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Wavelength tunable electroluminescence from randomly assembled n-CdS_xSe_{1-x} nanowires/p⁺-SiC heterojunction†

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Visible electroluminescence (EL) with tunable wavelength has been observed at room temperature from randomly assembled n-CdS_xSe_{1-x} nanowires grown on a p⁺-SiC substrate by the vapor transport technique. The dominant emission peaks can be tuned from ~720 to ~520 nm by varying the composition of the alloy nanowires.

One-dimensional semiconductor nanowires have shown great potential as building blocks for miniature optoelectronic devices, such as light-emitting diodes (LEDs), photodetectors, lasers and solar cells.^{1a-d} For these applications, it is essential to have the capability to tune the emission wavelength. It is well known that II–VI materials can form a series of solid solutions by adjusting their compositional ratios, allowing a continuous variation of the band-gap and subsequently the emission wavelength. As have been demonstrated in few reports, the Zn_xCd_{1-x}S,^{2a} CdS_xSe_{1-x},^{2b} and Zn_xCd_{1-x}S_ySe_{1-y},^{2c} alloy nanowires show color-tunable photoluminescence (PL) emissions spanning from ultraviolet to near-infrared regions of the electromagnetic spectrum.

Electrically driven LEDs based on individual nanowires have been realized in p⁺-Si/n-CdS,^{1a,3a} n-GaN/p⁺-GaN^{3b} crossed structures. However, the fabrication of these individual nanowire devices needs expensive techniques such as electron-beam lithography and a series of time-consuming processes including synthesis, sonication, and dispersal of ensemble nanowires on the target substrates with pre-fabricated electrodes. These fabrication techniques have built a platform for fundamental research but are rather complicated and irreproducible, which is unsuitable for large-scale manufacturing. The on-chip fabrication of randomly assembled nanowires into three-dimensional heterojunction has been proven to be powerful approach for the design of photodetectors and p–n junction light-emitting diodes. For example, an ultraviolet electroluminescence (EL)

emission from randomly assembled n-SnO₂ nanowires/p⁺-GaN:Mg heterojunction has been demonstrated in our recent report.⁴

In this communication, we present the fabrication and EL properties of n-CdS_xSe_{1-x} nanowires light-emitting diodes, in which the randomly assembled nanowires having variable compositions were grown on a single p⁺-SiC substrate by vapor transport technique. The EL measurements show that the heterojunction formed between n-CdS_xSe_{1-x} nanowires and p⁺-SiC substrate can produce visible light emissions at room temperature in the range of ~720–520 nm.

The CdS_xSe_{1-x} nanowires with spatially graded alloy compositions along the length of a single p⁺-SiC substrate (0.4 cm × 2 cm, Cree Inc., 4H) were synthesized by an one-step vapor transport process.^{1b} In a typical synthesis, a mixture of CdS and CdSe powders was placed in the center region of a small quartz tube (1 inch in diameter) furnace as the precursors for evaporation. A 2% H₂ in Ar gas mixture was used as carrier gas. The p⁺-SiC substrate coated with a 3 nm Au film was placed downstream of the gas flow. Before heating, the tube was flushed with the carrier gas repeatedly to decrease oxygen contamination. The optimum source temperature (*T*), time (*t*), and carrier gas flow rate (*k*_{flow}) for the growth of nanowires were *T* = 860 °C, *t* = 1 h, and *k*_{flow} = 5 sccm. After synthesis, the samples were cut into eight pieces and gold ohmic contact was sputtered at the back of the p⁺-SiC substrate. In-doped SnO₂ (ITO) glass mechanically pressed against nanowires was used as the top contact to form the device structure. This configuration was used to avoid direct sputtering deposition of ITO onto the n-CdS_xSe_{1-x} nanowires and avoid the annealing needed after the ITO deposition. For EL measurement, a constant voltage was applied to the sample and the EL signal was detected by a PDS-1 photomultiplier detector connected through a monochromator and collected from an optical fiber.

