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# Dependence of photoluminescence of CdSe/ZnS on excitation wavelength

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**Abstract**

We have found that the photoluminescence (PL) intensity of CdSe/ZnS nanocrystals placed on a thin film of insulator (GaAsOx/GaAs) depends on excitation wavelength through the interference effects of the excitation light. By employing the multi-reflection/interference calculation, the insulator thickness of the underlying non-uniform patterns can be evaluated by the simple observation of CdSe/ZnS PL with a couple of excitation wavelengths. Moreover, the differences observed for the temporal evolution of CdSe/ZnS PL (blue shifts and degradation) among the excitation wavelengths suggest that the photo-induced changes of chemical composition and surface ligands are responsible for blue shifts and degradation, respectively.


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*Keywords:* CdSe; Nanocrystals; Photoluminescence; Blue shift; Excitation wavelength; Interference; Excitation photon energy

## 1. Introduction

Photoluminescence excitation (PLE) spectroscopy is one of the powerful techniques to characterize the optical properties of semiconductor quantum structures, and many new findings have been obtained for low-dimensional structures, especially for self-assembled InAs/GaAs quantum dots [1–4]. However, for another quantum-dot system, i.e., the nanocrystals (NCs) of CdSe/ZnS [5], PLE has not been applied intensively, especially when the NCs are placed on solid surfaces. This is because the photoluminescence (PL) of CdSe/ZnS NCs on solid surfaces shows temporal evolution as well as spontaneous blinking [6–9], which makes the conventional PLE difficult to apply.

In this report, we show that the thickness of insulator patterns can be evaluated by the microscopic observation of CdSe/ZnS PL with a couple of excitation wavelengths, on the basis of multi-reflection/interference calculations. Differences in the temporal evolution of CdSe/ZnS PL by excitation wavelength are also described, and the mechanisms of blue shifts and degradation in CdSe/ZnS PL are discussed.

## 2. Experimental

The insulator patterns of GaAs-oxide (GaAsOx) were prepared on GaAs(0 0 1) substrates by droplet etching; a 10 μl droplet of etchant solution (1$NH_4OH$:1$H_2O_2$:100-$H_2O$) was placed onto the GaAs(0 0 1) surfaces for 20–60 s (Fig. 1a), evaporating slowly during the etching. The GaAsOx byproducts remained at the edge of the droplet, and a ring pattern of GaAsOx with diameter 4–6 mm and width 150–200 μm was formed on GaAs. The GaAsOx formed by the droplet etching was a mixture of $Ga_2O_3$ and $As_2O_3$ (primarily $Ga_2O_3$).

Trioctylphosphineoxide (TOPO)-capped CdSe/ZnS NCs dispersed in chloroform (30 μg/ml, supplied from Mitsubishi Chemical Co., PL peak = 2.18 eV and PL width = 130 meV for the suspension) were placed on the specimen with the GaAsOx ring pattern by dropping a 100 μl suspension of NCs. The suspension evaporated and CdSe/ZnS NCs with an area density approximately

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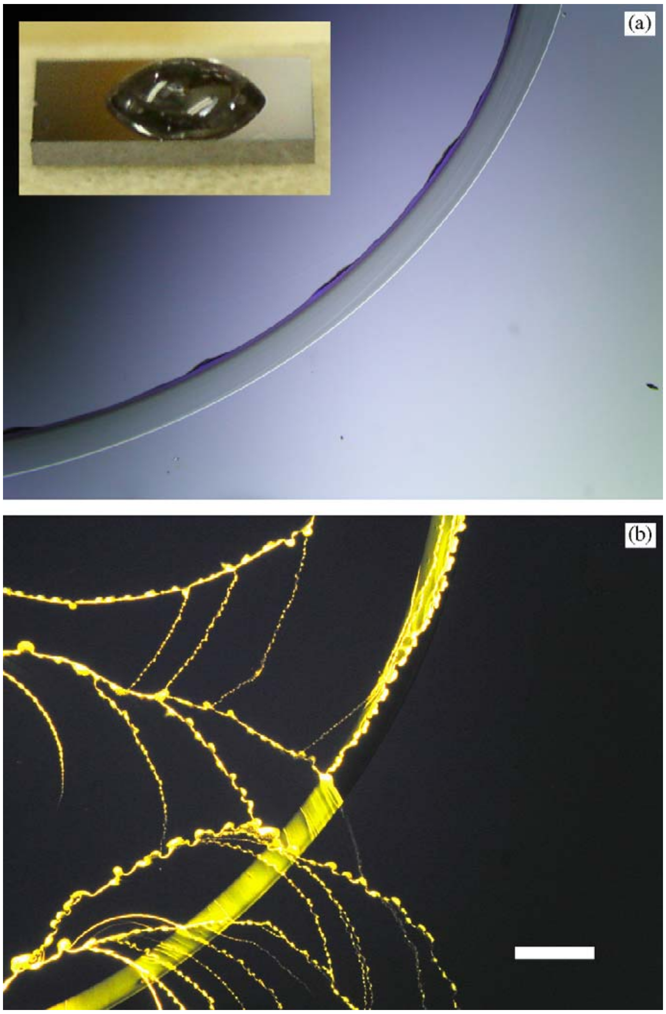


Fig. 1. Phase contrast image of GaAsOx/GaAs specimen (1/4th part of the GaAsOx ring pattern) (a) and photoluminescence image taken with 475 nm excitation (b). Only the GaAsOx ring can be seen to be bright in (b), while the CdSe/ZnS NCs were spread on the GaAs bare surface as well as on the GaAsOx ring. Many evaporation traces in (b) should be neglected. Scale bar in (b) shows 200 μm. The inset in (a) shows the droplet etching of a GaAs substrate in progress.

