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Selective growth of ZnSe and ZnCdSe nanowires by molecular beam epitaxy

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Abstract

Controlled growth of ZnSe and ZnCdSe nanowires is demonstrated by molecular beam epitaxy using Au or Ag catalyst films in the temperature range 400–550 °C. The highest density of small-diameter (10 nm), highly-crystalline ZnSe nanowires is achieved by using Au at 400 °C. Direct growth onto transmission electron microscope grids clearly indicates a tip-growth regime. Pre-patterning of the catalyst film allows highly selective ZnSe deposition as probed by photoluminescence and Raman spectroscopy. In similar conditions, the addition of Cd vapour in the MBE reactor allows the synthesis of ZnCdSe ternary nanowires.

1. Introduction

One-dimensional semiconducting nanostructures have attracted increasing interest in recent years both in terms of fundamental physics as well as device applications [1]. In particular, nanowires (NWs) and nanodots based on II–VI compounds are suitable candidates for applications in nano-optics and nanosensing [2, 3]. Due to their wide bandgap, ZnSe and ZnCdSe films have been extensively studied as materials for lasers and light-emitting diodes in the blue–green region of the visible spectrum [4, 5]. The controlled synthesis of ZnSe NWs, however, is still in its infancy [6–9]. To the best of our knowledge, the deposition of ZnCdSe NWs has not been reported so far, despite ZnSe/ZnCdSe quantum wells showing promising results as active layers for light-emitting devices [4, 5].

Different approaches have recently been proposed for the growth of single-crystal ZnSe NWs, including vapour phase growth [6], metal–organic chemical vapour deposition (MOCVD) [7, 8], and molecular beam epitaxy (MBE) [9]. In all cases, a metallic catalyst allows the growth of one-dimensional structures. However, the role of such a catalyst in the NW formation is still to be clearly understood. Generally, it is assumed that the catalyst-assisted NW growth follows the standard vapour–liquid–solid (VLS) model proposed by Wagner and Ellis [10]. Within this framework, it is

assumed that the precursor alloys with the catalyst, forming a eutectic melt and thus a preferential site for gas adsorption. The nanostructure grows by precipitation from the catalyst interface. There are, however, some reports which do not validate this model for the growth of ZnSe NWs [7, 8].

Molecular beam epitaxy has been widely used to deposit III–V and II–VI materials and devices and is well known to be an effective method to grow heterostructures with very sharp interfaces [4, 5]. Furthermore, single electron transistors and resonant tunnelling devices have been demonstrated with MBE-grown III–V semiconductor nanowires [11].

Gold has been shown to be one of the most effective catalysts for the low-temperature growth of semiconductor NWs [6, 7, 9, 11, 12]. Other metals have been considered as well. For example, the Ag-catalysed MOCVD synthesis of ZnSe NWs at a substrate temperature of 450 °C has been reported [8].

Here, we present the growth of Au- and Ag-catalysed ZnSe and ZnCdSe nanowires by MBE in the 400–550 °C temperature range. High densities of wires as thin as 10 nm are obtained using Au at 400 °C. Transmission electron microscopy indicates a tip-growth mechanism, leading to highly crystalline and defect-free NWs. The optical selectivity on patterned substrates is confirmed by photoluminescence and Raman spectroscopy measurements.

2. Experimental details

All samples are grown by solid-source MBE. A 20 nm-thick SiO₂ layer is sputtered on n-doped Si wafers, as well as on 300-mesh Mo TEM grids. The substrates are then coated with a thin (0.5–2 nm) catalyst layer. Elemental Zn, Cd and Se are evaporated on the sample surface for 1 h, with fluxes corresponding to an equivalent 2D growth rate of about 0.5 $\mu\text{m h}^{-1}$. The II/VI beam equivalent pressure ratio is 0.4. The growth temperature range is from 400 to 550 °C, as measured by an infrared pyrometer. The structural and optical properties of the resulting nanostructures are investigated by field-emission scanning electron microscopy (FE-SEM) coupled with energy dispersion x-ray spectroscopy (SEM-EDX), transmission electron microscopy (TEM, 400 kV), Raman spectroscopy (Renishaw, MicroRaman 1000), and photoluminescence (PL). PL was measured at 10 K with 1 mW laser power from an Ar-ion laser in the UV (333.6–363.8 nm). The Raman spectra were measured using a 514.5 nm Ar-ion laser excitation.

3. Results and discussion

Epitaxial ZnSe films are typically grown by MBE at about 300 °C and it is well known that higher growth temperatures are detrimental to the optical properties of the film [13]. Hence, we believe it is important to grow the ZnSe nanowires at similar temperatures.

