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Resonant Raman effect enhanced by surface plasmon excitation of CdSe nanocrystals embedded in thin SiO₂ films

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In this article, the Raman signal of CdSe nanocrystals well dispersed in a very thin SiO₂ film (20 nm) has been investigated by surface plasmon excitation in a resonant Raman spectroscopy experiment. In order to perform the excitation, the thin SiO₂ layer containing nanocrystals is deposited on a well-defined silver layer. The surface plasmon excitation increases the sensitivity of the Raman experiment, compared to the conventional setup, and allows the observation of a small number of nanocrystals (around 5000). The luminescence has also been measured and its dependence with the separation between the metal layer and CdSe nanocrystals is analyzed. In particular the quenching of the luminescence for thin film has been used to obtain only the Raman signal in resonant configuration.

INTRODUCTION

Semiconductor nanoparticles of type II–IV compounds are currently being intensively investigated for their applications in the field research of optics.^{1,2} This is because when nanocrystals have sizes comparable to the Bohr radius of the exciton in the bulk semiconductor which is 3.3 nm for CdSe nanocrystals, the resulting three dimensional confinement strongly modifies their optical properties. Raman spectroscopy has proven to be an excellent tool for the investigation of the vibronic properties of such low dimensional semiconductor structure. Nevertheless, in order to obtain a significant Raman signal in conventional Raman spectroscopy, it is necessary to work on a large number of particles and in a resonant configuration. This means that only rather thick and densely packed samples can be studied which reduces the applicability of this technique and that a luminescence signal is superposed to the Raman signal due to the resonant excitation. To reduce the number of nanocrystals necessary for detection, excitation techniques such as surface plasmon resonance (SPR) can be used to greatly enhanced the Raman scattering intensity.³

In this article, we investigate resonant Raman scattering of CdSe nanocrystals embedded in nanometric thick sol–gel SiO₂ films. In order to probe very small quantities of nanocrystals, we have studied their optical properties by coupling classical Raman spectroscopy with SPR. This method has two main advantages. First the SPR enhances of the Raman light scattering, improving significantly the detection sensitivity of a classical Raman experiment. Second, in adapted conditions, the luminescence can be quenched and only the Raman signal is observed. The SPR was obtained in the so-called Kretschmann geometry, which consists of a prism and a thin silver film covered by the sol–gel layer containing CdSe nanocrystals.³ This setup allows excitation of the metal/thin film interface surface plasmon polariton (SPP) with incident light coming from within the prism.

We first describe sample preparation: silver layer and thin film (SiO₂) are made by the sol–gel process in which CdSe nanocrystals are included. In order to determine the microstructural properties of CdSe nanocrystals embedded in the thin SiO₂ layer a transmission electron microscopy (TEM) study is conducted in the second part. In the third part, we present Raman scattering and luminescence results obtained when studying two different thickness layers containing CdSe nanocrystals. Finally, the different lumines-

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cence results are discussed and in particular, the efficiency of the various competing radiative and nonradiative energy transfer processes.

SAMPLE PREPARATION

Thin silver films were electron gun deposited onto a pre-cleaned Pyrex® glass with refractive index=1.472 at $\lambda=514.5$ nm under a vacuum of 10^{-6} Torr. The deposited thickness was 50 ± 0.5 nm and the evaporation rate was 0.5 nm/s as measured by a quartz balance. This thickness was chosen to optimize the light coupling effect. The growth rate was fixed to give a smooth metal surface. A detailed parameters study of this thin silver film is presented elsewhere.^{4,5}

The solution used to fabricate thin SiO₂ films has been prepared by the sol-gel route following the procedure already described.⁶ The preparation of CdSe particles added in this SiO₂ solution is presented in details by Ptatschek *et al.*⁷ Thin SiO₂ films embedded in CdSe nanocrystals are then deposited with a dip-coating apparatus^{8,9} on the silver layer preliminary evaporated onto a pre-cleaned glass. The resulting films were first dried at a temperature of 100 °C for 10 min. The films were continuous and crack free as proven by micro-optical observations. Their thicknesses were controlled by adjusting the SiO₂ sol viscosity. When the hydrolysis and condensation reactions had been performed, ethanol was added to the solution. This addition was made just to dilute the sol without changing the chemical reactions. The coated sample was then annealed under an infrared lamp at a temperature around 300 °C with a permanent O₂ flow for 15 min to densify the deposited film and to eliminate carbon residues without destroying the silver layer.

