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Quantitative Scanning (Transmission) Electron Microscopy:
Pushing the Boundaries of Nanoscale Chemical, Thermal, and Electrical Characterization

A dissertation submitted in partial satisfaction
of the requirements for the degree
Doctor of Philosophy in Physics

by

Yueyun Chen

2026

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ABSTRACT OF THE DISSERTATION

Quantitative Scanning (Transmission) Electron Microscopy:
Pushing the Boundaries of Nanoscale Chemical, Thermal, and Electrical Characterization

by

Yueyun Chen

Doctor of Philosophy in Physics

University of California, Los Angeles, 2026

Professor Brian C. Regan, Chair

As devices are scaled to ever smaller dimensions, their performance becomes increasingly governed by nanoscale heterogeneity in the materials they are made of. Rather than the bulk average, local variations in composition, structure, and electrostatic environment start to dominate the materials' properties. Understanding the behavior, locating the failure point, and predicting the scaling limits of next-generation microelectronic components therefore require quantitative, spatially resolved characterization techniques capable of measuring chemical bonding, temperature, and electrical properties at the relevant length scales. This work advances three such techniques, each leveraging the unique capabilities of scanning (transmission) electron microscopy—STEM and SEM—to push measurement precision and characterization capability beyond what is conventionally considered possible.

First, we demonstrate that energy-dispersive x-ray spectroscopy (EDS), despite its ~ 140 eV energy resolution, can detect sub-eV chemical shifts in transition energies through statistical averaging in the shot-noise-limited regime. Systematic measurements across compounds of tungsten, titanium, and aluminum reveal that EDS chemical shifts can be either positive or

negative—in contrast to EELS binding energy shifts—reflecting the differential perturbation of the two orbitals involved in each transition. We introduce a corrected paralyzable detector model accounting for the finite response time of the event discriminator, which enables accurate dead-time characterization and quantitative evaluation of pile-up artifacts. Built on top of the corrected paralyzable detector model, we develop a post-acquisition pile-up correction algorithm that improves data acquisition throughput by a factor of ten while preserving sub-eV energy precision.

Second, we introduce Kikuchi Diffraction Thermometry (KDTh), a non-contact nanoscale thermometry technique that operates on a standard SEM platform. By expanding the parameter space of cross-correlation-based pattern matching to include lattice constant variations, KDTh achieves $2.2 \text{ K}/\sqrt{\text{Hz}}$ temperature sensitivity and sub-20 nm spatial resolution—comparable to TEM-based techniques and surpassing all existing SEM-based thermometries. Dynamic temperature tracking under both stepped and continuous power ramps on Joule-heated graphite devices demonstrates linear thermal response consistent with Fourier heat conduction theory.

Third, we develop a methodology for predicting ferroelectric memory scalability through *in situ* STEM electron-beam-induced current (EBIC) imaging. An interleaved PUNDp/NDPUn pulse protocol enables pixel-wise hysteresis loop construction and extraction of local coercive and remanent fields across a functioning TiN/HZO/W capacitor. Statistical modeling of the distribution of device averaged polarization allows for predicting the manufacturing yield as a function of operating voltage and capacitor area. The analysis demonstrates that FeRAM cells with sub-1 V operation and sub-50 nm footprints can achieve >99.9% yield with the characterized 5-nm HZO film.

Together, these studies trace an arc from fundamental physical measurements to practical device metrology, forming a general toolkit for quantitative characterization of functional materials with electron microscopy.

The dissertation of Yueyun Chen is approved.

Sarah Tolbert

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HongWen Jiang

Brian C. Regan, Committee Chair

University of California, Los Angeles

2026

I dedicate this to my family.

Shiyun, your kindness and wisdom give me courage to move forward,

I couldn't have done this without you.

To my parents

who inspired my love for math and physics and supported me to pursue my dream,

I couldn't have started this without you.

And to my grandparents

who gave me love when I was young and gave me the strength to journey on.

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CHAPTER 1

Introduction

The relentless drive toward miniaturization in microelectronics has pushed critical device features well below the 100-nm mark. In this regime, the behavior of functional materials is governed less by bulk averages than by local variations in composition, structure, and electrical properties that manifest at the nanometer scale. As device dimensions approach the characteristic size of microstructural features—grain boundaries, domain walls, and interfacial layers—the variance of device performance increases, and techniques capable of characterizing chemical composition, thermal properties, and electrical response at these length scales become essential. Conventional optical and x-ray-based imaging and spectroscopy methods, however, are generally limited to spatial resolutions no better than 0.1 μm , constrained either by diffraction (for visible-light optics) or by severe aberrations arising from the engineering challenges of focusing short-wavelength radiation (for x-ray optics) [1, 2].

Electron microscopes are uniquely positioned to meet these demands. The wavelength of electrons accelerated through typical microscope voltages is on the order of a few picometers—five orders of magnitude smaller than visible light—enabling routine sub-Å spatial resolution [3], three orders of magnitude better than the diffraction limit of optical techniques. Scanning transmission electron microscopy (STEM) and scanning electron microscopy (SEM) are particularly well suited for quantitative analysis. In these instruments, a focused electron probe is rastered across the specimen, and spectroscopic signals, diffraction patterns, and electronic properties can be recorded at each beam position, producing spatially resolved maps in which every pixel preserves quantitative information.

Compared to conventional transmission electron microscopy (TEM), where parallel beam illumination simultaneously excites correlative signals from the entire illuminated area, scanning approaches offer a decisive advantage for correlative studies: they decouple the field of view from the spatial resolution of each measured signal. Because the specimen is excited one pixel at a time, the spatial resolution of correlative signals (such as spectroscopic signals) in a scanned map is determined by the probe size and the beam-specimen interaction volume rather than by the field of view. Each pixel thus represents an independent measurement, yielding spatially resolved chemical, structural, and electronic properties of a nanoscale region that cannot be isolated under parallel-beam illumination.

Equally important is the breadth of correlative signals accessible from a single scanning platform. The same inelastic scattering event can be detected as an energy loss in the primary electron—electron energy loss spectroscopy (EELS)—or as a characteristic x-ray photon—energy-dispersive x-ray spectroscopy (EDS). Elastically scattered electrons carry crystallographic information through diffraction patterns. Beam-generated electron-hole pairs, when separated by internal electric fields, produce a measurable electron-beam-induced current (EBIC) that reports on the local electrostatic environment. STEM and SEM instruments are compatible with *in situ* sample manipulations—electrical biasing, heating, cooling, and mechanical straining—enabling the study of materials under conditions that approximate their operational state. Moreover, the magnification-independent nature of these contrast mechanisms allows micrometer-scale device regions to be surveyed and atomic-scale features to be interrogated within the same experiment, bridging the gap between device-scale behavior and local properties.

The first of these correlative signals—spectroscopy—forms the basis of Chapter 2. EELS and EDS are the most accessible spectroscopic techniques in STEM, and they form a complementary pair, measuring the same inelastic scattering events from fundamentally different perspectives. EELS records the energy lost by the primary electron as it excites a core-level transition. With sub-eV energy resolution, it has long been the technique of choice for

mapping chemical shifts—the small changes in core-electron binding energies that reveal oxidation states and bonding configurations [4, 5]. EDS, by contrast, detects the characteristic x-ray photon emitted when the core hole is filled again. Its energy resolution—typically 30–100 eV for silicon drift detectors—is two orders of magnitude poorer than that of EELS, and it has consequently been regarded as a tool for elemental identification rather than chemical bonding analysis. However, EDS possesses several compensating strengths: it places no strict requirements on sample thickness, it can access transition energies of elements across the entire periodic table with standard accelerating voltages, and its energy axis, being defined electronically rather than optically, is nearly immune to temporal drift.

Extending EDS to chemical shift measurement would therefore open chemical bonding analysis to heavy elements and high-energy transitions that lie far beyond the practical reach of EELS, while simultaneously making the technique available to a much broader user base, as EDS is also a standard detector on SEM platforms. In Chapter 2, we pursue this goal by demonstrating that, in the shot-noise-limited regime, the precision of an EDS peak centroid—as distinct from its resolution—improves as $1/\sqrt{N}$ with accumulated counts, enabling sub-eV chemical shift detection despite a peak width two orders of magnitude larger. We further develop a corrected paralyzable detector model and a post-acquisition pile-up correction algorithm that together increase data throughput by an order of magnitude while preserving this precision, transforming EDS chemical shift mapping from a specialized measurement into a practical routine capability.

Chapter 3 shifts focus from spectroscopic analysis to thermal characterization. Temperature measurement in the electron microscope has been pursued through several modalities, each trading off sensitivity against spatial resolution and accessibility. In the TEM, thermal expansion varies Bragg angles with temperature, providing sub-Kelvin sensitivity [6, 7]. However, the parallel illumination employed restricts the sampling area to beam diameters exceeding 100 nm, precluding point-by-point thermal mapping. In the STEM, where the electron beam can be focused to an atomic-scale probe, plasmon energy expansion thermometry

(PEET) exploits the temperature dependence of the bulk plasmon energy in EELS to simultaneously achieve high temperature sensitivity and high spatial resolution [8]. However, the practical spatial resolution of any thermometry technique is bounded by the phonon mean free path—typically a few to tens of nanometers—below which temperature is no longer a well-defined thermodynamic quantity, rendering the atomic-scale probe unnecessary.

A SEM-based approach, operating at probe sizes comparable to the phonon mean free path, could therefore deliver the highest meaningful spatial resolution for thermal mapping while offering broader accessibility than TEM- or STEM-based alternatives. Prior SEM thermometry efforts using electron backscatter diffraction have been constrained to approximately 100 nm resolution by the large interaction volume of backscattered electrons in bulk specimens and constrained to relatively low temperature sensitivity by their reliance on the Debye-Waller effect or thermal diffuse scattering [9, 10]. In Chapter 3, we introduce Kikuchi Diffraction Thermometry, which circumvents these limitations by collecting forward-scattered electrons from a thin specimen in transmission geometry, improving resolution by more than an order of magnitude while employing cross-correlation-based pattern matching to extract temperature with $2.2 \text{ K}/\sqrt{\text{Hz}}$ sensitivity.

Chapter 4 addresses yet another facet of functional material characterization: the electrical properties. Characterizing the switching behavior of ferroelectric devices presents a distinct challenge because the property of interest is not a static material parameter but a dynamic response to an applied field that varies from one microscopic region to another. Macroscopic electrical measurements—positive-up negative-down (PUND) and first-order reversal curves (FORC)—probe the entire capacitor in parallel and therefore report only ensemble-averaged quantities. A large ferroelectric film with acceptable average remanent polarization may contain minority regions that fail to switch at the operating voltage. When the ferroelectric capacitor is scaled to dimensions approaching the characteristic size of these heterogeneities, device-to-device variability can cause the yield to collapse in ways that no ensemble measurement can predict [11, 12]. Atomic-resolution TEM can image the atomic

displacements that underlie ferroelectricity [13,14], but the field of view is restricted to tens of nanometers and the specimen must be extracted by destructive focused-ion-beam (FIB) milling, severing the connection to the original device’s electrical behavior.

Electron-beam-induced current (EBIC) imaging in the STEM offers a third path: when electron–hole pairs are generated by the beam–specimen interaction, the internal remanent field of a ferroelectric capacitor can separate these pairs to produce a measurable current at the device’s own electrodes. EBIC directly maps the polarization state with both electrodes intact, preserving the mechanical and electrostatic boundary conditions of the functioning device [15]. In Chapter 4, we combine STEM EBIC with an extended PUND switching protocol to construct pixel-wise hysteresis loops across an entire TiN/HZO/W capacitor, and then propagate the resulting spatial distributions of coercive field and remanent polarization through a statistical model to predict manufacturing yield as a function of operating voltage and device area.

Collectively, the studies presented in this work demonstrate that quantitative scanning (transmission) electron microscopy, when combined with rigorous physical modeling and statistical analysis, can deliver chemical, thermal, and electrical information at levels of precision and spatial resolution previously thought to be inaccessible. By pursuing precision beyond resolution in EDS, by expanding the parameter space of diffraction pattern matching for nanoscale thermometry, and by constructing statistical bridges between microscopic heterogeneity and device-scale performance, this work establishes a general methodology for extracting maximal information from beam–specimen interactions. The techniques developed here form a cohesive toolkit for characterizing the functional materials that underpin next-generation microelectronic devices.

CHAPTER 2

Advancing Energy-Dispersive X-ray Spectroscopy for Chemical Shift Analysis

This chapter is based on a published article [16] and a preprint [17].

2.1 Introduction

Elemental identification and chemical bonding analysis constitute two fundamental pillars of materials characterization in electron microscopy. While knowing which elements are present in a specimen is essential, understanding how those elements are chemically bonded provides the deeper insight necessary for correlating structure with function in nanoscale materials and devices. Transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM) can resolve atomic-level defects and interfaces inaccessible to other microscopy methods, and these boundaries contain critical chemical information [4]. X-ray spectroscopies for chemical detection, with energy resolution better than an eV, typically use absorption, emission, or photoelectron measurements and are spatially limited by x-ray sources and optics to micrometer probe sizes or greater [2, 18, 19]. Spatial resolution using x-ray sources often does not surpass diffraction-limited optical microscope resolution [1]. In the far field, only TEM can access elemental and chemical information at the atomic level.

STEM rasters a sub-Ångström sized probe to generate images in parallel with spectroscopic techniques like energy-dispersive x-ray spectroscopy (EDS) and electron energy loss spectroscopy (EELS) [20–23]. This pervasive pair of complementary spectroscopies measures

the same inelastic scattering events from fundamentally different perspectives. EELS measures core electrons' binding energies after a primary electron inelastically scatters from a quantum bound state into a magnetic prism that disperses electrons onto a camera. Combining high spatial and energy resolution, EELS delivers chemical shift mapping across atomically sharp interfaces [4,5]. EDS collects the emitted photon when an electron from a higher shell fills the hole that is created by ejecting a core electron from its bound state via inelastic scattering. EDS has a relatively poor energy resolution compared to EELS—typically 30–100 eV versus 0.01–1 eV—but it can detect a wider variety of elements and operates under less restrictive experimental conditions.

Different x-ray spectrometer technologies have been employed in electron microscopes. Microcalorimeters can achieve sub-10 eV energy resolution [24], but the cryogenic requirement and speed limitation make them currently unsuitable for everyday tasks [25]. Wavelength-dispersive x-ray spectroscopy (WDS) can also achieve sub-10 eV energy resolution [26], but its limited solid angle, serial collection, and moving parts make it ineffective for TEMs. Energy dispersive x-ray spectroscopy (EDS) had used silicon-lithium (SiLi) detectors [27] for years, which are recently replaced by silicon drift detectors (SDDs) [28]. Compared to SiLi detectors, SDDs have smaller collecting capacitors and larger detector areas, granting them higher speeds and larger solid angles. SDDs also do not need to remain at cryogenic temperature, which makes them easier to use. The solid angles of the EDS detectors (SiLi and SDD) have been increasing over time in the past fifty years following approximately exponential trajectories (Fig. 2.1). SDD-based EDS detectors are now widely deployed on TEMs across the world and are widely used by the semiconductor industry. Compared to EELS, EDS instrumentation is less expensive by roughly an order of magnitude and does not require electron optics or associated alignments, making it more accessible and easier to use than nearly any other spectroscopy [23].

Electrons captured in EELS must pass through the sample. To keep the signal-to-background ratio (SBR) high, the electrons should minimally scatter [39, 40]. For heavy

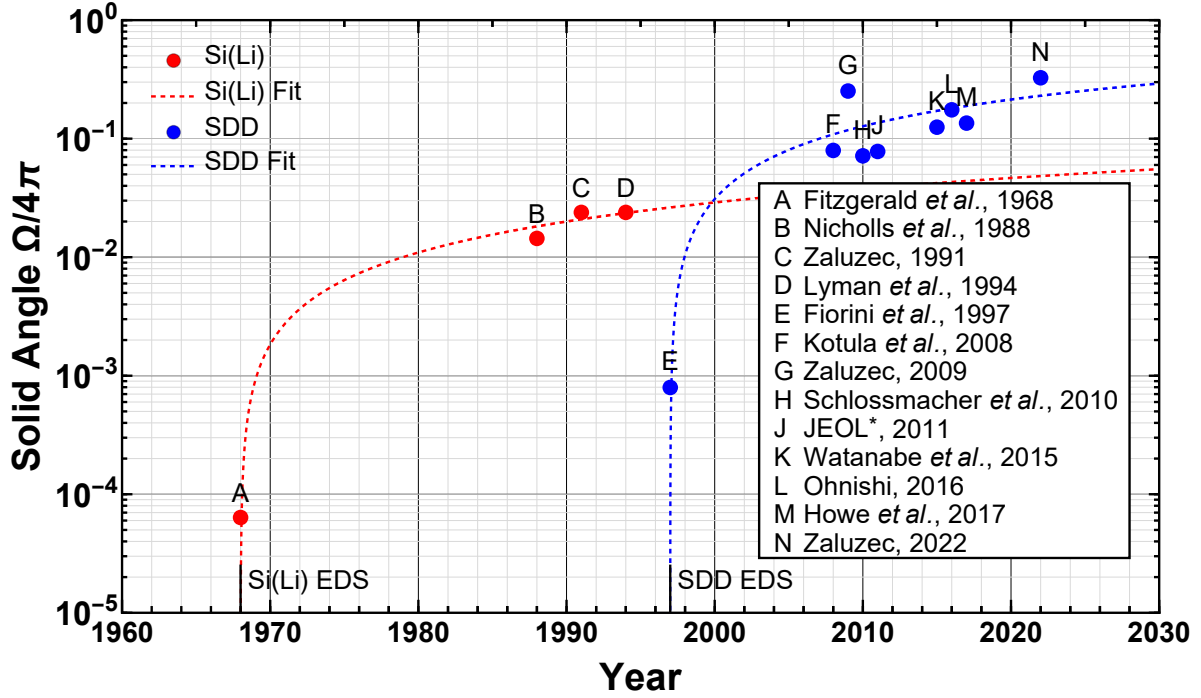


Figure 2.1: **EDS detector evolution.** The progress of x-ray detector's solid angle size over time, and a fit function for past interpolation and future extrapolation [22, 27, 29–38]. Silicon drift detectors (SDDs) have smaller collecting capacitors and larger detector areas. This gives access to faster acquisition speeds and larger solid angles than SiLi detectors.

elements, sharp edges from s and p orbital scattering have high energy losses. For these inelastic events, the primary electrons are usually scattered to relatively high angles and are not commonly captured by EELS. The characteristic scattering angle can be approximated as $\theta_s = \Delta E / 2\gamma KE$, where ΔE is the energy loss, KE is the kinetic energy of the incident electrons, and γ is the relativistic factor. For efficient signal collection, the scattering angles should fall within the optimal range (e.g., <10 mrad) [41]. Therefore, the collection efficiency of EELS drops significantly for a signal with high energy loss (which translates to high characteristic scattering angle). However, what is inaccessible to EELS can be complementarily captured by EDS, where only an overvoltage (beam energy divided by X-ray energy) of two

is needed to excite the transition (Fig. 2.2). EDS’s high SBR, even with thick samples or low accelerating voltages, makes it suitable for both scanning electron microscopes (SEMs) and TEMs [42]. At 30 kV accelerating voltage, which is accessible to both SEMs and TEMs, EDS can already access the L line of all naturally occurring elements, whereas EELS efficiency is roughly restricted to elements below titanium in atomic number.

However, the limited energy resolution of EDS has historically restricted it to elemental analysis. The central premise of this chapter is that insufficient resolution does not translate to insufficient precision. Since SDDs are nearly shot-noise limited, averaging more x-ray events can improve the measurement precision to a point where EDS becomes sensitive to sub-eV chemical shifts—changes in transition energies induced by different chemical bonding environments. By collecting enough counts in the shot-noise-limited regime, better than 100 meV energy precision can be achieved for well-isolated peaks. With enhanced energy precision, EDS can be used for chemical shift measurement on heavy elements and even chemical shift mapping complementary to EELS.

Achieving such precision, however, demands both sufficient total counts and minimal spectral artifacts. High count rates are essential for improving signal-to-noise ratios and for making chemical shift mapping practically feasible, but high input fluxes can lead to pulse pile-up—a phenomenon where multiple x-ray events arrive within the detector’s resolving time and produce spurious spectral features. Contemporary EDS systems employ hardware pile-up rejection, but this rejection system itself has finite response time, leading to imperfect discrimination at high count rates. Understanding and modeling the detector’s behavior under varying count rate conditions is therefore essential for optimizing data throughput while maintaining quantification accuracy.

This chapter presents a comprehensive investigation into advancing EDS for chemical shift analysis, encompassing both the demonstration of sub-eV chemical shift detection across multiple material systems and the development of an improved detector model that enables high-throughput acquisition with minimal artifacts. We first establish the theoretical frame-

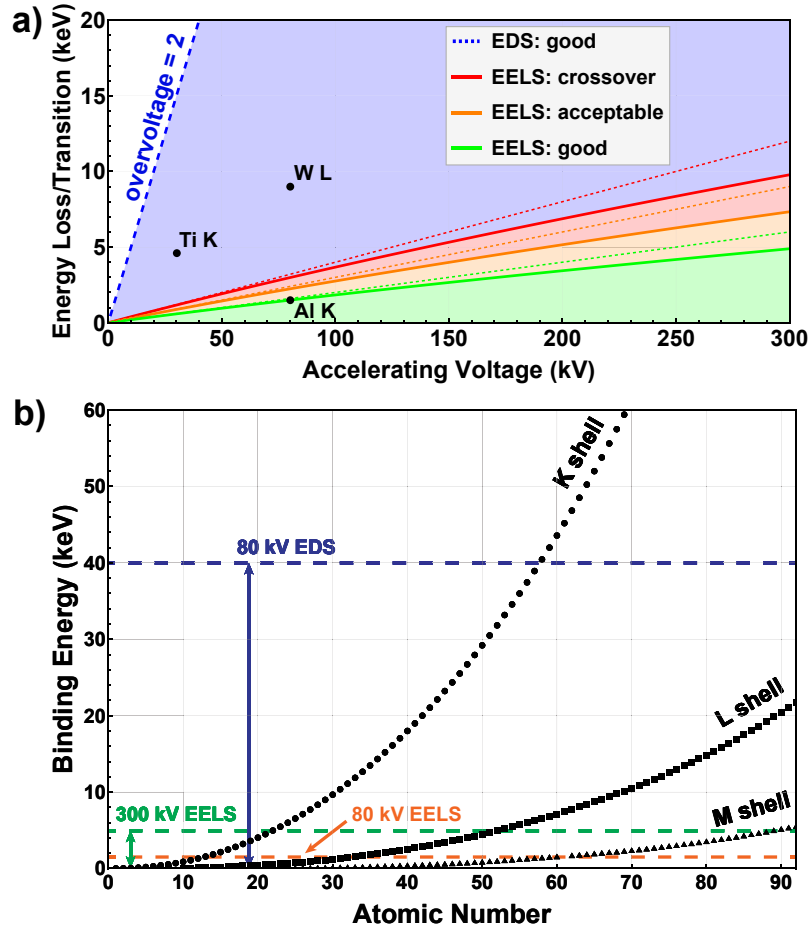


Figure 2.2: **EDS and EELS accessible energy range.** a) EDS and EELS accessible energy range plotted against the electron’s accelerating voltage. EDS peak-to-background ratios and ionization cross sections are good with an overvoltage between 3-5 [43]; 2 is shown as a lower bound. Approximate EELS good (10 mrad), acceptable (15 mrad) and crossover (20 mrad) cases for efficient collection angles are shown for relativistic (solid) and non-relativistic (dashed) cases [41]. b) Core shells of various elements accessible by EDS and EELS. At 80 kV, EDS can already access the L and M shells of all elements and the K shell of most elements; whereas EELS can barely access the L shell of germanium.

work connecting EDS resolution, precision, and the physics of chemical shifts in transition energies. We then demonstrate chemical shift measurements in compounds of tungsten,

titanium, and aluminum, spanning transition energies from 1 to 10 keV and covering parameter spaces inaccessible to EELS. Subsequently, we develop a corrected paralyzable detector model that accounts for the finite response time of the event discriminator, enabling accurate characterization of detector dead time and quantitative prediction of pile-up artifacts. Finally, we implement a post-acquisition pile-up correction algorithm based on this model and demonstrate that it enables an order of magnitude increase in data throughput while maintaining sub-eV peak energy accuracy.

2.2 Theoretical Framework

2.2.1 EDS Energy Resolution and the Detection Chain

The energy resolution of an SDD-based EDS system is fundamentally determined by the combined effects of electronic noise and the statistical fluctuations inherent in the photon-to-charge conversion process. When an x-ray photon is absorbed in the silicon drift detector, it generates electron-hole pairs through ionization. The number of pairs created fluctuates due to correlations in the ionization process, quantified by the Fano factor F [44]. The full width at half maximum (FWHM) of an EDS x-ray peak can be expressed as:

$$\text{FWHM}_{\text{EDS}}(\varepsilon_x) = \sqrt{\left(2\sqrt{2\ln 2} F\varepsilon_x\varepsilon_i\right)^2 + \varepsilon_S^2 + \varepsilon_{LW}^2}, \quad (2.2.1)$$

where $\varepsilon_S \approx 30$ eV denotes the FWHM of the strobe peak (the electronic noise peak), which arises from the electronic noise in the SDD [45], and ε_{LW} denotes the natural line width of the transition energy, which is typically a few eV and too small to contribute meaningfully in quadrature for most transitions. The remaining parameters describe the photon-to-electron-hole-pair conversion: $F \approx 0.12$ is the Fano factor quantifying ionization correlations in silicon [44, 46], ε_x is the x-ray energy, and $\varepsilon_i \approx 3.6$ eV is the silicon ionization energy (the average energy required to create one electron-hole pair with high energy electrons) [47, 48].

The first term under the square root in Eq. 2.2.1 represents the Fano-statistics-limited contribution, which scales as $\sqrt{\varepsilon_x}$. The second term ε_S , the strobe peak FWHM, represents the electronic noise floor that is independent of x-ray energy. The strobe peak width decreases monotonically with increasing processing time (the parameter controlling the pulse shaper time constant). At the longest processing time settings used in this work, $\varepsilon_S \approx 30$ eV provides near-optimal energy resolution, though at the cost of lower maximum throughput due to the longer dead time.

For a tungsten x-ray peak around 8 keV (W L_α), the EDS resolution $\text{FWHM}_{\text{EDS}} \approx 140$ eV. This is approximately two orders of magnitude larger than typical chemical shifts, which are on the order of a few eV or less. Directly resolving chemical shifts at the FWHM level is therefore impossible with SDD-based EDS. However, the resolution limit does not constrain the measurement precision when sufficient statistics are accumulated.

2.2.2 Precision Beyond Resolution: Shot-Noise-Limited Measurements

An isolated peak can be measured more precisely than the FWHM, just as the error in the mean of a distribution decreases as more samples are averaged. As the number of counts N in a peak increases, curve fitting improves the precision of the centroid determination in a nonlinear fashion. In the shot-noise-limited regime, the uncertainty carried by individual x-ray measurements disturbs the curve fitting and limits the achievable precision. As N increases, the precision improves proportional to $1/\sqrt{N}$, governed by Poisson statistics.

The energy precision as a function of counts can be expressed as:

$$\sigma_{\text{precision}} = \sqrt{\left(\frac{\sigma_p}{\sqrt{N}}\right)^2 + \sigma_0^2}, \quad (2.2.2)$$

where σ_p represents the Poisson noise contribution from a single x-ray event and σ_0 represents the asymptotic precision limit. The single-event uncertainty σ_p is closely related to the FWHM through the empirical relationship $\sigma_p \approx \text{FWHM}/\sqrt{2 \ln 2}$. Because of fluctuations

in the ionization process, photons with the same energy do not always generate the same number of charges [44], leading to an x-ray energy-dependent σ_p whose contribution to total uncertainty can be reduced by collecting more events [49, 50].

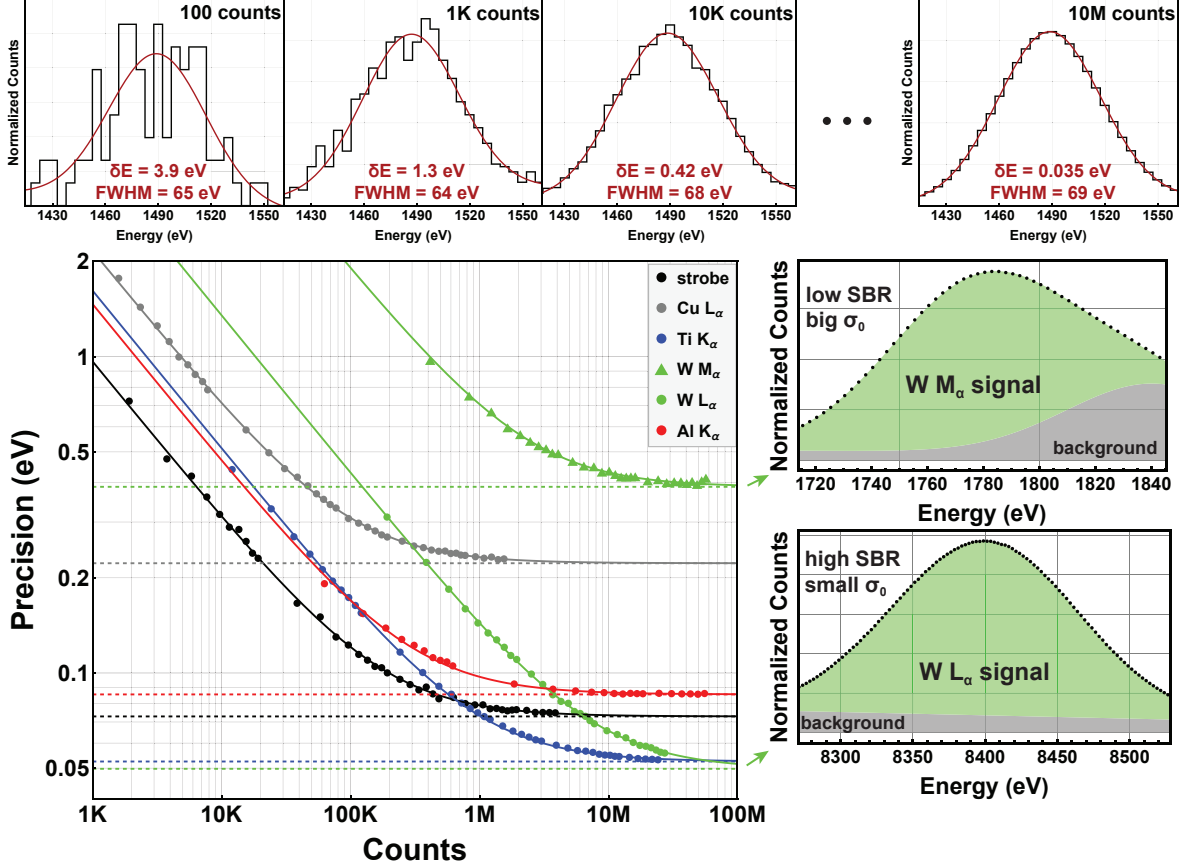


Figure 2.3: **EDS energy precision versus counts.** As more x-ray events are collected, the Poisson noise is reduced, and the peak center can be determined more precisely. The x-ray peak energy precision (fit error in the mean) as a function of the number of x-ray counts detected is plotted for various elements and lines. Peaks with a higher SBR tend to have a lower precision limit.

The precision-versus-counts relationship (Eq. 2.2.2) was validated across multiple elements and transitions spanning 1 to 10 keV (Fig. 2.3). In all cases, the precision improves with $1/\sqrt{N}$ at low counts before approaching the asymptotic limit σ_0 at high counts. Differ-

ent transitions exhibit different asymptotic limits, with the achievable precision negatively correlated with the SBR of the peak (Fig. 2.4). For well-isolated peaks with high SBR (such as W L_α at high energy where Bremsstrahlung background is minimal), sub-100 meV precision is achievable with sufficient counting statistics ($N > 10^5$). Peaks in crowded, low-energy spectral regions with substantial Bremsstrahlung background exhibit higher σ_0 values.

The SBR is found to semi-quantitatively correlate with both the asymptotic precision limit σ_0 and the agreement between the fitted peak standard deviation and the FWHM-derived value. A better SBR leads to a lower precision limit (smaller σ_0) and a better agreement with the standard deviation of the peak energy derived from the Gaussian FWHM. The single-event Poisson noise σ_p , normalized by the ratio to the standard deviation derived from the Gaussian FWHM, can exceed unity when a background model is included in the nonlinear fit, as this leads to a larger error estimation for the signal model parameters.

X-ray events in STEM are rare—approximately one x-ray photon is generated per ten thousand beam electrons [51]—but in solid-state detectors, collecting millions of counts is routine. With enhanced energy precision through statistical averaging, EDS can detect chemical shifts on the order of 0.1 eV for well-isolated peaks, which is approximately three orders of magnitude better than the FWHM resolution.

2.2.3 Accuracy versus Precision in Energy Measurement

A critical distinction must be drawn between the accuracy of absolute x-ray energy determination and the precision of measuring energy differences between two spectra. This distinction explains why EDS can measure sub-eV chemical shifts despite having eV-level absolute energy calibration uncertainty.

Pulses from the charge-sensing amplifier are sorted in a multi-channel analyzer (MCA). Each channel has an energy width set before data collection, and the lowest energies are offset to enable detection of the strobe peak, which defines the zero-energy reference. The

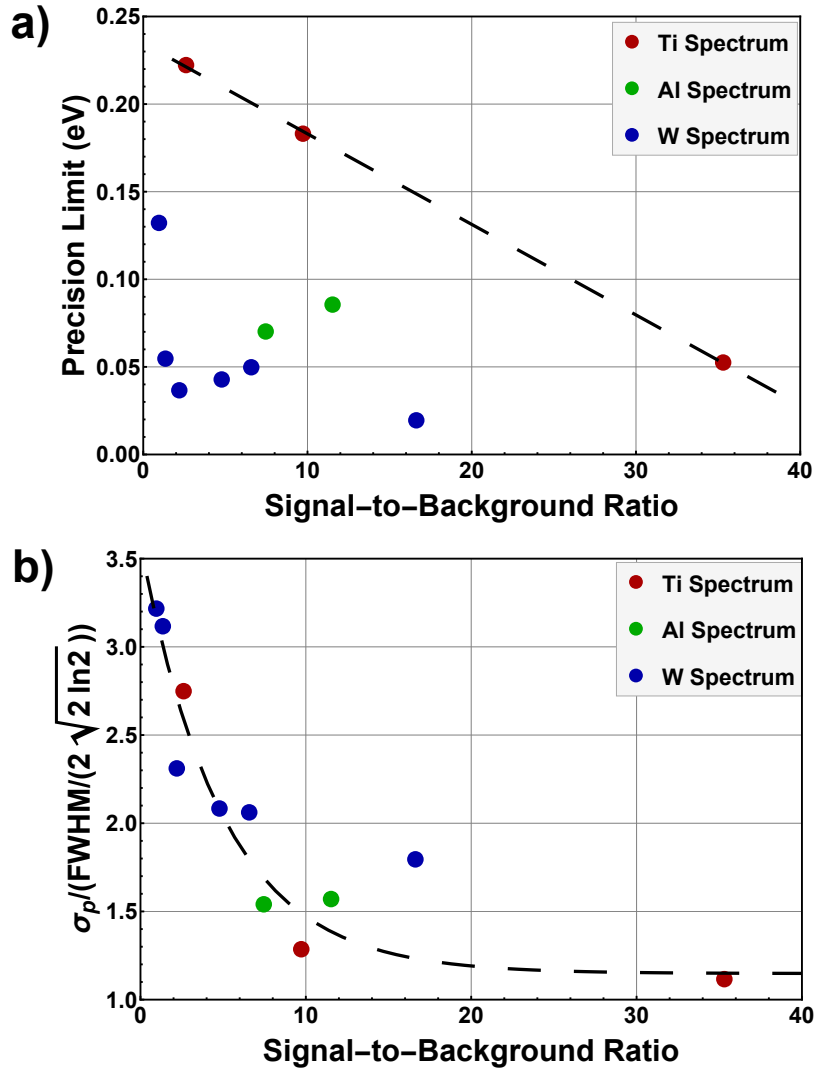


Figure 2.4: **EDS signal-to-background ratio.** The precision limit (in eV) and the normalized σ_p peak standard deviation ratio are plotted as a function of the signal-to-background ratio (SBR). Semi-quantitative correlations are given by the dashed lines in the plot. Although the exact relationship between these quantities is not given, the correlation is clear: a better SBR leads to a better precision limit and better agreement with the peak standard deviation.

x-ray energy is measured from the strobe peak to the fluorescence peak, center to center. The spanned channels are multiplied by a calibration factor D (in eV/channel, analogous to the dispersion in an electron energy-loss spectrometer). For a fluorescence peak at channel N_x and the strobe peak at channel N_s , the absolute x-ray energy is $\Delta E_{\text{accuracy}} = D(N_x - N_s)$. The error in this absolute determination is:

$$\delta \Delta E_{\text{accuracy}} = D \sqrt{\left(\frac{\delta D}{D}\right)^2 (N_x - N_s)^2 + \delta N_x^2 + \delta N_s^2}, \quad (2.2.3)$$

where $\delta D/D$ is the fractional error in the calibration factor (typically < 0.005 based on calibration fits). Although $\delta D/D$ is small in relative terms, it is multiplied by the large channel span $N_x - N_s$, making it the dominant term that limits absolute energy accuracy to approximately an eV or so.

However, chemical shift measurements do not require absolute energy accuracy—they only require precision in comparing two measurements of the same peak. For two measurements A and B (e.g., metal and oxide), the energy difference is:

$$\Delta E_{\text{precision}} = D(N_{x_A} - N_s) - D(N_{x_B} - N_s) = D(N_{x_A} - N_{x_B}). \quad (2.2.4)$$

The strobe peak position cancels, as does its associated uncertainty. The error in this relative measurement becomes:

$$\delta \Delta E_{\text{precision}} = D \sqrt{\left(\frac{\delta D}{D}\right)^2 (N_{x_A} - N_{x_B})^2 + \delta N_{x_A}^2 + \delta N_{x_B}^2} \approx D \sqrt{\delta N_{x_A}^2 + \delta N_{x_B}^2} \approx \sqrt{2} D \delta N_x. \quad (2.2.5)$$

The previously limiting $\delta D/D$ term is now negligible because the shift's span in channels is small, typically less than one channel. The precision error is therefore limited only by the error in the curve-fit peak centers. In this work, the spectrum offset is calibrated using a background peak with known energy for each dataset: Si K_α for Al, the strobe peak for

Ti, and Cu K_α for W. The offset peaks are selected based on SNR and proximity to the peaks of interest for maximum measurement accuracy. This cancellation of the dispersion uncertainty and reference peak energy uncertainty is the fundamental reason that EDS can achieve sub-eV precision in chemical shift measurements despite having eV-level absolute calibration uncertainty.

2.2.4 Chemical Shifts in Transition versus Binding Energies

Chemical shifts manifest differently in EDS and EELS due to the fundamental difference in what each technique measures. EELS measures the absolute binding energy of core electrons: as an atom forms more bonds, the energies of core electrons are further minimized, resulting in universally higher binding energies relative to the pure metal [52]. Consequently, EELS chemical shifts in binding energies are always positive for metal elements compared to their pure metallic state [53].

EDS, in contrast, measures the energy difference between two electron orbits—the transition energy. Whether the chemical shift in a given transition is positive or negative depends on which electron’s energy is minimized more when forming a new chemical bond. If the energy of the electron in the lower orbital is minimized more strongly than that of the higher orbital, the EDS chemical shift is positive; if the higher orbital is more strongly affected, the shift is negative.

The physical origin of chemical shifts involves several competing effects [54, 55]. A decrease in the valence electron density can decrease the Fermi energy, producing a negative chemical shift (smaller magnitude binding energy) [2]. In contrast, opening a band gap can increase the lowest unoccupied level relative to the core state, creating an increased chemical shift (larger magnitude binding energy). When a metal and oxide are brought together, electrons in the valence band move from the metal to the oxide [4], increasing the charge density in the oxide and causing the outer electrons to be less effectively screened, which in turn pulls all electrons closer to the nucleus and thereby increases the binding energy. There are

other smaller effects such as the core-hole being effectively repulsed by the screened nuclear potential leading to a small negative chemical shift (the relaxation case) [40]. Transitions between different atomic orbitals are further complicated because the two energy levels may shift in different directions; when examining changes in transitions rather than binding energies, one must recognize that the sign of the chemical shift can change because the orbitals involved can move independently.

