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Low threshold room-temperature lasing of CdS nanowires

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Abstract

The synthesis of CdS nanostructures (bands, wires, irregular structures) was investigated by systematic variation of temperature and gas pressure, to deduce a comprehensive growth phase diagram. The high quality nanowires were further investigated and show stoichiometric composition of CdS as well as a single-crystalline lattice without any evidence of extended defects. The luminescence of individual nanowires at low excitation shows a strong near band edge emission at 2.41 eV indicating a low point defect concentration. Sharp peaks evolve at higher laser power and finally dominate the luminescence spectrum. The power dependence of the spectrum clearly shows all the characteristics of amplified stimulated emission and lasing action in the nanowire cavity. A low threshold was determined as 10 kW cm$^{-2}$ for lasing at room temperature with a slope efficiency of 5–10% and a $Q$ factor of up to 1200. The length and diameter relations necessary for lasing of individual nanowires was investigated.

This study addresses the two key points: the systematic variation of the growth parameter for CdS nanostructures to achieve a cheap and reproducible routine for the synthesis of high quality nanowires, and the systematic study of their emission properties in relation to the nanowire dimensions. Significant effort has already been devoted to the synthesis of CdS nanostructures ([9] and reference therein), but a comprehensive growth phase diagram has not yet been reported. Furthermore, most previous experiments on stimulated emission properties have been performed on nanowire ensembles [4–6], meaning that the properties of the individual nanostructure were lost in the superposition of the ensemble. Clear evidence for lasing action at room temperature and its relation to the morphology, as reported for ZnO nanowires [10, 11], is not yet available for individual CdS nanowires.

1. Introduction

The miniaturization of light sources is one of the key tasks for the development of smaller optoelectronic devices with enhanced function and properties [1]. CdS nanowires are promising candidates as they offer efficient waveguiding [2], show light emission at electrical excitation [3], can achieve stimulated emission [4–6]; and even lasing at low temperatures [7] has been reported. The coupling of CdS nanowires to plasmonic substrates [8] resulted in the realization of a hybrid photonic plasmonic nanowire laser with extreme light confinement, but light amplification was only achieved at very high pumping due to the high optical losses of the plasmonic structure. For future integration of CdS nanowires into devices, two key points still have to be addressed: the investigation of the synthesis conditions for a cheap and reproducible production method for high quality nanowires and the systematic study of their emission properties in relation to the nanowire dimensions. Significant effort has already been devoted to the synthesis of CdS nanostructures ([9] and reference therein), but a comprehensive growth phase diagram has not yet been reported. Furthermore, most previous experiments on stimulated emission properties have been performed on nanowire ensembles [4–6], meaning that the properties of the individual nanostructure were lost in the superposition of the ensemble. Clear evidence for lasing action at room temperature and its relation to the morphology, as reported for ZnO nanowires [10, 11], is not yet available for individual CdS nanowires.

2. Experimental details

Cadmium sulfide (CdS) nanostructures were synthesized by a chemical vapour deposition (CVD) process using the
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Figure 1. Several different morphologies of CdS nanostructures can be synthesized depending on the chosen growth conditions (temperature and gas pressure), as presented in the growth phase diagram (a). Representative SEM images display the CdS nanobands (b), nanowires (c) and irregular worm-like structures (d).

The morphology and crystal structure of the CdS nanostructures grown was characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM), the stoichiometry was examined using energy dispersive x-ray spectroscopy (EDX). Single nanowires were dispersed on to clean silicon substrates by the imprint technique for subsequent microphotoluminescence (µPL) measurements performed with a home-built far-field epifluorescence microscope. The beam of either a HeCd laser (325 nm, cw) or a frequency-tripled Nd:YAG laser (355 nm, 10 ns pulses at 200 Hz) was focused by a 40× refractive microscope objective (NA = 0.7) to a spot size of 20 µm² diameter on the sample. The luminescence light was collected by the same objective, dispersed by a 500 mm monochromator (spectral resolution of 0.1 nm) and detected by a nitrogen cooled charge-coupled device (CCD). For investigation of the emission from the nanowire facet end, nanowires partially suspended in air were optically pumped (Nd:YAG) perpendicular to the nanowire axis by a 40× refractive objective focused to a 75 µm² laser spot. The emission of the nanowire was collected ‘head-on’ by a 36× reflective objective in the direction of the nanowire axis at the air suspended end. The laser power was determined behind the microscope objective using an Si diode power meter and the excitation density was corrected for the laser focus diameter, the pulse length and the repetition rate. All µPL measurements were performed at room temperature.

