Layer-by-Layer Assembled Films of HgTe Nanocrystals with Strong Infrared Emission

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Dispersions of nanoparticles of II−VI semiconductors are currently of great technological interest as emitting materials for thin-film electroluminescence devices,[1−3] and as optical amplifier media for telecommunication networks.[4] This interest arises from the convenience of varying optical properties of semiconductor nanocrystals by simply varying their size owing to the effect of quantum confinement.[5] The feasibility of light-emitting diodes (LEDs) with light generation in the range of 500−700 nm was demonstrated by using CdSe[1,3] and CdTe[6,7] nanoparticles.

HgTe nanocrystals have been recently synthesized in aqueous dispersions.[8,9] They demonstrated strong emission in the infrared part of the spectrum and can find applications in telecommunication industry, which is based on fiber-optical networks operating in the window of transparency at 1550 nm. In this communication, we propose utilization of the layer-by-layer assembly (LBL) as a method of processing HgTe dispersions into high-quality thin films with thicknesses controllable in nanometer scale. The layer-by-layer assembly is based on alternating adsorption of oppositely charged species, which was originally developed for positively and negatively charged polyelectrolyte pairs[10] and was later extended to the assembly of nanoparticles.[2,6,7,11−15] Due to exceptional versatility of LBL that can be equally effectively applied to the coating of planar substrates and highly curved surfaces such as optical fibers, this technique can be used in infrared optoelectronics for manufacturing all-fiber emitters, detectors, amplifiers, etc.

Aqueous colloidal solutions of thioglycerol-capped HgTe nanocrystals were prepared as described previously.[8] The average particle size was 3.5 nm with a size deviation of 30% as determined by TEM. Colloidal solutions were used as prepared, with the concentration of HgTe particles of 0.013 M referring to Hg^{2+}. To accelerate the LBL deposition, thioglycolic acid was added (0.1−40 mL of colloidal solution, keeping pH constant in the range of 10.0 ± 0.5), which resulted in an increase of the negative charge of the nanoparticles. For LBL deposition, poly(diallyldimethylammonium chloride) (PDDA) was found to be the best among other investigated polycations (polyethylenimine and poly(allylamine hydrochloride)) at adsorbing HgTe nanoparticles. A commercially available 20% aqueous solution of PDDA (M_w = 450 000−500 000, Aldrich) was diluted 40 times to obtain a 0.5% solution that was used for film preparation.

LBL films have been prepared according to the standard cyclic procedure: (i) dipping of the substrate into a solution of PDDA for 10 min, (ii) rinsing with water for 1 min; (iii) dipping into the dispersion of HgTe nanocrystals (pH = 10.0) for 20 min; (iv) rinsing with water again for 1 min. On each exposed surface, such a procedure resulted in a “bilayer” consisting of a polymer/nanocrystal composite. The cycle can be repeated as many times as necessary to obtain a multilayer film of desirable thickness.

As substrates, rectangular 2 × 4 cm ITO-covered glass slides (Delta Technologies Ltd.), gold-coated quartz monocrystals, and silicon wafers (Virginia Semiconductors) were employed. Glass slides were washed under sonication in 1% Alconox solution (30 min), pure grade ethanol (30 min), and water (30 min). Silicon wafers were cleaned for 5 min in piranha solution (2 volume fractions of 98% H_2SO_4 + 1 volume fraction of 3% H_2O_2), rinsed with water, and covered by thin conductive film of gold using Denton Desktop II sputterer (Denton Vacuum Inc.). Milli-Q deionized water was used for all the preparations and the cleaning of substrates.

The adsorption of HgTe nanocrystals was monitored in-situ by a quartz crystal microbalance (Maxtek Inc., Santa Fe Springs, CA) with a gold-coated 5 MHz resonator. During the measurements, only one side of the resonator was in contact with the nanocrystal solution. Mass change occurring on the active area of a quartz crystal causes a frequency change.[16] This change can be used to obtain an amount of material firmly bound to the resonator surface.