Thus, unlike EELS where chemical shifts are universally positive for metals, EDS chemical shifts in transition energies can be either positive or negative, as has been observed in x-ray spectroscopy studies spanning decades [2, 19, 56–60]. This bidirectional nature provides complementary chemical information: the sign and magnitude of the transition energy shift reflect the relative perturbation of the two orbitals involved, offering insight into the differential effects of chemical bonding on different electron shells. When paired with EELS measurements of binding energies, EDS transition energy measurements can be used to determine binding energies of shells not directly accessible by either technique alone.

An important practical consideration is that existing tabulated binding energies cannot be used to predict EDS chemical shifts. Table 2.1 compares the binding energy differences calculated from tabulated values [61] with directly measured x-ray transition energies [62]. Although these values agree to approximately eV level, the remaining discrepancies at sub-eV level are comparable in magnitude to the chemical shifts we seek to measure. This variation arises because the binding energy measurements and x-ray energy measurements were performed on different specimens under different conditions, each with their own systematic uncertainties. Consequently, chemical shifts in transition energies must be measured directly rather than inferred from tabulated binding energies.

Transition	Initial Binding (eV)	Final Binding (eV)	Δ Binding (eV)	X-ray (eV)
Al K $_{\alpha_1}$	73.1 ± 0.5	1559.6 ± 0.4	1486.5	1486.70
Al K $_{\alpha_2}$	73.1 ± 0.5	1559.6 ± 0.4	1486.5	1486.27
Ti K $_{\alpha_1}$	455.5 ± 0.4	4966.4 ± 0.4	4510.9	4510.84
Ti K $_{\alpha_2}$	461.5 ± 0.4	4966.4 ± 0.4	4504.9	4504.86
Ti K $_{\beta_{1,3}}$	34.6 ± 0.4	4966.4 ± 0.4	4931.8	4931.81
W M $_{\alpha_1}$	33.6 ± 0.4	1809.2 ± 0.3	1775.6	1775.4
W M $_{\alpha_2}$	36.5 ± 0.4	1809.2 ± 0.3	1772.7	1773.1
W M $_{\beta}$	36.5 ± 0.4	1871.6 ± 0.3	1835.1	1834.9
W L $_{\alpha_1}$	1809.2 ± 0.3	10206.8 ± 0.3	8397.6	8397.6
W L $_{\alpha_2}$	1871.6 ± 0.3	10206.8 ± 0.3	8335.2	8335.2
W M $_{\zeta_1}$	425.3 ± 0.5	1809.2 ± 0.3	1383.9	1383.5
W M $_{\zeta_2}$	491.6 ± 0.4	1871.6 ± 0.3	1380.0	1378.7

Table 2.1: **Comparison of EELS binding energies and EDS transition energies.** Binding energies from Bearden [61] and measured x-ray energies from Bearden [62]. The binding energy differences and measured x-ray values agree to approximately four digits but vary in the remaining precision by amounts sizable compared to EDS chemical shifts. This variation explains why existing measurements of binding energy differences cannot be used to predict x-ray chemical shifts; direct measurement of transition energies is required. Notation differences between Siegbahn, IUPAC, and atomic conventions are tabulated in Table. 2.2.

Element	Siegbahn	IUPAC (f-i)	Atomic (i-f)
Al	K_{α_1}	K-L _{III}	$2p^{3/2} \rightarrow 1s^{1/2}$
Al	K_{α_2}	K-L _{II}	$2p^{1/2} \rightarrow 1s^{1/2}$
Ti	K_{α_1}	K-L _{III}	$2p^{3/2} \rightarrow 1s^{1/2}$
Ti	K_{α_2}	K-L _{II}	$2p^{1/2} \rightarrow 1s^{1/2}$
Ti	$K_{\beta_{1,3}}$	K-M _{II,III}	$3p^{1/2,3/2} \rightarrow 1s^{1/2}$
W	M_{α_1}	M _V -N _{VII}	$4f^{7/2} \rightarrow 3d^{5/2}$
W	M_{α_2}	M _V -N _{VI}	$4f^{5/2} \rightarrow 3d^{5/2}$
W	M_{β}	M _{IV} -N _{VI}	$4f^{5/2} \rightarrow 3d^{3/2}$
W	L_{α_1}	L _{III} -M _V	$3d^{5/2} \rightarrow 2p^{3/2}$
W	L_{α_2}	L _{III} -M _{IV}	$3d^{3/2} \rightarrow 2p^{3/2}$
W	M_{ζ_1}	M _V -N _{III}	$4p^{3/2} \rightarrow 3d^{5/2}$
W	M_{ζ_2}	M _{IV} -N _{II}	$4p^{1/2} \rightarrow 3d^{3/2}$

Table 2.2: **Notation differences in EDS transitions.**

2.3 Experimental Methodology

2.3.1 Sample Preparation

To demonstrate EDS chemical shift detection across a range of elements and transition energies, three material systems were selected: tungsten (W), titanium (Ti), and aluminum (Al). These systems span a wide range of atomic numbers (13–74), transition energies (1–10 keV), and chemical bonding environments while covering parameter spaces both accessible and inaccessible to EELS.

Tungsten and titanium samples are prepared using commercially available nanoparticles from SkySpring Nanomaterials, with detailed information shown in Table 2.3. Each type of nanoparticle is deposited onto a 3 mm TEM grid with a 20 nm-thick carbon membrane using standard drop-casting methods. Approximately 10 mg of nanoparticles are suspended in 1 mL of isopropyl alcohol, sonicated for 15 minutes, and centrifuged with an Eppendorf Centrifuge 5417C. For each type of nanoparticle, 2 μ L of suspension from just above the precipitate is transferred to a TEM grid and dried. Considering impurities introduced during manufacturing and contact with air—particularly for W and Ti metal nanoparticles—each nanoparticle type is analyzed with hyperspectral EDS imaging to identify chemically homogeneous regions appropriate for chemical shift measurements.

The aluminum sample is fabricated on a silicon substrate using microfabrication techniques [63]. The silicon substrate is 200 μ m thick with an 800 nm-thick silicon dioxide film and a 25 nm-thick silicon nitride (SiN_x) film on each side. SiN_x on the backside is patterned with photolithography and removed with reactive-ion etching (RIE) to define electron-transparent windows. KOH wet etch and HF vapor etch are used to remove the silicon and silicon dioxide in the patterned region, leaving only the top SiN_x layer as the membrane for the electron-transparent window. The patterns of aluminum and aluminum oxide are defined with photolithography. A 100 nm aluminum film was deposited using electron-beam evaporation (CHA Mark 40) on the SiN_x membrane, and a 20 nm-thick alu-

Product Number	Material	Diameter (nm)	Centrifuge Condition
1123XH	Ti	40–60	2500 RPM for 20 min
7945HK	TiN	20	1000 RPM for 1 min
7920DL	TiO ₂	10–30	100 RPM for 10 s
9821XH	W	80–100	800 RPM for 20 min
8005DX	WC	80	800 RPM for 20 min
8010CN	WO ₃	<100	500 RPM for 2 min

Table 2.3: **Nanoparticle sample preparation parameters.** Commercially available nanoparticles (SkySpring Nanomaterials) used for W and Ti chemical shift measurements, along with their preparation conditions including suspension, sonication, and centrifugation parameters.

minum oxide film is deposited using atomic layer deposition (ALD, Ultratech Fiji Thermal and Plasma ALD System). There is a region on the electron-transparent window where the Al and Al₂O₃ films overlap.

2.3.2 Instrumentation and Data Acquisition

EDS data are collected on multiple instrument platforms to cover different beam energies and detectors. Tungsten measurements are performed at 80 kV accelerating voltage using an FEI Titan 80-300 TEM equipped with an Oxford X-MaxN 100TLE 100 mm² SDD detector. Titanium measurements are performed at 30 kV using a TFS Spectra Ultra S/TEM equipped with a TFS Ultra-X EDS detector. Aluminum EDS measurements are performed at 80 kV on the same Titan 80-300 platform. For comparison of EDS quantification with EELS in Al, an EELS spectrum image is collected in the same region at 200 kV using a JEOL 2100F with a Quantum Gatan Imaging Filter (GIF).

EDS spectrum images—where a full EDS spectrum is acquired at each scan point in a

raster pattern—are collected for Ti and Al specimens. For W specimens, single spectra are acquired in highlighted regions of interest (ROIs) or across the entire field of view (FOV). The spectrometer bin size and detector processing time are optimized to provide the best energy precision for each measurement. The longest available processing times are used in nearly all acquisitions to ensure the best energy resolution, as the strobe peak FWHM decreases monotonically with increasing process time.

Due to the detection chain’s finite dead time, there is a maximum rate of x-ray detection achievable for a given process time setting. The optimal counting dead time for an ideal paralyzable detector is $D_{\%} \approx 63\%$, corresponding to the maximum of Eq. 2.5.2. The probe size, sample thickness, specific transition, processing time, and beam current all determine the number of x-rays emitted per incident electron. This value is most easily set experimentally from the beam current, which then controls the number of x-rays entering the detector chain and sets the output count rate. For high-precision chemical shift measurements requiring minimal pile-up artifacts, lower input fluxes are used with the longest available processing time to ensure the best energy resolution. The FWHM expression (Eq. 2.2.1) is at or near the ideal processing time set by the spectrometer settings under these conditions.

2.3.3 Spectrum Processing and Curve Fitting

X-ray peak energies are determined through nonlinear least-squares curve fitting. Each peak is fitted with a Gaussian function on top of a linear background:

$$I(E) = A \exp \left[-\frac{(E - E_0)^2}{2\sigma^2} \right] + mE + b, \quad (2.3.1)$$

where $I(E)$ is the intensity at energy E , A is the peak amplitude, E_0 is the peak centroid (the measured transition energy), σ is the peak standard deviation related to the FWHM by $\text{FWHM} = 2\sqrt{2 \ln 2} \sigma$, and m and b describe the linear background.

For precision analysis, spectra are randomly subsampled to varying count totals to gen-

erate the precision-versus-counts curves described by Eq. 2.2.2. The centroid uncertainty $\sigma_{\text{precision}}$ is taken as the fit error in the mean position E_0 . The spectrometer channel dispersion (eV/channel) and energy offset are calibrated using known reference peaks for each dataset. For Al, the Si K_α peak from the substrate is used as a calibration reference. For Ti, the strobe peak served as the energy reference. For W, the Cu K_α peak from the microscope background is employed. The calibrated bin sizes agree with manufacturer presets (5 eV, 2 eV, 5 eV for Al, Ti, W datasets, respectively) to better than 1%. Each spectrum is offset by the manufacturer to include the full dispersion of the strobe peak, which can be useful for determining the energy offset. However, the strobe peak is not always used for energy offset determination because of detector-specific background noise in the low-energy regime; background peaks closer to the peaks of interest are preferred for determining the offset (Fig. 2.5).

Stoichiometry determination follows the Cliff-Lorimer method [42, 64], using the integrated intensities of relevant peaks with theoretically calculated k -factors. Assuming oxygen adopts its most common valence of -2 , the averaged valence of the metal element was calculated from the measured oxygen-to-metal ratio. For tungsten carbide (WC), the carbon support membrane made independent valence measurement infeasible; the manufacturer’s stated 99.95% purity was used to assign a nominal valence of $+4$. The determined chemical composition of various samples used in this study is shown in Fig. 2.6.

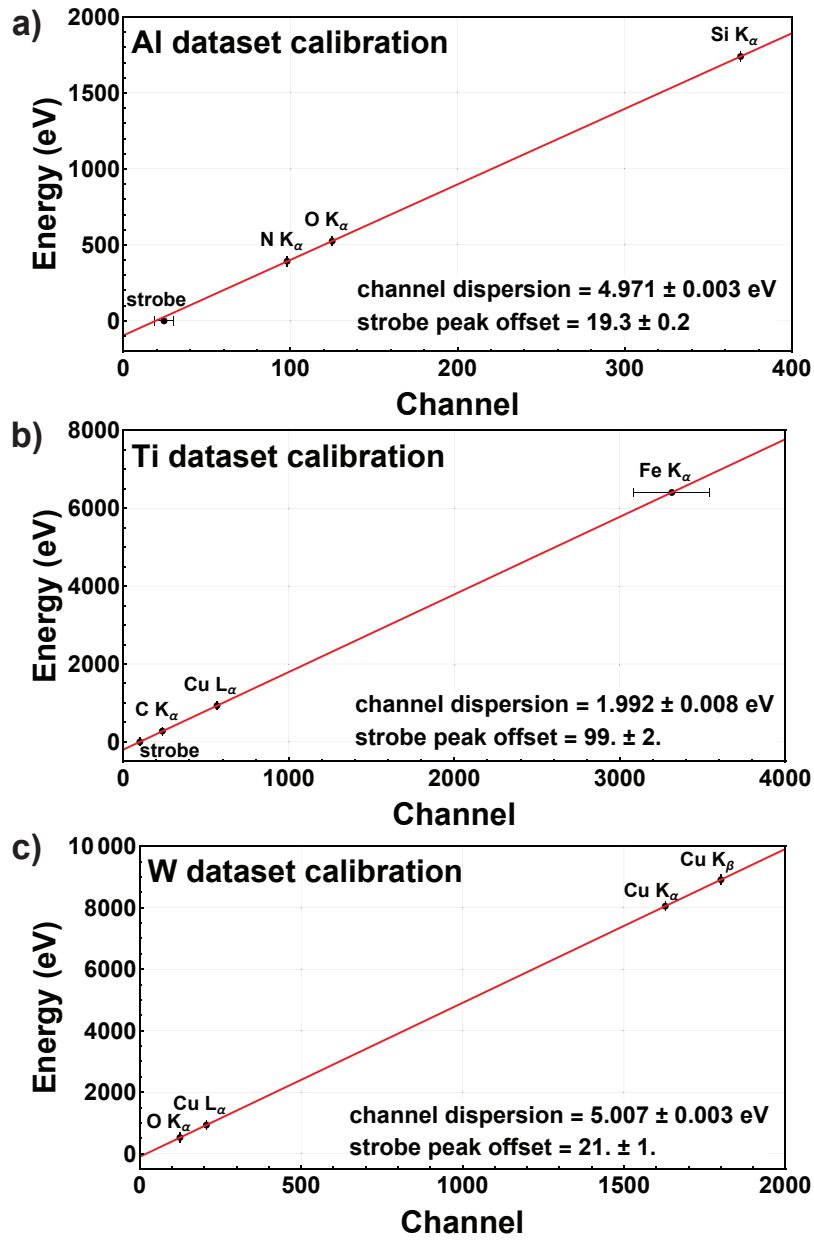


Figure 2.5: **Spectrometer calibration.** Precise determination of the spectrometer channel size is necessary for accurately determining the x-ray energy. The bin size in each case is calibrated from background elements that are either uniformly distributed on the sample or from the microscope background.

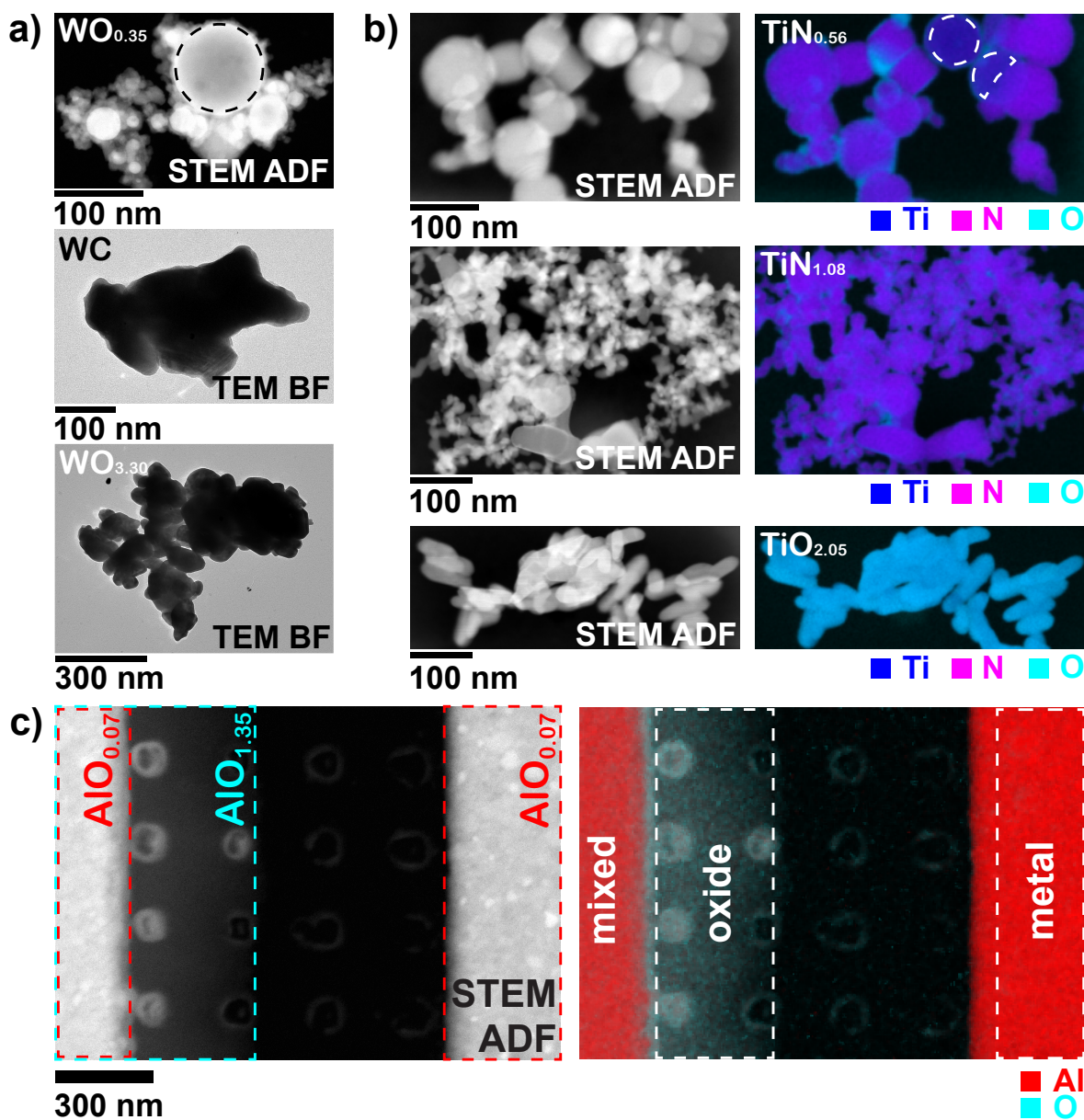


Figure 2.6: **Stoichiometry determination.** Bright field TEM or annular dark field STEM survey images and EDS element concentration maps of the tungsten, titanium, and aluminum specimens. The labelled chemical compositions are measured within the ROI or across the entire FOV when no ROI is present. a) Tungsten nanoparticles survey images. b) Titanium nanoparticles survey images and EDS maps. c) Aluminum films survey image and EDS map.

2.4 Results and Analysis

2.4.1 Chemical Shift Detection in Tungsten Compounds

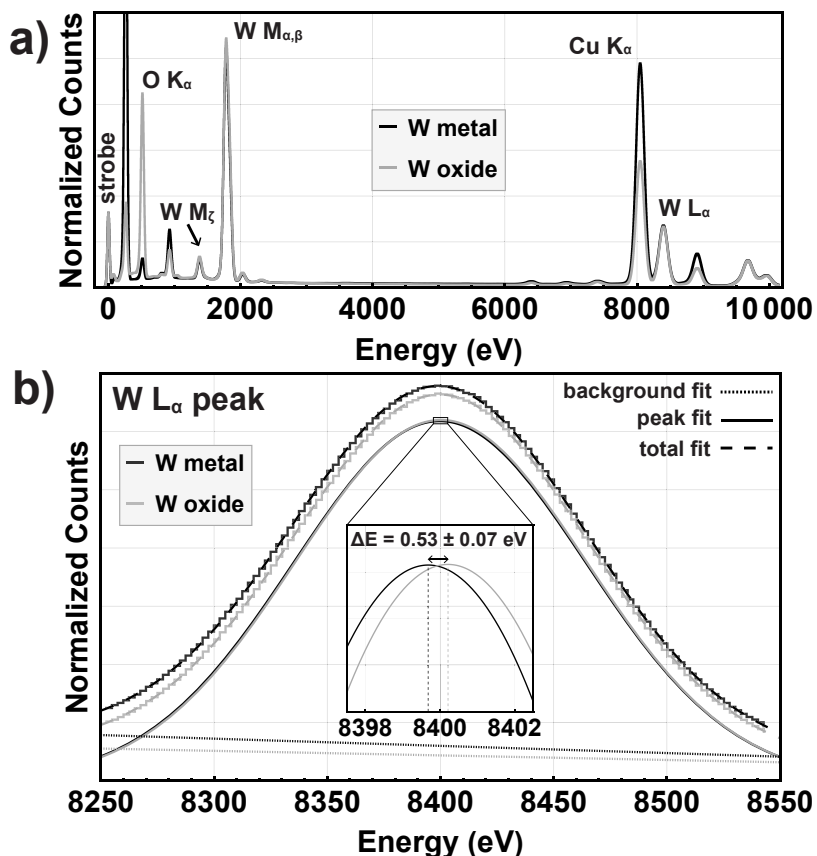


Figure 2.7: **EDS curve fits in tungsten compounds.** a) Full EDS spectra from tungsten metal (black) and tungsten oxide (gray) acquired at 80 kV. b) Gaussian-plus-linear-background curve fit to the W L α peak, revealing a chemical shift of 0.53 ± 0.07 eV between metal and oxide.

Three tungsten compounds—W metal, WC, and WO₃—are investigated to determine how transition energies respond to different chemical bonding environments. For the W metal sample, the spectrum is acquired in the ROI to maximize compositional homogeneity (Fig. 2.6a top). The W L α and O K α peaks are used to determine stoichiometry, yielding

compositions of $\text{WO}_{0.35}$ and $\text{WO}_{3.30}$ for the metal and oxide specimens, corresponding to averaged W valences of +0.7 and +6.6, respectively (Fig. 2.6a). The carbon support membrane prevented independent valence measurement for WC, so the manufacturer’s purity specification is used.

Fig. 2.7a shows representative EDS spectra from W metal and tungsten oxide acquired at 80 kV. Despite the ~ 140 eV FWHM of the W L_α peak at 8.4 keV, curve fitting reveals a chemical shift of 0.53 ± 0.07 eV between the metal and oxide (Fig. 2.7b)—a shift of approximately 0.4% of the peak width.

Chemical shifts are systematically measured across five W transition lines spanning energies from approximately 1 to 10 keV (Fig. 2.8). The three W L lines— L_α , $L_{\beta 2}$, and L_λ —all have energies above 7 keV, placing them in the inaccessible regime for EELS at 80 kV (Fig. 2.2). W L_α and W $L_{\beta 2}$ exhibit positive chemical shifts of less than +1 eV, while W L_λ shows a pronounced negative chemical shift reaching -2.6 eV. Chemical shifts were also observed in the lower-energy W M_γ and W M_2N_4 lines, both negatively signed.

The observation of both positive and negative chemical shifts is consistent with the theoretical framework established in Section 2.2.4: EDS measures the energy difference between two electron orbitals, and the sign of the shift depends on which orbital’s energy is perturbed more strongly by the changing chemical environment. The magnitude of the W L_λ shift (-2.6 eV, approximately one spectrometer bin) demonstrates that EDS chemical shifts can be substantial for certain transitions. Because of tungsten’s high elastic-to-inelastic scattering cross-section ratio and short mean free path, W edges are extremely difficult to measure precisely with EELS, making these EDS measurements uniquely valuable for chemical analysis of heavy elements.

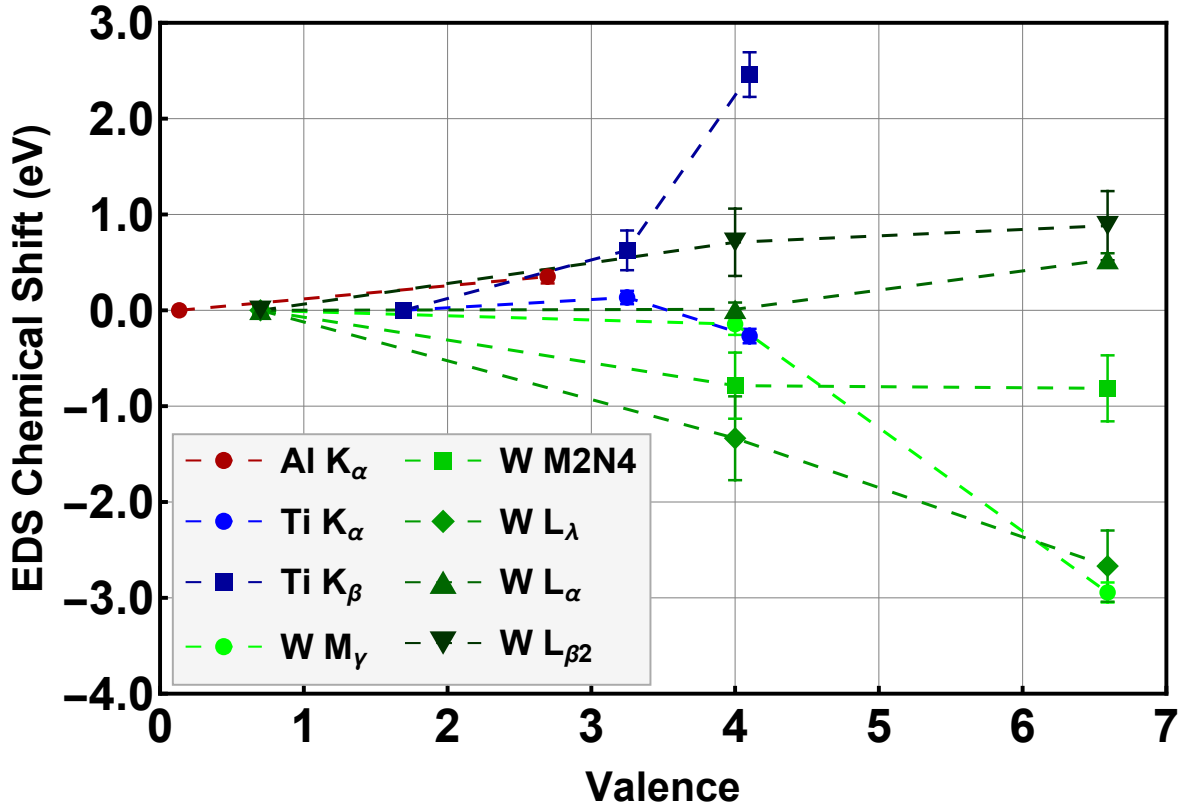


Figure 2.8: **EDS chemical shifts in W, Ti, and Al compounds.** EDS chemical shifts as a function of valence measured between covalently bonded compounds shown in Fig. 2.6. EDS measures the chemical shifts in transition energies, and these shifts can be either positive or negative, unlike the EELS chemical shifts being universally positive.

2.4.2 Chemical Shift Detection in Titanium Compounds

Spectrum images are acquired on Ti, TiN, and TiO₂ nanoparticle samples at 30 kV accelerating voltage. For the Ti metal specimen, an ROI is applied to select nanoparticles with low nitrogen concentration to differentiate from the TiN sample. Spectra are summed within each ROI or across the entire FOV, and the peak energies of the Ti K_{α} (4.51 keV) and Ti K_{β} (4.93 keV) lines are determined by curve fitting.

The Ti K_{β} line exhibits a pronounced chemical shift of up to +2.4 eV (approximately one

spectrometer bin at 2 eV/channel dispersion) with increasing oxidation state, while the Ti K_α line shifts by less than 0.5 eV (Fig. 2.8). The differential behavior of these two transitions—both originating from the same K shell (1s) but terminating in different shells ($M_{II,III}$ for K_β versus $L_{II,III}$ for K_α)—provides direct evidence that the chemical shift magnitude depends on the relative perturbation of the orbitals involved in the transition. At 30 kV accelerating voltage, the 5 keV Ti K lines lie well beyond the accessible regime for EELS (Fig. 2.2), yet EDS provides precise chemical information about the K shell.

2.4.3 Chemical Shift Mapping of the Aluminum Metal-Oxide Interface

To demonstrate chemical shift mapping capability, an Al EDS spectrum image is acquired across a patterned metal-oxide overlapping region. The spectrum image is binned to accumulate sufficient counts for pixel-level fitting of the Al K_α line at approximately 1.5 keV. Three distinct regions are visible in the resulting Al K_α energy map (Fig. 2.9a): a mixed region (very left), an oxide region (middle left), and a metal region (right). The oxide region exhibits a higher transition energy than the metal region, indicating that the Al K shell (1s) energy is minimized more than the L shell (2p) during oxidation.

The column-averaged profile (Fig. 2.9b) reveals a smooth transition between the oxide and mixed regions, with a distinct oxide edge detected at the boundary of the metal region. In the histogram of measured transition energies (Fig. 2.9c), a skewed normal distribution (for Al metal, reflecting the asymmetric peak shape at this energy) and a normal distribution (for Al oxide) can be fitted to the bimodal distribution, yielding a chemical shift of +0.36 eV between the two peak centers. This histogram-based measurement is in excellent agreement with the summed-spectra measurement from ROIs, which gives +0.35 eV, and is consistent with previous measurements from the literature [2, 57]. The EDS Al K_α chemical shift is approximately 1/14th of the 5 eV spectrometer bin size.

The spatial resolution of the EDS chemical shift map, experimentally limited by the binning needed to reach the high enough energy precision to resolve chemical shift, is ap-

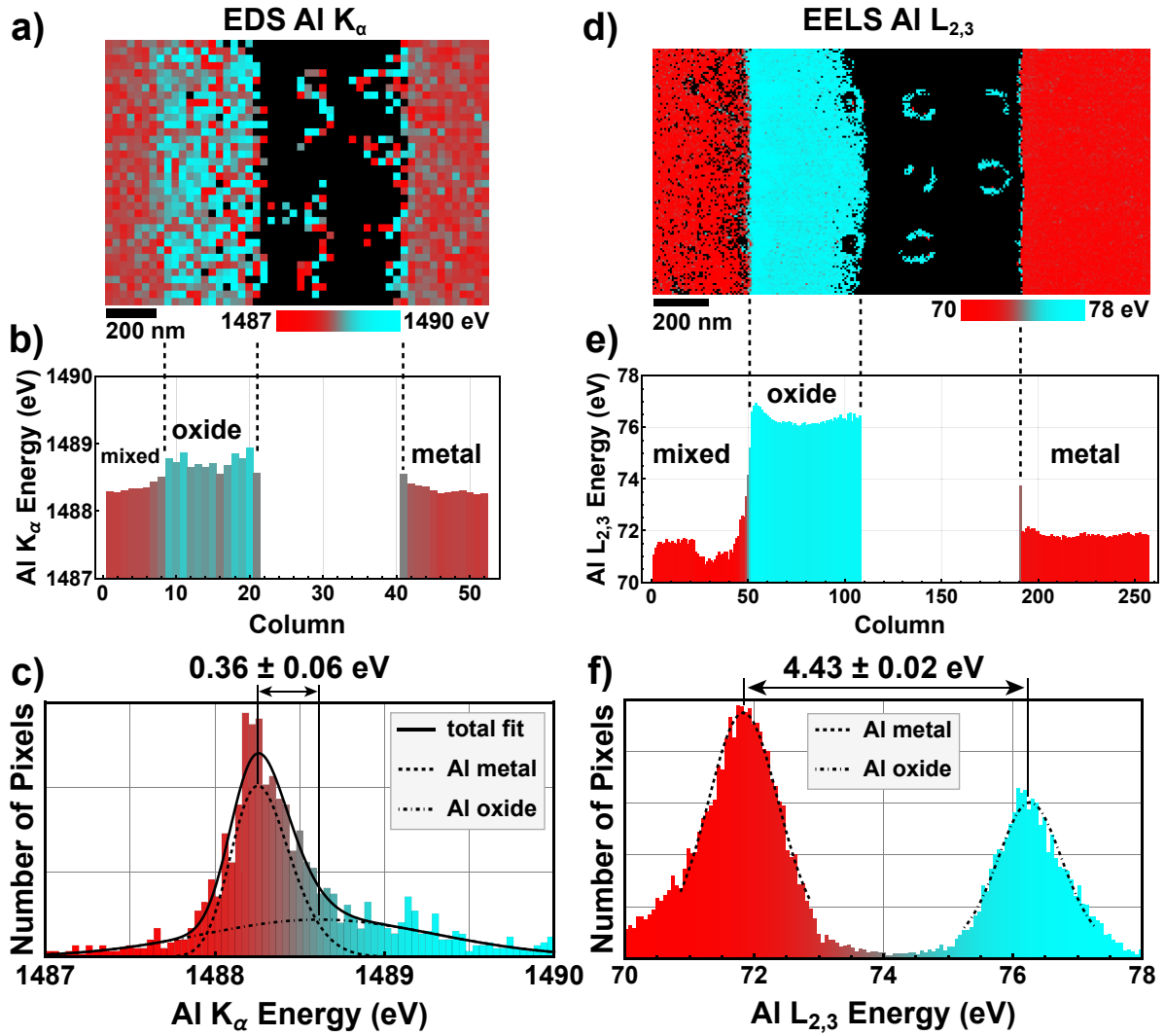


Figure 2.9: EDS and EELS chemical shift mapping across Al metal and oxide. a) and d), EDS Al K_{α} energy map and EELS Al $L_{2,3}$ energy map. b) and e), column average plots of the energy maps above (columns with less than 50% convergent fits were omitted). Three distinct regions are visible in both EDS and EELS plots. c) and f), histograms of the energy maps a) and d). Both histograms are fitted to two peaks representing the Al metal and oxide respectively. The EDS chemical shift is detectable despite being 12 times smaller than the EELS chemicals shift.

proximately 30 nm in this measurement. State-of-the-art SDDs capable of collecting more than a million counts per second [22] could reduce the pixel dwell time required for chemical shift detection by orders of magnitude, enabling higher-resolution maps and time-resolved measurements.

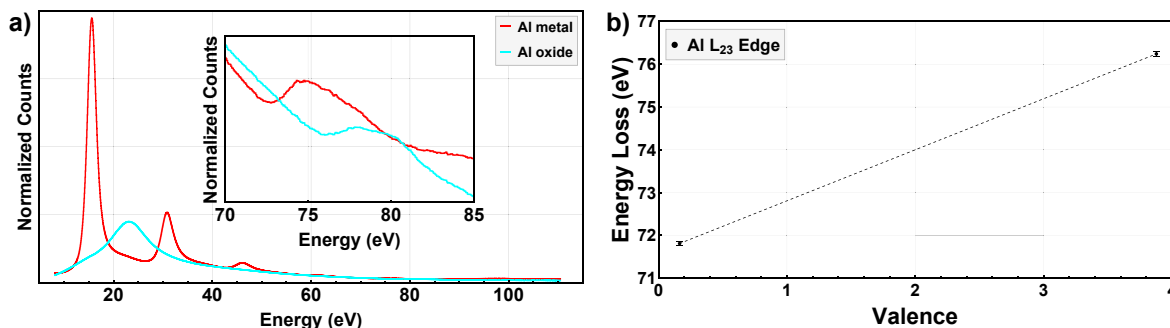


Figure 2.10: **EELS analysis of Al L_{2,3} edge.** a) EELS spectra from Al metal and oxide acquired at 80 kV, showing the Al L_{2,3} edge with a clear chemical shift (inset). b) Al L_{2,3} edge energy (defined as the energy corresponding to 10% of the rising edge) as a function of valence.

An EELS spectrum image is also collected in the same region under identical microscope settings (80 kV) to directly compare with the EDS analysis. At this accelerating voltage, EELS is borderline acceptable for measuring the Al K edge at 1.5 keV, so only the Al L_{2,3} edge around 75 eV is captured (Fig. 2.10a). The EELS Al L_{2,3} energy map (Fig. 2.9d–f) shows a similar three-region structure, with the oxide and metal regions clearly differentiated. The EELS chemical shift in the Al L_{2,3} edge is approximately 4.4 eV (Fig. 2.9f and Fig. 2.10b)—roughly 12 times larger than the EDS chemical shift in the Al K_α transition. This larger shift magnitude explains why the EELS histogram shows better peak separation. However, this does not imply superior energy precision: for the Al metal region, the EDS energy map actually achieves a factor of three better precision in the centroid determination.

The EDS Al K_α line measures the K–L_{2,3} transition energy, and the EELS Al L_{2,3} edge measures the L_{2,3} binding energy. Combining these independent measurements, the Al K-

shell (1s) binding energy is determined to be 1559.95 ± 0.03 eV for Al metal and 1564.88 ± 0.04 eV for Al oxide. These values are consistent with prior EELS-based results for the Al K edge [18], demonstrating that EDS can match EELS energy precision while accessing binding energy information for shells that are not directly measurable by EELS at the available accelerating voltage.

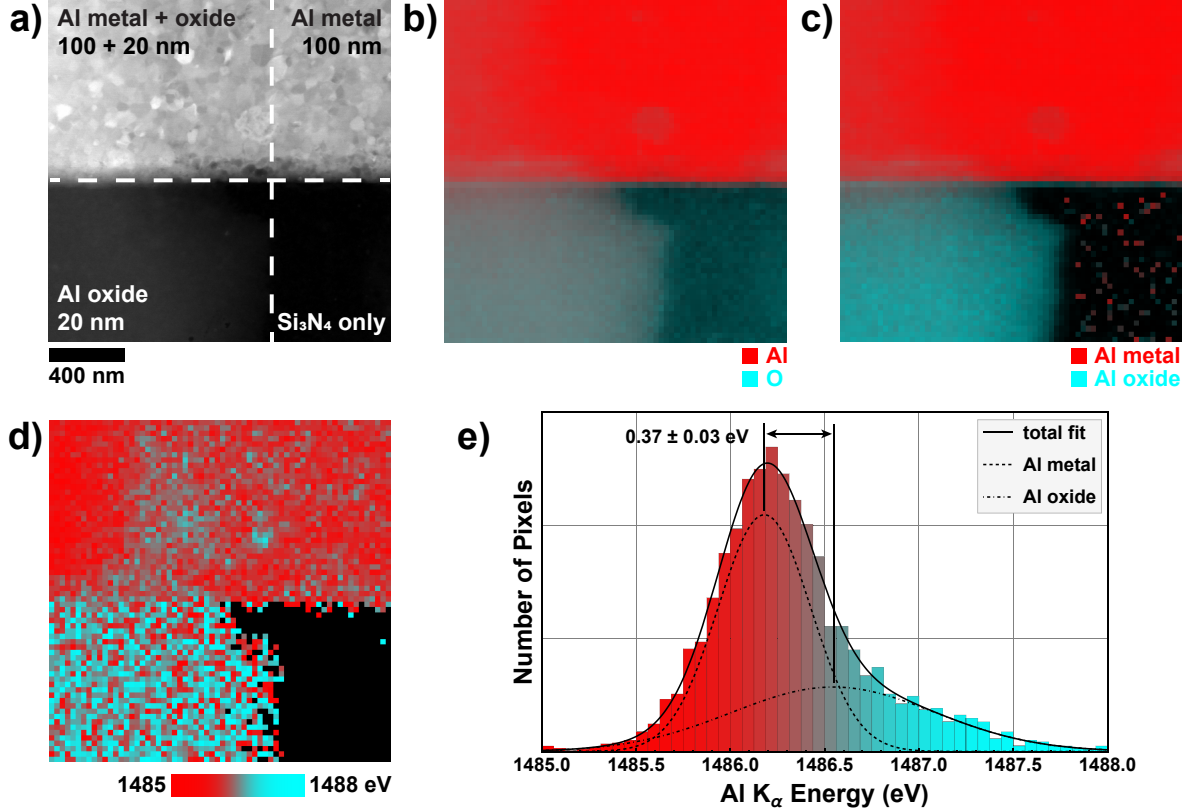


Figure 2.11: **EDS chemical shift mapping on an additional Al sample.** a) Shows the simultaneously acquired ADF image and only the Al metal (~ 100 nm thick) is visible. b), c) a layer of Al oxide was deposited on the left hand side. The EDS determined location is shown in atomic element map b) and the oxide map c). d) Shows the EDS chemical shift map in the two regions. e) The associated histogram of d). The measured shift between the Al metal and oxide is in good agreement with a separate dataset shown in Fig. 2.9 and result from the literature [57].

