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Bandgap measurement of high refractive index materials by off-axis EELS

Maryam Vatanparast[a,*], Ricardo Egoavil[b], Turid W. Reenaas[a], Johan Verbeeck[b], Randi Holmestad[a], Per Erik Vullum[a,c]

[a] Department of Physics, NTNU (Norwegian University of Science and Technology), 7491 Trondheim, Norway
[b] EMAT, University of Antwerp, Groenenborgerlaan 171, 2020 Antwerp, Belgium
[c] SINTEF Materials and Chemistry, 7065 Trondheim, Norway

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ABSTRACT

In the present work Cs aberration corrected and monochromated scanning transmission electron microscopy electron energy loss spectroscopy (STEM-EELS) has been used to explore experimental setups that allow bandgaps of high refractive index materials to be determined. Semi-convergence and –collection angles in the µrad range were combined with off-axis or dark field EELS to avoid relativistic losses and guided light modes in the low loss range to contribute to the acquired EEL spectra. Off-axis EELS further supressed the zero loss peak and the tail of the zero loss peak. The bandgap of several GaAs-based materials were successfully determined by simple regression analyses of the background subtracted EEL spectra. The presented set-up does not require that the acceleration voltage is set to below the Čerenkov limit and can be applied over the entire acceleration voltage range of modern TEMs and for a wide range of specimen thicknesses.

1. Introduction

The developments of aberration corrected and monochromated TEMs were expected to revolutionize the access to information about semiconductor bandgaps and optical properties at the nanoscale. Technically, this is the case, scanning transmission electron microscopy (STEM) with a Cs aberration corrected and monochromated electron beam can in combination with electron energy loss spectroscopy (EELS) be used to collect spectroscopy maps that have atomic spatial resolution and an energy resolution that is in the tens of meV range. Even if the spatial resolution of losses in the bandgap regime is limited by inelastic delocalization, the various bandgaps of nanoscale structures can in principle be mapped both easily and quickly. Moreover, since the low-loss region of the EEL spectrum is described classically by the energy-loss function that is determined by the material's dielectric function [1–3], Kramers–Kronig analysis can be used to determine the material's optical response.

However, many semiconductors are also high refractive index materials. The phase velocity of light in the sample material scales with the refractive index, and beam electrons which move faster than this phase velocity of light will suffer from Čerenkov losses (CLs) and Čerenkov photons generated in the low energy range of the loss spectrum [4,5]. Besides the pure relativistic CLs, further low-energy losses appear due to retardation of the beam electrons from surface and interface plasmons (these losses also have relativistic contributions) and from excitation of guided light modes [6]. The probability of generating Čerenkov photons increases with the acceleration voltage (i.e. the speed of the electrons), but disappears below a critical acceleration voltage (Čerenkov limit) determined by the sample's maximum value of the real part of the dielectric function [6]. However, surface and interface plasmon losses and excitation of guided light modes will still be present at acceleration voltages below the Čerenkov limit [6]. For a large and important group of high refractive index materials, such as Ge, Si, GaAs, GaP and many other semiconductors, the Čerenkov limit is below the typical acceleration voltage range of modern TEMs. The Čerenkov limit for GaAs is only 11 keV if the maximum value of the refractive index is used, and 20.6 keV if the refractive index at the bandgap is used [7].

The scattering cross-section for volume losses, including Čerenkov radiation, is further dependent on the thickness of the TEM specimen. If the specimen thickness has a similar magnitude as the wavelength of the emitted Čerenkov photons, the surfaces will damp the CLs. For h-GaN with a Čerenkov limit of 51 keV it has therefore been shown that the correct bandgap at 3.43 eV can

* Corresponding author.
E-mail address: maryam.vatanparast@ntnu.no (M. Vatanparast).

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be obtained for a specimen thickness up to 0.5 t/λ (λ = the inelastic mean free path) at 200 kV [8]. For GaAs it has been reported that the onset of the Čerenkov radiation is moved to energies above the bandgap if the specimen thickness is below 100 nm at 200 kV [9]. However, later simulations [10] and experimental data obtained with a specimen thickness as low as 0.4 t/λ [1] have shown that relativistic losses and guided light modes contribute with significant signal to the EEL spectrum below the bandgap energy in GaAs.

Another complication is the extremely low signal of the interband transitions compared to the intensity of the zero loss peak (ZLP). Even if the full width half maximum (FWHM) of the ZLP is very low, a careful procedure for handling the tail of the ZLP is important in order to extract a correct bandgap signal [11]. A vacuum-recorded ZLP is always different from the ZLP in an EEL spectrum acquired from the sample due to phonon and exciton losses, as well as imperfections in the spectrometer, converting elastic scattering which changes the incoming angles into seemingly inelastic signals. Hence, a vacuum-recorded ZLP cannot simply be used to subtract the ZLP and its tail from spectra acquired from the sample. Generally, a fitting procedure for the ZLP, and especially the tail of the ZLP, is preferred. Several methods have been attempted to extract the bandgap by various fitting routines. These routines include the use of a Lorentzian function [12], a seven parameter fit function for ZLP deconvolution [13], a power law background in front of the bandgap [3], and mirroring the left-side tail of the ZLP to the energy loss side [14]. Even if some of these fitting methods can remove phonon and exciton losses in the ZLP tail, relativistic losses present both below and above the bandgap of high refractive index materials cannot reliably be removed by any fitting routine [15].

