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A cathodoluminescence study of the influence of the seed particle preparation method on the optical properties of GaAs nanowires

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Abstract
Cathodoluminescence at 8 K is used to compare the optical properties of AlGaAs-capped GaAs nanowires, grown by metal–organic vapour phase epitaxy and seeded by gold particles prepared by different methods. Six different methods were used to fabricate and deposit gold seed particles onto GaAs substrates: colloid particles, aerosol particles and particles defined by electron beam lithography. The nanowires were grown with and without an in situ annealing step prior to the nanowire growth. The morphology showed no significant differences between the nanowires. The emissions from ensembles of nanowires have the same peak position, irrespective of seed particle type. Without the in situ annealing step prior to the nanowire growth, there are significant differences in the emission intensity and emission patterns from nanowires grown from different seed particles. When an in situ annealing step is included, all the resulting nanowires show identical optical emission intensity and emission patterns. This shows the importance of using an in situ annealing step prior to growth. This study demonstrates that different preparation methods for gold seed particles can be used to produce GaAs nanowires with highly similar optical properties. The choice of particle preparation method to be used can therefore be based on availability and cost.

Online supplementary data available from stacks.iop.org/Nano/23/265704/mmedia

(Some figures may appear in colour only in the online journal)

1. Introduction and background

Semiconductor nanowires (NWs) have been predicted to become an important part in future electronic devices, both in optoelectronic (as emitters [1], detectors [2] and solar cells [3, 4]) and in transistor [5] applications. This has generated much interest lately [6–8], mainly related to the ease with which the NWs are produced and their small footprint. The latter enables combinations of (lattice-mismatched) semiconductors not possible in bulk material. The small diameter of the NWs is a major strength, making it possible to utilize quantum mechanical effects, as well as to continue the downscaling of devices [9]. To be able to use NWs to their full potential, it is essential to optimize their structural, electrical and optical properties, depending on the application. Semiconductor NWs are often grown with the aid of metal seed particles, where gold is by far the most commonly used metal [10]. The seed particles to be deposited onto substrates for growth can
be prepared in many ways, where colloid particles, aerosol particles, particles generated by the annealing of a thin metal film and particles made by lithographic methods are generally used [10]. The optical properties of GaAs NWs grown by both metal–organic vapour phase epitaxy (MOVPE) and molecular beam epitaxy (MBE) have been studied by several groups. Most of the studies have been done using photoluminescence (steady state and time resolved), mostly spatially resolved to access individual NWs [11–16]. In order to achieve a higher spatial resolution, cathodoluminescence (CL) studies have also been carried out [17–20].

In this paper, we have investigated the influence of the different seed particle preparation methods on the optical properties of the resulting NWs using low temperature CL spectroscopy and imaging. In CL measurements, the total intensity of the emission from the NWs can be recorded and variations in the intensity and the peak energy position along the NWs can be studied on a sub-micron scale [21]. We have previously reported a comparison of GaAs NW growth by MOVPE using gold seed particles, fabricated by a variety of preparation methods [22]. In that study it was shown that the morphology, growth rate and crystal structure of the NWs were almost identical for all the different seed particle preparation methods that were studied. In the current study, we have grown GaAs–AlGaAs core–shell NWs by MOVPE. We have used six different preparation methods to fabricate and deposit gold particles onto a substrate: two ways of preparing aerosol particles, three ways of preparing colloid particles, and particle fabrication by electron beam lithography. These will be referred to as different types of seed particles. In order to have strong emission intensity from the NWs and also to ensure that the emission is stable under the electron beam, the NWs were all coated with a thin AlGaAs shell. The growth of a high-bandgap shell is known to improve the emission intensity by several orders of magnitude [23]. The emission intensity from uncoated GaAs NWs has a tendency to decrease permanently (generally referred to as bleaching) when subjected to an electron beam [24]. With a sufficiently thick shell, this bleaching can be avoided, at least for the typical SEM energies and probe currents used in the present study. We have also studied the effects of in situ annealing on the optical quality of the NWs. The annealing procedure is recommended by the wafer manufacturer in order to remove the oxide on the wafer surface to obtain a pristine GaAs surface for the growth. However, the annealing can also have negative effects. We have previously observed that particles can move and even split on the surface [22]. The movement can destroy predesigned patterns and the splitting will result in NWs with smaller diameters than intended. It is therefore important to study the influence of the in situ annealing on the optical properties of the resulting NWs.

