First Light on the Argonne PicoProbe and the X-ray Perimeter Array Detector (XPAD)

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From the late 1960's to the 1990' X-ray Energy Dispersive Spectroscopy (XEDS) in the electron microscope was dominated by the Lithium Drifted Silicon Si(Li) detector [1-4] . For the last two decades these detectors have been slowly displaced by implementations of Silicon Drift Detectors SDDs [5-12]. During this time SDD performance with respect to drift, deadtime, and resolution has continuously improved and they have become routine ancillary x-ray detectors in most new implementations. The early work at Argonne, focused on interfacing SDD's to the Analytical Electron Microscopes (AEMs), the first, a prototype windowless SDD system, was to the ANL HB603Z 300kV instrument. By today's XEDS standards, not only was the use of a SDD novel at that time, it also benefited by the fact our custom SDD had a large active area (50 mm^2) and was relatively thick (1 mm). Both of which improved the solid angle and the high x-ray energy (> 20 keV) detection efficiency. At that time because of its size and proximity to the specimen, the system attained a solid angle ~ 0.45 sR. This was an improvement over the previously installed Si(Li) detector on the HB 603Z which reached ~ 0.3 sR. Since that time, in order to generally improve the geometrical collection efficiency (and thus increase the available signal) various configurations of x-ray detectors have become available which range from single large (60 -> 150 mm^2) to multiple small SDD sensors. In all cases, the objective has been to increase the effective solid angle and thus the measurable signal/nA [10-14], the largest of which to date has been the π steradian detector [15]. Today, a wide range of implementations are commercially available, however, all are constrained by limits imposed by having to engineer around existing technology.

Since 2004, Argonne has been working on designs of linear arrays of SDD's in order to maximize the solid angle as well as mitigate artifacts. Evolving the π steradian detector solution, the X-ray Perimeter Array Detector (XPAD) combined with a custom electron optical pole piece (ZTwin) has improved upon the π steradian detector performance and is operating in the prototype instrument which is located in the Materials Design Laboratory at Argonne. PicoProbe locally achieved *First Light* on December 17th of 2020. In order to provide a specimen independent and reproducible evaluation of XEDS performance we employ a commercially available test specimen which is a 20 nm thick ultra-nanocrystalline Germanium film sputter deposited onto a 20 nm thick SiNx microporous self-supporting 0.5 mm^2 window on 100 µm thick Silicon disc [17]. This flat uniform test specimen has been described previously and allows robust testing and performance assessment of x-ray detectors in all analytical electron microscopes [18].

Figure 1 compares experimental results of the Ge Ka signal (integrated full peak intensity / nA-sec) from that test specimen for three different instruments all operating at 200 kV:

- the Argonne Tecnai F20 with a Single 60 mm^2 SDD
- the Argonne Talos F20x with Quad 30 mm^2 SDD
- the Argonne Analytical PicoProbe with the XPAD

Using the 60 mm^2 detector as a reference base (1x), we have found that the *XPAD* improvement is greater than 20 times the 60 mm^2 SDD system and exceeds the performance metrics of the original π steradian detector, reaching Argonne's design target. Numerically, the performance of those three systems achieve the following representative metrics for a flat untilted Ge/SiNx specimen in optimized specimen holders characterized by the following integrated Ge Kα intensity:

- Single 60 mm2 ~ 600 cnts/nA-sec
- Quad 30 mm2 ~ 2100 cnts/nA-sec
- *Argonne XPAD* ~ 13500 cnt/nA-sec

Due to the increased collection efficiency of the *XPAD*, there is also a corresponding improvement in the minimum detectable mass fraction. Illustrated in Figure 2 are two experimental measurements both done of gold nanoparticles drop cast onto a 20nm thick SiNx support membrane at 80 kV. The solid lower curve was measured using a Quad 30 mm^2 detector system, while the upper dashed line was measured using the *XPAD*. An improvement of an order of magnitude (from ~ 2 $x10^{-3}$ to ~ 2 $x10^{-4}$) has been realized as was predicted [19]. In addition, the functional dependence of the x-ray signal as well as the peak to background with incident beam energy from 30 to 300 keV, as discussed in that earlier work has also been verified.

Judicious design of collimation and shielding minimizes systems peaks, however they are not completely eliminated due in part to the large subtending solid angle. These peaks which result from peripheral scattering events are difficult to completely mitigate due to the optimization of the collection solid angle, however they can be minimized with appropriate design.

