VEELS band gap measurements using monochromated electrons

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Abstract. With the development of monochromators for transmission electron microscopes, valence electron energy-loss spectroscopy (VEELS) has become a powerful technique to study the band structure of materials with high spatial resolution. However, artefacts such as Cerenkov radiation and surface effects pose a limit for interpretation of the low-loss spectra; also the inelastic delocalisation restricts the spatial resolution on band gap mapping. For direct semiconductors, spectra acquired at thin regions can efficiently minimize the Cerenkov effects. Examples of h-GaN spectra acquired at different thickness showed that a correct band gap onset value can be obtained for sample thicknesses up to about 60 nm. For indirect semiconductors, the correct band gap onset can be obtained in the dark-field mode when the required momentum transfer for indirect transition is satisfied. At low energy-loss range the spatial resolution of this technique, which is mainly limited by the inelastic delocalisation, can be improved by dark-field VEELS at high collection angles.

1. Introduction
Low-loss electron energy-loss spectroscopy (EELS) investigates the energy-loss range of less than 50 eV, which contains fundamental material information including band gap values, surface and volume plasmon excitations, interband and intraband transitions and excitation of Cerenkov radiation [1]. Traditionally, semiconductor band gaps are measured by optical methods which have high energy resolution (~2 meV) but poor spatial resolution (~0.2 µm). This spatial resolution is clearly not sufficient for measuring band gaps in modern nanostructured devices with scales in the nanometer range. Valence electron energy-loss spectroscopy (VEELS) provides both high energy and high spatial resolution and thus makes this technique ideally suited for band gap measurements, particularly in microelectronic devices.

The energy spread of the electron source is one of the most important aspects to be improved for VEELS, since the tail of the zero-loss peak makes it difficult to separate the signal from the background. Recently, several types of monochromators were developed and advantages of using monochromated electron energy-loss spectroscopy were also demonstrated [2-5]. Despite the technological breakthrough, there are still restrictions for VEELS band gap measurements. The ultimate obtainable spatial resolution is limited by the inelastic delocalization phenomenon, especially for the energy-loss range close to the semiconductor band gap region. In addition, Cerenkov radiation and surface effects impose artefacts on band gap measurements for a wide range of semiconductors and insulators.
2. Experimental details
The h-GaN thin film was grown on [0001] sapphire by metal-organic chemical vapor deposition (MOCVD). Cross-sectional TEM specimens were prepared by double dimpling with final thinning using a precision-ion-polishing system (PIPS, Gatan, Pleasanton, USA). The ion-polishing process was carried out at 3.8 keV energy and followed by a 1.8 keV cleaning procedure.

All spectra presented within this paper were acquired using a Zeiss Libra 200FE transmission electron microscope (operated at an accelerating voltage of 200 keV) equipped with an electrostatic omega-type monochromator (CEOS GmbH), an in-column corrected 90° energy-filter, and a 2k×2k CCD camera (Gatan, Pleasanton, USA). The energy resolution of the microscope is 135 meV under normal operation conditions (acquisition time ≤ 1 s). All the EEL spectra were acquired at a dispersion of 0.032 eV/channel and a collection angle of 3 mrad in image mode. For the ω-q maps the specimen was raised above the eucentric position in image mode with spot illumination [6].

3. Results and discussion
3.1. Direct semiconductors
For direct semiconductors, no momentum transfer is required to launch the electron from the valence band into the conduction band. Peaks in the VEEL spectrum are expected at energy losses where the joint density-of-states (JDOS) exhibits maxima.

h-GaN is a direct band gap semiconductor for applications in high-temperature and high-power microelectronics as well as in light-emitting devices. In this study, the h-GaN band gap was measured at liquid nitrogen temperature and the onset value was determined to be 3.3 eV using a deconvolution method. Zero-loss deconvolution was applied for GaN spectra using the Richardson-Lucy method (DeConvEELS v2.0, HREM-Research, Higashimastuyama, Japan). During the deconvolution process a smoothing width of 0.2 eV was used in order to prevent the amplification of noise by the deconvolution algorithm. The iteration cycles were constrained manually to prevent apparent artefacts. Figure 1 shows a raw and a deconvoluted spectrum of h-GaN.

