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Photoluminescence enhancement in nanocomposite thin films of CdS–ZnO

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We show that the photoluminescence emitted from a dense, two-component quantum dot ensemble on a thin film is significantly higher and decays much faster than that from quantum dots of either of the two pure systems (CdS and ZnO). The semiconductor nanocomposite, in which the characteristic grain size of each species was 2–3 nm, was deposited directly on Si wafers by high-pressure magnetron sputtering, and exhibits a single, relatively short optical absorption edge. © 2005 American Institute of Physics. [DOI: 10.1063/1.1899248]

I. INTRODUCTION

The electronic and optical properties of quasizero-dimensional semiconductors or quantum dots are fairly well understood. Yet there is an overwhelming interest in these systems, largely due to the size-controlled tunability of their band gap and the high quantum efficiency for photoluminescence (PL) arising from quantum confinement. Exciting applications are envisaged for such systems in optoelectronic devices, lasers, optical communications, and quantum computing. Of particular interest is the lasing action arising from photon localization in an ensemble of light-emitting particles. Repeated scattering of light from grain boundaries in such systems could result in random lasing. Since lasing originates from interference effects, it is essential for the emitted light to have some degree of coherence. Coherence is also important for applications related to quantum-information processing. Such applications demand a high luminescence output with appreciable coherence from a nanocrystalline semiconductor in a device-compatible, thin film geometry. In this article we show that the PL emitted by an optically flat, quantum dot solid (QDS) thin film deposited on Si wafers shows a significant enhancement due to quantum confinement. Further, in a separate article we show that the light emitted from such a nanocrystalline ensemble has an appreciable degree of spatial coherence. It is important to note that while the optoelectronic properties of low-dimensional semiconductors have been investigated widely, this is one of the few studies on dense ensembles of QDs or QDSs.

A major problem with isolated semiconductor nanoparticles is that they often have surface electronic states within the highest occupied molecular orbital/lowest unoccupied molecular orbital (HOMO–LUMO) gap that provide nonradiative decay channels and lead to a severe degradation in optoelectronic properties. This problem has been addressed by “capping” the semiconductor nanoparticle with a thin layer of a higher band gap material. Techniques involving semiconductor-doped glasses, zeolite encapsulation, sol–gel synthesis, and colloidal precipitation can produce capped, nearly monodisperse nanoparticles suitable for basic studies, but are not very useful for fabricating large area thin films that can be integrated into devices. Here, we demonstrate a single-step process (without the necessity of forming a core–shell structure) for the deposition of nanocomposite thin films directly on Si wafers. The nanocomposite film is constituted of a random assembly of nanoparticles of two distinct semiconductors (CdS and ZnO), and we show that the larger band gap component of the nanocomposite effectively passivates the component with the smaller band gap.

II. SYNTHESIS AND MICROSTRUCTURE

Bulk CdS is a direct band gap semiconductor (Eg = 2.42 eV at 300 K) with a hexagonal wurtzite structure. It undergoes a size-induced structural transformation to a cubic zinc blende structure below 2–3 nm. The larger band gap component in our nanocomposite was ZnO (Eg=3.44 eV at 300 K), a semiconductor with a crystal structure similar to CdS. Nanostructured films (average grain size ~2–20 nm) of most metals, semiconductors, and oxides can be sputtered onto desired substrates by dc/rf sputtering at relatively high gas pressures (~10–200 mTorr) and low substrate temperatures (77–300 K). In particular, uniform, nanocrystalline films of pure CdS can be synthesized by this technique, but need to be chemically passivated by a prolonged in situ exposure to H2+N2 gas mixture. The present study reports the deposition of CdS:ZnO nanocomposite thin films on Si wafers or quartz plates by rf magnetron sputtering, typically carried out in flowing Ar (99.999%) at 170 mTorr, the substrate being held at 0 °C. The sputtering targets were sintered 2 in. pellets composed of a mixture of CdS and ZnO in the molar ratios 45:55, 40:60, and 33:67.

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The x-ray diffraction (XRD) spectra of the sputter-deposited nanocomposite films show a single broad hump, which could arise from a superposition of the stronger diffraction lines of CdS and ZnO, substantially broadened due to small particle size. The microstructure and chemical composition of the ion-milled nanocomposite CdS:ZnO film were obtained using transmission electron microscopy (TEM) in the imaging and diffraction modes, respectively. A FEI CM-200 TEM (200 keV) with a LaB₆ emitter was used. Bright-field TEM micrographs of a typical nanocrystalline CdS:ZnO film (Fig. 1, top) indicate that the average in-plane grain size is ≈3 nm and the size distribution is quite narrow. Note that it is not possible to obtain images at higher resolution since this results in electron beam induced annealing of the densely packed nanoparticles. However, the almost monodispersed, individual nanocrystals can be more clearly identified as white dots in dark field TEM micrographs (Fig. 1, center) formed by intensity contributions from a single diffraction ring. All the distinct rings in the selected area diffraction pattern from the sample (Fig. 1, bottom) can be indexed consistently to the hexagonal and cubic polymorphs of CdS and ZnO. We point out that the TEM diffraction patterns were recorded using a selected area aperture of diameter ~500 nm. Hence the compositional data refer to an approximate estimate of the particle size distribution obtained from a statistically significant number of nanoparticles. Energy dispersive x-ray spectrometry indicated that the CdS and ZnO phases were approximately stoichiometric, with Cd:S = 1:1.20 and Zn:O = 1:1.18.