Lastly, penumbra effects are paramount in limiting the performance of XEDS detectors in all AEMs, particularly due to the physical constraints imposed by specimen holders and their respective detector configurations which vary in all microscopes. Figure 3 compares the experimentally measured (and appropriately normalized) response of the three configurations when an optimized holder is used with the Ge/SiNx test specimen. Again, the XPAD demonstrates a superior functionality. This substantial improvement in performance with holder tilt, augments the improved solid angle and MMF results and also provides an improvement path for both quantification (by mitigating the need for tilting and thus absorption corrections) as well as enhancing the ability to measure tomographically resolved elemental distributions.

Additional work is in progress to further delineate the performance metrics [20].

References

[1] Fitzgerald R., Keil K. & Heinrich K.F.J. ;(1968). Solid-state energy-dispersion spectrometer for electron-microprobe X-ray analysis. Science 159(3814), 528–530.

[2] Lorimer G.W., Razik N.A. & Cliff G. ; (1973). The use of the analytical electron microscope EMMA-4 to study the solute distribution in thin foils: Some applications to metals and minerals. J Microsc 99, 153–164.

[3] Zaluzec,N.J. ; (1991) Progress on the ANL Advanced AEM Project - Proc. of Microbeam Analysis Society, San Francisco Press, 137

[4] Lyman C.E., Goldstein J.I.,Williams, D.B., Ackland, D.W., von Harrach H.S., Nicholls A.W. , Statham, P.J.; (1994) High-performance X-ray detection in a new analytical electron microscope. J Microsc 176, 85

[5] Gatti E., Rehak. P,; (1984), "Semiconductor Drift Chamber – An Application of a Novel Charge Transport Scheme", Nucl. Instr. And Meth. In Phys. Res. 225 608.

[6] Chen W. , Kraner H. , Li Z., Rehak P., Gatti E., Longni A., Sampietro M., Holl P., Kemmer J., Faschingbauer U., Schmitt B., Woner A. , Wurm J.P., (1992) ;"Large Area Cylindrical Silicon Drift Detector," IEEE Trans. on Nucl. Sci. V39 , 619.

[7] Iwanczyk J.S., Patt B.E., Vilkelis G., Rehn L., Metz J., Hedman B. , Hodgson K.,; (1996) "Simulation and Modeling of a New Silicon Drift Chamber X-ray Detector Design for Synchrotron Radiation Applications", Nucl. Instr. & Meth. in Phys. Res. A380 (1996) 288

[8] Iwanczyk J.S., Patt B.E., Tull C.R., Barkan S., (2001), "High-Throughput, Large Area Silicon X-Ray Detectors For High-Resolution Spectroscopy Applications", Micro. Microanal. 7, S2, 1052.

[9] Barkan S., Saveliev V. D., Iwanczyk J. S., Feng L., Tull C. R., Patt B. E., Newbury D. E., Small J. A., Zaluzec N. J. ; (2004) "New Improved Silicon Multi-Cathode Detector, (SMCD) for Microanalysis" ; Microscopy Today, 12, (6), 36,

[10] Watanabe, M. , Wade, C.A. (2013). “Practical measurement of X-ray detection performance of a large solid-angle silicon drift detector in an aberration-corrected STEM” , Microsc Microanal 19(Suppl 2), 1264

[11] Tordoff, B., Beam, S., Schweitzer, M., Hill, E., Kugler, V. & Png, K. (2012). “Introducing twin X-ray detectors and fast backscattered electron imaging through a new field emission SEM from Carl Zeiss”. Proceedings of EMC-2012, Manchester, September, PS2.2.

[12] von Harrach, H.S., Dona, P., Freitag, B., Soltau, H., Niculae, A. & Rohde, M. (2009). “An integrated silicon drift detector system for FEI Schottkey Field Emission Transmission Electron Microscopes”, Microsc Microanal 15(S2), 208–209.

[13] Zaluzec N.J.; (2004), “XEDS Systems for the Next Generation Analytical Electron Microscope”, Micro. Microanal., 10, S2, 122

[14] Zaluzec, N.J. (2009). “Innovative instrumentation for analysis of nanoparticles: The π steradian detector”. Microscopy Today 17(4), 56.

[15] Argonne National Laboratory. (2010). High collection efficiency X-ray spectrometer system with integrated electron beam stop, electron detector and X-ray detector for use on electron-optical beam lines and microscopes, US Patent 8,314,386,

[16] See the WWW sites of leading manufacturers of electron microscopes and x-ray systems.

