Preliminary results for in situ cleaning of B_4C-coated FEL mirrors using oxygen plasma.

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Synopsis Carbonaceous contamination stripes were removed by in situ plasma treatment, for a total of 5 hours, and mirror reflectivity quantitatively improved. Preparatory studies show high selectivity against B_4C erosion, with no change in treated/untreated surface roughness.

Abstract An in situ oxygen plasma cleaning process has been applied to LCLS B_4C-coated Kirkpatrick-Baez (KB) mirrors. After a total of five hours treatment, the initial carbonaceous contamination stripes, acquired over 7 years of FEL beam irradiation, were visibly reduced to barely detectable. After treatment, the output photon flux showed a reflectivity improvement between ~20% and ~170%, depending upon the photon energy. Further characterization, including detection of possible sputter-deposited impurities and improvement in KB focusing properties, are planned following return of FEL beams, at the conclusion of the current six-month downtime, in June, 2017. Preparatory, off-line measurements suggest that the process is both "safe and effective" for B_4C-coated mirrors. Test depositions of 50 nm amorphous carbon could be removed with high selectivity against B_4C erosion, with no change in treated/untreated surface roughness. Nevertheless, sputter-deposited impurities from adjacent components may be an issue, as seen in soft x-ray reflectivity studies, where surface reflectivity restoration remained imperfect.

Keywords: B_4C-coated mirrors; carbonaceous contamination stripes; in situ plasma treatment.

1. Introduction

Like synchrotron radiation user facilities, the Linac Coherent Light Source (LCLS) FEL user facility has seen build-up of carbonaceous stripes on UHV mirror optics. Stripes form preferentially in regions illuminated by the FEL beam.

This phenomenon is perhaps most detrimental on the LCLS bendable, soft x-ray Kirkpatrick-Baez (KB) mirrors (Kelez, *et al*., 2009), which tend to have greater exposure to carbon-containing gases, due to close proximity of the experimental station (2.1 and 1.4 meters), and the nature of experiments conducted. In these systems, contamination stripes affect not only general mirror reflectivity but also KB mirror system ability to focus to a small spot, due to a Gaussian height profile of the longitudinal deposited contamination stripe (consequence of FEL Gaussian transverse intensity profile), which may not be adequately correctable through our "2-moment" mirror bending mechanics.

We would like to remove this contamination in situ, to restore both reflectivity and focus. We seek an in situ mirror surface cleaning process which would ideally:

1) Remove deposited carbonaceous contamination, due to FEL illumination under UHV conditions with residual gases.

2) Leave reflective coatings unaffected, i.e.:

a) pristine surface roughness maintained/restored after cleaning

b) pristine surface reflectivity maintained/restored after cleaning

c) pristine surface composition unaltered

3) Have minimal erosive/mechanical effect on hydrocarbon-containing compounds used in the existing KB mirror system:

a) kapton-insulated wiring

b) epoxy potting compound

c) structural adhesive used to bond mirror substrates to bending mechanism

An additional, general complication for this at the LCLS is the use of B_4C reflective coatings on all soft x-ray FEL transport and focusing mirror optics. This low-Z, refractory coating is used because it is much more resistant to FEL single-shot damage than more conventional metal coatings, such as Ni, Rh, and Pt.

However, the carbon content of B_4C opens the risk that a process effective at removing carbonaceous contamination may also attack B_4C.

Recent studies from the ALBA Synchrotron report significant success with in situ optics cleaning (Pellegrin, *et al.*, 2014 and González Cuxart, *et al.*, 2016) using a commercial plasma source, the ibss Group, Inc., Model GV10x (ibss, undated). In the GV10x, 13.56 MHz RF energy ignites and sustains a plasma in the flow of input gases. Plasma products exit the source through an orifice, and flow into and through the user vacuum system, to interact with surfaces. Using the ALBA studies as a foundation, and after performing off-line studies of our own, using a B_4C test sample, we recently performed an in situ cleaning procedure on the LCLS AMO KB Mirror System using the GV10x, and obtained encouraging preliminary results.

What we did, the preliminary results, and some observations and cautionary warnings, will be presented below.

