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# Automated approaches for band gap mapping in STEM-EELS

Cecilie S. Granerød*, Wei Zhan, Øystein Prytz

*Department of Physics, Centre for Materials Science and Nanotechnology, University of Oslo, P. O. Box 1048 Blindern, N-0316 Oslo, Norway*

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ABSTRACT

Band gap variations in thin film structures, across grain boundaries, and in embedded nanoparticles are of increasing interest in the materials science community. As many common experimental techniques for measuring band gaps do not have the spatial resolution needed to observe these variations directly, probe-corrected Scanning Transmission Electron Microscope (STEM) with monochromated Electron Energy-Loss Spectroscopy (EELS) is a promising method for studying band gaps of such features. However, extraction of band gaps from EELS data sets usually requires heavy user involvement, and makes the analysis of large data sets challenging. Here we develop and present methods for automated extraction of band gap maps from large STEM-EELS data sets with high spatial resolution while preserving high accuracy and precision.

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## 1. Introduction

The optical band gap, defined as the onset of absorption in a semiconductor material, is a central property in the development and improvement of a large number of technologies. Many common techniques for measuring band gaps in semiconductors are based on interaction with light and hence do not offer a spatial resolution better than on a μm scale [1–4]. However, the demand for high efficiency and small size of new devices requires a fundamental understanding of the material and band gaps at smaller length scales. With a (Scanning) Transmission Electron Microscopes ((S)TEM's), band gap measurements performed using Electron Energy-Loss Spectroscopy (EELS) have a spatial resolution which in principle is limited only by the delocalization of the energy transfer process [5–8]. For band gaps in common semiconductors, this delocalization is on the order of 5–10 nm [6], thereby making band gap measurements in TEM a powerful method for studying new semiconductor devices.

In low-loss EELS the energy lost by the transmitted electron corresponds to energy transfer for excitations in the sample. The dominating feature in EELS is usually the zero-loss peak (ZLP), which contains transmitted electrons that have lost little or no energy to the specimen. The tail of this feature forms a background to the excitations which one usually wishes to study. If only single electron transitions from the valence to the conduction band are considered, the energy loss is related to the joint density of states, and the minimum of the observed energy loss corresponds to the optical band gap of the specimen.

The task of measuring the band gap using EELS is then to identify the onset of energy loss in a precise and accurate manner, a process that usually relies on fitting of models for both the background and edge to the experimentally obtained data. In performing the fitting, several choices must be made and complications may arise:

a) To achieve the highest accuracy in band gap extraction, a good model for the background (ZLP) should ideally be fitted as close to the edge onset as possible [9]. If the onset shifts, so should the background fitting region.
b) An optimal energy range must be identified for fitting of the energy loss model to the data. As with the background modelling, this energy range will vary with the position of the edge onset (the band gap value) [7,10]. Depending on the shape of the edge, this fitting region may also be relatively small, making precise positioning of the fit region important.
c) Even after background subtraction, intensity may remain below the onset of the band gap transitions. This may be due to losses to Cherenkov radiation, excitations of surface plasmons, guided light modes, amorphous surface effects, or transitions to and from defect states [11–13]. In any band gap extraction process a determination needs to be done on how to handle such effects.
d) Depending on the experimental conditions, the obtained spectra may have a high level of noise, both in the edge itself and in the energy loss range below [9,14,15]. The noise level must be evaluated and factored into the errors reported together with the extracted band gap values.

* Corresponding author.
*E-mail address:* cecilie.granerod@fys.uio.no (C.S. Granerød).

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If only a small data set containing a handful of spectra is analysed, each spectrum can be manually inspected and an optimal band gap extraction strategy can be identified individually. However, if the data is collected in a 2D scan with a spectrum at each scanned position, called Spectrum Image mode, the data set can contain thousands of spectra. The manual approach is then not viable. Furthermore, if the spectra are obtained from different parts of a chemically inhomogeneous specimen, band gap extractions based on one or a few optimal parameters are likely to give inaccurate results.

STEM-EELS has previously been applied in measuring band gaps with high spatial and energy resolution [7,16], but very few works have attempted to put forward an efficient computational method for band gap mapping [8]. In this work, an automated approach for STEM-EELS band gap analysis is presented, with the aim of extracting band gap maps from large Spectrum Images. Methods, referred to as the Sliding interval method, the Fixed endpoint method, and the Dynamic background subtraction method, have been implemented in MATLAB and are available on Github [17].

## 2. Experimental methods

ZnO has a direct optical band gap of 3.25–3.30 eV at room temperature, and Cd-alloying has been shown to increase the lattice spacing, thereby decreasing the band gap [18–20]. An MOVPE-grown sample with films of ZnO and $Zn_{1-x}Cd_xO$ ($x \simeq 0.1 - 0.2$, referred to as ZnCdO) was prepared by cutting and mechanical polishing, before ion milling with Ar gas in a Fishione model 1010. The sample was plasma cleaned for 4 min in a Fishione model 1020 in order to avoid carbon contamination.

