doi:10.1017/S1431927622010327
Microsc. Microanal. 28 (Suppl 1), 2022


# Elemental Quantification and Experimental Measurement of Mean Free Path Using EELS and CBED at 30 keV

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STEM is normally a technic that is used in most of the modern transmission electron microscope (TEM) which used high electron beam voltage (80-300keV). Even though this high-energy electron beam is useful to achieve atomic resolution, it becomes problematic in beam sensitive material. This is because when high energy electrons interact with the material, they are scattered through large angles and transfer their energy to the material which could induce atomic displacement. This atomic displacement call ''knock-on damage'' become important specially into low Z materials. [1] This becomes an important issue especially in the field of battery material where most materials are lithium-based. In those cases, the structural changes induced by the beam damage are similar to the changes induced by the charge-discharge cycle of the batteries which could lead to wrong conclusion. To prevent beam damage such as knock-on damage, it is well known that the beam energy needs to be below the energy threshold of atomic displacement. [1, 2] Computational calculation such as density functional theory (DFT) showed that for low Z elements such as boron and nitrogen in h-BN, the threshold energies for atomic displacements are < 19 eV and < 23 eV [3] which correspond to a beam voltage around 80 keV. This means that to reduce the knock-on damages on low Z elements, we need to turn to low beam voltage electron microscopy.

Using the Hitachi SU-9000EA microscope, which is 30keV cold-field emission STEM-EELS instrument with a 0.5eV energy resolution, EELS spectra and CBED pattern of $TiC_{0.63}$ and h-BN were acquired to investigate the validity of the EELS quantification method with a 30keV accelerating voltage. To determine the elemental ratio, the integration method described by Egerton [4] was used. The generalize oscillator strength (GOS) based program SIGMAK3 and SIGMAL3 [4] were used to determine the partial-cross sections of the respective K and L edges of our sample.

In total, 1700 spectrum showing both C K edge and Ti $L_{3\text{-}2}$ edges (Fig 1a) were acquired on multiple particles of TiC. Edges were background substrated and deconvoluted using the Fourier ratio method prior being integrated. Fig 2b shows the C/Ti elemental ratio distribution from all measurement which gave a mean value of 0.70 with a standard deviation of 0.07. This value is in an acceptable range from the expecting ratio 0.63 determined by the relation between the unit cell length measure by XRD and the composition of TiC [5].

Following the results obtain with the TiC, a beam sensitive material such as h-BN [3] was investigated using the 30 keV electron beam. EELS spectra of the boron K edge and nitrogen K edge were acquired (Fig 1c). However, the elemental ratio obtained using the integration method was not as expected. Two hypotheses were postulated following this observation to explain the incorrect quantification.

The first hypothesis is that the partial cross-section obtain from SIGMAK3 for the boron edge might be off due an approximation used the relationship between the dipole oscillator strength and the electron-scattering cross-section that might not stand for low energy edges such as the boron K edge. The second hypothesis is that even though working at 30 keV considerably reduce the risk of knock-on damage, it is well known that lowering the beam voltage generates more radiolysis damage. Doing so, we might damage the material and change its composition with our electron beam.

To validate our hypothesis, experimental measurements of the electron mean free path were done using the EELS zero-loss peak and convergent beam electron diffraction pattern (CBED) (Fig 1d) and was compared with the theoretical mean free path value using the Malis equation[6]. A large variation in the values of the experimental mean free path measurement shown in table 1, which also are far from Malis's value, could be a good indication that our second hypothesis is right and could confirm the presence of radiolysis damage. Furthermore, following the mean free path measurement, holes were observed on the material (Fig 1e) which again points towards our second hypothesis. To confirm that irradiation damage is causing the inaccuracy of our results and hopefully achieved EELS quantification on a beam sensitive material, the same measurements are in progress using a cryo-stage, since it was shown to be effective in restraining radiolysis damage [1], and will be presented at the conference.

