RESEARCH ARTICLE | JANUARY 15 2019

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AIP Conf. Proc. 2054, 060010 (2019)
https://doi.org/10.1063/1.5084641

Removal of carbon contamination on oxidation-prone metal-coated mirrors using atomic hydrogen

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Abstract. In synchrotron radiation (SR) optical devices coated with oxidation-prone metal, such as Ni and Cr, the UV-O_3 ashing method cannot be used for removal of the contaminated carbon film deposited during use in the beamline. We have demonstrated that surface treatment technology using atomic hydrogen is effective as a new contaminated carbon film removal technology. Hydrogen gas was flowed into contact with a tungsten mesh (catalyst) heated to 1700°C to obtain atomic hydrogen. By flowing this atomic hydrogen on the surface of the SR mirror, deposited contaminants could be almost completely removed. The reflectance of the mirror recovered from about 14% to about 70% at the C-K absorption region. The reflectance also increased by about 20% at a photon energy greater than 300 eV because of the removal of carbon film and the reduction of native oxide at the mirror surface.

INTRODUCTION

Optical elements such as metal-coated mirrors installed in synchrotron radiation (SR) beamlines are contaminated with a film, consisting mainly of carbon, that is deposited during use; therefore, the reflectance of the mirrors decreases. In many SR facilities, efforts have been made for a long time to deal with this problem [1-3], but it has not yet been completely solved. When the coating material of the mirror is a noble metal, such as Au or Pt, an ashing method using ozone gas under ultraviolet irradiation (UV-O_3 ashing) is used to remove the contaminants [4]. However, when the coating material is an oxidation-prone metal, such as Ni or Cr, there is concern that the reflectance may be lowered due to oxidation of the metal surface. In fact, as will be described later, it was found that when the UV-O_3 ashing method was applied to the Ni-coated mirror, the reflectance at the soft X-ray region decreased. In a recent study, Toyoshima succeeded in removing contaminants *in situ* by introducing oxygen gas into a mirror chamber at 8×10^{-2} Pa and an irradiating undulator light to a Cr-coated mirror [5]. However, in order to realize such a mechanism, it is necessary to install a large differential pumping system, and oxidation of the coating material has still been observed. Additionally, Swaraj reported that contaminants were removed and the reflectance was recovered by keeping a small amount of oxygen gas ($\sim 4 \times 10^{-6}$ Pa) for 2 years in the beam line during the time of beam operation [6]. However, this method takes time to recover reflectance, and the problem of surface oxidation for easily oxidizable metal remains unsolved.

On the other hand, the problem of carbon contamination has been investigated as a problem to be solved also in the field of extreme ultraviolet (EUV) lithography, and they have examined a contaminant removal method using atomic hydrogen [7, 8]. We investigated a carbon contamination removal method by treating a synchrotron radiation mirror with atomic hydrogen (AH treatment, AHT). It is possible that AH can prevent oxidation even for a metal film

Proceedings of the 13th International Conference on Synchrotron Radiation Instrumentation – SRI2018
AIP Conf. Proc. 2054, 060010-1–060010-4; https://doi.org/10.1063/1.5084641
Published by AIP Publishing. 978-0-7354-1782-3/$30.00

which is easily oxidized. We report the AH treatment of mirrors that actually received carbon contamination during the beamline operation and evaluate the reflectance of the mirror before and after the treatment.

EXPERIMENT

The sample, which is a Ni-coated mirror (L100 × W30 × T50 mm, Si substrate) with contaminants deposited on its surface, has been used at the beamline BL-09 of the NewSUBARU SR facility [9]. To clean up the contamination, we used the AH exposure equipment [10] of the faculty of engineering at the University of Hyogo. Hydrogen gas was introduced into a stainless steel chamber through a nozzle at the side of the treatment chamber. The base pressure of the chamber was about 1×10^{-3} Pa. A 55×55 mm^2 tungsten (W) mesh with a wire diameter of 0.03 mm and having 50 holes per inch was used as a catalyst. The mesh was heated electrically to 1700°C. H_2 gas was passed through the catalyst mesh with flow rate of 150 sccm and at a gas pressure of 30 Pa to obtain atomic hydrogen. The distance between the W mesh and the treated sample was 90 mm, and the heating of the sample was not performed. The temperature increase during the treatment was estimated to be less than 100°C.

The evaluation of the mirror before and after the AH treatment was carried out with visual observation (photograph), surface profile measurement by optical interferometer (Zygo, NewView7300), surface roughness measurement by atomic force microscope (AFM, Veeco, Dimension 3100), evaluation of the thin film structure for depth direction using hard X-ray reflectometry at grazing incidence (XRR, PANalytical, X'pert Pro MRD), and surface composition analysis by X-ray photoelectron spectroscopy (XPS, PHI 5000 VersaProbe). Because the mirror is too large to be introduced into the XPS chamber, we used a dummy Ni-coated mirror for XPS that has slightly contaminated with carbon and has been placed with the SR mirror during the AH treatment.