The nanocomposite CdS:ZnO thin films therefore consist of densely packed, randomly intermixed, nearly uniformly sized arrays of individual CdS and ZnO nanoparticles, the characteristic grain size for each phase being about 3 nm. An approximate estimate of the particle size distribution obtained from an analysis of the XRD line shape and the optical absorption spectra is 3(±1) nm. In the case of nanocrystalline CdS thin films deposited under similar conditions, the size distribution was measurably broader: 4(±2) nm. Competing growth of the two crystallographic phases in the nanocomposite probably leads to a narrower size distribution. A core–shell structure is not expected to originate from the sputtering process; neither is there any evidence for such a structure or for the formation of a solid solution between CdS and ZnO. Since the ZnO phase [whose HOMO–LUMO gap is quantum shifted deep into the ultraviolet (UV)] essentially provides a passivating matrix (see below), the system can be modeled as a random, three-dimensional ensemble of nearly identical CdS quantum dots. Such a system has been termed a disordered quantum dot solid and is described by coexisting discrete (localized) and band-like (delocalized) electronic states.

III. OPTICAL PROPERTIES

The optical absorption spectrum of a typical nanocomposite CdS:ZnO (40/60) thin film deposited on quartz shows a single, sharp absorption edge at 405 nm (Fig. 2), which corresponds to the quantum shifted excitonic energy in nano-CdS. In particular, the absorption edge is much sharper than that from the pure nano-CdS sample, indicating a narrower size distribution in the former. The absorption edge from a large particle (bulk) CdS film is also shown for comparison. Using standard expressions, we find that the observed blueshift in the gap energy (from 514 to 405 nm) in the nanocomposite film corresponds to a particle diameter of 3 nm for CdS nanoparticles, which is in excellent accordance with the size obtained from TEM. Clearly, the observed absorp-
growth in particle size in the sputtered films with increasing film thickness. However, the presence of two components in the nanocomposite film effectively retards the particle growth for either phase.

The external PL quantum efficiency (QE) for the nanocomposite sample was measured using the second harmonic of a Ti:sapphire laser (400 nm, 80 fs). The spectrally integrated PL produced by an incident power of 10 mW was detected with a calibrated photodiode, the scattered laser light being blocked by a suitable long pass filter. Appropriate corrections were made for the absorption cross section at the excitation wavelength and the filter transmission. The angular variation in the PL signal was also measured and used in the calculation of the QE. The external QE at room temperature for the nanocomposite (40/60) sample was found to be \( \approx 0.1\% \), which is at least five times more than that measured for nano-Cds under similar conditions. The internal quantum efficiency of all the samples is expected to be higher due to self absorption within the samples. This compares favorably with the value of external QE (=0.22\%) measured from light emitting diodes made with CdSe(CdS) core–shell structures.\(^{20}\)

We also carried out time-resolved fluorescence measurements using the second harmonic from a Ti:sapphire laser (440 nm, 1 ps) as excitation source. The majority species in the CdS:ZnO (40/60) nanocomposite was found to have a lifetime \(<50\) ps (as obtained from an exponential fit), while both nano-Cds (166 ps) and nano-ZnO (329 ps) had substantially longer lifetimes. The short decay time in the nanocomposite appears to be a direct consequence of the enhanced oscillator strength in this system. The enhanced PL and fast relaxation are both desirable for device applications. An earlier measurement of time-resolved PL in nanocrystalline CdS and CdSe also yields a decay time in the picosecond range.\(^{21}\) In that case too, the authors invoked the participation of “intrinsic nanocrystalline states or intrinsically unpassivated interface states.”

In a separate article,\(^{5}\) using the Young’s double slit experiment, we have shown that the PL emission from the nanocomposite thin films has significant spatio-temporal coherence, a fact that would be crucial for their use in quantum information processing as well as for lasing action from light-emitting particles.

**IV. CONCLUSIONS**

The optoelectronic properties of a nanoscale dispersion of two different semiconductors (in which we expect an appreciable overlap of wave functions between particles) cannot be expressed simply as a linear superposition of the properties of the individual components. This therefore opens up a region of phase space with both the crystallite size as well as the component fraction as coordinates. The CdS:ZnO nanocomposite exhibits much higher photoluminescence emission and shorter decay times than individual CdS or ZnO nanocrystals of similar dimensions. The increase in the PL due to decreasing size can be empirically related to the faster relaxation dynamics, while a further increase takes place in the nanocomposite due to efficient surface passiva-

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**FIG. 3.** Normalized photoluminescence emission spectra recorded with an excitation wavelength of 391 nm (second harmonic of Ti:sapphire laser) from (A) bulk CdS film \((r=1.3 \mu m, d_w=5 \mu m)\), (B) nanocrystalline CdS film \((r=0.5 \mu m, d_w=4 \mu m)\), (C) CdS:ZnO nanocomposite film \((r=45/55, t=0.6 \mu m, d_w=3 \mu m)\), (D) CdS:ZnO nanocomposite film \((r=40/60, t=1.3 \mu m, d_w=3 \mu m)\), and (E) CdS:ZnO nanocomposite film \((r=33/67, t=1.5 \mu m, d_w=3 \mu m)\). Here \( r \) is the molar ratio of two semiconductors. Curve (A) has been multiplied by 5.
tion, which reduces the effect of the nonradiative surface-mediated decay channels. The self-passivated nanocomposite thin film structure can also be formed more efficiently and in a device-compatible manner than the core–shell structure.

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