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Abstract

The application of semiconductor quantum dots in important new areas such as random lasing and quantum-information processing requires knowledge of the coherence of the optical emission from such systems. We report the first direct experimental estimation of the coherence in the light emitted by a nanoparticle ensemble. The photoluminescence from a two-phase nanocomposite CdS–ZnO thin film (with a characteristic grain size of 2–3 nm for both the chemical phases) possesses an appreciable degree of spatial and temporal coherence at room temperature. The degree of spatial coherence was estimated from the classical Young's double slit experiment. We also discuss a simple technique for estimating the degree of spectral coherence of the photoluminescence from thin films.

1. Introduction

Photon localization in microstructured systems leading to laser action is a subject of active theoretical and experimental research. In an ensemble of particles emitting light, recurrent light scattering from grain boundaries may provide coherent feedback and result in lasing. Macroscopic coherent emission from such particle ensembles has been called 'random lasing' [1, 2]. Since the lasing action originates from interference effects, it is essential for the emitted light to have some degree of coherence, i.e., a well-defined phase and amplitude correlation for each spectral component [3]. In addition to the fascinating random laser phenomenon, much attention has been attracted by the coherent excitation and control of quantum dots, which are candidates for quantum-information processing [4–6]. Clearly, it is very important to determine the degree of temporal and spatial coherence in the optical emission from a quantum dot ensemble. To our knowledge, this is the first quantitative study of the nature and extent of coherence in the photoluminescence emitted by a dense aggregate of semiconductor nanoparticles.

The coherence of the light emitted from an ensemble of particles is destroyed by different types of phase relaxation processes that occur in individual particles [6]. The temporal

and spatial scales over which phase correlation is lost due to such relaxations determine, respectively, the temporal and spatial coherence lengths. There have been a number of studies of dipolar dephasing and quantum state coherence in spatially confined systems [7, 8]. However, there are no quantitative studies of the spatial and temporal coherence of light emitted by nanoparticles, even though such data would obviously be extremely important for applications of quantum dots in lasers and opto-electronics [9, 10]. The *temporal* coherence length (or time) of an ensemble of fluorescing particles can be estimated using well-established techniques such as the measurement of the spectral width of the photoluminescence (PL) spectrum, and from experiments based on interference by division of amplitude (e.g., Michelson interferometer and interference due to multiple reflections) [3, 8]. The existing methods for investigating *spatial* coherence are based on confocal microscopy [6], near-field coherent spectroscopy [11], and time- and space-resolved pump–probe experiments [12]. These techniques, however, require spatial resolution of the order of the wavelength of light, and are not suitable for studying coherence in ensembles covering areas larger than about a micron. In this paper we present a measurement of the degree of spatial coherence in the space–time domain for a nanocomposite semiconductor (CdS–ZnO) thin film. We also show how the degree of spatial coherence in the space–frequency domain (otherwise known as the degree of spectral coherence) may be estimated by a simple technique based on photoluminescence spectroscopy. Finally, we discuss our coherent back-scattering measurements in the CdS–ZnO nanocomposite thin films and compare these with the corresponding properties in pure nano-CdS and nano-ZnO thin films to show that the spatial coherence is lost in ZnO due to inherent scattering within the thin film.

The sample selected for this measurement is a nanocomposite thin film consisting of a random ensemble of closely aggregated 2–3 nm nanoparticles of two different semiconductors: CdS and ZnO. We show in a separate communication that such a nanocomposite produces a substantially higher level of PL than similarly synthesized individual nanoparticulate thin films of either CdS and ZnO. In this paper, we focus our attention on the experimental measurement of the coherence of the PL emission from the nanocomposite sample.

