Hot-carrier separation in heterostructure nanowires observed by electron-beam induced current

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Abstract
The separation of hot carriers in semiconductors is of interest for applications such as thermovoltaic photodetection and third-generation photovoltaics. Semiconductor nanowires offer several potential advantages for effective hot-carrier separation such as: a high degree of control and flexibility in heterostructure-based band engineering, increased hot-carrier temperatures compared to bulk, and a geometry well suited for local control of light absorption. Indeed, InAs nanowires with a short InP energy barrier have been observed to produce electric power under global illumination, with an open-circuit voltage exceeding the Shockley-Queisser limit. To understand this behaviour in more detail, it is necessary to establish control over the precise location of electron-hole pair-generation in the nanowire. In this work we perform electron-beam induced current measurements with high spatial resolution, and demonstrate the role of the InP barrier in extracting energetic electrons. We interprete the results in terms of hot-carrier separation, and extract estimates of the hot carriers’ mean free path.

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Due to the short timescale available for carrier extraction, the fabrication of such energy filters demand an ability to perform band-engineering at the nanoscale. In many cases, nanostructuring has also been used with the aim of increasing the hot-carrier life time [3–5]. Semiconductor nanowires are a promising platform for HCPV devices for three main reasons: 1) nanowires provide freedom in band gap engineering with atomically sharp heterostructure interfaces [6] and great tolerance for lattice-mismatch [7]; 2) reducing the nanowire diameter increases the hot-carrier temperatures, possibly by the formation of a phonon bottleneck [8, 9]; 3) the geometry is well suited for controlling the location of light absorption.

Previous work [10, 11] has realized InAs (small bandgap) single-nanowire HCPV devices, by implementing a short InP (large bandgap) segment, resulting in a potential barrier [12, 13] that serves as an energy filter. The proposed mechanism...
of current generation is described in figure 1(a). By generating electron-hole pairs in a smaller region within the nanowire, the resulting variations in hot-carrier concentration will drive a diffusion of hot carriers in both directions along the nanowire. Depending on their initial energy and relaxation time, hot carriers have a chance of diffusing across the barrier before thermalising with the lattice (figure 1(a)), eventually trapping them on the other side of the barrier. In zinc blende InAs the effective mass is expected to be greater for holes than electrons, with a ratio m_h/m_e on the order of 0.1 at the band edges (for transport along the nanowire) [14]. During photoexcitation, holes will thus receive a smaller portion of the excitation energy than electrons and be less likely to cross the barrier, resulting in a separation of charges. Once separated, electrons are extracted through the drain contact while holes are expected to recombine with electrons from the source contact. The resulting current is then set by the rate at which electrons escape over the barrier.

In previous studies [10, 11], such devices have been observed to yield a photocurrent response under global illumination of the entire device. To confirm the mechanism proposed in figure 1(a), and to rule out alternative explanations such as current generation at the contacts, it is necessary to control the location of electron-hole pair generation relative to the position of the barrier. This would allow for more direct observation of the barrier’s role in separating charges and investigate the typical distances within which hot carriers can diffuse and reach the barrier before relaxing.

By use of electron-beam induced current (EBIC) [15], a beam of highly energetic electrons (kV range) is focused onto the sample while simultaneously detecting any resulting current in the material, in our case a nanowire (see figure 1(b)). The incoming electrons deposit their energy via a cascade of inelastic scattering events that excite electron-hole pairs, where one single incoming high-energy electron may excite on the order of 10^5 electron-hole pairs [15]. These excited carriers are initially presumed to not be in thermal equilibrium with the lattice and considered as hot carriers. The beam’s spot size can be very small (order of a few nm), but the resolution is limited by the larger excitation volume resulting from secondary electrons spreading out as they scatter through the sample, which may vary on the scale of nm to μm depending on acceleration energy and material [15]. If the sample contains some mechanism whereby electron-hole pairs are separated from each other, a resulting current can be detected without applying any biasing voltage. EBIC has previously been employed to study nanowires containing p-n junctions [16–19], nanowire-metal Schottky contacts [20], and nanowires containing different types of heterostructures [21, 22].

In this work, we employ EBIC to locally excite carriers in single InAs nanowire devices containing a single, axial InP–InAs barrier. The results confirm that the barrier embedded in the nanowire separates energetic electrons from holes, in agreement with the model for current generation proposed in figure 1(a). Further, our results yield a hot-electron relaxation length in InAs nanowires on the order of 100 nm, which provides valuable information for the design of future, optimised devices.