We also repeat the EDS chemical shift mapping on a second Al metal and oxide sample. This time, the Al metal and oxide films are patterned to form four different quadrants (Fig. 2.11a): metal only (top right), oxide only (bottom left), mixed (top left), and none (bottom right). The EDS Al K_α energy map (Fig. 2.11d) again shows apparent difference between the oxide only region and the metal only region, and the chemical shift measured (Fig. 2.11f) is consistent with the previously shown dataset.

A critical practical advantage of EDS over EELS is measurement stability. Because EELS is optically defined through the magnetic prism, spectra must be acquired quickly to avoid drift in the optical components [39]. The magnetic prism, although μ -metal armored, is highly susceptible to changes in the local magnetic field, and these changes—along with scan deflections—can shift the spectrum in energy space enough to cause systematic effects that appear as chemical shifts. In contrast, the zero-energy position in the EDS spectrum, not being optically defined, is nearly imperturbable, allowing spectra from any time or position to be summed together without misalignment in energy [28]. Typically, EDS (EELS) is acquired over many frames (one frame) and a drift correction is applied between frames (rows). EDS’s immunity to energy-axis drift makes it particularly well-suited for chemical shift mapping, where spatial variations in transition energy must be reliably distinguished from instrumental artifacts.

2.5 Corrected Paralyzable Detector Model

The precision of radiation counting experiments inherently improves with increasing count number, making count rate maximization the most important route toward improving signal-to-noise ratios. However, high count rates can lead to artifacts due to pulse pile-up [65]. The optimal data acquisition parameters represent a compromise between maximizing data throughput and minimizing artifacts [65, 66]. As demonstrated in the previous sections, chemical shift measurements via EDS can be achieved. However, acquiring enough data

to map the chemical shift as shown in Fig. 2.9 can take hours, making such quantification inconvenient to perform on a daily basis. Therefore, it is important to study how to maximize data acquisition speed while maintaining high data quality. And a precise understanding of the detector's behavior under varying count rates is essential for achieving this optimization.

2.5.1 Classic Paralyzable Detector Model

With an ideal detector that measures every incident radiation quantum (Fig. 2.12a, top), a user could increase the input flux without limit to boost data throughput. However, real-world detectors require a finite time to measure each detected event. Sequential events occurring during this measurement period might not be counted, or might interfere with the first measurement. This measurement time is called the detector dead time τ [67]. Two fundamental dead time models describe the behavior of such detectors: the non-paralyzable and paralyzable models [68, 69].

In the non-paralyzable detector model, events arriving during the dead time are simply not counted (Fig. 2.12a, middle). As a result, the output count rate C_{out} increases monotonically with the input count rate C_{in} , asymptotically approaching $1/\tau$. The relationship is given by:

$$C_{\text{out}} = \frac{C_{\text{in}}}{1 + \tau C_{\text{in}}}. \quad (2.5.1)$$

In the paralyzable detector model, events arriving during the dead time are not counted *and* also reset the dead time (Fig. 2.12a, bottom), leading to a decrease in C_{out} when C_{in} exceeds a certain limit. The probability that no event arrives within a dead time τ following a given event is $P = e^{-\tau C_{\text{in}}}$ according to Poisson statistics, giving:

$$C_{\text{out}} = C_{\text{in}} e^{-\tau C_{\text{in}}}. \quad (2.5.2)$$

The maximum of C_{out} for a paralyzable detector occurs at $\tau C_{\text{in}} = 1$, where $(C_{\text{out}})_{\text{max}} =$

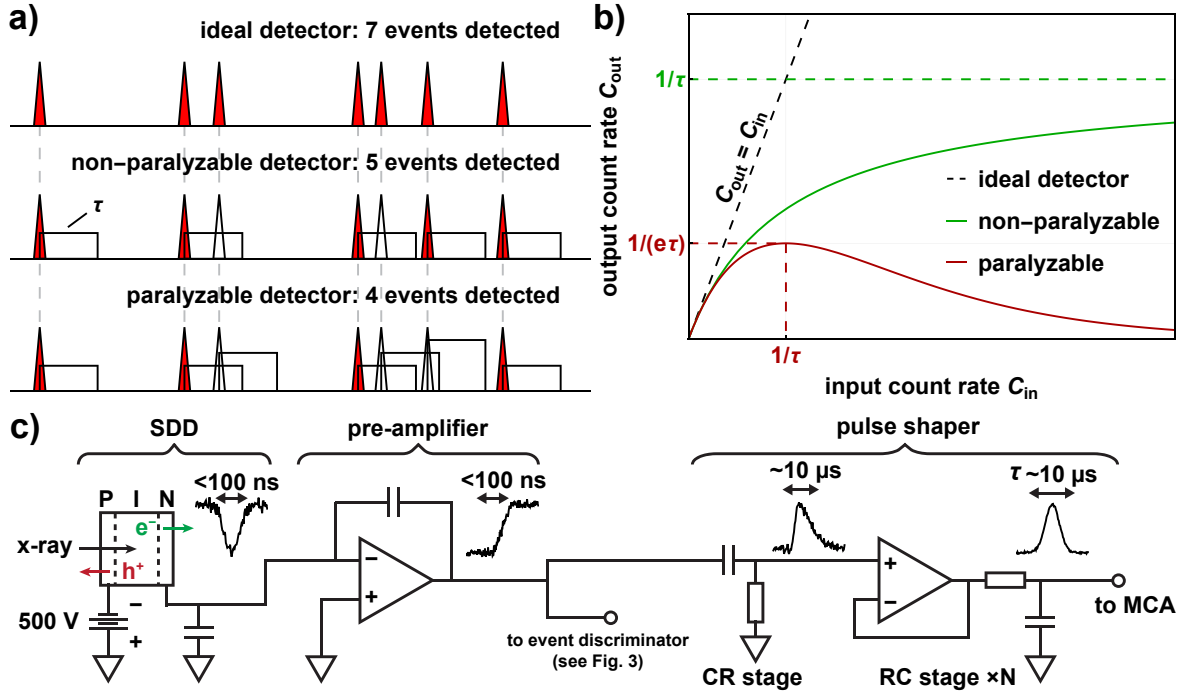


Figure 2.12: **Fundamental detector models and EDS detection chain.** a) The same event sequence arrives at different types of detectors. The red and white triangles represent detected events and missed coincidence events, respectively. The rectangular box represents the recovery time (the dead time τ). b) Output count rate C_{out} as a function of input count rate C_{in} for different types of detectors. The green dashed line marks the C_{out} asymptote of the non-paralyzable detector, and the red dashed lines mark the position of maximal C_{out} of the paralyzable detector. c) A schematic of a typical EDS system, where the progression of signal and approximate time constant is illustrated as an inset after each stage [70, 71]. This schematic can be generalized to other radiation detection systems by substituting the SDD with other types of detectors, such as neutron and electron detectors.

C_{in}/e . Defining the dead time percentage $D_{\%}$ as:

$$D_{\%} = \left(1 - \frac{C_{out}}{C_{in}}\right) \times 100\%, \quad (2.5.3)$$

it follows that C_{out} of an ideal paralyzable detector is maximized at $D\% = 1 - 1/e \approx 63.2\%$ [16]. This simple, dead-time-independent relationship is commonly used as a rule of thumb to optimize EDS acquisition throughput. For any given process time setting, operating at $D\% \approx 63\%$ corresponds to the maximum output count rate (Fig. 2.12b).

The physical origin of paralyzable behavior in EDS systems can be understood by examining the detection chain (Fig. 2.12c). The incoming photon is completely absorbed by the SDD and converted to a current pulse. The current is integrated by a capacitor (or JFET) and converted to a voltage step through a charge-sensitive pre-amplifier. A subsequent pulse shaper minimizes noise and converts the voltage step to a voltage pulse whose height is proportional to the energy of the incident photon. A semi-Gaussian pulse shaper, a classic analog design offering short dead time and high SNR [72, 73], is commonly employed. Other types of pulse shapers or digital signal processors can be implemented, but all are subject to a finite dead time that limits the output rate [74]. The voltage pulse is then processed by the MCA and added to the corresponding energy bin in the spectrum. Because the pulse shaper has a finite time constant, only well-separated x-ray events produce well-resolved pulses. Excessive input rates create pile-up pulses (multiple pulses merging into one), and massive quantities of pile-up pulses lead to a characteristic decrease in C_{out} at high C_{in} .

2.5.2 Corrected Detector Model with Event Discriminator

By fitting the C_{out} versus C_{in} data of an EDS system, the detector dead time can be experimentally determined. We record the input and output count rate of an Oxford X-MaxN 100TLE EDS detector on a FEI Titan 80-300 TEM. The count rates are taken from the Oxford AZtec v4.3 software. This detector features six adjustable dead time options (labeled as “process time” in the manufacturer’s software), though the exact values of τ are not publicly disclosed. In Fig. 2.13, the data is fitted with the classic one-parameter paralyzable detector model (Eq. 2.5.2) to determine the value of τ for each dead time option.

The classic model works reasonably well for long dead times but fails systematically as the

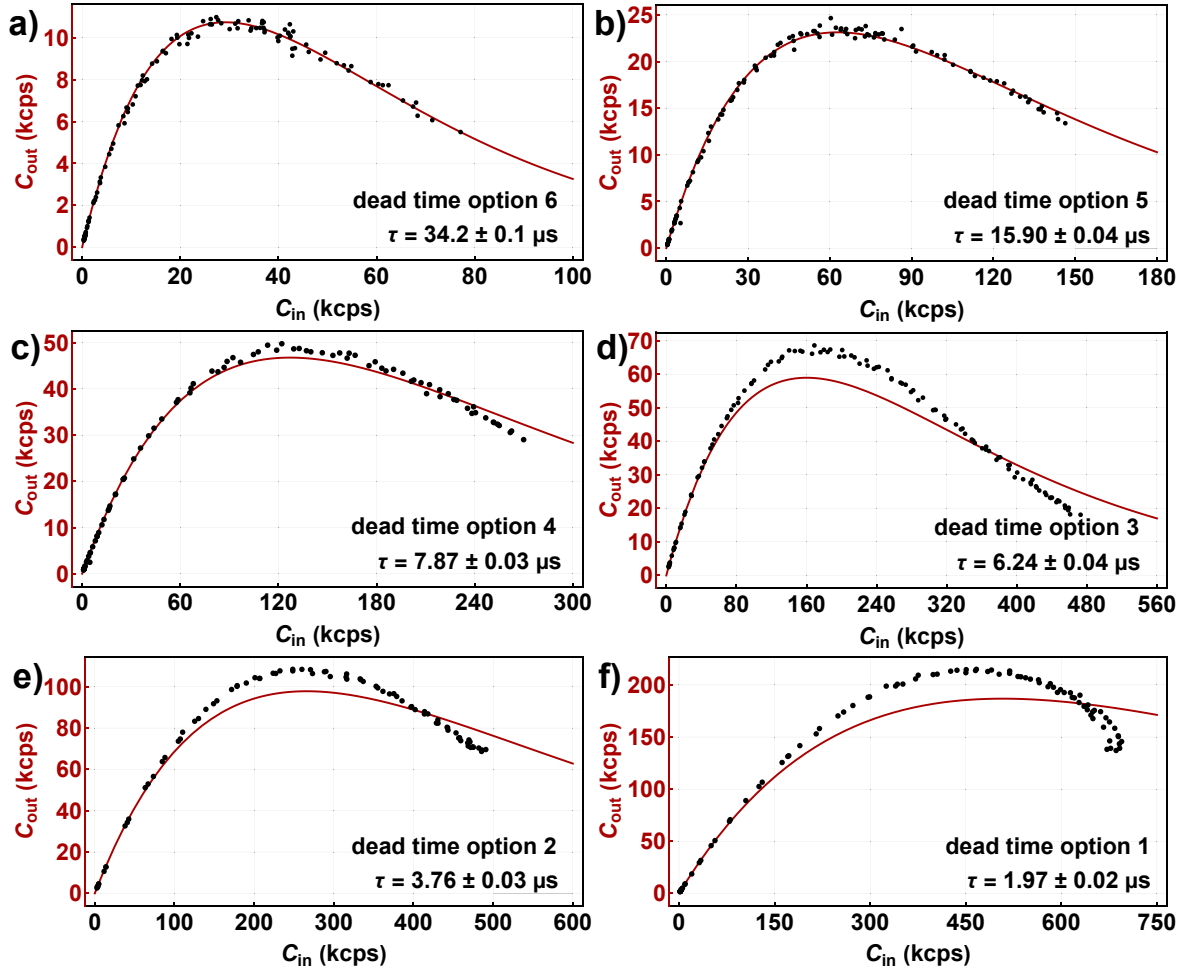


Figure 2.13: **Classic analyzable detector model fits.** The experimental data (black dots) and corresponding fits (red curves) using the paralyzable detector model (Eq. 2.5.2). The data is obtained on an Oxford X-MaxN 100TLE EDS detector for its six dead time options, and the measured dead time is labeled at the bottom right corner of each plot. The classic paralyzable detector model cannot accurately represent the data of shorter dead times.

dead time shortens. The failure of this model indicates that the input count rate measured by the detector, C_{hit} , deviates significantly from the actual input rate C_{in} at shorter dead times. The failure of the model affects the rule of thumb 63.2% dead time to maximize

throughput. More importantly, it also suggests that the input count rate measured by the detector C_{hit} deviates significantly from the actual input rate C_{in} at shorter dead times. This deviation means that the pulse processor is unable to distinguish all input x-ray events, leading to failures in hardware pile-up rejection [75].

To account for this inaccurately detected input count rate, we introduce a finite response time t_{dis} to model the input event discriminator of the system. The event discriminator is a subsystem parallel to the pulse shaper (Fig. 2.14a). It has a faster response and is used specifically to discriminate input events for hardware pile-up rejection [70]. The output of the pre-amplifier splits into two parallel pathways: one with a pulse shaping linear amplifier used for energy measurement, and another with a fast amplifier used for input event discrimination. The fast amplifier has a shorter response time t_{dis} , which is better for discriminating adjacent events at the expense of pulse height-energy linearity.

Modeling the event discriminator as a paralyzable detector following Eq. 2.5.2, the relationship between the measured input count rate C_{hit} and the actual input count rate C_{in} is:

$$C_{\text{hit}} = C_{\text{in}} e^{-t_{\text{dis}} C_{\text{in}}}. \quad (2.5.4)$$

To illustrate how the detector sorts input events into different categories, we plot the probability density function (PDF) and cumulative distribution function (CDF) of having a sequential event arriving within a time t after a leading event (Fig. 2.14b,c). The PDF area can be divided into three regions, each corresponding to a distinct event fate.

The green region indicates the probability that no subsequent event arrives within the dead time τ , meaning the leading event is well resolved and becomes a clean output event:

$$P(\text{clean}) = e^{-\tau C_{\text{in}}}. \quad (2.5.5)$$

The yellow region indicates the probability that a subsequent event is detected by the

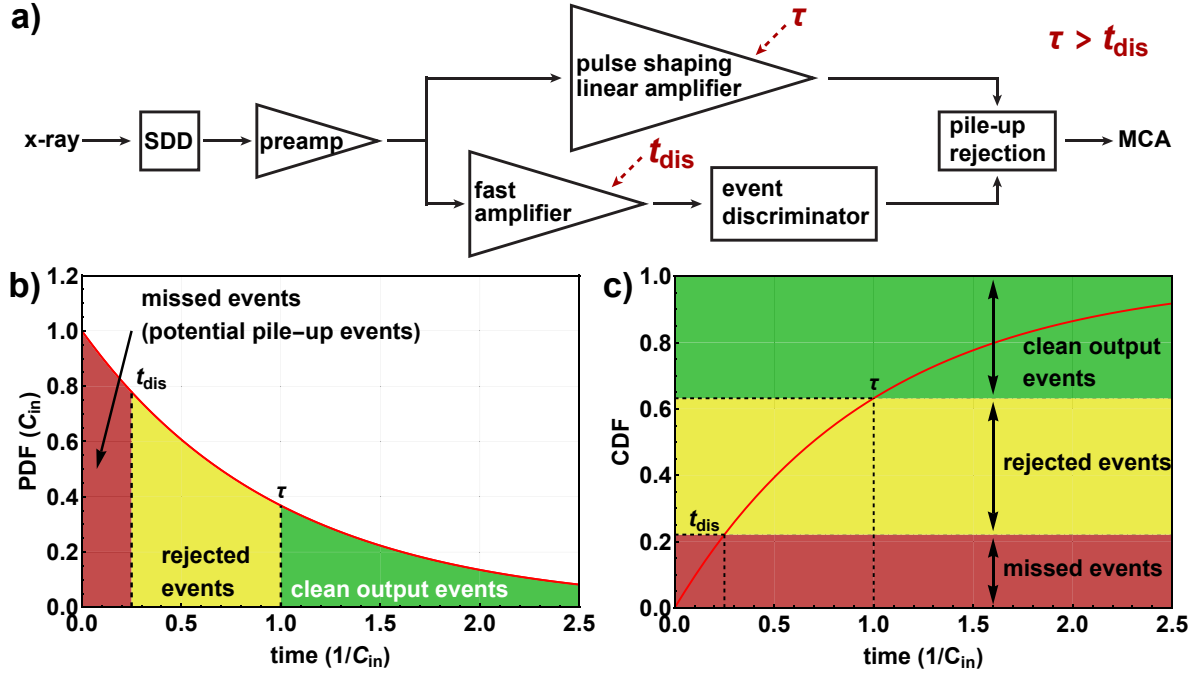


Figure 2.14: **Event probability distributions of EDS system with event discriminator.** a) Simplified schematic of an EDS system with event discriminator and hardware pile-up rejection [70]. The pre-amplifier output feeds two parallel pathways: a pulse shaping linear amplifier for energy measurement (dead time τ) and a fast amplifier for input event discrimination (response time t_{dis}). b) Probability density function (PDF) and c) cumulative distribution function (CDF) of having a sequential event arriving within time t after a leading event. The time axis is in units of $1/C_{\text{in}}$. The PDF area is divided into three regions: green (clean output events), yellow (correctly rejected pile-up events), and red (events missed by discriminator). Sequential events arriving within t_{dis} are missed and can become pile-up events.

event discriminator (arrives after t_{dis}) but within the dead time τ , causing the leading event to be correctly rejected by the hardware pile-up rejection system.

The red region indicates the probability that a subsequent event arrives within the discriminator response time t_{dis} and is therefore missed:

$$P(\text{missed}) = 1 - e^{-t_{\text{dis}} C_{\text{in}}}. \quad (2.5.6)$$

In order to provide a complete vision of how incident events are classified based on their proximity to a leading event, all possibilities are graphed in Fig. 2.15 with examples shown.

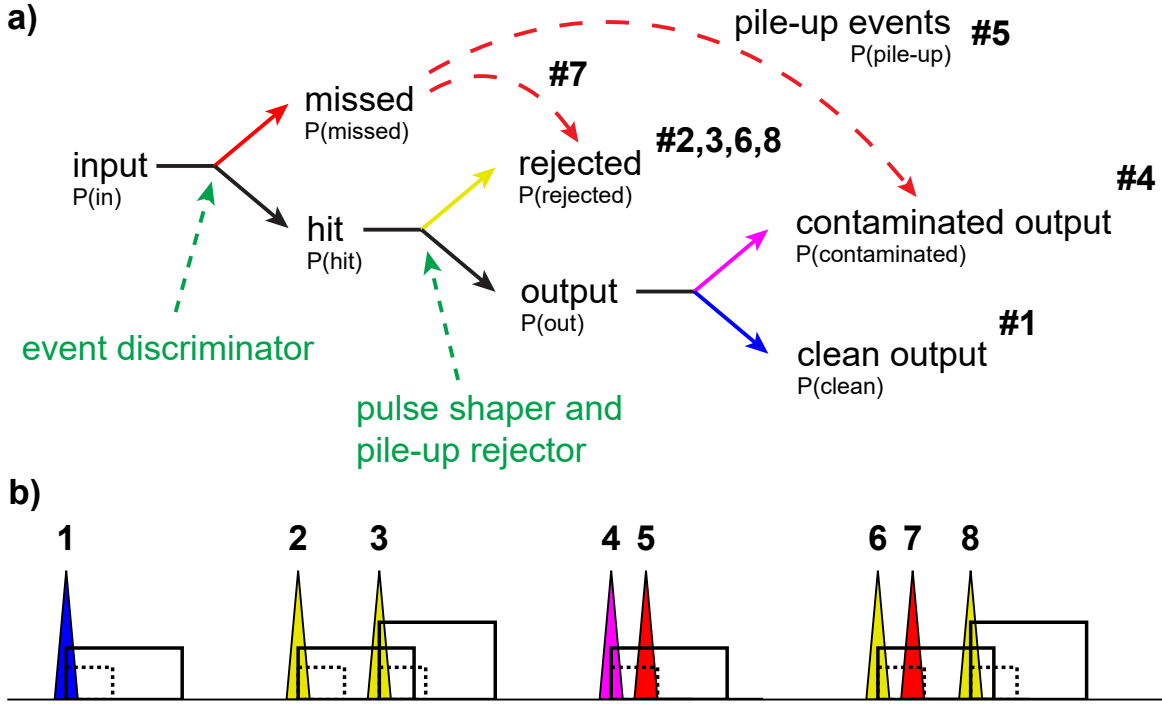


Figure 2.15: **Event classification diagram.** a) The x-rays reaching the detector can be classified basing on their proximity to the leading event and how they are treated by the event discriminator and the pile-up rejection system. b) An event sequence similar to the ones in Fig. 2.12a. They are color coded to indicate which category they end up being in the diagram above, and their indices are also labeled next to where they belong. The solid and dashed line boxes indicate the pulse shaper dead time τ and the event discriminator response time t_{dis} , respectively.

The times of arrival of input events are first registered by the event discriminator. During this process, events arriving within time t_{dis} following a previous event are missed by the

event discriminator (Fig. 2.15b #5, 7). They sneak into the pulse processing system without being registered and can potentially become pile-up events. If a second event is detected within time τ following a registered event, then the pile-up rejector will discard both to prevent overlap (Fig. 2.15b #2, 3, 6, 8). If no event is detected within time τ , then the first event will be sent to the output spectrum (Fig. 2.15b #1, 4). In the case where a missed event follows the output event, the output event is contaminated by pile-up (Fig. 2.15b #4).

The probability of an input event ending up in each category can be derived as a function of τ , t_{dis} , and C_{in} .

$$P(\text{in}) = 1 \quad (2.5.7)$$

The probability that an event is detected by the discriminator is:

$$P(\text{hit}) = e^{-t_{\text{dis}}C_{\text{in}}} \quad (2.5.8)$$

When a subsequent event is missed and no other events are detected between t_{dis} and τ , the leading event becomes a pile-up output event—it passes through the pile-up rejection system (which saw no subsequent events) but is contaminated by the missed event. The probability of an event becoming any output event (clean or contaminated) is:

$$P(\text{out}) = \frac{P(\text{clean})}{1 - P(\text{missed})} = e^{-(\tau - t_{\text{dis}})C_{\text{in}}}. \quad (2.5.9)$$

The probability of an event becoming a pile-up pulse that is missed by the hardware pile-up rejection and contaminates the output spectrum is:

$$\begin{aligned} P(\text{pile-up}) &= \frac{P(\text{missed})}{1 - P(\text{missed})} P(\text{out}) \\ &= e^{-(\tau - t_{\text{dis}})C_{\text{in}}} (e^{t_{\text{dis}}C_{\text{in}}} - 1). \end{aligned} \quad (2.5.10)$$

The probability of an event being correctly rejected (detected by the discriminator but falling within the dead time) is:

$$\begin{aligned} P(\text{rejected}) &= P(\text{hit}) - P(\text{out}) \\ &= e^{-t_{\text{dis}}C_{\text{in}}} - e^{-(\tau-t_{\text{dis}})C_{\text{in}}}, \end{aligned} \quad (2.5.11)$$

The probability that an output event is contaminated by pile-up (rather than clean) is:

$$\begin{aligned} P(\text{contaminated}) &= P(\text{out}) - P(\text{clean}) \\ &= e^{-(\tau-t_{\text{dis}})C_{\text{in}}} - e^{-\tau C_{\text{in}}} \\ &= e^{-\tau C_{\text{in}}}(e^{t_{\text{dis}}C_{\text{in}}} - 1). \end{aligned} \quad (2.5.12)$$

2.5.3 Derivation of the Corrected Output Rate

Assuming operation on the ascending branch of the input event discriminator ($t_{\text{dis}}C_{\text{in}} < 1$, see Fig. 2.12b and Eq. 2.5.2), Eq. 2.5.4 can be inverted for C_{in} using the principal branch of the Lambert W function, which has been shown useful for inverting the classic paralyzable detector model [76]:

$$C_{\text{in}} = -\frac{1}{t_{\text{dis}}}W_0(-t_{\text{dis}}C_{\text{hit}}). \quad (2.5.13)$$

The total output count rate is the product of the actual input rate and the probability of an event becoming an output:

$$C_{\text{out}} = C_{\text{in}} \times P(\text{out}) = C_{\text{in}} e^{-(\tau-t_{\text{dis}})C_{\text{in}}}. \quad (2.5.14)$$

Combining Eq. 2.5.13 and Eq. 2.5.14, the total output rate as a function of the measured input rate is:

$$C_{\text{out}} = -\frac{1}{t_{\text{dis}}} W_0(-t_{\text{dis}} C_{\text{hit}}) e^{\frac{1}{t_{\text{dis}}} W_0(-t_{\text{dis}} C_{\text{hit}})(\tau - t_{\text{dis}})}. \quad (2.5.15)$$

Using the Lambert identity $W(z)e^{W(z)} = z$, this simplifies to:

$$C_{\text{out}} = C_{\text{hit}} e^{\frac{1}{t_{\text{dis}}} W_0(-t_{\text{dis}} C_{\text{hit}})(\tau - 2t_{\text{dis}})}. \quad (2.5.16)$$

Eq. 2.5.16 provides a two-parameter analytical model corrected for a system with a real-world event discriminator and hardware pile-up rejection, which is the most common configuration for contemporary EDS systems [70]. This model can independently determine both the discriminator response time t_{dis} and the pulse shaper dead time τ , critical parameters for understanding detector performance that are often not publicly disclosed by manufacturers.

2.5.4 Corrected Paralyzable Detector Model Fitting

A simultaneous fit of the corrected two-parameter model (Eq. 2.5.16) to all six dead time datasets was performed, assuming that all six options share the same event discriminator response time t_{dis} (Fig. 2.16a). The individual fits for each dead time option are shown in Fig. 2.16b–g. Compared to the classic model (Fig. 2.13), the corrected model achieves excellent agreement with the data across all dead time options, even though the fitted τ values change by only about 5% between the individual fits. The event discriminator response time is determined to be $t_{\text{dis}} = 0.479 \pm 0.002 \text{ } \mu\text{s}$, which falls between the $\sim 100 \text{ ns}$ SDD charge collection time and the microsecond-level pulse shaper dead time, consistent with physical expectations for a fast discriminator circuit.

Being a generalized model, the corrected paralyzable detector model (Eq. 2.5.16) provides a way to measure the response time of the event discriminator and the dead time of EDS system without knowing the detailed structure of each system component. It also provides a new way to measure the dead time of radiation detectors with similar structures, without the need for two standard radiation sources (two-source method) [77]. More importantly, it

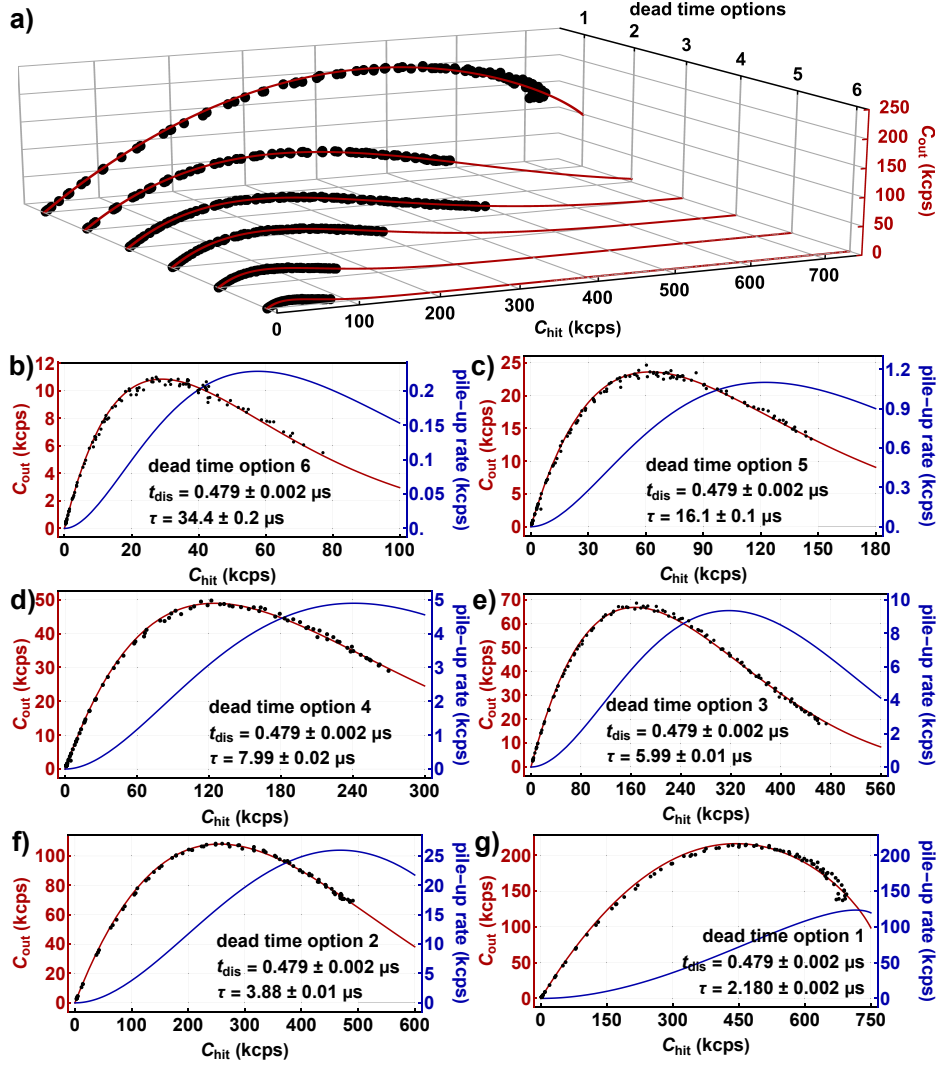


Figure 2.16: **Corrected paralyzable detector model fits.** Experimental data in Fig. 2.13 is fitted again using the corrected model in Eq. 2.5.16 which accounts for an event discriminator and pile-up rejection system. a) A simultaneous fit to all six dead time options to determine the common parameter t_{dis} . It is assumed that all six dead time options use the same event discriminator. b-g) C_{out} vs C_{hit} fit (red) and predicted pile-up rate (blue) for each dead time option. Compared to the classic paralyzable detector model in Fig. 2.13, the corrected model accurately represents the data even to the shortest dead time.

helps to maximize throughput more accurately and offers the ability to quantify the pulse pile-up effect, which negatively impacts the spectrum quality. Pulse pile-up generates false peaks that can be misidentified as elements do not exist in the specimen, for example the sum peak. It can also lead to shifts in peak energy and changes in peak intensity, which introduce errors in elemental composition quantification [65, 78]. Thus, it is helpful to quantify the rate of pile-up events for evaluating spectrum quality. The rate of pile-up events that enter the output spectrum is:

$$\begin{aligned} C_{\text{pile-up}} &= C_{\text{in}} \times P(\text{pile-up}) \\ &= C_{\text{in}} e^{-(\tau - t_{\text{dis}})C_{\text{in}}} (e^{t_{\text{dis}}C_{\text{in}}} - 1), \end{aligned} \quad (2.5.17)$$

where C_{in} is the actual input count rate, expressible in terms of the measured input rate C_{hit} via Eq. 2.5.13. The blue curves in Fig. 2.16b-g are the pile-up event count rate predicted by Eq. 2.5.17. Note that $C_{\text{pile-up}}$ can in principle exceed C_{out} because multiple pile-up events can contribute to the same output event, though this only occurs far beyond the optimal data acquisition condition.

The optimal data acquisition condition is defined as the point where the clean output rate $C_{\text{clean}} = C_{\text{in}} \times P(\text{clean})$ is maximized (Eq. 2.5.5). Fig. 2.17 shows the key optimization parameters as a function of the ratio $n = \tau/t_{\text{dis}}$ under the optimal condition. The measured dead time percentage,

$$\text{measured } D_{\%} = \left(1 - \frac{C_{\text{out}}}{C_{\text{hit}}}\right) \times 100\%, \quad (2.5.18)$$

is plotted rather than the actual $D_{\%}$ (Eq. 2.5.3) because commercial software is typically unaware of the difference between C_{hit} and C_{in} and reports the measured value to users. The smaller the ratio $n = \tau/t_{\text{dis}}$, the more the measured $D_{\%}$ at the optimal condition (red curve) deviates from the ideal ($t_{\text{dis}} \rightarrow 0$) 63.2% prediction (dashed line), and the higher the pile-up percentage (number of pile-up events divided by total output events, or $P(\text{pile-up})/P(\text{out}) \times 100\%$) at optimal throughput (Fig. 2.17b). The data points along the curves represent the ratios measured on the Oxford X-MaxN 100TLE detector for the six dead time options.

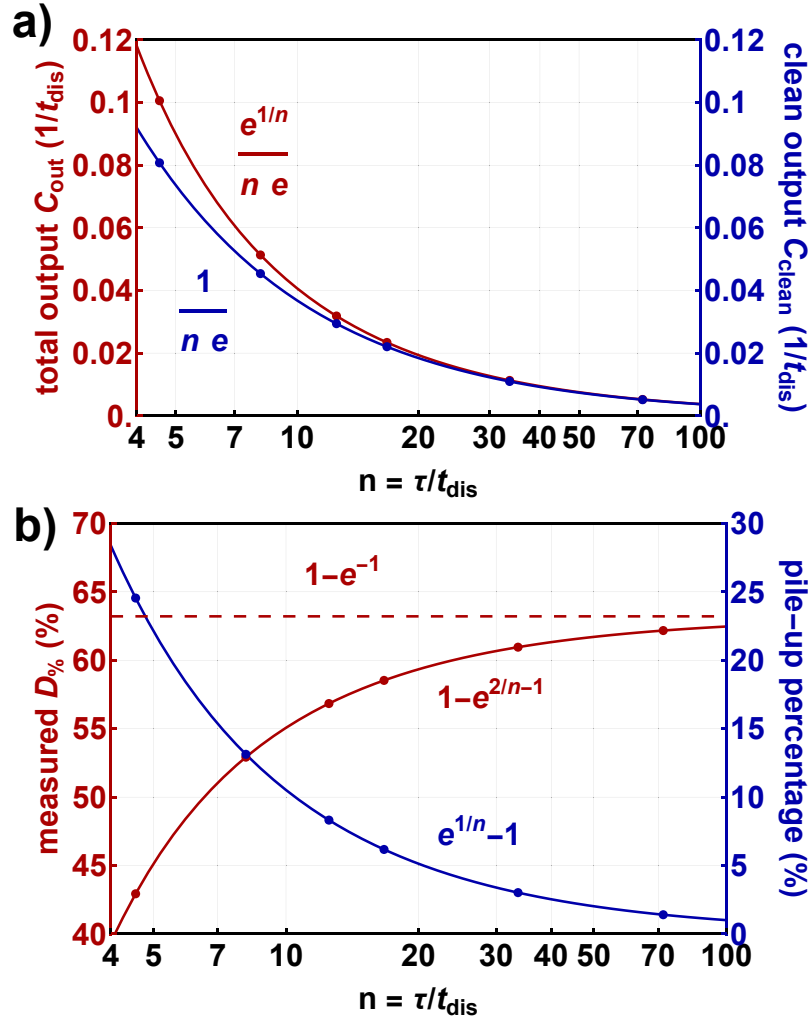


Figure 2.17: **Maximizing clean events throughput.** Maximizing the count rate of clean output events as a function of the ratio of dead time τ and the response time of the event discriminator t_{dis} . The dots along the curves represent the ratios measured on our Oxford X-MaxN 100TLE EDS detector for different dead time options. These plots guide users to maximize the data throughput and estimate the pile-up effect in the acquired spectrum. The dimensionless formulas can be derived with the probabilities shown in Section 2.5.3.

This optimization framework guides users to select acquisition parameters that balance throughput against spectral quality. For applications where pile-up artifacts must be min-

imized (such as chemical shift measurements requiring sub-eV precision), the framework identifies the input flux that maximizes clean output while keeping the pile-up percentage below an acceptable threshold. Furthermore, being able to quantify how many pile-up events are added to the spectrum provides a method to apply post-acquisition correction, which can largely eliminate pile-up artifacts and maintain the accuracy of EDS measurements even with ten times higher throughput.

2.6 Post-acquisition Pile-up Correction Algorithm

2.6.1 Post-Acquisition Pile-Up Correction

Post-acquisition pile-up correction methods have been developed by detector manufacturers [78–80], but the algorithm details are often not made public, and the corrected spectra are often not accessible for further analysis outside of the commercial software. Following the determination of t_{dis} and τ using the corrected paralyzable detector model, combined with the measured count rates, it is possible to perform a quantitative post-acquisition correction for two-photon coincidence events that the hardware pile-up rejection system failed to eliminate. The correction algorithm is based purely on probability and does not require any knowledge of the specimen composition.

Consider an energy spectrum with N bins starting at 0 eV. Pile-up always shifts photon events toward higher energy bins, so bin k is only affected by pile-up from photons with energy between 0 eV and the energy of bin $k - 1$. Denoting the uncorrected and corrected counts from bin 1 to bin $k - 1$ as $uc_{1:k-1}$ and $c_{1:k-1}$, respectively. Assuming the spectrum has been corrected up to bin $k - 1$, the number of pile-up events contributing to the spectrum with energy up to bin $k - 1$ is:

$$pu_{1:k-1} = [c_{1:k-1} / P(\text{clean})] \times P(\text{pile-up}). \quad (2.6.1)$$

Because the input event sequence is random, these pile-up events are randomly distributed

among all output events. For a pile-up event with energy corresponding to bin m to contribute to bin k , it must sum with an output event having energy corresponding to bin $k - m$. The probability that pile-up events contribute to bin k is therefore:

$$ap_{1:k-1} = [c_{k-1:1} / P(\text{clean})] \times P(\text{out}) / \sum_{i=1}^N uc_i. \quad (2.6.2)$$

Since the algorithm corrects only for two-photon coincidence events (the dominant pile-up mechanism), the probability that a pile-up event is a two-photon rather than multi-photon coincidence must be accounted for. The probability that exactly one missed event follows a detected event (with no additional events within t_{dis}) is:

$$P(\text{two-photon}) = e^{-t_{\text{dis}}C_{\text{in}}}. \quad (2.6.3)$$

The correction for bin k is then:

$$c_k = uc_k - (pu_{1:k-1} \cdot ap_{1:k-1}) \times P(\text{two-photon}). \quad (2.6.4)$$

Starting from bin 1 (which is unaffected by pile-up since no lower-energy events exist, so $c_1 = uc_1$), the algorithm iterates from $k = 2$ to $k = N$, correcting the entire spectrum for two-photon coincidence events. In cases where the spectrum contains negative energy bins to capture the entire strobe peak (electronic noise peak), these negative energy bins are simply ignored during the iterative correction.

A normalization factor can be applied at the end to effectively redistribute all coincidence events back into their correct single-photon bins:

$$n_0 = [P(\text{out}) + P(\text{pile-up})] / P(\text{clean}). \quad (2.6.5)$$

This normalization does not affect EDS quantification (which relies on relative peak intensities) but is applied to all corrected spectra shown here for ease of visual comparison. In most of the equations above, the actual input rate C_{in} is directly referenced for notational simplicity. Although C_{in} is not directly measurable, it can be derived from t_{dis} , τ , and C_{out} using Eq. 2.5.13 and Eq. 2.5.16.

