Plasma cleaning of carbonaceous samples using a shield

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Plasma cleaning is a useful technique to clean transmission electron microscopy (TEM) sample surfaces from carbon hydroxide. However, selective material removal rates can be hard to establish. As a result, carbonaceous samples are significantly impacted by the plasma process since by the very nature of an oxygen plasma it chemically reacts with carbon structures. We propose the use of a shield, provided by Fischione Instruments, to see whether this reduces significantly the plasma cleaning speed without reducing its effectiveness and without the need for a delicate tuning of the gas mixture or instrumentation parameters. Plasma cleaning could then be applied to carbonaceous samples such as graphite, diamond, amorphous carbon films as well as to any sort of powder deposited on holey carbon films. Tests were performed by electron energy-loss spectroscopy (EELS) using a post-column GIF attached to a Philips CM 30-UT and by high resolution imaging (HREM) with a top-entry JEOL 4000 EX.

We evaluated the time necessary to remove a carbon film deposited on formvar on copper grids such as used in TEM. The film still proved completely stable under the electron beam even after 6 minutes of plasma cleaning with the shield and no re-contamination was observed indicating cleaning did indeed take place. In order to seek for any changes in the bonding EELS measurements of the carbon K-edge were performed on amorphous carbon, highly oriented pyrolytic graphite (HOPG) and plastically deformed natural diamond. Carbon K-edge spectra show the transitions from the 1s occupied electronic state to the unoccupied states above the Fermi level. The first two peaks represent the transitions to the π^* and σ^* states, respectively. Figures 1a, b clearly show that the bonding signatures of the amorphous carbon film and the HOPG samples are unchanged when plasma cleaned for several minutes.

During sample preparation of diamond by ion milling an amorphous surface layer of considerable thickness (5 to 10 nm) can be created. Although this is not a real issue in conventional TEM, it becomes critically important when performing HREM or EELS. In the diamond sample the amorphous layer is visible on the carbon K-edge spectrum by a peak or shoulder at the position of the graphite's π^* peak and representative of the sp^2 contribution of the amorphous layer. Figure 2a shows a complete disappearance of that peak after a plasma cleaning time of 6 minutes with the shield, while the diamond ELNES remains unchanged. Also, the overall quality of HREM images remains approximately the same. However, although plasma cleaning refreshes the surface by removing amorphous layers, it also seems to differentially react with the surface on an atomic scale. This is a function of the disassociated oxygen, created by the plasma, chemically reacting with the diamond (C) to form CO and CO_2. The appearance of randomly distributed bright contrast changes in the HREM image indicates that differential removal of carbon atoms might have taken place.

Figure 2b shows these changes in contrast near a pair of stacking faults. Further, the thickness of the sample was measured using the low-loss spectrum of a given area. Repeating the thickness measurement after subsequent cleaning steps yields a thinning rate of approximately 10 to 15 $nm.min^{-1}$.

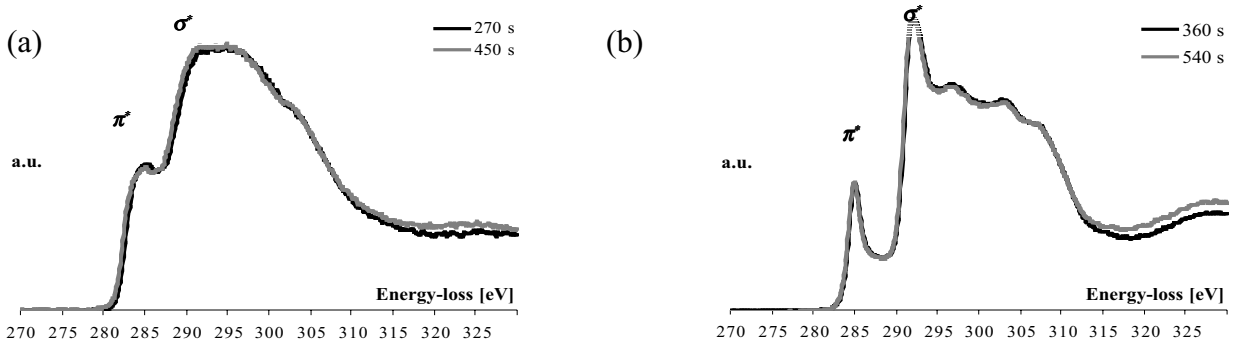

Fig. 1: (a) Amorphous film, carbon K-edge spectra after 270 and 450 s of plasma cleaning with shield. (b) HOPG, carbon K-edge spectra after 360 and 540 s of plasma cleaning with shield: no changes of peak positions, shapes and relative intensities are seen.

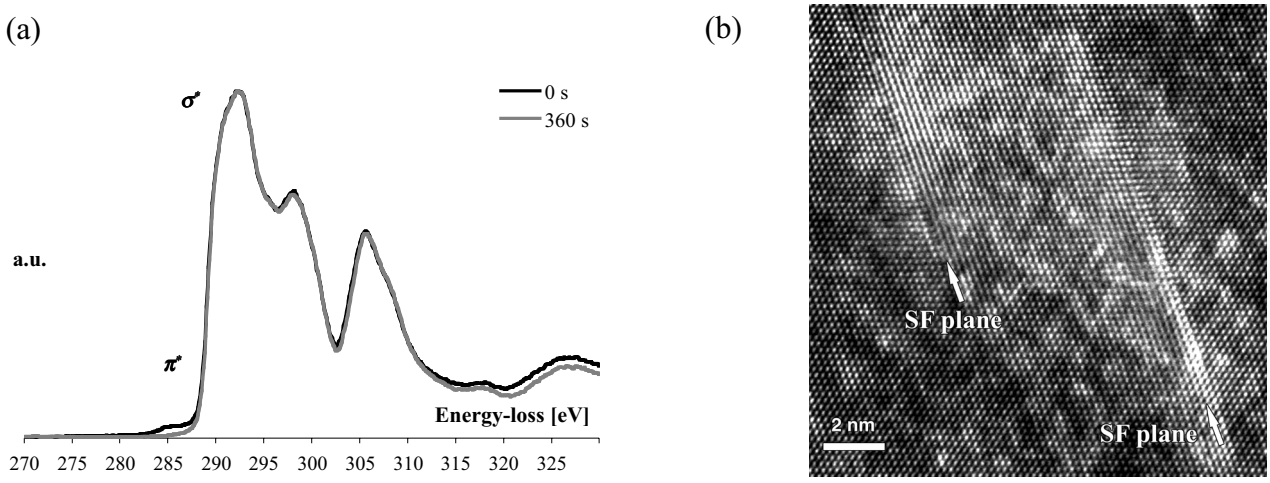

Fig. 2 (a) Diamond, carbon K-edge spectrum. The π* shoulder at 285 eV due to the sp^2 contribution of an amorphous layer (before plasma cleaning) disappears (360 s of plasma cleaning with shield), while the typical diamond peaks remain unchanged. (b) <110> plan-view HREM image of two stacking faults in diamond. An additional spotty white/black contrast, possibly due to the differential reaction of the oxygen with the surface, can be observed in the entire image.