3. Results and discussion

The substrate surface was covered with a wool-like yellow layer of CdS nanostructures after synthesis. The morphologies were systematically characterized by SEM and linked to the growth conditions (temperature and Ar gas pressure) to extract a clear phase diagram for VLS grown CdS nanostructures as presented in figure 1(a). No growth occurred above substrate temperatures of 720°C or below 600°C, indicating that these temperatures are limits of the CVD process used [9, 13]. Above 720°C, the temperature is too high for a significant condensation of the source material; whereas below the lower limit, it is likely that the Au did not melt to form the droplets necessary for catalysing the nanostructure synthesis [14]. Within the growth temperature limits, several CdS nanostructure morphology types were found: band-like structures (‘nanobands’; figure 1(b)) with a thickness around 100–300 nm, a width of 10 µm on average and lengths of more than 100 µm were synthesized at temperatures above 680°C. The high growth temperatures and rich CdS vapour supply enable not only fast VLS growth along the band axis, but also slower lateral vapour–solid (VS) growth at the energetically favourable crystal sides leading to the formation of band-like structures [15–17]. At lower growth temperatures, the nanobands could only be found at low Ar pressures. Long and straight nanowires (figure 1(c)) were synthesized with diameters between 70 and 500 nm and lengths of more than 50 µm at temperatures around 650°C and pressures of 50–100 mbar. The intermediate temperature and the lower gas pressure, and therefore reduced CdS vapour supply, seem favourable for suppression of VS growth, enabling the synthesis of straight nanowires [13]. The remaining catalyst dots on top of many wires reveal growth by the VLS mechanism [12, 9]. Shorter nanostructures with highly irregular morphology (‘nanoworms’; figure 1(d)) occur at low temperatures and high pressures. In the transition area, a mixture of the morphologies described, e.g. tapered nanowires, was found between the conditions for nanowire and nanoband growth.

The morphology and stoichiometry of the straight nanowires was further examined by TEM and selective
area EDX measurements, as summarized in figure 2: the nanowires show a smooth and straight surface without extended imperfections (figure 2(b)). The remaining dot on top of the nanowire was identified as the Au catalyst, further confirming the VLS growth of the nanowires [12, 9]. No impurities or residuals of the source material could be found in the Au dot (figure 2(a)). The composition of the nanowire is close to the stoichiometric ratio for CdS without any traces of the Au catalyst and other elements. The selected area diffraction pattern (figure 2(c)) of the nanowire body shows a large number of diffraction spots revealing a high quality crystal lattice. The assignment of the spots was performed by evaluation of the angles and distances to the central spot and matches very well to the spacing of the (0002) and \( \bar{2}10 \) planes (zone axis \([1010]\)) of the wurtzite CdS crystal lattice, verifying growth of the nanowires along the c-axis. (d) The high resolution TEM image shows the crystal lattice; no extended defects such as stacking faults or dislocations could be observed.

Figure 2. (a) EDX point analysis on a single nanowire in the TEM confirms the 1:1 stoichiometry of the CdS; whereas the remaining catalyst Au dot on top of the nanowire does not contain impurities. (b) The TEM image of a typical nanowire shows a very smooth surface without imperfections. (c) The SAED pattern of the nanowire body reveals the high quality lattice structure. The reflexes could be assigned to the spacing of the (0002) and (0220) planes (zone axis \([1010]\)) of the wurtzite CdS crystal lattice, verifying growth of the nanowires along the c-axis. (d) The high resolution TEM image shows the crystal lattice; no extended defects such as stacking faults or dislocations could be observed.

