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In situ MOCVD growth of III-V semiconductor nanowires in the Lund ETEM

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Abstract

A new environmental transmission electron microscope has been installed in Lund in order to investigate the growth of III-V semiconductor nanowires by metal-organic chemical vapour deposition. We report here on the concepts behind the design of the facility and on details of the operation, and we refer to early results to highlight the new information that can be accessed from in situ studies. The installation includes a gas handling system that delivers the precursors to III-V semiconductor growth under controlled conditions. The core microscope is a Hitachi HF-3300S 300 kV TEM with additional pumping that can handle up to 6 Pa of gas injected into the specimen area, or up to 400 Pa if an apertured lid is fitted to the holder. Various custom specimen holders incorporate precursor gas lines, a heating chip or a double tilt mechanism. The polepiece gap has been expanded to accommodate the holders, while the combination of an imaging aberration corrector and a cold field emission gun delivers a point resolution of 86 pm. Single images with atomic level detail are collected by one camera while another camera provides real-time video recording. A scanning unit offers high angle annular dark field and secondary electron images, and compositional microanalysis is performed with energy dispersive spectroscopy. In summary, III-V nanowires have been grown successfully in situ across a range of controlled conditions such as substrate temperature and precursor partial pressures. Atomic resolution images and movies, and spectroscopy data taken during this growth allow detailed measurements of structures, compositions and growth rates – data that are otherwise hard or impossible to obtain from ex situ studies – and further our understanding of the mechanisms of crystal growth.
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Keywords: ETEM, MOCVD, nanowires

1. Introduction

Electron microscopy is an important tool for investigating the structure of semiconducting materials. The open lattices of semiconductors - diamond cubic for Si or zinc blende for GaAs – meant that these materials were well suited to high resolution observations in the early transmission electron microscopes (TEMs) [1]. The typical epitaxial layer structures had to be thinned to electron tranparency, and this preparation of plan-view and cross-section specimens was time-consuming. But a new area of nano-structured semiconducting materials then developed, where nanoparticles or nanowires were formed “bottom up”. This means that the growth proceeds atom by atom in order to generate the nanostructure, as opposed to a nanostructure being milled or etched from a bulk structure [2]. These finished nanostructures are then particularly suitable for TEM studies since very little specimen preparation is needed. Furthermore, the combination of TEM-readiness of the samples and the “bottom up” nature of their formation permits in situ observations of the growth.

In situ TEM studies of Si and Ge nanowire growth have been reviewed by Ross [3]. Subsequently, in situ III-V nanowire growth by metal-organic chemical vapour

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deposition (MOCVD) was reported, *e.g.* for GaP by Hillerich *et al.* [4] and for GaAs by Jacobsson *et al.* [5]. The in situ III-V growth was performed on an existing TEM instrument that had been modified, and video was used to record conventional bright/dark field images. The determination of the role that growth mechanisms played in the formation of different crystal phases showed the feasibility and power of the in situ technique as applied to nanowire growth.

Recent developments in in situ microscopy [*e.g.* 6] meant that a *custom* instrument became feasible which could incorporate improvements in the gas handling, specimen holder design and imaging capabilities. The two principle requirements of the instrument were the following. First, the growth conditions should be comparable to those found in normal MOCVD equipment and they should be tunable with the same precision. Second, the microscope, including holder, should allow high resolution imaging of the growth. At Lund University, significant expertise had developed in the MOCVD growth of III-V semiconductor nanowires under the auspices of the NanoLund consortium formed in 1988. Parallel to this development, the characterisation of nanowire structures had been performed at the national center for high resolution electron microscopy (nCHREM), established in 1987.

A pilot project for the in situ growth of InAs nanowires was made by Lenrick *et al.* [7], employing a standard JEOL 300 kV TEM. The source material was enclosed between two Si dies with thin SiN windows which were mounted in a standard heating holder. The successful outcome, which included a video of InAs nanowire growth from the seed particle, was a useful step in the planning of the custom instrument. The new Hitachi HF-3300S 300 kV microscope was delivered in 2015. Over the following two years the gas handling infrastructure was installed and an inauguration held in 2018.

Nanowire structure and composition had been up to that time investigated in Lund only *after* growth in a separate apparatus, and these studies might be called "ex situ". In situ observations on the other hand reveal phenomena that cannot be observed ex situ, such as catalyst particle size and composition at elevated temperatures. Also, multiple observations can be made in situ during a single growth run, for example nanowire length as function of time, whereas multiple growth runs and TEM specimens would be needed for the same data to be collected ex situ.

In this report, we discuss the design of the instrumentation with sections concerning microscope, MOCVD equipment and specimen holder. We then refer to a selection of early results and consider future plans.

2. Design of Microscope

The microscope is capable of recording high resolution images and movies from large areas of sample, *e.g.* an entire nanowire growth front. It achieves this combination through transmission electron microscopy; scanning TEM (or STEM) is not suited to delivering the same amount of information at such high frame rates. Figure 1 shows an image of a nanowire recorded during in situ growth in the Lund ETEM. The GaAs crystal lattice is resolved and the width of the nanowire and its interface with the catalyst particle is captured. The video camera used here captured an image of size 1024 by 1024 pixels. A larger and faster camera is to be fitted, as discussed later.