2.6.2 Validation on Simulated Spectra

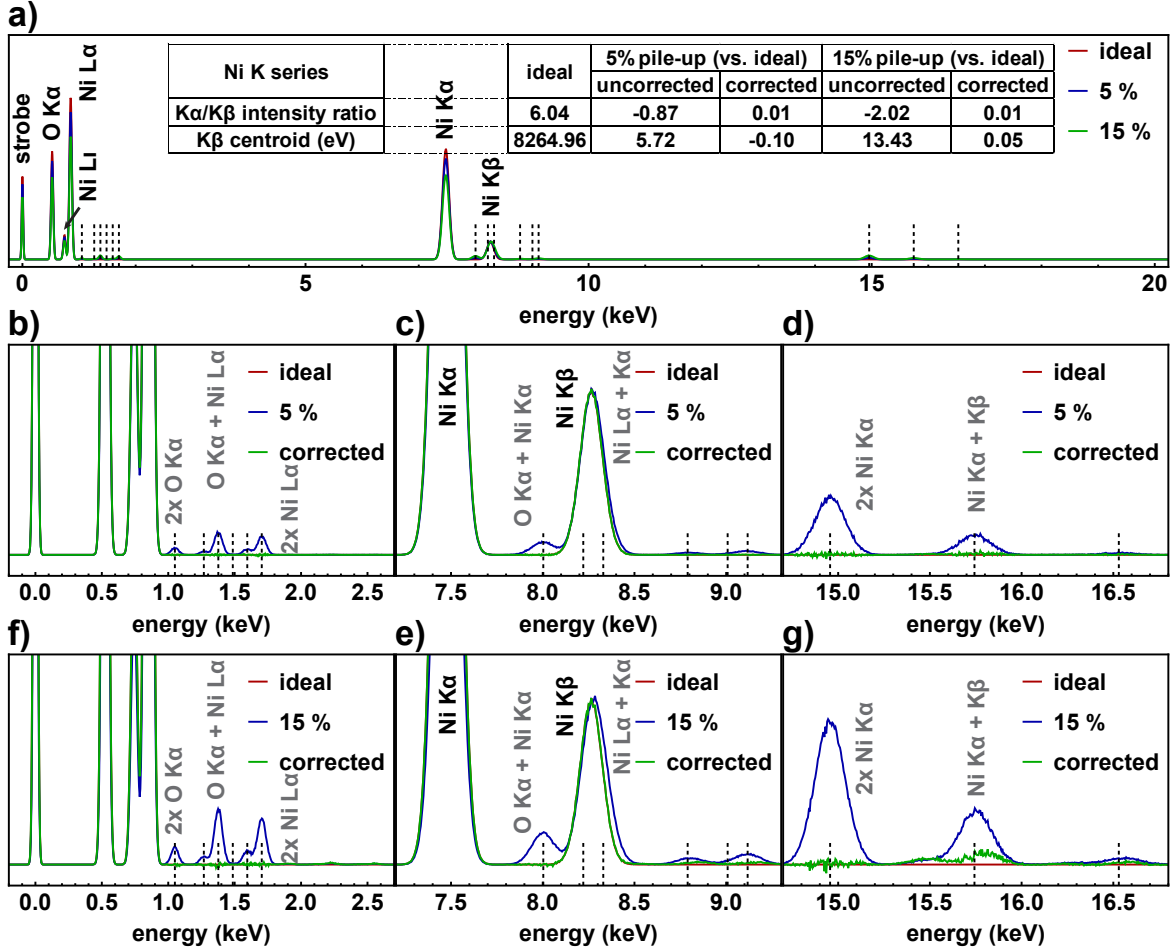


Figure 2.18: **Pile-up correction on simulated EDS spectra.** a) Simulated EDS spectra of NiO_x with 0% (ideal, red), 5% (blue), and 15% (green) pile-up events. Dashed lines indicate the locations of all two-photon pile-up peaks. The Ni K_β peak at 8265 eV is affected by three nearby pile-up peaks. The inset table shows that pile-up correction reduces quantification deviations by approximately two orders of magnitude. b–d) For spectrum with 5% pile-up, all two-photon pile-up peaks are effectively removed. e–g) For spectrum with 15% pile-up, minor three-photon pile-up residuals remain visible in panel g). Several selected pile-up peaks are labeled with gray texts. All y-axes are counts.

The correction algorithm is first validated on simulated spectra where the ground-truth ideal spectrum is known (Fig. 2.18). A high-quality NiO_x reference spectrum is constructed with five million events distributed among the major peaks: strobe peak, O K_α , Ni L_α , Ni L_β , Ni K_α , and Ni K_β , with intensity ratios of 2:4:1:6:12:2. Peak energies are taken from the literature [62,81], and peak widths are determined using Eq. 2.2.1 with $\text{FWHM}_{\text{strobe}} = 30$ eV, $\varepsilon_i = 3.6$ eV [82], and $F = 0.12$ [83]. Events are randomly generated following normal distributions around each peak center. A specified percentage of events are randomly selected as pile-up events and randomly added to the remaining events, then sorted into a 4096-bin spectrum with 5 eV bin size spanning -242.5 to $+20242.5$ eV.

For detector parameters $t_{\text{dis}} = 0.5$ μs and $\tau = 2$ μs (similar to dead time option 1 of the Oxford detector), 5% and 15% pile-up correspond to actual input count rates of 98 kcps and 280 kcps, respectively. Three spectra with 0% (ideal), 5%, and 15% pile-up are generated (Fig. 2.18a). The locations of all two-photon pile-up peaks are indicated by dashed lines. Pile-up peaks at 1.7 keV, 8 keV, and 15 keV can be misidentified as Si K_α (1.74 keV), Cu K_α (8.05 keV), and Y K_α (14.96 keV), respectively [62]. Pile-up artifacts also change the Ni $\text{K}_\alpha/\text{K}_\beta$ intensity ratio and shift the Ni K_β peak centroid to higher energy.

The pile-up correction algorithm is applied to both the 5% and 15% pile-up spectra. Comparisons between the ideal, uncorrected, and corrected spectra are shown in three different energy ranges for each case (Fig. 2.18b–g). The correction effectively eliminates all two-photon pile-up peaks for both cases, and the corrected spectra overlap with the ideal spectrum within the noise level. Some three-photon pile-up peaks, which are not accounted for by this implementation, remain visible in the 15% case (Fig. 2.18g), but their intensity is negligible.

Without pile-up correction, the Ni K_β centroid is shifted to higher energy. For the 15% pile-up case, this shift is on the order of 10 eV (Fig. 2.18a inset table). Such artifacts would severely impede efforts to detect fine shifts in peak energy using EDS and would force chemical shift studies to be performed with ultra-low throughput to limit pile-up contamination.

After applying the pile-up correction, sub-eV level peak centroid accuracy is recovered even for the spectrum with 15% pile-up. The Ni K_α/K_β intensity ratio, which should be constant for a given material, also shows one to two orders of magnitude improvement in accuracy after correction.

2.6.3 Validation on Experimental Spectra

The pile-up correction algorithm is subsequently validated on twelve experimental NiO_x spectra acquired on the same Oxford X-MaxN 100TLE detector using a PELCO NiO_x test specimen (No. 650) under varying dead time options and x-ray fluxes (Fig. 2.19). The detector parameters t_{dis} and τ determined from the corrected model fits (Fig. 2.16) are used to calculate the pile-up percentage for each spectrum. Three spectra with pile-up percentages similar to the simulated cases are selected for detailed comparison.

The ideal (0.4% pile-up), 5.7%, and 16% pile-up spectra are acquired with dead time option 6 at $C_{\text{out}} = 5.83$ kcps, dead time option 3 at $C_{\text{out}} = 60.8$ kcps, and dead time option 1 at $C_{\text{out}} = 182$ kcps, respectively. The raw data of the ideal spectrum is acquired with a very low input x-ray flux to minimize pile-up events; even this spectrum has the pile-up correction applied (estimated residual pile-up 0.4%). Because of the continuous Bremsstrahlung x-ray background [70] accounting for approximately 40% of total counts, even though each experimental spectrum contains the same five million total counts as the simulated ones, the experimental spectra are subject to more Poisson noise. The channel dispersion and offset are calibrated using the centroids of O K_α and Ni K_α peaks, and the background intensity (determined with an energy window of 8.55–8.65 keV) is subtracted when quantifying Ni K series peaks.

The post-acquisition pile-up correction effectively removes all visible pile-up peaks from the spectrum with 5.7% pile-up (Fig. 2.19b–d) and substantially suppresses those in the spectrum with 16% pile-up (Fig. 2.19e–g). Despite some incomplete correction visible around 1.5 keV for the 16% pile-up spectrum, the pile-up correction significantly reduces both the

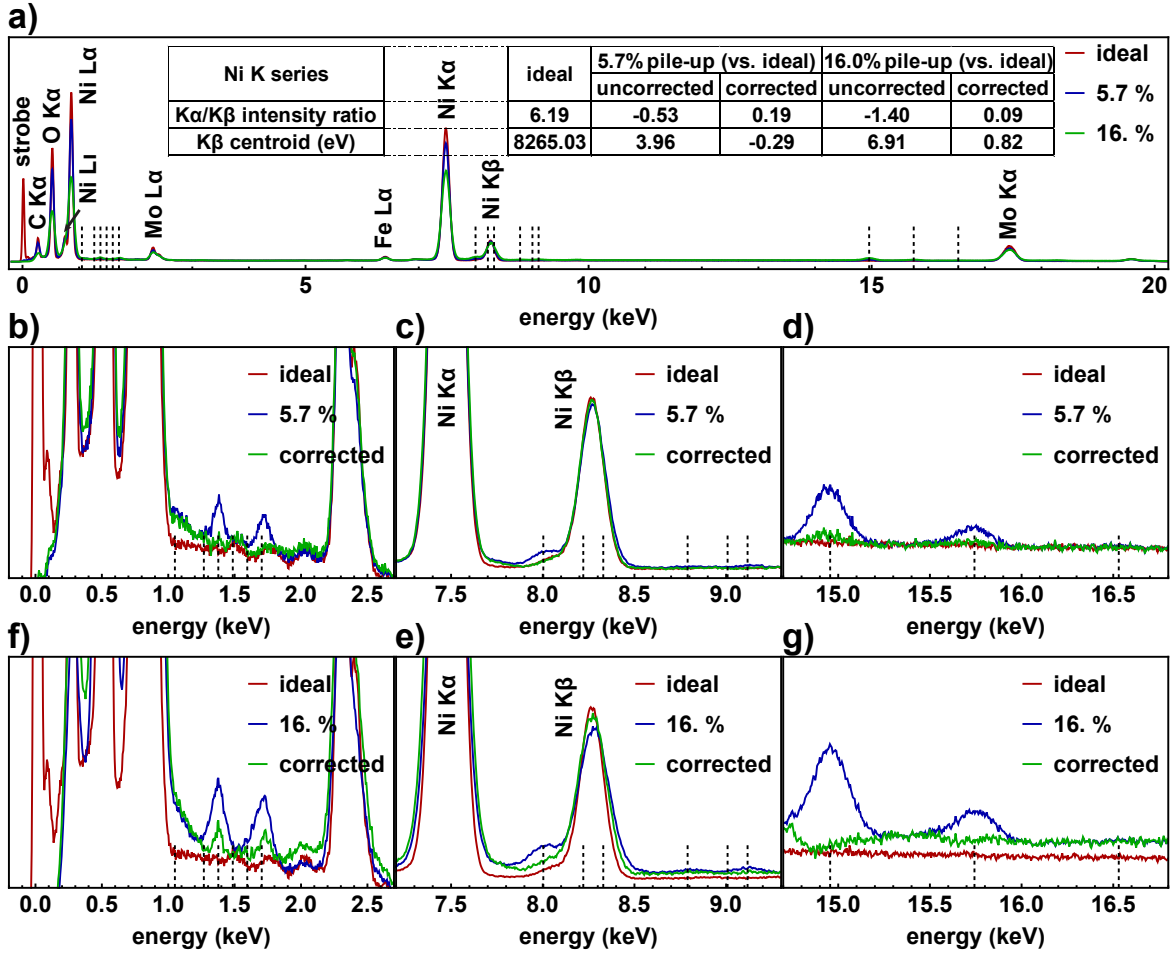


Figure 2.19: **Pile-up correction on experimental EDS spectra.** a) Experimental spectra acquired on a NiO_x standard with pile-up percentages similar to the simulated spectra in Fig. 2.18. Extra EDS peaks from C, Mo, and Fe originate from the carbon support membrane, molybdenum TEM grid, and the TEM objective lens, respectively. Dashed lines indicate the locations of the same two-photon pile-up peaks shown in Fig. 2.18. b–g) Comparison of the spectra with 5.7% or 16% pile-up before and after post-acquisition correction. The post-acquisition pile-up correction significantly reduces the intensity ratio and centroid deviations of the Ni K_β peak, with sub-eV peak energy accuracy preserved even for the 16% pile-up spectrum. All y-axes are counts.

Ni K_β centroid deviation and the Ni K_α/K_β intensity ratio deviation for all experimental spectra.

Fig. 2.20 summarizes the quantification accuracy across all twelve experimental spectra. The Ni K_β peak centroid deviation and Ni K_α/K_β intensity ratio deviation are plotted as a function of pile-up percentage, both before and after pile-up correction. The pile-up correction provides one to two orders of magnitude improvement in both metrics. Sub-eV accuracy in the Ni K_β peak centroid is preserved even for the spectrum with 16% pile-up, whose data throughput is approximately 30 times higher than the condition used for the ideal spectrum acquisition.

This result demonstrates that the complete data analysis pipeline—from quantifying detector dead time using the corrected paralyzable detector model to applying post-acquisition pile-up correction—enables high-throughput EDS acquisition while maintaining the quantification accuracy necessary for chemical shift measurements. With a state-of-the-art EDS detector whose output rate can exceed one million counts per second, the data acquisition time for a chemical shift measurement can be reduced from hours to minutes, making routine EDS chemical shift analysis practically feasible.

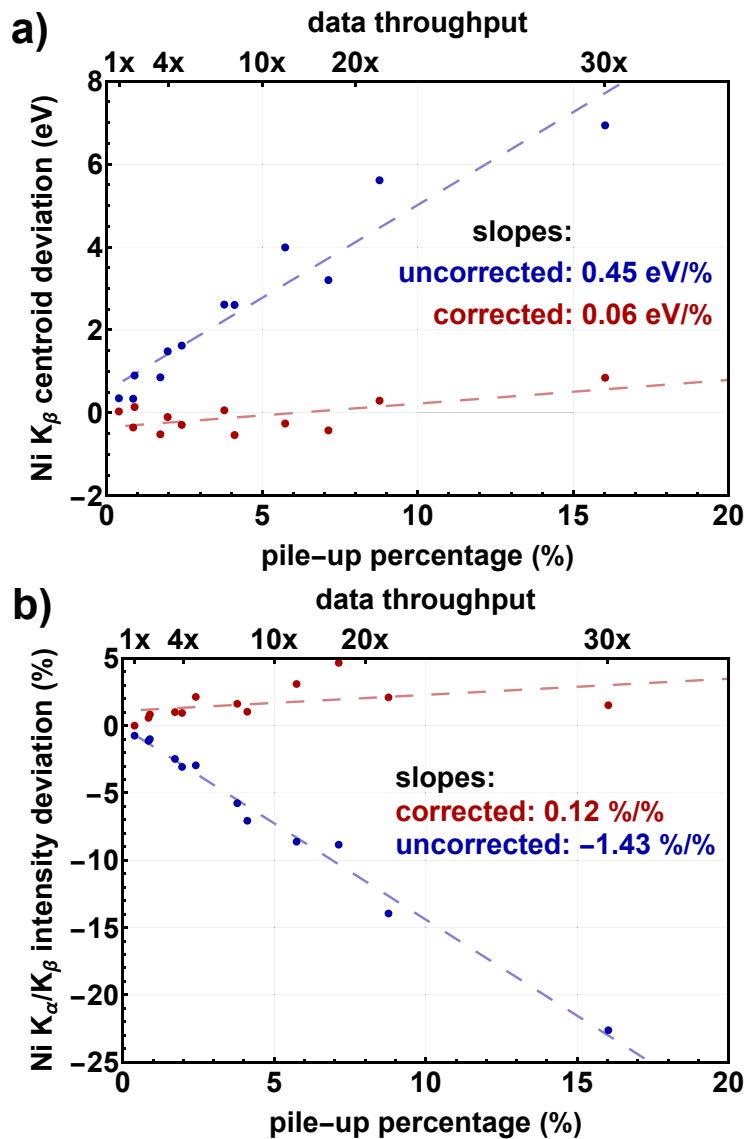


Figure 2.20: **Quantification accuracy improvement through pile-up correction.** a) Deviation of the Ni K_β peak centroid from the reference value is reduced by an order of magnitude with pile-up correction, leading to more reliable chemical shift measurements at high data throughput. b) The accuracy of Ni K_α/K_β intensity ratio is also improved by an order of magnitude, which implies more accurate elemental composition analysis under high data throughput scenarios.

2.7 Discussion

2.7.1 Complementarity of EDS and EELS for Chemical Analysis

The results presented in this chapter establish EDS as a viable platform for chemical shift analysis that is highly complementary to EELS across multiple dimensions: energy range, sample constraints, measurement stability, and cost.

In terms of energy range, EELS is only efficient with period 4 elements and below at commonly used accelerating voltages, with accessible edges limited by both the scattering cross-section and the collection angle constraints of the magnetic prism [41]. EDS, by contrast, can access transitions across the entire periodic table, with the only requirement being sufficient overvoltage (a factor of 2–5 times the transition energy) to efficiently excite the transition [43]. The W L lines measured in this work (7–10 keV) lie far beyond the practical range of EELS at 80 kV, yet EDS provides precise chemical shift information for these transitions. Similarly, the Ti K lines at 5 keV, acquired at 30 kV accelerating voltage, also represents information (high transition energy at low accelerating voltage) that is fundamentally inaccessible to EELS. The wide energy range accessible to EDS makes it particularly valuable for studying heavy elements, where EELS is fundamentally limited by scattering cross-sections. In semiconductor devices, where heavy metal interconnects, diffusion barriers, and contact materials are common, EDS chemical shift analysis could provide critical information about interfacial chemistry, oxidation states, and degradation mechanisms under operational conditions.

In terms of sample constraints, EELS requires thin electron-transparent samples ($t < 100$ nm) to maintain adequate SBR, as multiple inelastic scattering events rapidly degrade the spectral quality [39]. EDS is far more tolerant of sample thickness, as x-rays can escape from relatively thick specimens without significant energy loss. This makes EDS chemical shift analysis applicable to analyzing bulk samples in SEMs, such as nanoparticles on thick supports and device structures that cannot be thinned to be electron transparent. The

inelastic scattering that produces a problematic background in EELS actually contributes to greater x-ray generation, making it beneficial for EDS.

In terms of measurement stability, EELS spectra are defined optically through the magnetic prism, making them susceptible to drift from environmental magnetic fields and scan deflections. EDS spectra, in contrast, have a nearly imperturbable energy reference defined by the detector electronics, allowing spectra to be summed across arbitrary times and positions without energy misalignment. This stability is particularly valuable for chemical shift mapping, where spatial variations in transition energy must be reliably distinguished from instrumental artifacts.

Furthermore, when paired with EELS measurements of the same specimen, EDS transition energy measurements can be combined with EELS binding energy measurements to determine the binding energies of shells not directly accessible by either technique alone. This is demonstrated for the Al K-shell: combining the EDS Al K_α transition energy with the EELS Al $L_{2,3}$ binding energy yielded the Al 1s binding energy with ~ 30 meV precision, comparable to direct EELS measurements of the K edge. This synergistic approach extends the reach of electron microscopy-based spectroscopy to new parameter spaces without requiring higher accelerating voltages or advanced electron optics.

2.7.2 Signal-to-Background Ratio and Precision Limits

The precision of EDS chemical shift measurements is governed by two factors captured in Eq. 2.2.2: the Poisson statistics of photon counting and the asymptotic precision limit imposed by the SBR. The Poisson term $\sigma_p/\sqrt{N}$ can always be reduced by collecting more counts, but the SBR-limited term σ_0 represents a hard ceiling for a given experimental configuration.

The SBR is determined by the ratio of characteristic x-ray intensity to background intensity within the energy window of the peak. The background is dominated by Bremsstrahlung

x-ray at low energies and by the tails of neighboring peaks at high energies. For well-isolated peaks at high energies, $\text{SBR} > 10$ is easily achievable, and tens of meV precision is demonstrated (Fig. 2.3). However, for peaks in crowded spectral regions—such as W M_α at 1.8 keV, where the tail of W M_β peak contributes significantly to the background—the SBR is lower and the achievable precision is correspondingly degraded.

This precision limit, which depends on both the sample and the experimental configuration, constitutes the primary constraint on EDS chemical shift analysis. Because the typical peak width in EDS is ~ 100 eV, closely spaced peaks inherently overlap, making them difficult to measure precisely. Consequently, M- and N-shell transitions, where the energy separations are small, generally yield lower precision. In contrast, the more isolated K- and L-shell transitions can achieve excellent energy precision. This distinction further emphasizes the complementarity of EDS with EELS: EDS provides high precision for well-separated high-energy peaks, whereas EELS offers superior energy resolution for low-energy closely spaced edges.

2.7.3 Optimizing Data Throughput While Maintaining Accuracy

The corrected paralyzable detector model and associated pile-up correction algorithm provide a complete framework for optimizing EDS data acquisition across the competing demands of throughput, precision, and spectral purity. The traditional rule of thumb—operating at $D_\% \approx 63.2\%$ to maximize output rate—assumes an ideal paralyzable detector with instantaneous event discrimination. However, as shown in Fig. 2.17, the actual optimal condition depends sensitively on the ratio $n = \tau/t_{\text{dis}}$. For detectors with short dead times relative to the discriminator response time, the measured $D_\%$ at optimal throughput can deviate significantly from 63.2%.

More importantly, maximizing total output rate does not necessarily maximize the clean output rate, which is the relevant metric for most quantitative analyses. As n decreases, the pile-up percentage at the optimal clean-output condition increases (Fig. 2.17, blue curve).

Users must therefore balance the competing demands of throughput and spectral purity based on the requirements of their specific measurement. For elemental quantification with moderate accuracy requirements, a higher pile-up percentage may be acceptable if the pile-up correction is applied. For chemical shift measurements requiring sub-eV precision, minimizing pile-up is essential, though the correction algorithm substantially relaxes this constraint.

The post-acquisition pile-up correction algorithm provides a powerful solution to this trade-off. As demonstrated in Fig. 2.20, applying the correction can recover sub-eV peak energy accuracy and accurate intensity ratios even for spectra acquired with 16% pile-up, representing a 30-fold increase in data throughput compared to the near-ideal (0.4% pile-up) acquisition condition. This throughput improvement is transformative for practical EDS chemical shift analysis: measurement times that would otherwise require hours can be reduced to minutes, making routine chemical shift mapping and point measurements feasible.

2.7.4 Future Directions

Several avenues exist for extending the capabilities demonstrated in this chapter. It would be interesting to see, when paired with post-acquisition pile-up correction, how fast can EDS chemical shift mapping be done with a state-of-the-art high throughput SDD detector. If a 10-min acquisition is proven to yield a precise enough chemical shift mapping, then this would truly become a handy tool for chemical characterization.

In addition, the corrected paralyzable detector model provides a foundation for automated acquisition optimization. Knowing t_{dis} and τ for a given detector, the acquisition software could dynamically recommend the optimal dead time setting and input flux for a user’s specified requirements regarding precision, throughput, and acceptable pile-up percentage. This would eliminate the trial-and-error process currently used to optimize acquisition parameters and ensure consistent data quality across different users, instruments, and laboratories.

Finally, the corrected paralyzable detector model is general and applicable to any particle

detector that measures energy spectra with single-particle sensitivity and employs a similar event discrimination and pile-up rejection architecture. This includes not only EDS systems using SDDs but also high-purity germanium (HPGe) gamma-ray spectrometers [84] and scintillator-based SiPM detectors [85]. The model’s ability to independently determine both the discriminator response time and the pulse shaper dead time from simple count rate measurements makes it a valuable diagnostic tool for characterizing detector performance without requiring detailed knowledge of internal components.

2.8 Conclusion

This chapter has presented a comprehensive advancement of energy-dispersive x-ray spectroscopy for chemical shift analysis, encompassing both the experimental demonstration of sub-eV chemical shift detection across multiple material systems and the development of an improved detector model enabling high-throughput acquisition with minimal spectral artifacts.

Key achievements include:

1. Demonstration that EDS, despite having energy resolution (~ 140 eV at 8 keV) approximately two orders of magnitude larger than typical chemical shifts, can achieve sub-100 meV measurement precision through statistical averaging in the shot-noise-limited regime, with precision following $\sigma_{\text{precision}} = \sqrt{(\sigma_p/\sqrt{N})^2 + \sigma_0^2}$.
2. Systematic measurement of EDS chemical shifts in compounds of tungsten (five transitions spanning 1–10 keV, including W L_α , $L_{\beta 2}$, L_λ , M_γ , and M_2N_4), titanium (K_α and K_β transitions), and aluminum (K_α transition), demonstrating that EDS chemical shifts in transition energies can be either positive (up to +2.4 eV for Ti K_β) or negative (down to –2.6 eV for W L_λ), in contrast to the universally positive shifts observed in EELS binding energies. The sign and magnitude of the shift reflect the differential

perturbation of the two orbitals involved in the transition.

3. Chemical shift mapping across an Al metal-oxide interface with ~ 30 nm spatial resolution, showing three distinct chemical regions (oxide, mixed, metal) consistent with EELS measurements of the same area. Combining EDS Al K_α transition energy with EELS Al $L_{2,3}$ binding energy determined the Al 1s binding energy to be 1559.95 ± 0.03 eV (metal) and 1564.88 ± 0.04 eV (oxide), demonstrating that EDS can match EELS precision while accessing energy ranges and sample conditions inaccessible to EELS.
4. Development of a corrected two-parameter paralyzable detector model (Eq. 2.5.16) that accounts for the finite response time t_{dis} of the event discriminator, overcoming the systematic failure of the classic one-parameter model at short dead times. The complete event classification framework derives probabilities for distinct event categories.
5. Application of the corrected model to an Oxford X-MaxN 100TLE EDS detector, determining $t_{\text{dis}} = 0.479 \pm 0.002$ μs and accurate dead time values for all six processing time options. The model achieves excellent agreement with experimental data across all dead times while the classic model systematically fails at short dead times.
6. Derivation of optimal data acquisition conditions as a function of the dimensionless time constant ratio $n = \tau/t_{\text{dis}}$, showing that the traditional 63.2% dead time rule deviates increasingly from the true optimum as n decreases, and quantifying the trade-off between clean output throughput and pile-up contamination.
7. Implementation and validation of a post-acquisition pile-up correction algorithm that removes two-photon coincidence events from EDS spectra, demonstrated on both simulated and experimental NiO_x spectra. The correction improves Ni K_β peak centroid accuracy and Ni K_α/K_β intensity ratio accuracy by one to two orders of magnitude, and enables an order of magnitude increase in data throughput while maintaining sub-eV energy precision.

The corrected paralyzable detector model and pile-up correction algorithm together form a complete data acquisition and processing pipeline that dramatically improves the practicality of EDS chemical shift measurements. With a state-of-the-art EDS detector whose output rate can exceed one million counts per second, the data acquisition time for a chemical shift measurement can be reduced from hours to minutes. This throughput improvement, combined with EDS’s inherent advantages in sample compatibility, energy range, instrumental stability, and cost efficiency, positions EDS as a powerful and broadly accessible technique for nanoscale chemical analysis that is highly complementary to EELS.

The corrected paralyzable detector model is not unique to x-ray silicon drift detectors but is generally applicable to particle detectors that measure energy spectra with single-particle sensitivity, including HPGe gamma-ray spectrometers and scintillator-based SiPM detectors. Future work can focus on extending the chemical shift database to additional elements and compounds and developing automated acquisition optimization based on the corrected detector model. The implications for non-destructive chemical characterization of operating devices and in-situ experiments open substantial avenues for advancing our understanding of nanoscale chemistry and bonding in technologically relevant materials.

CHAPTER 3

Nanoscale Temperature Mapping via Transmission Kikuchi Diffraction Thermometry

This chapter is based on a preprint [86].

3.1 Introduction

As the relentless miniaturization of electronic devices pushes feature sizes into the nanometer regime, highly localized heat accumulation and dissipation cannot be adequately characterized by macroscopic thermal models and bulk material properties. Understanding these microscopic thermal dynamics is critical for maximizing the performance, reliability, and operational lifetime of next-generation microelectronics, particularly in applications ranging from high-performance computing to high-density power delivery. However, measuring temperature at the nanoscale remains a formidable metrological challenge that sits at the intersection of condensed matter physics, materials science, and electrical engineering. Traditional thermometry techniques are broadly classified into two categories: contact-based and non-contact methods, each presenting distinct limitations when applied to nanoscale systems under operational conditions.

Contact thermometries, such as scanning thermal microscopy (SThM), rely on direct physical interaction between a sensor probe and the device under test (DUT). In SThM configurations, a specialized atomic force microscope tip equipped with integrated thermocouples or resistive heaters is brought into intimate contact with the sample surface. Heat

transfer across this interface induces a measurable voltage or resistance change that correlates to local temperature through calibrated thermal conductance models [87]. While these techniques offer high sensitivity and can resolve sub-micron features, the physical contact inevitably perturbs the thermal equilibrium of the nanoscale system being measured. The probe itself acts as an additional heat sink, fundamentally altering the very temperature distribution it seeks to measure. Furthermore, signal interpretation is complicated by spatially varying thermal contact resistance that changes dynamically as the probe scans across topographically heterogeneous surfaces, introducing significant artifacts and systematic errors into reconstructed temperature maps [88]. Calibration procedures often require reference samples with known thermal properties, which may not accurately represent the complex material interfaces present in actual operating devices.

Non-contact thermometries circumvent sample perturbation by detecting temperature-dependent radiation without requiring physical interaction or introducing additional thermal pathways. Techniques such as infrared thermography [89], Raman spectroscopy [90], and fluorescence-based nano thermometry [91] collect emitted photons to infer local thermal states through established spectroscopic relationships. Although these methods preserve the native thermal environment and enable measurements on opaque bulk samples, their spatial resolution is fundamentally diffraction-limited by the optical wavelength of the collected light, typically restricting practical resolution to approximately $1\text{ }\mu\text{m}$. This fundamental limitation makes them unsuitable for resolving temperature gradients across modern nanoscale device architectures where critical features such as transistor channels, interconnect lines, and phase-change memory elements are often smaller than 50 nm . Consequently, there is a pressing need for non-contact thermometry techniques that combine sub-optical spatial resolution with high thermal sensitivity, fast acquisition speeds, and minimal system perturbation to enable in-situ characterization of operating nano devices.

Electron microscopes provide an exceptionally ideal platform for developing high-resolution non-contact thermometries due to their atomic-scale spatial resolution, versatile imaging

modalities, and compatibility with in-situ sample manipulation stages. Transmission electron microscopy (TEM), scanning transmission electron microscopy (STEM), and scanning electron microscopy (SEM) each offer distinct advantages and constraints for thermal mapping applications, necessitating careful consideration of experimental requirements when selecting the appropriate modality. In conventional TEM configurations, where samples are illuminated by a parallel electron beam spanning hundreds of nanometers to micrometers in diameter, temperature can be inferred from systematic variations in reciprocal-lattice vectors measured through high-resolution diffraction patterns [6, 7] or through analysis of the Debye-Waller effect [6]. The Debye-Waller effect quantifies the attenuation of coherent Bragg diffraction intensity due to atomic thermal vibrations, providing a direct relationship between scattering factor reduction and mean-square displacement of atoms. Despite their demonstrated high sensitivity capable of resolving sub-Kelvin temperature changes, TEM-based thermometries suffer from fundamentally limited spatial mapping capabilities because the parallel beam diameter typically exceeds 100 nm. This large illumination area effectively averages thermal information across extended device regions, preventing point-by-point temperature scanning and making it impossible to resolve localized hotspots or steep thermal gradients that characterize modern nanoscale devices.

In STEM and SEM configurations, a highly convergent electron probe is rastered across the sample surface in a controlled grid pattern, enabling sequential acquisition of thermal information at each beam position with independent spatial localization. STEM-based thermometries utilizing electron energy loss spectroscopy (EELS) can map temperature distributions with atomic-scale probes by analyzing the precise energy of the plasmon excitation, which exhibits a characteristic temperature-dependent shift [8, 92]. However, having atomic resolution in STEM-EELS does not imply having the same spatial resolution in the temperature measurement. The temperature being mapped is only well-defined at length scales larger than the mean free path (MFP) of primary heat carriers (usually phonons), which is typically a few nanometers or above depending on material properties. When probe sizes

approach or fall below these characteristic MFPs, thermal transport becomes inherently delocalized through ballistic rather than diffusive mechanisms, limiting well-defined temperature gradients to exist only across nanometer scale or above.

SEM-based thermometries offer compelling advantages that make them particularly attractive for practical device characterization: minimal sample preparation requirements compared to TEM/STEM techniques, wide field of view enabling mapping across entire device architectures, and straightforward electrical connections facilitating in-situ heating or biasing experiments. Electron backscatter diffraction (EBSD) has been successfully employed to detect temperature-induced changes through analysis of the Debye-Waller effect and thermal diffuse scattering patterns [9, 10]. Nevertheless, accurately quantifying inelastic scattering contributions remains experimentally challenging due to overlapping elastic and inelastic signal components, detector efficiency variations, and complex multiple scattering effects. Furthermore, the spatial resolution of conventional EBSD is fundamentally limited to approximately 100 nm by the large interaction volume generated when backscattered electrons emerge from bulk sample volumes, restricting its applicability for mapping thermal gradients across nanoscale features.

Transmission Kikuchi diffraction (TKD), a technique that collects forward-scattered electrons from electron-transparent thin films as the focused beam raster scans across the sample, overcomes many of these fundamental limitations while retaining compatibility with standard SEM platforms. TKD exhibits a significantly smaller interaction volume compared to conventional EBSD configurations, enabling sub-10 nm spatial resolution and substantially higher pattern quality due to reduced inelastic scattering and interaction volume within thin specimens [93, 94]. Building upon this robust experimental foundation, we introduce Kikuchi Diffraction Thermometry (KDTh), a novel non-contact method for mapping temperature distributions in an SEM that combines measurement speed, exceptional precision, and broad experimental accessibility. KDTh leverages the existing pattern-matching algorithms routinely used in crystal orientation determination to directly detect temperature- or stress-

induced lattice strain by systematically expanding the parameter space of cross-correlation-based indexing routines to include continuous lattice constant variations as optimization variables.

This chapter presents a comprehensive investigation into the theoretical foundations, experimental implementation, data analysis pipelines, and performance characteristics of KDTh. We demonstrate the technique’s capability to map nanoscale temperatures and strains on Joule-heated graphite devices with sub-pm precision in lattice parameter determination.

3.2 Theoretical Framework of Kikuchi Diffraction Thermometry

3.2.1 Principles of Electron Diffraction in SEMs

The physical basis of KDTh rests on the interaction between a focused electron probe and the crystalline lattice of a thin sample, resulting in the formation of Kikuchi diffraction patterns. When electrons with kinetic energy in keV range impinge upon a crystalline material, they undergo multiple scattering events characterized by both inelastic thermal diffuse scattering (TDS) and coherent Bragg diffraction. The combination of these scattering mechanisms generates Kossel cones, which intersect with the Ewald sphere to produce Kikuchi bands. These bands appear as projected lines on the detector plane and collectively form a geometric map that encodes information about crystal phase, orientation, and lattice parameters [95].

Unlike single-scattered electrons that form discrete Bragg spots in selected area diffraction patterns (SAED), multiple-scattered electrons generate the continuous Kikuchi bands observed in SEMs. The width of each Kikuchi band equals twice the Bragg angle (θ_B), which is directly sensitive to hydrostatic strain. Similarly, the angle between two intersecting Kikuchi bands corresponds to the interplanar angle between the respective lattice planes, making it sensitive to shear strain and anisotropic strain. Temperature and stress changes induce both types of strain simultaneously, manifesting as measurable shifts in band widths

and inter-band angles within the diffraction pattern.

The network of Kikuchi lines scattered from a focused electron probe (typically a few nanometers in diameter) in SEM provides information extending to the highest scattering angles, surpassing 1000 mrad. This extensive angular coverage is fundamentally inaccessible in TEMs or STEMs due to geometric and physical constraints. Atomic thermal motion and quantum zero-point vibrations introduce an uncertainty of $d_{DW} \sim 10$ pm in atomic positions [96,97]. These small positional variations produce correspondingly large momentum attenuation in coherent diffraction, limiting Bragg diffraction to scattering angles of $\lambda/d_{DW} \sim 200$ mrad. Furthermore, the bottom pole piece of TEM objective lenses restricts collection angles to $\theta_{max} \approx (D/2)/f \approx (0.4 \text{ mm}/2)/2 \text{ mm} \approx 100$ mrad, where D is the bore diameter and f is the back focal length of the lower objective lens [98]. In contrast, without a bottom pole piece limiting collection angles, SEMs allow the acquisition of electrons scattered at angles an order of magnitude greater than TEMs, corresponding to two orders of magnitude greater reciprocal space area.

Collecting high-angle scattered electrons is highly advantageous for phase identification, Euler angle measurements, and orientation mapping [99,100]. The wide reciprocal space field of view provided by SEM-based Kikuchi diffraction enables the detection of minute crystal structure changes. By fitting the entire Kikuchi pattern collectively rather than measuring individual lines, KDTh achieves precision in temperature and strain measurements that surpasses what has traditionally been possible with SEMs [9,10].

3.2.2 Collection Angles and Reciprocal Space Coverage

The efficiency of orientation determination and strain measurement in Kikuchi diffraction depends critically on the collection semi-angle (β) and the resulting reciprocal space field of view (FOV). Table 3.1 summarizes typical imaging conditions and reciprocal space coverage for 4D STEM, TKD, and X-ray diffraction configurations. In x-ray diffraction using Cu $K\alpha$ radiation ($\lambda = 154$ pm), the Ewald sphere radius is small compared to the captured angular

		convergence semi-angle α (mrad)	collection semi-angle β (mrad)	reciprocal space FOV radius ($\text{\AA}^{-1}$)	FOV radius/Ewald sphere radius
4D STEM (300 kV, $\lambda = 1.97$ pm)	parallel beam	0.5	40	2.0	3.9%
	strain mapping	5	30	1.5	3.0%
	high resolution	20	30	1.5	3.0%
TKD (30 kV, $\lambda = 6.98$ pm)		5	850	11	75%
XRD (Cu K_α , $\lambda = 154$ pm)		NA	1400	0.64	98.5%

Table 3.1: **Collection angle.** Typical imaging conditions and reciprocal space field of view for 4D STEM and TKD. In x-ray diffraction, the Ewald sphere radius (x-ray wavevector) is small compared to the diffraction space field of view. Multiple zone axis poles are seen simultaneously on a diffraction pattern. In TEM, a single zone axis pole is seen, but in TKD/EBSD the scattering angles are close to the Ewald sphere radius. TKD and EBSD are more similar to x-ray diffraction in the sense of having a high diffraction sphere coverage, and absolute orientation determination is possible with high efficiency.

range, allowing multiple zone axis poles to be observed simultaneously on a single diffraction pattern. Similarly, in TKD and EBSD, scattering angles approach the Ewald sphere radius, enabling orientation determination with high accuracy by capturing three or more pole regions simultaneously [99].

