Method for precise extraction of optical functions from transmission electron energy loss spectroscopy

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Abstract. We have developed a spectrum analysis method for transmission electron energy loss spectra. The method involves a deconvolution process optimized for extracting the optical functions. The advantages are equivalent to those of the monochromator-installed systems, and were successfully demonstrated in HfSiON amorphous high-k films as well as well-known crystalline materials, i.e., Al2O3 and SrTiO3.

1. Introduction

Valence electron energy loss analysis with Kramers-Kronig (K-K) relations yields the complete characteristic of the dielectric function. Optical and electrical properties such as the complex permittivity, the band-gap energy, and the interband transition strength are derived. However, the analysis results of electron energy loss spectroscopy (EELS) obtained using a transmission electron microscope (TEM) usually include uncertainty and errors originated from the experimental or the numerical processes. Many efforts have been made to establish a reliable analysis. Though the poor energy resolution has not been recognized as an important factor, we pointed out that the energy broadening deforms optical functions, especially in the case of the Lorentzian type broadening [1]. In practical measurement, typical energy resolution (full width at half maximum: FWHM) with parallel detection EELS is 1eV or worse, which is insufficient for accurate analysis, because the EEL spectrum with wide energy range and high signal to noise ratio (long acquisition time) is required for the K-K transformation. In dielectric formulation, single scattering distribution (SSD) \( S(E) \) of the energy loss spectrum is related to the energy loss function (ELF) in the Born approximation:

\[
S(E) \propto \text{ELF} = \text{Im}[-1/\varepsilon(E)],
\]

where \( \varepsilon = \varepsilon_1 + i\varepsilon_2 \) is the complex dielectric function. First of all, SSD is extracted from a raw spectrum. The next step is normalizing SSD to ELF. Then Re\([-1/\varepsilon]\) is obtained by K-K transformation and \( \varepsilon \) is calculated from a set of loss functions in simple algebra. Appropriate normalization has to be determined for each sample independently whereas the extraction of SSD depends on the TEM-EELS metrology itself. In this report, we focus on a practical method for extraction of the optical function combined with a deconvolution and its application for insulating materials such as high-k thin films. It is noteworthy that our analytical technique drastically improves both energy resolution and quantitativity even in the case of using a commercially available TEM-EELS system without a monochromator.
2. Method
The analysis method we propose here is based on the assumption that only one loss spectrum is given. No extra experimental technique is needed.

2.1. Fitting method for Zero-loss peak and deconvolution
Deconvolution of the valence electron energy loss spectrum (VEELS) is expected to give the ideal loss spectrum by using the zero-loss peak as the resolution function. For sharpening the peak shape, a simple resolution function such as the Gaussian or the Lorentzian is sufficiently effective. However for K-K transformation, a correctly deconvoluted spectrum is needed, because the error components significantly degrade the results of transformation. Therefore we have to extract the complete zero-loss peak from the loss spectrum. A zero-loss peak $Z(E)$ can be described as a convolution of incident electron energy distribution $f(E)$ and an instrumental function $g(E)$:

$$Z(E) = \int f(E') g(E-E') dE'.$$

Our TEM was equipped with a cold field emitter and a parallel detection photo-diode array with scintillator. The energy broadening caused by instrumental instability is about 0.7eV during acquisition time. Thus we assume that the incident electron energy distribution is described by the Fowler-Nordheim equation, and the instrumental function is a convolution or mixed function of the Lorentzian and the Gaussian. The fitting range is below the band gap energy since it should be free from the electron excitation. Implementation of nonlinear parametric fitting gives very good agreement with the measured zero-loss peak over the whole energy range (Fig.1). Deconvolution based on the maximum entropy method (MEM) was performed with DeConvEELS (HREM Inc.)\textsuperscript{[3]}. MEM-deconvolution enables not only resolution enhancement but also noise reduction.

