

Fabrication and investigation of nanocomposites of conducting polymers and GaSb nanocrystals

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Abstract

Nanocomposites consisting of GaSb nanocrystals in conducting polymer matrices were fabricated and investigated. Optical absorption and electrical properties of the samples were analyzed. Electroluminescence with a spectral maximum near 1600 nm was observed for both bias polarities. Infrared electroluminescence from GaSb/polymer nanocomposites points to possible applications in fibre-optic communications.

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1. Introduction

Composite systems comprising semiconductor nanocrystals embedded in conducting polymers are the object of active experimental investigation (see, e.g., [1–4]) as promising materials for mechanically flexible large area optoelectronic, particularly light-emitting, devices. In most experimental works, nanocrystals are fabricated from relatively wide-gap II–VI semiconductors so that the spectrum of the resulting light-emitting and photosensitive devices lies in the visible spectral region. In contrast, today's optical communication systems use the region 1.3–1.6 μm , so that designing active composites operating in this spectral region is of significant applied importance. Recent

work on InAs/ZnSe/polymer nanocomposites [5] has led to important progress in this direction.

In this work we present the first results on the fabrication and investigation of composites containing GaSb nanocrystals in conducting conjugate polymers. The band gap of bulk GaSb produces light of wavelength 1.75 μm . This prospectively allows access to today's low-loss fibre-optic communications spectral window with only modest exploitation of size quantization. Simple estimates suggest that light emission in the 1.3–1.5 μm spectral range may be achieved using nanocrystals ranging from 8 nm down to about 6 nm.

2. Sample preparation

GaSb nanocrystals were fabricated by temperature-controlled synthesis [6] in solution using $\text{Sb}(\text{SiMe}_3)_3$ prepared as per [6], in combination with commercially available GaCl_3 . The solvents were carefully dried, distilled, and degassed prior

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to use. 2 mmol GaCl_3 was dissolved in 50 ml di(isopropyl)benzene and cooled to -50°C . To this solution, 2 mmol $\text{Sb}(\text{SiMe}_3)_3$ was dropwise added via syringe, immediately followed by formation of a white solid. Slow mixing during warming to ambient temperature led to a darkening of both the solid and solution, finally yielding a brown mixture. Heating this mixture to reflux yielded a black solid collected by filtration, washed with pentane, dried in the vacuum and eventually dissolved in toluene for storage, investigation and further processing.

Preliminary microscopic observations revealed that the GaSb phase obtained was not monodisperse but contained nanocrystals of various sizes

partially aggregated in large precipitates. For this reason the samples were subjected to two different procedures: (a) filtering through a 5- μm micropore filter to eliminate large agglomerates; (b) extraction of a fine component from the suspended nanoparticle solution. Together with the initial unfiltered fraction, they were used in the preparation of three groups of samples.

Fig. 1 demonstrates the images obtained by atomic force microscopy (Nanoscope IIIa in tapping mode) for all three above-mentioned groups. They show a considerable difference in nanocrystal sizes between the groups and confirm that even this simple separation procedure allows us to obtain nanocrystals with a characteristic radius

