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Electroluminescence from Sol–Gel Derived Film of CdS Nanocrystals

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Nanocrystals (NCs) of II–VI semiconductors (CdSe, CdS, ZnS, etc.) have efficient and widely spectrally tuneable (controlled by mean size of NCs) photoluminescence (PL). They can be potentially applied to fabricate cheap light-emitting diodes (LEDs) and displays. Electroluminescence (EL) devices based on II–VI NCs were already demonstrated by embedding NCs in conductive polymer [1] or ITO layer [2], by close packing of NCs [3] etc. In this note we demonstrate, for the first time, EL from CdS NCs prepared in Al_2O_3 matrix on Si substrate by the sol-gel method. The advantage of this method is relatively low-cost fabrication of highly concentrated films of NCs on different types of substrates.

The preparation started with mixing of $Cd(CH_3COO)_2$ solution with $Al(OCH_2CH(CH_3)_2)_3$ under dry nitrogen to produce a composition with a molar ratio Al:Cd of 4. The sol was filtered and used immediately for the deposition. Thin films were deposited on a highly doped n-type Si substrate by the dip-coating technique (withdrawal speed of 6 cm/min) with subsequent drying and heat-treatment. The deposition procedure was repeated until film with thickness of about 0.7 μm was achieved. The samples were calcined at 450 °C in air for several hours and then treated with gaseous H_2S at 120 °C (several hours) to convert the CdO nanocrystals into the CdS. Finally, the samples were annealed at 500 °C (2 °C/min) and indium-tin oxide (ITO) transparent contacts (diameter of 2 mm) were evaporated on top of the film.

EL was excited by a continuous dc voltage applied between the ITO contact and the Si substrate. A cw He–Cd laser (325 nm) was used to excite PL. Emitted light was collected by a microscope objective, then dispersed by a grating or imaged by a mirror. The signal was detected by a CCD camera. All spectra were measured at room temperature and corrected for spectral sensitivity of the detection system.

Panel A of Fig. 1 shows the PL image of a 60×20 μm^2 area of the CdS layer (observed outside the ITO contact, in order to avoid its influence). There is an apparent inhomogeneity of the emission, which becomes even more pronounced in the EL image (Fig. 1B, conditions: 16 V, 17 mA – negative polarity on the ITO contact, the same magnification as for Fig. 1A but different part of the sample).

The PL and EL spectra are compared in Fig. 1C. The two PL emission bands are commonly observed in small CdS NCs and interpreted in the literature to be due to quantum-confined delocalized excitons (the narrow high-energy band) and surface trapped e–h pairs or donor–acceptor recombination (the wide low-energy band) [4]. The ratio of intensities of the two PL bands varies in dependence upon location of an observed spot on the sample. On the other hand, EL spectra contain always only one broad emission band centred around 1.9 eV, the shape and position of which are not significantly changed with varying bias and polarity.

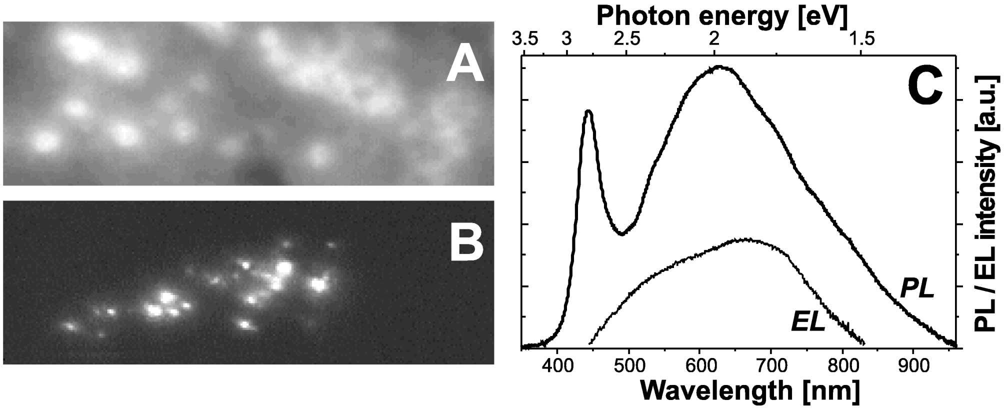

Fig. 1. PL and EL images of the CdS NCs film (part A and B, respectively). The images correspond to 60 × 20 μm^2 area of the sample. Panel C shows the corresponding PL and EL spectra

