

An Ion Chamber Dedicated to Carbon NEXAFS: Removal of High-Order X-Rays and Reliable Flux Measurement

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Abstract. The difficulty of performing a reliable carbon NEXAFS measurement for thin films and adsorbate systems has long been recognized. The difficulty is typically related to lower S/B, carbon buildup in beamline optics, dirty mesh, presence of the high-order x-rays, etc. To alleviate the experimental difficulty, we have constructed an intensity-monitoring ion chamber situated between the beamline and sample chamber. The ion chamber is filled with argon up to a working pressure of 10^{-3} Torr and terminated with $0.1\text{ }\mu\text{m}$ thick Ti foils at both ends. Titanium foils and the filled argon gas effectively remove the high-order x-rays. Consequently, the data are acquired with predominant 1st-order x-rays and thus free of the aforementioned interference, leading to a more reliable data analysis.

Keywords: NEXAFS technique, carbon K-edge, ion chamber, x-ray intensity monitor

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INTRODUCTION

Carbon K -edge NEXAFS spectroscopy is a powerful technique in determining molecular conformation for the organic films [1]. Unfortunately, the main experimental difficulty is the relatively low S/B ratio, particularly for thin films and adsorbate systems. In order to recover the signal solely attributed to the adsorbate, up to three normalization schemes are often needed to eliminate the influence from time-varying x-ray flux and substrate absorption [1]. A key element needed for implementing such an operation is to have a device that faithfully reproduces the variation of x-ray flux, i.e. an I_o monitor. Gold mesh outputs photocurrent in proportion to photon flux but the mesh cleanliness is often an issue. Moreover, the high-order x-rays, a common occurrence in soft x-ray beamlines, also results in spurious spectral features that further complicate the data analysis. Taken together, it cannot be overstated that there is always an uncertainty about how to relate mesh current, even measured in clean mesh condition, to the photon flux of the first-order component only.

PROBLEM ANALYSIS AND DESIGN CONSIDERATION

For the soft x-ray beamline based on spherical grating monochromator, the high-order components of x-rays can be quite pronounced. For the carbon K -edge

NEXAFS measurement (from 270 to ~ 325 eV), up to fourth-order component of x-rays can be found. Both the presence of high-order light and the contaminants in the beamline optics are detrimental to a reliable determination of absorption features in NEXAFS spectrum.

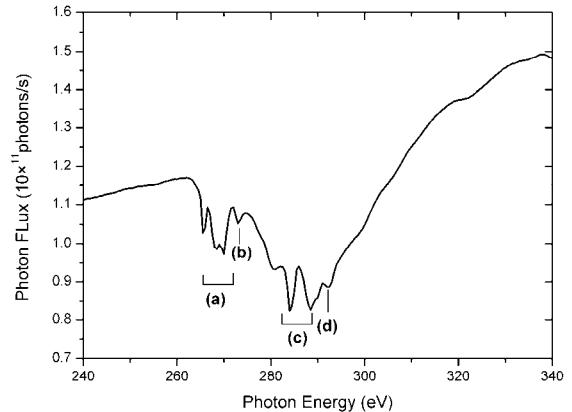


FIGURE 1. Energy-dependent x-ray flux for the 400 line/mm grating measured with a photodiode [2]. Both the entrance and exit slit openings set at $100\text{ }\mu\text{m}$ with storage ring operating at a current of 200 mA.

Shown in Fig. 1 is the distribution of x-ray flux from the 400 line/mm grating in the wide range beamline (BL24A) of NSRRC. X-ray flux is measured with a commercial photodiode [2]. There are many

absorption features spanning across the carbon K -edge region. For example, in the region (a) located between 265 and \sim 270 eV, several sharp dips are found to be associated with the absorption of 2nd-order x-rays (530 to 540 eV, accordingly) by oxygen-containing species residing in the beamline optics. The dip (b) originates from the N_3 absorption edge (546.3 eV) of gold coating in the beamline mirrors, excited by the 2nd-order x-rays. Consequently, the presumably flat, pre-edge region of carbon NEXAFS is subject to distortion, which will cause difficulty in performing an edge-jump normalization procedure. The dips in region (c) starting from \sim 282 eV are due to the x-ray absorption by the carbon species in the optics. These carbon-related flux dips are ubiquitous, which is the main difficulty to be overcome when performing carbon x-ray absorption experiment for thin films. The feature in region (d) is due to the excitation of Cr $L_{2,3}$ core levels (binding energy at 583.8 and 574.1 eV, respectively) by the 2nd-order x-rays again. Chromium layer is present underneath the topmost gold reflective coating to help achieve a uniform coating of gold in the beamline optics.

