The University Of Sheffield.

Mini-project report

Nanowire Photovoltaics

Correlating the Optical and Structural Properties of GaAs Nanowires Containing InGaAs Quantum Dots

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18/05/2012

Research Councils UK Energy For a Low Carbon Future

Abstract

GaAs nanowires with InGaAs inserts were to be studied using micro-photoluminescence (μPL) and transmission electron microscopy (TEM) in order to determine and correlate their optical and structural properties. The preparation of the nanowire samples for this analysis became the chief focus of this project. A reasonably successful method was established for transferring the wires from the growth substrate onto the grid required for TEM. Unfortunately, issues with the positioning of a solid immersion lens over the transferred wires were not fully resolved, meaning that μPL measurements of the samples were not possible. Some TEM measurements were performed, and it was found that – for phosphorous capped or phosphine cooled wires – the ends of the wire could be distinguished by looking at phosphorous composition, allowing for identification of which end of the wire was previously attached to the growth substrate. In addition, stacking faults were seen clearly as might be expected from the literature on these wires. No quantum dots were located.

Introduction

At present, silicon panels dominate the photovoltaic market; however their cost currently makes them financially uncompetitive with conventional fossil fuel based electricity generation, and - in many scenarios - with other intermittent renewables. Nanowire (NW) geometry offers numerous potential advantages over standard plat panel devices, in particular in the area of reducing costs, allowing cells to be fabricated using less material and relaxing the stringent requirements on the materials used. Quantum dots (QDs) also have many properties which could be useful in photovoltaic applications. Solar cells incorporating NWs and QDs have been produced, but with efficiencies generally only reaching a few percent[1], much work still needs to be done if they are going to become commercially competitive.

Sample Fabrication

A 20nm layer of SiO_2 is deposited on a (111)B GaAs substrate. Arrays of holes (diameter 100-120nm, pitch 4μm) are then produced in the SiO_2 layer using electron beam lithography and reactive ion etching, and it is in these locations that GaAs NWs form in a MOVPE (metalorganic vapour phase epitaxy) reactor. QDs were formed by growing an InGaAs insert within the NW. Finally either a capping layer of GaAsP was grown on the samples, or they were cooled in a PH_3 overpressure; this is to ensure passivation of surface states which would affect the optical properties of the samples. Nanowire arrays are arranged in grids of 12 arrays in a 4x3 pattern.

Methods of Analysis

The optical properties of the structures under investigation are studied using micro-photoluminescence (μPL). This involves using a laser to excite electrons in the sample (photo-) and studying the photons emitted as those electrons relax back down to lower energy states (-luminescence). This information gives details about the electronic structure, and thus optical properties, of the material.

The structural properties are studied using transmission electron microscopy (TEM) which uses electrons rather than light to probe the structures under investigation. Since the de Broglie wavelength of electrons is much shorter than that of photons, TEM allows us to image right down to individual columns of atoms in the sample, meaning the details of the crystal structure can be determined. In addition, the TEM set-up allows investigation of the composition of a sample using energy dispersive x-ray spectroscopy (EDX), which involves studying the x-rays given off when the sample is bombarded with electrons. TEM measurements must be performed after the μPL measurements since it involves prolonged exposure high energy electrons which could create defects and thus affect the optical properties of the sample.

In order to perform TEM on a nanowire sample, the wires must be broken off from the substrate and placed on a TEM grid. This consists of a thin mesh copper grid with a 10nm thick carbon film sputtered onto one side.

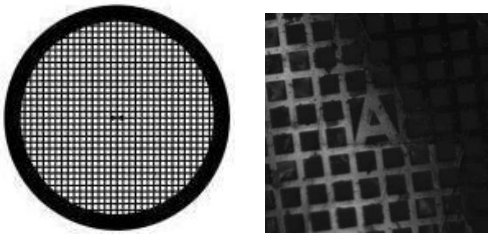

FIG. 1: The TEM grids used in the investigation. The grid is roughly 3mm in diameterand the centre is marked with an ‘A’ as shown which assists locating the wires.

