Efficient field emission and optical properties of In-doped cadmium sulphide nanopens and nanopencils

Ismathullah Khan Shafiq, Yan-Cheong Chan

Department of Electronic Engineering, City University of Hong Kong, Hong Kong SAR, People’s Republic of China
E-mail: eeycchan@cityu.edu.hk

Published in Micro & Nano Letters; Received on 22nd June 2011; Revised on 1st August 2011

Quasi-aligned indium (In)-doped cadmium sulphide (CdS) nanostructures synthesised by the gold (Au) metal-catalysed vapour–liquid–solid growth method on silicon (Si) substrates under different experiment conditions are reported. X-ray diffraction analysis on the as-prepared samples indicated the nanostructures as ‘wurtzite-type’ CdS crystal structures. Characterisation of the morphology and structure revealed the growth of two different geometries; nanopens and nanopencils with tip diameters ranging from 50–100 nm which can be varied through experimental conditions. Electron field emission measurements on the indium-doped quasi-aligned nanopencils and nanopens exhibit low turn-on electric fields of 5.5 and 4.5 V/µm (at the current density of 0.01 mA/cm²) for nanopens and nanopencils, respectively. This low turn-on field can be attributed to the sharp tip and higher indium doping level in the nanostructures. In addition, the indium doping into the CdS lattice was analysed by low-temperature photoluminescence spectroscopy (LT-PL). Temperature-dependent PL measurements showed that the PL spectra have three emission peaks at 9 K, which can be attributed to band edge exciton emission and shallow donor levels donor–acceptor pair exciton emission because of doping. The result presents the promising application of these materials in the field of optoelectronics as efficient electron field emitters.

1. Introduction: Semiconductor materials of 1D vertically aligned nanostructure have been a field of intense research in recent years because of the possibility of using them as field emission displays because of their high efficiency, economical fabrication cost and compact device size compared with conventional thermionic emitters. Carbon nanotubes (CNTs) have emerged as a potential candidate for cold cathode field emission in recent years because of their unique electrical and mechanical properties [1]. Electron field emission (EFE), one important application of nanomaterials, is of great commercial interest because of its application in displays and electronic devices. In the past decade, research on EFE properties has mainly focused on carbon-based materials, because of their low work function, high mechanical stability, high aspect ratio and high conductivity. Aligned CNTs with a high density of emitting tips have been proved to have enhanced uniform current emission [2].

Recently, 1D semiconductor nanostructures have also been investigated as potential electron field emitters, as they possess a low electron affinity, high aspect ratio and are chemically stable in harsh environments [3, 4]. Different methods have been reported for the fabrication of arrays of well-aligned nanowires, including template, thermal-evaporation, vapour-transport, condensation, metal-organic chemical vapour deposition, buffer-layer-precoated, solution and laser-ablation methods [5–11]. Similar to CNTs and ZnO, CdS-based nanostructures can be fabricated with small curvature radii, high aspect ratios and high field enhancement factors (β). Furthermore, CdS has a lower work function (4.2 eV) compared to the CNTs (5 eV) which can be exploited for fabricating efficient field emitters. Synthesis of well-aligned CdS nanowire or nanorod arrays has generated particular interest because of their unique electrical and optoelectronic properties. Although 1D CdS nanowire or nanorod arrays have been synthesised by the template-confined method, the use of such method increases the complexity of the synthesis procedures.

In the work reported in this Letter, quasi-aligned indium (In)-doped CdS nanopens and nanopencils were synthesised and their morphology and structure were examined. The synthesised nanostructures have a tip diameter in the range of 50–100 nm, making them potential candidates for field emitters. Electron microscopy studies revealed that the nanopens and nanopencils were single crystals growing along the [001] direction. Field emission studies and optical characteristics were also performed and the growth mechanism is illustrated.

2. Materials and methods: Doped CdS nanopens and nanopencils were synthesised by controlled thermal co-evaporation of analytical-grade CdS and In₂S₃ (10% by weight) powders placed in a ceramic boat located in the central region of a quartz tube mounted inside a horizontal three-zone temperature alumina tube furnace. The substrates were Si wafer pre-coated with Gold (Au) (10 nm) as the catalyst, placed at a distance of 25 cm from the ceramic boat in the downstream end of the gas flow. The tube was evacuated by a mechanical rotary pump to a pressure of 4 × 10⁻² Torr and was flushed with high-purity Ar gas for 1 h to eliminate oxygen (O₂). The quartz tube was then backfilled with Ar pre-mixed with 5% H₂ to a pressure of 175 Torr and at a flow rate of 30 SCCM (standard cubic centimetre per minute) throughout the experiment. Temperature at the central part of the furnace was increased at a rate of 30°C min⁻¹ until 860°C and held at that temperature for 15 min and again ramped to 950°C and maintained at that temperature for 45 min, while the pressure was decreased to 75 Torr. The substrates were kept in the downstream zone and the temperature was maintained between 750 and 650°C. After reacting in flowing Ar gas for 2 h, the furnace was cooled down to room temperature and an orange–yellow sponge-like product is formed on the silicon substrates. Samples under the working conditions of constant temperature and pressure (860°C; 175 Torr) were also fabricated.