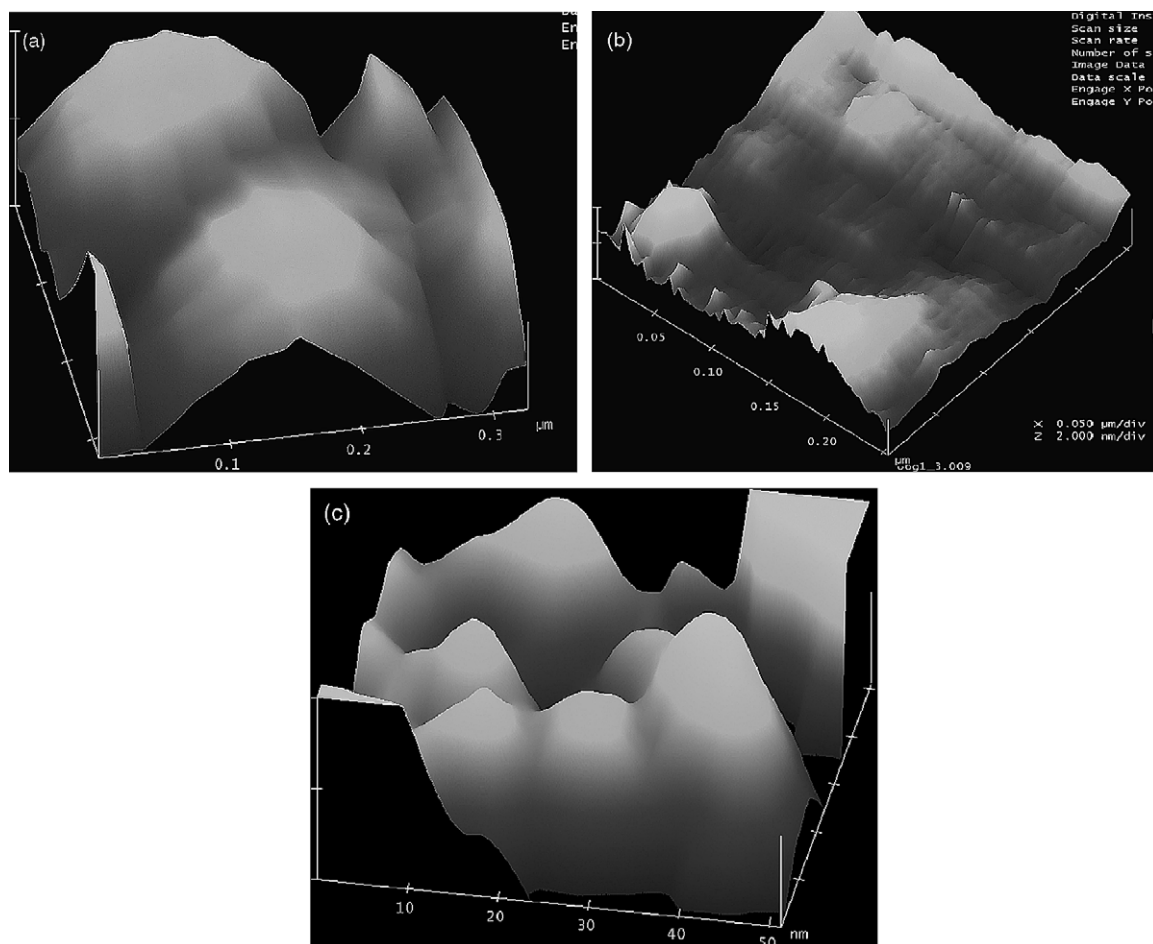


Fig. 1. AFM images of GaSb nanocrystals directly after growth process (a), after microfiltering (b) and after settling followed by phase separation (c). Note the difference in spatial scale for different figures.

around 5 nm (Fig. 1c) in which quantum size effects might be expected.

We used poly(2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene (MEH-PPV) as polymer matrix. Composite samples were prepared by mixing the nanocrystal powder with a polymer precursor, followed by sonication for 1.5 h and spin coating onto glass or quartz substrates with final annealing for 2 h in vacuum.

The structures for electrical and electroluminescent measurements comprise quartz or glass substrates covered by an ITO (indium-tin oxide) layer used as the anode contact, nanocomposite layers 100–700 nm thick, and upper cathode contacts fabricated by vacuum evaporation of Mg protected from the ambient atmosphere with a thin capping Ag film. Electrical measurements were performed using the Agilent semiconductor parameter analyzer 4155C.

3. Optical absorption

Fig. 2 demonstrates the absorption spectra for the same three samples as shown in Fig. 1 compared with the spectrum of pure bulk GaSb [7]. The peak around 500 nm corresponds to absorption in the MEH-PPV matrix. At longer

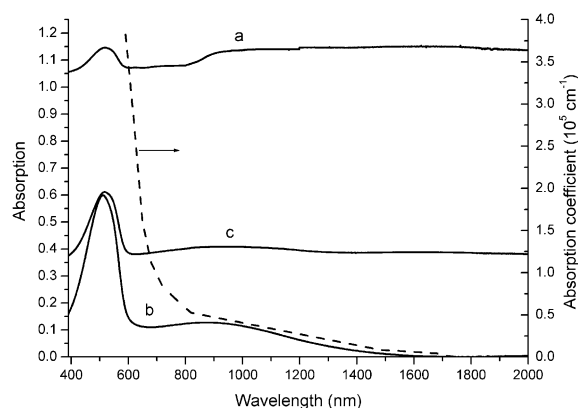


Fig. 2. Absolute values of optical absorption for three different GaSb/MEH-PPV nanocomposites. Letters a, b, c are related to the samples described and shown in the corresponding parts of Fig. 1. The samples have different thicknesses, so that quantitative comparison of the curves is not informative. The dashed line shows the absorption spectrum of pure bulk GaSb [7] (for scale see right ordinate axis).

wavelengths where the matrix is transparent, the spectrum differs noticeably from that of bulk GaSb and for two samples has no edge related to the GaSb bandgap. Initially we attributed this observation to molecules absorbed at the nanocrystal surface, which can play an important role in polymer-nanocrystals composites, including in deliberate passivation of the nanocrystal surface [8,9]. However, absorption below the GaSb gap disappears after microfiltering the nanocrystal solution (curve b) which eliminates large agglomerates and for this reason only increases the relative role of interface effects. We therefore attribute our observations at long wavelengths to strong scattering; microfiltering eliminates large particles with the size comparable to optical wavelengths and hence suppresses scattering.