In order to correlate the optical and structural properties of the NWs, it is necessary to perform both μPL and TEM on the *same* nanowire. In addition, the logistics of the TEM means that the location of a dot within a particular wire must have been determined already in PL measurements in order to facilitate finding it in TEM. Due to the limited field of view and difficulty in scanning around in both PL and TEM, images of the grid are first taken using a scanning electron microscope (SEM) on which it is comparatively easy to zoom in and out and thus find any NWs and record their positions and orientations. The SEM also allows for

rough diameters of the wires to be measured in order to find appropriately thin wires for TEM investigation (around 100-150nm or less in diameter). Only four studies appear to have performed μPL and TEM on the same nanowire ([2,3,4,5]) and none of these investigated quantum dots within the nanowires.

Sample Preparation

Unfortunately, the samples to be studied had been grown in a pattern which meant that the arrays of nanowires thin enough to be studied in TEM were very close to arrays of NWs with larger diameters. This complicates preparation, as great accuracy is required to ensure the transfer of the target NWs from the growth substrate to the TEM grid. In addition, the wires to be studied must be isolated, single wires; this is important to note as some preparation methods tend to aggregate the wires together into clumps, leaving them inaccessible for PL and TEM measurements. Finding and perfecting a repeatable method of transferring a good number of the target wires proved very difficult, and became the main focus of this project.

Methods tried include:

- Simply knocking the wires over with a scalpel – this can successfully knock over the wires, but they are scattered over a wide area. If less force is used the wires are simply not knocked over. Using a scalpel fixed on a platform controllable by a micrometre - in order to find the optimum level of force - was not successful.
- Knocking over the wires with a scalpel within a droplet of deionised water – this successfully retains the wires within the droplet, avoiding them spreading out, but leads to aggregation (clumping together) of wires (see FIG. 2). This effect is reduced if isopropanol or ethanol is used instead of deionised water, however neither of these solvents form small droplets due to their significantly lower surface tensions. In addition, transferring the wires to the grid did not work well as the wires seem to be stuck down after the droplet has dried. Wire transfer was tired by swiping the grid through the droplet, leaving the grid on the droplet as it evaporated and sucking up the droplet and depositing it on the grid, however all methods left the vast majority of the wires on the substrate rather than transferring them to the grid. In addition, allowing a second droplet to roll down the angled substrate and onto a grid was tried, the idea being that this droplet might pick up wires on the way. Again this was not successful – a small water droplet would simply not move whilst IPA failed to form a droplet, and after spreading out failed to move any fallen wires in a significant manner.

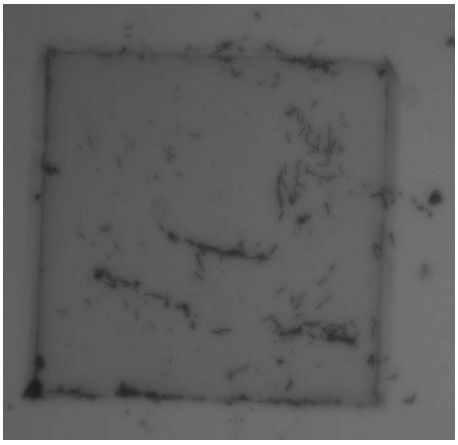

FIG 2. Optical image of the array after wires were knocked over within a droplet. It can be seen that some wires are knocked over without being moved greatly, but that there is also a large amount of aggregation of wires.

- Freezing the wires in a droplet, then removing the droplet and placing it on a grid to melt – the idea being that the frozen droplet will contain the wires, allowing them to be removed easily. However when the frozen droplet is removed from the substrate there is generally a thin layer of ice left on the substrate which is likely to contain the wires. This is not easily removed and transferred onto the grid.
- Using a solid immersion lens (SIL) – the lens can be used to accurately knock over the array, and some wires stick to the bottom of the lens and are lifted from the growth substrate. Unfortunately, however, these wires are not easily released onto the TEM grid.
- Using the TEM grid itself to knock over the wires (the ‘brute force’ method) – simply placing the grid over the target NW arrays, applying moderate pressure and agitating the grid slightly. This method met with some success, however there are also some major issues: much of the carbon film is removed from the grid (FIG. 3), leaving many areas which are unusable; the transferred NWs have a tendency to stick to the Cu grid rather than the carbon film (FIG. 3); many wires are not transferred; the knocking over of the wires is fairly uncontrollable and it would be possible to knock over adjacent arrays whilst not successfully transferring a target array. Greater success was achieved when less pressure was applied and the grid only moved or agitated slightly. As an extension of this, after using the ‘brute force’ method, it is possible to swipe a second TEM grid over the wires which have been knocked over but not picked up by the first grid. This succeeds in picking up a few wires, however only a very small fraction of those lying on the substrate.

