Chemical Shifts Observed Using Energy Dispersive Spectroscopy

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Chemical Shifts Observed Using Energy Dispersive Spectroscopy

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Chemical shifts, small relocations of atomic energy levels due to bonding, are observed using energy-dispersive x-ray spectroscopy. This widely used photon counting technique has poor energy resolution (more than 10-100 times) compared to the natural broadening in x-ray transitions (typically a few eV or less). However, just as exoplanets are detectable despite insufficient resolving power to separate planet and star, detecting x-ray chemical shifts with energy-dispersive x-ray spectroscopy (EDS) is possible despite the inseparability of the spectrometer's intrinsic linewidth and transition's natural linewidth. The energy of an individual counted photon can be measured with a precision between 30-100 eV; counting millions of photons using a nearly shot noise-limited electron detector chain improves this precision to sub 0.05-0.5 eV. Curve fitting analysis detects chemical shifts between metallic Al, Ti, and W and similarly bonded compounds. Mapping of transition energy chemicals shift are correlated with binding energy chemical shifts acquired by electron energy-loss spectroscopy (EELS), but are generally different in sign and magnitude. X-ray counting spectrometers (widely used in non-destructive testing) can access a wider range of atomic information (especially at higher transition energies) than can other spectroscopic methods. By extending chemical shift measurements to the realm of silicon drift detectors, reaching out beyond 20 keV transitions, it is possible to access shifts from a wide array of bonded elements using more varied sources and samples.

EDS is less expensive than EELS by roughly an order of magnitude and requires no electron optics or associated alignments, making it more accessible than nearly any other spectroscopy. This does not mean EDS is superior to EELS, the latter can access a plethora of effects unobservable with EDS, rather they are complimentary. EDS's high signal-to-background ratio (SBR) even with thick samples and using low accelerating voltages make it suitable for both SEMs and TEMs. At 30 keV beam energy, accessible to SEMs and modern TEMs, EDS can efficiently access (in reasonable time and fluence for mapping) the L line of all naturally occurring elements, which is not the case for EELS. Large solid angle detectors are increasing the collection angles to roughly 1/3 of the total possible 4π [1], making them capable of capturing more photons per incident electron.

Chemical analysis has long been the domain of EELS [2]. EDS is used over a wide range of accelerating voltages, sample thicknesses, and atomic numbers. Through collecting large numbers of counts, EDS chemical shifts can be measured from a variety of compounds with sub-100 meV precision [3]. The increase in precision with increasing number of counts is shown as a series in Figure 1. EDS chemical shifts can be either positive or negative, depending on the specific transition and chemical environment. The spatial resolution of EDS chemical shift mapping, fundamentally limited by the sample dependent x-ray generation volume, ranges from atomic level (sub-Å) to a few nanometers. Chemical shift maps shown in Figure 2, limited by number of counts per unit area under the Al K_α peak (using a single 100 mm^2 detector), have a spatial resolution of about 30 nm. With more counts (larger detectors) this can be improved down to the atomic scale. Comparisons between chemical shift mapping with EELS and EDS are shown in Figure 2b and c. The extension of precision in different detected elements is shown in Figure 2e. State-of-the-art SDDs can collect more than a million counts per second [1]. With such a detector, the minimal number of counts needed for chemical shift detection (10k per peak) can be collected in 100 ms. This opens up new avenues to detect chemical shifts near defects and interfaces that would be inaccessible using other techniques, in particular in thick high-Z materials [5].

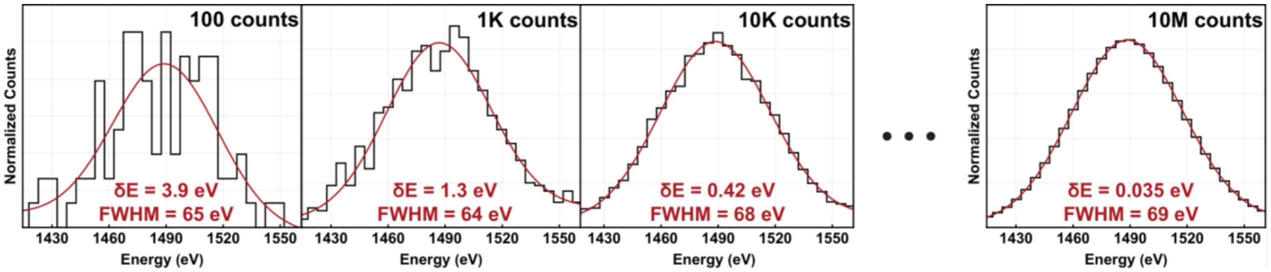

Fig. 1. An example of increasing the counts acquired and the change in precision in an Al K_α line. The natural linewidth is 0.4 eV and its convolution with the full width at half maximum of 70 eV erases identification by direct resolution. The peak's position can be determined with enough precision, after 10^7 counts, to identify chemical shifts and map them.

