Controlling optics contamination at the PolLux STXM

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ABSTRACT: Contamination of X-ray mirror surfaces by carbon is a common issue that can significantly degrade the optical performance of the instrument. The effects can be severe at photon energies near the carbon K-edge (ca. 300 eV), where the X-rays are strongly attenuated, but also significant at higher photon energies where the carbon coating affects the reflectivity and surface shape of the mirrors. [1] The Swiss Light Source has typically relied on in-situ plasma cleaning to control mirror contamination and the PolLux scanning transmission X-ray microscopy (STXM) beamline has also been employing further contamination reduction strategies in recent years. In particular, in 2014 we installed a $1 \times 10^{-8}$ mbar background pressure of O$_2$ on the PolLux first mirror chamber. We present a history of efforts to control optical contamination at the PolLux beamline and report on the observed efficiencies of the different processes employed both for the in-vacuum optics and critical components of the frequently vented STXM experiment chamber.

KEYWORDS: Instrumentation for synchrotron radiation accelerators; X-ray transport and focusing

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1 Introduction

The deposition of carbon films on X-ray optics is commonly observed, despite the use of an ultra high vacuum (UHV) environment. Such contamination impacts the performance of the optics, both at the carbon K-edge (due to strong absorption) and at higher energies due to changes in the surface reflectivity and focus distortions. [1] The contamination films have been characterised as amorphous carbon (with 15–20% hydrogen content), with increasing irradiation resulting in a loss of hydrogen and a more graphitic structure. [2–6] The general mechanisms of the carbon contamination deposition involve the adsorption of precursor molecules, which are then decomposed and reduced to a solid phase by the incident ionising radiation and the subsequent photo-emitted electrons. [2–4, 7] The rate of contamination deposition has been shown to be dependent on the pressure and composition of the residual gas, as well as the temperature of the substrate and the radiation flux. [2–4]

Recent efforts in cleaning carbon contamination from X-ray optical surfaces have tended towards a strategy of reacting the carbon with reactive oxygen species in order to transform the carbon into volatile gasses such as CO\textsubscript{2} that can be pumped away. These reactions are being driven by energy provided through either a plasma [8] or ionising radiation from a UV lamp [1, 8] or synchrotron radiation. [7–13] In-situ cleaning treatments are strongly preferred since breaking UHV provides opportunities for further carbon species to enter the vacuum environment and cause further contamination. Risterucci et al. [7] provide an excellent demonstration of the surface chemistry of CO and O\textsubscript{2} leading to carbon deposition or removal on an X-ray irradiated Pt surface, while Matsunari et al. [2] showed that heavier organic molecules tend to deposit carbon at higher rates. In this article we present the accumulated experience of dealing with carbon deposition at the PolLux scanning transmission soft X-ray spectro-microscopy (STXM) beamline at the Swiss Light Source (SLS).
1.1 A short history of the PolLux beamline

Figure 1. Current layout of the PolLux beamline. The components within the STXM endstation (indicated by a grey dashed box) are typically positioned to have separations of a few millimetres. Note that the HOS was not part of the initial 2006 beamline, but was added in May 2009. The beamline upstream (left) of the vacuum window is kept under UHV, while the endstation typically operates at $10^{-5}$ mbar, but is periodically vented for exchange of samples and accessory apparatus.

The PolLux beamline [14, 15] was installed in the spring of 2006, obtaining first light on June 13th and beginning regular STXM experiments in November 2006. The design of the beamline, shown schematically in figure 1 uses a bend magnet source with a typical heat load on the first mirror of 30 W. The beamline was optimised for an energy range of 200–1400 eV for experiments focusing on X-ray magnetic circular dichroism in the transition metal L-edges (e.g. Fe, Co and Ni L$_{2,3}$-edges at approximately 710, 780 and 860 eV), and organic materials at the C, N and O K-edges (approximately 285, 400 and 530 eV). The first mirror and monochromator grating chambers were each constructed with an RF antenna for driving an in-situ O$_2$ plasma, which was used to clean these vacuum chambers before installing the optics and subsequent baking at 120°C. After performing experiments for about half a year, a significant build-up of carbon contamination was observed and so in-situ O$_2$ plasma cleaning of the first mirror chamber was performed in August 2007. In-situ O$_2$ plasma cleaning was performed again in January 2008 on both the first mirror and monochromator chambers. The O$_2$ plasma cleaning of the monochromator chamber was followed by an in-situ H$_2$ plasma in order to chemically reduce the Ni coating on the monochromator grating.

