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Vapour-liquid-solid growth of ZnO-ZnMgO core–shell nanowires by gold-catalysed molecular beam epitaxy

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Abstract

Nanowire heterostructures, combining multiple phases within a single nanowire, modify functional properties and offer a platform for novel device development. Here, ZnO/ZnMgO core–shell nanowires are grown by molecular beam epitaxy. At growth temperatures above 750 °C, Mg diffuses into ZnO making heterostructure growth impossible; at lower shell-growth temperatures (500 °C), the core–shell structure is retained. Even very thin ZnMgO shells show increased intensity photoluminescence (PL) across the ZnO band-gap and a suppression in defect-related PL intensity, relative to plain ZnO nanowires. EDX measurements on shell thickness show a correlation between shell thickness and core diameter which is explained by a simple growth model.

Keywords: nanowires, ZnO, heterostructure, MBE

(1. Introduction)

Nanowire heterostructures, where multiple chemistries are combined within a single nanowire, allow for the modification and enhancement of nanowire functional properties [1–3]. There are broadly two types of nanowire heterostructure, defined by the quasi-one-dimensional nanowire geometry: axial heterostructures (where the chemistry changes along the axis of the nanowire) and radial or core–shell heterostructures (where the chemistry changes in a direction perpendicular to the nanowire axis).

Such heterostructures are typically grown in a step-wise manner: a nanowire of one material is grown first and then the growth conditions are changed to deposit a chemically distinct secondary material. Nanowires are frequently grown via variants of the so-called vapour liquid solid (VLS) mechanism. Axial growth occurs when a liquid particle at the nanowire tip absorbs reactants, becomes super-saturated and thus deposits a crystalline layer at the nanowire tip. Radial growth occurs when mobile reactants adsorbed on the sample surface react before reaching the liquid particle and are deposited on the sidewalls of the nanowire. By varying the growth conditions the relative rate of these alternatives may be controlled. This approach provides, in principle, a straightforward way to grow different types of heterostructure with a high degree of control.

Zn1−xMgxO is a wide band gap semiconductor in which the band gap, $E_g$ increases with $x$, the Mg concentration, whilst maintaining a wurtzite structure. The room temperature band gap is determined [4] to depend on $x$ as $E_g = 3.30 + 2.36x$. At large values of $x$, the rock-salt phase of MgO starts to segregate, although the precise value of $x$ depends on film thickness and the substrate; films with $x = 0.61$ have been reported without segregation [5]. ZnO/ZnMgO heterostructures, therefore, allow band-gap mis-aligned epitaxial heterointerfaces to form. ZnO/ZnMgO nanowire heterostructures have been previously grown by...
metal organic vapour phase epitaxy [6–8] and pulsed laser deposition [9]. In these heterostructures, ZnO quantum wells are sandwiched between ZnMgO layers leading to quantum confinement. In this case, no catalyst was used and growth is likely driven by vapour–solid mechanisms. Thermal evaporation has been used to grow core–shell $\text{Zn}_x\text{Mg}_y\text{O}/\text{Zn}_w\text{Mg}_o\text{O}$ with $y > x$ where the core had wurtzite and the shell cubic crystal structures, likely due to phase segregation [10]. ZnO/MgO core–shell nanowires have also been grown by MBE with VLS growth [11]. But again, the shells had the rock-salt structure precluding an epitaxial interface around the full wurtzite core.

In this manuscript, ZnO/ZnMgO core–shell nanostructures are grown via a two-stage VLS process based on molecular beam epitaxy, in the form of forests deposited on a substrate. The effects of growth conditions on core/shell dimensions, and interface sharpness are explored with transmission electron microscopy. The intensity of photoluminescence is expected to form axial heterostructures [12, 13]. C-axis sapphire coated with a ~3 nm film of thermally evaporated gold is used as the substrate. Upon heating the sample, the gold melts and detwets from the substrate forming self-assembled liquid nanoparticles. Elemental Zn flux with beam equivalent pressure (BEP) $\sim 3 \times 10^{-7}$ Torr and an oxygen plasma (300 W power, flow of $5 \times 10^{-8}$ m$^3$ s$^{-1}$) are directed towards the sample. The gold nanoparticles act as reservoirs for incident Zn and O radicals. Upon supersaturation of the gold nanoparticle a layer of ZnO forms on the base of the nanoparticle resulting in axial nanowire growth by the VLS mechanism. ZnMgO is grown by introducing an elemental Mg flux with a BEP typically 1%–10% of the Zn BEP whilst maintaining the Zn flux and oxygen plasma. Nanowires grown by this technique form forests of nanowires with lengths 0.5–2 $\mu$m and diameters 20–100 nm.