The as-prepared samples were characterised by scanning electron microscopy (SEM; Philips XL 30 FEG), transmission electron microscopy (TEM; Philips CM202 FEG), high-resolution transmission electron microscopy (HRTEM; CM200 FEG) and X-ray diffraction (XRD, Siemens D-500 with Cu Kα radiation and a normal 2θ scan). Photoluminescence (PL) measurements were conducted at room temperature using the fourth harmonic of an Nd: yttrium–aluminium–garnet (Nd:YAG) laser (266 nm wavelength) with a 6 ns pulse width as the excitation source. The PL was collected using an ultra-violet optical fibre and detected with a 0.5 m spectrometer (Acton Research Corp., Spectra Pro 500i) with dispersion gratings of 1200 and 150 grooves mm⁻¹ for high (~0.1 nm) and low (~0.8 nm) resolution and a Peltier cooled (~20°C) intensified charge-coupled device (ICCD) camera (Roper Scientific). The measurements were performed using normal incident excitation and 10° angular detection (all angles were measured with respect to the sample surface). Low temperature photoluminescence (LT-PL) measurements were carried out on an APD Cryogenics system reaching up to 9 K helium temperatures.
3. Characterisation and discussion: The morphology and the structure of as-prepared samples were analysed using the SEM. As shown in Fig. 1, quasi-aligned well-hexagonal faceted nanopen structures of uniform size were found to be grown on the Si substrate. The nanopen structures have average diameters of 700 nm to 1 μm (aspect ratio 8–9) and the tips are in a range of 60–100 nm in diameter. A closer view on the nanopen structures, as shown in Fig. 1b, reveals the hexagonal prism morphology, which is because of the preferential growth along the principal c-axis, normal to the basal plane. The samples fabricated at constant temperature and pressure conditions were also characterised to study the effect of experimental conditions on the growth of the nanostructures. Figs. 1c and d, show the SEM image of hexagonal nanorods at high and low magnification. The growth of pen tips on the top of the nanorods occurred at the 600 °C temperature zone, when the working pressure was decreased. Under this condition, the prism growth may stop owing to the shortage of the source vapour. However, the cadmium source still evaporated with a slower rate during the cooling process, the (0001) platform on the top of the prism could act as an ideal site for the secondary nucleation resulting in pen-like morphologies. When the hexagonal axis of a crystal is along the geometrical axis, it results in the growth of pen-shaped crystals. Larger concentration of cadmium enhances the pen shaped growth as the growing surface tends to certain dissolved cadmium and hence molecules of cadmium sulphide can easily adhere to the growth surface via sulphur atoms.

Fig. 2a shows the XRD spectrum of the nanopen structures. All strong peaks can be readily indexed to the hexagonal ‘wurtzite-type’ structure of CdS with lattice constants of \( a = 4.14 \) Å and \( c = 6.72 \) Å, which are close to the standard values for bulk CdS in the JCPDS (Joint Committee on Powder Diffraction Standards) card No. 41-1049. TEM and HRTEM characterisation were done to study the microstructure. Fig. 2b shows a low magnification TEM image of the nanorod. The wurtzite structure of CdS is favourable for needle-shaped crystal growth [12] because of the only preferred growth direction (the [0001] plane) of wurtzite CdS. Thus, the CdS crystals have a strong tendency to grow in the c-direction, which is shown in Figs. 2b and c. An electron diffraction pattern of the nanopen is shown in the inset of Fig. 2c and the HRTEM image in Fig. 2d exhibits the characteristics of single crystal growing along the [0001] plane growth direction.

The SEM images of the products obtained from the 700 °C temperature zone were examined using SEM. Figs. 3a and b are the tilted SEM image of well-hexagonal faceted nanopencils with a penholder diameter of 250–350 nm (aspect ratio 8–9) and the pencil diameter of 50–100 nm with uniform size at higher and low magnification, respectively. The TEM image nanopencil tip is shown in Fig. 4a. The initial growth stage is believed to be growth governed by the vapour–liquid–solid mechanism because of the presence of Au particle as identified by EDX. The growth mechanism of the nanopen and nanopencils is illustrated in Fig. 4b. EDX analysis shows the nanopencils consist of Cd and S with indium dopant concentration as little as 0.34%, as shown in Fig. 4c.
3.1. EFE measurements: The EFE measurements were performed in a spherical vacuum chamber pumped down to $7.0 \times 10^{-8}$ mbar. The ZnO NW array samples were installed onto a copper stage using a vacuum-compatible and electrically conducting glue to form the cathode. The anode was formed with a cylinder-shaped platinum probe (1 mm in diameter) which can be horizontally levelled and positioned by linear step motors. In all our field emission measurements we used a fixed cathode–anode distance (100 mm). The voltage was applied across the cathode and anode electrodes using a power source (Keithley 248), and the current was recorded by an electrometer with sensitivity of the order of picoamperes (Keithley 6514). Each sample was measured in ten different positions to verify the reproducibility and determine average EFE current characteristics.