2. Method

The nanowires used for this study were grown using chemical-beam epitaxy (CBE) from 40 nm diameter Au aerosol seed particles deposited on InAs (111)B substrates. The nanowires typically contain some non-intentional n-type dopants, resulting in resistances on the order of 10^2–10^3 Ωcm for InAs nanowires without any InP segment [23]. Whether these dopants originate from carbon incorporated from the organometallic III–V sources or from vacancies in the crystal structure is still a subject of discussion [23]. The three-dimensional band structure is influenced by Fermi-level pinning about 50–100 meV above the InAs conduction band edge. TEM images of similar growths show that the nanowires are generally of high crystalline quality and free from defects except for some stacking faults in the direction of nanowire growth [6, 23, 24]. The wurtzite (WZ) InAs nanowires are roughly 2 μm long, and a 25 nm long WZ InP segment was grown in the center of the nanowires (see inset of figure 1(b)). The length of the InP segment is chosen so that tunneling through the barrier is not expected.
Device fabrication was conducted as detailed in [24, 25]. Nanowires were mechanically deposited on a Si substrate covered with a 100 nm thick SiO$_2$ layer for electrical insulation. The nanowires were contacted to pre-defined gold pads by one step of electron-beam lithography (EBL) followed by metal evaporation of 25 nm Ni followed by 100 nm Au. We present results from four such devices, all of which were fabricated simultaneously and with nanowires from the same growth run to ensure uniform results. Additional devices, including from other growth runs, were also studied with qualitatively consistent results.

The EBIC measurements were performed at room temperature inside a Hitachi S8010 scanning electron microscope (SEM), operating at an acceleration voltage of 3 kV and a probe current of about 20 pA. These parameters were chosen in order to optimize the image quality. Specifically, we chose the beam current to be just high enough to yield reasonable signal to noise ratio, and a relatively low acceleration voltage to limit the interaction volume to mainly within the nanowire. Whereas no simple relationship can be expected between acceleration voltage and the hot-carrier dynamics, the energy of a single incoming electron is expected to excite a significant number of electron-hole pairs. For electrical measurements, two tungsten nano-probes with piezoelectronic positioning (Kleindiek Nanotechnik) were used to make electrical contact to each gold pad at each side of the NW device. One contact was grounded and EBIC current was measured at the other contact using a current amplifier-and-measurement-system from Point Electronic. No external bias voltage was applied across the nanowire. As the electron-beam was scanned over the sample, secondary electrons were detected to create a standard scanning electron microscope (SEM) image. Simultaneously, the short-circuit current through the nanowire was measured and mapped to the position of the rastering electron beam (figure 1(b)).

The EBIC data was smoothed to reduce noise likely caused by charging of the insulating SiO$_2$ substrate, as previously observed in EBIC measurements [21]. The smoothing was done by subtracting the median background signal along each line scan (see supplementary information for details available online at stacks.iop.org/NANO/39/394004/mmedia).

3. Results

Figure 2(a) shows the results of the EBIC measurement from one device as a composite SEM image with EBIC data overlaid (results from three additional devices can be found in figure S3 of the supplementary information). The red and blue contrast scale represents EBIC data with positive and negative current direction, respectively. We note that if the contacts are swapped such that current is measured on the opposite side of the device, the EBIC reverses sign as well. Based on TEM images of nanowires from the same growth, the InP segment is expected to be located roughly in the center of the nanowire, where we also observe the change of polarity of the current.

Figure 2(b) shows a line profile of the EBIC signal along the nanowire in-between the Au contacts. The maximal current detected is around 1 nA which is on the order of 100 times greater than the probe current. This ratio provides strong evidence that the majority of the current originates from electron-hole pairs generated by the electron beam, whereas any contribution of the probe current itself is expected to be no more than 1% of the signal. Additionally, if no hot carriers crossed the barrier, the barrier would be expected to act as a current divider, where any current detected would originate from electrons injected by the electron beam itself. In this work we present identical measurements carried out on four devices, but qualitatively matching behavior has been observed in about ten devices. For all measured devices, the maximum EBIC current is on the order of a few nA and the spatial peak-to-peak distances on the order of 100 nm. A slight asymmetry in peak height of the EBIC signal on each side of the barrier can be seen in most samples, but without any significant correlation to the wire’s growth direction, the electric grounding point, or the symmetry of the barrier position relative to the contacts.

4. Discussion

The observed switch in current polarity around the location of the InP segment in the center of the nanowire (figure 2), along with the subsequent decay in current as the excitation source moves further away, is consistent with the mechanism for
current generation proposed in figure 1(a). According to this model, the electron beam excites hot electron-hole pairs at a given location, with electrons expected to receive a higher portion of the kinetic energy than the holes (due to the asymmetry in effective mass). Because of their higher kinetic energy, electrons that travel towards the barrier have a higher chance of surmounting it than the holes, leading to charge separation. This matches well with the observation that locating the source of excitation on the left (right) side of the barrier results in a net flow of electrons toward the right- (left-) hand side of the device.

Importantly, we observe no current generation when the electron beam is positioned near the contacts. We can thus rule out the possibility that the observed current is generated at the metal-semiconductor interface, for example due to a Schottky contact. As an additional control, EBIC was performed on devices made from pure InAs (WZ) nanowires that contained no InP barrier. No signal resembling that of figure 2 could be observed (see supplementary information for details).