In contrast, TEM configurations typically capture only a single zone axis pole due to the limited collection angle imposed by the objective lens aperture and bottom pole piece geometry. Fig. 3.1 illustrates this limitation, showing that the angular range of Kikuchi lines accessible in a TEM is substantially smaller than those available in an SEM. The presence of at least three visible poles in SEM-based TKD/EBSD provides redundant geometric constraints that significantly improve the robustness and precision of pattern matching al-

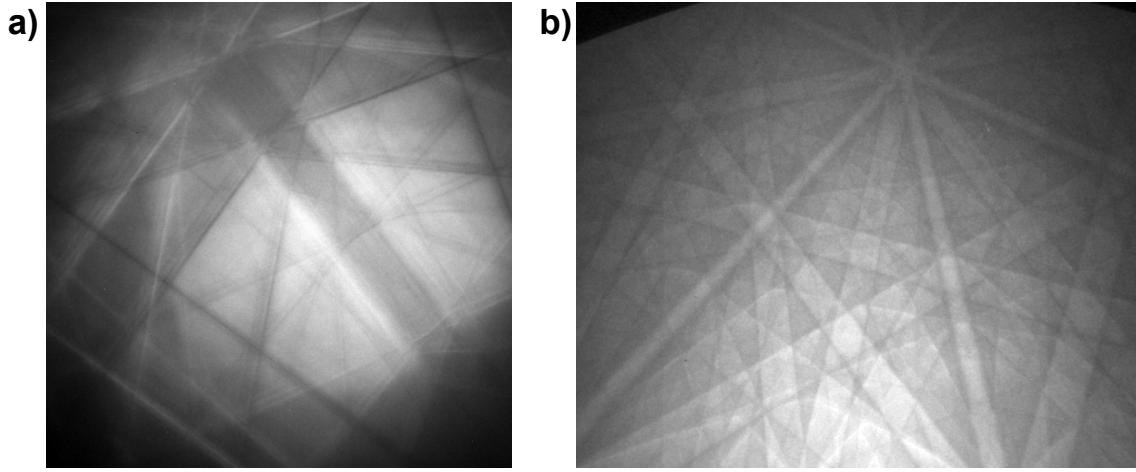


Figure 3.1: **Comparison of Kikuchi patterns acquired in TEM and in SEM.** a) Kikuchi pattern of copper acquired in TEM (FEI Titan 80-300) at 300 kV, only one major pole is fully captured. b) Kikuchi pattern of copper acquired in SEM (Helios G4) at 30 kV, multiple poles are visible.

gorithms.

The reciprocal space FOV radius for different techniques can be calculated based on the electron wavelength (λ) and collection semi-angle (β). For TKD operating at 30 kV ($\lambda = 6.98$ pm) with $\alpha = 5$ mrad and $\beta = 850$ mrad, the reciprocal space FOV radius reaches $11 \text{ \AA}^{-1}$, corresponding to a coverage of 75% relative to the Ewald sphere radius. This extensive coverage ensures that multiple Kikuchi bands intersect the detector plane simultaneously, providing abundant data points for cross-correlation optimization and lattice parameter refinement.

3.2.3 Cross-Correlation Pattern Matching vs. Hough Indexing Optimization

The core computational engine of KDTh is a cross-correlation-based pattern matching algorithm that searches for the best match between experimental TKD patterns and a library of simulated master patterns. A master pattern represents the diffraction sphere equal-

area projected onto 2D Cartesian coordinates, generated for a specific crystal structure. The normalized cross-correlation coefficient (NCC) ranges from -1 to $+1$ and quantifies the similarity between experimental and simulated patterns. Maximizing the NCC yields the optimal orientation and lattice parameter that best reproduce the observed diffraction features [101–103]. However, pure cross-correlation-based indexing is extremely computationally intensive and slow (a few patterns per second), making it impractical for mapping spatially and temporally varying signals in in-situ experiments.

Traditional Kikuchi indexing relies on the butterfly filter and Hough transform algorithm to enhance line contrast and detect Kikuchi bands, respectively. Developed by Lassen in 1994 [104,105], this approach calculates interplanar angles between detected bands (typically 6–12 bands) and compares them to a lookup table generated from candidate crystalline phases [99]. Crystal orientation is determined by minimizing the mean angular deviation (MAD), defined as the average interplanar angle mismatch between the experimental pattern and the candidate phase at a given orientation. While Hough indexing operates at high speed (thousands of patterns per second) on contemporary systems, it provides at best a fraction of the angular precision that cross-correlation method does, and it is insensitive to changes in Kikuchi band widths induced by hydrostatic strain.

To overcome these limitations while maintaining computational feasibility, we employ a hybrid two-step analysis routine. First, the Hough indexing algorithm determines the approximate phase and orientation, providing a starting point close to the optimal solution. This initial estimate dramatically reduces the number of iterations required for convergence in the subsequent cross-correlation optimization step. By combining the speed of Hough indexing with the precision of cross-correlation analysis, we can efficiently expand the parameter space beyond crystal orientation to include lattice constant variations without prohibitive computational overhead [106].

3.2.4 Fundamental Sensitivity Limits Imposed by Gun Brightness

The ultimate sensitivity of any electron-based measurement is constrained by the number of electrons available per unit time, quantified by the gun brightness (β_{gun} in A/m²/sr). In this section, we derive the fundamental sensitivity limits imposed by electron source brightness when performing physical measurements such as lattice parameter determination.

The current density on the specimen is given by:

$$J = \pi\alpha^2\beta_{gun} \quad (3.2.1)$$

where α is the convergence semi-angle and β_{gun} is the gun brightness. Assuming a diffraction-limited probe radius r :

$$r = \frac{0.61\lambda}{2\alpha} \quad (3.2.2)$$

Substituting Eq. 3.2.2 into Eq. 3.2.1 yields current density as a function of electron wavelength λ , probe radius r , and gun brightness β_{gun} :

$$J = \pi \left(\frac{0.61\lambda}{2r} \right)^2 \beta_{gun} \quad (3.2.3)$$

Rewriting with beam current I :

$$I = \left(\frac{0.61\pi\lambda}{2} \right)^2 \beta_{gun} \quad (3.2.4)$$

Using the definition of current $I = Ne/t$, where N is the number of electrons, e is the electron charge, and t is measurement time:

$$N = \left(\frac{0.61\pi\lambda}{2} \right)^2 \frac{\beta_{gun}t}{e} \quad (3.2.5)$$

For a measured physical quantity Q , sensitivity is defined as $S = \delta Q/\sqrt{B}$, where δQ is measurement uncertainty and $B = 1/t$ is bandwidth. Substituting t from Eq. 3.2.5:

$$S_{lim} = \delta Q\sqrt{t} = \delta Q \frac{2}{0.61\pi\lambda} \sqrt{\frac{Ne}{\beta_{gun}}} \quad (3.2.6)$$

For shot-noise-limited measurements where uncertainty follows Poisson statistics ($\delta Q = Q/\sqrt{N}$):

$$S_{\text{lim}} = \frac{2Q}{0.61\pi\lambda} \sqrt{\frac{e}{\beta_{\text{gun}}}} \quad (3.2.7)$$

Defining relative sensitivity $R = S/Q = 1/\sqrt{NB}$, the gun brightness limited relative sensitivity becomes:

$$R_{\text{lim}} = \frac{S}{Q} = \frac{2}{0.61\pi\lambda} \sqrt{\frac{e}{\beta_{\text{gun}}}} \quad (3.2.8)$$

S and S_{lim} have units of $[Q]/\sqrt{\text{Hz}}$, while R and R_{lim} are measurement-independent with units of $1/\sqrt{\text{Hz}}$. Therefore, R_{lim} serves as a standardized metric for comparing sensitivity limits across different electron gun types. The dashed lines in Fig. 3.8f represent relative sensitivity limits for various guns (W LaB₆, FEG, Cold FEG) at 100 keV, with brightness values sourced from Carter and Williams [3].

3.3 Experimental Methodology and Instrumentation

3.3.1 In-Situ Biasing Microchip Design and TKD Geometry

To demonstrate TKD strain and temperature mapping capabilities, we develop a custom in-situ biasing setup for an SEM (Helios G4 PFIB UXe DualBeam FIB/SEM). The sample holder is tilted at 20° relative to the electron beam axis, and an electron-transparent sample is mounted upside down on the back of the holder (Fig. 3.2). This inverted geometry ensures that the sample itself serves as the exit surface rather than the support membrane, significantly improving the quality and contrast of collected Kikuchi patterns [107].

The microchip is fabricated from a 200 μm -thick silicon wafer featuring a 20 nm-thick silicon nitride (SiN_x) membrane on each side. Electron-transparent windows are defined from the backside using optical lithography, followed by reactive ion etching (RIE) to remove SiN_x in corresponding regions. Silicon is subsequently removed from the backside using KOH wet etching, leaving the 20 nm-thick SiN_x on the top side to serve as a robust support membrane.

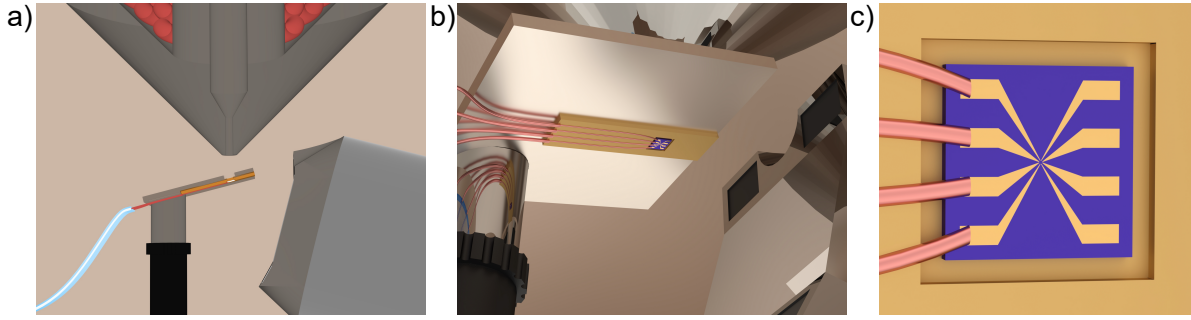


Figure 3.2: **Microchip Design and Electrical Connections.** The microchip holder with an electron transparent window. a) as shown in profile, b) from the underside of the holder, and c) a close-up of the chip.

Cr/Au electrodes are patterned on the front side via optical lithography and deposited using electron-beam evaporation. Electrical connections are established through a flexible ribbon cable attached to contact pads, enabling precise current sourcing during TKD acquisition (Fig. 3.2).

An Oxford Symmetry EBSD detector collects TKD patterns at a detector distance of 14.4 mm. The off-axis geometry provides an equivalent collection semi-angle of 740 mrad and covers a solid angle two orders of magnitude larger than achievable in TEMs. This wide collection angle ensures that multiple Kikuchi bands intersect the detector simultaneously, providing redundant geometric constraints for robust pattern matching and lattice parameter extraction.

3.3.2 Electron Probe Characterization and Aberration Analysis

Spatial resolution in SEMs and STEMs is determined by both the electron probe size and the beam spread within the sample. Understanding probe characteristics is essential for evaluating the theoretical limits of KDTh spatial resolution. The total probe size d_t can be

estimated using:

$$d_t = \sqrt{d_g^2 + d_d^2 + d_s^2 + d_c^2} \quad (3.3.1)$$

where d_g is the gun brightness-limited probe size, and d_d , d_s , d_c represent broadening due to diffraction limit, spherical aberration, and chromatic aberration, respectively [3]. d_g is primarily limited by the electron gun brightness β_{gun} (in the unit of A/m²/sr) and the convergence semi-angle α . From geometry, we know that

$$\beta_{gun} = \frac{I}{\pi(d_g/2)^2 4\pi \sin^2(\alpha/2)} \approx \frac{I}{\pi(d_g/2)^2 \pi \alpha^2} \quad (3.3.2)$$

where I is the beam current. From Eq. 3.3.2, we can derive

$$d_g = \frac{2}{\pi \alpha} \sqrt{\frac{I}{\beta_{gun}}} \quad (3.3.3)$$

We use a 64 μm condensing aperture and a 7.5 mm working distance, which gives a convergence semi-angle of $\alpha = (64 \mu\text{m}/2)/7.5 \text{ mm} = 4.3 \text{ mrad}$. All data are acquired on a Helios G4 PFIB UXe DualBeam FIB/SEM equipped with a Schottky field emission gun (FEG). The typical brightness of an FEG is $\beta = 10^{12} \text{ A/m}^2/\text{sr}$. With 1.3 nA beam current, $d_g = 5.3 \text{ nm}$.

The broadening terms are given by

$$d_d = \frac{0.61\lambda}{\sin \alpha} \quad (3.3.4)$$

$$d_s = 0.5 C_s \alpha^3 \quad (3.3.5)$$

$$d_c = C_c \frac{\Delta E}{E} \alpha \quad (3.3.6)$$

λ is the electron wavelength. C_s and C_c are spherical aberration and chromatic aberration, respectively. E and ΔE are the beam energy and energy spread, respectively. For modern SEM with FEG, the typical values are $C_s = 5 \text{ mm}$, $C_c = 5 \text{ mm}$, and $\Delta E = 0.7 \text{ eV}$ [3,108,109]. Beam energy from 15 to 30 kV is used for the data presented in the main text, which yields d_d around 1.0 to 1.4 nm, d_s and d_c around 0.2 to 1 nm. The total probe size d_t is dominated by the d_g term and is determined to be 5.6 nm.

3.3.3 Modeling Beam Spread: TKD versus EBSD

The spread of the electron beam inside the sample, which determines the effective sampling area for thermal information, is another factor that limits the spatial resolution of temperature mapping. To quantify the beam spread, we performed Monte Carlo simulations using CASINO V2 software [110] comparing TKD and EBSD configurations under identical illumination conditions.

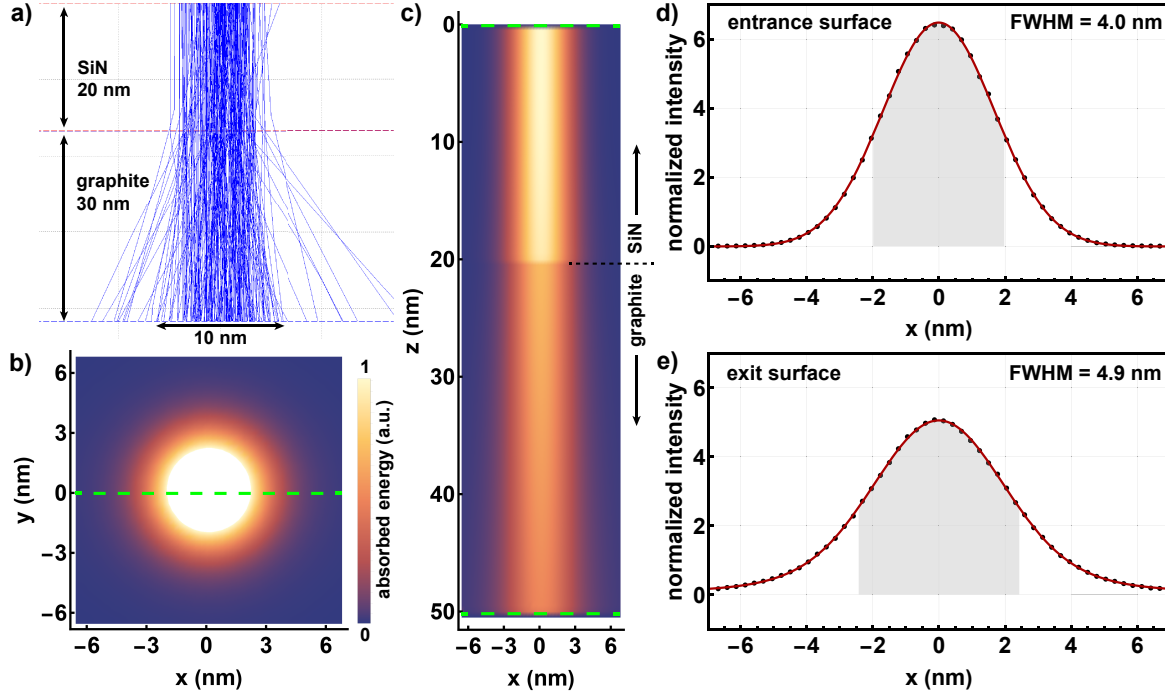


Figure 3.3: **TKD interaction volume.** a) Trajectories of incident electrons hitting a 30 nm graphite flake on a 20 nm SiN_x membrane. The sample is loaded upside down to allow the graphite being the exit surface. b, c) Absorbed energy of the specimen projected onto xy-plane and xz-plane, respectively. The green dashed lines indicate where the line profiles in d, e) are taken. d, e) Line profile of the electron probe intensity at the entrance surface and the exit surface, respectively. The shaded area highlights the FWHM of the beam.

For the TKD simulation, we adapted our actual sample geometry: a 30 nm graphite flake supported on a 20 nm SiN_x membrane. The 20 keV incident electron beams have an initial diameter of 5.5 nm and are set perpendicular to the sample surface for simplicity in modeling. The ignored 20° sample tilt introduces an underestimation of beam spread to within 10%. Trajectories of 10 million electrons are generated to map absorbed energy from inelastic scattering.

Fig. 3.3 illustrates the TKD interaction volume. Beam spread effects are confined to the 10-nm scale, with absorbed energy projected onto xy- and xz-planes showing tight confinement around the incident beam path. Line profiles of electron probe intensity at the entrance surface (FWHM = 4.0 nm) and exit surface (FWHM = 4.9 nm) confirm minimal lateral spreading through the thin film. By fitting a Voigt distribution to account for both initial Gaussian beam profile and limited spreading, the spatial resolution is quantified as 4.9 nm at the exit surface using the full-width at half-maximum (FWHM) standard.

In contrast, EBSD simulations model a bulk graphite flake $5\text{ }\mu\text{m}$ thick in the z-direction and $8\text{ }\mu\text{m}$ wide in the xy-plane. Backscattered electrons are generated throughout a large 3D volume, with beam diameter varying by orders of magnitude at different depths. Fig. 3.4 shows that electron trajectories extend beyond $1\text{ }\mu\text{m}$ laterally. To account for BSE generation from depth, we consider the distribution of backscattered electron counts as a function of maximum penetration depth (Fig. 3.4d). A weighted-average line profile extracted from the top $2\text{ }\mu\text{m}$ of the sample yields an FWHM of 97 nm (Fig. 3.4e), fitted to a double Gaussian distribution representing both tight incident beam and wide-spread deep material interactions.

A separate note is that even though FWHM is commonly used for determining the spatial resolution, the areal intensity of the beam spreads faster than it does in the 1D line profile. The discrepancy between the 1D line profile and 2D areal intensity simply arises because the intensity at a given radius is proportional to dr and rdr , respectively. A more representative beam diameter can be defined as the diameter enclosing 75% of areal intensity (rather than

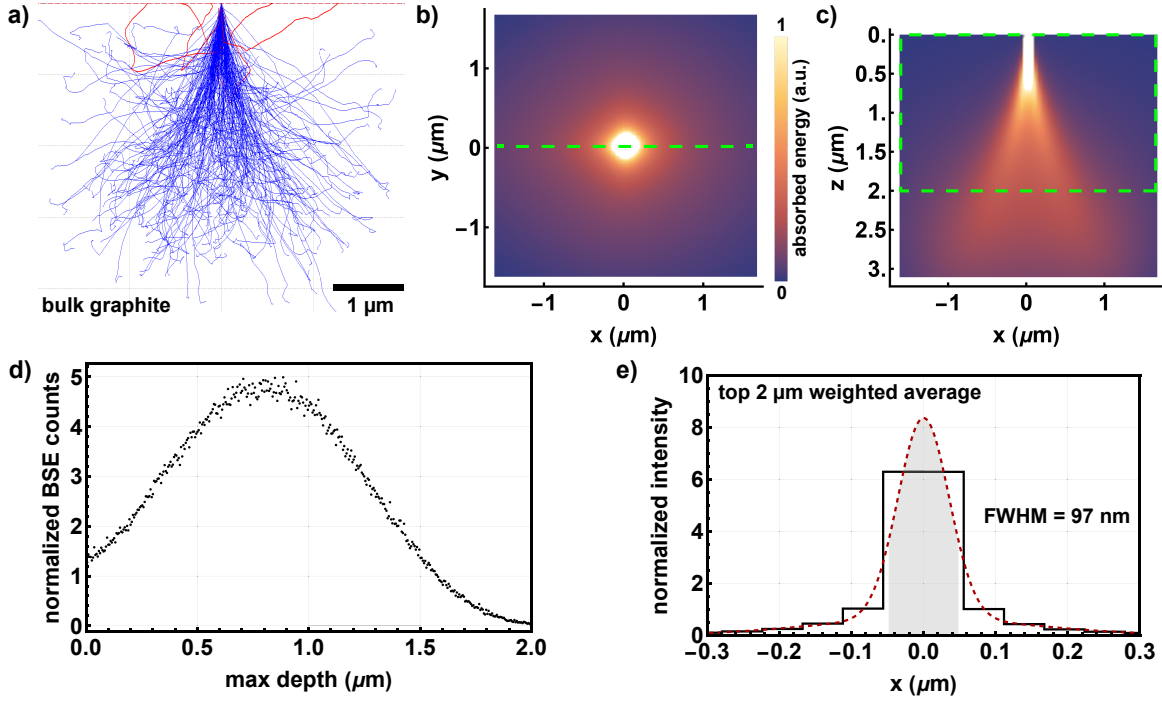


Figure 3.4: **EBSD interaction volume.** a) Trajectories of incident electrons hitting bulk graphite flake for EBSD analysis. b, c) Absorbed energy of the specimen projected onto xy-plane and xz-plane, respectively. The green dashed line and square indicate where the weighted-average line profile in e) is extracted from. d) Normalized backscattered electron (BSE) counts as a function of the max depth reached by the BSE before ejecting from the top surface. e) Normalized BSE intensity from the top 2 μm graphite, weighted averaged along the z direction based on d). The shaded area highlights the FWHM of the distribution.

using the 1D FWHM which encloses 75% intensity in a line profile). For reference, the diameter of the incident beam that encloses 75% areal intensity is 5.5 nm, consistent with the setup of the incident beam (vs. a 4.0 nm diameter shown in Fig. 3.3d that encloses 75% intensity in 1D).

By the areal intensity standard, the TKD beam diameter is 16 nm, compared to 380 nm for EBSD. Under identical imaging conditions, TKD offers improvements exceeding an order

of magnitude in spatial resolution by both FWHM and areal standards. This dramatic reduction in beam spread enables KDTh to resolve temperature gradients across features that would be averaged out in conventional EBSD measurements, taking full advantage of the nanometer spatial resolution of SEMs.

3.4 Results and Analysis

3.4.1 Strain Mapping on MoS₂ Flakes

Before demonstrating temperature mapping capabilities, we validate the lattice parameter and strain measurement precision of our TKD pipeline using an exfoliated MoS₂ flake dry transferred onto an electron-transparent SiN_x window (Fig. 3.5b). Electrons with 20 keV kinetic energy are focused to form a probe with 4.3 mrad convergence semi-angle. Scanning proceeds with a step size of 72 nm and a dwell time of 49 ms per pixel. The acquired TKD map is first indexed using Oxford AZtecHKL software employing the Hough indexing algorithm, which rapidly determines phase and approximate orientation across the entire field of view. The Hough indexing algorithm returns a uniform (0001) orientation across the MoS₂ flake as expected for exfoliated hexagonal crystals. The [0001] zone axis is positioned below the bottom of the detector image (outside the field of view), while the (1 $\bar{1}$ 00) band is clearly visible and highlighted in diffraction patterns (Fig. 3.5c,d). This initial indexing step provides a robust starting point for subsequent refinement.

To extract precise lattice parameter variations, we extend the cross-correlation-based pattern matching routine to include lattice constant as an optimization parameter. A library of master patterns is generated for the target crystal structure (hexagonal MoS₂, space group No. 194, P6₃/mmc) with systematically varied out-of-plane lattice constants spanning 60 pm around the expected room-temperature value. The master patterns are dynamically simulated in Oxford MapSweeper following the routine described by Winkelmann et al. [111] For each experimental TKD pattern, the orientation is optimized for every master pattern

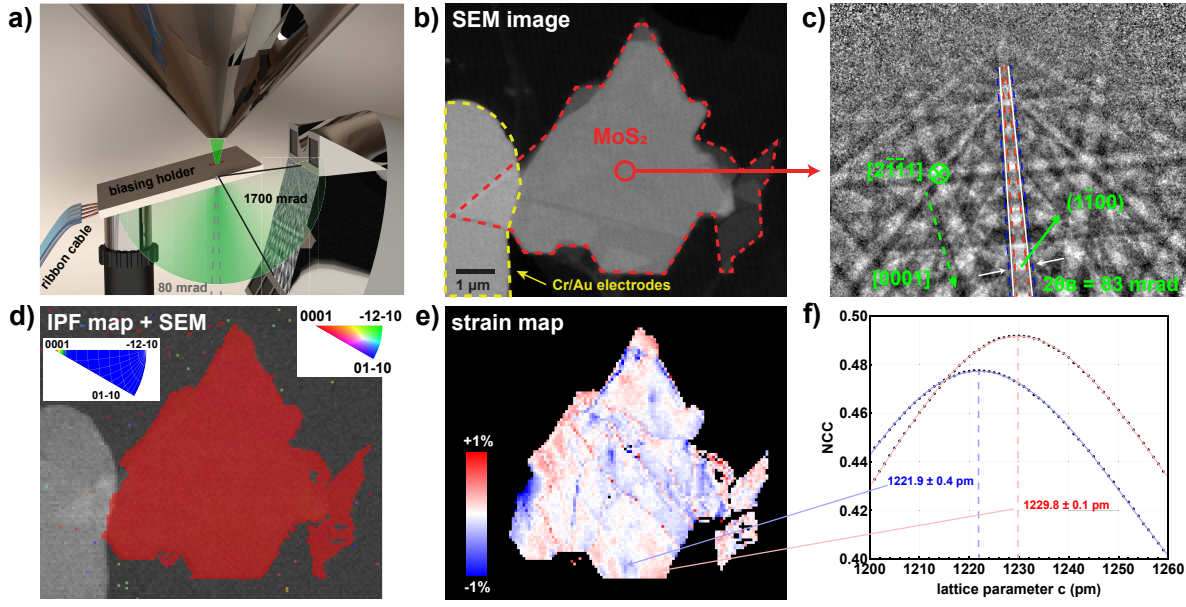


Figure 3.5: **Strain mapping with TKD.** a) Diagram of *in-situ* biasing setup in the SEM chamber. The sample is attached to the back of the holder, and the electrical connection is established through a ribbon cable (Fig. 3.2). The setup utilizes an off-axis TKD detector geometry. The black solid lines and gray dashed lines indicate collection angles for typical TKD and 4D-STEM systems, respectively. b) SEM image of a MoS₂ flake collected by forward-scatter detectors. c) A TKD pattern from the middle of the MoS₂ flake. A high-symmetry zone axis [0001] is at the bottom of the pattern outside of the collection region. The band highlighted with solid white lines corresponds to the family of lattice plane (1 $\bar{1}$ 00). The width of the Kikuchi bands varies with strain, with red and blue dashed lines indicating the directions of change that correspond to positive and negative strain respectively. d) Inverse pole figure (IPF) map overlaid with SEM image and IPF (inset) showing (0001) alignment. e) Strain map of the MoS₂ flake. f) Normalized cross-correlation coefficient (NCC) plot from two different pixels in e), the position of the max NCC is the best fit lattice parameter.

in the library with dynamic template matching (DTM, a cross-correlation based pattern matching algorithm [106] using Oxford MapSweeper, and the NCC of the best-matching orientation for each lattice constant is recorded.

Plotting the maximum NCC as a function of corresponding lattice constant yields a characteristic curve with a distinct peak (Fig. 3.5f). We fit this NCC curve to a Gaussian function with a linear background and take the position of the maximum as the local lattice parameter at that beam position. This approach determines local variations in the out-of-plane lattice parameter c with sub-pm precision, which is subsequently converted to strain using standard elasticity relations (Fig. 3.5e). The map reveals deformation features invisible in the corresponding orientation map (Fig. 3.5d), demonstrating that lattice parameter variations can be resolved independently of crystal rotation effects.

The two-step analysis routine combines the speed of Hough indexing with the precision of cross-correlation optimization. Providing an initial orientation estimate close to the optimal solution dramatically reduces the number of iterations required for convergence, enabling efficient expansion of the parameter space beyond crystal orientation to include lattice constant variations without prohibitive computational overhead. This methodology forms the foundation of KDTh, allowing simultaneous determination of phase, orientation, and precise lattice parameters across extended device regions.

3.4.2 Temperature-Induced Thermal Expansion in Graphite

To demonstrate temperature sensitivity, we prepare a graphite flake connected to Cr/Au electrodes on a SiN_x electron-transparent window (Fig. 3.6a) and subject it to Joule heating using a Keithley 6430 source measure unit. TKD maps are acquired at three distinct power levels: 0 mW (room temperature baseline, Fig. 3.6b), 12.8 mW, and 25.6 mW. Applying the cross-correlation pipeline to these datasets yields strain maps revealing temperature-induced positive strain of approximately 0.5% due to thermal expansion (Fig. 3.6c).

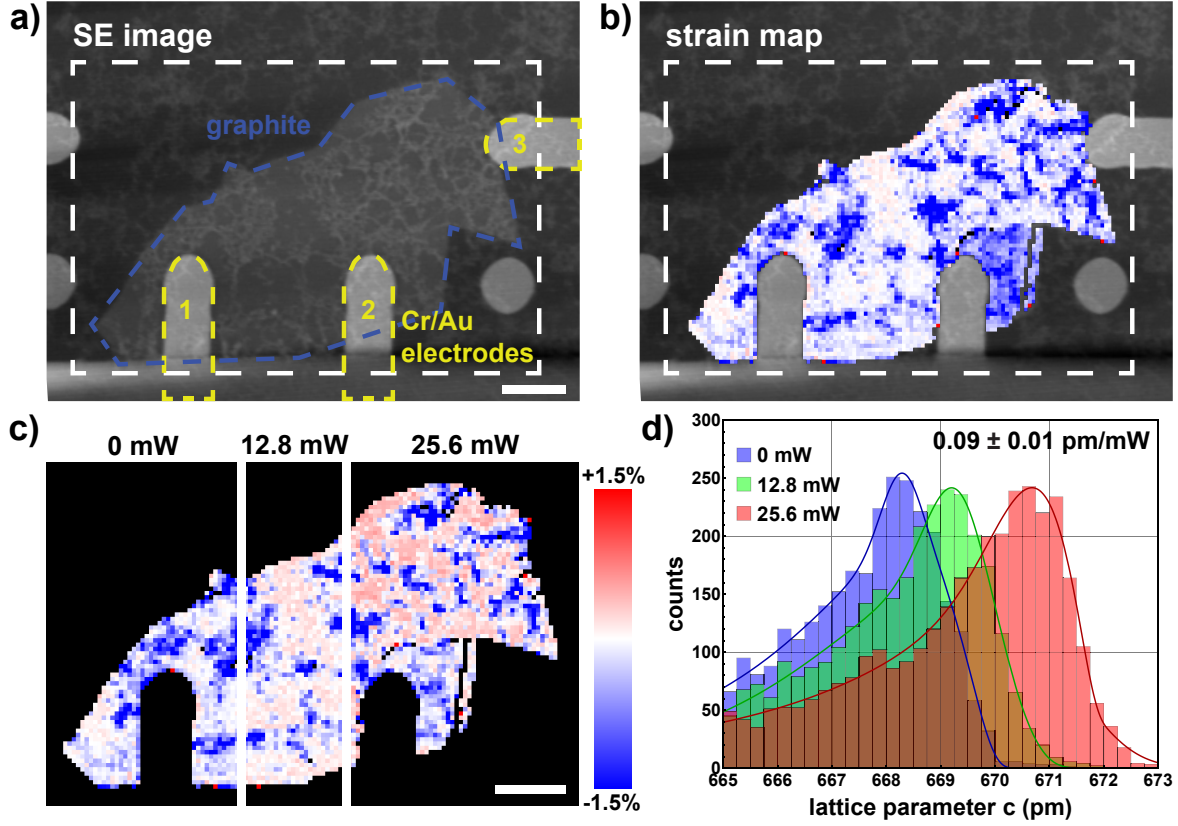


Figure 3.6: **Detection of thermal expansion.** a) SEM image of a graphite flake connected to three Cr/Au electrodes. Electrode 1 and 2 are used to bias the graphite flake. The white box highlights the region where TKD maps are acquired. b) Strain map of the graphite flake without electrical bias, overlaid on the SEM image. c) Strain maps of the graphite flake at different applied heating powers (see Fig. 3.7 for complete maps). The strain increases with applied power due to thermal expansion. d) Histogram of lattice parameter c measured at different heating powers. All scale bars are $5\mu\text{m}$. The color bar applies to both b) and c).

Histograms of the graphite lattice parameter c measured at different heating powers show a significant right-hand shift as power increases (Fig. 3.6d). Quantitative analysis reveals that for every mW power sourced, the lattice parameter c expands by 0.094 ± 0.009 pm, corresponding to $0.0140 \pm 0.0013\%/mW$ temperature-induced strain. Considering the out-of-plane Young's modulus of graphite (36.5 GPa [112]), we determine the thermal stress to be 5.1 ± 0.5 MPa/mW.

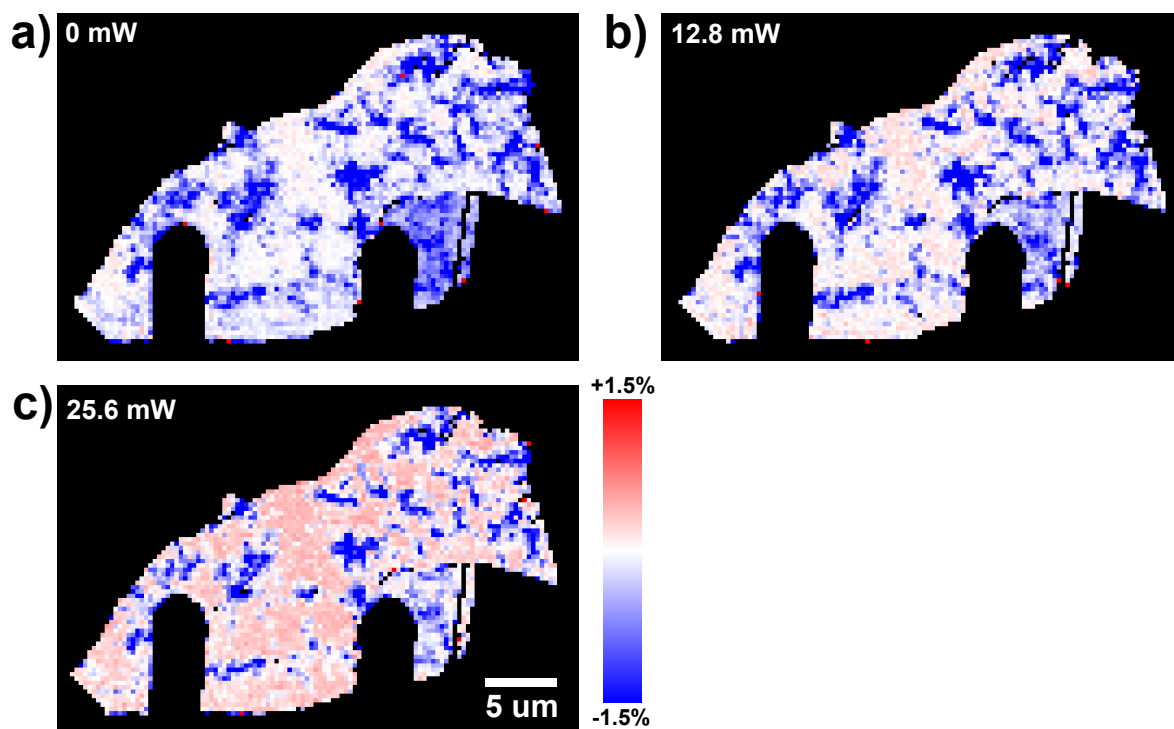


Figure 3.7: **Complete strain maps for Fig. 3.6c.** As heater power increases, a positive strain induced by thermal expansion is observed.

3.4.3 Dynamic Temperature Tracking Under Stepped and Continuous Power Ramps

To evaluate temperature mapping capabilities, we perform experiments where heating power is varied during single TKD acquisitions. In the stepped power experiment (Fig. 3.8), we source 50 mW prior to the start of the acquisition, then step down by 10 mW every two to three minutes until reaching 0 mW. The resulting temperature map shows six distinct horizontal stripes parallel to the SEM’s fast scan direction, each corresponding to a different heating power level (Fig. 3.8b). Row-averaged profiles confirm uniform temperature within each stripe and clear correspondence between the measured temperature and the applied power (Fig. 3.8e).

Temperature changes near the graphite edges show lower values due to proximity to heat sinks (Cr/Au electrodes) or negative strain from edge warping ($\sim 0.1\%$). These effects produce the characteristic roll-off observed at acquisition boundaries. Linear regression of the temperature change against the applied power yields a conversion factor of 2.7 ± 0.2 K/mW (Fig. 3.8d) using the known coefficient of thermal expansion for graphite ($\alpha_c \approx 25$ ppm/K) [127–129].

In continuous ramp experiments (Fig. 3.9), we supply 70 mW through a graphite flake initially, maintain it for three minutes, decrease to 0 mW, hold at room temperature for two minutes, then ramp back to 70 mW. The row-averaged lattice parameter tracks the varying power with sub-pm sensitivity, corresponding to strain precision on the 0.01% level (Fig. 3.9b). Histograms of lattice parameters show two well-resolved peaks at 0 mW and 70 mW separated by 1.86 ± 0.02 pm, corresponding to a temperature difference of 101 ± 1 K (Fig. 3.9c).

The measured temperature exhibits linear dependence on heating power (1.5 ± 0.1 K/mW), consistent with Fourier’s law of heat conduction (Fig. 3.9d). The ramp-down branch shows excellent linearity, while the ramp-up branch exhibits slight disturbance from temperature-

independent strain near electrodes. A small (~ 10 K) temperature difference between the two 70 mW regions is attributed to spatial thermal gradients across the flake. The bottom half of the field of view lies closer to the electron-transparent window edge, where sample thickness rapidly increases to 200 μm due to the silicon substrate acting as a room-temperature heat sink. Considering sample geometry and in-plane thermal conductivity of graphite, the heat flow corresponding to this 10 K difference is approximately 1 mW, aligning with theoretical expectations.