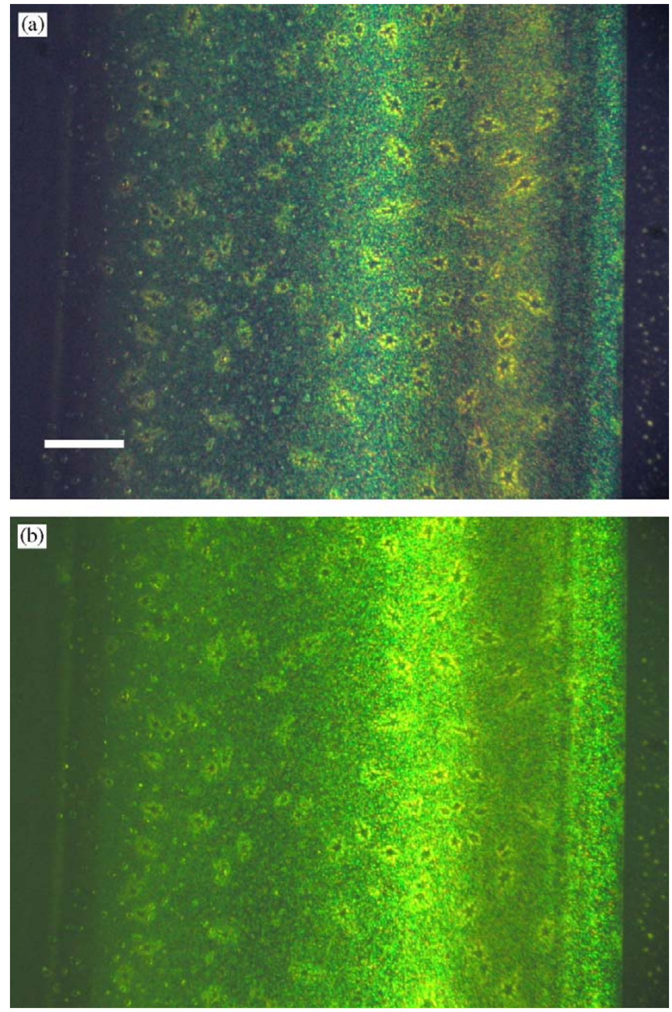


Fig. 2. Photoluminescence images for the GaAsOx ring with excitation wavelength 365 nm (a) and 435 nm (b). Scale bar in (a) shows 20 μm. Small patterns due to surface roughness are observed on the surface, but they were eliminated in the line profile of PL intensity in Fig. 3 by area averaging. Left side on the image corresponds to the inside direction of the GaAsOx ring.

$2 \times 10^{12}\,cm^{-2}$ remained on the surfaces of GaAsOx and GaAs. Evaporation traces with the aggregation of NCs were excluded for the PL measurements.

A fluorescent microscope (Olympus, IX71) was used for PL measurements, with four mirror units and an Hg lamp for excitation with 365, 405, 435, and 475 nm, individually. PL images and spectra can be taken through the microscope by CCD camera (Olympus, C4040Z) and a linear CCD array (Oceanoptics, USB2000), respectively.

## 3. Results and discussion

PL image taken with 475 nm excitation was given in Fig. 1b. The GaAsOx ring pattern on the specimen surface was brightly observed by the CdSe/ZnS PL. Since the excitation lights cancel out by the interference of incident/reflected at conductive surfaces, the effective excitation power for CdSe/ZnS NCs on GaAs was negligibly small compared with that on GaAsOx, which results in the bright PL images only for the insulator pattern (GaAsOx ring). The clear contrast in Fig. 1b indicates that the insulator patterns on semiconductor surfaces can be visualized through the photoluminescence of CdSe/ZnS, which should be useful to recognize the nm-scale conductive/insulating patterns through an optical microscope.

The bright PL images on GaAsOx pattern have coaxial undulations as well as in the phase contrast images, as shown in Fig. 2a. It is not due to the density fluctuation of CdSe/ZnS NCs, since when the wavelength of excitation light was switched among the four we used, the undulation showed a slight change in its location and brightness (Fig. 2a and b). In order to analyze the dependence on the excitation wavelength, the line-scan profiles of PL intensity are taken along the line crossing the GaAsOx ring pattern from inside to outside, as given in Fig. 3.