Our intuitive model for the current generation (figure 1) is based on the notion that hot carriers gradually lose energy as they approach the barrier. In the following, we show that our data are consistent with such a model. In an EBIC experiment, the actual energy of excited carriers is not well specified and may well have a large spread. The rate of energy loss will depend on the inelastic carrier-carrier and carrier-phonon scattering rates, typically occurring at a timescale of 10–100 fs and ~1 ps respectively [1]. In addition, electron-hole pairs that recombine before being separated cannot contribute to the current. All of these rates are processes that decay exponentially and can be characterized with a relaxation length. In our model, we therefore describe energy decay by a single, effective hot-electron relaxation length \( L_e \), containing the total effect of all the relaxation mechanisms.

Due to the higher effective mass of holes in InAs [14], we assume that the majority of the excitation energy goes towards electrons, such that electrons are the majority charge carrier in the resulting EBIC. For the initial distribution of excited electrons \( G_e(x) \), at location \( x \) in the nanowire, we use a Gaussian curve centered on the location of the electron beam, \( x_e \).

\[
G_e(x) = A e^{-\frac{(x-x_e)^2}{w^2}}
\]

(1)

Here, \( A \) is a normalization constant that is chosen such that the highest current value of data and model are aligned. For the root mean square width we use \( w = 60 \) nm, based on Monte Carlo simulations of the electron beam excitation volume with CASINO v2.5.1 [26] (see supplementary information). As the origin of \( x_e \) and \( x \) we choose the point where the EBIC current reverses direction, presumed to be the location of the InP barrier.

Based on the initial distribution, we assume a probability for electrons to cross the barrier that decreases exponentially with their distance from the barrier, \( x \). The net current, i.e., generated by the electron beam at location \( x_e \), is then proportional to the difference in the flow of electrons crossing the barrier from the left and right side, respectively.

\[
\int_0^{L_e} G_e(x) e^{-x/L_e} dx - \int_0^{L_e} G_e(x) e^{-x/L_e} dx
\]

(2)

Figure 3 shows the EBIC current along four different nanowires together with fits of equation (2) and the fit value \( L_e \) (see supplementary information for fitting procedure). The overall good quality of the fit supports the model based on figure 1(a) and equation (2). Averaged over the four presented measurements (see supplementary information), we find \( L_e = (110 \pm 30) \) nm.

This value, found here for electrons, agrees well with a hole diffusion length for holes of about 100 nm in InAs found in a similar EBIC study of an axial InSb/InAs heterojunction [22]. However, it is likely that the energy relaxation length depends on the excitation method and on the initial energy distribution of hot carriers, as well as defects and impurities in the material. For example, a recent study in which plasmonic elements were used to optically excite electron-hole pairs (photon energy between 1 and 1.3 eV), found an effective relaxation length on the order of 30–40 nm for electrons in InAs [27]. An EBIC signal qualitatively similar to that of figure 2 and figure 3 has previously been observed in InAs nanowires containing an axial double InP barrier [21]. We believe that a similar mechanism as described in figure 1(a) and equation (2) may have played a role also in that case.

5. Conclusion and outlook

The presented results, enabled by the high spatial resolution of an electron beam, support the concept that a potential barrier embedded in a nanowire can be used to separate hot charge carriers. The results support the model illustrated in figure 1(a)
and the interpretation of previous observations of photocurrent generation when the device was globally illuminated by optical light [10, 11].

The $L_e \approx 100$ nm extracted here for electrons in InAs, and in [16] for holes, serves as a quantitative guide for the region available for effective hot-carrier extraction. The model used to interpret the data assumes transport in only one dimension (along the nanowire), employs a single effective relaxation length, and contains no information about the excitation energy. For this reason it will be valuable to repeat similar studies using optical excitation. Using optical light as an excitation source will allow for high spectral resolution and probing of the energy using different energy regimes, as well as for simultaneous measurement of power generation and efficiency [26]. In such a study, we envision the study of energy regimes where transport across the barrier is dominated either by hot carriers that are transmitted ballistically (internal photoemission), or by hot carriers that have thermalised amongst each other (photo-thermionic emission). For sufficient control over the excitation source we envision the use of various methods such as optical beam-induced current (OBIC), scanning nearfield optical microscopy (SNOM), and the use of plasmonic elements along the nanowire to focus the absorption of light in small regions. It will then also be interesting to explore the role of barrier height, thickness and geometry in effectively separating carriers.

Finally, the effective hot-carrier relaxation length found will guide us in the design of future nanowire hot-carrier devices. Specifically, we envision a nanowire containing two barriers, one that selectively transmits hot electrons (as the InP barrier in this work), the other one blocking hot electrons but transmitting hot holes. For electron-hole pairs created between the barriers, such a structure is expected to yield a substantially higher quantum efficiency than our present device, as carriers are prevented from diffusing away from the barrier. Based on the presented results, such barriers should have a separation on the order of a few 100 nm, leaving enough space for the implementation of plasmonic antennas to focus light absorption between the barriers [27].

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