Detecting Chemical Shifts with Energy Dispersive Spectroscopy

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Detecting Chemical Shifts with Energy Dispersive Spectroscopy

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In analytical transmission electron microscopy (TEM), energy dispersive spectroscopy (EDS) is widely used to identify and quantify the chemical elements present in a sample. However, EDS can be extended beyond mere elemental identification, enabling it to determine the chemical bonding state of the elements detected.

Fast silicon drift detectors (SDDs) are sensitive enough for atomic elemental mapping [1]. They are compact, cryogen free, inexpensive, and are thus widely available on modern TEMs. However, the energy resolution of EDS is poor because the x-ray peaks are broadened by the electronic noise of the detector and the uncertainty in the ionization process, which is proportional to the square root of the x-ray energy. The FWHM of the x-ray peaks is far broader than the natural linewidth of most atomic transitions, yet through precise measurements small chemical shifts can be observed. Although other x-ray spectrometers, microcalorimeter for example, have better energy resolution, they cannot compete with the near universality of EDS in TEM. EDS also cannot come close to the energy resolution of EELS, which is the standard spectroscopic technique for chemical shift measurements. However, EDS can detect a wider range of elements at a lower accelerating voltage than EELS [2]. Here we present results of a chemical shift as small as 0.4 eV measured between aluminum metal (Al) and its oxide (Al_2O_3) using EDS in a scanning transmission electron microscope (STEM).

A 100 nm thick Al film and a 20 nm thick Al_2O_3 film are deposited on a 20 nm thick electron-transparent silicon-nitride window via electron beam evaporation and atomic layer deposition, respectively. A 300-nm overlap region of the two films is defined with optical lithography. We collect an EDS spectrum image with an Oxford X-MaxN 100TLE EDS detector on a Titan 80-300 TEM. The Al, Al_2O_3, and overlapping regions are all visible in the field of view (Fig. 1a). By summing the spectra in the non-overlapping regions separately and fitting the x-ray peaks to a normal distribution with a linear background, we determine the aluminum K_α peak energy with a precision of 0.06 eV with 36 million counts. We measure a chemical shift of 0.41 ± 0.08 eV between the pure metal and the oxide (Fig. 1b). After binning the spectrum image by 4, the aluminum K_α peak energy can be determined at each pixel. The two labelled regions in Fig. 1a are distinguishable in Fig. 1c histogram, and the chemical shift is measured to be 0.37 ± 0.03 eV by fitting the two populations separately, which matches Fig. 1b result. These results agree with x-ray chemical shifts in Al and Al_2O_3 obtained by other methods [3].

EDS measures the transition energy between two different electron orbitals, whereas EELS directly measures the electron binding energy. Thus, chemical shifts in EDS and in EELS are slightly different concepts. The chemical shift commonly seen in EELS is the change in electron binding energy due to different chemical environment [4], while the shift in EDS is a change in transition energy. And this means the chemical shift measured in EDS is expected to be smaller than that seen in EELS. EDS K_α peak marks the transition between K and $L_{2,3}$ orbitals. To confirm our result, we compare it with the shift in binding energy of these two levels as measured with EELS.

The key to achieve precise transition energy measurement in EDS is to gather more counts. Even though current EDS detectors have a bin size of a few eV, and the x-ray peaks are broadened to approximately 100 eV, given enough counts in a high-quality spectrum, the peak energy can be determined to a hundredth of the bin size. Fig. 2a inset shows the fit of Al K_α peak with counts from one thousand to ten million. As the total count increases, the data resembles a normal distribution better and better, and the precision of the peak energy determination improves from approximately 1 eV to 0.04 eV. As the total number of counts increases, the precision of the measurement gradually moves from the shot noise limit to the instrumental limit (Fig. 2b). Thanks to the rapid development in high-throughput EDS detectors, achieving the high number of counts needed for precise energy measurement is more and more feasible [5].