Fig. 1a shows a typical SEM image of the as-synthesized CdS_xSe_{1-x} nanowires. The length of the nanowires is up to several tens of micrometres and the diameter varies from 30 to 200 nm. Systematic SEM observation indicated that the sample throughout the substrate has similar morphology and density. Fig. 1b shows the normalized PL spectra of the CdS_xSe_{1-x} nanowires collected from different locations along the length of the substrate. The dominating peaks in the PL spectra are all due to the near-band-edge (NBE) emission, suggesting the high crystalline quality of the nanowires. With decreasing *x*, the NBE emission continuously red-shifts from 519 nm to 683 nm as a result of the band gap narrowing. Energy gaps of CdS_xSe_{1-x} nanowires, calculated from the PL peak positions, are

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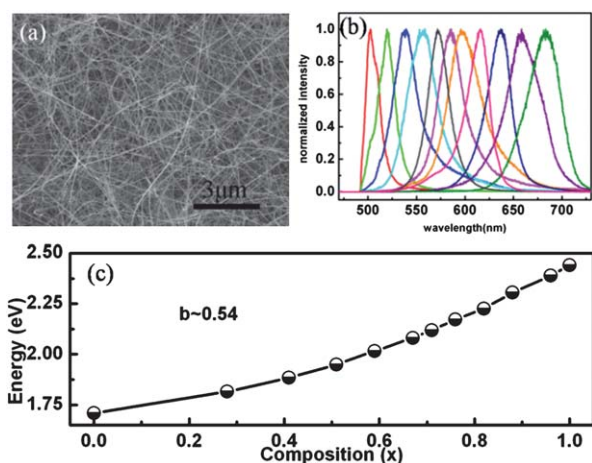


Fig. 1 (a) SEM image of the $\text{CdS}_x\text{Se}_{1-x}$ nanowires. (b) Room-temperature PL spectra of the as-synthesized $\text{CdS}_x\text{Se}_{1-x}$ nanowires of different compositions along the length of the $\text{p}^+\text{-SiC}$ substrate excited with a 457 nm Ar^+ laser. (c) Compositional dependence of the NBE emission energy.

plotted in Fig. 1c. The variation of the energy gaps with x displays a nonlinear feature that can be fitted using the quadratic function:^{1b}

$$E_g^{(x)} = xE_g^{\text{CdS}} + (1-x)E_g^{\text{CdSe}} - bx(1-x), \quad (1)$$

where E_g^{CdS} , E_g^{CdSe} , and $E_g^{(x)}$ are the energy gaps of CdS (2.44 eV), CdSe (1.72 eV) and their alloy, respectively, and b is an optical bowing parameter. The best fit yields $b = 0.54$ eV in our experiment, which is consistent with earlier reports.⁵ With the x values increasing from 0 to 1, the real color of the sample along the length of the substrate changes from dark to red and yellow, as shown by the digital photograph of the sample under office light conditions (Fig. 2a). It is noted that, the EL and PL measurement were conducted using two separate systems. For accuracy, we do not use the x -values that are calculable from PL for the EL plot.

Fig. 2a also shows the photo of EL from samples 1 to 8 in dark room after an applied voltage. Wavelength tunable EL is observed from yellow to orange and red from sample 8 to 1. To see this spectroscopically, Fig. 2b shows the normalized EL spectra from the heterojunctions from different samples at the forward bias range of 25–40 V. A peak of ~ 538 nm is observed for sample 8 and red shifts to ~ 578 , ~ 594 , ~ 614 , ~ 640 , ~ 660 , ~ 688 , and ~ 714 nm for sample 7 to 1, respectively. It is noted that scattered light spots were observed instead of luminescence in the whole sample surface, suggesting that EL can only take place when certain transport mechanism is met. Different onset voltages (or turn on voltage) were needed for different samples. This can be confirmed by the current–voltage (I – V) characteristics shown in Fig. 3.

For the measurement of I – V characteristics of the $\text{CdS}_x\text{Se}_{1-x}$ nanowires/ $\text{p}^+\text{-SiC}$ substrate heterojunction, the inset of Fig. 3 illustrates the device structure and the test configuration. As seen from Fig. 3, low leakage currents were observed when the devices were reversely biased, except for sample 2 with a considerable amount ($>100 \mu\text{A}$) of leakage current when the applied voltage is larger than -15 V. There is no light emission under reversed bias for all samples. These I – V curves can be divided into three groups according to their current levels at the bias beyond their turn on voltages. Sample 1 & 2 form a group while sample 3, 5 & 6 form another and sample 4, 7 & 8