The soft X-ray reflectance of the mirror before and after the treatment was measured using the soft X-ray reflectometer of NewSUBARU BL-10 [11]. The reflectometer can measure a wide in-plane reflectance distribution of over 50 mm. However, in order to measure the distribution at a shallow grazing angle of incidence of 3 °, we developed a new, dedicated mirror holder. The measurement was performed at a grazing angle of incidence of 3 °, and the reflectance and its in-plane distribution at a photon energy of 150 to 750 eV were investigated.

RESULTS AND DISCUSSION

First, as a preliminary experiment, a reference mirror was prepared by coating a Si wafer substrate with Ni to a thickness of 100 nm, and AH treatment (1 hr) or UV-O_3 ashing treatment (Ushio, SJG01, 172 nm) [12] was carried out on these mirrors. The effects of both treatments were compared. Figure 1 shows the soft X-ray reflectance spectra of the reference mirror before and after the AH treatment or UV-O_3 ashing. When the UV-O_3 ashing treatment is performed, the reflectance of the O-K absorption edge region (~540 eV) decreased by 10% or more. This is because absorption by oxygen atoms occurred due to surface oxidation of Ni. Analysis of grazing incidence reflectance of hard X-rays (XRR) revealed that an oxide film about 3 nm thick formed on the coated Ni surface.

On the other hand, in the sample subjected to the AH treatment, the reflectance in the O-K region was increased by about 1% as compared with the original mirror. This is because the native oxide film on the Ni mirror surface was reduced and removed by AH treatment. The surface roughness of these samples was measured using AFM and compared. The surface roughness of the mirror was 0.317 nmRMS before AH treatment and 0.327 nmRMS after the treatment. It was

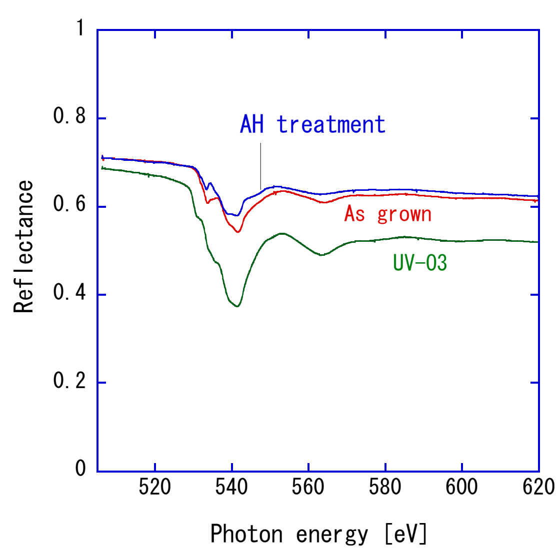
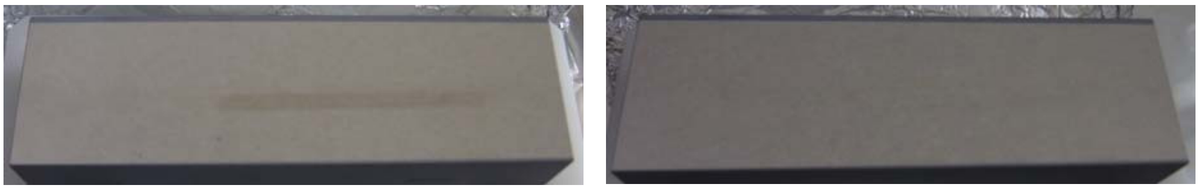


FIGURE 1. Soft X-ray reflectance spectra of the reference mirror before and after the AH treatment or VU-O_3 ashing.

found from this that the surface roughness was hardly changed by AH treatment.