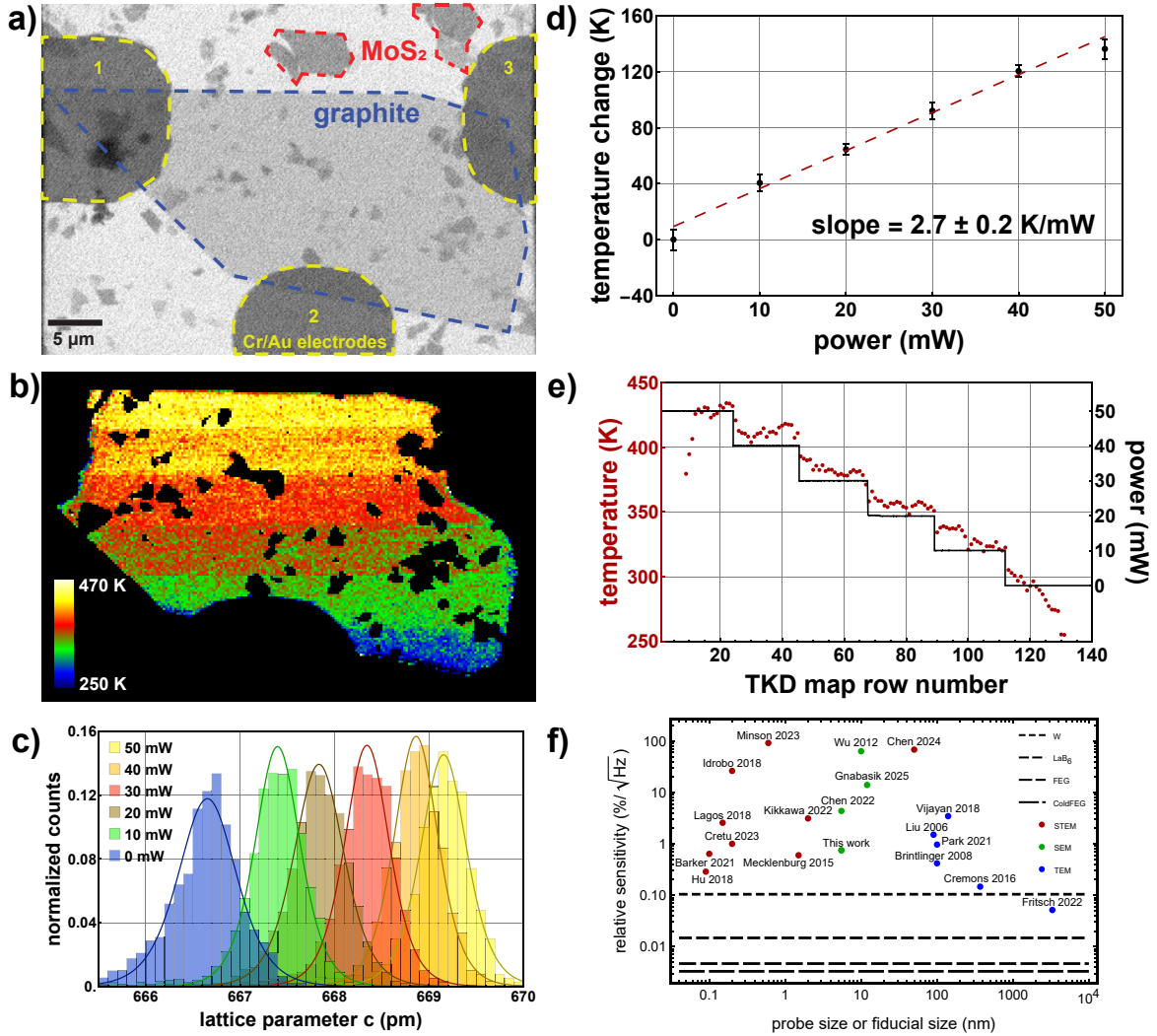


Figure 3.8: **In-situ temperature mapping while stepping the power.** a) A graphite flake connected to three Cr/Au electrodes. MoS₂ flakes scattered around the window are ignored in this study. b) Temperature map of the graphite flake while the heating power is varied six times during a TKD scan. The six different temperatures are visually distinguishable. c) Histogram of the measured lattice parameter c for the six different regions in b). The peaks correspond to different heating powers are clearly separated. d) Temperature change as a function of biasing power. e) Row-average temperature plotted with corresponding heating power. f) A summary of temperature measurements done in electron microscopes [6–10, 113–126]. The dashed lines represent relative sensitivity limit for different types of electron guns (see Section 3.2.4 for details).

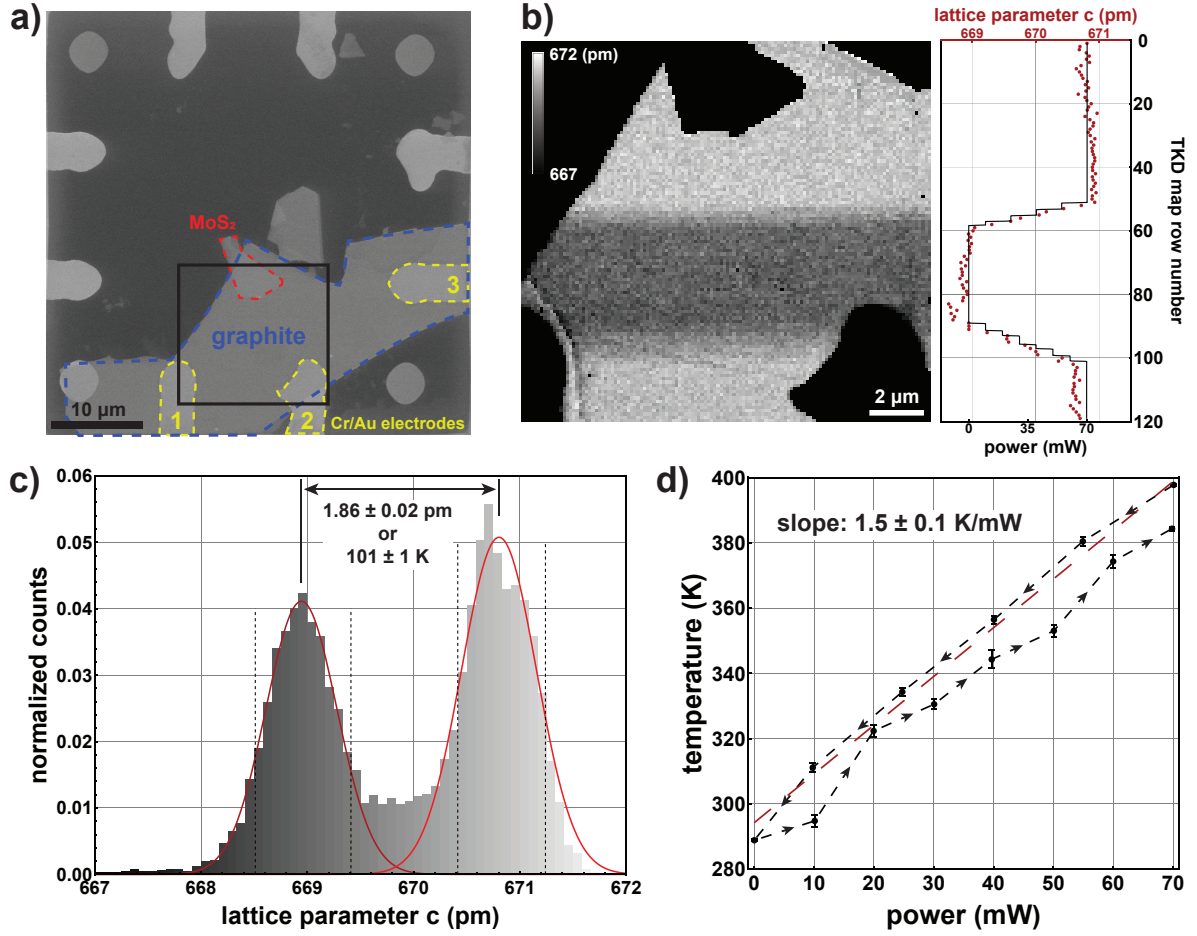


Figure 3.9: **Continuous temperature ramp.** a) SEM image of a graphite flake in contact with three Cr/Au electrodes. The black rectangle indicates the field of view where TKD mapping is performed. b) A map of lattice parameter c of the graphite flake derived from the TKD map as the heating power varies. The row-average of the lattice parameter tracks the varying heating power, indicating the temperature induced thermal expansion. c) Histogram of b). The two peaks, corresponding to 0 mW and 70 mW, respectively, are separated by 1.86 ± 0.02 pm, which corresponds to a temperature difference of 101 ± 1 K. The dashed lines indicate the fit window around each peak, and the red curves represent fits to a Gaussian distribution. d) Temperature versus heating power. The temperature change induced by Joule heating is 1.5 ± 0.1 K/mW. Black arrows indicate the chronology of the power ramp.

3.5 Discussion

3.5.1 Temperature Sensitivity and Spatial Resolution

Temperature sensitivity and spatial resolution constitute the two critical parameters for evaluating thermometry technique performance. For Fig. 3.8 data, we achieve a temperature uncertainty of $\delta T = 14$ K per acquired TKD pattern with 24-ms exposure time, yielding temperature sensitivity of $2.2 \text{ K}/\sqrt{\text{Hz}}$ (or relative sensitivity of $0.75\%/\sqrt{\text{Hz}}$, see Section 3.2.4). This matches the sensitivity achieved with TEM-based techniques (Fig. 3.8f).

Comparing various thermometry techniques, the 5.5 nm probe size in this work is superior to TEM mode techniques using parallel beams or fiducial markers [6, 7, 113–116], but it is eclipsed by STEM-based thermometries utilizing atomic-scale probes [8, 119–126]. However, actual spatial resolution of temperature mapping depends critically on phonon mean free path and beam spread, which relate to material properties, sample thickness, and electron beam energy.

Phonon mean free paths in different materials typically range from a few nanometers to several micrometers; therefore, sub-nanometer probe sizes achievable in STEMs provide none-to-marginal improvement in spatial resolution for temperature mapping. Among SEM-based techniques, EBSD generally exhibits beam spreads of $0.1\text{--}1 \mu\text{m}$, severely limiting spatial resolution. TKD achieves beam spreads less than 10 nm by collecting transmitted electrons through thin samples (<100 nm). The beam spread of our setup is estimated to be $5\text{--}16$ nm (Section 3.3.3), approaching the smallest possible feature size for temperature mapping in common materials, which is fundamentally limited by phonon mean free paths.

3.5.2 Comparative Analysis with High-Resolution EBSD and Other SEM Thermometries

Precise strain measurement using EBSD was first proposed by Wilkinson, Meaden, and Dingley in 2006 [130]. This technique, later termed high-resolution EBSD (HR-EBSD), measures zone axis shifts relative to a reference pattern and solves for strain components inducing such shifts. HR-EBSD demonstrates $\sim 0.01\%$ precision and sensitivity to c/a ratio changes [131, 132]. However, because it only captures interplanar angle variations, HR-EBSD remains insensitive to hydrostatic strain. Additionally, orientation optimization and strain measurement are performed as separate steps in HR-EBSD, meaning simultaneous optimization of lattice rotation and strain is not guaranteed.

KDTh overcomes these limitations by searching for the best match solution in a combined parameter space of crystal orientation and lattice constant, improving accuracy of both determinations while achieving $\sim 0.01\%$ precision in lattice constant determination. KDTh utilizes all information within Kikuchi patterns during optimization, making it sensitive to band width changes induced by hydrostatic strain.

Compared to other SEM-based thermometries, KDTh achieves superior temperature sensitivity ($2.2 \text{ K}/\sqrt{\text{Hz}}$) relative to Chen’s $21 \text{ K}/\sqrt{\text{Hz}}$ [118], Wu’s $170 \text{ K}/\sqrt{\text{Hz}}$ [9, 117], and Gnabasik’s $41 \text{ K}/\sqrt{\text{Hz}}$ [10] (Fig. 3.8f). Differences arise from platform choice (TKD vs EBSD), sample composition/crystal quality, technique methodology, and camera architecture. Wu and Gnabasik’s works rely on Debye-Waller effect and TDS quantification. While temperature measurement via TDS can be more general (applicable to non-crystalline materials as crystallinity is not required), all coherent scattering information that is temperature-dependent and possesses high signal-to-noise ratio remains unused in those approaches.

Before employing cross-correlation NCC optimization, two alternative attempts have been made to extract temperature information. The first is by measuring the line width of individual Kikuchi bands in butterfly-filtered Hough space [133]. Butterfly filter is critical

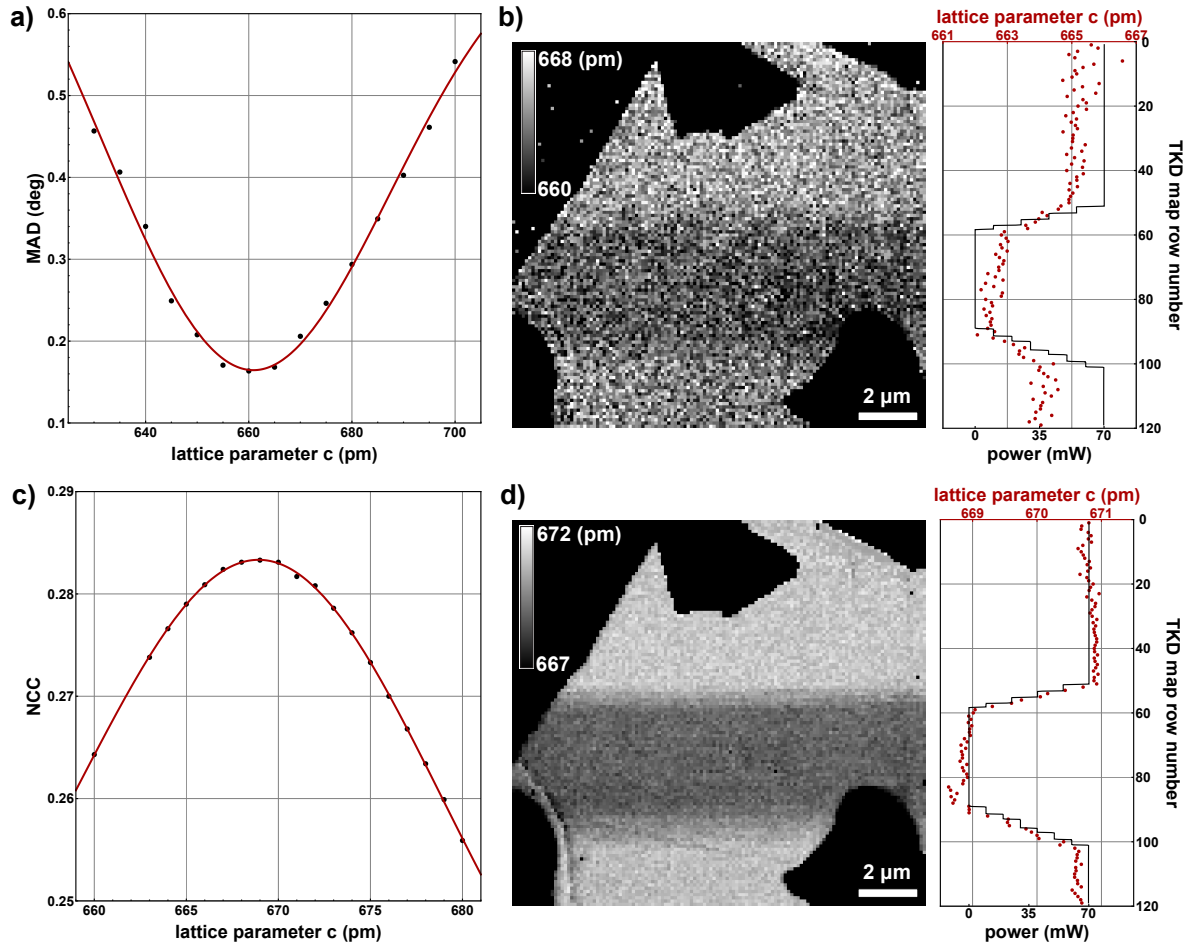


Figure 3.10: **Comparison of MAD and NCC optimization methods.** a) Minimizing MAD to determine the best fit lattice parameter using Hough indexing. b) Lattice parameter map generated with MAD minimization method shows a temperature signal corresponding to the drop of power in the middle of the acquisition. c,d) Same data processed with cross-correlation-based NCC optimization method shows good agreement with Hough MAD optimization method (0.3% temperature induced strain). However, NCC optimization yields an order of magnitude higher precision. Panel *d*) here is the same as Fig. 3.9b).

for improving SNR and facilitating Kikuchi band identification, but its own characteristic length convolves with the Kikuchi band width, complicating the extraction of actual

lattice parameters. The second attempt is employing Hough-indexing based MAD optimization [118]. Compared to cross-correlation pattern matching, Hough indexing yields one order of magnitude lower angular precision and is insensitive to Kikuchi band width changes. It therefore leads to a lower temperature sensitivity, $15 \text{ K}/\sqrt{\text{Hz}}$ for Hough vs $2.2 \text{ K}/\sqrt{\text{Hz}}$ for cross-correlation (Fig. 3.10). However, Hough indexing requires significantly less computational power. On contemporary TKD/EBSD systems achieving thousands of patterns per second via Hough indexing, real-time MAD optimization implementation remains feasible for scenarios prioritizing speed over ultimate precision.

3.5.3 Detector Architectures and Their Impact on Measurement Precision

Camera architecture represents a critical factor influencing KDTh sensitivity limits. Older EBSD/TKD systems utilize lens-coupled CCD cameras, which have largely been replaced by fiber-coupled CCDs. These systems offer decent read noise performance with large dynamic range (16-bit) but operate slowly compared to newer detector technologies.

Direct electron detectors operating in counting mode provide low dynamic range (and lower than CCDs in integrating mode) but deliver high speed and exceptional sensitivity. Recent studies indicate that electrons undergoing high energy loss yield lower band contrast, necessitating energy filtering to maintain Kikuchi pattern quality in counting mode [134]. Since EBSD/TKD often requires large beam currents for adequate pattern statistics, direct electron detectors are not always optimal solutions despite their advantages.

Hybrid-pixel detectors combine large dynamic range, high speed, and low read noise, potentially representing the best solution for future KDTh implementations, particularly at lower kV operations. However, widespread implementation remains limited by cost and availability. Future work should systematically evaluate how these advanced detector types improve precision in temperature and strain mapping measurements.

3.5.4 Sample Preparation Optimization and Data Processing Considerations

Beyond the fundamental methodology described above, two critical considerations can significantly enhance KDTh performance and measurement reliability. Sample preparation represents a foundational requirement that directly affects pattern quality and spatial resolution. Electron-transparent samples must be carefully fabricated to minimize thickness variations across the field of view while maintaining structural integrity. Significant variations in sample thickness lead to variations in inelastic scattering and electron coherence, which varies the Kikuchi pattern quality and potentially the band width. Minimizing sample thickness variation helps reduce potential systematic errors.

Pattern center (position on the detector plane that is the closest to the scan point on the sample) uncertainties are known to cause systematic errors in strain measurement [135]. For datasets presented in this work, the pattern centers are measured before acquisition and then refined during indexing. No measurable pattern center shift as a function of beam position is observed within a single map. Considering the 44 μm camera pixel size (Oxford Symmetry S2 detector at bin 2) and our sub-30 μm FOV, any projection center shift will be at sub-pixel level and only pose minimal influence on the strain measurements. But when applying this technique to larger FOVs (such as at mm level), pattern center shift needs to be carefully mapped to avoid artifacts.

3.5.5 Future Directions: Polycrystalline Samples and Extended Parameter Space Extraction

Kikuchi diffraction thermometry demonstrates high potential for extension to polycrystalline samples. Thanks to existing pipelines for phase and orientation mapping using Kikuchi patterns, KDTh proves easier to implement with polycrystalline materials than 4D STEM, where reliable pattern indexing remains a major challenge. However, characterizing polycrystalline samples containing extremely small grains (<10 nm) may remain the exclusive

regime of TEM-based techniques. Limited by SEM optics and interaction volume, TKD and EBSD can only easily resolve grains down to ~ 10 nm and several hundred nanometers, respectively [136, 137].

Moreover, KDTh provides a general methodology for adapting commercially available TKD/EBSD analysis pipelines for specialized research applications. By customizing the library of simulated patterns for pattern matching, structural information such as axial strain, shear strain, film thickness, or physical properties like the Debye-Waller factor can potentially be extracted simultaneously with temperature and orientation. The capability to measure temperature in microelectronic devices without destruction opens numerous avenues for further thermal investigation into heat transport mechanisms, dissipation pathways, and reliability assessment under operational conditions.

3.6 Conclusion

This chapter has presented a comprehensive development and validation of Kikuchi Diffraction Thermometry (KDTh), a novel non-contact method for mapping nanoscale temperatures and strains in scanning electron microscopes. By expanding the parameter space of cross-correlation-based TKD indexing pipelines to include lattice constant variations, we demonstrated precise detection of temperature-induced thermal expansion on micrometer-scale graphite devices with sub-pm precision in lattice parameter determination. The technique establishes a robust foundation for future nanoscale thermal characterization studies.

Key achievements include:

1. Development of a two-step indexing routine combining Hough phase/orientation determination with cross-correlation NCC optimization for simultaneous orientation and lattice parameter extraction.
2. Demonstration of $\sim 0.01\%$ strain measurement precision.

3. Achievement of a temperature sensitivity of $2.2 \text{ K}/\sqrt{\text{Hz}}$ in SEM while reaching highest useful spatial resolution for temperature mapping. The temperature sensitivity achieved surpasses all existing SEM techniques and is on par with TEM-based techniques.
4. Quantification of beam spread via Monte Carlo simulations showing TKD offers over $10\times$ improvement over EBSD (5–16 nm vs 97–380 nm by FWHM/areal standards).
5. Successful tracking of dynamic temperature changes under both stepped and continuous power ramps with linear response consistent with Fourier heat conduction theory.

KDTh operates in both transmission (TKD) and reflection (EBSD) modes, offering flexibility for different sample geometries and resolution requirements. The technique’s compatibility with commercially available SEM platforms, minimal sample preparation requirements, and ability to provide concurrent crystalline phase, orientation, strain, and temperature information make it a powerful tool for nanoscale thermal metrology in microelectronic devices.

Future work can focus on extending KDTh to polycrystalline materials, optimizing detector architectures (hybrid-pixel detectors), exploring real-time processing capabilities via algorithmic acceleration, and extracting additional physical parameters such as Debye-Waller factors through customized simulation libraries. The implications for non-destructive thermal characterization of operating electronic devices open substantial avenues for advancing our understanding of nanoscale thermodynamics and improving device reliability in next-generation technologies.

CHAPTER 4

Predicting Ferroelectric Memory Scalability via STEM EBIC Imaging of Switching Heterogeneity

4.1 Introduction

Ferroelectric hafnium oxide (HfO_2) and its derivative compounds, particularly hafnium zirconium oxide (HZO), have emerged as leading candidates for next-generation non-volatile memory technologies due to their compatibility with complementary metal–oxide–semiconductor (CMOS) processing and excellent endurance [138–142]. By replacing the dielectric material in a one-transistor-one-capacitor (1T1C) dynamic random-access memory (DRAM) cell with ferroelectric HZO, logical states can be stored as nonvolatile polarization states, extending the refresh interval from milliseconds to hours and enabling reduced power consumption [143–145]. The discovery of ferroelectricity in silicon-doped HfO_2 [138] and the subsequent demonstration that its orthorhombic $\text{Pca}2_1$ phase is responsible [139] have triggered an intense research effort spanning material science, device engineering, and process integration.

As ferroelectric random-access memory (FeRAM) cells are scaled down to sub-micrometer dimensions to increase storage density, the statistical variation of ferroelectric properties becomes a critical failure mechanism [11, 146–149]. At these scales, switching behavior is no longer governed by bulk averages but by the clustering of switchable domains and local variations in coercive fields [12]. A ferroelectric film with a nominal remanent polarization of $20 \mu\text{C}/\text{cm}^2$ may contain regions where the local coercive field exceeds the operating voltage

or where domains are pinned and cannot switch. When the device dimensions approach the characteristic size of these heterogeneous regions, device-to-device variability increases dramatically, and the yield—defined as the fraction of devices that meet the minimum switched charge requirement—can drop precipitously.

Standard transport characterization techniques, such as macroscopic positive-up negative-down (PUND) measurements [150] or first-order reversal curve (FORC) measurements, provide polarization loops and coercive field distributions that are ensemble-averaged over the entire capacitor area [151–156]. Although these techniques reveal heterogeneity in the aggregate—for example, through the width of the coercive field distribution—they do not reveal how ferroelectric properties vary from place to place. Consequently, predicting how yield varies with scaling based solely on macroscopic transport measurements is fraught with difficulty: the ensemble-averaged parameters may suggest adequate switched charge at a given operating voltage, while local variations cause individual devices to fail. There is a pressing need for characterization techniques capable of spatially resolving switching thresholds and polarization distributions at nanometer length scales in real devices.

Several microscopy techniques have been applied to map ferroelectric properties with spatial resolution. Piezoresponse force microscopy (PFM) [157, 158] is a variant of atomic force microscopy (AFM) that scans a conductive probe across the test specimen while applying a time-varying voltage and detecting the piezoelectric response. PFM can map ferroelectric domain patterns with sub-micrometer resolution and has been extensively used to study HfO_2 -based ferroelectrics. However, to achieve sub-100 nm resolution with PFM, it is often necessary to remove the top electrode—a destructive act that clouds subsequent interpretation of the results in terms of the original device behavior [159–162]. The top electrode plays a crucial role in clamping the ferroelectric film, providing mechanical confinement, and setting the electrostatic boundary conditions; removing it fundamentally alters the system under study.

Atomic-resolution transmission electron microscopy (TEM) can map ferroelectricity by

locating the atomic displacements associated with dipole switching [13,14]. Such high spatial resolution comes with a correspondingly small field of view. Moreover, atomic resolution can only be achieved by imaging cross-sections that must be extracted from the original device through focused ion beam (FIB) milling or similar destructive preparation. Because the sample areas are necessarily small and the sample preparation is necessarily destructive, TEM also struggles to link the microscopic properties it images with the original device’s dynamic electrical behavior.

Scanning transmission electron microscopy electron-beam-induced current (STEM EBIC) imaging addresses both of these limitations, as it can be performed on functioning devices and its contrast mechanisms are largely magnification-independent [15]. In this technique, a focused electron beam is rastered over the sample and beam-induced currents are collected from the device’s own electrodes. The incident electron beam generates electron-hole pairs within the sample; in a ferroelectric capacitor, the remanent electric fields from imperfect screening of the polarization charge drive the separation of these electron-hole pairs, generating a measurable current at the electrodes. By combining STEM EBIC with *in situ* electrical switching, the remanent and coercive fields can be mapped at nanometer spatial resolution across an entire functioning capacitor [15].

In this chapter, we investigate the scalability of TiN/HZO/W ferroelectric capacitors using STEM EBIC imaging combined with statistical modeling. We employ a specialized *in situ* switching protocol based on the PUND method to program the capacitors with varying set voltages, and in each programmed state we map the ferroelectric fields across the capacitor. From the resulting spatially resolved coercive and remanent field maps, we extract statistical distributions of local remanent polarization and switching fraction. We model the switching fraction with a beta distribution parameterized by the mean switching fraction and the intra-cluster correlation—a measure of domain clustering that controls device-to-device variability. By convolving these distributions, we derive device-scale polarization probability mass functions (PMFs) that enable accurate yield prediction as a function of operating

voltage and device size. This approach bridges the gap between microscopic material properties and macroscopic device performance, offering quantitative metrics to guide process optimization for highly scaled, low-voltage FeRAM devices.

4.2 Theoretical Framework

4.2.1 EBIC Contrast Mechanism in Ferroelectric Capacitors

The contrast mechanism in STEM EBIC imaging of ferroelectric capacitors originates from the separation of electron-hole pairs generated by the incident electron beam. When the focused electron probe irradiates the sample, primary electrons undergo inelastic scattering events, generating numerous electron-hole pairs. In a non-polar material, these generated carriers recombine or diffuse without any preferred direction, producing no net current. In a ferroelectric material, however, the bound polarization charge at the electrode interfaces is imperfectly screened by the free carriers in the metal electrodes, leaving a residual electric field within the ferroelectric film [163, 164]. This remanent field drives the separation of the beam-generated electron-hole pairs: electrons drift against the remanent field and holes drift along the remanent field, producing a measurable current in the external circuit.

The magnitude of the EBIC current is proportional to the local remanent field, which in turn is proportional to the local remanent polarization. The sign of the current indicates the direction of the remanent field, which points opposite to the polarization direction. Thus, a positive current (flowing from the bottom electrode to the top electrode) corresponds to a polarization pointing “down” (toward the bottom electrode), and a negative current corresponds to a polarization pointing “up” (toward the top electrode). By acquiring the EBIC signal at each scan position, a two-dimensional map of the remanent polarization state is constructed concurrently with conventional STEM imaging signals such as bright field (BF) and high-angle annular dark field (HAADF).

An important practical enhancement to the EBIC technique is the acquisition of signals

from both the top electrode (TE) and the bottom electrode (BE) simultaneously. When the TE and BE currents are subtracted, common-mode noise is largely rejected. Furthermore, the subtraction cancels out the secondary electron EBIC (SEEBIC) signal, which is primarily a surface effect unrelated to the bulk ferroelectric polarization [165]. The resulting EBIC difference image, where the intensity is proportional to the net current flowing from BE to TE, provides a robust measure of the local remanent field.

4.2.2 Ferroelectric Switching and the PUND Method

At the microscopic level, a ferroelectric unit cell has exactly two equilibrium polarization states. The polarization switching has an intrinsically abrupt character, as predicted by the mean field theory. Macroscopic hysteresis loops typically show a gradual transition between the two polarization states only because they represent the ensemble average of many domains switching at slightly different electric fields. With a probe size comparable to or smaller than the domain size, STEM EBIC can capture this abrupt switching behavior at the pixel level.

To map the coercivity distribution of a ferroelectric film, the sample must be systematically programmed into different polarization states, and the resulting remanent field must be measured after each programming step. The positive-up negative-down (PUND) method [150] provides a well-established framework for separating the ferroelectric switched charge from the linear dielectric displacement and leakage contributions. A standard PUND sequence consists of a pair of positive pulses followed by a pair of negative pulses: the first pulse of each pair measures both the switching and non-switching contributions, while the second pulse measures only the non-switching contribution, allowing the switching component to be isolated by subtraction (Fig. 4.1).

In this work, we extend the PUND method to incorporate a variable set pulse. We denote a “PUNDp” sequence as one where the sample is first initialized in a fully polarized “down” state by a large negative pulse, then set into a partially “up” state by a variable-amplitude

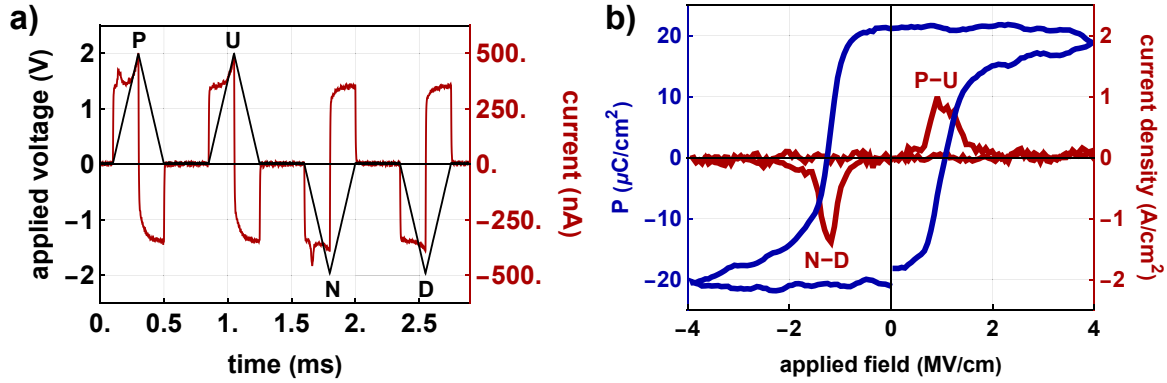


Figure 4.1: **Standard PUND waveform.** a) A standard PUND sequence used to probe a ferroelectric sample consists of two positive and two negative triangular voltage pulses (black). The current response of sample is captured (red), where the ferroelectric contribution only lies in the response to the first positive or negative pulse. b) Separation out the ferroelectric switching current (red) and integrate to get the hysteresis curve (blue).

positive pulse (Fig. 4.2). The inverse sequence, denoted “NDPUn,” initializes the sample fully “up” and then sets it partially “down” with a variable-amplitude negative pulse. As different ferroelectric domains switch at different applied fields, by varying the set pulse voltage and sequence polarity, we can put the sample in any intermediate state. By iterating this procedure over a range of set voltages and acquiring EBIC images after each PUNDp or NDPUn sequence, we obtain field maps of the specimen at many different states, which allows us to construct pixel-wise hysteresis loops that relate the local remanent field to the applied electric field history.

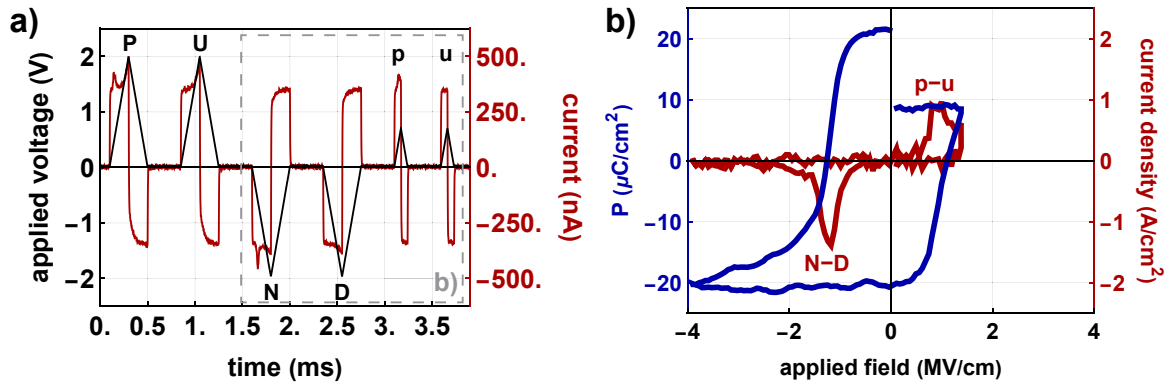


Figure 4.2: **Extended PUNDp waveform.** a) We extend the standard PUND sequence by adding a pair of variable set pulses at the end. The set pulses have voltages smaller or equal to the initial PUND sequence, and are therefore denoted as “p”. b) By isolating the switching component in the pulses in the gray dashed box in a), the hysteresis curve tell us the end state of the sample, which can be varied by changing the set pulse voltage and the pulse polarity.

4.2.3 Statistical Framework for Yield Prediction

For successful read operations in a ferroelectric memory cell (e.g., a 1T1C DRAM cell), the switched charge Q_{sw} from the ferroelectric capacitor must exceed the sensing threshold of the sense amplifier [166]. This sense limit, Q_{sense} , is determined by the bit-line and sense-circuitry design and, given a memory window of ~ 100 mV, typically falls between 10 and 100 fC [167–170]. In advanced process nodes, the capacitor’s active area is scaled down to increase memory density, while the operating voltage is reduced to curb power consumption. These trends lead to a decrease in total polarization and a degradation of the spatial uniformity of ferroelectricity, which together reduce Q_{sw} and increase device variability. To predict FeRAM yield as a function of operating voltage and device area, we require a statistical description of how the switched charge varies from device to device. For a ferroelectric capacitor of area A , the switched charge released during a read operation is:

$$Q_{sw} = 2\langle P_r \rangle A, \quad (4.2.1)$$

where $\langle P_r \rangle$ is the average remanent polarization over the device area. The factor of two accounts for the fact that during a read operation, the polarization is switched from one state to the other, releasing twice the remanent polarization charge.

The device-average remanent polarization $\langle P_r \rangle$ is not a single-valued material constant but rather a random variable whose distribution depends on both the operating voltage V_{op} and the device area A . Two distinct sources of variation contribute to this randomness. First, the local remanent polarization P_r varies spatially across the film due to variations in crystalline orientation, grain boundaries, and local strain. Second, not all regions of the film are switchable at a given operating voltage—the switching fraction sf , defined as the fraction of the device area where the local coercive field is less than the applied field, also varies from device to device due to the spatial clustering of switchable and non-switchable domains.

By mapping the spatially resolved ferroelectric properties of a HZO film, we can determine the distributions of P_r and sf under different operating voltages or device areas. From these two distributions, we can further compute the probability mass function of $\langle P_r \rangle$, which is proportional to the switched charge Q_{sw} , and derive the yield.

4.3 Experimental Methodology

4.3.1 Sample Fabrication

Ferroelectric capacitors are fabricated on a substrate of 200- μm -thick, (100)-oriented silicon with 800-nm-thick SiO_2 and 25-nm-thick SiN layers on both sides. An additional 5 nm of thermal atomic layer deposition (ThALD) Al_2O_3 protects the top SiN layer during the reactive-ion etching (RIE) that defines the bottom electrode. The top SiN layer serves as the electron-transparent support membrane for the completed device. For electrical connection, 5/25 nm Ti/Pt leads are deposited with electron beam evaporation.

The metal/ferroelectric/metal (MFM) stack consists of: a 20-nm-thick plasma-enhanced atomic layer deposited (PEALD) titanium nitride (TiN) bottom electrode (BE), 5 nm of PEALD $\text{Hf}_{0.5}\text{Zr}_{0.5}\text{O}_2$ (HZO), and an 85-nm-thick sputtered tungsten (W) top electrode (TE) (Fig. 4.3a). All features are defined with optical lithography and liftoff, except for the BE TiN layer, which is defined by RIE. After deposition, the sample undergoes rapid thermal annealing (RTA) at 550°C in N_2 for 1 minute to stabilize the ferroelectric $\text{Pca}2_1$ phase.

To make the sample electron-transparent for STEM imaging, SiN and SiO_2 are removed with RIE from the backside in areas defined by optical lithography. Then the Si is etched with 30% KOH at 80°C. Finally the top SiO_2 layer is etched from the back with HF vapor. The resulting electron-transparent window is a 30- μm -wide square with walls inclined at 54.7° (the characteristic angle of anisotropic KOH etching of (100) Si). Each window holds two devices with the same vertical stack; the lower one is imaged in this study (Fig. 4.3b). This architecture allows the electron beam to pass through the active capacitor area (Fig. 4.3c)

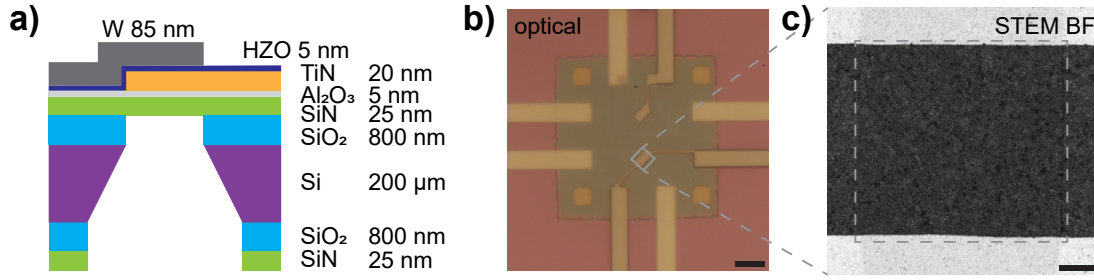


Figure 4.3: **Sample geometry.** a) Cross-section schematic of the TiN/HZO/W ferroelectric capacitor and Si substrate with electron-transparent window. b) Optical image of the electron-transparent window (green), with each window holding two devices with the same vertical stack. Scale bar: 5 μm. c) STEM BF image of the device, rotated 45° clockwise with respect to the optical image. The dark horizontal strip is the W TE, and the light vertical strip is the TiN BE. The simultaneously acquired EBIC image of the active area (dashed box) is shown in Fig. 4.4. Scale bars: 500 nm.

while maintaining electrical contact for voltage pulsing.

4.3.2 Instrumentation and Data Acquisition

The experiments are performed in an FEI Titan 80-300 STEM with the sample mounted in a Hummingbird biasing holder. EBICs are collected by a NanoElectronic Imaging (NEI) dual-channel system with 10^{11} gain. PUND transport measurements are performed with an arbitrary waveform generator (Keysight 33522B), a transimpedance amplifier (NF CA5351), and a digital oscilloscope (Rigol DHO1074). The experimental setup is illustrated schematically in Fig. 4.4. The top electrode and bottom electrode are switchable between two different sets of electronics: one set performs transport measurements and device programming, while the other set performs the subsequent EBIC imaging.

The imaging condition is optimized for a balance between spatial resolution, EBIC signal-to-noise ratio (SNR), and acquisition speed. A 300 keV beam energy, 23 pA beam current,

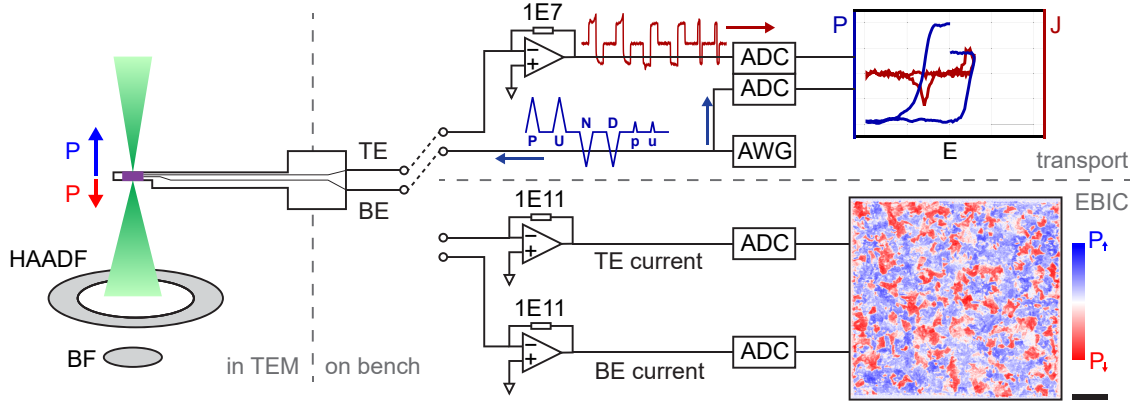


Figure 4.4: **STEM EBIC experimental setup.** Illustration of the *in situ* STEM EBIC setup. The top electrode (TE) and bottom electrode (BE) are switchable between two different sets of electronics: one for transport measurements and device programming, and another for subsequent EBIC imaging. The EBIC image is acquired simultaneously with standard STEM BF and HAADF, and the region shown is cropped to the gray dashed box in Fig. 4.3c. Scale bars: 500 nm.

and 10 mrad convergence angle are used. The dwell time is set to 250 μ s, so that the Nyquist frequency matches the bandwidth of the EBIC preamplifiers.