A current–voltage characteristic (Fig. 2A) shows no clear rectifying property, but there is some asymmetry. Current passing through the device is higher when the negative potential is applied to the Si substrate (let us call this polarity "forward" bias). For both polarities the current has been found to grow approximately quadratically with the applied bias (see the inset in Fig. 2A). These observations indicate that electron injection from Si substrate is more efficient than from the ITO contact. We recall that ITO is a degenerate wide-gap semiconductor of n-type [5] and the substrate is strongly doped n-type Si. Therefore, there should be no electric rectifying property in our structure and the asymmetric behaviour arises probably from different contact barriers.

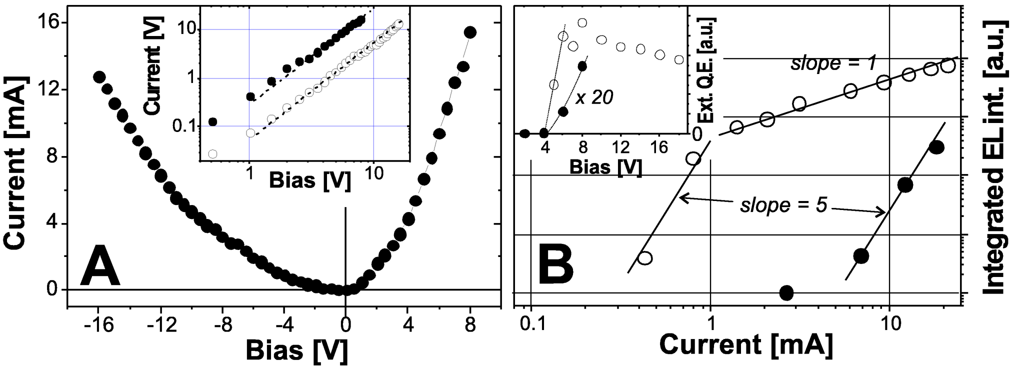

Fig. 2. A) Current–voltage characteristics of the device, the inset plots the same data in log–log scales. (Positive bias means that positive polarity is on the ITO contact.) B) Integrated EL intensity vs. current for reverse and forward bias (open and full circles, respectively). The inset shows external quantum efficiency (EL intensity divided by current density) vs. bias indicating a threshold voltage of about 4 V

EL emission is observed under dc voltage of both polarities for bias of 4 V and higher (Fig. 2B). The intensity is much stronger under “reverse” bias despite the less efficient electron injection. Integrated EL intensity increases rapidly with current for voltages close to the threshold, but a linear dependence is typical for higher voltages (Fig. 2B). Recently, we reported on similar behaviour (EL was observed for negatively biased ITO contact only) of EL devices containing silicon NCs in SiO_2 matrix on the n-type Si substrate with the ITO top contact [6]. As the architecture of both devices is similar, we propose the same model for EL in CdS NCs: EL occurs in points where the percolation of NCs takes place accidentally. Electrons and holes can be injected to such conductivity channels from the ITO and the substrate, respectively, and recombine radiatively in NCs. On the other hand injection of holes from ITO is negligible and almost no emission is observed under “forward” bias.

The absence of the high-energy emission band in EL spectra can be understood as the consequence of the low efficiency of formation of free excitons from separately injected electrons and holes. Also high electric field in the sol–gel layer should cause fast separation of excitons. This experimental observation therefore seems to confirm the interpretation of the narrow high-energy emission band in terms of free delocalized excitons.

We can estimate the external quantum efficiency of our device to be about 10^{-4} %. (Values as high as 0.1% were reported for CdSe NCs in organic PPV film [7].) Future development of our device will concentrate on improvement of layer homogeneity and growth of increased concentration of CdS NCs on different types of substrates. If successful, the sol–gel CdS NCs composites could become an alternative to novel organic EL devices in certain applications.

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