STRUCTURAL STUDY

Results were obtained on two samples hereafter denoted as samples A and B prepared in nearly the same way. For sample A, only one layer of the sol was deposited on the silver layer after which the annealing treatment described above was realized. For sample B, two sol-gel layers were deposited with a heat treatment made after each deposit. The SiO₂ film thicknesses, d_i , and refractive indices, n_i , were measured by a solid phase epitaxy (SPE) optical setup described previously.¹⁰ The optogeometric parameters of samples A and B were measured to be $d_a=19.3\pm 0.5$ nm and $n_a=1.52\pm 0.01$ and $d_b=31.5\pm 0.5$ nm and $n_b=1.50\pm 0.01$, respectively. These measurements have been performed with a He-Ne laser at a wavelength of 632.8 nm. Conventional TEM (CTEM) studies have been performed on a TOPCON EM-002B working at 200 kV to obtain a representative picture of the samples and to study the CdSe nanocrystals dispersion and structure. For this study, the sol-gel thin films were peeled off and deposited onto a 3 mm copper grid for direct observation.

One image from the study is presented in Fig. 1. The CTEM micrograph shows clearly CdSe nanocrystals in dark embedded in the amorphous SiO₂ matrix. The CdSe nanoparticles were well resolved in the CTEM images. The size distribution is presented in Fig. 2 which shows an average diameter of 3.1 nm. The number of CdSe nanocrystals in-

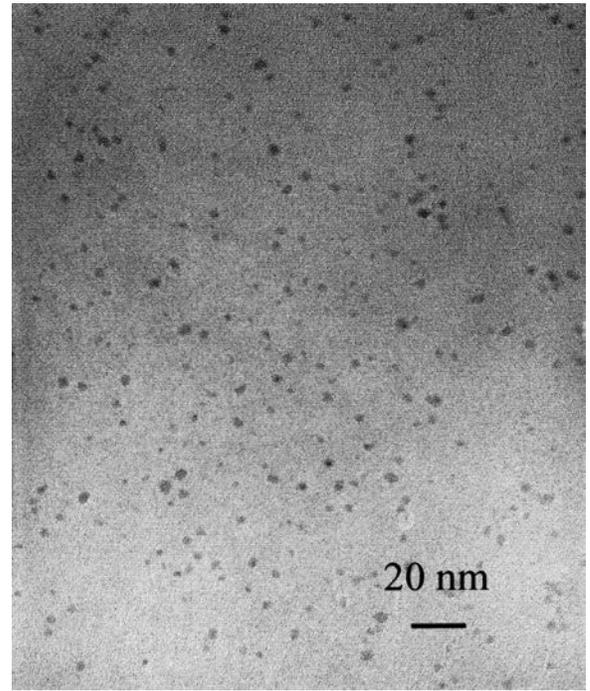


FIG. 1. CTEM micrograph of sample A.

cluded in a volume of $1 \mu\text{m}^3$ can be measured from Fig. 1. Considering that particles exhibit a rather spherical shape with a mean diameter of 3.1 nm, we can calculate that the volume occupied by the particles represents 1.7% of the total volume of sample A, assuming a homogeneous dispersion of the nanocrystals in the sol, then in the layer. This value is very close to the 1.5% chosen for the sample elaboration during the doping process.

In order to determine the crystalline phase of CdSe nanocrystals, a high resolution TEM study has been conducted on sample A. A typical micrograph is shown in Fig. 3. The crystalline phase is the cubic zinc blende with indexed planes (220) and (311).

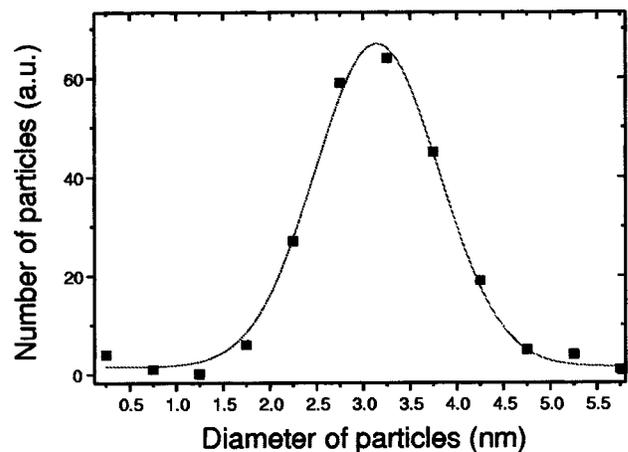


FIG. 2. Size distribution of CdSe nanocrystals embedded in the sol-gel SiO₂ ultrathin film (sample A).

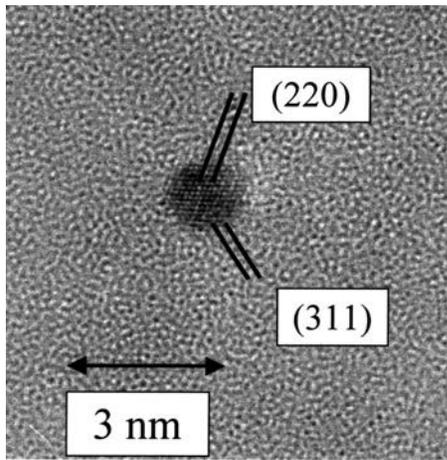


FIG. 3. Typical CdSe nanocrystals measured at 3 nm diameter embedded in the sol-gel matrix.