The measurements were performed with a monochromated and probe-corrected FEI Titan G2 60 – 300 kV TEM. The microscope was operated at a high tension of 60 kV in order to increase the interaction cross-section, while also reducing any Cherenkov losses [21,22]. The final sample thickness of less than 30 nm further minimized such unwanted retardation loss effects efficiently. STEM was set up with a convergence angle of 66 mrad, and EELS was measured with a Gatan Quantum 965 GIF with a collection angle of 16.8 mrad. The signal was dispersed to 0.01 eV per channel, and the exposure time of each spectrum in the Spectrum Image was set to right below the overexposure limit of the CCD. By using the monocromator, the energy resolution was 0.12 eV by measuring the full width at half maximum (FWHM) of the ZLP. After measurements, the data sets were corrected for dark current and energy calibrated by aligning the maximum of the ZLP of each spectrum to the same channel.

## 3. Results and discussion

### 3.1. Manual fitting of background and edge onset

Our starting points are two low-noise spectra obtained from ZnO and ZnCdO. From the 10× binned data in Fig. 1A it can be seen that the edge onsets are located around 3.2 eV in ZnO and 2.9 eV in ZnCdO. A successful removal of the background can be achieved with a good model, fitted to an energy range close to, but not overlapping with, the edge onset. We chose a decaying power-law model, and by manual inspection of the residual intensity (Fig. 1B), suitable background fit ranges were found at 2.5 – 2.8 eV and 2.0 – 2.3 eV for ZnO and ZnCdO, respectively. If regions closer to or further from the edges were chosen, we observe that the background is often over- or underestimated. This underlines the importance of the choice of fitting range for the background subtraction: the background in a Spectrum Image where the onset varies should be fitted relative to the edge and not in a fixed range of energy loss.

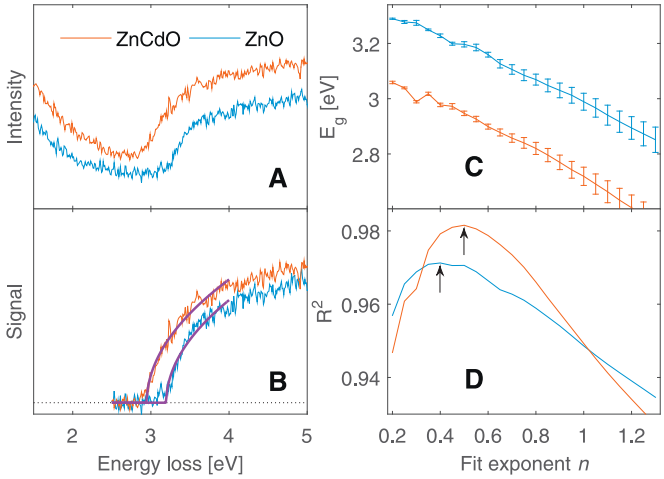


**Fig. 1.** (A) Low-loss EELS in ZnO and ZnCdO, 10× binned, and (B) background-subtracted spectra with least squares onset fit, $n = 0.5$. (C) Fitted band gap as a function of curve exponent $n$ from least squares fit, and (D) corresponding goodness-of-fit parameter $R^2$. The arrows indicate the maximum.

To identify the band gap, we build on the work of Rafferty and Brown [23]. Based on an idealized band structure consisting of two parabolic bands describing the valence and conduction states, the observed energy loss intensity is described as

$$I(E) = c(E - E_g)^n \quad \text{for } E \geq E_g. \tag{1}$$

Here $E$ is the energy loss, $E_g$ is the band gap, and $c$ is a constant. The exponent $n$ is ideally 1/2 for a direct band gap and 3/2 for an indirect band gap. The model describes the ideal EELS edge in a short energy range above the onset, where the parabolic approximation holds. Below the onset, the ideal intensity is zero. In the present work, we limit ourselves to direct band gaps. Indirect band gap materials usually have a gradual onset of energy loss (Eq. (1)) which is easily masked by noise, background, or Cherenkov losses. Modified experimental setups are often needed to study these, such as allowing only specific momentum transfers to contribute to the spectrum [12].

To test the suitability of Eq. (1), we first manually identify an acceptable edge fitting range for both materials as 2.5 – 4.0 eV. As edge onset is a one-sided fitting, any remaining intensity below the onset will shift the result down in energy. It is therefore more likely to find a lower than a higher onset of the edge. Hence, we seek both a high goodness-of-fit and a high onset when performing the fitting. By varying the exponent $n$, we find the band onsets as shown in Fig. 1C, and the corresponding goodness-of-fits ($R^2$) shown in Fig. 1D. The maximum of $R^2$ is found at $n = 0.45$ in ZnO and $n = 0.55$ in ZnCdO, and this is seen to vary with the choice of onset fit range. As both materials are direct band gap semiconductors, and the model is limited to a small energy range above the onset, we assume that it is sufficient to use $n = 0.5$ in both cases.

### 3.2. Automated approach for edge onset extraction

From Eq. (1) the intensity below the onset is ideally zero, however, this is rarely the case for experimentally obtained spectra. In addition to noise and residual signal after background subtraction, the energy resolution of the experiment is assumed to introduce a spectral broadening which affects the edge. The simulated impact of spectral broadening is shown in Fig. 2, where the ideal onset convoluted with a Gaussian (FWHM is set to 0.15 eV) can be compared with the ZnO spectrum. Here the energy broadening creates a tail to the ideal spectrum, which leads to intensity below the onset. When making a curve fit to this edge, this intensity

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