2. Experimental results

Nanocrystalline films of most metals, semiconductors and oxides can be sputtered onto desired substrates by dc/rf sputtering [13]. Nanostructure formation is promoted by carrying out the sputtering at relatively high gas pressures (20–200 mTorr) and low substrate temperatures (100–300 K). In particular, the CdS–ZnO nanocomposite thin films were rf-sputter-deposited typically in 100–200 mTorr Ar, from a composite target of CdS and ZnO on quartz and Si substrates maintained at 300 K [14]. Transmission electron micrographs of the deposited films show a uniform distribution of closely aggregated, individual CdS and ZnO nanoparticles with an average size of 2–3 nm [14]. The band gap obtained from optical absorption data was 2.8 eV. Single-component nano-CdS and nano-ZnO thin films, with an average size in the 2–5 nm range, were also prepared under similar conditions. Both the mean particle size and the size distribution are measurably smaller in the nanocomposite than in the single-component nanocrystalline systems, probably due to competing grain growth of the two phases in the former. Thus, the particle size distribution (obtained from absorption measurements as well as x-ray diffraction line shape analysis) in the nano-CdS film was 4.8 ± 2.0 nm, whereas in nanocomposite CdS–ZnO, it was 3.0 ± 1.0 nm.

Figure 1 shows the room temperature PL emission spectra for the nanocomposite CdS–ZnO as well as pure nanocrystalline CdS and ZnO thin films. The PL was excited by the 457.8 nm line from an Ar^+ laser and the spectra were recorded using a 0.85 m double monochromator. All three samples show a broad band PL in the 460–700 nm range. In
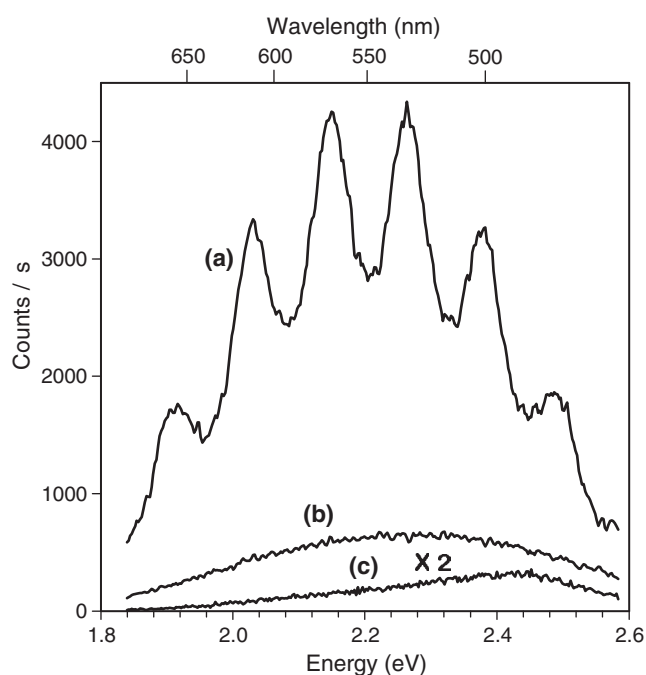
Figure 1. Photoluminescence emission spectra from (a) CdS–ZnO nanocomposite film ($t =$ 1.8 μm, $d_{av} = 2.8$ nm), (b) nanocrystalline CdS film ($t = 0.2$ μm, $d_{av} = 2.4$ nm) and (c) nanocrystalline ZnO film ($t = 0.9$ μm, $d_{av} = 3$ nm). Here t is the film thickness and d_{av} is the crystallographic domain size.

all cases it is clear that the gap states (and not the band-to-band transitions) are responsible for the PL excited at 458 nm [15, 16]. The PL emission from ZnO is actually due to states associated with oxygen vacancies [17]. Since the PL spectra of nano-CdS and the CdS–ZnO nanocomposite have similar spectral characteristics, we conclude that the same type of gap states is responsible for the observed PL in both the samples. These states are likely to arise from Cd vacancies in the sample [16]. As the PL spectrum originating from transitions from the conduction band to the mid-gap states is red shifted (with respect to the band gap) in CdS, an additional non-radiative transition must be involved in the process [18]. Note also that the spectral width of the PL emitted from the nanocomposite ($\sim$120 nm) is less than that from nano-CdS ($\sim$150 nm), due to the narrower size distribution in the former.

