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Optimization of Liquid Cell Transmission Electron Microscopy for Energy Dispersive X-Ray Spectroscopy

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Over the last decade, liquid-cell transmission electron microscopy (LC-TEM) has grown from a curiosity to a fundamental tool in the repertoire of materials and life sciences research. LC-TEM enables direct imaging of hydrated and liquid samples using a TEM without the need for vitrification or other preparatory embedment of the sample. The primary benefit of this technique is that samples are able to move and react freely under observation, enabling real-time process such as growth, degradation, interaction and fine movements to be observed at a resolution of a few nanometers. Typical LC-TEM sample preparation involves sandwiching a thin layer of liquid between two electron transparent membranes, such as silicon nitride or graphene. These membranes are integrated into microchip devices called E-chips contained within dedicated in situ sample holders which provide a hermetic seal from TEM column vacuum. Such closed cell in situ holders enable the introduction of liquid and/or stimuli such as heating or electrical currents to be delivered to the sample during imaging enabling a broad range of real-time dynamic studies to be observed using TEM.

However, a significant limitation of such closed cell environmental TEM holders has been the shadowing of the sample by the penumbra of the holder and the silicon frame of the E-chips themselves. This shadowing blocks line-of-site to the electron dispersive spectroscopy (EDS) detector. Modifications to holder design which reduce the penumbra of the holder tip have enabled users to obtain EDS maps in liquid in liquid (1, 2), however the sample holder must be tilted in order to obtain a direct line of site from the sample to the detector. In order to improve the collection efficiency of closed cell in situ holders for EDS, we introduced an E-chip fabricated using a modified process flow which removes more silicon from around the viewing window of the E-chip. This unique E-chip design, when combined with a low penumbra in situ holder (Protochips' Poseidon Select), results in a six-fold improvement in the counts per second obtained by the EDS detector and enables EDS maps to be obtained without tilting the specimen. Improved collection efficiency reduces the time necessary to obtain elemental spectra thus reducing the cumulative electron dose to which the sample is exposed. These modifications enable users to take full advantage of the analytical capabilities of the transmission electron microscope during in situ and operando LC-TEM experiments.

References:

[1] Zaluzec *et al*, Microscopy Microanalysis **20.2** (2014), p. 323.
[2] Lewis *et al*, Chemical Communications **50.70** (2014), p. 10019.

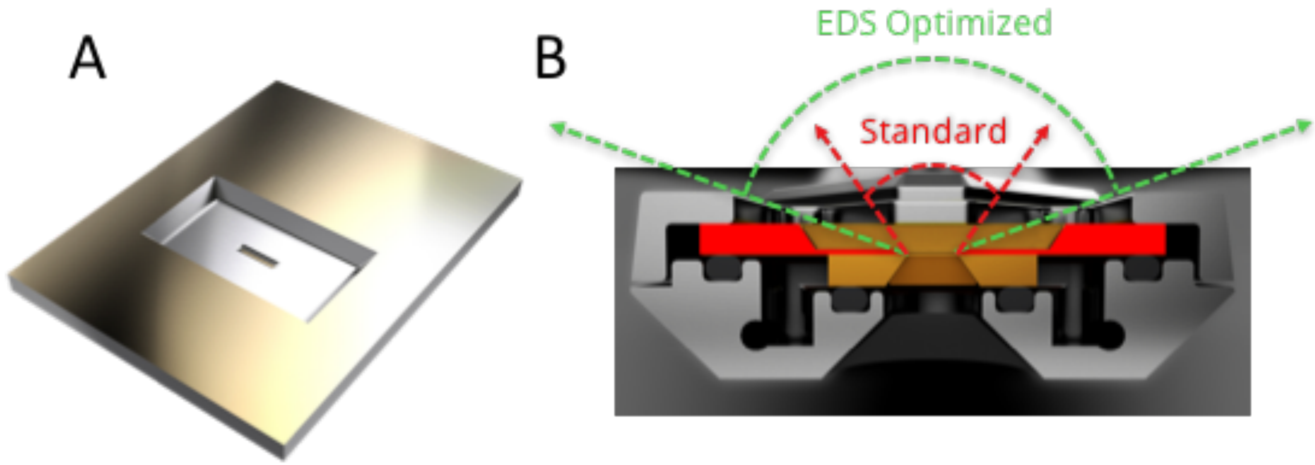

Figure 1. EDS optimized E-chip for LC-TEM. A) Back view of the optimized EDS E-chip. Silicon material is etched away from window on the back of the E-chip (the vacuum side) to provide a unique geometry. which allows a larger volume of x-rays to reach the detectors, improving counts per second over tradition E- chips, regardless of microscope. B) Cross section of the EDS optimized E-chip in a Protochips' Poseidon LC-TEM holder. The x-ray exit angle for the EDS optimized (double-etched) E-chip is indicated in green and the exit angle for the standard, single-etched E-chip is superimposed in red.