The EFE measurements were carried out inside an ultra-high vacuum chamber, which was pumped down to $5 \times 10^{-7}$ Torr. The ZnO NWs were glued to a copper stage. The anode was formed with a cylinder-shaped platinum probe (1 mm in diameter) which can be horizontally levelled and positioned by linear step motors. In all our field emission measurements we used a fixed cathode–anode distance (100 mm). The voltage was applied across the cathode and anode electrodes using a power source (Keithley 248), and the current was recorded by an electrometer with sensitivity of the order of picoamperes (Keithley 6514). Each sample was measured in ten different positions to verify the reproducibility and determine average EFE current characteristics.

The EFE measurements were carried out inside an ultra-high vacuum chamber, which was pumped down to $5 \times 10^{-7}$ Torr. The CdS nanopen and nanopencil arrays grown on Si substrate are glued to a stainless steel substrate using a vacuum-compatible and electrically conducting silver paste. The distance ($d$) between the emitting surface and the probe was determined by making an electric contact by nearing the two electrodes and using it as reference, thereby to raise it to a desired value. The distance between electrodes in our case was around 100 μm. The electric field ($E$) was estimated by dividing the applied voltage by the anode–cathode separation ($V/d$). The emission current density ($J$) was calculated from the obtained emission current and the cathode surface area. A variable positive voltage up to 5 kV was applied to the anode and the emission current ($I$) was indirectly determined by measuring the voltage across a 500 kΩ resistor. The schematic of the EFE setup is shown in Fig. 4d.

The field emission property of the CdS nanostructures was measured with a 100 mm gap between the anode and the cathode. The plot of the field emission current density ($J$) against the applied electric field ($E$) for quasi-aligned nanopen and nanopencils is shown in Figs. 4f. As for the aligned nanopencils and nanopen, turn-on electric fields of 5.5 and 4.5 V/μm (at the current density of 0.01 mA/cm$^2$) were observed, with
The calculated field enhancement factor ($b$) of the parameters are known. The absolute value of the slope decreases of the slope to an increase of a FEE mechanism of tunnelling over a barrier. The data roughly follow the Fowler–Nordheim (F–N) theory

$$J = (AE^2/\phi) \exp(-B\phi^{1/2}/|E|)$$

where $J$ is the local current density; $E$ is the local applied electric field; $\phi$ is the work function; $A$ is the field enhancement factor; $A = 1.543 \times 10^{-6} \text{AeVV}^{-2}$, and $B = 6.83 \times 10^{2} \text{eV}^{-3/2} \text{V}\mu\text{m}^{-1}$ [14]. The insets of Figs. 4a and b show the corresponding F–N curves $\ln(J/E^2)$ against $1/E$ of the quasi-aligned nanopencils and nanopens. The data roughly follow the Fowler–Nordheim equation indicating a FEE mechanism of tunnelling over a barrier. The $\phi$ and $B$ can be derived from the slope $(-B\phi^{1/2} / \phi)$, if either of the parameters are known. The absolute value of the slope related to the nanopens is smaller than that of the nanopencils. The calculated field enhancement factor ($b$) of the nanopencils is 6295 compared to the nanopencils with 5741. The work function was assumed to be 4.2 eV. Since they both are CdS-based nanostructures differing only in their geometries, we can thus attribute the decrease of the slope to an increase of $b$, which can be related to the geometry, structure and density of the nanostructures [15].

3.2. Optical properties investigation: LT-PL measurements were performed on the nanopens and nanopencils to explore the optical emission characteristics of the nanostructures. The measurements were performed in the 9–293 K temperature range with excitation power of 85 kW/cm² and spot size of 250 μm. The PL spectra in Figs. 5a and b illustrate the peak shift and intensity quenching as a function of temperature for doped CdS nanopens and nanopencils. Since the sizes of the nanostructures are significantly larger than the Bohr exciton radius of CdS ($\sim 2.8$ nm), no quantum confinement effects are expected to be observed. The room temperature PL spectrum of the doped nanostructures shown in the inset of Fig. 5c consists of a band edge FX emission around 517.8 nm (2.394 eV) and a very weak and broad luminescence around 696 nm (1.78 eV) [16]. The broad red emission band is too weak to be resolved in comparison to the intensity of the other emissions at room temperature (293 K). When doped with indium, high density of excess carriers are supplied to the conduction band of CdS which results in a red shift of the PL energy, which could be caused by band gap renormalisation [17] or impurity mediated transitions. When a higher percentage of dopant is introduced into the CdS crystal, changes in the band gap and lattice distortions are expected to enhance the red shift.