The nanocomposite sample not only produces a much higher PL emission than single-phase nanocrystalline CdS and ZnO (even after thickness normalization), but also shows sharp intensity modulations in its emission spectrum due to multiple-beam, thin-film interference effects, indicating that the PL emission is measurably coherent. As expected in such interference patterns, the spectral fringe spacing is inversely proportional to the film thickness. No fringes are visible in the nano-CdS emission spectrum since the fringe spacing corresponding to a thickness of 0.2 μm is more than 200 nm. Interference modulations were, however, observed for the thicker CdS films. Interestingly, no fringes were observed from even the thicker (0.9 μm) nano-ZnO thin film, though we expect at least three fringes for this thickness. Fringe contrast in the multiple beam interference depends on the reflectivity of the substrate, difference in refractive indices at the interfaces, surface quality and the spatial and temporal coherence properties of the material [3]. Since the synthesis conditions and
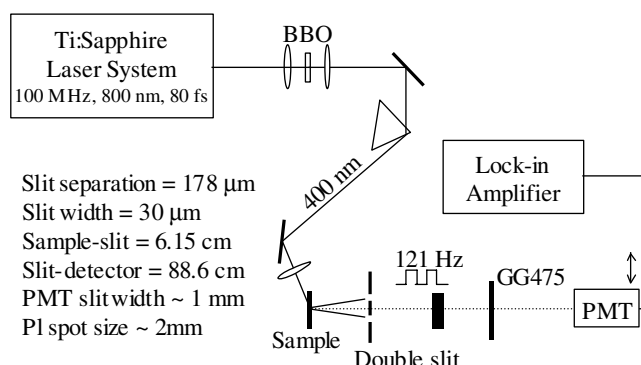
Figure 2. Schematic diagram of the Young's double slit experiment for measuring the degree of spatial coherence.

microstructural parameters are comparable in the case of the CdS–ZnO nanocomposite and the nano-ZnO sample, the absence of fringes in the latter case presumably indicates that the emission from ZnO nanoparticles has poor temporal and/or spatial coherence.

The temporal coherence length calculated [3] from the width of the PL spectra (figure 1) is ≈3 μm in all the samples. Since the PL spectra probably undergo some broadening due to particle size distribution, we should consider 3 μm to be the *lower limit* of the temporal coherence length. The thickness of even the thickest sample is 1.8 μm, which is less than the temporal coherence length. Clearly, in the case of ZnO, the absence of interference is *not* due to a lack of temporal coherence. It therefore appears that the *spatial* coherence in ZnO is inherently low.

We employed the celebrated Young's double slit experiment [3] to investigate the extent of spatial coherence in the nanocrystalline thin films. Since the two sources in the double slit experiment are generated by a division of wavefront, it can be used to study the spatial coherence of a sample, provided the light retains temporal coherence over the path difference of the two secondary sources at the point of observation. Figure 2 provides a schematic representation of the set-up for the double slit experiment. The PL was excited by the second harmonic of a Ti:sapphire laser with a fundamental wavelength of 800 nm and pulse duration of 80 fs. The spot size on the sample was ≈2 mm. A yellow filter (GG475) was used to block the scattered laser radiation from entering the detector. We replaced the sample by a scattering plate to check that the laser light was *completely* blocked by the filter. This is a necessary requirement since the PL signal reaching the PMT is rather weak, having passed through 30 μm slits and covering an experimental path length of about 90 cm. Thus, if any part of the highly coherent laser radiation enters the PMT, it would not only produce a high background but also lead to a wrong estimate for the degree of coherence.

Figure 3 shows the two-beam interference pattern produced by the PL emitted by the CdS–ZnO nanocomposite. The figure also shows the theoretical fit to the data, from which one can calculate the degree of spatial coherence ($|j_{12}|$)—a complex quantity related to the fringe contrast in the double slit experiment [3]. A value of $|j_{12}| = 1$ corresponds to perfect coherence, that is 100% contrast in the fringe pattern. The fitted curve in figure 3 yields a value of $|j_{12}| = 0.2$ for the CdS–ZnO nanocomposite.

