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Unraveling electronic band structure of narrow-bandgap p-n nanojunctions in heterostructured nanowires

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Experimental details

Nanowire growth – The nanowires are grown by metal-organic vapor phase epitaxy (MOVPE), using aerosol Au nanoparticles as catalysts on InAs (111)B substrates. First, wurtzite InAs nanowires are grown. Afterward, GaSb is deposited. GaSb forms a zinc-blende axial segment, as well as a tapered wurtzite shell on the wurtzite InAs cores (following the same crystal structure). The full growth procedure is described in a previous report [1].

TEM specimen preparation – The nanowires are transferred from the substrate to lacey carbon grids by mechanical approximation. Thereafter, they the specimen is baked for several hours at an elevated temperature (~130˚C) in high vacuum (~$2x10^{-6}$ Torr) prior to the insertion to the electron microscope, in order to gently remove hydrocarbon contaminations without damaging the nanowires.

EELS – The beam is monochromated in a way that energy resolutions of 30-40 meV are achieved, while an energy dispersion of 5 meV/channel was used for the spectra presented in the main text. It is possible to reach much higher energy resolutions (down to 5-8 meV [2]) by decreasing the monochromator's slit width, however, this is not ideal for our experiments as the electron beam intensity, and consequently signal to noise ratio, decrease dramatically. The optimal experimental conditions can vary for different specimens with different thicknesses or chemical compositions. It should be observed and adjusted during the experiment. The acceleration voltage was 60 kV. The probe convergence and EEL spectrometer aperture semi-angle were 31 mrad and 44 mrad, respectively. While including the intense ZLP in a recorded spectrum aids in calibration and estimation of the energy resolution, the finite dynamic range of the CCD EELS camera used was found to severely limits the signal-to-noise of the comparatively much weaker signal in the bad-gap region. To address this, we used the so-called "Dual-EELS" approach [3], where two spectra including different energy loss ranges are acquired in rapid succession, for each pixel in an EEL spectrum image. Acquisition times can be independently chosen for these two spectra so that the signal-to-noise is optimized for each. In our case we chose to acquire spectra of the band gap region where (1) the full ZLP

was included and where (2) the ZLP maximum was shifted off the camera so that only parts of the energy loss tail of the ZLP was detected.

Line scans are acquired on target regions of the nanowires. It is important to avoid the amorphous carbon film of the TEM grid as this will significantly complicate the interpretation of resulting spectra. Therefore, the spectra are acquired on nanowires in which the target regions are hanging on vacuum, several tens of nanometers away from the amorphous carbon film.

ZLP subtraction – An important parameter to take into account is the consistency of the shape of the ZLP as it is required to be subtracted. In order to ensure that the ZLP is subtracted correctly, it is recorded in identical conditions (within the same dataset) in vacuum, at least 100 nm away from the nanowire and the carbon film. This is used as a reference to model and subtract the ZLP from the low-loss spectrum obtained on the nanowire after scaling. The resulting spectra are compared to the relativistic EELS calculations. The methodology described by Rafferty and Brown is used in order to determine the band gap value [4]. This procedure is applied in Figures 2e, and 3d,g.

Spectrum fitting – Since InAs and GaSb materials have direct bandgaps in both wurtzite and zinc-blende structures, a square root model, $(E-E_g)^{1/2}$, is used to fit the spectrum near the intensity onset that reveals the bandgap value, i.e. E_g [3]. Apart from the square-root function, the shape of the EELS spectra near the intensity onset contains several other contributions. First and foremost, the contribution of the ZLP tail has to be considered. We use a power-law background that contains only a few parameters but provides enough flexibility to extrapolate this contribution from a short range before the onset indicating the bandgap. Additionally, we observe some pre-onset intensity before the direct bandgap edge in GaSb in the experimental data, not reproduced in the relativistic calculations, and thus likely unrelated to retardation losses. The origin of this intensity is not clear, however, we propose that it is mainly due to indirect transitions before the direct bandgap onset from defects in the crystalline structure or few ångströms of amorphous material around the nanowire. For this reason, we model it using an indirect transition model that follows a $(E-E_g)^{3/2}$ dependency [4]. In order to fit the EELS data in the vicinity of a bandgap transition, $s(E)$, we propose to use the following model,

$$s(E) = \frac{\Theta(E - E_g)(E - E_g)^r}{1 + e^{k(E - E_g)}},$$

where Θ is the Heaviside step function and $r = 0.5, 1.5$ depending on the type of bandgap transition observed, direct or indirect, respectively. A sigmoid function controlled by the parameter k allows the intensity away from these transitions to decay, improving the agreement with the experimental spectra. This approach is inspired by Fermi-Dirac statistics and the energy-loss simulations from Tauc-Lorentz models used for fitting the dielectric properties of semiconductor materials [5]. These contributions are fitted in a sequential fashion. First, the power-law parameters estimated from the pre-onset region. Direct and indirect band gap are pre-fitted using the Levenberg-Marquardt algorithm. Finally, dual annealing is employed to optimize the parameters of the final model (5% allowed variation). These models are implemented using HyperSpy and an extension module available upon request [6].

The standard deviations for the measured direct bandgaps are usually in the order of the energy dispersion which was around 5 meV/ch. Nevertheless, as the ZLP width was larger than that and thus energy resolution

is ultimately around 30 meV. Therefore, for the bandgap values with a standard deviation within the limits of our instrumental resolution, the tolerance can be ±3 meV.

References

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