[17] http://www.temwindows.com/category_s/55.htm

[18] Zaluzec N.J., Wen J., Wang J. , Miller D.J.; (2016) “ Quantitative Measurements of the Penumbra of XEDS Systems in an AEM “ Microsc. Microanal. 22 (Suppl 3), 278-

[19] Zaluzec N.J. (2019) “Improving the sensitivity of X-ray microanalysis in the analytical electron Microscope*” Ultramicroscopy V203 163*

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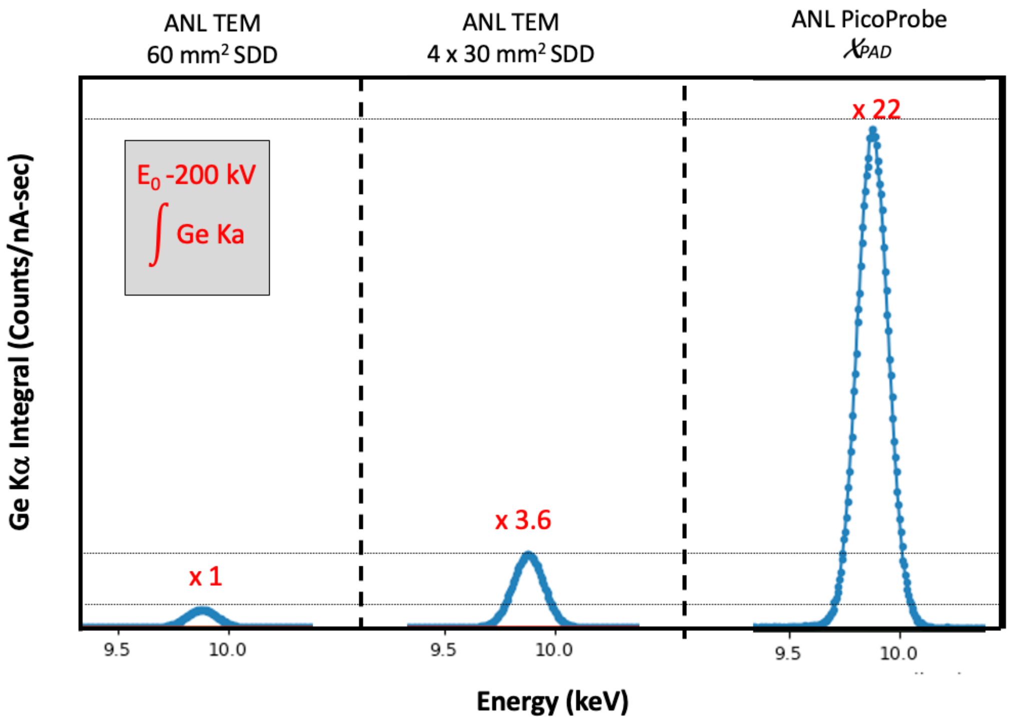

Figure 1 : Normalized performance of XEDS Collection for Ge Ka (Integrated Counts/nA-sec) from a 20nm thick ultra-nanocrystalline Ge film on SiNx for Single, Quad and XPAD systems.