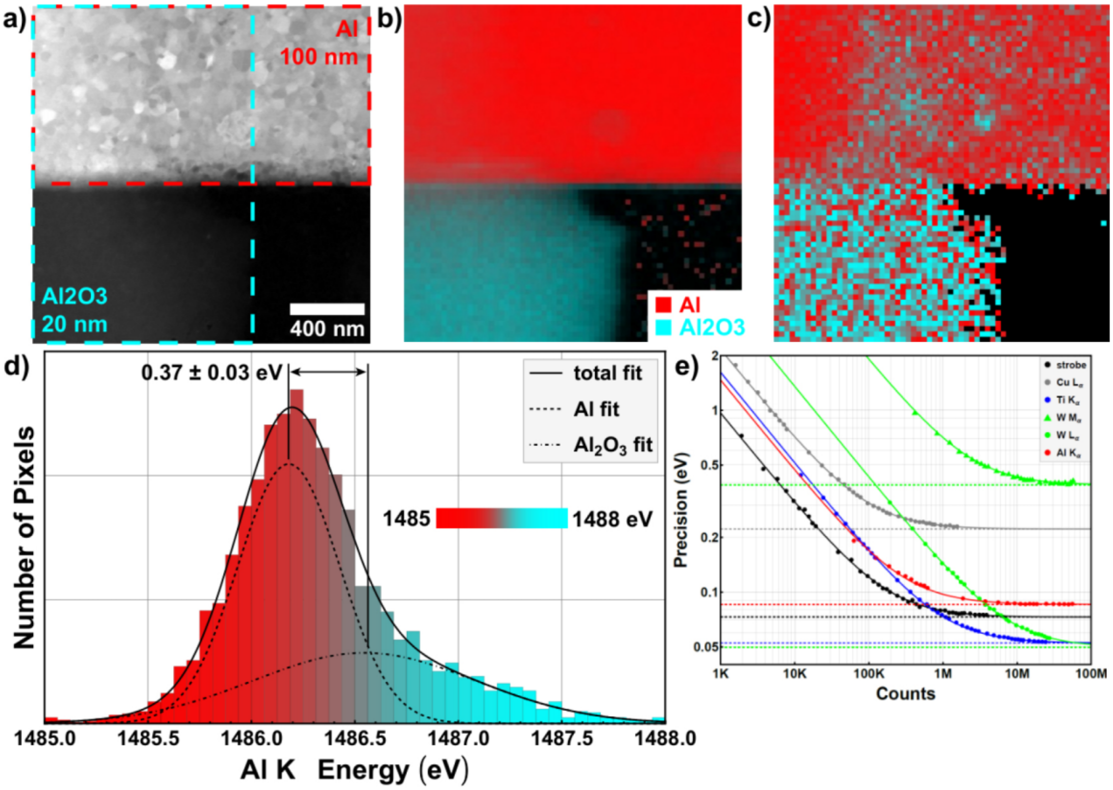

Fig. 2. a) An annular dark field STEM image of the orthogonal overlapping strips of Al and Al_2O_3 atop a 20 nm thick Si_3N_4 membrane. b) EELS chemical shift map showing the ALD deposited oxide next to the metallic region. The surface oxide is visible at the edge of the metal, but the thin layer atop makes it invisible as displayed. c) An EDS chemical shift map of the same region. The SNR is poor because the overlap between the Al and Al_2O_3 peaks is only 0.4 eV, as detailed in d). This chemical shift agrees with that measured by x-rays generated from bombardment with $^4He^+$ ions [4]. e) A comparison of precision in various measured x-ray lines as they vary with counts. With sufficient counts many chemical shifts are accessible.

References

1. Zaluzec NJ. *Microscopy and Microanalysis* (2023) **29** 334-340. https://doi.org/10.1017/S143192762200068X
2. Egerton RF. *Ultramicroscopy* (2007) **107** 575-586. https://doi.org/10.1016/j.ultramic.2006.11.005
3. Chen Y *et al. arXiv* (2024), https://doi.org/10.48550/arXiv.2409.15639, preprint: not peer reviewed.
4. Brukhalter PG *et al. Physical Review A* (1972) **6**. https://doi.org/10.1103/PhysRevA.6.2093
5. The data were acquired at the Core Center of Excellence in Nano Imaging (CNI), University of Southern California. This work was supported by National Science Foundation (NSF) Science and Technology Center (STC) award DMR-1548924 (STROBE) and by NSF award DMR-2004897. The authors acknowledge support from the Electron Imaging Center for Nanosystems (EICN) at the University of California, Los Angeles's California for NanoSystems Institute (CNSI) (RRID:SCR_022900).