Scanning tunneling microscopy images were taken by using a Nanoscope IIIa (MultiMode Scanning Probe

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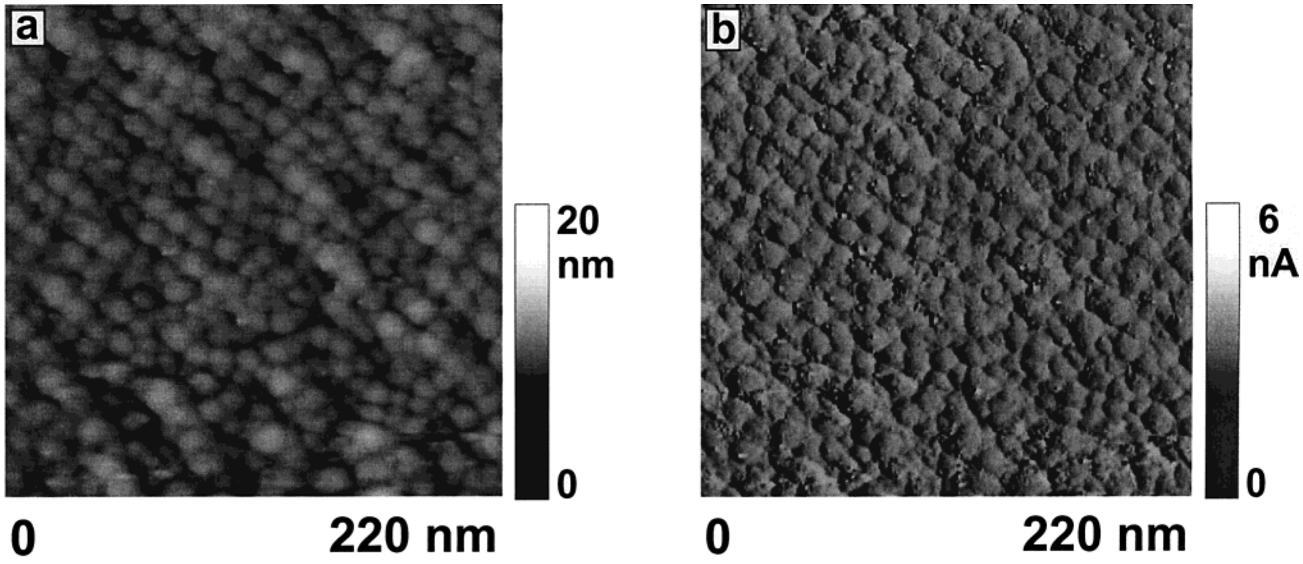

Figure 1. STM height (a) and STM current (b) images of a PDDA/HgTe LBL layer.

Microscope) instrument (Digital Instruments/Veeco) with standard Pt/Ir tips.

UV−vis absorption spectra were taken by using a HP8453 diode array Hewlett-Packard spectrophotometer. Photoluminescence spectra were recorded using a chopped Ar ion laser as the excitation source. The resulting emission from the PDDA/HgTe film was collected through a Bentham M300 monochromator and detected using liquid nitrogen cooled InAs photodiode.

The adsorption kinetics of HgTe nanocrystals on a foundation layer of PDDA was monitored by the frequency shift of a quartz crystal microbalance (QCM) resonator crystal carrying an adsorption layer of PDDA. The deposition curve for HgTe nanocrystals reaches the saturation point in ~80 min. The mass of the *saturated* layer of adsorbed nanoparticles corresponds to a layer of bulk HgTe with a thickness of ~8 nm. This translates into adsorption of 2−3 monolayers of nanoparticles despite electrostatic repulsion between them. The formation of a fairly thick layer in one deposition cycle can be attributed to the fact that the substrate/water interface is likely to act like a polyelectrolyte brush,[13] with positively charged groups spreading into solution and been able to catch more than a monolayer of nanocrystals.

Thick nanoparticulate film adsorbed in one cycle ensures efficient switching of the surface charge from a positive—characteristic of PDDA—to a negative, determined by the charge of HgTe nanoparticles. In turn, this facilitates the efficient adsorption of the polyelectrolyte in the subsequent deposition cycle. The thickness of the adsorption layer of the polyelectrolyte on HgTe nanoparticles in the saturation reaches 1 ± 0.5 nm as estimated from QCM measurements of LBL film in air.

For making LBL films, we used a 20 min adsorption time for HgTe deposition step. Under these conditions, the thickness of the HgTe approaches that of a monolayer of nanoparticles. The thinner HgTe layer improves the degree of control over the overall film thickness and shortens the time for film preparation.

The topography of the PDDA/HgTe layer can be seen in scanning tunneling microscopy (STM) image (Figure 1a). The rms roughness of the film is 6.5 nm, which is slightly above the quantum dot diameter. The HgTe particles form a densely packed film, where each nanocrystallite is in contact with adjacent ones, which can be seen particularly well in the current image (Figure 1b). The good quality of the STM images indicates high conductivity of the film.