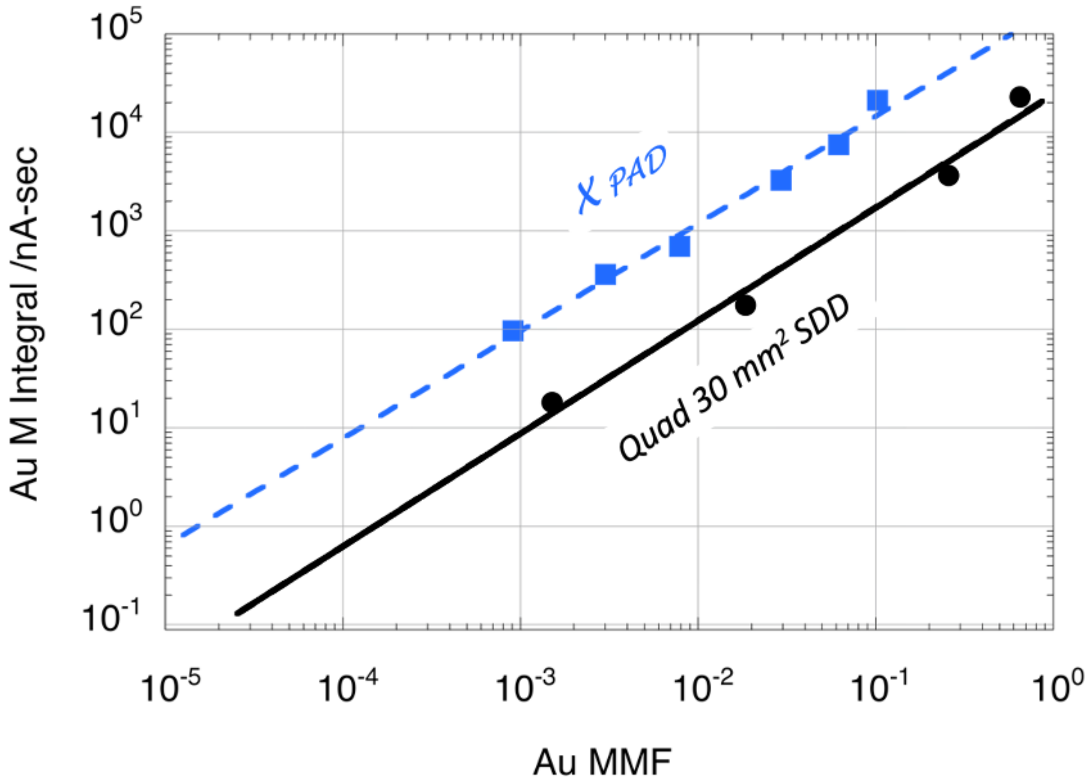

Figure 2: Improvement of MMF of Au nanoparticles on SiNx at 80 kV. Solid line Quad 30 mm^2 SDD, Dashed line XPAD

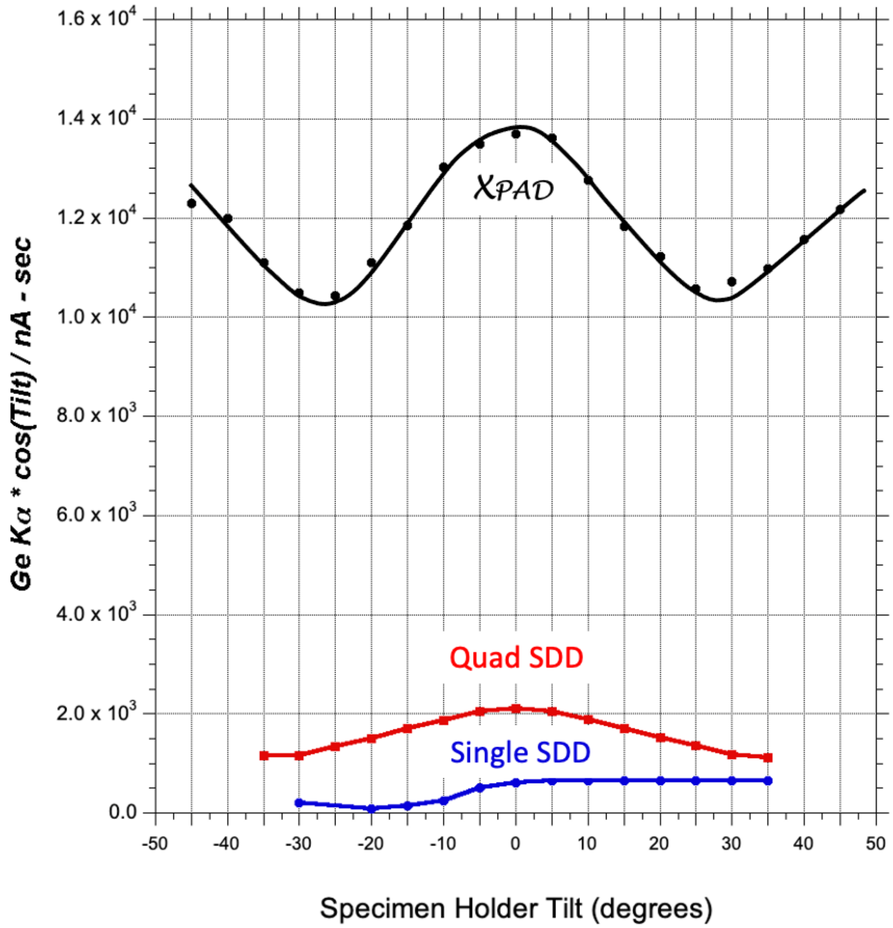

Figure 3. Experimental Penumbra effects as a function of specimen holder tilt for Argonne Instruments: Single 60 mm^2 SDD, Quad 30 mm^2 SDD and XPAD