In the Young's double slit experiment, the detector is scanned in a direction normal to the axis of the set-up. The fringe pattern is formed by the *spectrally integrated* PL and the fringe spacing corresponds to the *mean* wavelength of the PL spectrum. Now, if the spectrum
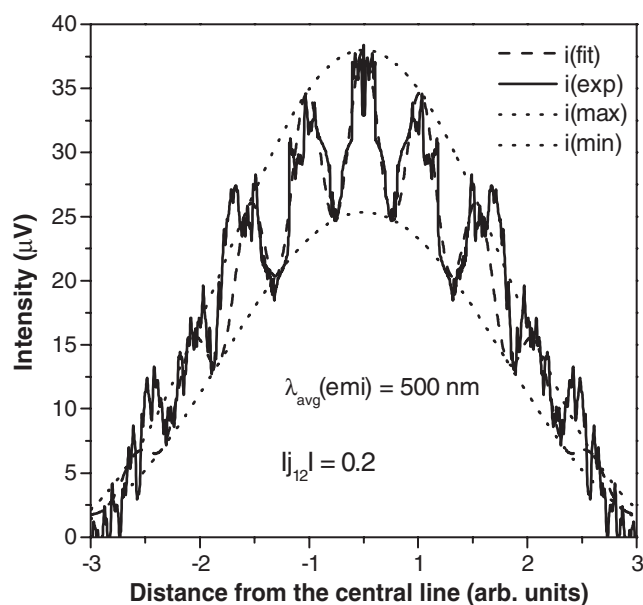
Figure 3. Two-beam interference pattern generated from the photoluminescence emitted from the CdS–ZnO nanocomposite thin film.

is recorded using a monochromator and the detector is kept away from the axis, the spectrally resolved signal would also be modulated. The experimental set-up in this case is similar to that used for recording a PL emission spectrum. Such an experiment would produce a fringe pattern similar to that obtained in the double slit experiment, except that the intensity would vary as a function of wavelength instead of position. The fringe contrast in the latter case would also be related to the spatial coherence of the emitted light. However, in this case the contrast is given by the degree of *spectral* coherence, $|\mu_{12}|$, which provides information about spatial coherence in the space–frequency domain and is related to $|j_{12}|$ by a Fourier transform [3]. The signals from our samples were not strong enough to record the spectrally resolved data and measure $|\mu_{12}|$ directly.

Both $|j_{12}|$ and $|\mu_{12}|$ are Bessel functions of wavelength, slit separation, slit width, slit–source separation and angular size of the source [3]. In addition, for a polychromatic source, $|j_{12}|$ also depends on the spectral width of the PL spectrum: a larger spectral width leads to a lower contrast. For a broad, top-hat type PL profile, the Young's double slit experiment would produce fringes with poor contrast even though the light is spatially coherent, as the peak for one wavelength would overlap with the valley for another. In our case, the comparatively low value of $|j_{12}| = 0.2$ may be ascribed to the rather broad PL spectrum. For a broadband source, the more relevant quantity is $|\mu_{12}|$, as it gives a measure of the coherence of each wavelength component. In other words, $|\mu_{12}|$ gives the correct information about the spatial coherence of a broadband source irrespective of its spectral width and shape. The lower the angular dimension of a source, the better is the fringe contrast, which indicates that spatial coherence is lost above a certain source size. The characteristic length scale over which it is lost is actually the spatial coherence length.

Recall that interference fringes were observed (figure 1) in the broadband PL spectra of nanocomposite (CdS–ZnO) and nano-CdS films but were absent in nano-ZnO and that the experimental set-up for PL emission spectroscopy of thin films is the same as that for measuring
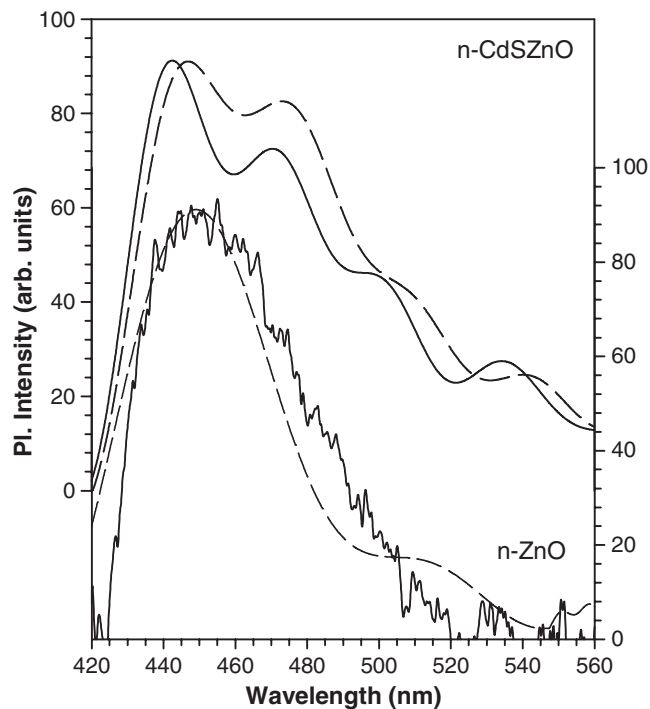
Figure 4. Photoluminescence spectra from thin films of nanocomposite CdS–ZnO (top) and nanocrystalline ZnO (bottom) for excitation spot sizes of 20 μm $\times$ 10 μm (solid curve) and 2 mm $\times$ 1 mm (dashed curve).

