XANES Study of Carbon Contamination on EUVL Optical Mirror Surface

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Abstract

Carbon accumulates as contamination on optical mirror of Extreme Ultraviolet Lithography (EUVL) instrument when the mirror surface is irradiated with EUV light in vacuum. The accumulated carbon was investigated by C K-edge XANES spectroscopy. Characteristic peaks were found in the spectra of mirror samples. The XANES data indicated that the deposits on the mirror were organic compounds partly decomposed into graphite. As a model sample, a silicon wafer was prepared on which carbon films were deposited by EUV irradiation with different durations. It was found that the chemical state of the contaminant carbon depended on the irradiation time.

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1. Introduction

One of the problems concerning optical mirrors used for EUVL process is formation of contaminant film on the mirror surface by photochemical reaction of residue organics in the vacuum. The film grows on the surface because the mirrors are placed under comparatively low vacuum condition (at about 10^{-5} Pa) and irradiated with high energy photons (about 92 eV). The surface contamination leads to reduced throughput and degradation in exposure quality of the EUVL process. Therefore, it is considered that techniques to control and remove the contamination are very important It is important for the development of these techniques to understand the condition under which the contamination occurs and its reaction process.

Our group, Semiconductor Leading Edge Technologies (Selete), has been developing the EUVL process using Small Field Exposure Tool (SFET) and Full Field Exposure Tool (EUV1). In the course of the development the surfaces of the exposed optical mirrors used for SFET and EUV1 were studied by several analytical methods. By using Ellipsometry, TEM, RBS, XPS, ERDA and TOF-SIMS [1-2] it was found that deposited carbon contained hydrogen and had density of 1.3 and thickness of 20 nm. We further have studied chemical structure of the carbon by using X-ray Absorption Near Edge Structure (XANES) spectroscopy and the results will be reported here.

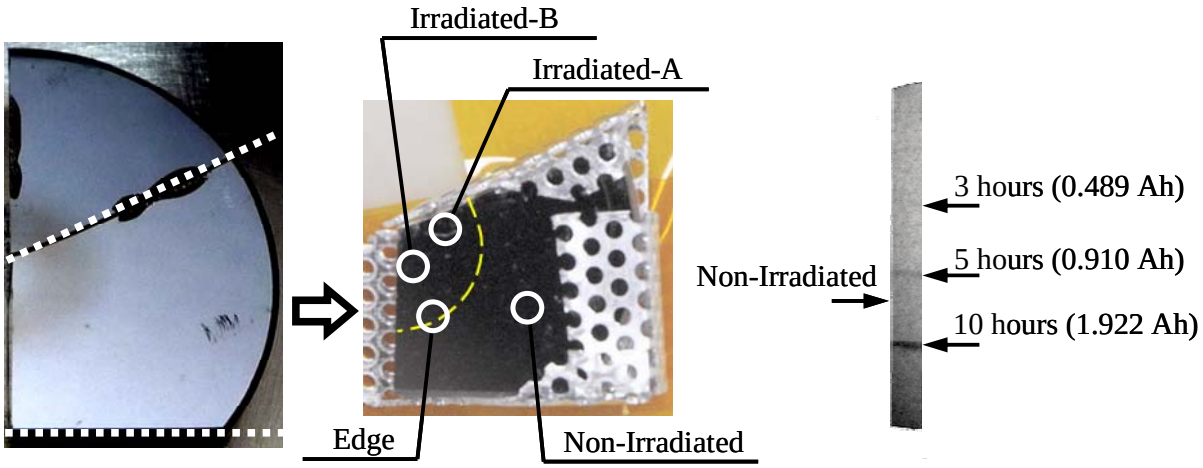

Fig. 1. Photographs of the used mirror for SFET process (left) and a silicon wafer exposed to EUV light at BL-6 of Ritsumeikan SR (right). The total photon numbers given to the silicon wafer are proportional to the exposure time (in hour) and the SR ring current (in ampere), thus they are expressed in Ah.

2. Experimental

An optical mirror used for SFET for about 9 months was segmented into a few pieces (Fig. 1). C K-edge XANES spectra in the total electron yield mode were obtained for one of the pieces using a beamline No. 2 (BL-2) of the SR Center at Ritsumeikan University. The spectra were obtained for four different points of the sample, two EUV irradiated, a non-irradiated and a border (edge) points.

In addition to the SFET sample, a model sample was prepared: A silicon wafer was placed in a vacuum chamber ($10^{-1} \sim 10^{-2}$ Pa) of BL-6 at Ritsumeikan SR. The wafer was irradiated with EUV light for three different time durations as indicated in Fig.1. Dependence of the chemical character of imitated contamination grown on the wafer on the irradiation time was investigated. A carbon-free gold plate was used as a reference sample to monitor the photon beam intensity [3].

3. Results

Fig. 2 shows C K-edge XANES spectra of the SFET mirror and graphite over 280 ~ 294 eV. The spectral intensities for irradiated areas were four times stronger than that of the non-irradiated, however, for the comparison purpose all the spectra were normalized in intensity at around 292 eV. Four characteristic peaks, α, β, γ and δ, may be identified in the spectra. The peaks are assigned to (α) π* of C＝C, (β) π* of C－C＝O, (γ) σ* of C－H, (δ) π* of O－C＝O, respectively. From the comparison of the spectra for EUV irradiated and non-irradiated areas, it is obvious that the EUV irradiation reduced the relative intensities of γ and δ components and on the other hand enhanced α and β components. This result suggests that the EUV photon breaks the bonds of C－H and O－C＝O of the organic compounds adsorbed on the mirror surface and leaves C＝C and C－C＝O bonds. The EUV irradiation changes the compound to graphite-like substance, however, it is precisely not graphite because if the β, γ and δ components of Irradiated-A and B are compared to that of α, they are far stronger than those of graphite.