2. Preparatory tests/experimental procedure

2.1. Preparatory tests

Initial tests were made using a B_4C test sample, in a small treatment chamber, both illustrated in Figure 1.

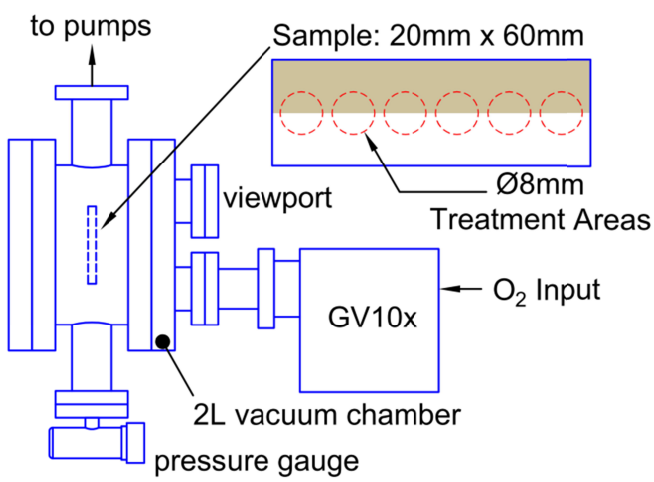

Figure 1 Schematic illustration of test vacuum system used for initial, preparatory tests, and test sample detail. Plasma gases from the GV10x source enter the vacuum chamber, flow past the sample, and into a turbomolecular pumping station. The sample is a 5 mm thick silicon substrate with 50 nm deposited B_4C. The upper half of the sample was coated with an additional ~50 nm amorphous carbon. ϕ8 mm treatment areas on the sample could be exposed one at a time.

Approximately 50 nm amorphous carbon was separately vacuum deposited over half the B_4C sample using conductively-heated, pointed graphite electrodes. The B_4C sample was held in a stainless steel carrier, which also defined the six, ϕ8 mm treatment regions. A UHV aluminium foil mask exposed a single, ϕ8 mm sample region at a time for treatment. The treatment region approximately faced the GV10x plasma source, not directly on axis to the source, but certainly perpendicular to the GV10x source axis. The presence of the deposited carbon could be seen through a viewport; its disappearance during a treatment procedure was readily determined visually.

The plasma treatment conditions used are summarized in Table 1.

Table 1 Summary of plasma treatment conditions

Plasma source	ibss Group, Inc., Model GV10x
Plasma gas	Pure oxygen
Treatment chamber pressure	3.8 mTorr †
Gas flow rate	~Few standard cubic centimeters per minute (sccm) ‡
Plasma source RF power	70 W, at 13.56 MHz

† Read using Granville-Phillips Convectron gauge

‡ Estimated from turbomolecular pump pumping speed and conductance of hardware between pump and chamber

Under the plasma conditions in Table 1, the amorphous carbon visually disappeared after 15 minutes of treatment. During this time, the presence of the amorphous carbon was easy to see, until the very end, when in <1 minute, the carbon disappeared quite uniformly over the exposed sample region. Treatment was continued, however, for a full hour total.

Erosion/mechanical degradation of hydrocarbon materials used in the LCLS KB system was also tested in the same small treatment chamber, again using the plasma conditions in Table 1. Kapton insulation, epoxy potting compound and structural adhesives were only eroded at rates of ~few µm/hour of plasma treatment, maximum. This was considered acceptable.

Mechanical shear strength test samples were designed, and assembled using the KB system structural adhesive. Half the samples were plasma treated for one hour, while half were left untreated. Stress/strain curves for both sets were measured with a universal testing machine (Instron, undated); no systematic differences between the two sets were detected.

Plasma treated B_4C sample regions were further characterized. Surface roughness and etching were quantified using an interferometric 3D profiling microscope (Coherent Scanning Interferometry), Zygo

NewView 8300. Surface roughness was unaffected by oxygen plasma treatment (~5 nm rms, for distortion wavelengths between 6 mm and 4 µm.) The removed carbon created a step height of ~55 nm. The boundary between treated and untreated B_4C was detectable, with a step of at most a few nm, which suggests slight B_4C etching.