In 2009, a number of changes were made to improve the available photon flux at the carbon K-edge. First, in January, the translation stages in the endstation were disassembled and the lubricants...
were replaced with MoS$_2$ in order to minimise the outgassing of carbon containing species. Second, in April, we began routine ex-situ cleaning of the zoneplates with a UV/ozone treatment. Finally, a set of additional mirrors were installed in the beamline in May, to act as a higher order suppressor (HOS) \cite{16} and ensure the spectral purity of the X-ray beam at photon energies below 600 eV. The HOS chamber was cleaned with an in-situ O$_2$ plasma before installing the mirrors. These measures dramatically improved the spectroscopy (and spectroscopic contrast for imaging) measurements at the carbon K-edge and a jump in publications the following year. In July of 2011, in-situ O$_2$ plasma cleaning was performed again on the first mirror, monochromator and HOS chambers.

In September 2012, the scanning stages for the coarse motion of the sample along the X- and Y-axes were replaced. The old stages involved stepper-motors driving a screw to slide the stages along rails, while the new stage is based on a flexure design that is driven by piezo-walker drives. The new stage eliminated sliding motions and hence the need for lubricants that could outgas. A 2012 report by Leontowich et al. \cite{17} indicated that the detector efficiency at the carbon K-edge was low. In response to this, we replaced the phosphor coating in front of the photomultiplier tube (PMT) detector and increased the sensitivity of the pulse discriminator in September 2012. The phosphor was again replaced in November 2017 after it was damaged in an accident while exchanging the detector shield.

In July 2013, a small partial pressure of O$_2$ was added to the PolLux first mirror chamber, which has been running continuously since then. The same type of continuous O$_2$ leak has also been operating in the first mirror chamber of the neighbouring (and nearly identical in design) NanoXAS beamline since June 2014.

2 Methods

2.1 Ex-situ UV/ozone cleaning

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\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2.png}
\caption{a) UV lamp in metal box for UV/ozone cleaning of zoneplates. Images of the upstream, flat membrane side of a 240 $\mu$m diameter zoneplate b) before and c) after 24 hours of UV/ozone cleaning.}
\end{figure}

