Performance of the HERMES beamline at the carbon K-edge

S Swaraj, R Belkhou, S Stanescu, M Rioult, A Besson and A P Hitchcock

1 Synchrotron SOLEIL, L’Orme des Merisiers, Saint-Aubin - BP 48, F-91192 Gif-sur-Yvette cedex, FRANCE
2 McMaster University, Hamilton, Ont. L8S 4M1 CANADA

Abstract. Contamination of soft X-rays beamline optics due to carbon cracking and deposition under X-ray irradiation is especially critical for spectromicroscopy operations near the carbon K-edge from organic materials, polymers and nanoparticles. In this paper we present the strategy and procedure followed on the HERMES beamline (Synchrotron SOLEIL) to minimize carbon contamination of the beamline optics. Measurements on a complex organic test sample are reported to demonstrate the performance of the beamline at the carbon K-edge in imaging, spectroscopy and spectromicroscopy modes.

1. Introduction

With the recent advances in brilliance, coherence and stability of synchrotron sources, it is becoming exceedingly important that the gained advantages are not lost downstream in the beamline due to contaminated optics. Carbon contamination of beamline optics is a well-known phenomenon that can significantly undermine the performance of a beamline, especially for soft X-rays. It not only affects the spectral and imaging performance near the carbon K-edge but can also result in reflectivity losses at higher energies [1]. Basic steps/conditions leading to the formation of these contamination layers are well established by various theoretical and experimental studies [2,3]. These include, (a) the presence of carbon radical precursor molecules, (b) the adsorption of precursor molecules onto the optics surface, and (c) cracking of the precursor molecules primarily by the electrons photo-emitted from the optics and contaminant at the positions where the X-ray beam hits the optics. Since the 1970’s various procedures have been proposed for cleaning beamline optics. These methods include UV-ozone [1], DC glow discharge [4-8], RF plasma [9], pulsed laser [10] and zero-order SR (synchrotron radiation) activated in-situ cleaning [11-15]. While all of these techniques have proven to be effective to various degrees, the choice of technique is often limited by ease of applicability, risk of optics damage and down time. From this point of view, the zero-order SR activated in-situ cleaning appears to be the most appropriate and effective [12]. This technique involves the use of SR generated, activated oxygen radicals as a chemically reactive cleaning agent that reacts with carbon to form CO and CO₂, which are then pumped away. Warburton et al. [15] were the first to suggest that exposing beamline optical elements to continuous flow of pure O₂, and not only during a specific cleaning procedure that involves zero-order SR, can suppress carbon contamination completely. Risterucci et al. [11] have experimentally shown that the use of intense monochromatic soft x-ray photon beams can have a cleaning effect on a Pt(111) surface and is highly effective at cryogenic temperatures. They also suggested that this procedure could have benefits for optics at room temperature as well.
However, it is important to state that preventive measures should take precedence to strategies for decontamination. This was followed at HERMES beamline by minimizing any contaminant source in the beamline. Wherever possible, all the motors, encoders and cables have been placed outside vacuum optical chambers. All the vacuum vessels of the beamline are made exclusively of Al and have undergone a reactive pre-treatment to have a ca. 300 nm thick Al$_2$O$_3$ passivated layer that acts as a barrier and prevents any absorption/desorption of carbon from the chamber walls [16,17]. Finally, all the optics vacuum chambers have been conditioned for several weeks under radiation with dummy mirrors. The real mirrors were installed only after achieving UHV with the X-ray beam present. These steps were aimed at improving the performance of the beamline in the so-called water-window energy domain. In this paper we present the monitoring of beamline contamination over a period of 4 years and demonstrate the effectiveness of these steps.

2. Experimental

Experimental observations were performed at the HERMES beamline with a ring current of 450 mA corresponding to the multi-bunch operation mode. A residual gas analyzer (RGA, MKS instruments) was used for partial gas pressure measurements. Carbon K-edge spectra were obtained either using a Si photodiode, installed downstream of the monochromator or using a photomultiplier tube at the Scanning Transmission X-ray Microscope (STXM) end-station. ~200 nm thin sections of a previously studied polyurethane test sample [18] embedded with Poly(Styrene-co-Acrylonitrile) (SAN) and Poly-isocyanate Poly-Addition (PIPA) nanoparticles were prepared and transferred on to silicon nitride window for STXM measurements. The Fresnel zone plate (FZP – the STXM focusing element) used for this measurement has an outer ring width of 30 nm. Data analysis software aXis2000 was used for the analysis of the presented STXM data [19].