The aim of this study is to establish similarities and differences in the optical properties of the resulting NWs. If a similar optical quality is achieved, the most suitable preparation method can be chosen in terms of availability, size of area to be covered, preparation time, and cost. In addition, similar optical quality would make it possible to compare experimental results achieved by different groups using various preparation methods to fabricate the seed particles.

2. Experimental details

2.1. Seed particle preparation methods and nanowire growth

In this study we focus on one single particle size, since the NW diameter has a significant influence on emission intensity [12]. In order to obtain as strong emission as possible from the NWs, we chose the largest diameter particles, 30 nm, that we can produce by all six preparation methods. A surface density of about 1 particle µm\(^{-2}\) was used, and each type of seed particle was deposited on a separate (111)B oriented GaAs substrate from the same batch of wafers. Apart from the preparation of the annealed colloid particles, the fabrication and preparation processes for the other particle types are described in detail elsewhere [22] and are therefore only summarized briefly here.

2.1.1. Direct deposition of colloid particles (DDC particles) [25]. The substrate is covered by a poly-L-lysine (PLL) solution and subsequently rinsed with de-ionized water before a droplet of a colloid suspension (water + stabilizing ligands) is spin-coated on the substrate.

2.1.2. Electro-spray deposition of colloid particles (ESC particles) [26]. A colloid suspension is soaked through a capillary and then atomized by an electric field into small droplets, carrying approximately one metal particle each. The particles are dried and transported to an electrostatic precipitator using an ultra-pure nitrogen carrier gas and deposited onto the substrate.

2.1.3. Electro-spray and annealing of colloid particles (ESAC particles). These particles are prepared slightly differently compared to the ESC particles described above. The difference is that the electro-sprayed colloid particles are transported through a furnace to include a short annealing step at 600 °C in order to remove contamination from the particles before they are deposited onto the substrate.

2.1.4. Evaporation/condensation generated aerosol particles (ECA particles) [27]. A gold vapour is produced by evaporating solid gold in a high temperature furnace. The vapour is transported in an ultra-pure nitrogen carrier gas and as the vapour cools down, particles nucleate. The particles are reshaped into compact spherical particles in a second furnace and then size-selected using a differential mobility analyzer [28] before being deposited onto the substrate.

2.1.5. Spark discharge generated aerosol particles (SDA particles) [29]. A spark discharge between two solid gold electrodes generates a gold vapour. The gold particles are formed, reshaped and deposited in the same way as described for the ECA particles above.
2.1.6. Electron beam lithography defined particles (EBD particles) [30]. Electron beam lithography (EBL) is used to create a dot pattern in a resist and a thin gold film is deposited. After lift-off, a regular pattern of flat gold discs remains in rectangular fields on the surface. These discs reshape into spherical gold particles when bringing the substrate up to the NW growth temperature or during an in situ annealing step.

2.2. CL studies

The CL studies were performed at 8 K in a dedicated SEM, equipped with a liquid He cryostat (base temperature of about 5 K) as described in [21]. The emission was dispersed through a monochromator and detected by a GaAs photomultiplier tube. The spectral resolution used in the study was typically 5–15 meV, which is less than the width of the emission peaks in the spectra. An acceleration voltage of 5 kV was used with a beam current of either 10 or 50 pA. The choice of 5 kV is related to the diameter of the NWs and the penetration depth of the electrons, as discussed in the supplementary information. These conditions result in a spatial resolution better than 100 nm. In most cases, the substrates containing the NWs were cleaved through the centre, and the sample was mounted on a sample holder with the fresh cleave upwards. This gives access to the NWs in side view while still attached to the substrate. This geometry gives access to literally thousands of NWs for the CL investigations. All the data were recorded from the middle of the substrate, avoiding the edges of the original substrate, where the growth may deviate. Spectra were recorded by scanning the beam over several NWs, over a single NW or by placing the beam at specific positions on a single NW. For all samples, a series of CL images was recorded covering the range of the emission peak. The supplementary information contains a more detailed reasoning behind the choice of excitation conditions, as well as more detailed information about how the measurements were performed. Note that in the CL images presented in the figures white represents the highest intensity in the individual images and black means no intensity.