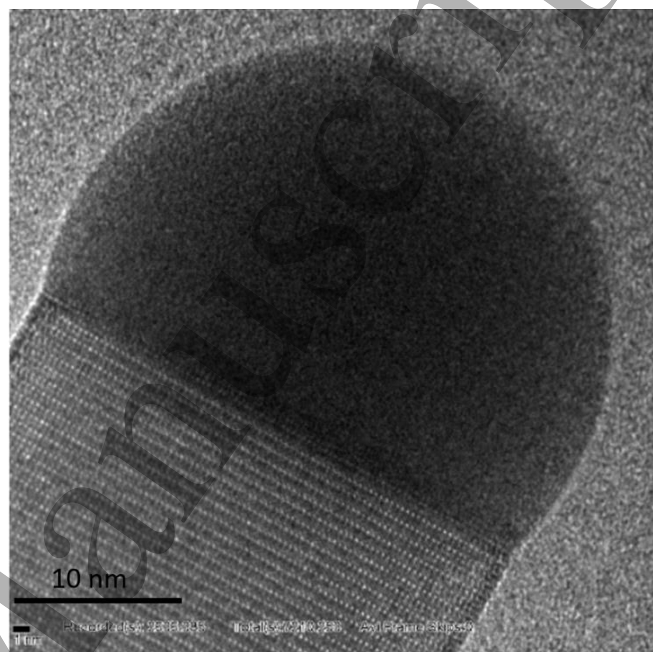

Figure 1. A single frame from a recording of growth where the entire width of growth front (30 nm) is imaged at high resolution. The hemispherical droplet is the gold catalyst or seed particle which may be alloyed with gallium. The GaAs nanowire has the wurtzite structure and is viewed along a {1 1 -2 0} direction .

The instrument chosen was a 300 kV Hitachi HF-3300S TEM fitted with a cold field emission emitter (FEG) as shown in figure 2. A C_s corrector "BCOR" for TEM imaging made by CEOS [8] was incorporated in order to improve resolution to the information limit of 86 pm, and to minimise image delocalisation.

A further advantage of aberration correction is the freedom to choose a larger polepiece gap since the resulting increase in the coefficient of spherical aberration C_s can then be corrected away. The larger-than-standard gap on the Lund ETEM is 10mm and it can accommodate the specialist sample holders that need to be thicker than standard holders. Furthermore, a prerequisite for lattice imaging is the ability to tilt the specimen in two axes in order to observe the crystal along low index zone axes and this tilting requires space in the polepiece. The medium voltage (300 kV) chosen for the microscope also

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permits a larger gap than a lower voltage with maintained resolution, and imaging of slightly thicker samples is possible.

At present, single images are recorded on a Gatan Orius SC1000B camera. The Gatan camera has a CCD sensor of size 4008 by 2672 pixels with a 9 μm pixel size. The sensor is fibre optically coupled to the phosphor scintillator and the camera is retractable. A rate of 14 frames per second (fps) is achieved only at 4x binning. Videos are therefore recorded on the AMT XR401 camera which, when binned by 2, can record video at 30 fps. The AMT camera has a sCMOS sensor of size 2048 by 2048 pixels with a 13 μm pixel size. The sensor is lens coupled to the phosphor and the camera is also retractable. Neither camera requires beam blanking for operating the "shutter" to record images Figure 1 is a single frame from a video taken on the AMT camera.

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Figure 2 The 300 kV ETEM instrument in Lund. A panel in the microscope enclosure box is open and reveals the sample exchange area. The operator has access to a viewing screen. Pipes into the wall at upper right are for ventilation of the cabinets that house the gas cylinders and the area around the specimen holder at the microscope.

A STEM unit is installed on the microscope. The probe forming lens is not corrected, but the resolution that can be achieved is sufficient for compositional mapping across a nanowire. Detectors include bright field, annular dark field (ADF) - typically used for high angle ADF - and secondary electron (SE). The secondary electron detector is useful in several ways [9]. At one level, areas of samples and holders (including faraday cage cups) may be too thick to transmit electrons, and SEM-style imaging becomes invaluable for initial navigation across the sample and sample holder. At another level, surface information available in the SE image is useful for three dimensional specimens – such as nanowires - and facets that are hidden in HAADF images can be readily observed in SE images, as shown in Figure 3.

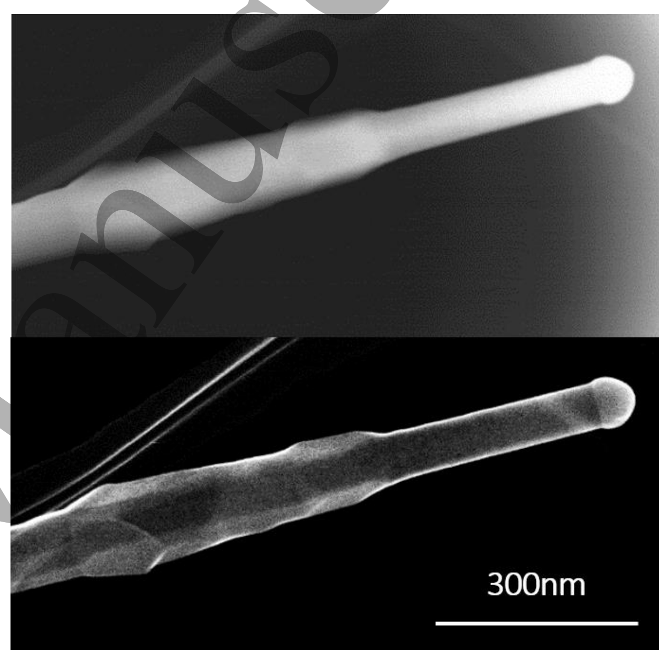

Figure 3 Top, standard HAADF image of a nanowire and bottom, an SE image that reveals surface facetting and surface overgrowth. The images were recorded simultaneously.