Zoneplates are delicate nanostructures that constitute the critical focusing element for a STXM. Since the zoneplate is exposed to both high X-ray flux and the poor vacuum environment of the endstation, it is to be expected that it will show a high rate of carbon deposition on both surfaces. Carbon deposits on a flat surface, such as the rear side of the zoneplates supporting membrane, are easily observable in a visible light microscope due to thin film interference effects, as shown in figures 2b and 3, while it is difficult to see on the structured side of the zoneplate. Cleaning
with UV/ozone is driven by a UV source, which creates ozone (O$_3$) from UV-illuminated oxygen molecules (O$_2$) and/or water (H$_2$O). Organic materials tend to react strongly with ozone, even at room temperature, to eventually produce CO$_2$ and water. Ozone directly attacks double and triple C-C bonds such that unsaturated carbon is more readily oxidised by ozone than saturated carbon species. [18, 19] This means that ozone is particularly effective at oxidising heavily unsaturated carbon layers, such as is typically observed on X-ray optical surfaces. [5, 6] The removal of carbon deposits by UV light has been previously demonstrated in a number of situations. The simple version implemented at PolLux consists of a non-reactive enclosure equipped with a UV light and a gas inlet and outlet, as pictured in figure 2a. In this case, the gas inlet is just a filter while the gas outlet is connected to a low-vacuum exhaust line. The UV lamp (Ozone Gen Pen-ray Lamp, model 90-0003-01) was purchased from Omnilab, Switzerland, and has an intensity of 2.8 mW/cm$^2$ at a distance of 25 mm. A small beaker of water increases the humidity, which improves the cleaning rate. A heatsink is attached to the opposite side of the lid from the UV lamp in order to help dissipate heat (The apparatus shown in figure 2a operates at ca. 35°C). The top hat shaped copper piece inside the box in figure 2a has a gold plated zoneplate mounted on the upper face, which is positioned to be well illuminated by the UV lamp (when the box is closed) and thus apply the cleaning treatment to the structured side of the zoneplate. To clean the rear side of the zoneplate, it is held upside-down (by a block with a hole through it) such that the nanostructured area of the zoneplate doesn’t touch anything. Images of the rear side of a zoneplate before and after 24 hours of UV/ozone treatment are shown in figures 2b and 2c respectively. Zoneplate materials of Au, Ir and Ni are in use at PolLux and all of these have been regularly cleaned by the UV/ozone method without noticeable degradation of their performance. However, small variations in the focal length parameter have been observed after removal of a heavy carbon film. This effect is suspected to be the result of a change the effective zone width (removal of carbon overlayer). In a variation of this effect, we have once observed an energy-dependent astigmatism of a zoneplate that we suspect was caused by oblique UV illumination of the zoneplate leading to asymmetric cleaning of the carbon film from the nanostructures (i.e. the effective zone width was asymmetric at photon energies where
carbon film was strongly absorbing). To avoid such issues, we recommend placing the zoneplate directly under the UV lamp, so that the illumination is parallel to the optical axis of the zoneplate, and also to occasionally rotate the zoneplate ca. 90° while cleaning the structured surface in order to ensure even and symmetric cleaning between the zone walls.

In November 2017, there was an incident in which temperature control of a heater failed, causing kapton and epoxy to be evaporated into the STXM chamber and resulting in strong carbon contamination of the zoneplate. It was initially believed that the order selecting aperture (OSA) had shielded the zoneplate from the contamination and so measurements using 800 eV X-rays continued for a few days further. Figure 3 shows the UV/ozone cleaning progress of the Au, 240 µm diameter zoneplate, first of the upstream, flat membrane side (figure 3a-f) and then of the sample-facing nanostructured side (figure 3g-k), which ended with the failure of the supporting membrane (figure 3k-l). We assume that the UV/ozone treatment caused changes in the tension of the contamination layer that eventually overcame the tensile strength of the membrane.

2.2 In-situ UHV O₂ leak

![Figure 4](image)

**Figure 4.** Oxygen leak cleaning on the first mirror chamber of the NanoXAS beamline (identical to PolLux). a) The oxygen leak is installed as a lecture bottle together with a leak valve. Photographs of the first X-ray mirror b) before and c) after 37 hours of bend magnet radiation with a 1×10⁻⁸ mbar background pressure of O₂.

A leak valve and small bottle of O₂ have been installed on the the first mirror chambers of the PolLux and NanoXAS beamlines and adjusted to increase the pressure within the respective chambers to 1 × 10⁻⁸ mbar (from a base pressure of 5 × 10⁻¹⁰ mbar). This oxygen leak has been constant since that time, regardless of the operation of the beamline for experiments and it is expected that X-ray illumination performs the same role in the carbon removal process as the UV illumination discussed in the above section. Figure 4a shows the leak valve and O₂ lecture bottle attached to the NanoXAS beamline (the PolLux first mirror chamber is closer to the wall of the hutch and so more difficult to take photographs). The baffle in front of the NanoXAS first mirror
was narrowed at the same time as the O$_2$ leak was installed such that the illuminated stripe across the mirror was reduced in height. The carbon removal effectiveness of the O$_2$ leak is well illustrated by comparing photographs of the NanoXAS first mirror before (4b) and after 37 hours of X-ray exposure (4c), with a bright band of clean mirror surface clearly visible through the center of the dark stripe caused by carbon deposition.

