doi:10.1017/S1431927622003555
Microsc. Microanal. 28 (Suppl 1), 2022

Detectability & Sensitivity vs Incident Beam Energy in Modern Analytical Electron Microscopes

Nestor J. Zaluzec*

Photon Sciences Directorate, Argonne National Laboratory, Lemont, Il, USA
* Corresponding author: zaluzec@microscopy.com

Modern Analytical Electron Microscopes (AEM's), especially those equipped with aberration correctors can, today, operate routinely at incident beam accelerating voltages between 30 – 300 kV and at extremely high-performance levels [1]. At the same time the new generation of high collection angle x-ray energy dispersive spectrometer (XEDS) detectors based upon silicon drift detector technology (SDD) have provided unprecedented capabilities for x-ray microanalysis and can be interfaced to many of these instruments [2-11]. A paramount question given this range of experimental capabilities becomes: Is there an optimum set of conditions for x-ray microanalysis in the AEM? Generically the answer would be no, as a particular experiment will be dictated by not only the specimen, the spatial resolution desired, the sensitivity of the detection but also any deleterious effects of related to the instruments operating parameters and their affects to the specimen (i.e. contamination and /or beam damage). A detailed analysis of that range of parameters is beyond the scope of any simple study, however, in the absence of deleterious effects we can experimentally determine how the sensitivity of x-ray analysis varies with incident beam energy by a set of measurements on a representative specimen.

To assess this question, experimental measurement of x-ray emission from a uniformly thick amorphous Ge/SiNx standard test specimen [13] has been undertaken in the Analytical PicoProbe/XPAD instrument (the prototype of the ThermoFisher Spectra UltraX) [12] over the operating range of 30-300 kV. While the results of these measurements are specific to this particular instrument, the general principles obtained herein will apply to all instruments, with judicious adjustments due to their varying capabilities. In this work, all measurements were carried out at constant beam current of 100 pA as determined using a faraday cup calibrated beam and identical acquisition live times for each measurement. The integrated Ge signal and corresponding fitted background were both measured over the full width at tenth maximum (FWTM) at the Ge Kα. All data was acquired for 300 detector live seconds and repeated a minimum of four times to confirm reproducibility, as well as to confirm the absence of electron damage. The results of these measurements are plotted in Figure 1. As expected due to the increase in K shell Ionization Cross-section with decreasing incident beam energy the net intensity of the characteristic x-ray emission increases (having a nominal maximum at ~ 2-3 the excitation edge energy) while the Peak/Background (Pk/Bgnd) decreases (as predicted by the changing angular distribution of Bremsstrahlung) [14]. In this figure, the Peak/Background ratios reported are specifically measured using FWTM integration windows, this is due to the large collection solid angle (> 4sR) of the XPAD system. FWTM integration for the background is slightly different to the often used "Fiori" Peak/Background measurements. The Fiori definition, which uses a 10 eV window under the peak, is more suitable for comparison of smaller solid angle detectors [15] and for the XPAD is inappropriate. Throughout the course of the measurements the region of interest on the uniformly thick and flat specimen neither contaminated nor damaged.

Traditionally, the Peak/Background (Pk/Bgnd) ratio is frequently used as a measure of performance and sensitivity of XEDS in an AEM. From figure 1, taken at face value, using Pk/Bgnd alone as a measure of sensitivity would logically force one to conclude that sensitivity decreases with accelerating voltage. While the Pk/Bgnd ratio is indeed a measure of signal *detectability* above background, in the presence of a high background signal, it is not the analytical expression needed to assess either the *minimum detectable mass* (MDM) or the *minimum mass fraction* (MMF) which are measures of *sensitivity* [16]. This is particularly true of the recent generation of XEDS/SDD systems which have novel geometries as well as solid angles which can range from 0.3 to in excess of 4 sR. In figure 1, we see that while the Pk/Bgnd ratio decreases approximately three fold from 300->30 kV, at the same time the absolute signal of the net characteristic Ge x-ray signal (Pk) increases nearly eight fold. Instead of the Pk/Bgnd ratio, the relationship between detectability/sensitivity and Pk & Pk/Bgnd is more appropriately expressed by the relationship [16]:

$$\frac{\Delta P_K}{P_K} = \frac{2.33}{\sqrt{\frac{P_K{}^2}{P_K + Bgnd}}}$$

From this equation, we can see that in the limit of ultra-thin specimen's, such as 2D materials, a situation where the background is near zero then the sensitivity is dominated by the inverse of the signal $(Pk)^{1/2}$. This is clearly demonstrated by the experimental solid curve in Figure 1. At the other extreme, for specimens with appreciable background signal, (i.e. the background is significant) then the inverse product of $(Pk*Pk/Bgnd)^{1/2}$ more applicable. This measure of ΔPk/Pk is plotted in Figure 2. Here one can see that in this non-zero background limit, nearly a factor of two improvement is measured (dashed curve) as the accelerating voltage is decreased, contrary to the conclusion one would draw based solely upon Pk/Bgnd ratios. So, if spatial resolution, which would be limited by probe size and multiple scattering, is not key to the measurement, then reducing the incident beam energy will increase the analytical sensitivity of a measurement, all other things being equal.