B_4C sample surface reflectivity and surface composition were characterized using soft x-ray reflectivity and total electron yield, measured at BL 6.3.2 at the Advanced Light Source (ALS) at Lawrence Berkeley National laboratory (LBNL) (Underwood, *et al.*, 1996).

Absolute reflectivity was measured from ~60 eV to 1300 eV, at 1.5° grazing angle, which overlaps a reasonable portion of the photon energy range required for the LCLS AMO KB System, ~300 eV to 2000 eV. Below ~600 eV, the reflectivity of plasma-treated regions matched that of untreated B_4C regions on the sample, within a few percent, however above ~600 eV, treated regions consistently showed decreased reflectivity, by 5% to 10% over untreated B_4C. This is attributed to sputtered stainless steel contamination of the treated sample surface, which is inferred from the clear absorption signatures of Cr, Ni, Fe, and Mn in the treated surfaces. Ideally, features from only B, C, and perhaps O from the plasma, and O and N from atmospheric exposure, are expected.

Angle scans of surface reflectivity also suggest some slight etching of the B_4C surface by oxygen plasma. Untreated B_4C regions display Kiessig fringe interference structure consistent with a B_4C surface layer 55 nm thick, while plasma-treated regions clearly infer a thinner layer, 52.2 nm thick.

2.2. Experimental procedure

Taken altogether, the promising aspects of these off-line, preparatory studies prompted us to proceed with plasma treatment of the LCLS AMO KB Mirror System, but with two important procedural changes, designed to help reduce risk:

1) When mounted to the KB system mirror chamber, the axis of the GV10x plasma source was always oriented at grazing incidence to mirror optical surfaces, unlike the facing, ~normal-incidence geometry used with the B_4C test sample. This was intended to significantly reduce any ion sputtering of contaminants from internal structures onto the mirror surface, and follows the advice given in González Cuxart, *et al.*, 2016.

2) Plasma treatment was performed for the minimum reasonable time, i.e. only until the contaminated stripe was barely visible. This was intended to minimize any etching of the B_4C coating.

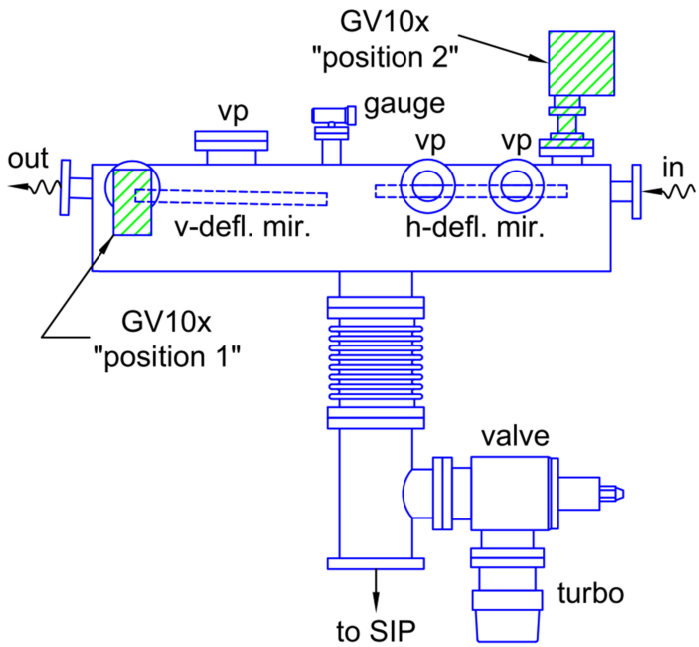

Figure 2 Schematic illustration of plasma treatment set up for LCLS AMO KB Mirror System. Plasma gas products, produced by the GV10x source, flow between the source and the turbomolecular pump. Treatment was initially made with the source installed in "position 1", and subsequently in "position 2". Viewports associated with each of the KB mirrors allowed visual monitoring of the mirror reflective surface during plasma treatment.