2.3 In-situ plasma cleaning

![Figure 5](image)

**Figure 5.** a) Rendering of the in-situ RF antenna design for plasma operation in UHV chambers, including the vacuum flange interface (blue, grey) and carrier gas inlet (green). b) Image of a plasma in a 40% O$_2$ and 60% Ar gas mixture.

The first mirror, monochromator and HOS chambers are each equipped with an RF antenna for in-situ plasma treatments. The RF antenna, shown in figure 5, consists of a cylindrical mesh that is capped at one end where the RF input and vacuum feedthrough is located. It is 177 mm long and 121 mm in circumference, but the precise dimensions are not important since they simply determine the impedance of the device, which is matched by the matchbox unit. An O$_2$ plasma treatment is performed by isolating the chamber by closing valves and then filling it with 40% O$_2$ and 60% Ar to about 2.5 × 10$^{-2}$ mbar. 50 W of RF power was applied to the antenna (at 13.52 MHz and a bias of about 100 V) by a PRG-RF RF generator and PFM 1500-A Matchbox (Hüttinger, Germany). Once ignited, the plasma was kept running for about 16 hours. An O$_2$ plasma treatment in the monochromator chamber would be followed by a 2-hour H$_2$ plasma treatment in order to try to reduce the surface of the Ni coated grating. This was performed by pumping the chamber again before refilling it with 5% H$_2$ and 95% He to about 2.5 × 10$^{-2}$ mbar and applying RF power in the same way as for the O$_2$ plasma. Plasma treatments were typically followed by baking the chamber(s) to 120°C for about 4 days, if permitted by the beamtime schedule. Note that in-vacuum screw threads and valve seals are commonly coated with silver or gold in order to avoid vacuum welding. Silver is readily oxidised to a black powder by an O$_2$ plasma and so gold coatings are recommended in vacuum chambers where O$_2$ plasma cleaning treatments are intended.

Due to a design mistake, the RF antenna in the PolLux HOS chamber was initially not properly shielded, causing Ti (probably from the mechanical supports for the optics) to be sputtered onto the mirror surfaces during the plasma cleaning treatment in July 2011. This shield was replaced with a
wider one before repeating the plasma cleaning and baking the chamber. The presence of Ti on the HOS mirrors can be clearly observed by the appearance of strong Ti L\textsubscript{2,3} absorption near 460 eV in the more recent spectra shown in figure 8b (but notably absent when the HOS is not in use, as shown in figure 8a).

We have also used an ex-situ H\textsubscript{2} plasma in a Diener Atto plasma cleaner (Diener, Germany) for cleaning the inner surfaces of channeltron electron multipliers. The channeltrons were used for experiments in PolLux [20, 21] and NanoXAS [22, 23] and strong performance improvements were observed after H\textsubscript{2} plasma treatments.

### 2.4 In-situ endstation O\textsubscript{2} backfill

![Figure 6](image)

**Figure 6.** Spectra measured before and after a cleaning procedure can be converted into an optical density in order to quantify the amount of carbon removed. In-situ cleaning procedures were carried out on contaminated vacuum windows in a-b) June 2015 and c-d) November 2017 by backfilling the chamber with 10 mbar of O\textsubscript{2} and then exposing to intense X-rays via the zero-order monochromator reflection for a-b) 3.5 hours or c-d) 1 hour.

The PolLux STXM endstation is designed for use in low- or high-vacuum, and to be routinely vented (with dry N\textsubscript{2}) for the exchange of samples and accessory apparatus. Hence, the vacuum environment of the endstation tends to be relatively poor and the deposition of carbon onto samples is commonly observed when performing repeated scans. In order to combat this issue, experiments on samples that are not oxygen sensitive are now often performed with 1 mbar of O\textsubscript{2} backfilled into the endstation. This is especially useful for magnetisation dynamics measurements in which the same micron-scale object was repeatedly imaged for a number of days, [24–27]