3. Results and discussion

3.1. HERMES beamline

HERMES is an undulator beamline (2 APPLE-II type undulators of 42 & 64 mm period) covering an overall energy range of 70-2500 eV. It is a dual-branch beamline that has XPEEM (X-ray Photoemission Electron Microscope) and STXM end-stations. Full details are given in Belkhou et al. [20]. Briefly, the first M1 optics presents three mirrors in chicane mode working in pairs depending on the energy range (M1A/B for low energy at 2.5° incidence; M1A/C for high energy, 1.2° incidence). M1A is a plane mirror (SiC substrate, with Ni and Rh stripes) while M1B (Si substrate, Ni coating) and M1C (Si substrate, Rh coating) are toroidal mirrors focusing the beam horizontally 0.5 m after the gratings and collimating the beam vertically for parallel incidence on the gratings. The PGM (Plane Grating Mirror) monochromator has two VLS-VGD (Variable Line Spacing – Variable Groove Depth) gratings (450 l/mm and 600 l/mm) coupled with a M2 plane mirror (Si substrate, Ni and Rh coatings). An additional M3 toroidal mirror (Si substrate, Au coating) is used inside the monochromator optics vessel to focus the beam to the exit slits. The deflection chamber further downstream has M5 cylindrical mirror (Si substrate, Au coating) and M4 toroidal mirror (Si substrate, Au coating). When inserted in the optical path, the M5 mirror deflects the beam to the KB focusing optics on the XPEEM branch. On the STXM branch the M4 mirror focuses the beam to a set of secondary slits that acts as a source for the FZP. The M1, monochromator, and the deflection chamber are all made of Al and have been reactively pretreated to obtain ~300 nm of Al$_2$O$_3$ coating internally. A partial pressure of pure oxygen, P(O$_2$) of ~4x10$^{-8}$ mbar is maintained during beam operation in all these chambers.

3.2. Discussion on the evolution of carbon contamination

An RGA is installed permanently on the M1 chamber since its installation in 2012. The partial pressures in the chamber are regularly monitored in order to follow the hydrocarbon contamination and the overall effects of continuous O$_2$ flow. Figure 1a presents the evolution of C, CO and CO$_2$
content over a period of 4 years. These measurements were obtained in the absence of X-rays and O$_2$ partial pressure. The partial pressures presented in Fig. 1a were normalized to the residual O$_2$ partial pressures. The plot indicates clearly that the carbonaceous content in the M1 chamber has decreased by at least an order of magnitude. A visual inspection of the M1 mirrors also confirms the absence of any carbon trace. In addition, reflectivity measurements on the M1 mirrors were performed after tuning the undulator harmonic to the carbon edge. No significant changes in reflectivity profile across the length of the M1 mirrors were observed, confirming the absence of any contaminating layer. This cleaning effect is expected since the source of precursor hydrocarbon molecules, initially present in the form of external contaminants, are likely to be significantly reduced during this extended period of time (48 months). This chamber has no in-vacuum motors or encoders installed that could be an additional contamination source. On the other hand, while the monochromator M3 optics receives much less monochromatic power load (<10 mW) compared to the M1 optics (c.a. 300W pink beam), the presence of in-vacuum encoders act as a major source of contamination. These encoders are unavoidable since high precision movements are necessary in the monochromator. Due to this proximity to a major source of contaminants, the monochromator optics were found to have a visually prominent carbon trace. Absorption by this carbon trace (which only existed on M3) resulted in a significant drop at the carbon K-edge (85%) near 285 eV as shown in figure 1b. It has to be noted that the visual carbon trace on the optics was already observed within the first two months of operation. Although the in-vacuum encoders and cables are claimed by manufacturers to be UHV compatible in terms of out-gassing rate, the manufacturers do not guarantee that these components will not desorb hydrocarbons when hit by X-rays. While the in-vacuum source of contaminants is significant in this chamber, it is nevertheless limited. On visual inspection after another two years of continuous operation, it was found that the carbon trace was completely removed in the region of the mirror M3 continuously exposed to X-rays for more than 2 years (Fig. 1c). Figure 1c shows a photo of the contaminated region that was created by the exposure of the mirror to X-rays during commissioning and initial alignment. The decontaminated part on the mirror is the region that was exposed to X-rays for more than two years. This was also observed as a reduction in the carbon dip from 85% to 15% (Fig. 1b). It has been shown recently that the presence of atomic oxygen on Au surfaces dramatically increases the dissociation rate of oxygen [21] at higher temperatures. Thus we speculate that although M3 receives only a small power load, it does lead to some temperature change, and even a few degree increase in temperature may aid the decontamination process.