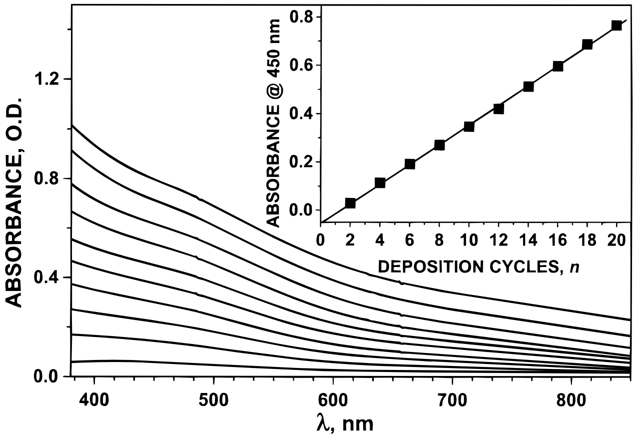

Figure 2. Absorption spectra of LBL assembled film of HgTe nanocrystals and PDDA as a function of a number of deposition cycles. Insert: Absorbance at 450 nm vs the number of deposited HgTe LBL layers.

Although STM is a surface imaging technique, these data provide insight into the internal structure of the multilayers, because both topography and packing of the films repeat in subsequent layers. In particular, one needs to point out that the multilayers of this sort can be considered as a very homogeneous composite material, which does not have sharp interfaces between the polymer and inorganic component. This feature differs them from spin-cast films prepared by mixing polymer and nanoparticles and is very valuable for light-emitting devices. It allows one to attain uniform charge transport through the film, which is extends longevity and reduces the turn-on voltage of LEDs.

Equality of amounts of nanoparticles and polyelectrolyte transferred in each deposition cycle can be seen from sequentially taken absorption spectra of the multilayers (Figure 2). Optical density at selected wavelength is linearly increasing with the number of deposited layers. There is no well-pronounced maximum in the absorption spectra as might be expected from a quantum-confined system—the "excitonic" features in nanocrystalline HgTe do tend to be rather weak and broad.[8] After 10 deposition cycles the coating has a dark glass appearance without any visible defects, opaque areas or color inhomogeneities. The film is robust and environmentally stable: no sign of peeling or oxidation have been observed for all the period of this work (several months).

Photoluminescence of HgTe nanocrystals in solutions has been observed from 1000 nm to over 1700 nm (depending upon the synthetic conditions of the sample) with quantum efficiencies up to 50%.[9] The LBL assembled films also displayed strong emission in the near-infrared, peaking around 1600 nm (Figure 3) and covering the entire telecommunications spectral region of interest. By observing the photoluminescence from a PDDA/HgTe film sample, the difficulties of solvent reabsorption which were observed previously[8,9] have been removed and the full extent of the spectrum is revealed. The IR luminescence can be detected from as few as two LBL layers of the nanoparticles. The demonstration of strong infrared luminescence from a solid, hybrid film, which could be a predecessor of many different types of devices, is significant in the context of optical telecommunications. LBL films of nanoparticles can be viewed as very inexpensive yet versatile technology, enabling implementation of cost-effective high capacity optical networks. Ultra-broad-band amplifiers for maximizing existing silica fiber bandwidth as well as cheap infrared LEDs for polymer fiber local area networks may become possible by using this technology.

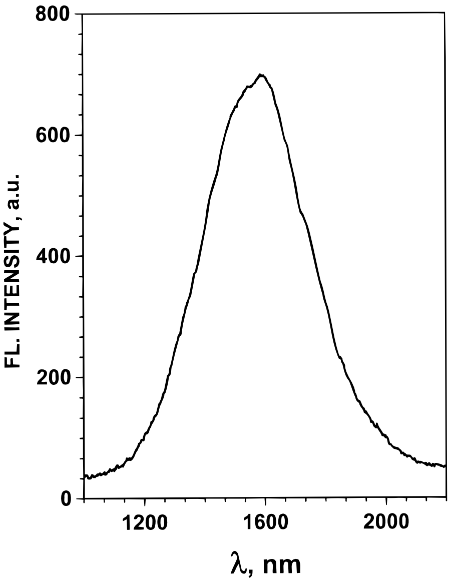

Figure 3. Photoluminescence of HgTe nanoparticles in the multilayer $(PDDA/HgTe)_{20}$ LBL film.

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