3. Results

Irrespective of the type of seed particles used and whether or not the in situ annealing step was performed, all NW samples that were studied in this work show remarkably similar emission spectra in terms of peak position and line shape. In fact, we could not detect any significant differences in the emission spectra, irrespective of seed particle type. All emission spectra from the NWs are dominated by a relatively broad peak (full width at half maximum, FWHM, of ~30 meV) centred in the range 1.470–1.480 eV. There are some minor variations (less than ±10 meV) in the peak position of the average spectra of the NWs grown from the different seed particles. Similar variations can be observed between individual NWs in the same sample, as well as among individual NWs, as will be discussed below. The origin of this peak will be discussed in detail elsewhere [33]. It is linked to the presence of twins in the zincblende structure of the core, as discussed by Heiss et al [34]. A typical spectrum from several NWs in side view on the substrate is shown in figure 1. The spectrum was recorded at 8 K with the beam scanning over an area of 2 × 2 μm², carefully avoiding exciting the substrate. The spectrum is dominated by a single emission peak centred at 1.475 eV, from the GaAs NW core [31]. At higher energies,
Figure 2. Low-magnification CL and SEM data from NWs grown from ECA particles with in situ annealing. (a) CL image of the core emission and (b) the corresponding SEM image recorded simultaneously. (c) The CL intensity integrated over the whole width of the image along the arrow in (a).

a broad and much weaker band covering 200 meV can be observed. This is attributed to the shell itself, as well as material grown axially when the AlGaAs shell is formed. Although radial growth is increased at the temperature used to grow the NW shell, growth also continues underneath the seed particle as it is difficult to decouple radial and axial growth for particle seeded NWs [20]. Whether a ternary layer grows axially or radially has a significant influence on the composition. We note that the broad emission at higher energies corresponds to an AlGaAs layer with an Al content in the range 15–30%. We attribute this variation in composition to significant differences in the Al content of the AlGaAs shell and the core material at the top of the NW, as well as possible domains in the shell material with different Al incorporation, similar to what has been observed for AlInP shells on GaAs cores [35].

3.1. Nanowires grown without in situ annealing

We first concentrate on NWs grown without in situ annealing. The peak position of the emission is the same for all NWs in this study, as discussed above and identical to the spectrum shown for NWs seeded by ECA particles in figure 1. There are some variations in the intensity between ensembles of NWs grown from the different seed particles, where the DDC- and ESC-seeded NWs are significantly weaker in intensity than the rest. There are also significant differences in the intensity variations along the NWs seeded by different types of seed particles. Figure 3 shows a series of typical images of NWs grown from all the different seed particle types. The lower parts of the images show the emission from the substrate and they all show a dark stripe above the substrate due to the AlGaAs material at the base of the NWs, as discussed above. It is worth pointing out that the further the NWs are from the cleaved edge of the substrate, the weaker the emission is in the images. This is a simple geometrical effect, as more of the emission from a NW is blocked from reaching the detection system by the NWs above it, as discussed in the supplementary information. This is also the main reason why adjacent NWs appear to vary in intensity.

As mentioned above (in section 2.2), the grey scale in a CL image is related to the intensity in that particular image, and therefore the intensity of two images cannot be compared directly from the grey scale. However, the intensity of the substrate at the bottom of the images serves as a reference for the relative intensity. For the DDC- and ESC-seeded NWs, the relative emission intensity from the substrate is stronger, compared with the NW emission (see figures 3(g) and (i)). These NWs show lower intensities as compared with the NWs
seeded by the other particle types. The emission patterns from the NWs are similar for all samples apart from the DDC- and ESC-seeded NWs. For the NWs grown from the other four types of seed particles (ECA, SDA, EBD and ESAC), the emission patterns are similar to that of figure 2(a), where the intensity is highest near the bases, gradually dropping towards the tops of the NWs. The DDC-seeded NWs show the reverse pattern, where the intensity increases from base to top. As the average intensity is significantly less for these NWs, the tops of these NWs are in fact similar in intensity to the tops of the rest of the NWs. For the ESC-seeded NWs, the emission is weak, but homogeneous along the entire NW. When the colloids are annealed during electro-spraying process (ESAC particles), the resulting NWs are almost identical to NWs grown from ECA particles. In figures 3(a), (c) and (e), the CL images show the same spotty emission intensity as in figure 2(a). We will discuss the origin of this feature in the section below.