The vacuum window that separates the UHV of the PolLux beamline from the endstation vacuum (shown in figure 1) can also be a challenge to keep reasonably carbon free on the endstation side. Its heavily enclosed position close to the zoneplate and within the central hole of the zoneplate
mount means that it experiences a poorer vacuum environment, while also transmitting a higher photon flux than the other optical components within the endstation. It is also difficult to access, being glued to a stainless steel block that is screwed to the zoneplate Z-axis stage. The vacuum window at PolLux is usually replaced, rather than cleaned (more details in the following section), although this involves breaking the UHV of the beamline and so requires about 6 hours to pump down again (no bake out). An alternative is to expose the vacuum window to a high X-ray flux (zero-order monochromator reflection) and a significant pressure of O\(_2\) back filled into the endstation. Figure 6 shows beamline spectra measured across the C K-edge region before and after exposing the vacuum window to 10 mbar of O\(_2\) and zero-order X-rays (from the Au coated grating) for 3.5 hours (figure 6a) and 1 hour (figure 6c). By treating the before and after spectra as \(I\) and \(I_0\) measurements, we can calculate the spectrum of the material removed (and/or chemically altered) by the cleaning process, as presented in figures 6b and 6d. The June 2015 experiment presented in figure 6a-b demonstrates the removal of about 0.43 optical density (OD) of carbon and 0.18 OD of other elements, while the November 2017 experiment presented in figure 6c-d demonstrates the removal of about 0.46 OD of carbon and 0.18 OD of other elements. Both of these experiments appear to have completely removed the carbon contamination, so even shorter X-ray exposure times may be sufficient and the actual etch rate is probably greater than 0.6 OD/h.

Note that exposing a zoneplate to a zero-order monochromator reflection is not recommended since it could provide sufficient heat load to melt the zoneplate.

2.5 Minimising contaminant availability

While most X-ray optics are installed in UHV environments, gas pressure is not the only factor that impacts the rate of carbon deposition. If we examine the ideal gas law in eq. (2.1), then we see terms for pressure \(P\), volume \(V\), number of moles \(n\), the ideal gas constant \(R\) and the temperature \(T\).

\[ PV = nRT \quad (2.1) \]

A dependence on the mass of the gas molecules is notably absent and therefore the number of carbon atoms present in the gas is not reliably indicated by the measured pressure. If we instead examine the rate at which gas molecules will collide with a surface:

\[ \Phi = \frac{PN_A}{\sqrt{2\pi MRT}} \quad (2.2) \]

where \(N_A\) is Avogadro’s number, we now see that there is a dependence on the molecular mass of the gas molecules, \(M\). However, this is only an inverse square root dependence and so a gas composed of organic molecules will increase the number of constituent carbon atoms faster than the resulting reduction in surface impacts. Therefore, at the same partial pressure, heavier organic molecules should be expected to deposit on X-ray illuminated surfaces at a higher rate than lighter organic molecules, as has been demonstrated by Matsunari et al. \[2\]. Of course, the vapour pressure of heavier molecules will also tend to be lower, but still significant at UHV pressures. Therefore, the composition of the residual gas is always important in regards to carbon contamination.

Residual gas measurements of UHV chambers typically show major contributions from H\(_2\), H\(_2\)O, CO and CO\(_2\), however, it has been demonstrated that the measured CO and CO\(_2\) are actually
produced by ion sources such as in the quadropole mass analyser (or residual gas analyser, RGA) used to perform the measurements, rather than being directly outgassed from the vacuum chamber walls. [28, 29] Other ionisation sources, such as ion-guages and X-ray radiation (and the resulting photoelectrons), are similarly responsible for CO and CO$_2$ production and so CO and CO$_2$ will still be real components of the UHV residual gas of any synchrotron beamline. Further, ion pumps are also suspected of producing hydrocarbons via a related mechanism. [12, 30] Chauvet et al. [1] provide a good example of the change in RGA spectra when surfaces inside a UHV chamber are exposed to X-rays. Whatever its chemical form may be, the carbon films observed on X-ray optics demonstrate that significant sources of carbon atoms must be commonly present in UHV systems.