OPTICAL STUDY

The optical device used to perform the Raman experiment is shown in Fig. 4. The sample is positioned on the back surface of the prism. The mirror M1 is then adjusted so that the laser beam is incident on the sample at the surface plasmon resonance angle. The Raman signal is collected on the top of the sample using a XY Dilor triple spectrometer followed by a nitrogen cooled charge coupled device. Details of the experimental setup are given in a previous article.¹¹ In Fig. 5, we compare Raman spectra obtained on sample A using Raman spectroscopy enhanced by SPP [Fig. 5(a)] and conventional backscattering Raman spectroscopy [Fig. 5(b)], respectively, using the 514 nm wavelength as excitation provided by an argon-krypton laser (power 40 mW). In the first case, we can observe the Raman longitudinal optical 1LO and 2LO peaks of CdSe nanocrystals. These peaks observed at 205 and 410 cm^{-1} correspond to the two first orders of CdSe nanocrystals lattice vibrations. In the second case, no Raman signal can be distinguished from the background noise. This figure confirms clearly the necessity to use surface plasmon excitation to enhance Raman intensity and then to perform the Raman experiment with a good resolution.

Optical results obtained on sample A in Raman spectroscopy enhanced by SPP excited using different wavelengths is shown in Fig. 6. For wavelength of excitations 488 and 514.5 nm, the two Raman peaks 1LO and 2LO can be observed. The determination of the full width at half maximum of the

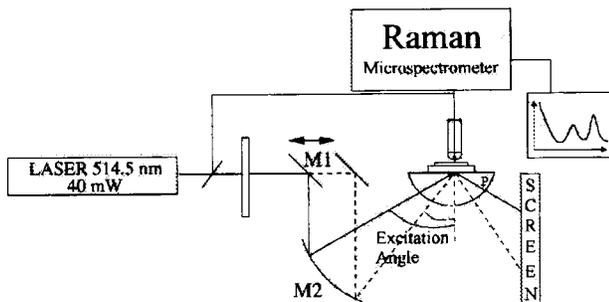


FIG. 4. Optical device used in micro-Raman experiment.

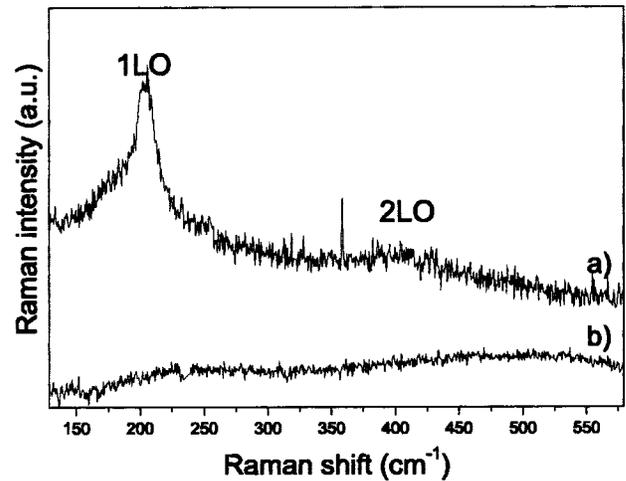


FIG. 5. Raman spectra of sample A in SPE configuration (a) and in conventional configuration (b).

first peak allows us to calculate the mean nanocrystals size at 3.1 nm.^{7,12,13} This value is in fair agreement with the mean diameter already deduced from TEM observation on the same sample. Furthermore, the shoulder on the asymmetry of the low frequency side of the peak 1LO has been attributed to other optical modes.¹⁴

For an excitation wavelength of 647.1 nm, no Raman signal has been observed. The absorption curve presented in Fig. 7 shows that this wavelength is far from the absorption bands of CdSe nanocrystals. This observation underlines the need to use the resonant Raman effect to produce a significant signal, especially when the amount of studied nanocrystals is low. At the contrary, in the case of excitation with wavelengths 488 and 514.5 nm inside to the absorption bands, the two Raman peaks 1LO and 2LO can be observed. Finally, the two previous figures show clearly that for a very low quantity of nanocrystals (≈ 5000), only the configuration of Raman resonant effect coupled with surface plasmon excitation allows the CdSe nanocrystals structure study.