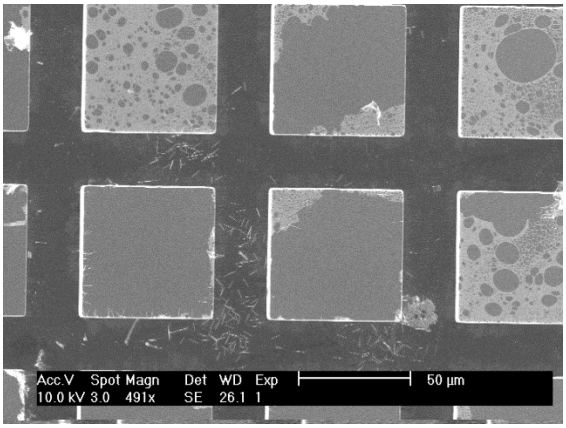

FIG. 3: SEM image of a TEM grid after an initial attempt to transfer the NWs onto the TEM grid using the 'brute force' method. The circular holes visible in the film are a natural part of the film, however the central squares of the grid have little or no film since it has been torn away during the process of knocking over the NWs. A high density of nanowires is visible on the copper grid near the squares where the film has been torn away.

In the end, using the TEM grid with minimal applied force proved to be the most successful method of transfer. In general NW transfer was most successful for thicker wires, and least successful for the thinner wires which would be better for TEM studies. The TEM grid was then mounted onto a p-doped silicon substrate using a tiny amount of conducting silver DAG as an adhesive (this ensures that the grid does not charge whilst acquiring SEM or TEM images). In order to achieve high resolution in the µPL measurements, it is necessary to place a solid immersion lens (SIL) over the target wires. Positioning the SIL over the desired wires is not easy, since it is around 1mm in diameter but with a field of view of only around 20µm. Simply sliding the SIL into place is awkward but can be done, though this can move some wires slightly and damage the carbon film in some areas. In order to avoid any movement of the SIL whilst loading the grid into the PL set-up, the lens must be stuck down in some way. Using a small amount of vacuum grease – slightly above and slightly to the side of the target square – was tried, however the SIL was found to have moved after the loading and vacuum pumping procedures. Unfortunately this issue was not resolved, and finding a solution to this problem should be the first goal of any continuation work.

Results and Discussion

TEM Results 1

The first TEM measurements were made on a sample of GaAs NWs with an insert of InGaAs to produce a QD half way up the nanowire. These were transferred using the 'brute force' method of using the TEM grid to knock over the wires, before it was realised that better transfer could be achieved by using less force.

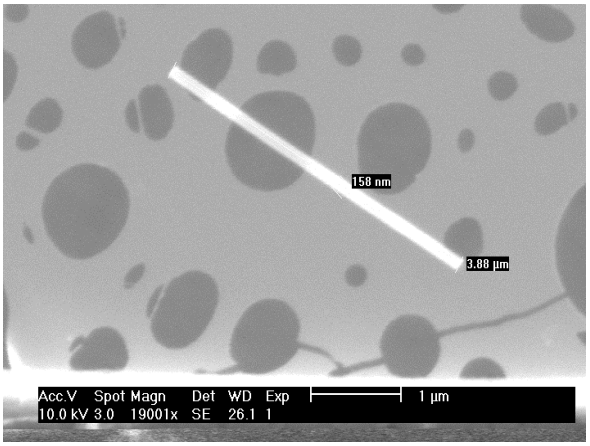

FIG. 4: The wire studied in detail with TEM, with approximate diameter 160nm and length 3.9µm.