$|\mu_{12}|$. The two sources that interfere and modulate the intensity as a function of wavelength are: (i) the direct PL emission from the sample, and (ii) the PL reflected from the film–substrate interface. Fringes are formed only if the emitted light is coherent in space as well as in time. Our experiments suggest that the PL emission from all the samples is temporally coherent but the emission from the nano-ZnO film is not spatially coherent. We could observe fringes from the nanocomposite films even when the excitation spot size was ∼1 cm $\times$ 2 mm. If the fringe contrast depends on $|\mu_{12}|$, it would improve if the spot size is reduced as other parameters such as reflectivity of the interface and the surface quality would remain the same [3].

The relation between the fringe contrast and the angular size of the PL spot was studied by recording PL spectra for different spot sizes; these were controlled simply by changing the size of the excitation beam on the sample. PL spectra are shown for two different spot sizes (2 mm $\times$ 1 mm and 20 μm $\times$ 10 μm) from the CdS–ZnO nanocomposite thin film (figure 4, top) and the nano-ZnO thin film (figure 4, bottom). In the case of the CdS–ZnO film, the spectra corresponding to both spot sizes show modulation, while the contrast is expectedly better for the smaller spot size (solid curve). In the nano-ZnO film the larger spot size (dashed curve) does not produce any modulations but weak fringes start appearing for the smaller spot size. Essentially similar results were obtained from measurements made at different parts of the films, and a small spot size was used to minimize the effect of thickness non-uniformity. Similar experiments on nano-CdS films also showed an enhancement in fringe contrast with a reduction in the excitation spot size. From the measurements of the degree of spatial coherence, we estimate the spatial coherence length to be ∼10 μm in the nanocomposite and ∼350 nm in nano-ZnO.
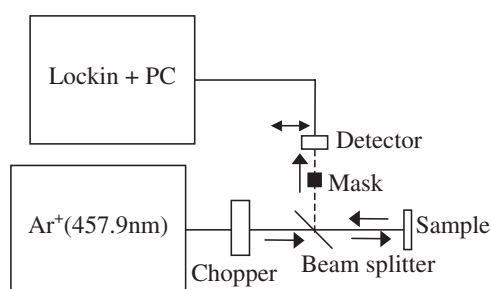
Figure 5. Schematic diagram of the experimental set-up for measuring the back-scattered intensity.

3. Discussions

Clearly, the CdS–ZnO nanocomposite shows a greater degree of spatial coherence than nano-CdS or nano-ZnO. It is, however, important to point out that in spite of the PL emission being appreciably coherent, we believe that it is a *spontaneously* emitting source [19]. The following observations [20] rule out the occurrence of stimulated emission:

(1) the integrated PL output varies *linearly* with intensity up to intensities much higher than those used for the measurement of coherence,
(2) the *nature* of the PL spectra does not change with intensity (i.e., there is no gain-narrowing), and
(3) no cavity modes are observed in the high resolution PL spectra.

To understand the origin of this enhanced coherence, we measured the coherent back-scattering from each sample. Spatial coherence is related to the phase correlations between two emitters separated in space. Random scattering within the sample destroys this phase relationship and thereby reduces the degree of spatial coherence [21, 22]. This can be easily seen by measuring the value of $|j_{12}|$ for He–Ne laser light scattered from a piece of ground glass (scattering plate). The scattered light showed $|j_{12}| = 0.65$, whereas the He–Ne laser itself has an extremely high value of 0.92. Our experimental set-up for measuring coherent back-scattering is shown in figure 5. The 457.9 nm line of an Ar^+ laser was used as the source. In order to optimize the sensitivity of the measurement, the central spot in the back-scattered light was blocked by a mask such that the back-scattering signal dropped to only 0.6% of the actual signal (without mask). During measurement, the back-scattering angle was varied by scanning the detector (photodiode) in a direction perpendicular to the beam. The samples used for this experiment were sputter-deposited on quartz plates.