3.2. Nanowires grown with in situ annealing

We now turn to the NWs grown using an in situ annealing step before growth. Figure 4 shows a series of images from six different sets of NWs, using all six types of seed particles. The images are similar to the ones in figure 3, but with NWs grown including the in situ annealing step. The images were recorded at slightly higher magnification than in figure 3, excluding the tops of the NWs in each image. The lower part of the images shows the emission from the substrate and they all show a dark stripe above the substrate due to the AlGaAs material, as discussed above. Our CL measurements show that the emission patterns and the emission intensities are very similar for all six NW samples. The intensity is strongest at the base, gradually reducing towards the top of the NW. As discussed in section 3.1, we attribute this to the change in core volume due to the tapering of the NWs. In addition, all NWs have a slightly spotty emission pattern, especially visible in the ECA- and EBD-seeded NWs ((a) and (e)). Each CL image was recorded at the peak energy position of the average emission from the area of the entire image. Therefore, the detection energy varies slightly from image to image.

As discussed above, there are differences in the peak emission position when comparing the emission from individual NWs. In addition, the emission varies randomly along the individual NWs within ±10 meV. This random variation in the energy leads to the spotty intensity variations,
Figure 5. Images recorded from the same area as figure 4(e), but at different energies: (a) 1.498 eV, (b) 1.480 eV, (c) 1.462 eV and (d) 1.445 eV. The intensity of (a) and (c) is enhanced by a factor of two and (d) by a factor of three with respect to (b). As the detection energy is varied, the pattern of spots changes slightly. The wires were seeded by EBD particles.

as observed in all the CL images. To illustrate this, we present a number of images recorded from the same area, but at different energies in figure 5. These four CL images were recorded at four different energies around the main emission peak from the NWs. They all show a spotty pattern, where a closer look reveals that the spots are at different positions in the different images. This can be studied in more detail by recording spot mode spectra by placing the electron beam at various positions along a single NW and recording a spectrum in each position. Though not shown here, such a set of spectra confirms that there are slight variations in the peak position of the core emission along individual NWs. This local variation in the emission peak explains why the emission pattern for a single emission energy, as in the CL images, appears spotty. At present, the origin of this variation is not completely understood but at least part of the explanation may be connected to variations in the crystal structure influencing the emission pattern along the length of the NWs [34]. As mentioned in the experimental section (section 2.1), the crystal structure is mostly zincblende with the inclusion of a high density of twin defects, stacking faults and occasionally, short wurtzite segments [22].

3.3. Stability under e-beam irradiation

NWs seeded by SDA particles show a major deviation in the emission behaviour, as they show sensitivity to exposure to the electron beam during the CL measurements. These NWs exhibit significant, and permanent, bleaching of the emission when exposed to the electron beam. This effect is general for all the NWs seeded by SDA particles that we have studied by CL, both with and without the in situ annealing step. This is illustrated in figure 6, where (a) and (b) were recorded after each other, with a pixel dwell-time of about 1 ms, where the bleaching takes place within less than a minute of exposure. In this case, the images are presented with the same intensity scale. It is clearly visible that the intensity in figure 6(b) is significantly reduced as compared to figure 6(a). Figure 6(c) shows a low-magnification image recorded after several scans were made of a smaller area at higher magnification. There is a dark area where the high-magnification images were recorded. Figure 6(d) shows the intensity profile across to the NWs in this image. Since the other types of NWs grown in the same growth runs do not show any bleaching, we can rule out that it is related to insufficient shell growth for some of the growth runs. We can therefore conclude that this effect must in fact be intrinsic to the SDA particle seeded NWs.

4. Discussion and conclusions

Earlier investigations have shown that general growth characteristics and crystal structure are almost identical for NWs grown using different types of seed particles [22].
The emission energies, patterns and intensities (with two exceptions) are the same irrespective of the type of seed particle. This means that the most suitable type of seed particle with respect to equipment available, area coverage, preparation time and fabrication cost can be used to seed NWs for optical applications and studies. Potentially, this also means that NWs grown from gold particles from different preparation methods using similar growth parameters can be compared. NWs grown by different groups can be compared, provided they were grown using identical growth conditions.