X-ray energy-dispersive spectroscopy (EDS) is installed for performing compositional analysis. The EDS system is the Oxford Instruments Aztec with 80 mm^2 SDD detector. EDS is a suitable technique for analysing the range of elements found in nanowires and indeed had been in routine use for nanowire work on the older 300 kV JEOL TEM in Lund. Elevated temperatures at the specimen holder tip lead to increased background counts in the X-ray spectrum and these counts interfere with the EDS signal. This background starts to become challenging to account for at 500 °C , and difficult at 700 °C . There are some procedures however, such as partial withdrawal of the detector, that reduce the problem and allow useful EDS collection at nanowire growth temperatures.

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3. Microscope room

Operators sit in the same room as the microscope and the gas handling system. In many HRTEM facilities, operators remain outside the microscope room in order not to disturb the environment of a high resolution instrument. At Lund however, the gas handling equipment and up to 6 computers are already sited in the microscope room making the presence of operators less likely to be the limiting factor regarding performance. The microscope is also shielded from noise, air movement and temperature fluctuations by the enclosure box seen in figure 2.

The precursor gas cylinders are enclosed in cabinets with gas monitors and independent ventilation. The microscope room and a small service room where hydrogen, oxygen and nitrogen are housed are kept at a small underpressure. With the doors closed, the air leak flow is from the surrounding rooms towards the instrument room. The two rooms have an air inlet and outlet separated from the rest of the microscopy facility.

A stable platform for the instrument is provided by a concrete block separated from the rest of the floor, and the microscope room is enclosed by internal walls and ceiling that lie within a larger equipment hall. One issue at Lund is the opening in 2020 of an electric tramway that will pass about 150 m from the microscope. The nature of the electric supply to trams can make the resulting fields especially hard to to compensate. Modifications were therefore made to the tramway design so that magnetic fields generated at locations close to sensitive scientific equipment are reduced [10]. The enclosure box for the ETEM microscope will also help mitigate effects.

4. Equipment for MOCVD growth

We turn to the specialist features that are in place to be able to grow nanowires by MOCVD. (The emphasis in Lund has been on growth by MOCVD, but an alternative method exists which is Molecular Beam Epitaxy. This method can also be studied in situ and the reader is referred to the work of Harmand *et al*. [11])

MOCVD relies on the delivery to the substrate of the group III and V species by gaseous precursors: trimethylgallium, trimethylindium, trimethylaluminium, trimethylantimony, arsine, phosphine as well as hydrogen as a carrier gas. Since the holder is of the "open type" (see next section) these gases must then be pumped away before they reach the high vacuum area housing the cold FEG. Compared to the standard HF-3300 microscope configuration, the HF-3300S microscope has an extra differential pumping aperture or orifice, and an extra ion pump (IP3) located below the gun valve (figure 4). In total there are three differential pumping stages between the sample area, where pressures may be up to around 6 Pa, and the gun area where pressures are around 10^{-9} Pa. (An exact figure for the pressure that can be maintained at the sample area is difficult to define. The figure depends on the gas type, how long the gun valve is to be kept open, and what rate of decrease in beam intensity can be tolerated for any particular observation.)

During operation in ETEM mode, the bulk of the gases entering the specimen area are pumped away through a turbomolecular pump (TMP). Some of the gas will be pumped away by the ion pumps, with IP3 as the main pump. If the gas pressure above the gun valve increases too much, IP2 will trigger a safety routine that closes the gun valve and stops emission to protect the FEG.

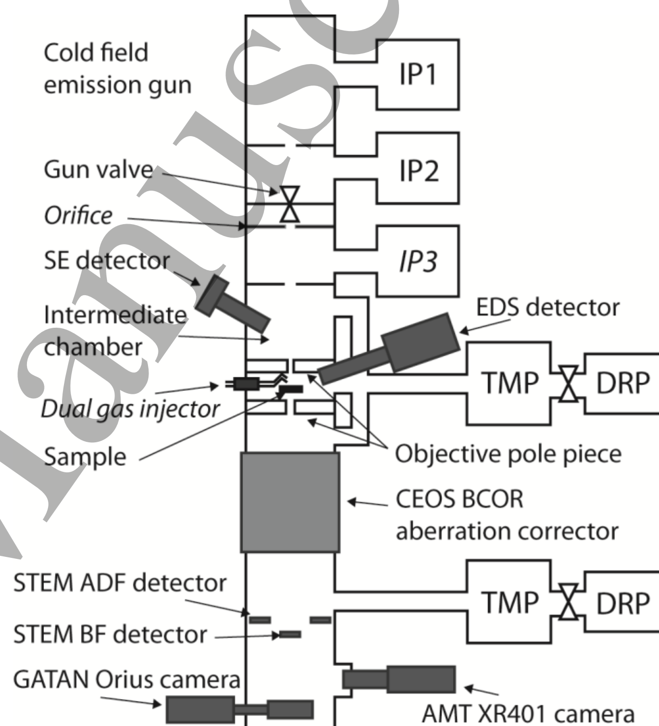

Figure 4 Schematic diagram of the pumping system in the microscope column between gun and sample area. Gases may be injected via the holder or via the dual gas injector. The increased pressures at the sample necessitate the addition of an orifice and IP3 pump (written in italics). A selection of other important components are shown, including the BCOR aberration corrector located below the objective lower pole piece [8] and the secondary electron detector located above the upper polepiece [9]