Figure 6 shows the back-scattered intensity as a function of angle for the quartz substrate, nano-CdS, nano-ZnO and the nanocomposite CdS–ZnO. Clearly, the nano-ZnO film gives rise to a much wider back-scattering angle than the other two samples, indicating larger scattering within the sample. Since it is possible for the enhanced scattering to be related to the surface quality of the film, we measured the surface roughness for the three samples using an atomic force microscope (AFM). We found that all the three samples showed a similar degree of surface roughness (∼30 nm), which indicates that the higher scattering in ZnO is an inherent property of the sample, unrelated to the surface quality. Random, local fluctuations in the refractive index may give rise to multiple reflections within the sample over a very short optical path [22, 23] and lead to the loss of phase correlation in ZnO. Since the substrate roughness in all the samples is similar, the film–substrate interface is expected to have essentially similar
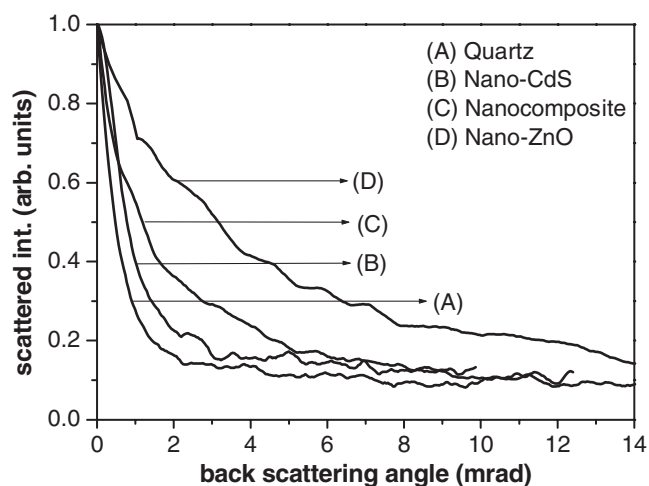
Figure 6. Back-scattered intensity as a function of angle for the quartz substrate, nanocomposite CdS–ZnO, nano-CdS and nano-ZnO thin films.

characteristics. The scattering from the nanocomposite sample is larger than that from nano-CdS, which is expected due to the presence of a second crystalline component (ZnO) in this sample. Note, however, that the presence of ZnO in the nanocomposite does not appear to affect the coherence length. On the contrary, it leads to a significant increase in the PL yield. It is also important to note that the average grain size in the three samples is similar. Since the scattering is the lowest from the nano-CdS films, it should have shown a higher degree of spatial coherence. However, the low yield and broad profile of the PL from this sample reduce the fringe contrast considerably. Thus the high spatial coherence from the nanocomposite film is not only intrinsic, but is also ascribable to the higher PL intensity and the comparatively narrower size distribution.

In summary, we have reported the first study of the temporal and spatial coherence properties of the photoluminescence from nanocrystalline systems. The samples studied include nanocrystalline thin films of CdS and ZnO as well as a CdS–ZnO nanocomposite. The nanocomposite shows a substantially enhanced photoluminescence and greater coherence compared to nanocrystalline CdS and ZnO. We also show that a simple measurement of the PL spectrum as a function of excitation spot size and back-scattering angle provides a direct estimate of the spatial coherence in thin films. This would be very useful for studying the optical properties of nanocrystalline thin films, which are important for many opto-electronic applications. We point out that the degree of spatial coherence can be further increased in such nanocrystalline samples by either

 (a) reducing the scattering at the scale of optical wavelengths (such as related to the sample porosity, etc), or

 (b) reducing the particle size distribution which would lead to a narrower PL band and increased coherence.

A larger degree of coherence is expected to be useful for several opto-electronic applications, including situations where the divergence or the size of the focused spot is important.

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