Case A) and 14 nm (blue curve, Case B) which are optimized for *DE* and *SF*, respectively, at 54.3 eV. For reference, *DF* of the Au-coated grating (orange curve) is also shown. *SF* for the grating having B_4C overcoating at 14 nm is plotted in the thin blue curve in the scale where *SF* coincides with *DF* at the peak angle of *DE*, 80.7°.

From the result for Case A, it can be safely confirmed the validity of B_4C overcoating because that a clear improvement of the maximum measured diffraction efficiency which close to that obtained by the calculation. However, a meaningful discrepancy in the incidence angle showing maximum *DE* for Case A and *SF* for Case B between the calculation and experiment, and it is considered to be attributed to the properties of the B_4C coating. To overcome this issue, we will procced to analyze the properties of the coating materials and coating process more carefully to reduce optimum incidence angle much closer to that estimated by the numerical calculation in near future.

Acknowledgements

The measurements of absolute diffraction efficiencies were performed as a part of the PF synchrotron radiation joint experiment of "Development of tailor-made keV region soft X-ray gratings using extreme techniques," (2020G013, April 2020-March 2022). A.S.P acknowledges the support of Strategic Grant (Creative Research) by President, QST (No.20, April 2018–March 2020).

References

[1] S. Sugawara, T. Kazama, M.Fujita, R. Sakamoto, S.er Goda, *Material technology and market prospects for large-capacity Li-ion batteries* (Ed. A. Yoshino, CMC Publishing, Tokyo, 2019), (in Japanese).

[2] M. Terauchi, S. Koshiya, F. Satoh, H. Takahashi, N. Handa, T. Murano, M. Koike, T. Imazono, M. Koeda, T. Nagano, H. Sasai, Y. Oue , Z. Yonezawa, and S. Kuramoto, Microsco. Microanal. **20** (3), 692–697 (2014).

[3] M. Terauchi, Isotope News **722** (6), 2–7 (2014).

[4] T. Hakari, Y. Fujita, M. Deguchi, Y. Kawasaki, M. Otoyama, Y. Yoneda, A. Sakuda, M. Tatsumisago, and A. Hayashi, Adv. Funct. Mater., 2106174 (2021).

[5] R. Kasada, Y. Ha, T. Higuchi, K. Sakamoto: Sci. Rep. **6**, 25700 (2016), (6 pages).

[6] T. Hatano, M. Koike, M. Terauchi, A. S. Pirozhkov, N. Hayashi, H. Sasai, T. Nagano, Appl. Opt. **60**, 4993–4999 (2021).

[7] T. Imazono, M. Koike, T. Kawachi, M. Koeda, T. Nagano, H. Sasai, Y. Oue, Z. Yonezawa, S. Kuramoto, K. Sano,Proc. of SPIE, **8139**, 81390V(2011), (9 pages).

[8] M. Koike, T. Murano, S. Koshiya, T. Hatano, A. S. Pirozhkov, T. Kakio, N. Hayashi, T. Nagano, K. Kondo, and M. Terauchi, Adv. X-Ray. Chem. Anal., Japan **53**, 69–76 (2022), (in Japanese).

*hatanotadashi@tohoku.ac.jp