4.3.3 Pulse Protocol for State Preparation

To map the coercivity distribution of the 5-nm HZO film, we use a specialized pulse protocol to set the state of the specimen prior to each STEM EBIC acquisition. The protocol is based on a standard PUND sequence but incorporates a variable-amplitude set pulse (see Section 4.2.2). Because of the micrometer-scale dimensions of the specimen, the capacitance measured by the test equipment is dominated by the stray capacitance of the TEM holder, so removing the linear part of the polarization is crucial for measuring the ferroelectric part accurately.

The sample is first woken up with 5×10^5 cycles at 2.0 V using triangular pulses. A PUNDp sequence then proceeds as follows (Fig. 4.5): 2.0 V negative initialization pulses prepare the sample in a fully polarized “down” state, after which a variable-amplitude positive set pulse (0.2–2.0 V) places it in a partially polarized “up” state. Subsequent readout pulses at the set voltage quantify the resulting remanent polarization without disturbing the final state. We denote this sequence as “PUNDp”, because it is equivalent to a PUND sequence followed by a positive set pulse “p” with a lower voltage. The inverse sequence, “NDPUn”, initializes the sample in the fully polarized “up” state and then sets it partially “down”. The voltage ramp rate is kept constant at 10^4 V/s for all pulses.

The PUNDp set voltages are varied from 2.0 V to 0.2 V in descending order and interleaved with NDPUn sequences at the same set voltages. After each pulse sequence, two standard STEM images (BF and HAADF) and a pair of STEM EBIC images (one from the TE and one from the BE) are acquired simultaneously. The sample then undergoes 10^4 cycles at 2.0 V to remove any potential imprint built up during the approximately 5-minute image acquisition time. This procedure repeats with an NDPUn sequence at the same set voltage and then continues with PUNDp and NDPUn sequences at the next lower set voltage.

Each pair of simultaneously acquired EBIC images is subtracted to obtain the EBIC difference image (Fig. 4.6), where the intensity is proportional to the net current flowing from BE to TE and hence to the local remanent field. A symmetric, diverging blue-white-red (BWR) colormap is applied to the difference images, encoding signal polarity with different color channels to better visualize the polarity and zero-crossing of the remanent field. It is important to note that the remanent field points in the opposite direction of the polarization: a positive current (flowing from BE to TE) corresponds to the polarized “down” state, and a negative current corresponds to the polarized “up” state.

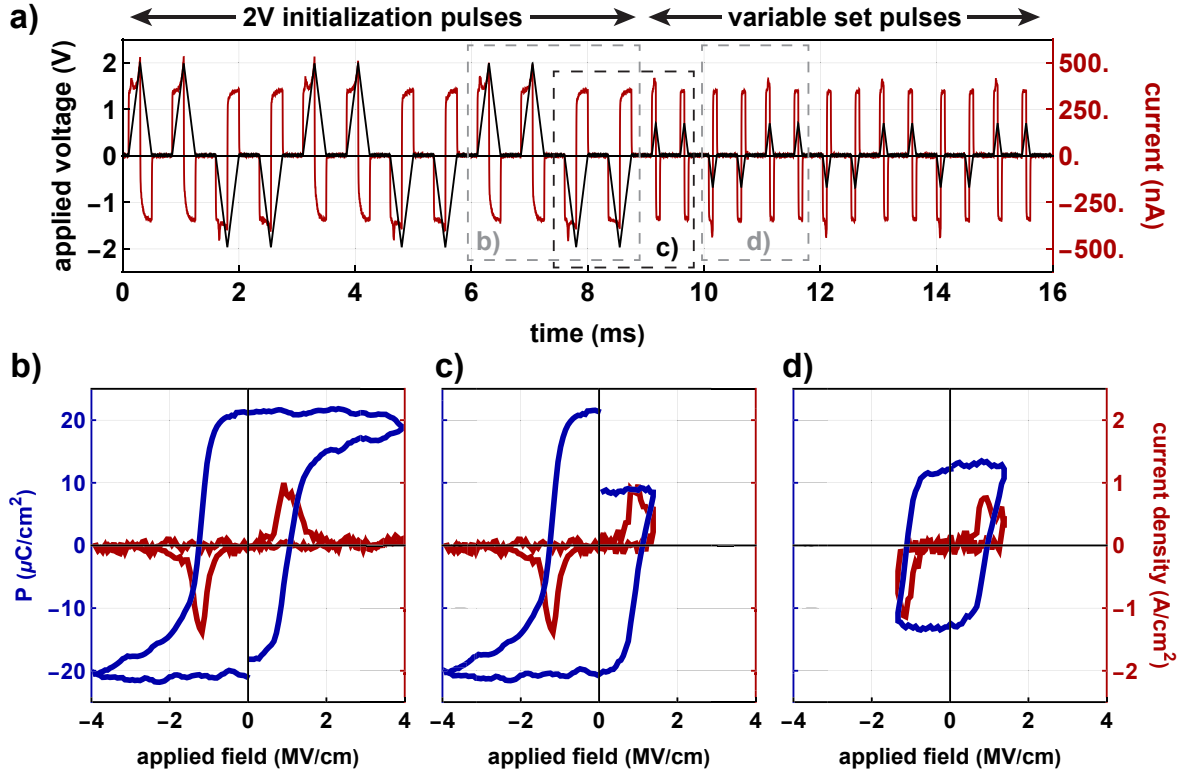


Figure 4.5: **Pulse sequence for state preparation.** a) An example PUNDp pulse sequence with 0.7 V set voltage and the corresponding current response. b–d) Polarization and current density plots corresponding to the three sub-sequences highlighted in panel a): b) the 2.0 V initialization pulses that polarize the sample fully down, c) the variable set pulse that programs the sample to a partially polarized up state, and d) the readout pulses that quantify the resulting remanent polarization without disturbing the final state.

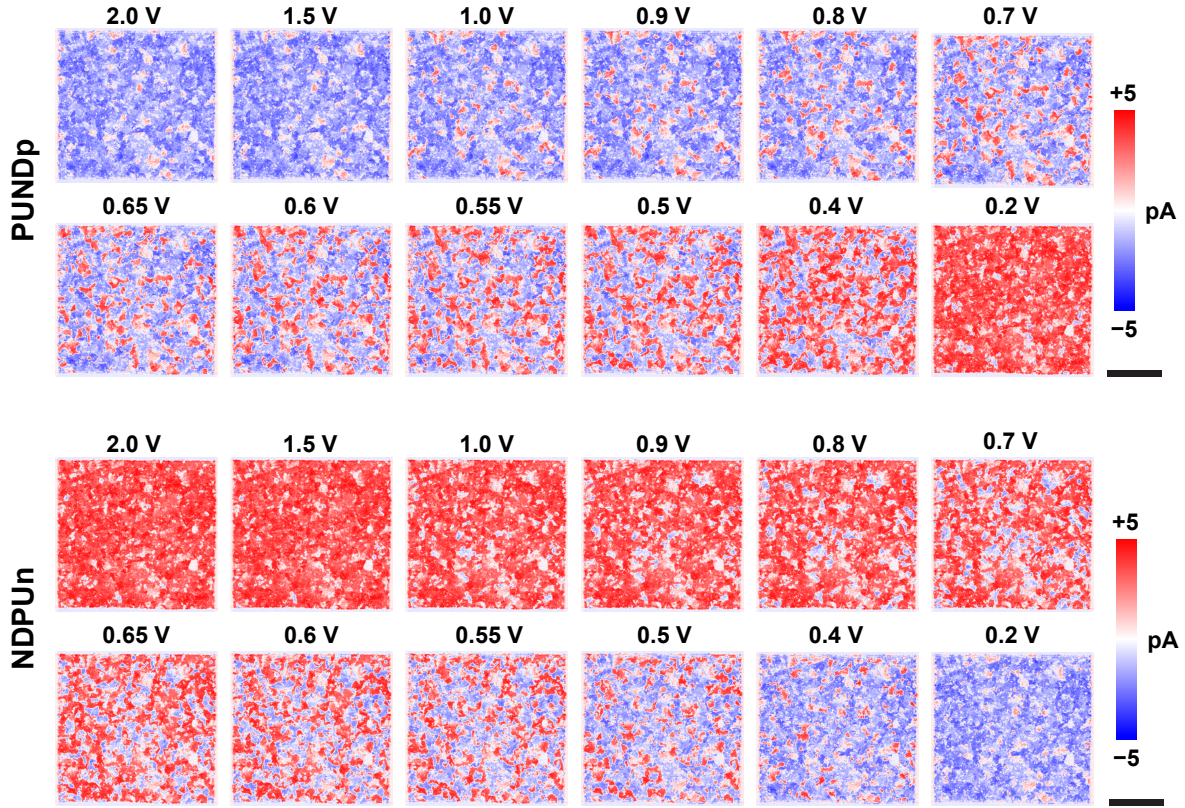


Figure 4.6: **EBIC images acquired at different set voltages.** EBIC difference images $((TE - BE)/2)$ acquired after the sample is set by different voltages. The PUNDp sequence (top half) initializes the sample in the polarized down state and then sets it partially up with a variable positive set voltage. The NDPUn sequence (bottom half) initializes it in the polarized up state and then sets it partially down. Combining the two sequences, we obtain spatially resolved positive and negative coercive field maps. Scale bar: $1 \mu\text{m}$.

4.4 Results and Analysis

4.4.1 Pixel-Wise Hysteresis Fitting and Ferroelectric Parameter Maps

For each pixel in the capacitor area (approximately $2.69\text{ }\mu\text{m} \times 2.84\text{ }\mu\text{m}$), we plot the EBIC intensity against the applied electric field to construct a pixel-wise hysteresis loop. The two branches (PUNDp and NDPUn) are each fitted to a step function to capture the binary switching behavior and to extract local ferroelectric parameters (Fig. 4.7). The step function model reflects the abrupt nature of ferroelectric switching at the microscopic level: as the applied field crosses the local coercive threshold, the polarization switches between its two equilibrium states, producing a step-like change in the remanent field.

From the step function fits, we determine four parameters for each pixel:

- The positive coercive field E_{c+} : the applied field at which the domain switches from the “down” to the “up” state (from the PUNDp branch).
- The negative coercive field E_{c-} : the applied field at which the domain switches from the “up” to the “down” state (from the NDPUn branch).
- The remanent field in the polarized “up” state E_{r+} .
- The remanent field in the polarized “down” state E_{r-} .

To simplify the physical interpretation, these four parameters are transformed into an orthogonal representation with magnitudes and offsets:

1. Coercive field magnitude $E_c = (E_{c+} - E_{c-})/2$, proportional to the energy barrier for switching.
2. Coercive field background $E_b = (E_{c+} + E_{c-})/2$, representing the background offset of the coercive field.

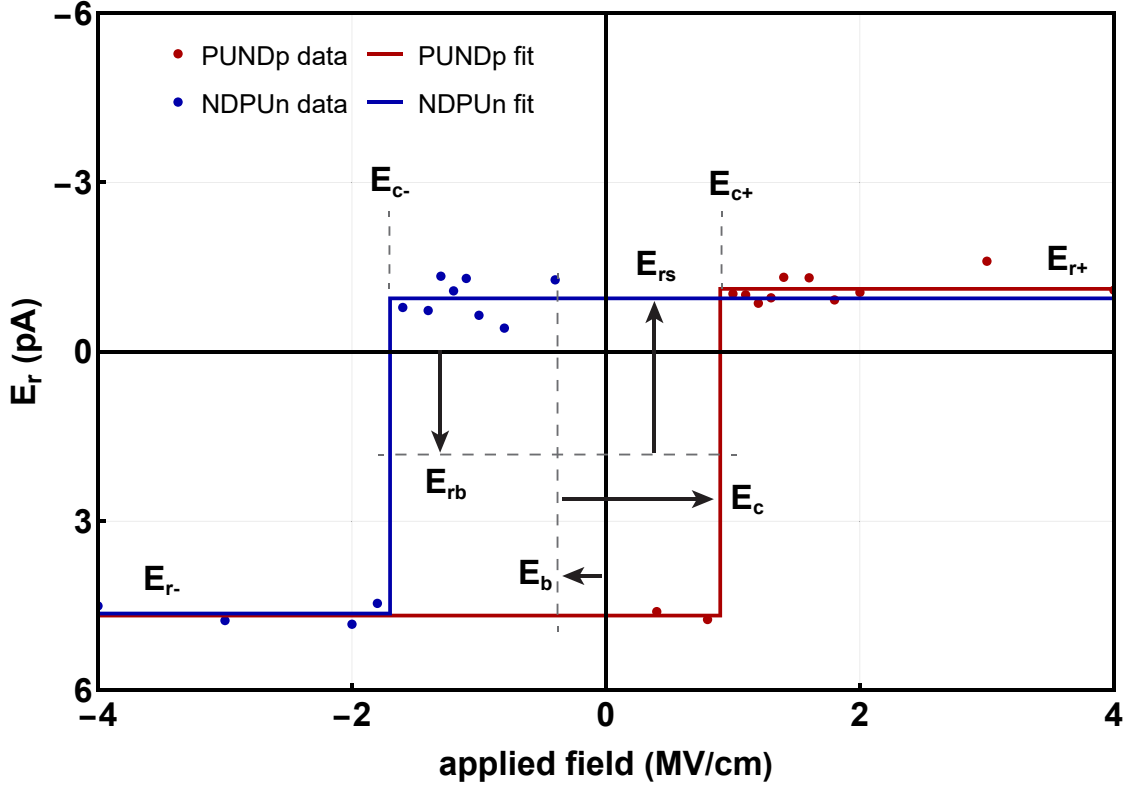


Figure 4.7: **Pixel-hysteresis fit illustration.** The remanent field E_r (or EBIC intensity, in pA) is plotted against the applied field. The PUNDp and NDPUn branches are each fitted with a step function. The remanent fields (E_{r+} , E_{r-}) and coercive fields (E_{c+} , E_{c-}) are determined from the fits, and they are then transformed into an orthogonal representation with magnitudes (E_{rs} , E_c) and offsets (E_{rb} , E_b).

3. Remanent switching field $E_{rs} = (E_{r+} - E_{r-})/2$, representing the magnitude of the remanent field that switches with polarity.
4. Remanent background field $E_{rb} = (E_{r+} + E_{r-})/2$, representing the background offset of the remanent field (originating from imprint or asymmetric electrode interfaces).

The remanent fields (E_{rs} and E_{rb}) are presented in current units (pA), as the electric field magnitude is directly proportional to the EBIC current [15].

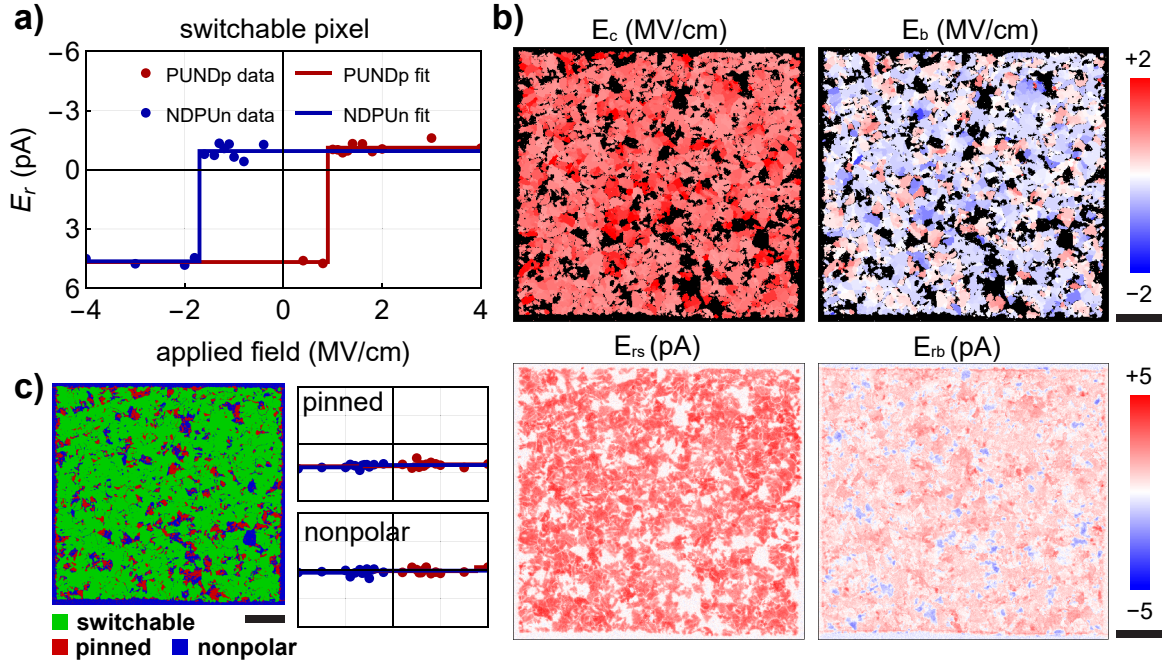


Figure 4.8: **Pixel-wise hysteresis fit and EBIC characteristic maps.** a) Hysteresis loop of a single pixel constructed by correlating the EBIC intensity with applied field history. The two branches (PUNDp and NDPUn) are each fitted to a step function to extract the local ferroelectric properties. The positive or negative coercive field is determined by the applied field at which the transition occurs, and the remanent fields corresponding to the poled up and poled down states are determined by the high and low E_r levels. b) Ferroelectric property maps obtained by applying the step function fits to every pixel. E_c and E_b represent the magnitude and offset of the coercive field. E_{rs} and E_{rb} represent the switching component and the offset of the remanent field. c) Pixel category map derived from the E_{rs} and E_{rb} maps. Typical data and fits for pinned and nonpolar pixels are shown in the same range as panel a). Scale bar: 500 nm.

The E_c map (Fig. 4.8b, top left) reveals significant spatial heterogeneity in switching thresholds across the film. The coercive field magnitude is found to center around 1.0 MV/cm, corresponding to approximately 0.5 V for the 5-nm-thick HZO film. This value

is consistent with the coercive fields reported for HZO films in the literature [139,140].

The E_{rb} map (Fig. 4.8b, bottom right) indicates a positive remanent background field throughout much of the active area. We attribute this bias to the asymmetry between the TE (W) and BE (TiN) materials, which leads to asymmetric Schottky barriers at the two electrode interfaces [171–173]. The positive E_{rb} implies that the HZO film is energetically favored to be polarized “up” (toward the W electrode) rather than “down” (toward the TiN electrode). This built-in asymmetry must be overcome when switching polarity, which explains the overall negative E_b observed in the coercive field background map (Fig. 4.8b, top right). The identification of this remanent background field provides insight into the interfacial physics of asymmetric electrode configurations—a common feature in practical FeRAM devices where the TE and BE materials are often different for process integration reasons.

4.4.2 Pixel Classification: Switchable, Pinned, and Nonpolar Regions

With the remanent field maps, we classify each pixel into one of three categories based on its local ferroelectric response. A threshold field E_{th} is set to three times the noise level of the E_{rs} measurement; any remanent field signal with an SNR greater than three is considered real and significant. The noise level of E_{rs} is determined by computing the standard deviation of E_{rs} in a region not covered by the electrodes (the top left corners of the field of view, see Fig. 4.9), where no electric field contrast exists.

The classification criteria are:

- **Switchable:** $E_{rs} \geq E_{th}$ —the pixel exhibits a switching remanent field above the noise threshold.
- **Pinned:** $E_{rs} < E_{th}$ and $|E_{rb}| \geq E_{th}$ —the HZO is polar (has a non-zero background field) but is not switchable at the applied voltages.

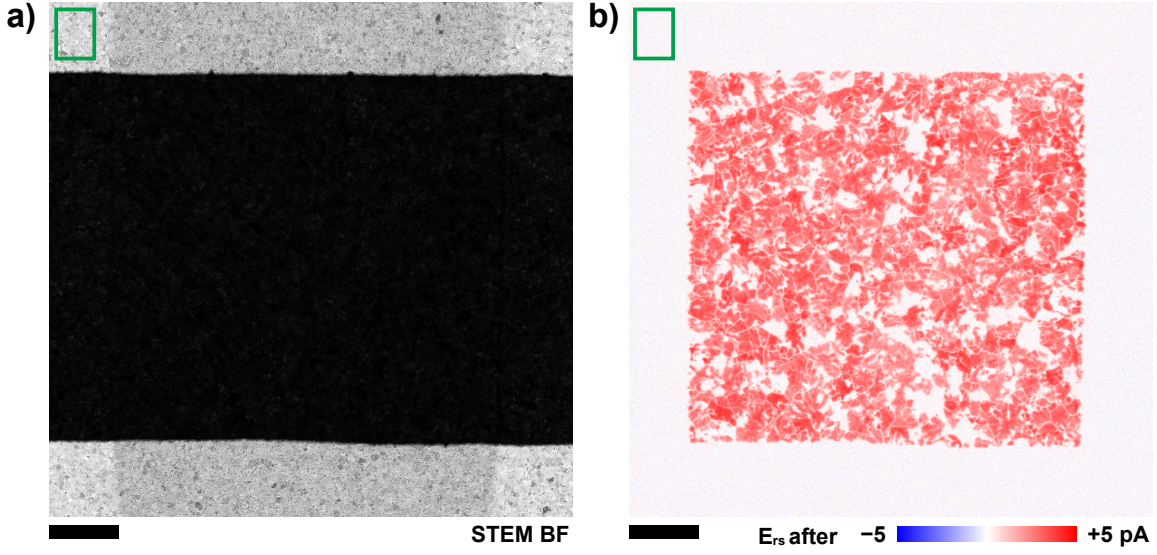


Figure 4.9: E_{rs} noise and E_{th} determination. a) A STEM BF image acquired simultaneously with EBIC images. The four corners are not covered by the bottom electrode (vertical stripe) or the top electrode (horizontal stripe), so those regions have no electric field contrast in EBIC. b) A full E_{rs} (after) map with the same FOV as the STEM BF image. The standard deviation of intensities within the green box is used as the noise level of E_{rs} measurement. The threshold field E_{th} is set to three times of the noise. Scale bar: 500 nm.

- **Nonpolar:** $E_{rs} < E_{th}$ and $|E_{rb}| < E_{th}$ —the HZO does not have a significant internal field.

The resulting pixel category map (Fig. 4.8c) reveals a complex spatial arrangement of switchable, pinned, and nonpolar regions across the capacitor. Typical EBIC hysteresis loops for pinned and nonpolar pixels (Fig. 4.8c, right panels) confirm the classification: pinned pixels show a finite background field but no switching, while nonpolar pixels show little to no remanent field.

4.4.3 Fatigue Analysis During Characterization

A subtle but important detail in the analysis is that the sample undergoes more than 10^5 cycles during the characterization process, and some domains degrade or “fatigue” during cycling. In such cases, the E_{r+} and E_{r-} values measured by the PUNDp and NDPUn sequences can differ because they probe the sample at different stages of the characterization process.

As we start with the 2.0 V set pulse and progressively step down the voltage, the PUNDp sequence measures the initial E_{r+} and the final E_{r-} , while the NDPUn sequence measures the initial E_{r-} and the final E_{r+} . Therefore, the fitting process generates a total of six field maps (Fig. 4.10): two coercive field maps (which are largely unaffected by fatigue) and four remanent field maps. E_{rs1} and E_{rb1} represent the state of the specimen at the beginning of the characterization process, while E_{rs2} and E_{rb2} represent the state at the end.

By comparing the before and after classification maps, we find that over 80% of the sample area is stable throughout the characterization process, while approximately 10% of the sample has fatigued (Fig. 4.11). Two distinct fatigue pathways are observed:

1. **Switchable to pinned:** The domain initially switches but becomes pinned over time, consistent with domain wall pinning by charged defects migrating under the applied field [174].
2. **Switchable to nonpolar:** The domain initially switches but loses polarity entirely, consistent with a local phase transformation from the ferroelectric $Pca2_1$ phase to a non-ferroelectric phase (e.g., the monoclinic or tetragonal phase) [175].

The rate of fatigue, quantified by plotting the switching fraction against the number of cycles, remains approximately constant for most of the experiment but drops to near zero at the end (Fig. 4.12f). This deceleration suggests that the most vulnerable domains—those with the lowest activation energy for defect migration or phase transformation—fatigue early,

leaving behind a population of more robust domains. For the scalability analysis, we use the after-characterization state of the sample (E_{rs2} and E_{rb2} maps with the “always switchable” region mask). This conservative choice avoids overestimating the scalability of the HZO film: the remaining switchable domains have survived nearly 10^6 cycles at 1 kHz and possess a reasonable lifetime for memory applications.

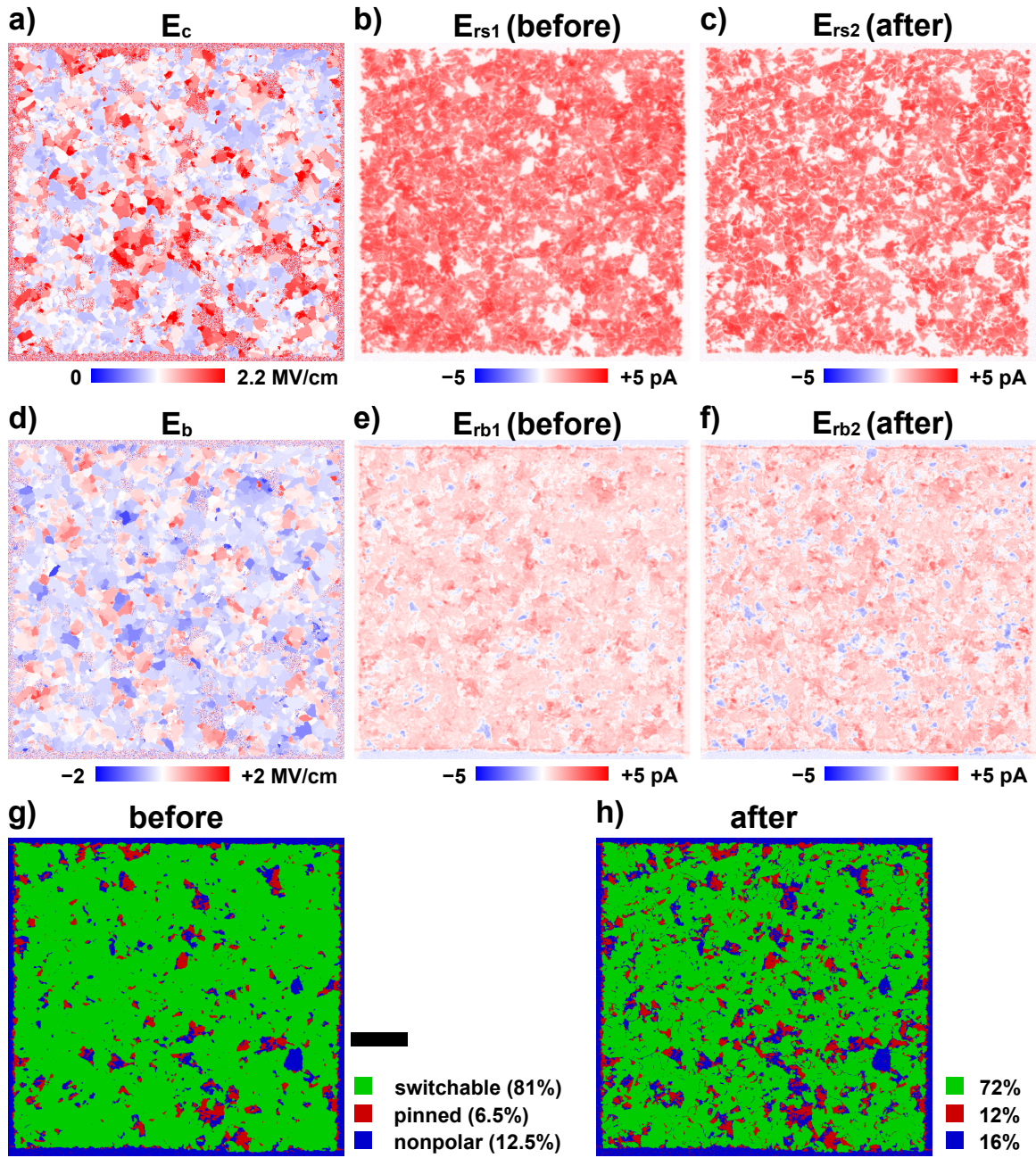


Figure 4.10: a-f) Pixel hysteresis fit maps. Comparing *b)* and *c)*, a visible amount of fatigue is observed. Pixel classification maps, which correspond to the state of the sample at the beginning (*g)*) and at the end (*f)*) of the characterization process, are generated from the before (*b,e)*) and the after (*c,f)*) E_{rs} and E_{rb} maps. Comparing *g)* and *f)* yields the classification maps in Fig. 4.11 below. Scale bar is 500 nm.

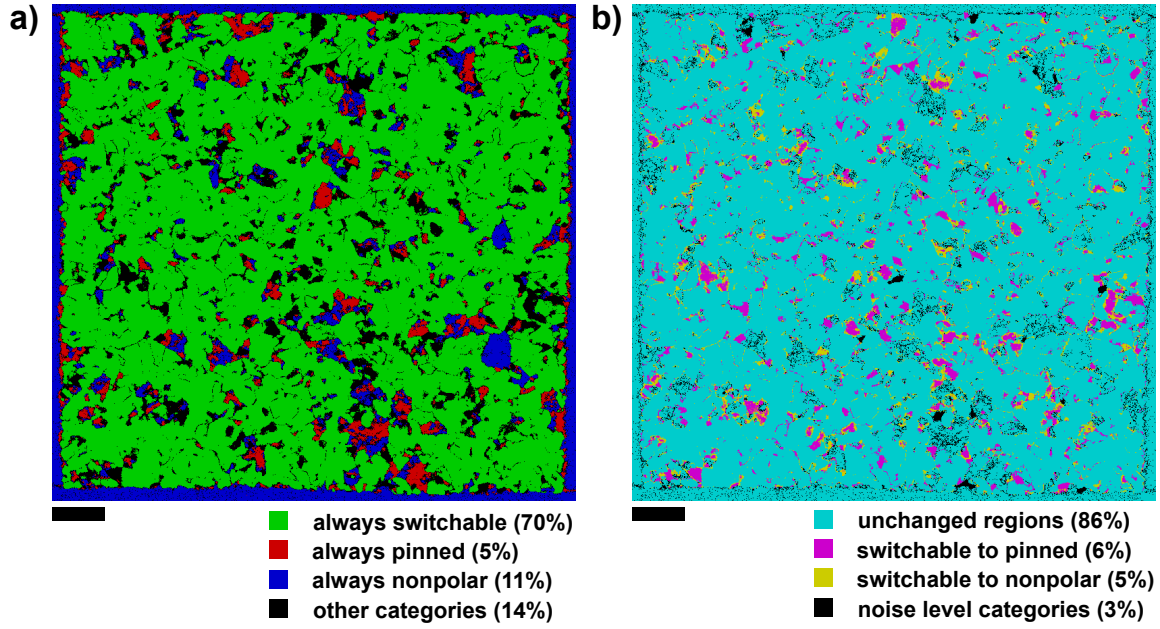


Figure 4.11: **Classification of ferroelectric regions and fatigue analysis.** a) Map of the regions that remain unchanged over the characterization process. b) Map of fatigued regions. Some ferroelectric regions become pinned (magenta) or nonpolar (yellow), possibly due to domain wall pinning or phase decomposition, respectively. Typical hysteresis curves of the five categories mentioned above are shown in Fig. 4.12. Noise level categories are pinned or nonpolar pixels turned into other types. Each of these categories is at 1% level or less and is therefore considered as noise. Scale bar is 300 nm.

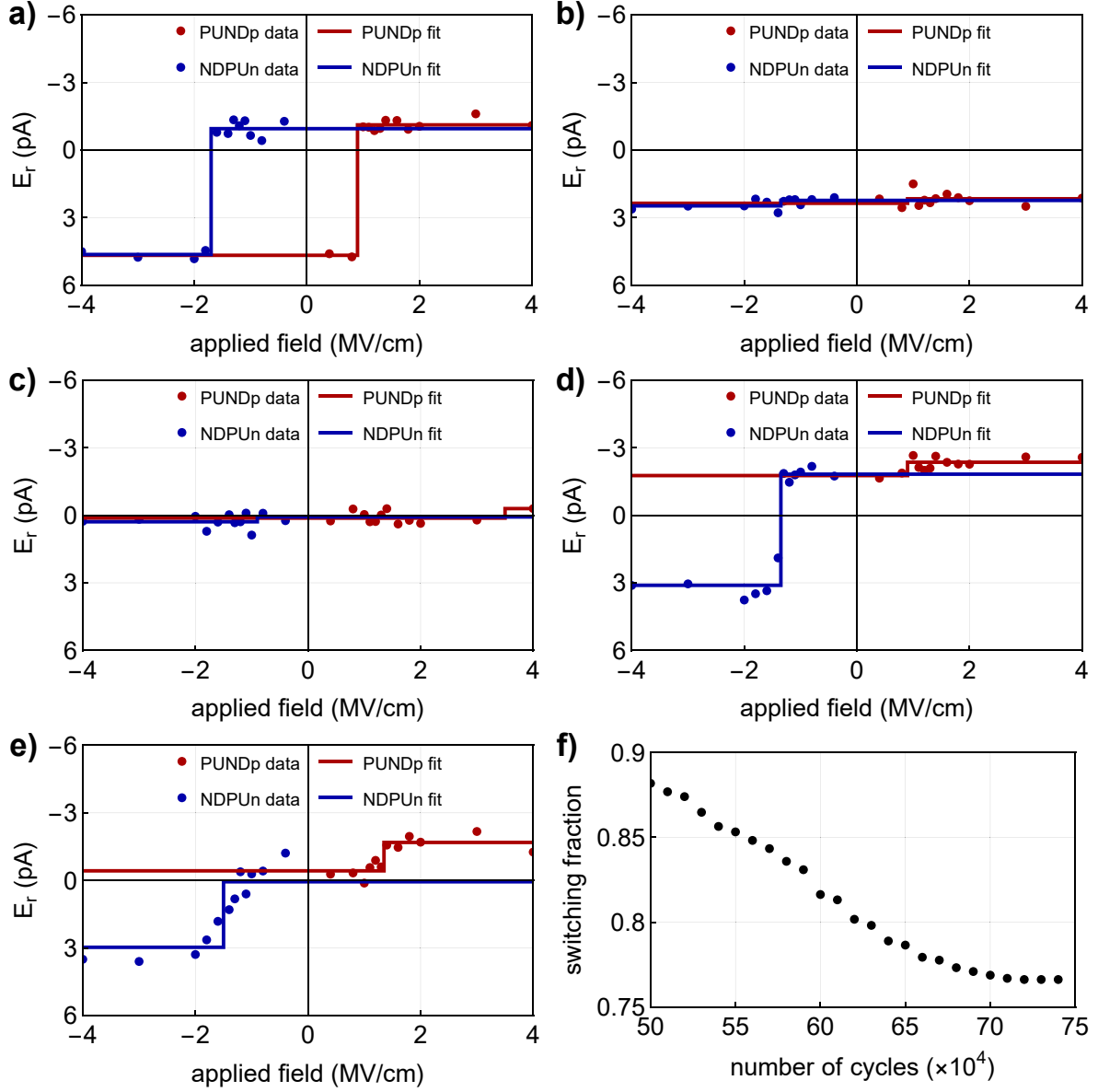


Figure 4.12: **Typical pixel-level hysteresis.** Typical pixel-level hysteresis for a) always switching, b) always pinned, c) always nonpolar, d) switchable to pinned, and e) switchable to nonpolar pixels. f) Switching fraction (normalized to the capacitor area) as a function of the number of cycles. Fatigue slows down significantly near the end of the characterization process.

4.4.4 Conversion of Remanent Field to Remanent Polarization

A previous study established that the remanent field measured by EBIC is proportional to the remanent polarization in a ferroelectric capacitor [15]. To convert the EBIC-derived E_{rs} maps into local remanent polarization values, we correlate the spatially averaged E_{rs} with the macroscopic P_r measured by transport PUND (Fig. 4.13).

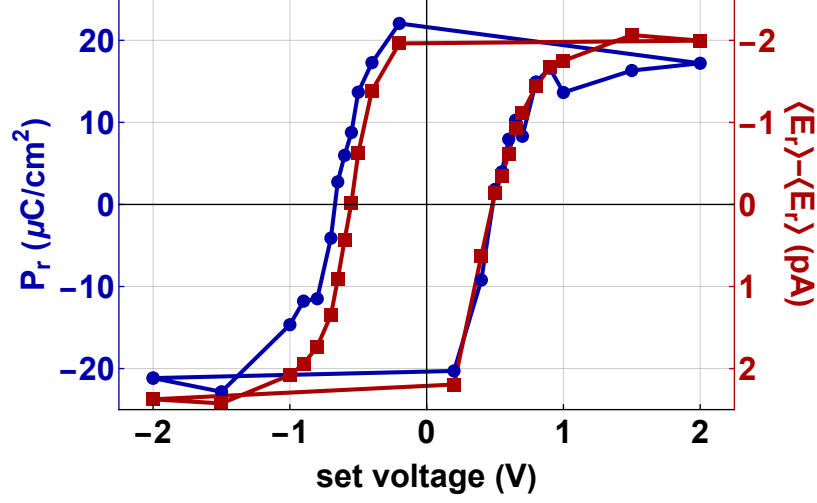


Figure 4.13: **Remanent polarization and remanent field proportionality.** The remanent polarization P_r measured by transport PUND and the mean remanent field $\langle E_r \rangle$ measured by EBIC are plotted as functions of the set voltage. The linear relationship confirms that EBIC intensity is proportional to the remanent polarization at the ensemble-average level. The mean of $\langle E_r \rangle$ is subtracted to align the zero positions of the two axes, as EBIC also measures the background field that is invisible to transport.

The linearity between P_r and $\langle E_r \rangle$ across the full range of set voltages confirms the proportionality at the ensemble-average level. At the end of the characterization process, the spatially averaged switching field is $\langle E_{rs} \rangle = 1.79$ pA, and the corresponding P_r measured by transport is $21.25 \mu\text{C}/\text{cm}^2$. The conversion factor is therefore determined to be $11.86 \mu\text{C}/\text{cm}^2/\text{pA}$. Applying this proportionality constant to each pixel in the E_{rs} map reveals the spatial distribution of the local remanent polarization P_r .

4.5 Statistical Modeling of Ferroelectric Heterogeneity

4.5.1 Local Remanent Polarization Distribution

With the coercive fields and switchable region mapped, we can determine which regions are switchable at a given operating voltage by applying the condition $|E_c \pm E_b| \leq V_{op}/d$, where $d = 5$ nm is the HZO film thickness. The distribution of local remanent polarization f_{P_r} within the always switchable region (Fig. 4.11a) is extracted and fitted to a skew normal distribution (Fig. 4.14).