PL measurements of these wires had not been taken, meaning that we could not be sure whether the samples had grown as intended and did indeed contain a QD, or the location of the dot if it had formed. In addition, it is unknown whether the wires snapped exactly at their base, meaning that it is difficult to be sure where a QD might lie. The samples were cooled using an overpressure of PH_3 in order to passivate surface states. This may have led to an increased composition of phosphorous at one end of the wire, and if this could be identified it would allow identification of which end broke from the substrate. This would give a reference for the position of any quantum dot, allowing confirmation of if the dot had grown in the expected location. Indeed, one end of the wire was seen to be flatter than the other, and in addition the flatter end has a stronger phosphorous signal, leading to the conclusion that this is probably the 'top' end of the wire, whilst the more irregular end is where the wire was broken off from the substrate when it was knocked over. Stacking faults can clearly be seen, as shown in FIG. 5, where the tone changes from dark to light and vice-versa. These occur when the GaAs crystal structure changes from zinc-blende (or wurtzite) to wurtzite (zinc-blende) and back again. Zinc-blende crystal structure is a cubic close packing structure (planes stack ABCABC and so forth), wurtzite on the other hand is a hexagonal close packing structure (planes stack ABABAB); for example an arrangement of planes ABCACBA is zinc-blende with a monolayer of wurtzite, and this is a stacking fault. This effect is commonly observed in other III-V NWs[6,7]. These stacking faults make it hard to locate a quantum dot in TEM, since it is not easily possible to spot a change in crystal structure between the GaAs and InGaAs regions when there is so much change in structure within the GaAs regions themselves. No QD or strong, localised indium signal was located during the TEM study.

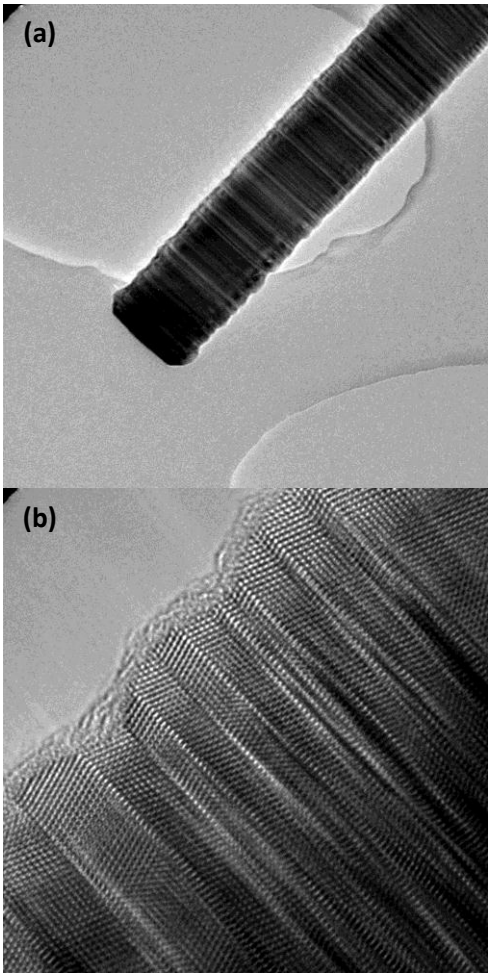

FIG 5: High resolution TEM Images showing stacking faults. (a) is 2000 times magnification, whilst (b) is 50000 times magnification.

TEM Results 2

These GaAs wires had had a GaAsP cap grown, and had been grown to contain 2 quantum dot InGaAs inserts, positioned approximately 1/3 and 2/3 of the way along the wire. The NWs were again transferred using the TEM grid itself to knock over the wires. This time less force and movement was used, with better results.

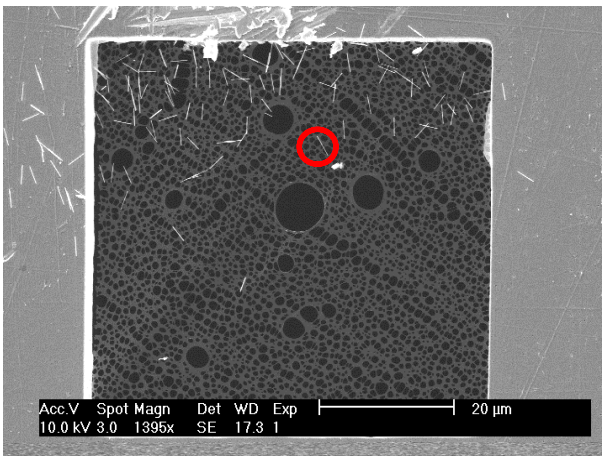

FIG 10: The wires selected for TEM investigation. The red circle shows the wire selected for more detailed study, which is approximately 3.3µm in length with a diameter of 105nm.