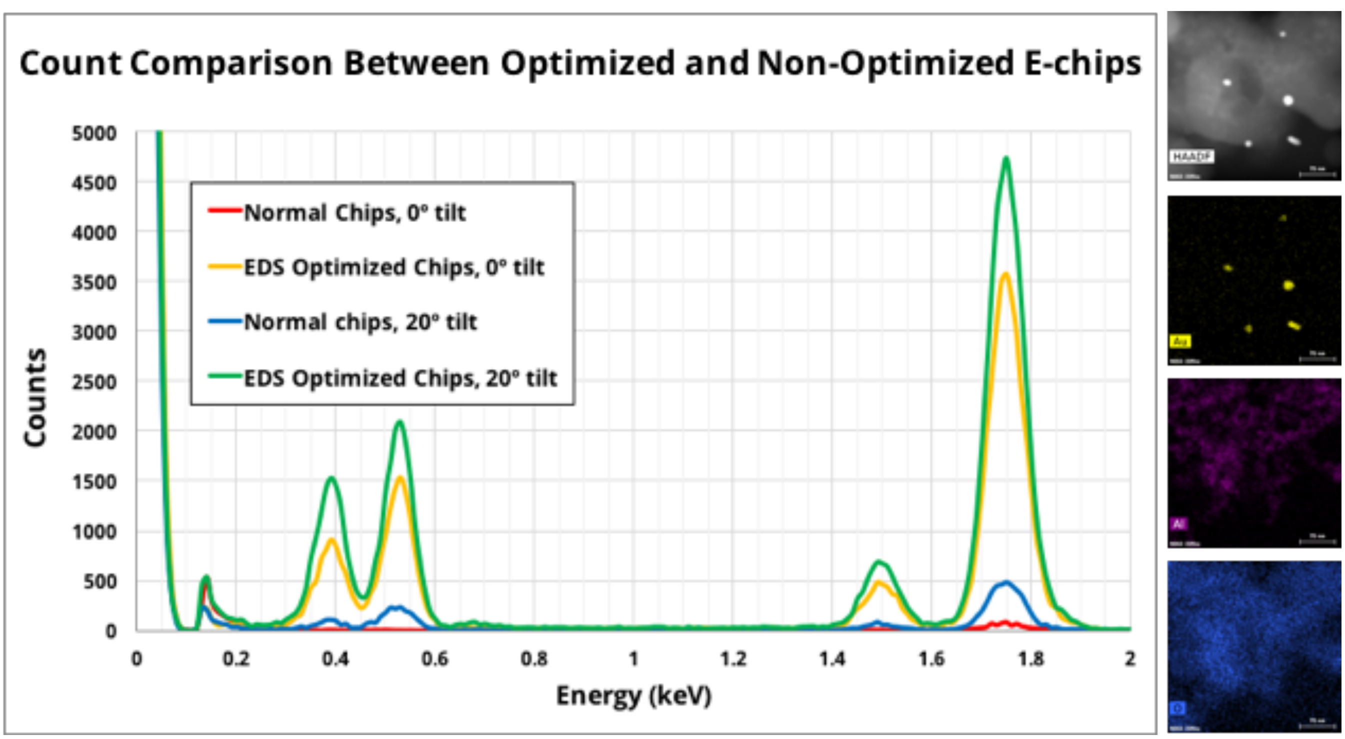

Figure 2. EDS spectra of gold nanoparticles and aluminum obtained using both normal, single etched, in situ liquid E-chips and EDS optimized, double etched in situ E-chips taken at 0° and 20° holder tilt. Images and spectra was obtained using an FEI Titan (200 KV and 60 pA beam current) equipped with a Super-X detector. Each data acquisition set was five minutes.