Microphotoluminescence measurements on single CdS nanowires (see supporting information figure S2 available at stacks.iop.org/Nano/23/365204/mmedia) at moderate cw excitation densities using the HeCd laser show a strong near band edge excitonic emission (NBE) centred at 2.41 eV [19, 20] as well as two weak defect-related emission bands at 2.08 and 1.67 eV arising from carrier recombination at interstitial Cd atoms and sulfur vacancies [21, 22]. Power dependent measurements show a saturation of the defect band emission intensity around 0.1–1 W cm\(^{-2}\) due to the limited number of defects in the crystal while the NBE still increases linearly with excitation power. At higher excitation above 10 W cm\(^{-2}\), the NBE emission dominates the PL spectrum, confirming the low defect concentration inside the nanowires.

High resolution \( \mu \)PL spectra of the NBE under pulsed excitation by the Nd:YAG laser of a single nanowire (diameter ~175 nm, length 15 \( \mu \)m; see the upper inset of figure 3(b)) are displayed in figure 3(a). At a low excitation density, the broad NBE emission increases linearly with laser power, as shown in the integrated PL intensity versus pumping power plot in figure 3(b). The luminescence originates mainly from the position of the laser spot and waveguide effects lead to an additional emission from the nanowire ends (lower inset of figure 3(b)) [2, 23]. At excitation above 6 kW cm\(^{-2}\), sharp and equidistant peaks appear in the \( \mu \)PL spectra and show superlinear growth in intensity, which is interpreted as the onset of amplified spontaneous emission (ASE). Upon a further excitation increase above 11 kW cm\(^{-2}\), the sharp modes dominate the PL spectrum. The respective luminescence image now shows the strongest emission at the nanowire facet ends (see the inset of figure 3(b)). The data points follow a clear linear trend as the sharp peaks dominate the spectrum at high pumping power. The evaluated dependence includes all characteristics of a classical macroscopic laser system [24]. The emission properties and power dependence are similar to those for previously examined ZnO nanowire lasers [10]; therefore we conclude that the gain mechanisms of the CdS nanolaser follow the same principles [25]. The experimental values of the integrated PL intensity can be fitted with a model developed for multimode laser oscillators [26] using a fit parameter of \( x_0 = 0.03 \). This parameter determines the dependence of laser powers on pump intensity and the value is comparable to that for ZnO nanowire lasers [10]. The power dependence of CdS nanowires on plasmonic substrates can be fitted with smaller...
nanowire facet end was collected from a nanowire partially Al-coated end facets [27]. A second possible explanation for the lower lasing threshold, compared to the ZnO nanowires case, is given by the longer emission wavelength of CdS: the inverse and lasing thresholds, necessary for gain and lasing, usually scale with the wavelength. In a 3D system, they are in fact inversely proportional to the wavelength squared [28], but for 1D systems this dependence is not that strong due to the reduced density of states of optical modes.

To gain further insights, the emission originating from the nanowire facet end was collected from a nanowire partially suspended in air in ‘head-on’ geometry (see the inset of figure 4(c)) without any scattering from the substrate, similar to what is reported in [11]. The nanowire output power was obtained by a calibration of the detection system using the reflection of a 532 nm laser of known power which simulated the nanowire laser emission; and subsequent conversion of the spectral data. Figure 4(a) shows the nanowire output power versus input pump power for a 17 µm long CdS nanowire with a diameter of ~700 nm (figure 4(b)). At an average excitation pump power below 10 nW, only spontaneous emission originates from the nanowire. The calculated ratio of nanowire light output to excitation laser input power increases from ≤1% for the spontaneous emission to a slope efficiency of 5–10% in the lasing regime, regarding only the emissions of the free standing nanowire end facet. This is also more than one order of magnitude higher than the value determined for a ZnO nanowire [11], which could further explain the lower lasing thresholds for CdS nanowires. The indirect measured ‘head-on’ data were confirmed by direct output power measurement using the Si diode power meter right behind the microscope objective (see the open triangles in figure 4(a)). The optical resonator can be characterized by the quality factor (Q factor) which is a common measure for the ratio of the stored to dissipated energy per oscillation cycle [29, 30]. The value was calculated for each lasing mode by using $Q = \frac{\lambda_0}{\Delta \lambda}$, using the central mode wavelength $\lambda_0$ divided by the mode width ($\Delta \lambda = $ FWHM). Q factors of up to 1200 were obtained using the spectral data given in figure 4(c) at 120 nW average input power, which is higher than the $Q$ factors observed in the literature [3, 31].