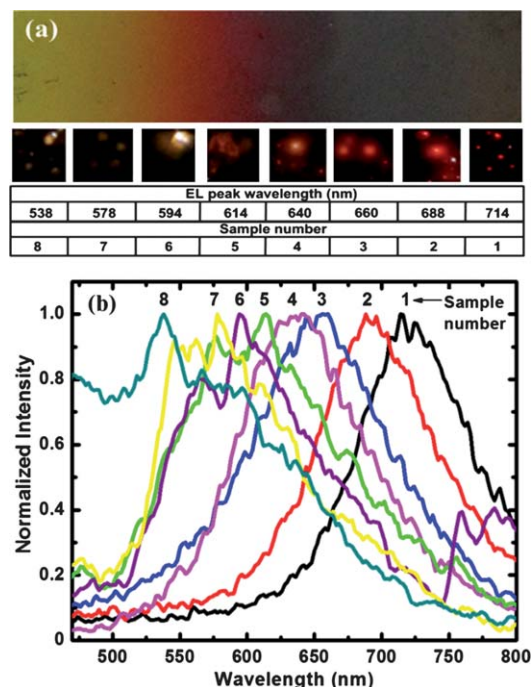


Fig. 2 (a) Optical photo of the $\text{CdS}_x\text{Se}_{1-x}$ nanowire samples under office light conditions. Smaller graphs show the wavelength-tunable electroluminescence (EL) under dark room condition with the EL peak wavelength and sample number. (b) Normalized EL spectra of the $\text{n-CdS}_x\text{Se}_{1-x}$ nanowires/ $\text{p}^+\text{-SiC}$ substrates from different samples at forward bias.

form the last group. The higher current level does not necessarily correspond to higher EL intensity. For instance, the current levels for sample 1 & 2 at 20 V are much higher than sample 3 & 4 while their EL intensities are about the same. This means that the emission efficiency of sample 4 $>$ sample 3 $>$ sample 1 & 2. The large forward current in sample 1 & 2 is probably due to the leakage current.

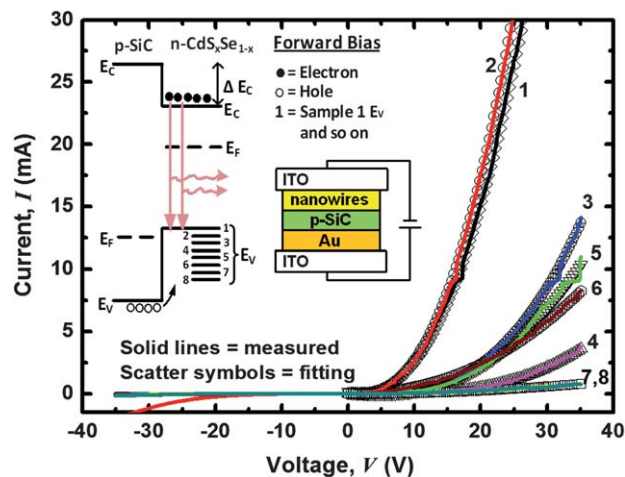


Fig. 3 I – V characteristics of the $\text{n-CdS}_x\text{Se}_{1-x}$ nanowires/ $\text{p}^+\text{-SiC}$ substrate heterojunction. Solid lines are the experimentally measured data, and scatter symbols denote the fitting results. The inset shows the band diagram at forward bias and test configuration of the LED device.

The energy-band diagram of the n-CdS_xSe_{1-x}/p⁺-SiC heterojunction at forward bias was illustrated schematically as exemplified by sample 1 (inset of Fig. 3). Other non-ideal factors like interface states are not considered for the ease of illustration. Band diagrams of other samples are not included except that their relative positions of valance bands (E_v) are drawn as a reference. Based on the known data of the bandgaps and electron affinities, a type-I heterostructure is formed. Under the forward bias, holes can be injected from the valance band of p⁺-SiC into those of n-CdS_xSe_{1-x}. Hence, electrons in the conduction bands of the n-CdS_xSe_{1-x} can radiatively recombine with the holes in their valance bands. The recombination originates dominantly from the n-CdS_xSe_{1-x} side, since the EL wavelengths depend on the nanowire composition (see Fig. 2b and also left inset of Fig. 4). The less-dominating bands near 400 nm might come from p⁺-SiC since electrons have certain probability to jump over to p⁺-SiC.