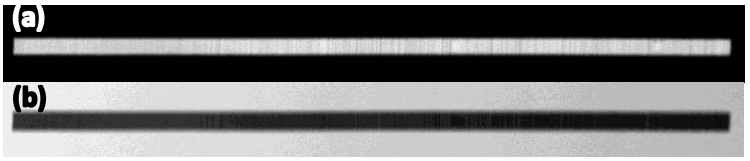

FIG 11: Dark field (a) and bright field (b) scanning TEM images of the nanowire under investigation. Again stacking faults are clearly visible.

Due to the lack of success at placing and fixing a SIL over the TEM grids, again these wires had not had PL measurements performed on them. EDX spectra were taken in a linescan along the whole wire. An indium signal might be expected at around 3-3.5keV if it were present. There is potentially a small signal here, but barely above background levels. Mapping of the signals in an attempt to locate a region with a higher than average indium signal was also unsuccesful, confirming that any quantum dot must definitely be located using PL measurements before it can be found in TEM.

Phosphorous composition was investigated at the ends of the wire. Again, one end shows no increase in phosphorous on the very end surface, whilst the other shows an increased signal, and thus we can conclude that the latter is the end which was exposed to the phosphorous, whilst the former is where the wire was broken off.

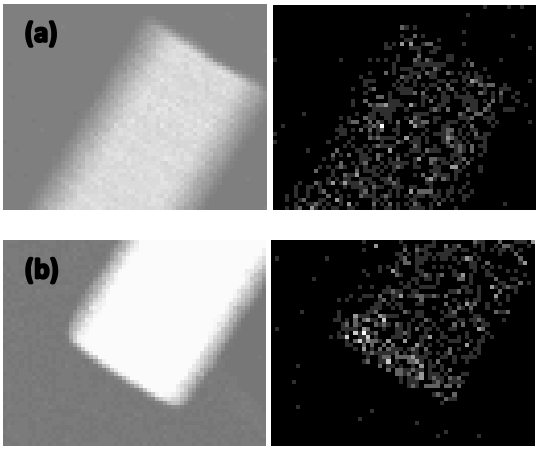

FIG 13: Images of the two ends of the wire under investigation. The images with a grey background show the wire, whilst the images with a black background show only the signal detected from phosphorous. Images (a) correspond to the end of the wire where it broke off from the substrate. Images (b) correspond to the 'top' end of the wire where a phosphorous cap was grown, as can be seen by the increase in phosphorous signal at the very end of the wire.

Conclusion

A fairly successful method has been established for transferring the wires from the growth substrate onto the TEM grids. Unfortunately a satisfactory method was not found for fixing a SIL in position over the target

wires, and this should be the first issue to be addressed in any future work. The lack of success at solving this issue meant that µPL measurements of the samples were not possible. Some TEM images were taken, and it was determined that using EDX to map phosphorous signals at the ends of the wires could be used to distinguish the ends. Stacking faults were seen clearly. No quantum dots or strong, localised indium signals were found.

Acknowledgments

Particular thanks go to Andrew Foster, Dr Luke Wilson, Dr Thomas Walther and Dr Maxim Makhonin. Also thanks to Scott Dufferwiel and Prof Anna Fontcuberta I Morral (École Polytechnique Fédérale de Lausanne).

[1] K Sun et al. *IEEE J. Selected Topics in Quantum Electronics* **17**, 1033-1049 (2011)
[2] J Bao et al. *Nano Lett.* **8**, 836 (2008)
[3] M Heiss et al. *Phys. Rev. B* **83**, 045303 (2011)
[4] J Todorovic et al. *J. Phys. Conf. Ser.* **326**, 012043 (2011)
[5] A Fasoli et al. *Nano Res.* **4**(4), 343-359 (2011)
[6] J Bao et al. *Nano Lett.* **8,** 836-841 (2008)
[7] R Algra et al. *Nature* **456**, 369-372 (2008)