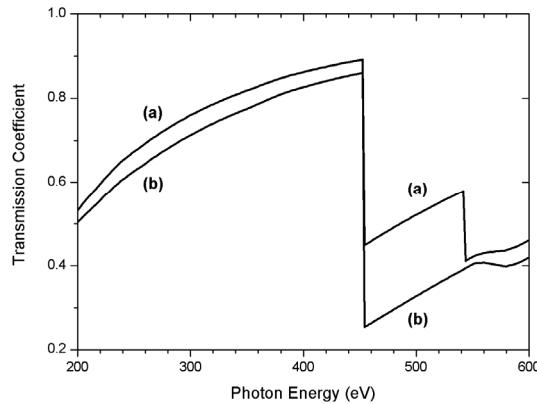


FIGURE 2. Change of x-ray transmission coefficient with the x-ray energy for a 0.1 μm thick titanium oxide foil (a) and 0.1 μm thick titanium foil (b), respectively. The spectra are obtained from reference [3].

Figure 2 shows the variation of transmission coefficient with the x-ray energy for titanium oxide (a) and titanium (b) foils of identical thickness of 0.1 μm [3]. For both foils, the drops of transmission coefficient occur at about 455 eV and are attributed to the Ti $L_{2,3}$ edges. For titanium oxide foil, one additional transmission drop at 543 eV is related to the O K -edge. For the Ti foils in use here, two foils mounted in tandem give a combined transmission coefficient of 0.5 at carbon K -edge and 0.14 at oxygen K -edge. Taking into account the argon absorption in the ion chamber, the intensity of x-rays when emerging from the working ion chamber is typically

attenuated from 2/3 to $3/4$, which is still satisfactory for monolayer adsorbate measurement.

The smooth variation of transmission coefficient across the carbon K -edge region is important to ensure a successful normalization. One advantage expected to gain from using Ti foils is that x-rays with energy around O K -edge, appearing at the carbon pre-edge region through the 2nd order reflection of grating, is to be significantly reduced in intensity. Titanium oxide is not chosen here because of the drastic change of transmission across the oxygen K -edge, leading to a possible difficulty in normalizing carbon pre-edge features.

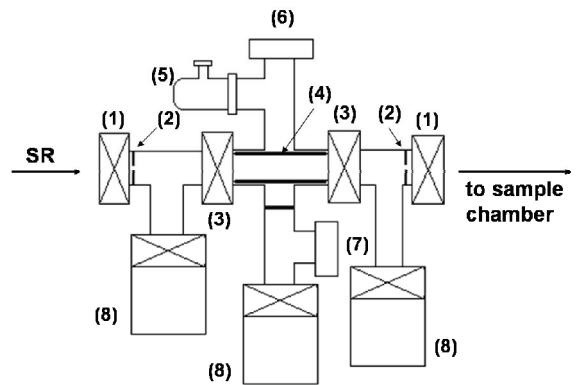


FIGURE 3. Schematic of argon ion chamber used for monitoring the intensity of incident x-rays and for removing the high-order x-rays during carbon K -edge measurement. (1) VAT shutoff valves, 2 places; (2) blank copper gasket with 5 mm diameter aperture in the center, for differential pumping, 2 places; (3) VAT window valves for mounting Ti foils, 2 places; (4) a rectangular-tubing electrode with ceramic standoffs, mounted inside the ion chamber constructed from a six-way cross; (5) Varian leak valve for admitting argon gas; (6) Convectron gauge; (7) hot cathode ionization gauge; (8) turbo-molecular pumps, 70 l/s, 3 places.