The length and diameter relations necessary for lasing action in CdS nanowires were obtained for measurements at 40 kW cm$^{-2}$ pump power and are displayed in figure 5. It is obvious from the data that the CdS nanowires must have a critical length of about 7 µm. Below this value, the resonator cavity is too short to achieve sufficient gain to overcome the losses at the nanowire ends. A further limit was found for nanowires with diameters smaller than 170 nm: no lasing

![Figure 3. (a) µPL spectra of a single CdS nanowire (diameter ~175 nm, length 15 µm) at room temperature show the spontaneous emission of the near band edge emission at low excitation power. Above 6 kW cm$^{-2}$, sharp peaks emerge indicating amplified spontaneous emission due to stimulated emission into the laser modes. At higher excitation, sharp, equidistant longitudinal laser modes dominate the emission spectra. (b) The s-shaped course of the experimental values in the integrated light intensity versus pump power plot clearly confirms lasing action of the CdS nanowire (SEM image of the respective nanowire with Au cap shown in the inset). The low threshold of 10 kW cm$^{-2}$ was determined by fitting of the data with a model developed for multimode laser oscillators [26].](image-url)
behaviour could be achieved below this value. Although some nanowires showed well defined waveguide modes on top of the strong ASE peak, the gain was insufficient to reach the lasing regime. The diameter threshold can be understood since the reflection coefficient at the nanowire ends and the waveguiding is related to the confinement of light in the nanowires [32]. As the nanowire diameter becomes smaller than a minimum diameter, light is no longer completely confined inside the nanowire, but propagates as an evanescent wave around the waveguide [23, 10]. This leads to a strong increase in the losses in addition to the reduction of the reflection coefficient, suppressing the gain and therefore the lasing. As a rule of thumb, the minimum diameter can be estimated as \( d_{\text{min}} \approx \frac{\lambda_0}{2n} \), where \( \lambda_0 \) defines the wavelength of the guided light (515 nm) and \( n \) the index of refraction \( (n = 2.76 \text{ for CdS} [33]) \). For CdS, the calculated minimum diameter is about 174 nm, which is in good agreement with the experimentally determined value. Lasing at smaller diameters can be achieved [8], but the pumping threshold increases inversely to the decreasing diameter. The estimated diameter limit for CdS nanowires is slightly larger than the value for ZnO nanowires of 150 nm [11], which is due to the longer emission wavelength of CdS.

The mode spacing of the sharp emission peaks depends on the nanowire length: shorter wires show only few resonant laser modes with a large spacing, while more resonant modes (with a smaller spacing) fit into the gain profile for longer wires. The mode spacing as a function of the inverse nanowire length evaluated is plotted in the inset of figure 5. The data for all CdS nanowire lasers follow a linear relation, which is typical for Fabry–Pérot type cavities [24]. From the data of figure 5, the dispersion for CdS at 517 nm is estimated as 
\[
\frac{\Delta \lambda}{\Delta L} = -7.4 \pm 0.8 \mu \text{m}^{-1},
\]
in good agreement with the literature value [33].

4. Conclusion

CdS nanostructures were synthesized via the VLS mechanism. The growth temperature and transport gas pressure were systematically varied and a phase diagram was evaluated for the morphologies of nanobands, nanoworms and nanowires found. EDX and TEM measurements show a stoichiometric composition of the high quality nanowires having a smooth surface and no extended crystal defects. Under optical excitation above the band edge, the nanowires emit a strong NBE emission and show a saturation of the defect emission at increased laser power. High pumping intensities lead to the appearance of sharp peaks on top of the broad emission, which were identified as lasing modes by the measured power dependence. The sharp modes dominate the emission spectrum above the low threshold of 10 kW cm\(^{-2}\) at room temperature. In the lasing regime, a slope efficiency of 5–10% and \( Q \) factors of up to 1200 were evaluated. The minimum diameter and length, required for lasing, were found to be 174 nm and 7 \( \mu \)m. The mode spacing shows all features of a Fabry–Pérot type cavity and the dispersion evaluated is in excellent agreement with the literature.

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