Examining the PL spectrum of the doped nanopens at low temperature (9 K), shown in Fig. 5a, it consists of distinct emission bands at $A$: 494 nm (2.510 eV), $B$: 517 nm (2.398 eV), with $C$: 524 nm (2.366 eV) and $D$: 536 nm (2.31 eV) as a shoulder of the peak towards the longer wavelength region. The emission at $A$: 494 nm (2.510 eV) can be assigned to the band edge FX emission of the wurtzite CdS crystal. The energy spacing between the peaks at $B$: 2.398 eV and $C$: 2.366 eV is around 0.032 eV and C: 2.366 eV and D: 2.310 eV is around 0.056 eV. The peak at $B$: 517 nm (2.398 eV) can be attributed to DAP, widely found in II–VI group semiconductors. One unique characteristic feature of the DAP emission is the longitudinal optical (LO) phonon appearing on the lower energy side. Hence the peaks at $C$: 524 nm (2.366 eV) and $D$: 536 nm (2.310 eV) are considered to be associated with the LO phonon replicas of the DAP emission because the

---

**Figure 5 PL spectra**

a Room temperature PL spectrum of the as-synthesised CdS nanostructures

b Temperature-dependent PL spectra of doped CdS nanopencil

c Temperature-dependent PL spectra of doped CdS nanopencil. The spectra are shifted vertically for clarity

d Temperature dependence of peak energy of the band edge emission (A) and the DAP emission (B)

e Temperature dependence of peak energy of the band edge emission (E) and the DAP emission (F)
energy difference between these two peaks is close to the LO phonon energy 0.027 eV (1LO) and 0.056 eV (2LO). For the low-temperature PL spectrum of nanopenicles at 9 K shown in Fig. 5b, the peaks are located at E: 497 nm (2.495 eV) and F: 518 nm (2.393 eV) with G: 524 nm (2.366 eV) and H: 536 nm (2.31 eV) as a shoulder of the peak towards the longer wavelength region. The emission at E: 497 nm (2.495 eV) can be assigned to the band edge FX emission. The energy spacing between the peaks at F: 2.393 eV and G: 2.366 eV is around 0.027 eV and G: 2.366 eV and H: 2.310 eV is around 0.056 eV. Similar to the PL spectra of nanopenicles, the peak at G: 524 nm (2.366 eV) and H: 536 nm (2.310 eV) can also be attributed to LO phonon modes of the DAP peak at F: 518 nm (2.393 eV). It is known that In doped into a CdS single crystal enters the lattice as an impurity, substituting the Cd on the cation sub-lattice to form shallow donor centres InCd [18]. As the temperature is lowered, electrons fill the donor centres and the probability of their thermal ionisation to the conduction band decreases and this gives rise to the formation of an additional PL band. It can apparently originate from the recombination of electrons (which occupy the InCd donor centres filled at low temperatures) with the valence-band holes. Centres with such PL peaks were also observed in CdS crystals doped by other impurities, which form shallow levels in the crystal bandgap [19, 20].

4. Conclusion: In summary, In-doped CdS nanopenicles were fabricated for the first time on silicon substrates. Quasi-aligned well-hexagonal faceted nanopenicles with an average diameter of 700 nm to 1 μm and the tips are in a range of 60–100 nm in diameter and uniform size distribution were found to be grown on the Si substrate placed at 600°C. Well-hexagonal faceted nanopenicles with a penholder diameter of 250–350 nm and the pencil diameter of 50–100 nm with uniform size were found to be grown on the Si substrate placed at 700°C. As for the aligned nanopenicles and nanopenicles, turn-on electric fields of 5.5 and 4.5 V/μm (at the current density of 0.01 mA/cm²) were observed, with corresponding threshold current density (1 mA/cm²) achieved at about 8.4 and 6.3 V/μm, respectively. The low turn-on current and the screening can be attributed to the sharp tip and higher indium doping level in the CdS nanostructures. The LT-PL studies on doped CdS nanopenicles show four distinct emission peaks at 494 nm (2.510 eV), 517 nm (2.398 eV), 524 nm (2.366 eV) and 536 nm (2.31 eV) denoting a shallow level doping of indium into CdS nanostructures.

5. Acknowledgments: The authors acknowledge the financial support provided by an RGC Applied Strategic Development Centre Grant (CityU ASDC Project No. 960003) and the research postgraduate studentship of the School of Graduate Studies at the City University of Hong Kong.

6 References