In low- or high-vacuum environments, the use of “vacuum grease” is commonly tolerated, since reasonably low pressures can be attained. It can even sometimes see restricted use in UHV environments. However, as demonstrated in equations (2.1) and (2.2), the vacuum pressure has little bearing on the availability of carbon for photo-deposition and very heavy molecules with extremely low vapour pressures can be particularly misleading in this regard. Replacing vacuum grease with a dry lubricant such as MoS$_2$ will reduce the availability of carbon in the vacuum system.

A design choice of the PolLux STXM, as well as the ALS-5.3.2 STXM design it was based on, is to minimise the optical path between the vacuum window and zone plate in order to reduce X-ray absorption by gases filling the chamber. This is because the ALS-5.3.2 STXM was designed to operate in a 300 mbar He environment in order to aid heat removal from the stepper motors driving the scanning stages. While PolLux has been adapted to operate in low- or high-vacuum, the small gap between the vacuum window and zone plate has been kept, resulting in a poorly pumped volume that sees high photon flux and hence a high carbon deposition rate on the downstream vacuum window and upstream zoneplate surfaces. A major contributor to carbon availability in this volume is outgassing from the glues used to mount the vacuum window and zoneplate. The PolLux strategy for mounting zoneplates is to use a minimal amount of silver paint on the corners of its frame. Applying glue at the corners, rather than between the mount and zoneplate substrate, keeps the glue further away from the problematic volume. The vacuum window is glued to its mount by Torr Seal (Agilent Technologies, U.S.A.), again using a minimal amount, but by drawing a circle of glue onto the mount using a needle in order to ensure a vacuum-tight seal. When mixing the Torr Seal, it is important to mix a relatively large amount (to ensure correct proportions), to heat the glue to about 40°C to make the components more fluid while mixing and to ensure the components are thoroughly mixed. Curing the Torr Seal for a few hours at 60°C is also recommended.

### 2.6 Detector phosphor recoating

The default detector in the PolLux STXM endstation uses a phosphor to convert soft X-rays into visible light for subsequent detection by a photomultiplier tube. [31] A fast decay, green emission UKL59 phosphor (Gd$_2$O$_2$S:Pr,Ce,F from Phosphor Technology, U.K.) with a mean particle size of 2.5 µm is deposited directly onto the PMMA light pipe by a suspended powder settling method. A small amount of phosphor powder is added to a 8:1 solution of water and ethanol and treated in an ultrasonic bath to ensure the powder is well dispersed. Areas of the light pipe not intended to receive a phosphor coating are wrapped in parafilm and the piece weighted to ensure it will not float. The solution is allowed to settle for 5 minutes after removal from the ultrasonic bath so that larger phosphor particles settle out of the dispersion. The wrapped and weighted light pipe is then lowered
into the solution and a cover is placed over it, as shown in figure 7a. The solution is left undisturbed overnight to fully settle so that the solution looks completely clear as shown in figure 7b.

The solution is then removed with a syringe to minimise disturbance of the settled particles by movement of the liquid and the remaining moisture allowed to evaporate. Once dry, the piece is removed from the beaker and the parafilm removed. In agreement with Leontowich et al. [32], we find the optimum coating to consist of the thinnest layer required to for almost full area coverage i.e. a few monolayers of phosphor particles. Note that the critical area to be coated is at the very top of the submerged piece shown in figure 7 and so the coating thickness will depend on the dispersed particle concentration and the height of solution above the application area. We prefer this dispersion-settling deposition method over the method described by Leontowich et al. [32] (plunging a greased tip into loose phosphor powder) because it does not rely on the use of vacuum grease and therefore doesn’t contribute to the amount of carbon in the residual gas of the experimental chamber.