Together with an assessment of the spatial resolution afforded by low voltage, aberration corrected AEM's, additional work is in progress to evaluate these results in lower Z and 2D layered materials [17].

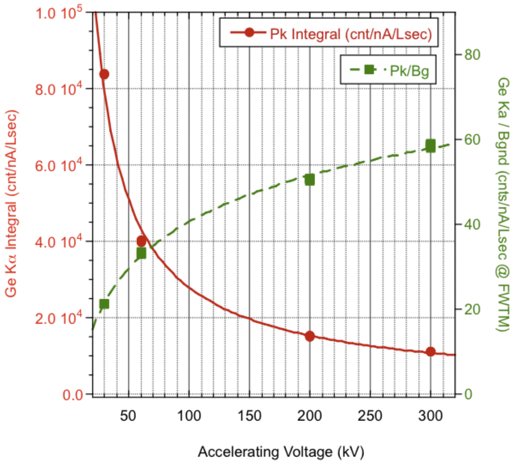

Figure 1. XEDS signal collection for Ge Kα (Integrated FWTM counts/nA-Lsec) from a 20nm ultra-nanocrystalline/amorphous Ge film on 20 nm of SiNx and the corresponding Ge Kα/Background (FWTM) ratio as a function of accelerating voltage. Note the error bars on the reproducibility of the

measurements are smaller than the symbols used to indicate the measurements. The solid and dashed lines are provided to illustrate trends.

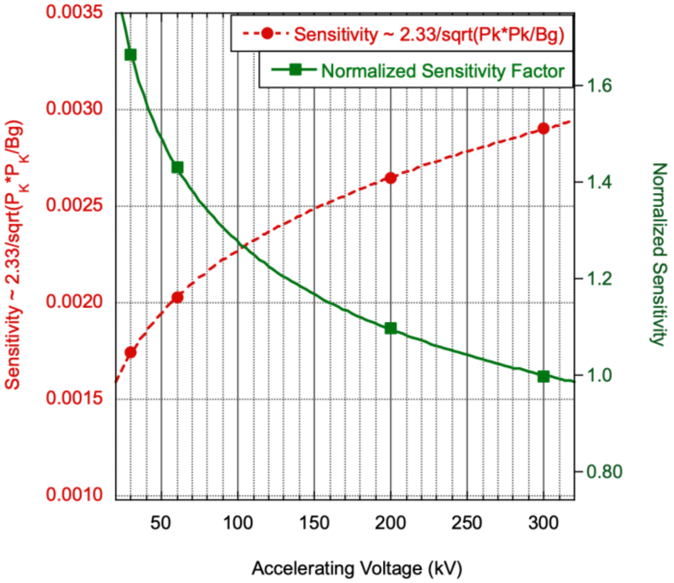

Figure 2. Improvement of the Detection Sensitivity of Ge SiNx as a function of accelerating voltage. Dashed line sensitivity, solid line normalized relative performance (300kV=unity).

References:

[1] See the WWW sites of leading manufacturers of analytical electron microscopes and x-ray systems.
[2] Gatti E., Rehak. P, "Semiconductor Drift Chamber – An Application of a Novel Charge Transport Scheme", Nucl. Instr. & Meth. In Phys. Res. **225** (1984), p. 608.
[3] Chen W. et al., IEEE Trans. on Nucl. Sci. **39** (1992), p. 619.
[4] Iwanczyk J.S. et al., Nucl. Instr. & Meth. in Phys. Res. **A380** (1996), p. 288.
[5] Iwanczyk J.S. et al., Micro. Microanal. **7, S2** (2001), p. 1052.
[6] Barkan S. et al., Microscopy Today **12(6)** (2004), p. 36.
[7] Watanabe, M., Wade, C.A., Microsc Microanal **19**(Suppl 2) (2004), p. 1264.
[8] Tordoff, B. et al., Proceedings of EMC-2012, Manchester, September, (2012), PS2.2.
[9] von Harrach, H.S. et al., Microsc Microanal **15(S2)**, p. 208.
[10] Zaluzec N.J., Micro. Microanal., **10 S2** (2004), p. 122.
[11] Zaluzec, N.J., Microscopy Today 17(4) (2009), p. 56.
[12] Zaluzec, N.J., Microsc. Microanal. **27** (Suppl 1), (2021), p. 2070; doi:10.1017/S1431927621007492
[13] Zaluzec N.J., Microscopy and Microanalysis (2021), p. 1. doi:10.1017/S143192762101360X
[14] Zaluzec N.J., Microsc. Microanal. 22 (2016), p. 230. DOI:10.1017/S1431927615015755
[15] Fiori, C.E. Swyt, CR, Willis JR, "The Theoretical to Characteristic Continuum Ratio in Energy Dispersive Analysis in the Analytical Electron Microscope." Microbeam Analysis-1982, SF Press 57-71 (1982)
[16] Zaluzec N.J., Ultramicroscopy **203** (2019), p. 163.
[17] Acknowledgements; This work was supported by the Photon Science Directorate and Laboratory Directed Research and Development (LDRD) funding from Argonne National Laboratory, provided by the Director, as well as the Office of Science, of the U.S. Department of Energy under Contract No. DE-AC02-06CH11357.