Nanowires were characterized by room temperature ensemble PL using a He/Cd laser with an excitation wavelength of 325 nm using a Renishaw fluorescence microscope. The fluorescence microscope has a spot size of approximately 2 $\mu$m and so simultaneously addresses approximately 10 nanowires as well as other material not growing in the nanowire geometry. However, similar PL spectra were acquired at multiple locations confirming consistent behaviour. Scanning transmission electron microscope (STEM) and energy dispersive x-ray spectrometry (EDX) measurements were performed in a JEOL 2100Plus. Nanowires were dispersed onto transmission electron microscope (TEM) grids (gold grids with holey carbon and a 2 nm amorphous carbon film) by sonicating as-grown nanowires in 2-propanol causing nanowires to break off and become dispersed. The nanowire dispersion was then pipetted onto the TEM grids and allowed to evaporate.

2. Experimental

ZnO nanowires are grown by gold-catalysed plasma-assisted MBE as previously reported [12, 13]. C-axis sapphire coated with a ~3 nm film of thermally evaporated gold is used as the substrate. Upon heating the sample, the gold melts and detwets from the substrate forming self-assembled liquid nanoparticles. Elemental Zn flux with beam equivalent pressure (BEP) $\sim 3 \times 10^{-7}$ Torr and an oxygen plasma (300 W power, flow of $5 \times 10^{-8}$ m$^3$ s$^{-1}$) are directed towards the sample. The gold nanoparticles act as reservoirs for incident Zn and O radicals. Upon supersaturation of the gold nanoparticle a layer of ZnO forms on the base of the nanoparticle resulting in axial nanowire growth by the VLS mechanism. ZnMgO is grown by introducing an elemental Mg flux with a BEP typically 1%–10% of the Zn BEP whilst maintaining the Zn flux and oxygen plasma. Nanowires grown by this technique form forests of nanowires with lengths 0.5–2 $\mu$m and diameters 20–100 nm.

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3. Results

3.1. Axial heterostructures

First, unsuccessful attempts to grow axial heterostructure nanowires are reported since the results highlight some constraints which must be considered when growing radial heterostructure nanowires. ZnO nanowires were grown as described above for one hour at a sample temperature of 750°C. After the first hour of growth, an Mg flux of $5.9 \times 10^{-9}$ Torr (corresponding to 1.6% of the Zn flux) was introduced while maintaining the Zn and O fluxes.

ZnMgO growth was continued for another hour (two hours total growth). Upon completion, Zn and Mg shutters were closed and the oxygen flow for the plasma terminated. In principle (although as shown later not in practice), this regime is expected to produce a nanowire where the lower-half is ZnO and the upper-half is ZnMgO.

PL measurements were performed on ensembles of many of such nanowires (blue curve figure 1(a)). The PL spectrum shows a single peak with maximum counts at 3.33 eV. If heterostructure nanowires had been successfully grown two peaks, one from ZnO and another from the wider-gap ZnMgO, would be expected. The PL spectrum of pure ZnO nanowires grown as a control, without the introduction of magnesium (black curve figure 1(a)) also shows a single peak with a maximum at 3.28 eV. The shift in the PL peak observed from the (intended) axial heterostructures indicates the presence of a homogenised ZnMgO only. The band-gap dependence on x from [4] implies Mg concentration in the heterostructures of ~1% close to the fractional Mg flux and significantly below the solubility limit of Mg in ZnO which can be up to 33% [4].

![Figure 1](image-url)
EDX maps show the Mg distribution within nanowires from this growth run (e.g. figure 1(b)). The EDX maps show that, rather than having discrete regions of ZnO and ZnMgO, magnesium is quite uniformly distributed throughout the nanowire. This observation is consistent with the PL measurement showing only a single peak at energies corresponding to ZnMgO.