There are currently four inlets for gases into the specimen area of the ETEM and the gas handling system can currently deliver gases to three. Two of the inlets are located near the

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tip of sample holders that are dedicated to nanowire growth. Two separate inlets are necessary so that premixing of the group III and the group V gases is minimised. The remaining two inlets are located in the column wall.

Figure 5 shows a schematic of the gas handling system (GHS). Precursors for III-V growth are supplied via temperature controlled bubbler cylinders or from gas bottles. Premixing within the same "family" of gases is possible so that alloys may be grown. For example trimethylaluminium and trimethylgallium may be mixed if AlGaAs growth is desired. On the other hand, premixing of the group III and group V precursors should be avoided, and hence two gas lines deliver to the holder, as mentioned earlier. For growth of indium-containing material, possible contamination by indium of the equipment has been considered. Inside the microscope, only the holder is close to the heated area and hence susceptible to indium deposition. Since the holder itself cannot be baked, a second gas holder is dedicated to growth involving indium. In addition, nitrogen purging procedures are used when changing material types.

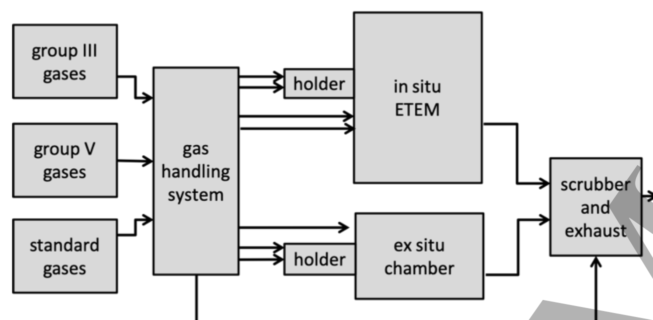

Figure 5 GHS schematic showing a simplified picture of possible gas flows.

An "ex situ chamber" is installed so that experiments may be performed at higher pressures than those allowed in the ETEM column. It also serves as a testing station for new holders or new process conditions.

Gases pumped from the in situ and ex situ chambers are directed to a scrubber unit which absorbs and neutralises the gases before expelling the clean remaining gases into the atmosphere. The bulk of the gases that are supplied by the sources in fact bypass those two chambers and go direct to the scrubber. The reason is as follows. The sources supply gases to the gas control unit at atmospheric pressure and standard technology is used for the mixing. A large fraction of the gas is then diverted to the bypass leaving a small fraction – at a lowered pressure – to enter the chambers.

There are sufficient safeguards in place for the handling of the gases and the required certificates from the relevant authorities have been obtained. The procedure requiring most precautions is the exchange of the hydride bottles, and experience acquired in Lund at the existing MOCVD facility has been useful. The more frequent procedure of removing the specimen holder from the microscope is preceded by extensive flushing with nitrogen of the pipes.

To keep the column clean from residues of the process gases, several different cleaning procedures can be employed. Standard bake out is used regularly where the microscope column is heated by operating the lenses at controlled currents without cooling water. Another procedure employs ozone created by UV radiation from a "Sparkle" cleaning system [12]. For standard high resolution imaging – *i.e.* not for ETEM work - two cold traps can be filled with liquid nitrogen to improve vacuum further.

5. Specimen Holder

There are multiple demands on the holder for in situ growth. To deliver the precursors, gases are transported along two microtubes running through the holder, with outlets or ports located at the end of the holder as shown in figure 6. For other ETEM work, gases may be delivered from the wall of the microscope column, as mentioned in the previous section.

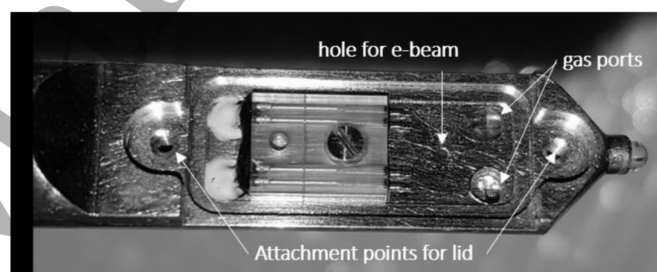

Figure 6 Detail of a single tilt specimen holder tip with two gas inlets for the group III and group V precursors. The MEMS heating chip on which the nanowires grow is attached to the underside. An optional lid with a hole for the electron beam may be attached to the top side.