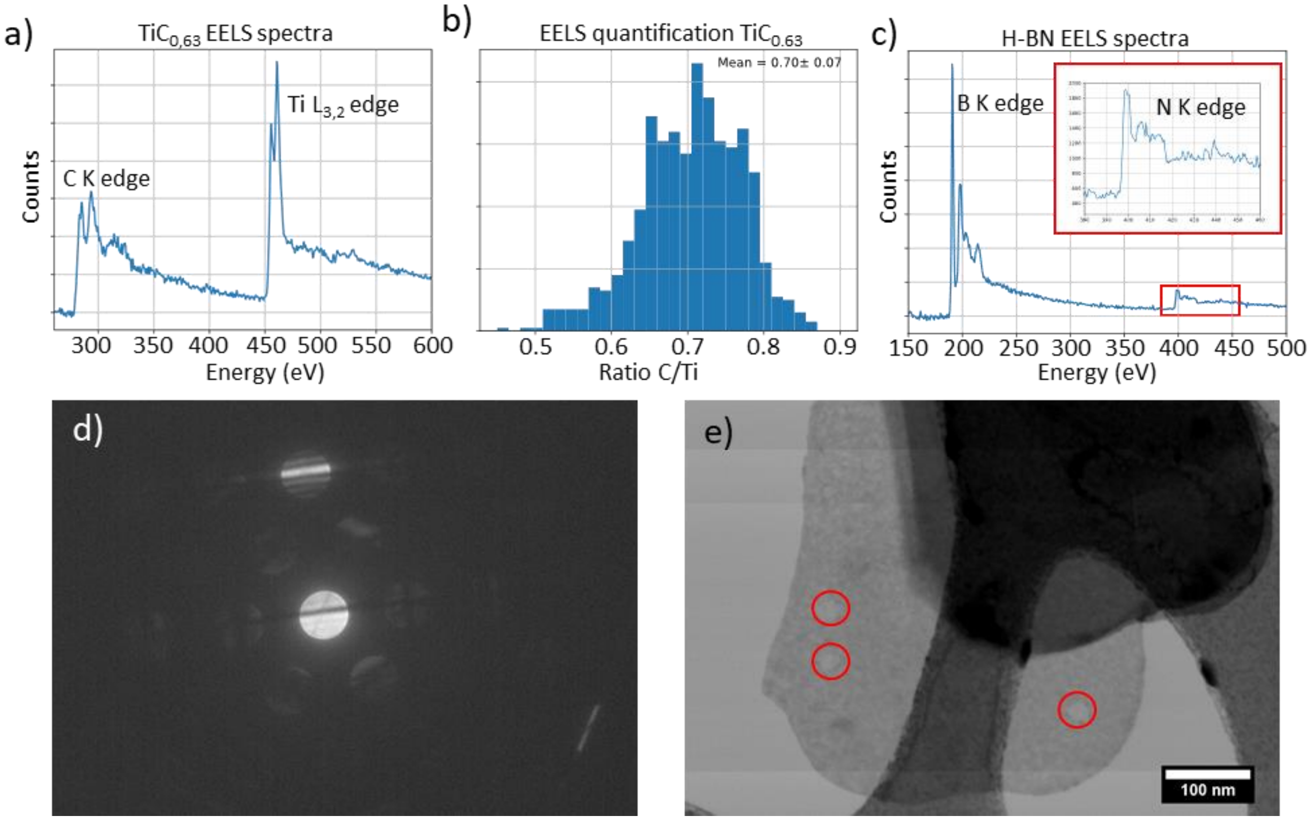


**Figure 1.** a) EELS spectra acquired at 30 keV of the background subtracted carbon K edge and titanium $L_{3,2}$ edge. b) Elemental ratio distribution C/Ti of the 1700 spectra c) EELS spectra acquired at 30 keV of the background subtracted boron K edge and nitrogen K edge d) CBED pattern of h-BN acquired at 30keV. E) h-BN BF images where holes are shown in red circle

https://doi.org/10.1017/S1431927622010327 Published online by Cambridge University Press

| ROI | λ (nm) | Malis Eq. (nm) |
|---|---|---|
| 1 | 158.8 | |
| 2 | 27.1 | 66.39 |
| 3 | 55.3 | |
| 4 | 10.9 | |

**Table 1.** Experimental mean free path measurement comparison with theoretical value

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