MBE growth of ZnSe NWs on GaP(111) substrates was first reported by Chan *et al* [9]. They proposed 530 °C as the lowest limit for Au-catalysed nucleation based on the onset of a molten state for the catalyst nanoparticles, reflecting the basic condition of the VLS framework. Zhang *et al* [7, 8] reported MOCVD of ZnSe NWs at 550 and 450 °C, by using colloidal dispersions of Au and Ag on Si substrates, respectively. The authors pointed out that a different growth mechanism could occur, as they could not detect Au or Ag particles at the wire tip and the temperature was suggested to be too low for the catalyst to melt.

Figures 1(a) and (b) show SEM images of our Au-catalysed ZnSe NWs, deposited by MBE at a substrate temperature of 400 and 550 °C, respectively. At 550 °C we observe the growth of only a few NWs. Conversely, at 400 °C their density strongly increases. Large quantities of randomly oriented NWs, longer than 1 μm , grow from the Au-coated regions. Figures 1(c), (d) show NWs grown at the same temperatures on Ag-coated Si substrates. In this case a very low density of wires is present, irrespective of the substrate temperature. Most of the evaporated ZnSe agglomerates on the surface, forming a very rough nanostructured layer. Thus, it seems that at our deposition conditions, Au is a better catalyst than Ag for the MBE growth of ZnSe NWs.

An SEM-EDX spectrum of the NWs of figure 1(a) is shown in figure 2. Zn and Se peaks are detected with relative intensity typical for stoichiometric ZnSe. The 1:1 ratio for Zn and Se is extracted by the SEM-EDX software. Additional x-ray photoemission spectroscopy (XPS) measurements (not shown), normalized to the Zn/Se ratio observed for bulk ZnSe epilayers grown by MBE, confirm that our wires are stoichiometric ZnSe crystals. The Si signal originates from the substrate. The small carbon peak is due to contamination.

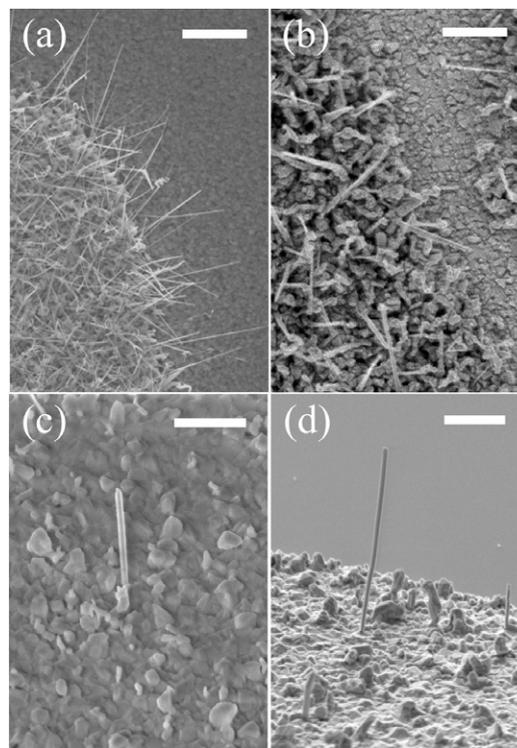


Figure 1. SEM micrographs of ZnSe NWs grown by using a thin Au catalyst layer at (a) 400 °C, (b) 550 °C, and by using a thin Ag catalyst layer at (c) 400 °C and (d) 550 °C. The scalebars are all 1 μm . The uniform grey background in the upper part of (d) is an Ag-free region of the oxidized Si surface.

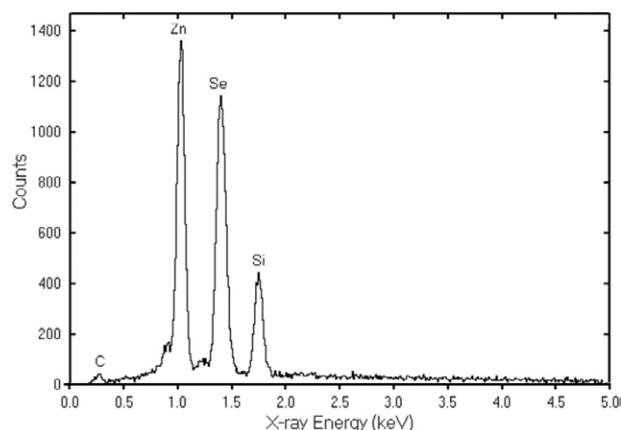


Figure 2. SEM-EDX spectrum measured for Au-catalysed ZnSe NWs grown at 400 °C. The Zn/Se intensity ratio indicates a stoichiometric ZnSe crystal.