The location for nanowire growth at the holder tip must allow for heating to suitable and controlled temperatures. The heating for the holder supplied by Hitachi is achieved on MEMS (microelectromechanical system) chips. The chip, manufactured by Norcada Inc., consists of a W heating coil embedded in SiNx. Blaze-based software by Hitachi is used to control the temperature using Joule heating in a constant power mode [13]. The resistance of the W heating coil is then used to measure the temperature of the chip, the original calibration employing the melting point of gold.

The central part of each chip is isothermal and it is here that an array of "pits" is located. At the end of each pit is an approximately 30-50 nm thick electron-transparent amorphous SiN_x window on which samples sit and through which growth may be observed. A second generation of the

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MEMS chips also includes a through-hole in the thin SiNx window, which allows for higher resolution imaging in vacuum.

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The advantage over earlier holders, where the entire tip was heated, is the improved stability not only at a particular temperature, but also during the heating from room to elevated temperature. The main effect is the SiN_x membrane "bulging" at elevated temperature and a correction of height or focus is then necessary. For temperature changes of only a few degrees per second, it is possible for the operator to keep the sample in focus by changing height.

A further required feature of the holder is double tilt. For HRTEM, the nanowire lattice must be oriented at a zone axis, and growth fronts must be aligned "edge-on" to the electron beam. The combination into a single holder of 1) a double gas supply b) double tilt and c) heating MEMS chip has yet to be realised. Nevertheless HRTEM imaging of nanowires has frequently been achieved with a *single-tilt,* two gas-inlet heating holder, such as the one shown in figure 6. How then are favourably-oriented nanowires found? One factor is that microscope operators can become expert at identifying correctly oriented nanowires. A second factor is that nanowires may settle with a facet flat on the support film and consequently there will be a zone axis perpendicular to that film and parallel to the beam.

The choice of the "open holder" rather than closed holder was made in order to allow the possibility of a double tilt mechanism and to permit the collection of X-rays and secondary electrons. There is an option to add a lid so that pressures under the lid may be increased from around 6 Pa of arsine up to an estimated 400 Pa. A small aperture in the lid allows the gases to be vented, and the electron beam to pass through. The present design of the lid has the disadvantage of blocking the line-of-sight to the X-ray detector.

Use of the MEMS chip in general may entail new approaches to TEM sample preparation compared to the standard methods used for a 3.00 mm grid. Seed particles for nanowire growth may be deposited on the chip in a similar way to the standard deposition onto III-V substrates. On the other hand, MEMS chips may be designed that themselves incorporate a crystalline substrate surface from which the epitaxial structures can grow, similar in concept to those of Kallesøe et al [14].

Gas piping to the holder has to fulfill several criteria. It must be inert, vacuum compatible and not leak gases. The pipes must also not transmit vibrations from the gas handling system. The solution adopted in Lund was PEEKsil as shown in figure 7. Earlier attempts with Teflon or stainless steel tubing failed on one or more of the criteria. PEEKsil tubing is based on PEEK tubing which is found on a number of TEM specimen holders. The PEEK material is a polymer and hence may be permeable to some gases. PEEKsil tubing incorporates a thin quartz tube inside the PEEK tube and the quartz layer reduces the permeability. The choice of tubing must also be compatible with the precursor gases used, and quartz is commonly used for liners in MOCVD systems.

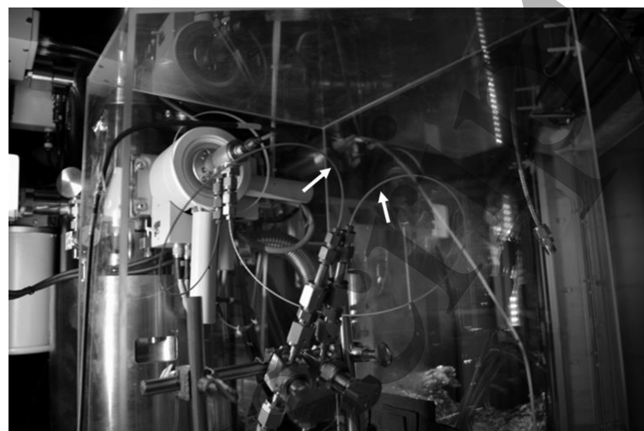

Figure 7 The two PEEKsil gas pipes (arrowed) that feed the precursors to the holder, seen through a opened panel of the microscope enclosure box. The clear perspex surround increases the efficiency of the ventilation from the area.

6. Results

This paper is intended primarily to present an overview of the concepts behind and operational aspects of the installation of the Lund ETEM. Experiments are underway to measure the technical performance of the ETEM and will be reported in a future publication [15]. One area of interest is the imaging resolution when observing the sample at different temperatures and when observing through different gases at various pressures. Another aspect is the influence of the electron beam on growth. Measurements and modelling of the pressure distribution at and around the specimen area are also in progress.

Some results from experiments on nanowire growth have been obtained already and they are presented here to illustrate the range of experiments and conditions that the ETEM instrument can offer. These in situ results build on work that has been performed ex situ, for example on the zincblende-to-wurtzite interface in GaAs nanowires [16], the stability of InAs nanowire growth [17]. A review of developments in the growth of semiconductor nanowires includes perspectives on the role of ex situ and in situ characterisation methods [18]

The seed particle at the growing end of a nanowire has been studied [19]. At the elevated temperatures for growth, the seed particle is often molten, taking the form of a droplet at the growing end of the nanowire, see figure 8. How the size, shape and composition of the droplet vary with parameters such as gallium supply and temperature was investigated. This particular kind of phenomenon is reversable, allowing experiments to be repeated and optimised during a single session.