Figure 2 schematically illustrates the LCLS AMO KB Mirror System, and details relevant to plasma treatment. Beam line sector valves, located immediately upstream and downstream of the KB system were closed and sealed for plasma treatment. The Convectron gauge was installed to monitor mirror chamber pressure, and chamber pumping was provided by the illustrated turbomolecular pump, throttled by the large adjacent right angle valve (the main sputter ion pump [SIP] was turned "off"). The GV10x plasma source was initially installed near the downstream end of the vertically-deflecting mirror, "position 1". Plasma treatment in this configuration was made for 2 hours, 15 minutes, using the plasma conditions in Table 1. The GV10x was then relocated to the upstream end of the KB mirror chamber, "position 2", as illustrated in Figure 2, and plasma treatment applied for an additional 2 hours, 30 minutes.

3. Preliminary results

Viewports on the KB mirror chamber allowed visual observation of the carbonaceous stripes, on both KB mirror surfaces, during plasma treatment. Initially "clean" mirror regions appeared dark blue/black; the deposited stripes looked orangish-brown at the thickest, and silver when thinner. As treatment continued,

the lengths of the orange and silver regions decreased, until all the orange disappeared. After that, the width of the remaining silver region decreased, until any sign of the initial stripe was difficult to see.

Plasma treatment with the GV10x in "position 1" was visually effective at removing the carbonaceous stripe on the downstream, vertically-deflecting mirror, but essentially ineffective on the upstream, horizontally-deflecting mirror. Only when the GV10x was relocated to "position 2" was effective cleaning of the horizontally-deflecting mirror seen. In addition, treatment in "position 1" was made until a faint stripe was still visible on the vertically-deflecting mirror; this stripe remained after 2.5 hour treatment with the GV10x in "position 2".

An initial, quantitative measure of plasma treatment effect on KB mirror reflectivity was obtained through experimental, FEL intensity measurements, made downstream of the AMO KB Mirror System five days before plasma treatment, and repeated six days after plasma treatment. The intensity measurements were made with power meters, UP10 from Gentec-EO. The results appear as Table 2. The reflectivity improvement is obtained from the ratio of the flux after treatment to that before treatment (each normalized by an upstream measurement of the incident flux), the excess of this ratio over 100%, i.e.:

Reflectivity improvement = $(\mathrm{Flux}_{\mathrm{after}}/\mathrm{Flux}_{\mathrm{before}}) - 100\%$.

Table 2 Reflectivity improvement in the LCLS AMO KB Mirror System, following in situ plasma treatment. FEL photon flux measurement downstream of the KB system was made before and after plasma treatment using experimental power meters.

Photon energy	350 eV	550 eV	1000 eV	1560 eV
Reflectivity improvement	51%	19%	77%	167%

4. Discussion

At this time, the LCLS is in the midst of a six-month down time, during which no FEL beams will be available. As a result, important characterization of the AMO KB mirrors, following the described plasma treatment, must wait. Our observed significant removal of the carbonaceous stripe should permit much improved KB mirror focus, as the original mirror figure may be substantially restored. This will be examined.

Preliminary tests showed sample surface contamination, presumably by sputter erosion of nearby surfaces. Testing for such contamination on the KB mirror system, using FEL beams, will also be important, as contamination could significantly limit the applicability of this cleaning technology.

Determining plasma conditions and geometry that result in sputtered contamination certainly deserves further study and consideration.

The described plasma process, for the test sample chamber, and for the LCLS AMO KB system chamber, very likely falls into the intermediate/Knudsen flow regime, i.e., between viscous flow and molecular flow. Yet clearly, from the way in which cleaning occurred in the present set up, "flow direction/path" is much more effective than diffusion in transporting the relevant chemical species to the surfaces to be cleaned, and removing the subsequently-generated reaction products. Consider the "flow path" from the GV10x source at "position 1" to the turbomolecular pump (see Figure 2). Plasma products flow past the vertically-deflecting mirror and down to the turbomolecular pump. Only by diffusion will these products significantly encounter the horizontally-deflecting mirror; it is out of the "flow path". We noted little cleaning effect on the horizontally-deflecting mirror for the GV10x at "position 1". In an entirely similar way, very little cleaning effect on the vertically-deflecting mirror was seen with the GV10x in "position 2"; this mirror is then out of the "flow path".

Therefore, it seems important that plasma cleaning set ups, using sources, parameters, and physical systems similar to those encountered here, be designed to place surfaces to be cleaned in the general "flow path" between the plasma source and the system pump.

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