Another result from this study is the importance of using \textit{in situ} annealing when growing NWs. NWs seeded by two types of colloidal gold particles (ESC and DDC particles) show significantly reduced emission intensities, and different emission patterns when the \textit{in situ} annealing is omitted. We attribute this reduction to an increase in competing non-radiative recombination introduced by contamination from the particle-deposition processes. The deposition of the DDC particles involves coating the surface with PLL, as well as the liquid (mainly water and ligands) from the colloidal solution. During the initial growth, it is quite possible that some of this contamination will be incorporated into the NWs during growth, causing a reduction in the intensity of the emission from the NWs. When depositing the ESC and ESAC particles, no PLL coating of the substrate was used, which in combination with the cleaner deposition process of electro-spraying can explain why the optical properties of NWs grown using these particles are less affected by omitting the \textit{in situ} annealing step, as compared to the DDC particle seeded NWs. NWs seeded by ESC particles show weaker emission intensities but not as severe as the ones seeded by DDC particles. This indicates that the optical properties of NWs grown from ESC particles are also deteriorated due to contamination from remnants of the colloidal solution. Annealing the colloids during the deposition process, as in the case of the ESAC particles, seems to remove the residues and make the resulting NWs comparable to the aerosol-seeded ones. The results discussed above strongly indicate that a cleaner substrate surface, from either a cleaner deposition method or from \textit{in situ} annealing, results in NWs with better optical properties. It is, however, a bit surprising that the optical properties of NWs seeded by EBD particles do not seem to require the \textit{in situ} annealing step. The lithography process involves patterning with a resist, and exposure to chemicals that could potentially leave residues on the substrate surface. It may be that these residues are more volatile and therefore leave the surface before the growth temperature has been reached. This is an important observation, as the annealing step can disrupt well-designed patterns, as the particles tend to move and even split during the annealing step, as discussed in section 2.1.

A puzzling difference that was observed between NWs seeded by the different particles is the fact that NWs grown from the SDA particles are so greatly affected by the electron beam, unlike the other NWs in this study. As all NWs grown from SDA particles that we studied rapidly lose the emission intensity when exposed to the electron beam, we can clearly say that this effect must be related to the properties of the original seed particles. Our group has done in-depth analyses of palladium SDA particles generated by the same spark generator and found significant amounts of carbon in the palladium SDA particles prior to growth [36]. Producing gold nanoparticles in this way may also result in carbon contamination and thereby in contamination of the NWs during the NW growth process. The carbon in the palladium most likely originates from the plastic parts of the particle generation chamber and is incorporated during the spark discharge process itself. It might be that the gold SDA particles suffer from the same type of carbon contamination, but until further studies are performed nothing can be concluded since gold/carbon is a very different system than palladium/carbon. It is not clear to us how and why the carbon contamination would affect the growth. One possibility is that the carbon is in the form of carbon compounds. If these compounds are incorporated into the NWs during growth, they can be modified by the electron beam and transformed to non-radiative recombination centres. The origin of this bleaching will be the subject of a future study, and is beyond the scope of this report.

5. Summary

We have performed optical studies of GaAs nanowires using cathodoluminescence measurements. We find that the emission intensity and pattern from all the resulting nanowires irrespective of gold seed particle type are highly similar when an \textit{in situ} annealing step is included before the growth. When the \textit{in situ} annealing step is omitted there are significant effects on the emission from the nanowires seeded by colloid gold particles. Directly deposited colloid particles result in
nanowires with less emission intensity than all other seed particles. By using the electro-spraying method instead of direct deposition, the effect is less pronounced. However, it is only when the colloid particles are annealed in the gas phase before being deposited using electro-spraying that these particles result in nanowires with similar emission intensities to the two types of aerosol particles and the electron beam lithography defined particles. We attribute the reduced emission intensity to contamination introduced on the substrate surface during the deposition processes for the directly deposited and electro-sprayed colloid particles.

The final conclusion is that the different types of gold seed particles result in the same quality nanowires with highly similar optical properties, providing proper in situ annealing is included in the growth process.

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