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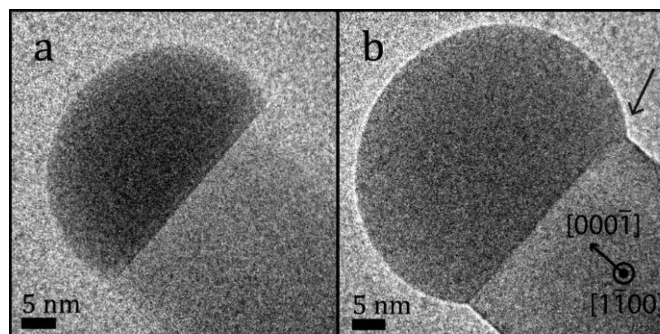

Figure 8 a and b. Liquid gold droplet at the end of a nanowire that has grown in size on the addition of gallium. The nanowire had a wurtzite structure and was oriented as indicated. Measurement of the contact angle at the junction , arrowed in b), allows the droplet surface energy to be calculated as a function of gallium content.

When growth of the nanowire was allowed to proceed, high resolution imaging, figure 9, revealed both the crystallography of the layers just grown in the nanowire and the changes in contact angle measured at the liquid/solid/vapour junction with the gold droplet.

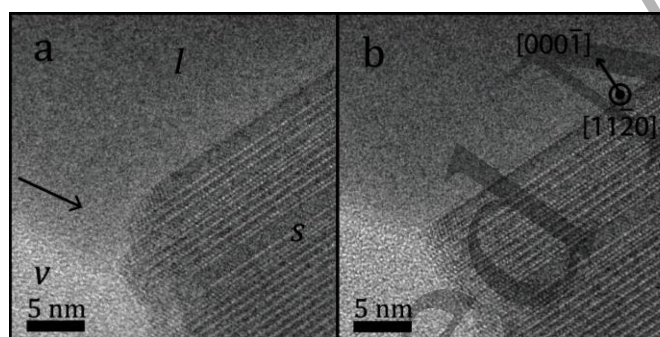

Figure 9 Detail of the liquid/solid/vapour junction between nanowire and gold droplet. The interface changes dynamically during crystal growth of a layer, with a truncation (arrowed) appearing and disappearing over a period of less than one second. The nanowire structure shown in the image is a mix of wurtzite and zinc blende, the directions indicated in b) referrring to the wurtzite structure.

The decomposition of GaAs nanowires has been another area of study. This process provides an alternative insight into the growth since the mechanisms of layer-by-layer removal and formation are similar. In situ TEM and EDS were used to measure the time and temperature-dependent rates of GaAs removal and the composition of Au−Ga particles on top of GaAs (-1 -1 -1) type facets at temperatures up to 420 °C. [20]

In another study the catalyst composition was investigated as a function of temperature and as a function of ratio of precursor flux. This type of data, obtained by EDS during growth, could only be obtained in situ, and not ex situ after growth has completed. An example of an EDS spectrum is shown in figure 10 and is taken from work by Maliakkal et al. [21]. The data were recorded in situ at 440 °C from a gold catalyst seed particle similar to the particle shown in figure 1. The peaks for the main elements in the particle, Au and Ga, can be clearly seen. The background signal at this temperature is low enough not to interfere with measurements of the Ga to Au peaks in the 9-10 keV range. (Peaks for Si and Cu come from material in the chip and holder.)

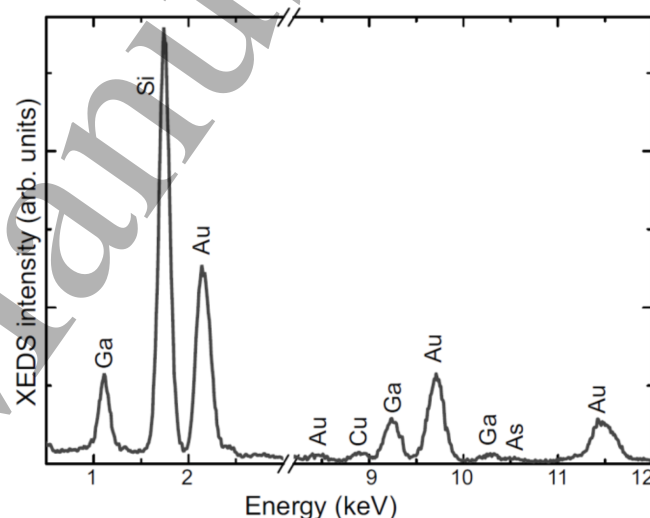

Figure 10. EDS spectrum of the catalyst particle taken in situ during growth at 440 °C. The atomic species giving rise to the peaks are indicated. This figure was first published in Nature Communications [21]

Spectra taken in the range 420 to 500 °C showed that the Ga content in the catalyst increased with increasing temperature. This increase was predicted by calculations of phase diagram. The Ga content was also found to increase with increasing pressure of the Ga precursor. Comparison of the measured Ga-Au content with calculated Au-Ga-As phase diagrams gave an estimate of the As concentration, which otherwise is below limits for detectability by EDS.