Based on these considerations, Fig. 2(b) provides a better picture of absorption in the nanocomposites, including the impact of possible interface effects on absorption. The spectrum shows a smooth maximum in the region of intrinsic absorption in GaSb and an edge slightly shifted from the absorption edge of bulk GaSb, due to size quantization in nanocrystals. In samples which possess more scattering, a similar maximum is revealed in magnification, as discussed below with reference to Fig. 4.

4. Electrical properties and electroluminescence

For detailed electrical and luminescent measurements, we focused our attention on the sample with the smallest size of nanocrystals (Fig. 1c). Electrical measurements demonstrated the almost symmetric (non-rectifying) but strongly non-linear current–voltage characteristics of our structures (Fig. 3). These results are consistent with those seen in known polymer-nanocrystal composites emitting in the visible spectrum [10].

For an applied bias exceeding 10 V and currents exceeding 200–300 mA (the exact values vary from sample to sample), noticeable electroluminescence is observed and reported below in both integral and spectral measurements. In contrast with structures emitting visible light, infrared emission in our samples is potentially attributable not only to the

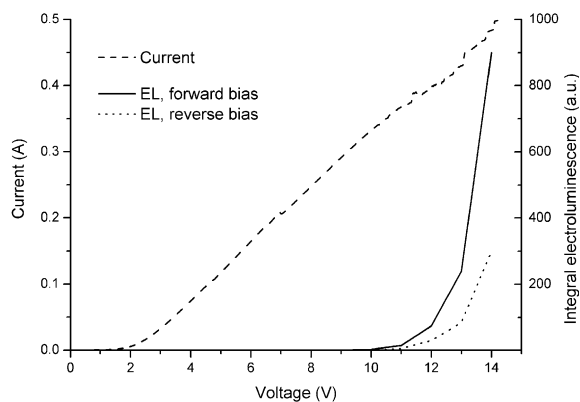


Fig. 3. The current–voltage characteristic (dashed curve) almost identical for forward and reverse bias and the integral intensity of electroluminescence for forward (solid line) and reverse (dotted line) bias. Forward bias corresponds to positive potential being applied at the ITO electrode.

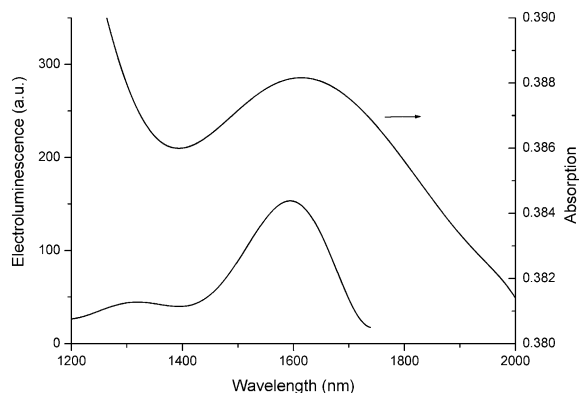


Fig. 4. The spectrum of electroluminescence (lower curve) compared to the spectrum of optical absorption (upper curve) in the GaSb/MEH-PPV nanocomposite.

luminescence from GaSb but could in principle contain a component of blackbody radiation from a Joule-heated sample. We see, however, that the voltage dependence of emission intensity is very steep, considerably steeper than it should be for blackbody radiation. Direct evidence of true electroluminescence from the nanocrystals is seen in the spectrum shown in Fig. 4.

The spectrum of electroluminescence (lower curve) has a distinct peak in the vicinity of 1600 nm. Comparison with the absorption spectrum (upper curve) shows that their spectral maxima essentially coincide.

5. Conclusion

To summarize, we have presented the results of first observation the infrared electroluminescence in nanocomposites GaSb/conducting polymer. These results point to the prospect of using this composite system for creating infrared light-emitting structures suited to optical communication in the spectral region 1.3–1.6 μm .

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