![Graph](image1.png)

Figure 1. (a) Normalized RGA data showing the evolution of C, CO and CO$_2$ content with time, (b) IO carbon dip over a period of two years measured after the monochromator exit slit. The Sep 2014 trace was after initial commissioning while the July 2016 trace was after in situ cleaning with O$_2$ and the X-ray beam (c) Contaminated and ‘X-ray beam decontaminated’ region of the M3 mirror.

3.3. Carbon K-edge measurements on a polyurethane test sample

In order to demonstrate the performance of the beamline at the carbon K-edge we performed STXM analysis of polyurethane samples embedded with SAN and PIPA nanoparticles. This sample was chosen because of the experimental challenges it presents due to the similarity in the C K-edge NEXAFS spectra of the components and the facile radiation damage of some of the components [18].
Figure 2(a-c) present individual chemical component maps extracted by fitting STXM stacks to reference spectra of the components. The SAN and PIPA particles were reliably differentiated and their average sizes, 50 - 300 nm, are consistent with previous results [18]. NEXAFS spectra of individual components extracted from the STXM stacks are presented in figure 2d. The sharp \( C_1s \rightarrow \pi^* \) transitions observed in the NEXAFS spectra for all three components span a range of 2 eV (285.1 to 287.2 eV). It is evident from the presented results that the beamline optics are sufficiently clean to allow differentiation of chemically similar components near the carbon K-edge.

![Individual chemical component maps and NEXAFS spectra](image)

Figure 2. Individual chemical component maps of (a) polyurethane matrix, (b) SAN and (c) PIPA (scale bar: 1 µm) and (d) NEXAFS spectra of each component extracted from the carbon K-edge STXM stack, and converted to an absolute scale (OD/nm).

4. Conclusion

The high quality images and spectra at the carbon K-edge are a consequence of \textit{in-situ} suppression and reversal of carbon contamination of the HERMES beamline optics. Avoiding in-vacuum sources of contaminants and maintaining a continuous flow of oxygen in the optics chambers are favorable conditions for an almost effortless and efficient cleaning of the contaminated optics. We stress that the \textit{in-situ} cleaning of the optics can be achieved even by monochromatic beam at room temperature.

References

[1] C. Chauvet et al., 2011, \textit{J. Synchrotron Rad.} 18 761.
[2] K. Boller et al., 1983, \textit{Nucl. Instr. and Meth.} 208 273.
[3] J. Hollenshead & L. Klebanoff, 2006, \textit{J. Vac. Sci. Technol. B} 24 64.
[4] T. Koide et al. 1986, \textit{Nucl. Instr. and Meth. in Phys. Res. A} 246 215.
[5] R. B. Gillette & B. A. Kenyon, 1971, \textit{Appl. Opt.} 10 545.
[6] W. D. Beverly et al. 1973, \textit{MIT press, Cambridge, Mass.} 31 159.
[7] W. R. hunter et al., 1973, \textit{Appl. Opt.} 12 2800.
[8] W. R. McKinney et al., 1982, \textit{Nucl. Instr. and Meth.} 195 371.
[9] E. Pellegrin et al., 2014, \textit{J. Synchrotron Rad.} 21 300.
[10] A. Singh et al. 2013, \textit{Applied Surface Science} 283 612.
[11] P. Risterucci et al., 2012, \textit{J. Synchrotron Rad.} 19 570.
[12] A. Toyoshima et al., 2015, \textit{J. Synchrotron Rad.} 22 1359.
[13] A. Toyoshima et al., 2012, \textit{J. Synchrotron Rad.} 19 722.
[14] Roger W.C. Hansen et al.,1994, \textit{Nucl. Instr. and Meth. in Phys. Res. A} 347 249.
[15] W. K. Warburton et al., 1992, \textit{Nucl. Instr. and Meth. in Phys. Res. A} 319 240.
[16] H. Ishimaru, 1989, \textit{J. Vac. Sci. Technol. A} 7 2439.
[17] H. F. Dylla, 1993, \textit{J. Vac. Sci. Technol. A} 11 2623.
[18] A. P. Hitchcock et al., 2001, \textit{Ultramicroscopy}, 88 33.
[19] A. P. Hitchcock, aXis2000 is freely available at http://unicorn.mcmaster.ca/aXis2000.html
[20] R. Belkhou et al., 2015, \textit{J. Synchrotron Rad.} 22, 968.
[21] X. Deng et al., 2005, \textit{J. Am. Chem. Soc.} 127 9267.