Fig. 3 shows C K-edge XANES spectra of the model samples and graphite. Here again the relative peak intensities of α and β increased, and that of δ decreased with an increase of X-ray irradiation time. This trend is the same as that of the SFET mirror, i.e. the organic compound having O－C＝O groups was so decomposed that the compound lost oxygen atoms to form C－C＝O and C＝C bonds and further into graphite-like compounds.

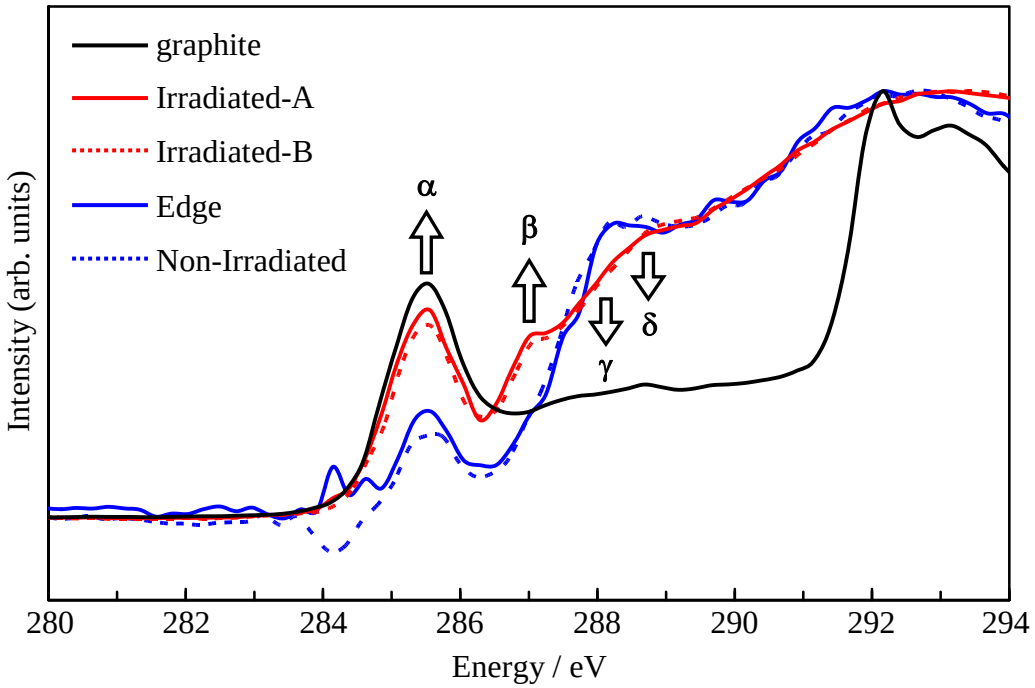

Fig. 2. C K-edge XANES spectra of the SFET mirror and graphite.

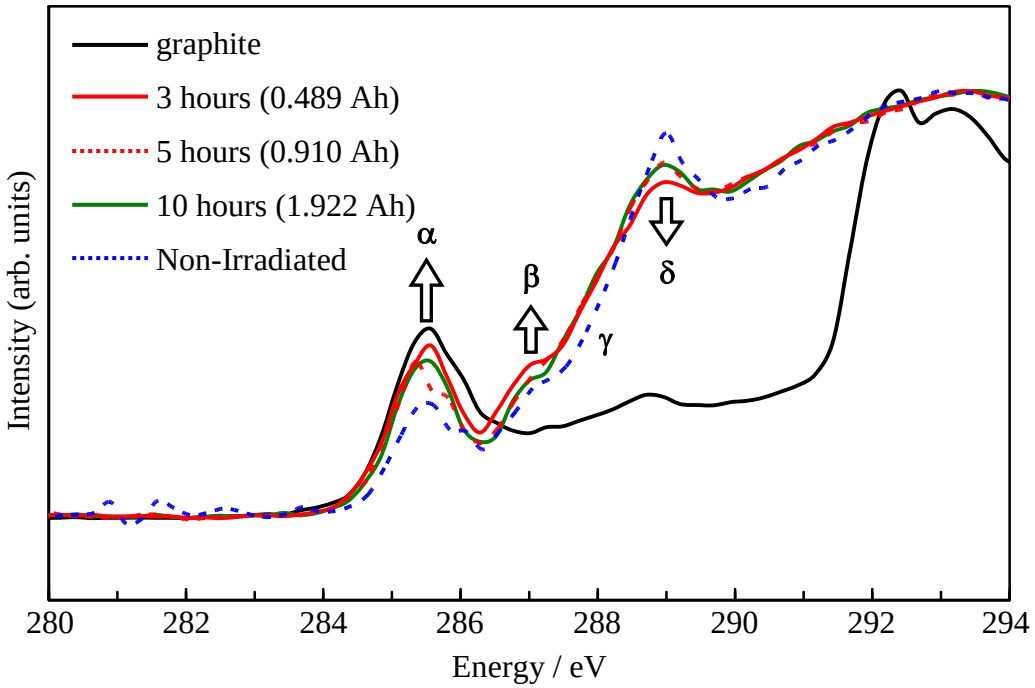

Fig. 3. C K-edge XANES spectra of the model samples formed on a silicon wafer with three different EUV irradiation durations and that of graphite.

4. Summary

C K-edge XANES spectra were measured for carbon deposits on EUVL optical mirror and a silicon wafer which was prepared as a model sample having carbon contaminant formed by EUV irradiation in a vacuum chamber. It was concluded that the deposit on the mirror was organic compound partially decomposed into graphite by EUV photons.

Acknowledgement

This research was supported by New Energy and Industrial Technology Development Organization (NEDO) and Open Advanced Research Facilities Initiative.

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