Clearly, in this case, a homogeneous, tertiary, nanowire grows instead of an axial heterostructure. At elevated temperatures (750 °C here), in addition to incorporation through the metal catalyst, Mg may also diffuse through the sidewalls into the already-grown-ZnO. This thermal diffusion means that during the ZnMgO growth phase, the ZnO is annealed in a Mg flux, Mg migrates into the ZnO and ZnMgO is formed. Mg diffusion has been reported upon annealing thin films of supersaturated ZnMgO where a rock-salt phase segregates out and ZnO/ZnMgO heterostructures which form uniform ZnMgO films with a lower Mg concentration [14]. Here, instead, the diffusion of adsorbed elemental Mg into the ZnO lattice resulting in uniform doping is shown.

An obvious solution to grow axial heterostructures is to conduct the second growth phase at a lower sample temperature. However, reducing the temperature much below 750 °C causes the gold catalyst particles to solidify and terminates axial growth. It therefore seems that ZnO/ZnMgO axial heterostructures may not be grown by gold-catalysed MBE. These considerations show that despite the large amount of control offered by VLS growth in MBE, the multiple processes occurring in nanowire growth makes heterostructure growth a challenge. An alternative strategy may be to use a metal catalyst with a lower melting point such as tin which does not give sufficient information to conclude that the nanowires are ZnO/ZnMgO core–shell heterostructures. EDX maps of nanowires from sample A and B were, therefore, collected as shown in figures 2(b), (c) respectively. Although there is no PL signature from ZnMgO in sample A, the EDX map of the edge of a nanowire from sample A (figure 2(b)) shows a significant increase in Mg counts. These nanowires are, therefore, assigned as core–shell structures with thin shells of ZnMgO coating a ZnO wire. For the thicker shells in sample B, the EDX map extending across the entire diameter of a nanowire (figure 2(c)) shows a clear increase in intensity of Mg at both sides of the nanowire. The Mg rich region is thicker in this nanowire than that shown in figure 2(b), as expected given the longer growth.

In STEM-EDX the primary electron beam penetrates the entire nanowire, with minimal scattering. X-rays may be generated at any point as the primary beam passes through the nanowire, meaning that EDX maps are projections of the elemental composition of a 3D object into a 2D map. When imaging with the electron beam perpendicular to the nanowire growth axis, the magnesium composition of a magnesium-rich shell is projected into 2D resulting in significant counts on the nanowire sides and fewer counts in the centre as seen comparable as data is collected on the same day with identical laser power and collection durations. Sample A shows only luminescence at these energies whereas sample B shows a distinct PL peak at higher energies with maximum intensity at 3.64 eV, corresponding to the bandgap of Zn0.3,Mg0.7O with 14% Mg content. These data indicate that, in at least in sample B, both ZnO and ZnMgO are present in the sample. The ZnMgO on this sample has a higher Mg concentration than the ZnMgO from the attempted axial heterostructures due to the larger Mg flux. X-ray diffraction collected from sample B shows no peaks from cubic ZnMgO or MgO indicating that the shells retain the wurtzite phase of the nanowire cores.

The limited spatial resolution of the PL measurements does not give sufficient information to conclude that the nanowires are ZnO/ZnMgO core–shell heterostructures. EDX maps of nanowires from sample A and B were, therefore, collected as shown in figures 2(b), (c) respectively. Although there is no PL signature from ZnMgO in sample A, the EDX map of the edge of a nanowire from sample A (figure 2(b)) shows a significant increase in Mg counts. These nanowires are, therefore, assigned as core–shell structures with thin shells of ZnMgO coating a ZnO wire. For the thicker shells in sample B, the EDX map extending across the entire diameter of a nanowire (figure 2(c)) shows a clear increase in intensity of Mg at both sides of the nanowire. The Mg rich region is thicker in this nanowire than that shown in figure 2(b), as expected given the longer growth.
these nanowires are cylindrical core–shell heterostructures, and the EDX profile of Fig. 3(c) shows a shell in red and nanowire cores in black. The thickness of four different nanowires from sample B is determined from the EDX Mg intensity profile taken across the nanowire core radius. The good agreement between the profiles of Fig. 3(c) and the radii data can be fitted to equation 1 with \( r_2 = 12.7 \) nm and \( r_1 = 9.7 \) nm.