Details of the VLS growth of GaAs nanowires have been investigated [22]. In situ observations showed that the nucleation and layer growth processes could be independently

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controlled. Nucleation can be controlled by the species that easily alloys with the catalyst, i.e., by varying the Ga precursor partial pressure. Layer growth is controlled by the other species, for which few atoms are required to supersaturate the droplet i.e. by using the flow of the As precursor. Both steps must be considered if material with particular properties such as crystal structure, composition and impurity incorporation is required from the growth.

Most experiments at this stage of the project concern III-V nanowire growth by MOCVD for that is the USP or "unique selling point" of the Lund ETEM. Other materials and reactions have been investigated too, making use of the more standard gases. In one project, in situ real-time oxidation of ethylene soot and carbon black samples was carried out at 600 and 900 °C, and at 1 and 10 Pa O_2. Observations at the atomic scale were made for the first time of mechanisms and phenomena such as surface fullerene formation and internal burning. [23]

7. Discussion

For an instrument where, historically, a good clean vacuum has been of the utmost importance, it would not be surprising that limits are encountered regarding gas pressures on the one hand and microscope performance on the other. There are perhaps two main areas of concern. The first is a decrease in image resolution caused by electron scattering by gas molecules. In the gas-experiments performed to date, the detail in the images at the 0.2 to 0.3 nm level required for viewing the zinc blende lattice at the 110 zone for example has not been affected by the pressures employed. Any deterioration from the 86 pm resolution is more likely to be caused by vibrations transmitted to the holder through the gas lines. Dedicated resolution tests with varying gas pressures using the most stable holders are underway.

The second area of concern is the function and longevity of microscope components. It has been found to be the field emission gun which limits the gas pressures allowed at the sample. The brightness of a cold FEG decreases over a period of several hours and a "flashing" procedure is then implemented to restore it to the original brightness. With gas pressures of 6 Pa at the sample, that period may be reduced to as low as 10 minutes. Fortunately, even with an increased frequency of flashing, the original cold FEG continues to function with no overall loss of brightness. Clearly, the rate of decrease in the emission will depend not only on pressure but also the nature of the gas, and the data are being accumulated [15].

A further consideration for in situ experiments is whether the reactions - growth rates in our case – proceed at a suitable pace. If the rate is too fast, the changes will not be captured at the frame rates offered by the camera. Too slow and the hours, or days, required for an experiment become problematic. For our work, the growth rate can generally be adjusted by the partial pressure of the limiting precursor, which is usually the trimethylgallium.

There is also a desire to keep the overall pressure within sight of the conditions used in "real world" MOCVD growth. The operating pressure of standard MOCVD equipment [see *e.g.* 24] is between 1 or 0.1 atmospheres (10^5 to 10^4 Pa) and some low pressure MOCVD operates at 0.01 atmospheres. The bulk of this pressure comes from hydrogen which is employed as a carrier gas for the precursors. For *planar* growth in standard equipment, the precursors have partial pressures in the region of 10s of Pa TMGa and 100s of Pa AsH_3. For *nanowire* growth - where catalysts play a role – precursors have partial pressures that are lower, typically around 10^{-2}-10^{-1} Pa TMGa and 1-6 Pa AsH_3, but in some cases up to tens of Pa AsH_3 [25]. The pressures of the precursors that can be used with the open holder in the ETEM, *i.e.* up to 6 Pa, are thus similar to the partial pressures of precursors used in standard MOCVD of GaAs nanowires, and a valid comparison can be made between the in situ ETEM and standard MOCVD processes.

It is only at the upper end of the AsH_3 range that the conditions are not reached with the open holder in the ETEM. Also, the *total* pressure in the ETEM is much lower as hydrogen carrier gas is not included. The addition of the apertured lid to the open holder converts it to a "semi-closed" holder. AsH_3 partial pressure can then be increased and hydrogen can be introduced up to around 400 Pa. This option, together with the ex situ chamber option (see figure 5) allow the conditions to meet or approach those of standard MOCVD equipment.

Finally, the question of the influence of the fast electron beam on in situ reactions is often raised. Overall, the effect of the beam on the growth of the nanowires has been found to be small or negligible. One way the effects were checked was to continue growth while the beam was blanked. When growth data are collected - at present by 8 bit video - the beam flux is noted independently. The installation of a new fast camera that records counts per pixel and hence electrons per unit area at the specimen will improve the accuracy and convenience of this measurement.

One effect of the beam flux on the specimen in general appears to be deposition of material on the SiN_x membrane. Possible mechanisms might be e-beam damage to the SiN_x and the formation of preferential sites for nucleation of droplets or crystals, or interaction of the e-beam with the precursor gases. Enhanced deposition onto the nanowire itself appears not to be a significant effect but any effects of the electron beam on axial or radial growth are being monitored and investigated.

8. Future developments

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Futher developments in equipment and instrumentation are planned or underway and we mention here two regarding the holder and two regarding signal collection.

MEMS chips with 2 μm diameter holes in the SiN windows have recently been developed. Instead of samples lying on top of a thin SiN layer, nanowires and other material lie over holes and are imaged over the void. It was found that imaging of soot aggregates without interference from the sample holder material was critical to obtain the desired high resolution information [23]

The present sample holder lid blocks the line of sight for X-rays, but a redesigned lid having a larger aperture for the beam could allow X-ray collection. The aperture may not be made too large, for then the upper limit of pressure allowed in the "semi-closed" holder would be reduced to a similar value to the pressure allowed for the open holder without lid.