The bandgap of GaAs has been retrieved in the literature before. In recent work, it has been argued that unwanted spectral contributions can be avoided by working below the Čerenkov limit [1], and that this simplifies credible measurement of bandgap energies. Nevertheless, in the relativistic simulations of valence electron energy-loss spectra of GaAs done by Rolf Erni it was found that the spectra could still be affected by excitation of guided light modes and retardation effects even with electron energies below the Čerenkov limit [10]. These energy losses are represented by a smooth thickness-dependent background, which is difficult to treat when removing the zero-loss peak from the spectra. Attempts to remove this background might be critical for materials with a weak bandgap feature like GaAs and could affect the measured bandgap energy.

CLs and light guided modes are only present at scattering angles below a few tens of µrad [8–10,15]. In normal STEM, the semi-convergence angles of the beam are normally so large [~several mrad] that the convergent beam electron diffraction (CBED) discs have a significant overlap. This also means that the extremely forward scattered CLs, surface losses and guided light modes are still present in the entire diffraction plane. Hence, normal STEM cannot be used to measure the bandgap of high refractive index materials in the standard acceleration voltage range of 60–300 kV for most modern TEMs. However, in this work we use a monochromated and probe corrected beam in low-magnification (Low-Mag) STEM mode. In low magnification STEM, semi-convergence and –collection angles in the µrad range are used. Off-axis conditions, i.e. dark field EELS, is further used to suppress the ZLP and to be outside the angular range where CLs and light guided modes hit the spectrometer. Furthermore, the low semi-convergence and -collection angles decrease the detection of phonons (they have a large angular distribution) and interband transitions with a significant momentum transfer. Dark field EELS means that we detect electrons with a momentum transfer. However, because the semi-angles are far down into the µrad range, we can still detect a part of reciprocal space that is close to the centre of the first

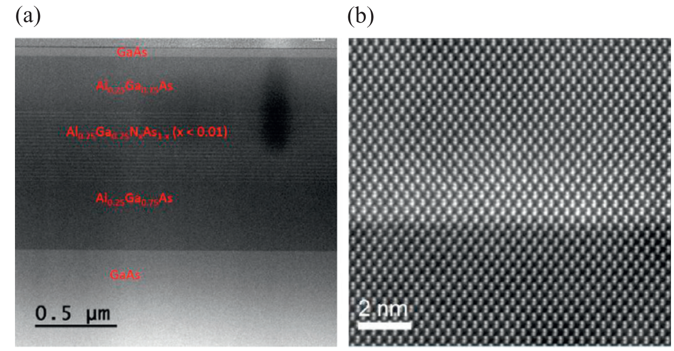

Fig. 1. (a) A high angle annular dark field (HAADF) STEM image of the sample structure. A 400 nm thick $Al_{0.25}Ga_{0.75}As$ layer is grown on top of a (001) GaAs substrate followed by a stack of 20 quantum dot (QD) layers. Each of the QD layers were grown as 2 monolayers thick InAs and they are separated by 20 nm thick $Al_{0.25}Ga_{0.75}N_xAs_{1-x}$ ($x < 0.01$) spacer layers. On top of the QD stack there is a 330 nm thick $Al_{0.25}Ga_{0.75}As$ layer followed by a 50 nm thick GaAs top layer. (b) High magnification HAADF-STEM image of an InAs quantum dot from layer 1, In is heavier than Ga, giving higher contrast.

Brillouin zone (BZ), the Gamma point (Γ), and far from any of the BZ boundaries. Since the valence and conduction bands both are very flat at the BZ centre, the measured bandgap would still be very close to the material's direct bandgap. One of the benefits of the presented methodology is that bandgap of high refractive index materials can be determined at any acceleration voltage and over the entire range of conventional TEM specimen thicknesses. Compared to EELS performed by conventional TEM in diffraction mode, low-mag STEM has important advantages: Most importantly, in Low-Mag STEM a much higher spatial resolution can be achieved than in conventional TEM mode. The resolution is typically a few nm and dependent on the convergence angle of the beam. Secondly, the camera lengths in conventional TEM mode are not large enough to provide the same small semi-collection angles that can be used in Low-Mag STEM.

After presenting the different experimental set-ups, we will in this paper systematically compare the results from these different methods of band gap measurements of GaAs-based materials.

2. Materials and method

The GaAs-based materials characterized in this work were grown by molecular beam epitaxy (MBE). A high angle annular dark field (HAADF) STEM image of the sample structure is shown in Fig. 1a). A 400 nm thick $Al_{0.25}Ga_{0.75}As$ layer is grown on top of a (001) GaAs substrate followed by a stack of 20 quantum dot (QD) layers. Each of the QD layers were grown as 2 monolayers thick InAs and they are separated by 20 nm thick $Al_{0.25}Ga_{0.75}N_xAs_{1-x}$ ($x < 0.01$) spacer layers. On top of the QD stack there is a 330 nm thick $Al_{0.25}Ga_{0.75}As$ layer followed by a 50 nm thick GaAs top layer.

Cross-section TEM samples were prepared both by focused ion beam (FIB) and by Ar ion-milling. The FIB samples were prepared by a FEI Helios Nanolab dual-beam FIB equipped with an Oxford Omniprobe. The coarse Ga^+ ion-beam thinning was done at 30 kV acceleration voltage followed by final thinning at 5 kV and 2 kV. A high resolution HAADF STEM image from one of the InAs QD layers is shown in Fig. 1b) and demonstrates that the samples made purely by FIB have very minor beam damage from the sample preparation. A PIPS II was used to thin the Ar^+ ion-milled samples. Coarse thinning was performed at 3 kV acceleration voltage before progressively reducing the acceleration voltage, finishing at 100 eV. The samples were cooled by liquid N_2 during milling.

The HAADF STEM images in Fig. 1 were taken with a double Cs corrected, coldFEG JEOL ARM 200CF, operated at 200 kV. EELS