With this idea in mind, we successfully constructed a single ion chamber filled with argon gas and terminated with Ti foils [4] on both ends. The schematic is presented in Fig. 4. The noble gas argon is chosen because of its relative ease of pumping and the absence of x-ray absorption features around the carbon K -edge. In fact, the argon absorption features located at 248.4 eV (L_3 edge), 250.6 eV (L_2 edge) and 326.3 eV (L_1 edge) can be further utilized to calibrate the x-ray energy around the carbon K -edge region.

During the operation, Ar gas is back-filled to a relatively high pressure of 3×10^{-3} Torr, yielding an appreciable ion current of 1 nA for the bias voltage of -80 V on the electrode. To avoid overloading both the sample chamber and beamline in particular with argon gas, several measures are taken. Pinhole-free Ti foils mounted on stainless steel grids of 94% optical

transmission are selected owing to their higher mechanical strength. Differential-pumping stages are also deployed to minimize gas intrush to the beamline if the foils rupture: two on the beamline side and one on the sample chamber side. As a result, the pressure rise in the beamline can be kept less than 2×10^{-9} Torr, but the pressure rise in the sample chamber is higher, $\sim 1 \times 10^{-8}$ Torr. Since the sample chamber is evacuated by turbo-molecular pumps during XAS measurements, high partial pressure of argon neither contaminates the sample nor causes harm to the pumping system.

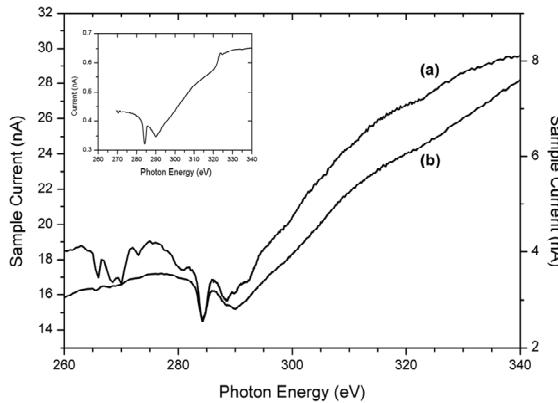


FIGURE 4. Drain current of clean Au(111) when irradiated by x-rays with the beam first passing through either a non-operational (a) or an operational (b) argon ion chamber. The inset shows the corresponding ion current obtained under a similar operation condition of the ion chamber.

Figure 4 shows the drain current of clean Au(111) when irradiated by x-rays, with measurements performed in either non-operational (a) or operational (b) modes of the argon ion chamber. When the ion chamber is not in operation, two Ti foils are moved out of the way and the ion chamber and the adjacent chambers are evacuated down to UHV pressure range. A clean Au(111) does not have any absorption feature for the x-ray energy ranging from 260 to 340 eV. The undesirable absorption features observed in the curve

(a) can be fully accounted for by invoking the excitation of the carbon with 1st-order x-rays and the excitations of the oxygen, gold, and chromium with 2nd-order x-rays. The deployment of the argon ion chamber clearly eliminates almost all the features derived from the 2nd-order x-rays, thus restoring a much simplified spectrum dominated by carbon absorption features, as shown in curve (b). Also shown in the inset is the ion current obtained under similar operation conditions. The clean-cut spectrum serves to monitor the intensity change of the x-rays very well. The current increase at 323.7 eV is related to the excitation of Ar *L*₁ edge, a naturally-present fiducial mark in the spectrum for calibrating photon energy. It is noted that the present setup has been in use for almost a year to determine the monolayer and submonolayer NEXAFS spectra for aromatic molecules on surfaces. The device has proven to be trouble-free besides the occasional need for replacing ruptured foils.

ACKNOWLEDGMENTS

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REFERENCES

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2. Silicon photodiode with model number AXUV 100, available from International Radiation Detector Inc.
3. X-ray transmission data were obtained from Eric Gullikson's website at the Advanced Light Source web site at University of California, Berkeley: http://www-cxro.lbl.gov/optical_constants/filter2.html.
4. Titanium foils were purchased from Lebow Company, Goleta, CA.