The collection of EELS data may offer several advantages over X-ray collection. The energy loss electrons would not be blocked by sample holder lids, nor would their spectra be suffer at elevated temperatures. Hydrogen gas could be monitored, and the EELS signal would derive from the electron path through the entire volume of gases, whereas it is less clear what is the volume of gas sample whose X-rays would be admitted into the X-ray detector. The additional capabilities of EELS need not be listed here, except to say energy resolution offered by the small energy spread of the cold FEG source will be advantageous for redox and other studies where the oxidation state of elements is important.

The advantages of an advanced camera were already referred to earlier in terms of electron counting and high frame rate imaging. A OneView IS camera by Gatan is to be installed in place of the Orius camera. The full detail of the BCOR corrected HREM images can then be captured since the size of the sensor increases to 4096 by 4096 pixels, and the larger pixel size (15μm) of the CMOS sensor gives an improved point spread function at 300 kV relative to the present cameras. The new camera will then be able to capture high resolution detail across a much larger field of view – 100nm or more – compared to the 40nm of the image in figure 1. The frame rate for full size (unbinned) images increases to 25 fps.

Figure 11 shows an HREM image taken on the currently installed Orius camera which has dimensions of 4008 pixels in one dimension (and 2672 pixels in the other). Correction of on axis aberrations is sufficient only for images taken on a 2K camera, as indicated by the dashed lines in figure 10. A 4K camera however records the image beyond that central area where off axial aberrations become important. The advanced BCOR corrects those off axis aberrations [26] and high resolution, aberration-free imaging right across the larger 4K dimensions becomes possible, as indicated by figure 11 and the magnified detail shown in the inset.

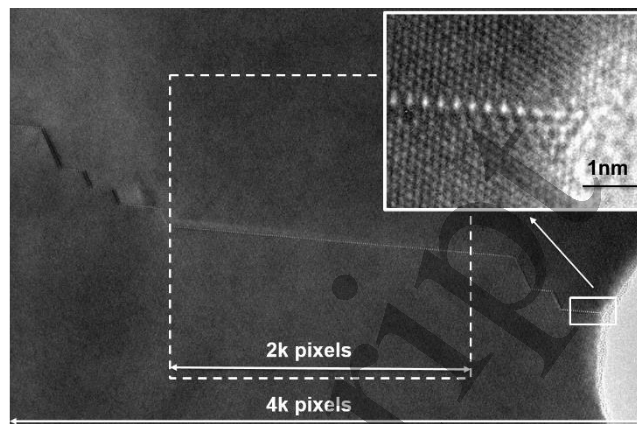

Figure 11 HREM image taken on the Orius camera of a 111 gold foil with a 11-2 type twin boundary. The field of view across the width is 100 nm. BCOR correction of aplanatic aberrations means that resolution is maintained *outside* the standard 2k inner square The inset image taken from near the edge of the camera shows {2 -2 0} fringes of spacing 0.144 nm.

9. Conclusion

The concept of placing a micro-MOCVD growth chamber into a high resolution TEM has, for the first time, been successfully realised. Many novel features were required in the design and construction of the facility.

The custom-built gas handling system delivers the group III and V precursors in a controlled manner and with the possibility of alloying. The gases pass though PEEKsil tubing, chosen to minimise the transmission of vibrations from the handling system across to the specimen holder. The holder is of the open-type and the upper limits to the partial pressures of gases introduced to the column is set by the frequency of FEG tip flashing that is acceptable for each experiment. The option of adding an apertured lid onto the holder, however, allows a significant increase in gas pressure. Significantly, these partial pressures are surprisingly close to those employed in "real world" MOCVD apparatus.

Heating holders based on MEMS chips allow the growth temperature to be selected and this design reduces drift of the sample to a level that allows high resolution imaging at elevated temperatures. Single tilt MEMS holders with gas supply lines to the tip have been mainly used for growth. A double tilt MEMS holder without gas lines can be employed for experiments where gases are supplied through the column inlets.

The high resolution performance of the microscope follows from the combination of a BCOR imaging aberration corrector and the highly coherent cold FEG. Data about nanowire growth are mainly recorded as video, and this is complemented by single image acquisition on a high quality

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camera and EDS mapping or spectra. A STEM unit is supplied for standard ADF and BF imaging, while the less common SE imaging capability has proved esecially useful for information about the topography and facetting of the nanowires.

The significance of the facility is the capability of examining samples at elevated temperatures and in an environment of precursor gases. In these conditions the material may have very different structures and composition - for example gold seed particles may be liquid and alloyed with gallium – and these phenomena could never be observed with standard ex situ microscopy.

Future developments of the facility include the addition of a fast 4k by 4k pixel camera that will fully exploit the BCOR corrected images and provide essential information on electron dose. New MEMS chips that have holes in place of the thin SiN layer will allow a "purer" image of any nanowire located over the hole, such an image being unobtainable in an instrument based on closed holders. Finally, gases other than the group III-V precursors – oxygen, hydrogen and nitrogen- are also available for use in more general types of in situ studies.

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