A simple model to explain this trend assumes that a gold film of uniform thickness \( t \) de-wets to form spherical catalyst particles of radius \( r_1 = (3At/4\pi)^{1/3} \) where \( A \) is the area of gold film contributing to the catalyst particle. It is reasonable to assume that flux incident on the same area \( A \) will contribute to the nanowire growth from this particle. The gold nanoparticle catalyses the axial growth of a nanowire of radius \( r_1 \) and length \( L \) which has total volume \( \pi r_1^2 L \). The volume is also determined by the integrated flux given by \( \pi r_1^2 L \) where \( r_1 \) and \( r_2 \) are respectively the incident flux in, and total time of, the first phase of growth. In the second growth phase a shell of volume \( \pi r_2^2 L \) grows where \( r_2 \) is the radius of the core–shell nanowire. This volume is then given by \( \pi r_2^2 L \) where \( r_2 \) and \( r_1 \) are the flux in and time of the second growth phase. Combining these relations gives a prediction for the relative radii of the core \( r_1 \) and the outer shell \( r_2 \):

\[
\frac{r_2}{r_1} = \frac{L}{\tau_2 - \tau_1} \approx \frac{1}{1.52},
\]

where \( \tau_1, \tau_2 \) are times of first and second growth phases. This approximate value of 1.38 is very close to the experimental value of 1.38. This excellent agreement, even for this simple model, supports the proposed mode of heterostructure growth.

Using this technique to determine the thickness of nanowire shells, the shell thickness of four different nanowires from sample B is determined (Fig. 3(c)). For these nanowires, thicker nanowire cores result in thicker shells.

A schematic showing a shell in red and nanowire generating x-rays is shown in Fig. 2. Detailed information could be determined, for example, using more elaborate sample preparation methods to create a FIB section to allow imaging with electrons parallel to the nanowire growth axis. For these samples, the nanowire with a cylindrical core encased by a shell of constant thickness and constant chemical composition. The 2D projection of Mg concentration from such a structure is given by

\[
I(x) = \begin{cases} 
0, & \text{if } |x| > r_2 \\
\sqrt{r^2 - x^2}, & \text{if } r_2 > |x| > r_1 \\
\sqrt{r_2^2 - x^2} - \sqrt{r_1^2 - x^2}, & \text{if } |x| < r_1
\end{cases}
\]

where \( r_1 \) and \( r_2 \) are the radii of the core and the whole nanowire respectively and \( x \) is the distance from the centre of the nanowire. This geometry is shown in Fig. 2 and 3(b). By fitting the measured EDX Mg intensity profile to equation 1 the shell thickness \( r_2 - r_1 \) can be extracted. The EDX line-scan intensity for the nanowire with EDX map shown in Fig. 2(c) is shown in Fig. 3(a) with a fit to equation 1 also shown. The extracted value of shell thickness is 3 nm. The good agreement between the profile considering an ideal radial heterostructure, and the EDX profile, indicates that these nanowires are cylindrical core–shell heterostructures.

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The ZnMgO shell passivates the nanowire surface as has been seen for core–shell ZnO/Al₂O₃ nanowires [18] due to the dielectric shell screening the charges of surface states and reducing the band-bending at the nanowire surface. The increase in PL emission is also seen for nanowires with cubic MgO or ZnMgO shells [10], indicating a general mechanism by which a wide-band shell may suppress band-bending and thus increase luminescence efficiency. Furthermore, as XRD measurements show no evidence of rock-salt phases these shells are wurtzite and are therefore compatible with a fully epitaxial interface which may be achieved with further growth.
refinements. Epitaxial shells with small lattice mismatch are compatible with defect free shells, important since shell defects have been shown to degrade optical properties [6].

4. Conclusion

ZnO/ZnMgO heterostructure nanowires were grown by plasma-assisted gold-catalysed MBE via the VLS mechanism. PL and STEM-EDX studies reveal the relationship between the structure and the electronic properties. Axial heterostructures are hard to access due to diffusion of Mg into the ZnO lattice at elevated temperatures and catalyst solidification at lower temperatures. In the future, catalysts with lower melting points such as tin may be used to grow these structures. However, core–shell heterostructures can be grown via a two-stage process: a ZnO nanowire core is grown axially by VLS before cooling the sample to a temperature below the melting point of the catalyst to grow the ZnMgO shell. PL measurements show an increase in optical quality of heterostructure nanowires over bare nanowires with more intense inter-band emission and a less intense defect peak. EDX maps show that nanowires grow with the core–shell structure and that the thickness of the nanowire shells varies systematically. The growth techniques reported here will aid future growth of heterostructures of ZnO/ZnMgO and other chemistries.

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