In order to perform TEM characterization, NWs are usually removed mechanically from their original substrate and dispersed on TEM grids (see [12], for example). This procedure, however, may lead to wire fragmentation and to a low density of measurable nanostructures. In order to overcome this problem, we directly grew the Au-catalysed NWs on TEM Mo grids. This circumvents any problems due to mechanical scratching of the substrate and allows a clear observation of a base- or tip-growth mode.

Figure 3(a) shows a bright-field TEM micrograph of ZnSe NWs grown at 450 °C. Most of the wires are straight,

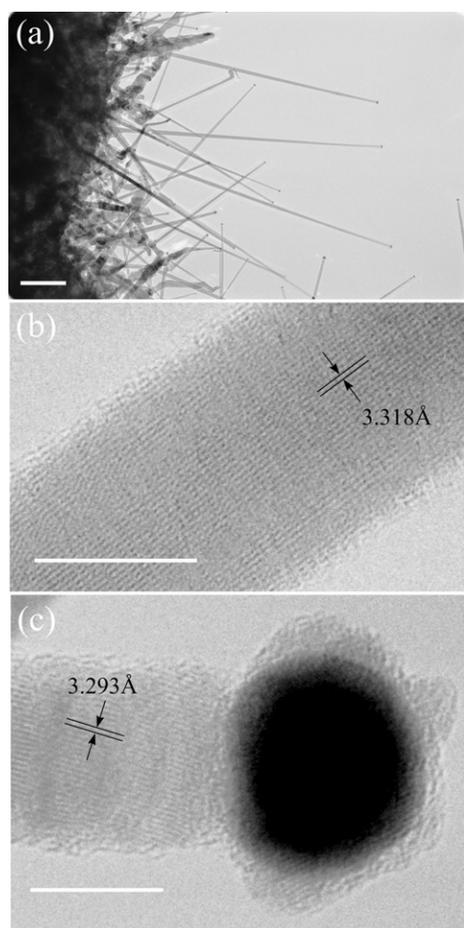


Figure 3. (a) Bright-field TEM micrograph of ZnSe NWs grown at 450 °C on an Au-coated Mo grid. The scalebar is 200 nm. A small catalyst particle is found at all tips, determining the wire diameter. (b), (c) HRTEM images of the NWs shown in (a). The scalebars are both 10 nm.

1–2 μm long and fairly uniform in diameter (10–30 nm). All of the NWs, even the shorter or kinked ones, have the Au catalyst at their tip.

High-resolution TEM (HRTEM) micrographs of highly crystalline NWs are shown in figures 3(b) and (c). The lattice fringes are compatible with both wurzite and zinc-blende ZnSe lattice structures. A thin amorphous layer is found around the wire core and the catalyst particle. This is probably due to post-growth oxidation, and is similar to what is found for Si NWs [12].

In order to achieve selectivity, the growth conditions must be carefully optimized to enhance NW growth and, at the same time, to suppress secondary nucleation events. Unlike chemical vapour deposition (CVD) methods (See, for example, [14], where NH_3 is used in carbon nanotube plasma-enhanced CVD growth to etch away the unwanted amorphous carbon deposited on the surface.), in MBE there is no etching gas available to remove any undesired ZnSe deposited on the catalyst-free substrate surface. Therefore, the substrate temperature must provide enough thermal energy to allow material desorption from such areas.

We performed PL and Raman measurements to further characterize the as-grown nanostructures as well as to probe

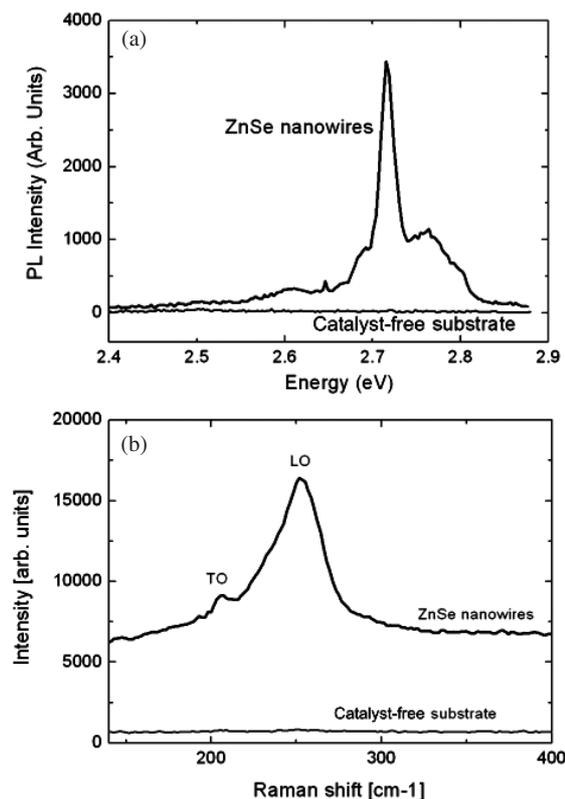


Figure 4. (a) PL and (b) Raman spectra of ZnSe NWs grown at 400 °C and of the respective catalyst-free surfaces where no NWs are found by electron microscopy. No signal is detected for catalyst-free areas, indicating a good optical selectivity and a ‘clean’ NW growth.