Fig. 4 shows the EL spectra evolution of sample 2 with the forward bias increasing from 10 to 25 V. Very weak EL was observed when a forward bias of 10 V was applied. As the voltage increased, the intensity of the EL spectra peaked at ~688 nm was enhanced significantly. The voltage dependencies of the integrated EL intensity (symbols) and of the current (solid line) of sample 2 are shown at the right inset of Fig. 4, from which one can see that the two dependence relationships are well correlated with each other, namely, they have nearly the same increase rates with the forward bias. Hence this indicates that the EL originates from the recombination of electrons and holes injected from the upper ITO gate and p⁺-SiC substrate, respectively. In addition to this dominating ~688 nm NBE peak, minor peaks could be seen as well (e.g., a peak at ~404 nm) when the applied voltage was higher than 20 V. By deconvolution of the EL spectrum measured at 25 V on sample 2, four peaks located at 402 nm, 541 nm, 694 nm and 791 nm were obtained (pink dotted line in Fig. 4), which were denoted as violet to blue band, green to orange band, orange to red band and near infra-red (IR) band, respectively. The convolution of all these bands was shown as a red solid line in Fig. 4.

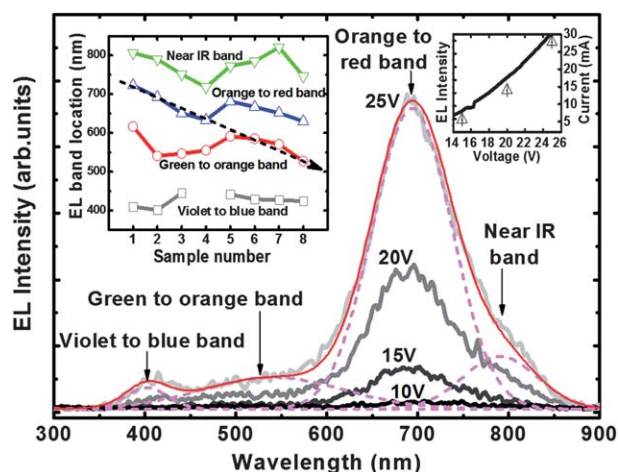


Fig. 4 Voltage dependence of the EL intensity from sample 2. The left inset shows the deconvoluted EL band locations from different samples where dash arrow line shows the shifting of majority band. The right inset shows the dependences of both integrated EL intensity and current on the forward bias.

Now we compare the EL bands between different samples. Shown in the left inset of Fig. 4 are peak positions for each deconvoluted band *versus* the sample number. All the four bands were consistently obtained with different integrated intensities from all samples except that no violet to blue band can be obtained from the deconvolution of sample 4 EL spectrum. Clearly, the violet to blue band and near IR band are not the major bands for all samples. The dash arrow line shows the shifting of the majority band from sample 1 to 8. The peak position from these major bands decreases from ~720 to ~520 nm, illustrating the wavelength tunability of the EL of our nanowire LEDs.

It is not possible that the ~400 nm emission (*i.e.* the violet to blue band) from the diode excites the NWs and gives rise to emissions at higher wavelengths. First, the EL emissions at ~400 nm were very weak and incapable of further excitation. Also, for sample 4, there is no emission at ~400 nm but other emission peaks are still observed at the visible range. This supports that the observed emissions from the heterojunctions should be due to EL of NWs.

The I - V characteristic of the heterojunction formed between n-CdS_xSe_{1-x} nanowires and p⁺-SiC substrate is found to follow a power law. The experimental data in Fig. 3 can be well fitted based on the power law,^{6a}

$$I = I_0 (V - V_T)^\xi, \quad (2)$$

where I is the measured current, I_0 is a coefficient, V is the applied voltage, V_T is the threshold voltage and ξ is the scaling component. The fitting yielded a value of ξ ranging from 1.81 to 3.06. This suggests that 2D or 3D transports^{6b} are responsible for the randomly distributed nanowires instead of 1D transport observed from single nanowire.^{6c} One scenario of the possible transport behavior is explained as follows: percolation paths form between nanowires and some of the percolation paths meet each other in certain locations/junctions. In this case, charge carriers transport in a collective manner to the ITO contact, resulting in higher current concentrations at those spots. Hence, the EL emissions appear at certain spots and have different intensities.^{6d-e}

In conclusion, we have shown that heterojunctions formed between n-CdS_xSe_{1-x} nanowires and the p⁺-SiC substrate can emit visible lights at room temperature in the wavelength range from yellow to orange and red. The EL intensities are well correlated with the measured I - V characteristics. By deconvolution of EL spectra from different samples, it is found that the peak of the major band ranges from ~720 to ~520nm, which is a result of composition variation of the nanowires. Several weaker bands are also obtained from deconvolution but their contributions to the overall EL spectra are small as compared to the major bands. It is hypothesized that the spot-like EL on the device surface originate from percolation paths between the random assembled nanowires.

Acknowledgements

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