3 Discussion

Figure 8 presents a series of PolLux beamline spectra from different years over the energy range covered by the Ni coated 300 l/mm grating, both without the HOS (only reflections from the Pt first mirror and Ni coated grating, 8a) and with the HOS (normal operation since 2009, 8b). The “2007-05” spectrum in figure 8a that was measured before any cleaning treatments were performed on the beamline optics is quite different from the spectra measured in later years. Firstly, the dip near 300 eV is stronger due to significant carbon contamination of the optics. It is somewhat misleading though, since all the other spectra shown except “2009-11” were taken soon after a cleaning treatment. Secondly the variation in photon flux observed near 400 eV changes after the initial plasma cleaning treatment and then remains stable thereafter (note that the “2009-11” spectrum was measured through a Si₃N₄ membrane and so has extra spectral features at the N K-edge). The strong variation seen in the “2007-05” spectrum near 400 eV is not well understood and the smaller variation seen in later spectra is more in line with calculations from the beamline design. [14] Near 530 eV, we observe structures at the O K-edge that are very weak in the “2007-05”
Figure 8. Wide range spectra demonstrate the transmission function of the PolLux beamline using the Ni-coated, 300 l/mm grating, both a) without the higher order suppressor (HOS), and b) using the HOS to obtain a pure spectrum. The 2009 spectra were measured with a diode in the endstation and therefore involve transmission through a Si$_3$N$_4$ membrane, while the others were measured with a diode just after the exit slits.

spectrum and grow in intensity over time. Spectra measured with the Au coated 600 l/mm grating (not shown) only display O K-edge features similar to the “2007-05” spectrum, indicating that the observed increase is due to oxidation of the Ni coated 300 l/mm grating. This oxidation suggests that the H$_2$ plasma treatment of the monochromator discussed in section 2.3 was not effective in reducing the Ni surface. The spectral features visible near 270 eV and 430 eV are due to the O K-edge and Ni L$_{2,3}$-edges interacting with the second order reflection from the monochromator grating. Ni L$_{2,3}$-edge features from third order light are also present near 290 eV, coincident with the C K-edge. Spectra measured with the HOS in figure 8b do not show these higher-order features, except for the second order O K-edge features near 270 eV. (Note that normal STXM operation with a zoneplate and order selecting aperture will further filter the higher order light to an insignificant level.) The “2009-11” spectrum in figure 8b shows spectral features near 300 eV due to strong carbon contamination on the beamline optics, near 400 eV due to N K-edge absorption by the additional Si$_3$N$_4$ membrane of the vacuum window and near 530 eV due to oxidation of the Ni coated 300 l/mm grating (as also observed in figure 8a). Spectra from later years show further features at 400 eV and 460 eV (also intensifying the features near 530 eV) that were likely introduced by the 2011 plasma cleaning incident described in section 2.3 where a significant layer of Ti was sputtered onto the HOS mirror surfaces (Ti L$_{2,3}$-edge is near 460 eV), which then reacted with nitrogen and oxygen.
(possibly during the venting to replace the RF antenna shield). On the positive side, the “2014-06” and “2017-05” spectra show relatively small dips at the C K-edge, indicating the beamline optics remain clean since the introduction of the in-situ O$_2$ leak was installed in the first mirror chamber in 2013. Examining the 2014 and 2017 spectra in more detail, the spectra without the HOS are very similar, indicating that the Pt first mirror and Ni coated grating are clean and stable over this three-year period. However, the HOS spectra show a deepening of the C K-edge and O K-edge dips, while the Ti L$_{2,3}$-edge dip decreased in intensity. This suggests progressive reaction of the Ti on the HOS mirrors with C and O, which in turn reduces the proportion of Ti in the composition of the mirror surface. This contamination of the HOS mirrors is likely intractable and will require ex-situ recoating the mirrors in order to recover the previous situation.

![Figure 9](image)

**Figure 9.** The archive of PolLux experiment data contains a time series of a) $I_0$ measurements (normalised at 283.5 eV). Comparing the available flux at 283.5 eV (just before the onset of carbon absorption) to 293 eV (the typical energy of the strongest absorption by the carbon contamination) provides a simple measure of the depth of the carbon dip. b) $I_0$ scans can therefore make a timeline of beamline contamination. The red line in mid-2011 indicates the application of an O$_2$ plasma treatment, while the period of operation of the O$_2$ leak in the first mirror chamber is indicated by a blue background.