detrimental film coverage on the catalyst-free substrate areas. PL in the blue region is observed from samples grown at 400–450 °C, where a high density of ZnSe NWs is present. Figure 4(a) shows the comparison between such blue emission and the spectrum taken from an uncoated Si surface after ZnSe deposition at 400 °C. No PL is found for the catalyst-free substrate. Raman spectroscopy has also been performed on the same samples (figure 4(b)). Raman spectroscopy allows the probing of the structure and diameter of nanowires [15]. We detect a broadening and downshift of the ZnSe LO and TO phonons compared to bulk material. This confirms the presence of ZnSe nanocrystals in the sample. No Raman signal is detected for the processed surface without catalyst (figure 4(b)), underlining the selectivity of the ZnSe deposition.

Figure 5(a) shows an SEM micrograph of Au-catalysed ZnCdSe NWs grown by MBE at 400 °C. The Cd concentration, as derived from the EDX data in figure 5(b), is $\sim 17\%$, in agreement with the Cd concentration expected for bulk ZnCdSe epilayers grown by MBE with a similar Zn/Cd flux ratio [16]. This indicates that the same approach used for conventional layer-by-layer MBE deposition is effective in growing ternary catalyst-assisted nanostructures. Figure 5(b) shows a close-up of the ZnCdSe NWs of figure 5(a). The ZnCdSe NWs look more irregular than the ZnSe NWs of figure 1(a). They often show a saw-like profile on one or both edges. We observe a similar morphology for ZnSe NWs when we increase the Zn flux while keeping the Se flux constant. Further optimization of the growth conditions are

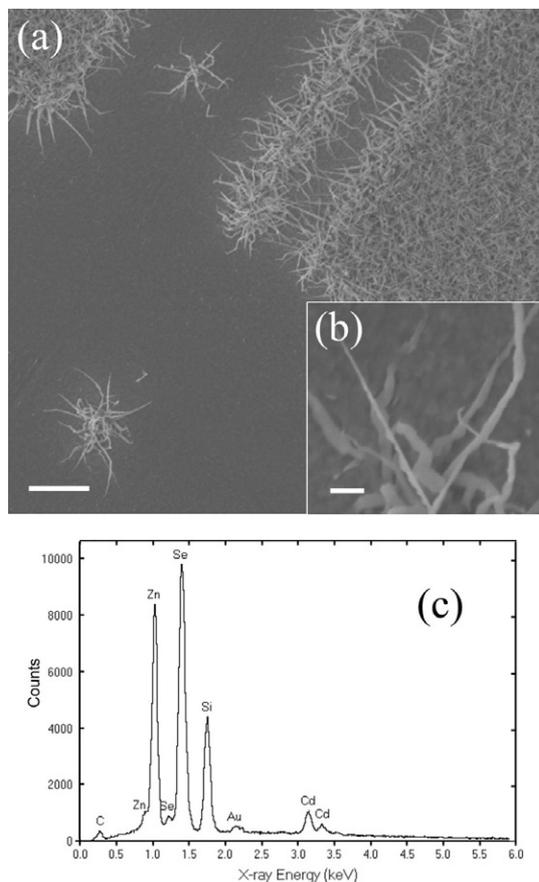


Figure 5. (a) SEM micrograph of Au-catalysed ZnCdSe NWs grown at 400 °C. The scalebar is 1 μm. (b) Close-up of (a). The scalebar is 100 nm. (c) SEM-EDX spectrum for ZnCdSe NWs shown in (a). The Cd and Zn molar fractions are 0.17 and 0.83, respectively.

required in order to fabricate high-quality ZnSe/ZnCdSe NW heterojunctions. This opens many promising optoelectronic applications since, for the ZnCdSe ternary nanowires, the bandgap is expected to be tunable as a function of the Cd concentration.

4. Conclusions

We have demonstrated selective growth of ZnSe NWs by MBE for substrate temperatures as low as 400 °C. For the

same growth conditions Au as catalyst gives a much higher NW yield than Ag. No PL and Raman ZnSe contribution is detected from catalyst-free substrate areas, indicating a good optical selectivity. We also were able to grow Zn_{0.83}Cd_{0.17}Se NWs, suggesting that composition-controlled ZnSe/ZnCdSe NW heterostructures are within reach.

Acknowledgments

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