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Comment

Comment on ‘Nanoscale mapping of optical band gaps using monochromated electron energy loss spectroscopy’

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In the above article [1] the authors attempt to measure the band gap of pure and of cadmium enriched zinc oxide from low-energy or valence electron energy-loss spectroscopy (VEELS) in a monochromated and aberration corrected scanning transmission electron microscope and claim a ‘spectral precision of 20 meV’. As this is a factor of 7.5 better than the quoted energy resolution of their spectrometer of 0.15 eV, this would be very impressive, and for investigating doping effects such a precision would be highly desirable. It is clear that the precision can be better than the resolution by several factors if the sampling is sufficiently fine, however, there are a few problems with the data that make this claim appear questionable. The whole situation is complicated by the fact that the manuscript shows only processed but no raw data and that essential experimental variables, such as convergence and collection angles, as well as relevant fitting parameters, such as begin and end positions of the fit range and R^2 values of the fits, are not provided. These points could have been picked up by a careful reviewer.

The authors have basically applied a standard approach of subtracting an exponential extrapolation of the zero loss peak and fitting a square root function to a 3.5 eV wide spectral range of the remainder. From the standard deviation of 0.02 eV of their data when repeating the same experiment at various points in the same specimen they conclude this to be the ‘precision’ of their experiment and add corresponding error bars to their plot. With comparison to cathodoluminescence data they then claim ‘both excellent accuracy and precision’.

Unfortunately, data interpretation is not easy and may not be so straightforward with VEELS. In the following, some aspects related to methodology, statistics and physics are considered.

Firstly, other methods of zero loss peak removal (deconvolution [2, 3], mirroring the peak tails and subtraction, which works well for a monochromator where the zero loss peak should be symmetrical [4, 5], different multi-exponential fittings as reviewed in [6], together with Cerenkov effects) could (and will) produce different numerical values for the band gap. The authors admit that ‘the exact fit range of the background model influences the extracted band gap value’, however, to what degree other methods of zero loss peak removal or other fitting ranges would influence the results seems to not have been explored. The statement that ‘for the most accurate results, this fitting region should be chosen close to the expected onset of the band gap transitions being studied’ is certainly correct but close to a tautology and perhaps not particularly helpful: this seems to imply that they can only measure the band gap precisely if they know it beforehand and so know where to place the fitting range! It means that the procedure described may, at the best work, for zinc oxide under the given (unknown) conditions of data acquisition and processing but is likely to fail for any other semiconductor and will probably not be able to predict unknown band gaps for methodological reasons. The general title of the publication, however, would have seemed to imply to readers a fairly widespread validity.

Secondly, the small spectral sections shown in the inset of one figure (figure 4) depict a strong rise of absorption near the suspected band gap of ∼3 eV but are then followed by a plateau from ∼3.5 to 5 eV, so the net signal does clearly NOT increase like a square root function. We have recently reported this for InGaN and pointed out that including an offset will alter but not improve the fit quality [7]. Hence, fitting such a function, of which no details are given, will not be very good (in terms of fit quality) and probably not be particularly reliable (in terms of reproducibility). It would be nice had the authors at least stated the R^2 values obtained, better still, explored the variation of R^2 values with extension and positioning of the fitting range [8]. This may have produced a much larger statistical error than the 20 meV stated, and it appears questionable whether a small scatter obtained by repeatedly applying their method to spectra extracted from pure zinc oxide from adjacent regions would also be useful to characterize the general precision of a technique that may significantly deteriorate in the case of small thickness, orientational and/or compositional variations within the specimen.

Thirdly, VEELS always shows strong plasmon peaks (for zinc oxide at 18.8 eV [9], for zinc at 17.2 eV [10]) the long tail components of which have been shown to also influence the numerical fitting results [7]. Moreover, for the specific materials system of zinc oxide under consideration here there are further, weaker valence interband transitions at 3.8, 5.5, 9.5 and 13.5 eV [9], and there may be a pronounced surface plasmon peak around 15.8 eV [11] in a thin foil sample, so fitting a simple square-root function to a small range which will inevitably contain several weak humps and shoulders makes physically rather limited sense. The underlying fundamental reason is that the free-electron approximation for a three-dimensional perfect bulk material implicitly assumed in the derivation of the square-root function for the density of states is not necessarily fulfilled in this crystalline material.

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References

[1] Zhan W, Granerød C S, Venkatachalapathy V, Johansen K M H, Jensen I J T, Kuznetsov A Y and Prytz Ø 2017 Nanoscale mapping of optical band gaps using monochromated electron energy loss spectroscopy *Nanotechnology* **28** 105703

[2] Dorneich A D, French R H, Müllejans H, Loughin S and Rühle M 1998 Quantitative analysis of valence electron energy-loss spectra of aluminium nitride *J. Microsc.* **191** 286–96

[3] Schamm S and Zanchi G 2003 Study of the dielectric properties near the band gap by VEELS: gap measurement in bulk materials *Ultramicroscopy* **96** 559–64

[4] Erni R and Browning N D 2005 Valence electron energy-loss spectroscopy in monochromated scanning transmission electron microscopy *Ultramicroscopy* **104** 176–92

[5] Walther T and Stegmann H 2006 Preliminary results from the first monochromated and aberration corrected 200 kV field-emission scanning transmission electron microscope *Microsc. Microanal.* **12** 498–505

[6] Stöger-Pollach M and Schattschneider P 2007 The influence of relativistic energy losses on bandgap determination using valence EELS *Ultramicroscopy* **107** 1178–85

[7] Walther T, Wang X, Angadi V C, Ruterana P, Longo P and Aoki T 2017 Study of phase separation in an InGaN alloy by electron energy loss spectroscopy in an aberration corrected monochromated scanning transmission electron microscope *J. Mater. Res.* **32** 983–95

[8] Amari H, Zhang H Y, Geelhaar L, Chèze C, Kappers M J and Walther T 2011 Nanoscale EELS analysis of elemental distribution and bandgap properties in AlGaN epitaxial layers *J. Phys.: Conf. Ser.* **326** 012039

[9] Hengehold R L, Almassy R J and Pedrotti F L 1970 Electron energy-loss and ultraviolet-reflectivity spectra for crystalline ZnO *Phys. Rev.* B **1** 4784–91

[10] Egerton R F 2011 *Electron Energy-Loss Spectroscopy in the Electron Microscope* 3rd edn (New York: Springer) p 420

[11] Wu C-T, Chu M-W, Liu C-P, Chen K-H, Chen L-C, Chen C-W and Chen C-H 2012 Studies of electronic excitations of rectangular ZnO nanorods by electron energy-loss spectroscopy *Plasmonics* **7** 123–30