2.2. Removal of plural scattering
To remove the plural scattering component, the Fourier log deconvolution is applied generally. A deconvolution or a modification function is often used for avoiding the noise problem \textsuperscript{[2]}. Strictly speaking, resolution enhancement is not achieved by these methods, e.g. commercial software EL/P (Gatan Inc. See Fig.2). A successfully deconvoluted spectrum could be regarded as the ideal spectrum with infinite resolution in the present channel width condition. Fourier log deconvolution for an ideal spectrum is described by a simple formula without using modification functions as below:

$$s(v) = I_0 \ln(j(v)/I_0),$$

where $j(v)$ is the Fourier component of an ideal loss spectrum, $I_0$ is the ideal zero-loss intensity equal to the total intensity of the resolution function. The inverse Fourier transformation of $s(v)$ gives an ideal single scattering distribution (SSD). Fig.2 shows the result of the present method and the raw data in a thick Al film. The removal of plural scattering after deconvolution is successfully achieved.
2.3. Normalization and K-K transformation

We implemented K-K transformation by the traditional Maclaurin (direct integration) method without using FFT, which is robust for noise. Recent PCs process K-K transformation with runtime of a few seconds. That enables us to easily optimize normalization calculations on any optical parameters at any energy. The integration range of the K-K transform and the normalization was the measured one. No extrapolation was applied. We checked the computational error through all procedures by using test dielectric function. The error deviation was 2 orders of magnitude smaller than that derived from the experiment.

3. Experimental

Measurements have been performed with HF-2000 microscope equipped with Gatan666 PEELS spectrometer. Typical PEELS measurement conditions for K-K analysis were as follows, photo diode counts were integrated up to 10000 at the principal loss peak, channel width was 0.1 or 0.2 eV over 1024 channels, collection semi-angle was within 10 mrad, and dark current and gain variation among channels are corrected before acquisition. Under these conditions, FWHMs of zero-loss peak were 1.0 to 1.2 eV. Specimens (α-Al₂O₃ [0001], SrTiO₃ [001], amorphous HfSiON films on Si(001)) were prepared by conventional argon ion thinning.

4. Results and discussion

4.1. Demonstration on well known crystalline specimens: α-Al₂O₃ [0001], SrTiO₃ [001].

![Graph of index of refraction and extinction coefficient for α-Al₂O₃ and SrTiO₃](image)

Fig.3 (a) The index of refraction $n$, (b) the extinction coefficient $k$ of α-Al₂O₃ [0001].

![Graph of index of refraction and extinction coefficient for SrTiO₃](image)

Fig.4 (a) The index of refraction $n$, (b) the extinction coefficient $k$ of SrTiO₃[0001].

We applied the method for the EELS data to commercial single crystals of α-Al₂O₃[0001] and SrTiO₃[001]. These optical properties were well investigated by French et.al. and Bentheim et.al., respectively. Complex refractive index $N(= n + ik)$ is shown (Fig.3, Fig.4). Similar results for shapes are obtained from EELS and vacuum ultraviolet (VUV) spectroscopy. However, the results of VUV represent highly resolved fine structure relative to those of conventional EELS as they pointed out. Our results of EELS reproduce those fine structures. This indicates both the energy resolution and the quantitativity were improved by the present method.
4.2. Evaluation for valence electronic structure in high-k thin films
We also tried to investigate the valence electron excitations of the high dielectric (High-k) materials. The nitrogen concentration dependence of the band offset in HfSiON was reported by coauthors[6], and the bandgap energy was determined by REELS measurement. TEM-EELS was measured with the same sample and analyzed by the current method. In this case, normalization constant is unknown. We applied the dipole sum rule for the normalization under the assumption that the dipole density is constant, which was determined by estimating the valence electron density of HfSiO. The bandgap energy was estimated by calculating the interband transition strength that is proportional to the probability of an electron excitation from the valence band to the conduction band (fig.5a):

\[ J_{cv}(E) \propto \varepsilon(E) \cdot E^2. \]

The bandgap dependence on N concentration agrees well with the REELS measurement within the experimental error (Fig.5b). This means the surface and the bulk electronic structure is uniform in this specimens. Fig.5a shows the cause of bandgap narrowing with increasing N concentration is not the band shift, but the peak broadening at the band edge. This gradual \( J_{cv}(E) \) onset indicates that the indirect transition may occur in the N20% sample. The changes of the band edge structure are clearly recognized even if the result is semiquantitative because of its uncertainty in normalization.

5. Summary
We have demonstrated that the extraction of the optical function from transmission electron energy loss spectra for Al₂O₃ and SrTiO₃ could be successfully improved by a numerical technique. The challenging analyses of the electronic structures were performed for HfSiON amorphous high-k thin films. These results lead us to conclude that TEM-EELS will become a more attractive tool for material science.

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