![Figure 1. A raw and a deconvoluted spectrum acquired from h-GaN.](image)

One of the major limitations for VEELS studies of semiconductor band gaps is Cerenkov radiation. Cerenkov radiation is emitted when the electron velocity v exceeds the phase velocity of light in the medium through which it is moving. Thickness-dependent VEELS spectra due to Cerenkov radiation losses have been discussed in detail in Ref. [7]. In order to overcome the difficulties associated with Cerenkov losses for direct semiconductors, thin regions of specimen should be used. Systematic studies on thickness dependent h-GaN VEELS spectra showed a consistent band gap value of ~ 3.3 eV up to about 60 nm. ω-q maps acquired at different thicknesses in Fig. 2 reveal great similarity for the plasmon losses as well as for the interband transitions. However, the more intensive Cerenkov losses in thick regions overlap severely with the band-gap transitions. This clearly explains the apparent shift of the band gap towards lower energies at increasing specimen thickness.
3.2. Indirect semiconductors

For indirect semiconductors, the fast electron has to transfer momentum to facilitate the electronic transition of a valence band electron into the conduction band. This implies that the cross section for interband transitions is lower than in the case of direct semiconductors, which, in turn, makes Cerenkov losses more prominent.

The scattering angle of electrons which suffer Cerenkov loss is very small: \( \theta = \theta_E (\varepsilon_1 v^2 / c^2 - 1) \), where \( \theta_E \) is the characteristic scattering angle, \( \varepsilon_1 \) is the real part of the dielectric function and \( v \) is the velocity of electrons. Since indirect semiconductors normally require a large momentum transfer \( q_\perp \) for band gap transitions, we suggest “dark-field VEELS” for band gap measurements of indirect semiconductors. Figure 3a shows the geometry of a star-shaped filter entrance aperture which can efficiently suppress the collection of Cerenkov losses while permitting the high-angle indirect band gap transitions. Corresponding results obtained using the star-shaped entrance aperture were shown in Ref. [7]. Based on dark-field VEELS, the silicon band gap of ~1.1 eV was measured by displacing the objective aperture in image mode along the Γ-X direction (Fig. 3b).

3.3. Spatial resolution

In the very low energy-loss range the ultimate spatial resolution for VEELS is limited by inelastic delocalisation which has its origin in the long-range Coulomb interaction. The inelastic collection angle has profound impact on spatial resolution that can be explained as inelastic “weak beam” imaging [8]. Taking advantage of the in-column Ω-type energy filter which allows an extra annular-
dark-field detector below the energy selection plane, an improved VEELS spatial-resolution has been obtained recently by energy-filtered scanning transmission electron microscopy (EFSTEM) at high collection angles. This technique can be quite useful especially for band-gap mapping of indirect materials with small band gaps. Recent experimental results indicate a spatial resolution well below 10 nm for an energy loss of 2 eV using a 1 eV energy slit (Fig. 4.). This is well below the theoretical prediction for “bright-field VEELS” using the $d_{50}$ ($d_{50}$ contains 50% of the inelastic signal) criteria which envisages the spatial resolution to be only about 12 nm [9].

![Figure 4.](image)

Figure 4. (a) Schematic of EFSTEM. (b) energy-filtered HAADF image of InP particles showing better spatial resolution than the $d_{50}$ prediction; inner collection angle of ~ 40 mrad.

4. Conclusions
For direct semiconductors, acquisition of VEEL spectra at thin regions can be a feasible way to minimize the Cerenkov effects. For indirect semiconductors, on the other hand, dark-field VEELS realized by a star-shaped filter entrance aperture was shown to be very effective. However one should keep in mind that despite these efforts, limitations still exist, including surface effects for very thin specimens and long acquisition times for dark-field spectroscopy. At low energy-losses, the spatial resolution of VEELS, which is mainly limited by the inelastic delocalisation, can be improved by dark-field spectrum imaging at high collection angles.

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