It is common practice to perform STXM measurements both with and without a sample, in order to be able to compare the sample-transmitted X-ray intensity to the X-ray intensity that would arrive at the sample and hence calculate the sample absorption. Therefore, the archive of experiment data for the PolLux beamline contains repeated measurements of the photon flux delivered by PolLux. Figure 9 presents a set of these “$I_0$” measurements over the time period from the installation of the HOS, which enables accurate spectroscopy at lower photon energies,
until the present. The general shape of the spectra (normalised at 283.5 eV, just before the onset of carbon absorption) is observed to be stable over time in figure 9a, with distinct resonances at about 285.1 eV, 286.7 eV and 288.5 eV, with a minimum intensity at about 293 eV. The ratio of photon flux intensities measured at 293 eV (maximum carbon absorption) to 283.5 eV (pre-edge region with minimum carbon absorption) provides a simple measure of the photon flux lost to carbon contamination, with a value of 1 corresponding to a perfectly clean beamline and lower values indicating increasing contamination. Plotting this value on a timeline (figure 9b) shows how the cleanliness of the PolLux beamline has varied over recent years. The rapid changes in the photon flux available at the C K-edge demonstrate how rapidly the carbon contamination builds up in the STXM endstation and requires regular maintenance to keep in check. An informative example is given by the set of three points in June 2015 that show a strong increase in available photon flux. The first, lowest data point is where the carbon dip was observed to be unacceptable. The increase to the second, middle data point was achieved by replacing the zoneplate with a clean one and the second improvement in available photon flux to reach the third, highest data point was produced by cleaning the vacuum window via the O$_2$ backfill method discussed in figure 6. Further, the rate of contamination is observed to have decreased since mid-2016, which we attribute to the use of backfilled O$_2$ in the STXM endstation for samples that are not oxygen-sensitive, as discussed in section 2.4.

A rapid downward trend is also observed in figure 9b in December 2010 where the available flux fraction at the C K-edge drops from 0.45 to 0.05 over the course of a week. It is unclear what caused this rapid contamination, which appears to have occurred within the STXM endstation because the plasma cleaning of the beamline in July 2011 (indicated in figure 9b with a dashed red line) had little impact on the available flux, which did not recover to previous levels until December 2011. The experiments performed during the period of rapid contamination involved polymer samples that typically show little outgassing. \[33–36\] The period over which the O$_2$ leak has been operating in the PolLux first mirror chamber is indicated in figure 9b by a blue background and there is a clear increase in flux available at the C K-edge with the O$_2$ leak (up to about 0.9) than before its installation (up to about 0.5).

4 Conclusions

A number of carbon contamination reduction and removal strategies have been implemented on the PolLux beamline and STXM endstation. The O$_2$ leak in the first mirror chamber and the ex-situ UV/ozone cleaning of zoneplates have clearly been very successful in improving the photon flux available at the C K-edge. Removing grease lubricants and backfilling the STXM chamber with 1 mbar of O$_2$ during experiments on samples that are not sensitive to oxygen have also contributed by reducing the rate of contamination. Plasma cleaning of the beamline has also been successful in removing carbon from the X-ray optics, but has come at the price of oxidising the surface of the Ni coated monochromator grating and contaminating the higher order suppressor (HOS) mirrors with Ti, which further associated with C, N and O that is likely intractable. On the other hand, the PolLux user community has a strong interest in the C K-edge, where performance is excellent, but very few measurements are made at the Ti L$_{2,3}$ or O K-edges where experiments are strongly
impacted by the HOS mirror contamination. We would therefore recommend the O\textsubscript{2} leak cleaning method over plasma treatments.

Removing sources of carbon from the endstation and also backfilling O\textsubscript{2} into the endstation when measuring samples that are not sensitive to oxygen have also been very successful. While in-situ cleaning of the vacuum window with backfilled O\textsubscript{2} and white light from the zero-order monochromator reflection has shown good results, further study is required to determine if the Si\textsubscript{3}N\textsubscript{4} membrane is weakened by such treatment. Further, zoneplates should not be exposed to zero-order light as they are likely to be damaged.

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References