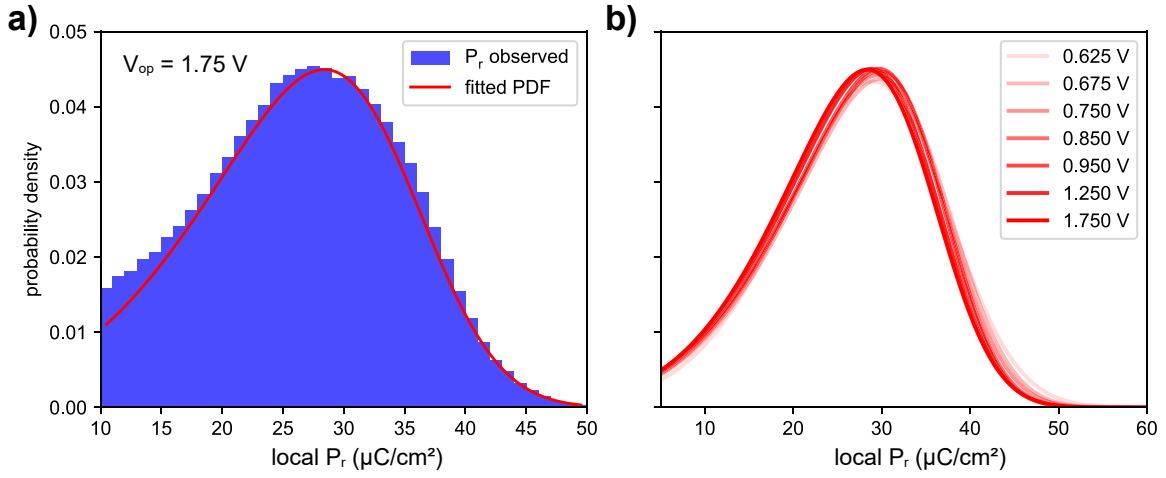


Figure 4.14: **Local remanent polarization distribution.** a) Observed local remanent polarization in the switchable region and the fitted skew normal distribution at $V_{op} = 1.75$ V. b) The local P_r distribution f_{P_r} is found to be independent of the operating voltage, which allows a single f_{P_r} to be used for modeling the local P_r distribution under any operating voltage.

A key finding is that the local remanent polarization distribution f_{P_r} is independent of the operating voltage (Fig. 4.14b), which implies that a single f_{P_r} distribution can be used for all operating voltages.

4.5.2 Switching Fraction Distribution and Beta Distribution Modeling

At a given operating voltage, the switchable region mask can be determined from the E_c and E_b maps. The switching fraction sf , ranging from 0 to 1, is defined as the ratio of the switchable area to the total area within a given region. To characterize how the switching fraction distribution f_{sf} varies with device area, we randomly sample the full active area with a window of a given size and compute the switching fraction within each sample (Fig. 4.15). By increasing the number of random samples, the statistical noise is reduced and the distribution is precisely captured.

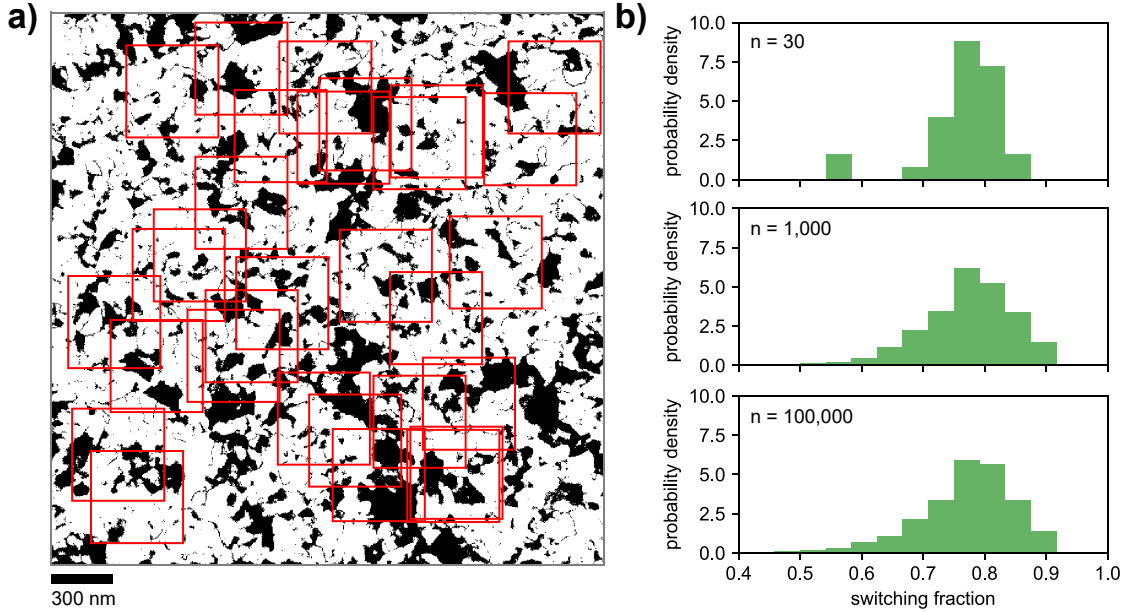


Figure 4.15: **Switching fraction subsampling.** a) A mask of the switchable region is generated for each operating voltage ($V_{op} = 1.75$ V is shown). By randomly sampling the whole film with a window (red box) of the same size, the distribution of switching fractions can be derived. b) The probability density of switching fractions with different numbers of samples.

The switching fraction distribution f_{sf} is the critical link between the microscopic spatial

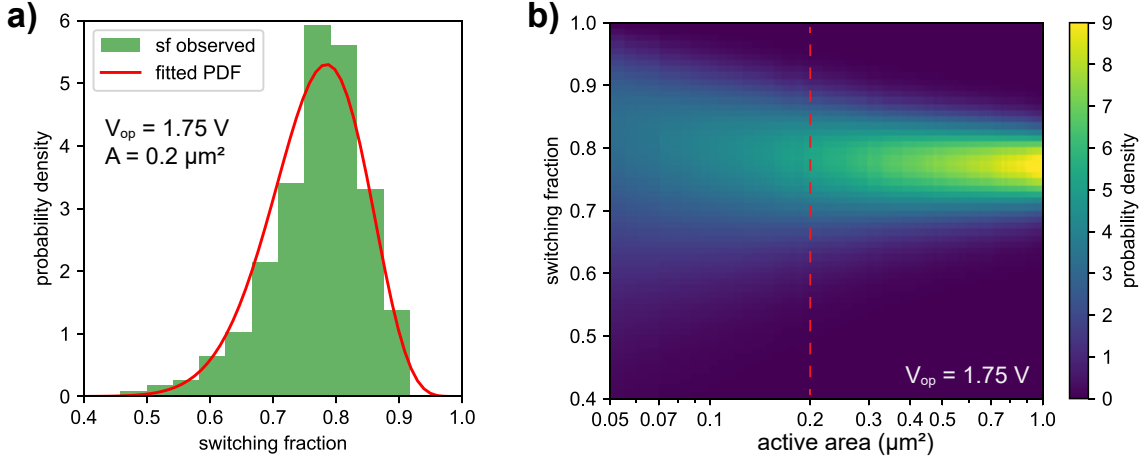


Figure 4.16: **Switching fraction distribution and beta distribution modeling.** a) Random sampling of the switchable region mask: by sliding a sampling window of the specified device area across the full capacitor, the distribution of switching fractions across many hypothetical devices is derived. b) The observed switching fraction distribution (histogram) and fitted beta distribution (red curve) at $V_{op} = 1.75$ V and active area = $0.2 \mu\text{m}^2$. c) The switching fraction distribution f_{sf} as a function of active area at $V_{op} = 1.75$ V. As the active area decreases, f_{sf} broadens due to increased device-to-device variation. The red dashed line marks the slice corresponding to the histogram and fit in panel b.

heterogeneity and the macroscopic device variability. If switchable domains were randomly distributed without any spatial correlation, sf would follow a binomial distribution. However, in ferroelectric materials, domains—microscopic regions where electric dipoles all align in the same direction and switch cooperatively—introduce spatial correlations. This clustering behavior causes f_{sf} to deviate from the binomial distribution, and the natural choice to account for the clustering behavior would be using a beta-binomial distribution. Since beta-binomial distribution converges to a continuous beta distribution (with the independent variable rescaled) when the number of trials is large, we therefore model f_{sf} with a beta distribution for simplicity (Fig. 4.16a):

$$f_{sf}(sf; V_{op}, A) = C sf^{\alpha-1} (1 - sf)^{\beta-1}, \quad (4.5.1)$$

where C is a normalization constant, and α and β are voltage and area dependent. The smallest sample size used in this study still consists of over 3,400 pixels, so the number of trials is sufficiently large for this approximation. At a given operating voltage, the mean switching fraction remains constant but the variance of sf increases as the active area decreases, representing an increase in device-to-device variability (Fig. 4.16b).

To make the parameters more physically interpretable, we reparameterize the beta distribution in terms of the mean switching fraction $\langle sf \rangle = \alpha/(\alpha + \beta)$ and the intra-cluster correlation $\rho = 1/(\alpha + \beta + 1)$. The mean switching fraction $\langle sf \rangle$ represents the expected fraction of the switchable area at a given operating voltage, while ρ is proportional to the variance and quantifies the dispersion of the distribution. The mean switching fraction $\langle sf \rangle$ increases with operating voltage V_{op} as more domains become switchable, saturating at higher voltages as all available ferroelectric domains are activated (Fig. 4.17a). The intra-cluster correlation ρ quantifies the degree of spatial clustering of switchable domains and is a function of both V_{op} and the device area A (Fig. 4.17b).

Both $\langle sf \rangle$ and ρ change continuously as we vary the operating voltage or the device area. By linearly interpolating these parameters between the experimentally measured V_{op} values, we can construct the estimated switching fraction distribution with finer voltage steps than those directly measured. This interpolation is essential for generating smooth yield contours, as the experiment is limited to a discrete set of voltages and extending the measurement to more voltage steps would substantially increase the experimental duration and push the limits of the device's endurance.

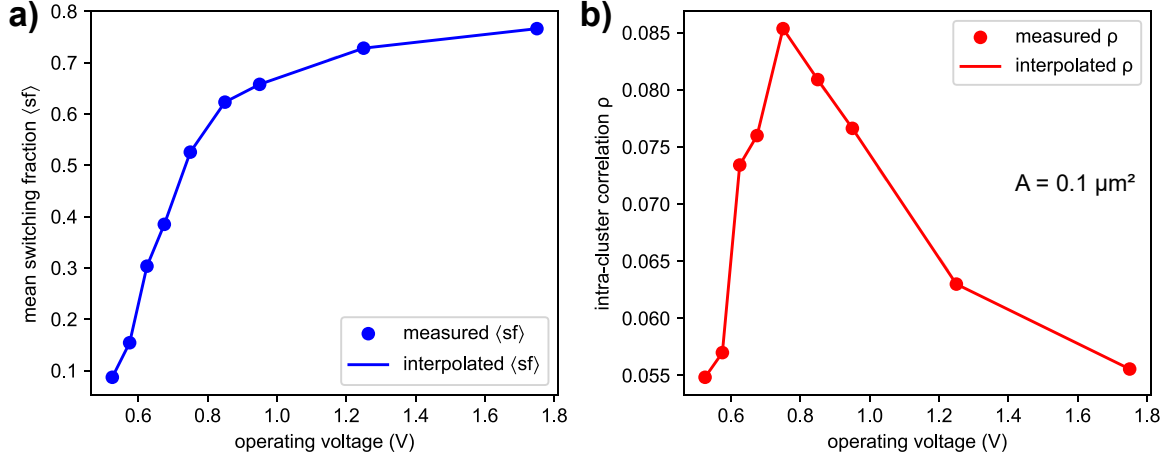


Figure 4.17: **Beta distribution parameterization and interpolation.** a) The mean switching fraction $\langle sf \rangle$ as a function of operating voltage. b) The intra-cluster correlation ρ as a function of operating voltage, shown for a device area of $0.1 \mu\text{m}^2$. Both $\langle sf \rangle$ and ρ change continuously with operating voltage, allowing linear interpolation between measured data points to overcome the experimental sampling limitations along the V_{op} axis. The solid lines represent the interpolated values used in the yield prediction model, and the data points represent the measured values.

4.5.3 Device-Scale Polarization Probability Mass Function

The distribution of device-scale polarization $f_{\langle P_r \rangle}(\langle P_r \rangle; V_{op}, A)$ can be determined from the local polarization distribution $f_{P_r}(P_r)$ and the switching fraction distribution $f_{sf}(sf; V_{op}, A)$. For a given active area A , the number of switchable pixels is $N = \frac{A}{a} sf$. The distribution of N is given by

$$f_N(N; V_{op}, A) = f_{sf}\left(\frac{a}{A}N; V_{op}, A\right), \quad (4.5.2)$$

where a is the pixel area from which the local remanent polarization distribution $f_{P_r}(P_r)$ is derived. Then, the distribution of $\langle P_r \rangle$ is given by N independent and identically distributed

(i.i.d.) draws from $f_{P_r}(P_r)$ weighted by $f_N(N; V_{op}, A)$:

$$f_{\langle P_r \rangle}(\langle P_r \rangle; V_{op}, A) = \int_0^{N_{max}} N_{max} \times f_{P_r}^{*N}(N_{max} \langle P_r \rangle) \times f_N(N; V_{op}, A) dN \quad (4.5.3)$$

f^{*N} denotes N -fold autoconvolution, and $N_{max} = A/a$ is the total number of pixels in the active area A .

To account for the discrete nature of i.i.d. draws and to reduce computation expenses, we can work with probability mass functions instead and use a normal distribution with reduced variance to approximate the N -fold autoconvolution. According to the central limit theorem, the distribution of the mean of N i.i.d. draws closely approximates a normal distribution for a sufficiently large N . Considering that the smallest sampling area used in this work still consists of over 3,000 pixels, this prerequisite is well satisfied. The mean of the normal distribution is given by the mean of the population $\mu = \mu_{P_r}$, and the variance of the normal distribution is scaled by the sample size $\sigma^2 = \sigma_{P_r}^2/N$. Then, the probability mass function of $\langle P_r \rangle$ can be written as

$$P_{\langle P_r \rangle}(\langle P_r \rangle; V_{op}, A) = \sum_N \mathcal{N}\left(\frac{aN}{A} \langle P_r \rangle; \mu_{P_r}, \sigma_{P_r}/\sqrt{N}\right) \times \Delta \langle P_r \rangle \times P_N(N; V_{op}, A), \quad (4.5.4)$$

where $\mathcal{N}(x; \mu, \sigma)$ denotes the normal distribution and $\Delta \langle P_r \rangle$ denotes the bin size.

With the local P_r distribution f_{P_r} and the switching fraction distribution f_{sf} in hand, the device-scale polarization PMF is constructed using Eq. 4.5.4. For each operating voltage V_{op} and device area A , the procedure is:

1. Determine the beta distribution parameters $\langle sf \rangle(V_{op})$ and $\rho(V_{op}, A)$ by interpolation from the experimentally measured values (Fig. 4.17).
2. Generate the switching fraction PMF $P_N(N; V_{op}, A)$ from the beta distribution, where $N = (A/a) \times sf$ is the number of switchable pixels.
3. Limit P_N to ten thousand discrete N value bins to reduce computation cost.

4. For each possible N , the distribution of $\langle P_r \rangle$ is approximated by a normal distribution with mean μ_{P_r} and standard deviation $\sigma_{P_r}/\sqrt{N}$, following the central limit theorem.
5. Sum the contributions from all N , weighted by $P_N(N; V_{op}, A)$, to obtain the full PMF $P_{\langle P_r \rangle}(\langle P_r \rangle; V_{op}, A)$.

The resulting PMFs are shown in Fig. 4.18a–b for selected operating conditions. For a fixed active area, as the operating voltage is lowered, the mean of $\langle P_r \rangle$ decreases because the switching fraction is reduced—fewer domains are switchable at lower fields (Fig. 4.18a). For a fixed operating voltage, the distribution of $\langle P_r \rangle$ becomes broader at smaller active areas due to increased device-to-device variation (Fig. 4.18b). This broadening is a combined effect of reduced active area and domain clustering, a small device may by chance contain a disproportionately high or low fraction of switchable area.

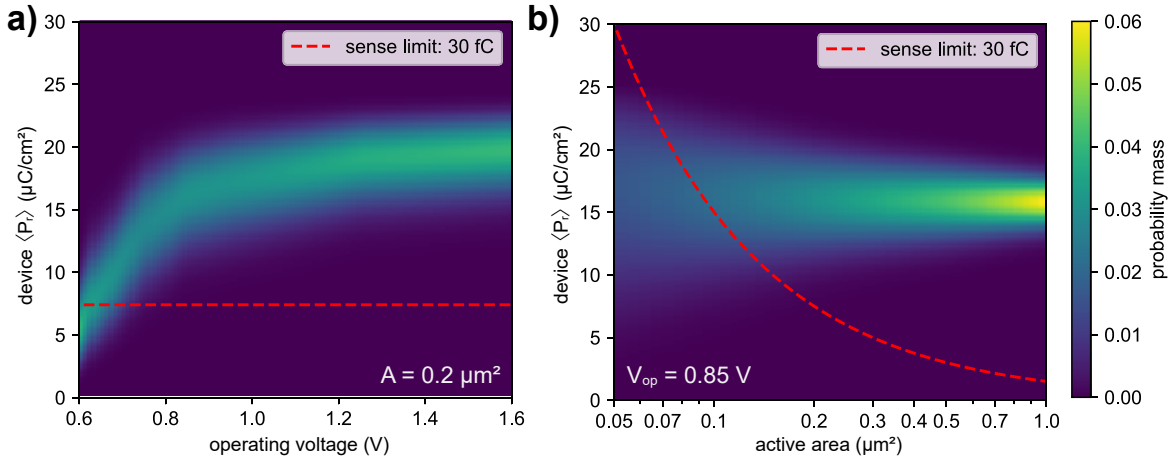


Figure 4.18: **Device $\langle P_r \rangle$ PMF.** The probability mass function of device-average remanent polarization $P_{\langle P_r \rangle}$ (a) at $0.2 \mu\text{m}^2$ active area as a function of operating voltage, and (b) at $V_{op} = 0.85 \text{ V}$ as a function of active area. Devices with $\langle P_r \rangle$ above the sense limit (red dashed curve) are functional.

4.6 Scalability Analysis and Yield Prediction

4.6.1 Yield Map and Operating Voltage–Area Trade-offs

The yield $Y(V_{op}, A)$ is obtained by integrating the device polarization PMF above the sense limit (Eq. 4.6.1). The resulting two-dimensional yield map (Fig. 4.19) reveals the trade-off between operating voltage and device area for achieving a target manufacturing yield.

$$Y(V_{op}, A) = \sum_{2A\langle P_r \rangle > Q_{sense}} P_{\langle P_r \rangle}(\langle P_r \rangle; V_{op}, A). \quad (4.6.1)$$

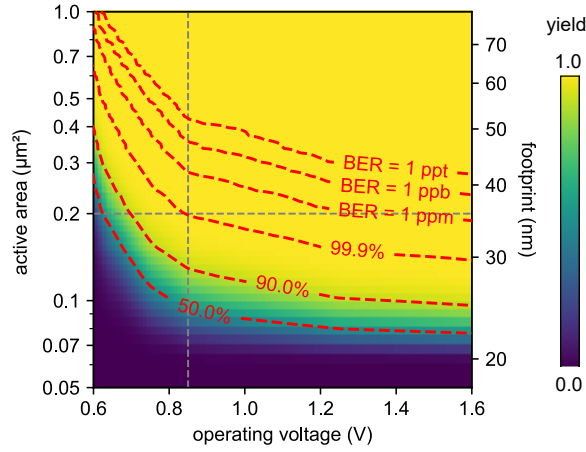


Figure 4.19: **Device yield map at 30 fC sense limit.** Integrating the probability mass above the sense limit (see Fig. 4.18) generates the predicted yield map for the tested HZO film at a 30 fC sense limit. Contours for 50% to 99.9% yield and for 1 ppm to 1 ppt bit error rate (BER) are shown. The device footprint (cylinder diameter) is calculated for cylindrical capacitors with a 50:1 aspect ratio, providing a direct link to realistic device geometries. The horizontal and vertical gray dashed lines highlight the slices corresponding to panels a and b in Fig. 4.18, respectively.

We find that the operating voltage and the active area can be reduced to 0.8–1.0 V and 0.2–0.3 μm^2 , respectively, while maintaining a 99.9% yield at a 30 fC sense limit. For a

cylindrical capacitor geometry with a 50:1 aspect ratio—similar to structures used in contemporary DRAM technology [145,176]—this active area corresponds to a capacitor footprint of 35–40 nm in diameter. This result demonstrates that low-voltage operation and aggressive area scaling can be achieved simultaneously in FeRAM fabricated from the characterized 5-nm HZO film.

An important observation from the yield map is that the active area needs only a relatively modest increase to achieve orders of magnitude reduction in bit error rate (BER), defined as $\text{BER} = 1 - Y$. For example, at 1.0 V operating voltage, increasing the capacitor footprint from 40 nm to 50 nm reduces the BER from one part-per-million (ppm) to one part-per-trillion (ppt) (Fig. 4.19). This dramatic improvement with a small area increase arises because the tail of the $\langle P_r \rangle$ distribution decays rapidly: a slightly larger device area both increases the total switched charge (through the factor of A in Eq. 4.2.1) and narrows the $\langle P_r \rangle$ distribution (through the $1/\sqrt{N}$ scaling of the standard error), pushing the failing tail of the distribution below the sense limit.

This behavior has important implications for FeRAM process development: if the intra-cluster correlation ρ can be reduced through process optimization—for example, by refining the annealing conditions to produce smaller, more uniformly distributed domains—the tail of the switching fraction distribution would narrow further, improving yield at the most aggressively scaled dimensions.

4.6.2 Validation: Comparison of Statistically Inferred and Directly Subsampled Yield

To verify that the statistical modeling approach does not introduce significant systematic error, we compare the yield map obtained from direct subsampling of the experimental data with the yield map computed from the modeled P_r and sf distributions (Fig. 4.20). The direct subsampling approach randomly samples the capacitor area with windows of the specified device size, computes the average P_r for each window, and tallies the fraction of

windows exceeding the sense limit.

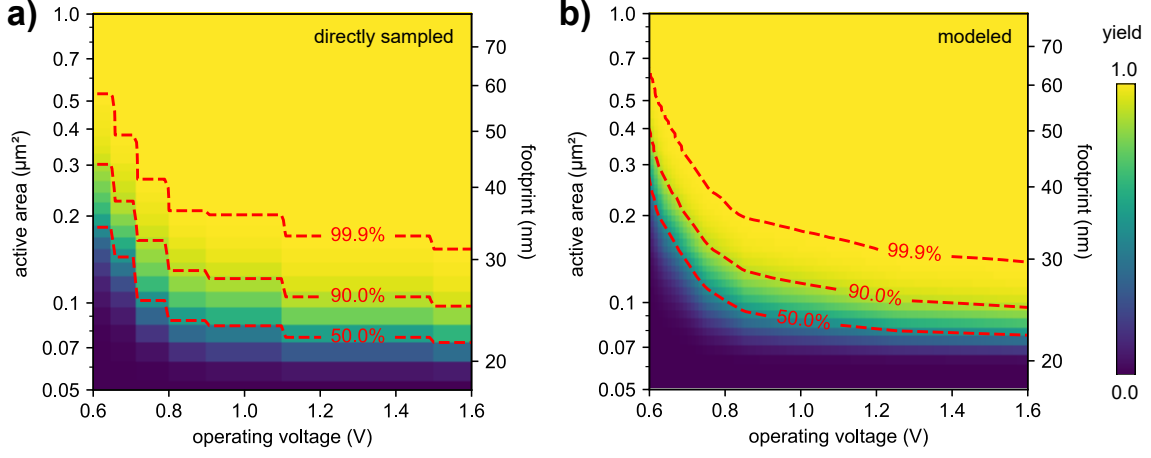


Figure 4.20: **Comparison of direct subsampling and statistical modeling approaches.** Predicted yield map for the tested HZO film at a 30 fC sense limit obtained by (a) directly subsampling the experimental data and (b) modeling the P_r and sf distributions. The two approaches match reasonably well for predicting yield contours up to 99.9%. The direct sampling approach has limited resolution along the V_{op} axis and cannot infer contours for yields $\gg 99.9\%$ due to insufficient sample count. With modeled distributions, we achieve finer voltage steps and can predict contours corresponding to ppm- and ppt-level bit error rates.

The two approaches show little to no quantitative difference for yield contours from 50% to 99.9%, validating the beta distribution model and the assumption of statistical independence between P_r and sf . The directly sampled map has very limited resolution along the V_{op} axis because data is only available at the discrete set voltages used in the experiment. Furthermore, the direct sampling approach cannot infer contours for yields $\gg 99.9\%$ (i.e., BER below 10^{-3}) because the finite sample size means that yields near 100% are indistinguishable: once all sampled windows exceed the sense limit, the directly estimated yield saturates at 100%. The modeled yield map, by contrast, can predict contours at the

ppm and ppt level because the beta distribution model extrapolates the tail behavior from the bulk of the distribution.

4.7 Discussion

4.7.1 The Role of Intra-Cluster Correlation in FeRAM Scalability

The intra-cluster correlation ρ emerges from this analysis as a critical material parameter governing FeRAM scalability. For a given device area, ρ quantifies the degree to which switchable domains are spatially clustered rather than randomly distributed. In a film with strong clustering (high ρ), two devices may have vastly different switching fractions—one may lie entirely within a large switchable domain while the other falls in a nonpolar region. In a film with weak clustering (low ρ), the switching fraction varies more gradually from device to device, reducing the variance of $\langle P_r \rangle$ and improving yield at small areas.

The physical origin of ρ lies in the microstructure of the HZO film. The Pca2₁ orthorhombic phase, which is responsible for ferroelectricity in HZO, forms as nanoscale grains within a matrix that may also contain non-ferroelectric monoclinic and tetragonal phases [139]. The grain size distribution, the spatial arrangement of these grains, and the crystallographic texture all influence ρ . Process conditions that promote a fine, uniform grain structure with a high fraction of the Pca2₁ phase would be expected to reduce ρ and improve scalability. The quantitative framework developed here provides a means to evaluate the effect of such process changes on scalability without fabricating and testing millions of nanoscale devices.

4.7.2 Advantages of STEM EBIC for Ferroelectric Characterization

The STEM EBIC approach demonstrated here offers several distinct advantages over alternative characterization techniques for ferroelectric memory development.

First, STEM EBIC is performed on functioning devices with both electrodes intact,

preserving the mechanical and electrostatic boundary conditions that govern ferroelectric behavior in real devices. This contrasts with high-resolution PFM, which often requires top electrode removal, and with atomic-resolution TEM, which requires destructive cross-section preparation.

Second, the magnification-independent contrast mechanism of EBIC means that the same technique can survey an entire micrometer-scale capacitor while retaining nanometer-scale spatial resolution. This multi-scale capability is essential for bridging the gap between local domain properties and device-scale performance.

Third, the *in situ* electrical access enables the construction of complete pixel-wise hysteresis loops through the interleaved PUNDp and NDPUn protocol. This direct measurement of both coercive and remanent fields at every pixel provides richer information than imaging techniques that measure only the polarization state at a single condition.

4.7.3 Implications for FeRAM Technology Development

The yield prediction framework developed in this chapter provides a quantitative tool for determining the minimum viable device size and operating voltage for FeRAM technology based on a given HZO film. By characterizing a single large capacitor with STEM EBIC and applying the statistical modeling pipeline, device manufacturers can assess the scalability of their ferroelectric film without fabricating and electrically testing millions of nanoscale capacitors.

The yield map in Fig. 4.19 indicates that FeRAM cells with operating voltages below 1 V and capacitor footprints below 50 nm are feasible with the characterized 5-nm HZO film at a 30 fC sense limit. These dimensions are competitive with the most aggressively scaled DRAM technology nodes. The ability to predict bit error rate (BER) at part-per-million level or below is particularly valuable for memory applications, where a high density of defective bits can overwhelm redundant circuits and render a chip non-functional.

4.8 Conclusion

In this chapter, we present a comprehensive methodology for predicting FeRAM scalability through *in situ* STEM EBIC imaging of ferroelectric switching heterogeneity combined with statistical modeling. By mapping local coercive fields and remanent fields across a functioning TiN/HZO/W capacitor, we establish that device-scale polarization is governed by two statistically independent distributions: the local remanent polarization distribution f_{P_r} and the switching fraction distribution f_{sf} .

Key achievements include:

1. Demonstration of pixel-wise hysteresis loop construction through an interleaved PUNDp and NDPUn pulse protocol combined with STEM EBIC imaging, enabling the extraction of four local ferroelectric parameters—coercive field magnitude E_c , coercive field background E_b , remanent switching field E_{rs} , and remanent background field E_{rb} —at every pixel across a functioning ferroelectric capacitor.
2. Classification of the HZO film into switchable, pinned, and nonpolar regions, revealing a complex spatial arrangement that governs the device-to-device variability at small length scales. Fatigue analysis identifies two distinct degradation pathways (switchable $\rightarrow$ pinned, switchable $\rightarrow$ nonpolar) and shows that the fatigue rate decelerates after the most vulnerable domains have degraded.
3. Identification of a positive remanent background field E_{rb} throughout the active area, attributed to asymmetric Schottky barriers at the W/HZO and TiN/HZO interfaces. This built-in field favors the polarization “up” state and must be overcome for switching, contributing to the observed negative coercive field background E_b .
4. Extraction of the local remanent polarization distribution f_{P_r} , found to follow a skew normal distribution and to be independent of operating voltage, confirming the statistical independence of P_r and switching fraction.

5. Modeling of the switching fraction distribution f_{sf} with a beta distribution parameterized by the mean switching fraction $\langle sf \rangle$ and the intra-cluster correlation ρ , where ρ quantifies the degree of spatial domain clustering and is identified as a critical material parameter governing FeRAM scalability.
6. Derivation of device-scale polarization probability mass functions through f_{Pr} and f_{sf} .
7. Generation of a yield map predicting functional device fraction as a function of operating voltage and device area, demonstrating that FeRAM cells with operating voltages of 0.8–1.0 V and capacitor footprints of 35–50 nm can achieve 99.9% yield at a 30 fC sense limit with the characterized 5-nm HZO film. The model further predicts that modest area increases can reduce the bit error rate from ppm to ppt levels.
8. Validation of the statistical modeling approach through comparison with directly subsampled experimental results, showing excellent agreement for yield contours up to 99.9% and demonstrating the model’s unique capability to extrapolate to ultra-low BER regimes inaccessible to direct sampling.

The STEM EBIC methodology and statistical framework developed in this work provide a powerful platform for evaluating the scalability of ferroelectric memory materials. By characterizing a single large capacitor, the complete device-to-device variability can be quantified and used to predict manufacturing yield across the entire operating voltage–device area parameter space. This approach bridges the critical gap between microscopic material characterization and macroscopic device performance, offering a quantitative tool to guide process optimization for future FeRAM technology. The identification of the intra-cluster correlation ρ as a key material parameter suggests that process improvements aimed at reducing domain clustering could extend FeRAM scalability beyond current limits.

CHAPTER 5

Conclusion

Here we presented three complementary studies united by a common conviction: the boundaries of what can be measured in an electron microscope are defined not only by the nominal specifications of the instrument, but also by the ingenuity with which signals are acquired, modeled, and interpreted. In each chapter, a technique whose conventional limits appeared to preclude a class of measurements was re-examined from first principles. By disentangling precision from resolution, by expanding the parameter space of established algorithms, and by constructing statistical bridges between microscopic heterogeneity and macroscopic performance, we demonstrated that scanning (transmission) electron microscopy techniques can deliver quantitative, spatially resolved information at a level previously thought to be attainable only with more specialized or more expensive instrumentation.

Chapter 2 addressed a question that, at first glance, seems to have an obvious answer: can energy-dispersive x-ray spectroscopy, with its ~ 140 eV energy resolution, detect chemical shifts of less than one electron volt? The conventional wisdom—that EDS is a technique for elemental identification while chemical bonding analysis is the exclusive domain of electron energy loss spectroscopy—rests on the assumption that a signal must be resolved to be detected. We show that it is not necessary. By accumulating sufficient counting statistics and fitting peak centroids with nonlinear least-squares methods, the precision of an EDS peak energy determination improves as $1/\sqrt{N}$ in the shot-noise-limited regime, asymptotically approaching a limit set by the signal-to-background ratio rather than by the FWHM of the detector response. On well-isolated peaks with high signal-to-background ratios—such as

the W L_α line at 8.4 keV—we achieved sub-100 meV energy precision, roughly three orders of magnitude better than the peak width.

This precision enabled systematic measurement of chemical shifts across five tungsten transitions spanning 1 to 10 keV, two titanium transitions at approximately 5 keV, and the aluminum K_α transition at 1.5 keV. A finding of particular physical significance is that EDS chemical shifts in transition energies can be either positive (up to +2.4 eV for Ti K_β) or negative (down to −2.6 eV for W L_λ), in contrast to the universally positive shifts observed in EELS binding energies. This bidirectional behavior arises because EDS measures the energy difference between two orbitals rather than the absolute binding energy of one: the sign and magnitude of the shift reflect the differential perturbation of the two orbitals involved, providing chemical information complementary to that available from EELS. Moreover, because EDS requires only an overvoltage of approximately two to efficiently excite a transition, it can access energies far beyond the practical range of EELS. The W L lines at 8–10 keV, measured in this work at 80 kV, lie in a regime where the EELS collection efficiency is negligible, yet EDS provides precise chemical information of this heavy element.

Recognizing that the practical utility of EDS chemical shift mapping is limited by acquisition speed, we developed a corrected paralyzable detector model that accounts for the finite response time of the event discriminator—a subsystem that registers input events for hardware pile-up rejection but has a characteristic time constant that is generally not disclosed by manufacturers. By simultaneously fitting the output-versus-input count rate relationship across all six processing time options of an Oxford X-MaxN 100TLE detector, we determined both the discriminator response time ($t_{\text{dis}} = 0.479 \pm 0.002$ μs) and the pulse-shaper dead times. The corrected model exposes a critical deviation from the widely used 63.2% dead-time rule for maximizing throughput: as the ratio of dead time to discriminator response time decreases, the optimal measured dead-time percentage deviates increasingly from the ideal value, and the pile-up contamination at the optimum grows. From this model we derived a post-acquisition pile-up correction algorithm that removes two-photon coinci-

dence events based purely on probability, requiring no knowledge of specimen composition. Applied to both simulated and experimental NiO_x spectra, the correction improved Ni K_β peak centroid accuracy and Ni $\text{K}_\alpha/\text{K}_\beta$ intensity ratio accuracy by one to two orders of magnitude, enabling a factor of ten increase in data throughput while preserving sub-eV energy precision. This throughput improvement transforms EDS chemical shift mapping from a specialized, hours-long measurement into a technique that can realistically be performed in minutes on a routine basis.

Chapter 3 addressed a different metrological challenge—nanoscale thermometry—and a different instrument platform—the scanning electron microscope. Temperature measurement at the nanoscale is essential for understanding heat dissipation, reliability, and failure mechanisms in modern microelectronic devices. However, the resolution of conventional optical thermometry is diffraction-limited to approximately one micrometer, and contact-based scanning probes perturb the thermal equilibrium they seek to measure. Electron microscopy-based thermometries have demonstrated impressive sensitivity: TEM-based Debye-Waller measurements achieve sub-Kelvin precision, and STEM-based plasmon energy shift measurements offer atomic-scale probes. However, TEM and STEM platforms require electron-transparent specimens and expensive, specialized instrumentation, limiting their accessibility for routine device characterization.

We introduced Kikuchi Diffraction Thermometry (KDTh), a technique that operates on a standard SEM equipped with an EBSD detector. The key innovation was to expand the parameter space of cross-correlation-based pattern matching—an algorithm traditionally used to determine crystal orientation—to include the lattice constant as an additional optimization variable. By generating a library of simulated master patterns with systematically varied lattice parameters and maximizing the normalized cross-correlation coefficient between experimental and simulated patterns at each scan position, we extracted local lattice constants with sub-picometer precision, corresponding to strain sensitivity of approximately 0.01%.

The spatial resolution of SEM KDTh varies with the imaging condition and the specimen mass thickness. With Monte Carlo simulations, we evaluated the most common Kikuchi diffraction geometries: the transmission Kikuchi diffraction (TKD) configuration with an electron-transparent specimen and the conventional EBSD configuration with a bulk specimen. We found that the TKD geometry reduces the beam spread by more than an order of magnitude: on graphite sample, the areal beam diameter enclosing 75% of the signal is 16 nm for TKD versus 380 nm for EBSD under identical illumination conditions. The spatial resolution of TKD, combined with the high angular precision of cross-correlation pattern matching, enabled temperature mapping on Joule-heated graphite devices with a sensitivity of $2.2 \text{ K}/\sqrt{\text{Hz}}$, surpassing all existing SEM-based thermometries and matching the performance of TEM-based techniques. We demonstrated dynamic temperature tracking under both stepped and continuous electrical power ramps, observing linear thermal response consistent with Fourier’s law of heat conduction.

Chapter 4 focused on characterizing the electrical properties of ferroelectric capacitors. Ferroelectric hafnium-zirconium oxide (HZO) has emerged as a leading candidate for next-generation non-volatile memory, but as FeRAM cells are scaled to sub-micrometer dimensions, the spatial variation of ferroelectric properties becomes a critical failure mechanism. The major challenge is that macroscopic transport measurements—such as PUND and FORC—are ensemble averages that are insensitive to the spatial heterogeneity governing device-to-device variability. A large film with acceptable average remanent polarization may contain regions where the local coercive field exceeds the operating voltage, and when device dimensions approach the characteristic size of these heterogeneous regions, yield can drop steeply.

We addressed this challenge by combining *in situ* STEM electron-beam-induced current imaging with an extended PUND pulse protocol. The interleaved PUNDp and NDPUn sequences programmed a functioning TiN/HZO/W capacitor into a series of intermediate polarization states, and EBIC images acquired after each sequence captured the result-

ing spatial distribution of remanent fields. Pixel-wise fitting of the EBIC intensity against applied field history yielded four local ferroelectric parameters at every pixel across the capacitor: the coercive field magnitude and background, and the remanent switching field and background. From these maps, we classified each pixel as switchable, pinned, or nonpolar, revealing a complex spatial arrangement that governs device variability.

The key insight of this chapter was to treat device-scale polarization not as a single-valued material parameter but as a random variable drawn from two statistically independent distributions: the local remanent polarization distribution f_{P_r} , found to follow a skew normal distribution and to be independent of operating voltage, and the switching fraction distribution f_{sf} , modeled with a beta distribution parameterized by the mean switching fraction $\langle sf \rangle$ and the intra-cluster correlation ρ . The intra-cluster correlation—a measure of the degree to which switchable domains are spatially clustered rather than randomly distributed—emerges as a critical material parameter governing scalability. With f_{P_r} and f_{sf} derived from STEM EBIC imaging, we constructed device-scale polarization probability mass functions (PMF) that depend on operating voltage and device area. We integrated the PMFs above a representative 30 fC sense limit to generate a two-dimensional yield map spanning operating voltages from 0.6 to 1.6 V and device areas from 0.05 to 1.0 μm^2 . The map predicts that FeRAM cells with sub-1 V operating voltage and sub-50 nm capacitor footprints can achieve >99.9% yield with the characterized 5-nm HZO film, and that modest area increases can reduce the bit error rate from parts-per-million to parts-per-trillion level. Fatigue analysis conducted in parallel revealed two distinct but coexisting degradation pathways—switchable domains becoming pinned, consistent with charged defect migration, and switchable domains becoming nonpolar, consistent with local phase decomposition—with the fatigue rate decelerating after the most vulnerable domains have degraded.

Looking ahead, extending each of the studies presented above could further benefit nanoscale characterizations. The EDS chemical shift methodology would benefit from a systematic database of transition-energy chemical shifts across a broad range of compounds,

analogous to the extensive EELS chemical shift literature, to establish reference values for identifying unknown specimens. The KDTh technique is poised for extension to polycrystalline materials and to the simultaneous extraction of all types of sample details – lattice constants, phase, orientation, thickness, strain, and temperature, for example – through detailed simulation libraries. The FeRAM scalability framework can be strengthened by correlating the EBIC-derived switching heterogeneity with grain orientation maps from 4D-STEM and with longer-term endurance cycling data to establish quantitative structure–property–reliability relationships.

Together, these studies trace an arc from fundamental physical measurements to practical device metrology. In the field of electron microscopy, all information needed to understand and predict the behavior of nanoscale materials is already present in the signals generated by beam–specimen interaction. It only remains to collect the signals intelligently, model them with sufficient fidelity, and analyze them with appropriate statistical rigor. The work presented represents progress along these three axes. The methodologies developed here—precision through statistics, throughput through detector physics, yield prediction through heterogeneity modeling—extend beyond the specific materials studied, forming a general toolkit for quantitative electron microscopy in the service of functional material characterization.

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