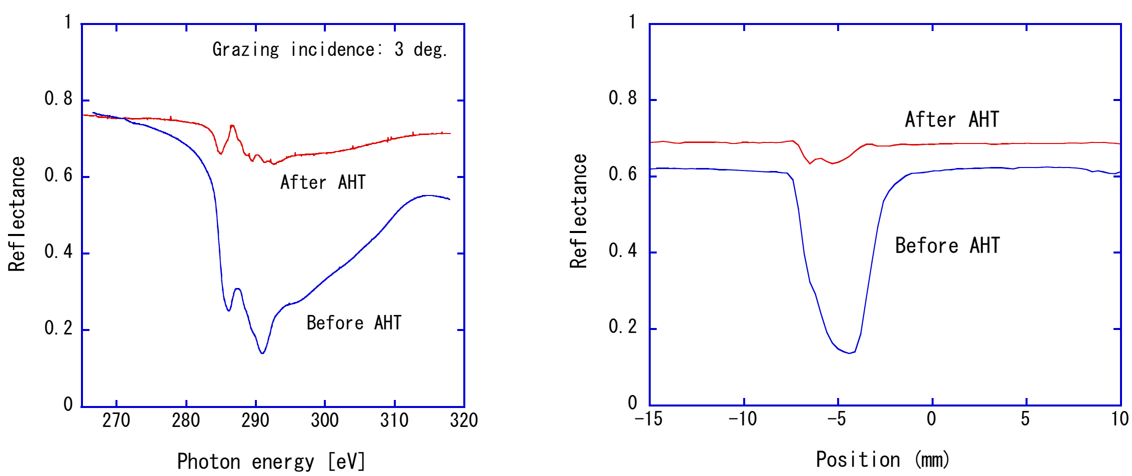
Next, we attempted AH treatment of the Ni-coated sample mirror used in the beamline. The thickness of the contaminants was 11 nm at the maximum point as measured with an optical interference profiler. Figure 2 shows photographs of the Ni-coated sample mirror surface used in the beamline of the NewSUBARU SR facility (a) before and (b) after the AH treatment. By exposure to 1 hr of AH, contaminants could be removed to such a degree that traces are slightly visible by visual observation. According to the surface profiler analysis, in this treatment, deposited contaminants remained at about 1 nm at maximum. Composition analysis of the reference mirror simultaneously introduced by XPS showed that only the signal of C1s decreased and the signal of Ni2p increased, and no special compound formation was observed.



(a) (b)

FIGURE 2. Photographs of Ni-coated mirror surface used in the beamline of the NewSUBARU SR facility (a) before and (b) after the AH treatment.

Figure 3 shows the soft X-ray reflectance spectrum of the C-K region (~290 eV) of the Ni-coated sample mirror before and after the AH treatment. As shown in Fig. 3 (a), even in the region where the contaminants were thickly deposited, the reflectance could be recovered to about 14 → 70%. Figure 3 (b) shows the in-plane distribution of the reflectance of the sample mirror before and after the AH treatment. The incident angle was 3°, and the measured photon energy was 291 eV. Before AH treatment, the reflectance decreased significantly at the position of -5 mm in the graph. On the other hand, by performing the treatment, the reflectance was almost recovered with small decrease of several percent at the contaminated position.



(a) (b)

FIGURE 3. The soft X-ray reflectance spectrum (a) and its in-plane distribution (b) of the C-K region (~300 eV) of the Ni-coated sample mirror before and after the AH treatment. The incident angle was 3°, and the measured photon energy for the distribution was 291 eV.

Figure 4 shows reflectance spectra before and after AH treatment in a wide photon energy range from 150 to 750 eV. From this, it can be seen that the reflectance decreased to about 50% due to accumulation of carbon contamination even at an energy of 310 eV or higher above the C-K absorption edge due to the accumulation of contaminants. With this AH treatment, we could recover this reflectance to about 70%, and this value is close to the theoretical reflectance. From the above, it was found that the AH treatment is an excellent method as a contaminant-removal method for a metal-coated mirror that is easily oxidized.

After this experiment, we also succeeded in removing the contamination film by conducting AH treatment on the Ni-coated diffraction grating (L150 × W30 × T20 mm, Si substrate), which also had a carbon-contamination film.

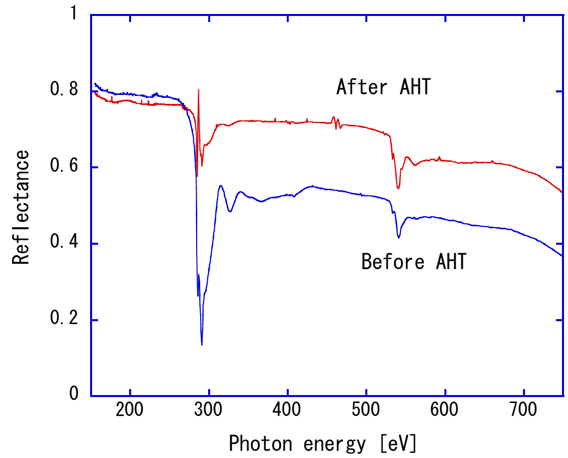


FIGURE 4. Reflectance of Ni-coated mirror at the wide photon energy region before and after AH treatment.

SUMMARY

We attempted a new cleaning method called atomic hydrogen treatment and could successfully remove carbon contaminants deposited on synchrotron radiation mirrors. The damage (roughening or compound formation) of the AH treatment to the mirror was very small. This method is very simple, and there is a possibility that contamination can be removed *in situ* without installing a differential pumping system or irradiation of intense undulator radiation.

ACKNOWLEDGMENTS

This work was strongly supported by the staff of the NewSUBARU Synchrotron Radiation Facility at the University of Hyogo.

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