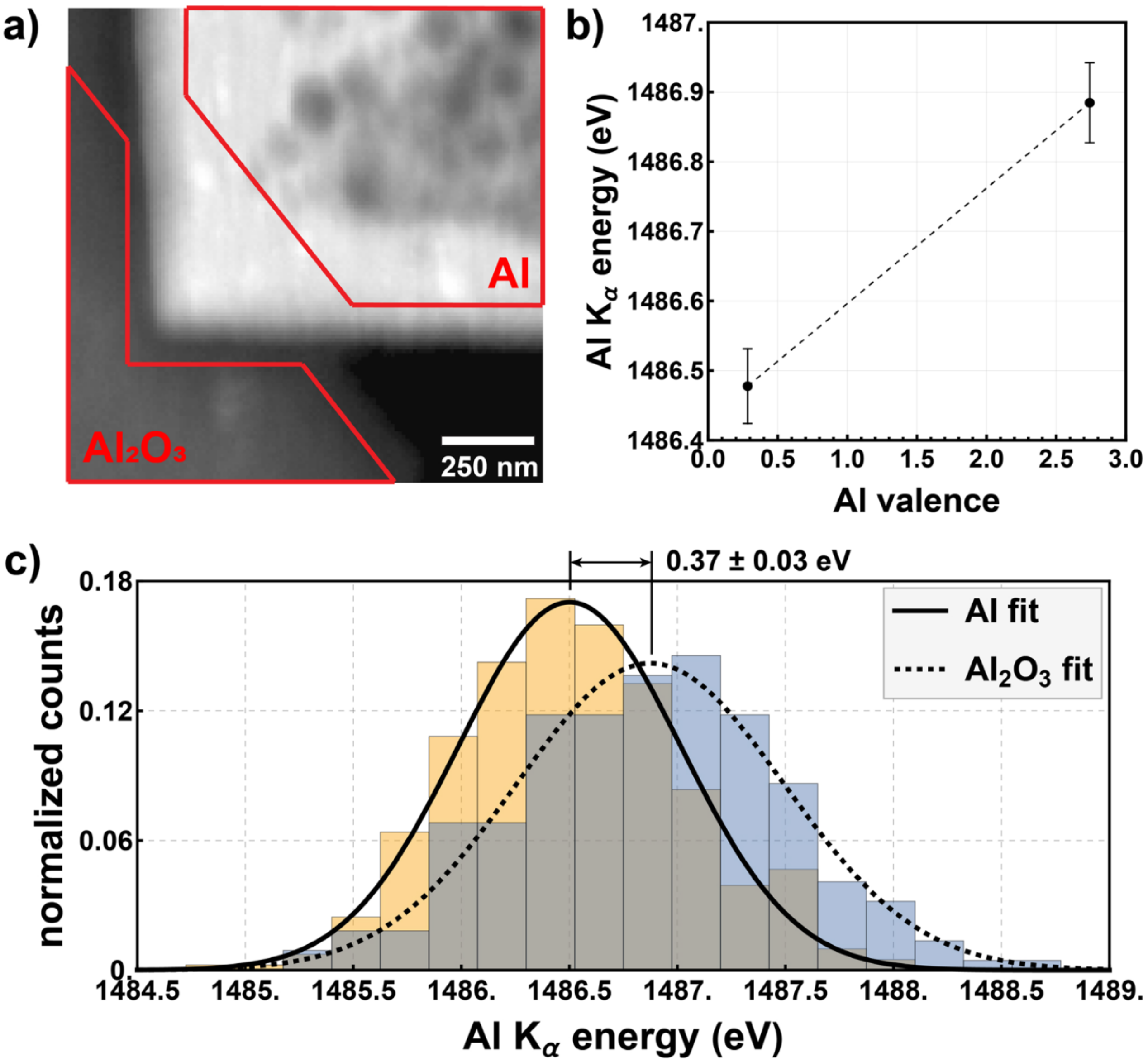

Fig. 1. a) An EDS spectrum image with a 200-eV energy window around Al K_α peak. The Al and Al_2O_3 regions used for Fig. 1b and 1c analysis are labelled. b) By fitting the summed spectrum in each region, the energy of Al K_α peak is determined with a 0.06 eV precision. The Al valence is estimated through the Cliff-Lorimer method. The chemical shift between Al and Al_2O_3 is determined to be 0.41 ± 0.08 eV. c) Population of Al K_α energy determined at pixel level (binned by 4) in the Al and Al_2O_3 regions. Fitting the histogram yields the same chemical shift as shown in Fig. 1b within a standard deviation.

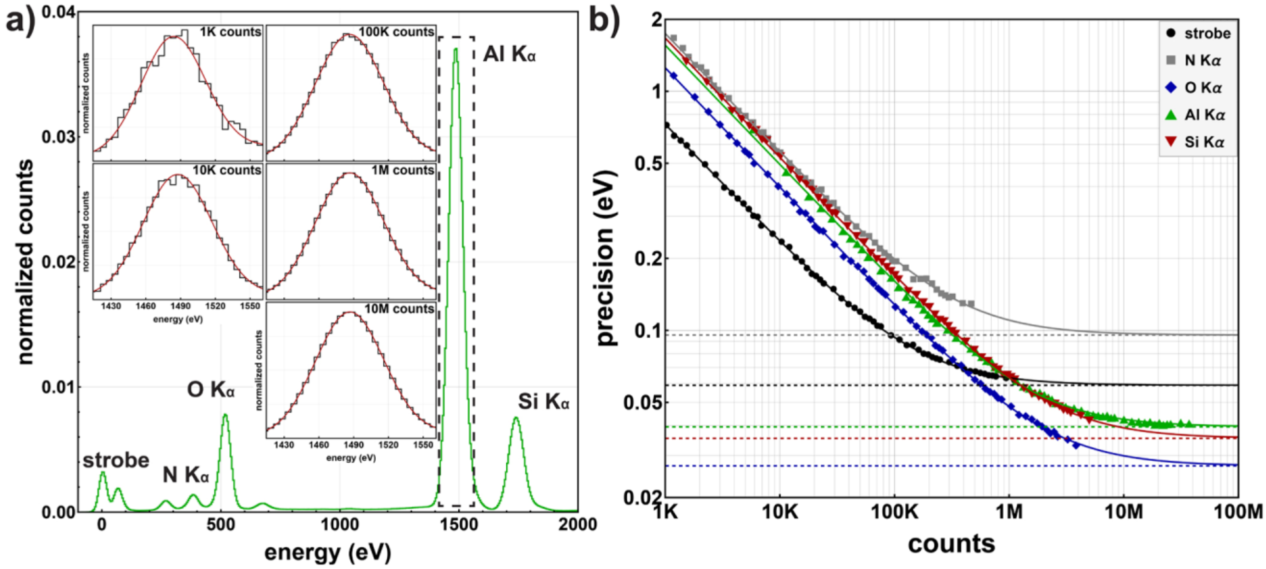

Fig. 2. a) A summed spectrum with approximately 10 million counts in the Al K_α peak. The inset shows the Al K_α peak in the boxed region with different total counts in the peak. The black histograms are the acquired data, and the red curves are the fit. As the total number of count increases, the precision in the measured peak energy approaches the instrumental limit. b) Precision in peak energy as a function of counts in the peak. The dashed lines are the asymptote of each curve, which is the best achievable precision for these experimental conditions.

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