In order to compare optical results in the two Raman experimental configurations, a thicker sample was made to obtain significant signal in the conventional backscattering Raman configuration. Figure 8 is devoted to a comparison of the curves (a) and (b) corresponding to the Raman spectra of

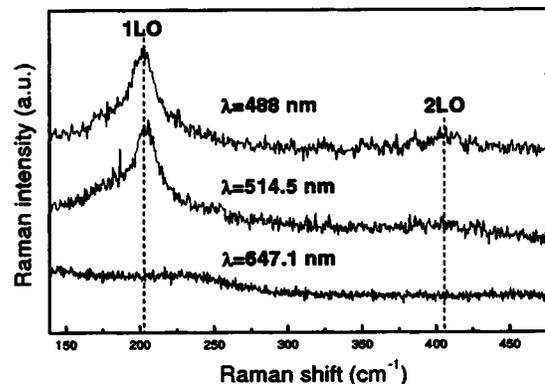


FIG. 6. Raman spectra of sample A obtained at different excitation wavelengths: 647.1, 514.5, and 454 nm.

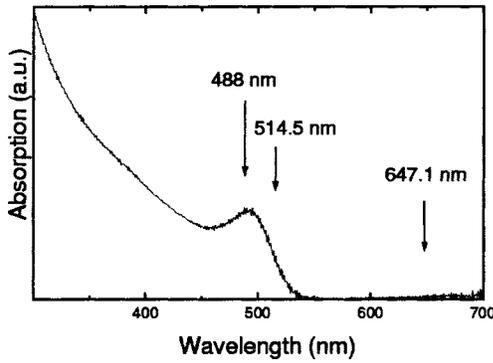


FIG. 7. Absorption spectra of CdSe nanocrystals embedded in a bulk SiO₂ matrix.

a bulk sample (thickness around 20 μm) composed of CdSe nanocrystals embedded in a SiO₂ sol-gel matrix, and the Raman spectra of sample A, respectively. The Raman spectrum Fig. 8(a) has been obtained in a conventional Raman spectroscopy experiment with an excitation at 514.5 nm without excitation of surface plasmons. For comparison, the Raman spectrum Fig. 8(b) corresponds to the one reported in Fig. 6 at 514.5 nm in our configuration of resonant Raman excited by surface plasmon. In the spectrum associated to bulk study, an intense luminescence background caused by radiative recombination is observed in Fig. 8(a). In this case, the luminescence background is an undesirable effect for the observation of the 2LO Raman peak of CdSe nanocrystals. Moreover, the asymmetry of the 1LO peak is not as well resolved as in sample A. When studying sample A, this luminescence background is not observed, allowing the well-resolved observation of peaks 1LO and 2LO. Compared with Raman spectra of the similarly doped bulk samples, these measurements allow better resolution of Raman peaks without luminescence contribution.

In order to explain this lack of luminescence emission, we have to take into account the metal layer. The behavior of the CdSe nanoparticles excited by surface plasmon depends on its local environment and thus on the efficiency of the various competing radiative and nonradiative energy transfer processes as a function of the metal-nanocrystals separation. Generally, two contributing factors are in competition:¹⁵

- (1) the enhancement of the particle absorption energy due to the surface plasmon resonance and
- (2) the nonradiative energy transfer processes from the particle to the metal.

The first effect will be maximum if the particle is located very close to the metal, e.g., where the electromagnetic field enhanced by SPR is the more intense. However, the part of this absorbed energy which can be radiatively dissipated will achieve the highest value for a precise metal-particle separation distance depending on the system geometry. This distance is governed by the relative rate of the decay channels available. Theoretical and experimental results¹⁶⁻¹⁸ in our study, taking into account a planar geometry, show that placing the particle close to the metallic film will introduce additional nonradiative decay channels, causing the fluorescence intensity quenching. An important nonradiative decay channel for a particle very close to the metal is the direct coupling of the excited particle to SPP; this decay channel typically becomes dominant for metal-particle separation around 20 nm.^{18,19} If this separation decreases below 20 nm, other nonradiative decay channels become important such as a direct Joule heating of the metal or an excitation of electron-hole pairs in the metal.^{20,21}

In order to confirm and analyze the evolution of the luminescence signal intensity as a function of the metal-particle separation distance, we have realized the sample labeled B which exhibits a 31.5 nm thickness. Luminescence spectrum of this sample B has been excited using a 454 nm wavelength (power \approx 40 mW). The conventional luminescence spectrum of CdSe nanocrystals embedded in the bulk SiO₂ matrix is shown in Fig. 9(a). This spectrum presents two broadbands. The first band labeled α is due to direct “intrinsic” recombination, and the second, at lower energy, is due to trapped carrier recombination in levels band gap. This band is labeled β in Fig. 9(a). In Fig. 9(b), the spectrum obtained when studying sample B in SPR configuration is presented and only exhibits the peak β . This β band corresponds to the surface defects of CdSe nanoparticles embedded in a SiO₂ ultrathin film. The SiO₂ matrix is necessary for the luminescence emitting process because of its interaction with the CdSe nanoparticles. Moreover, taking into account the CdSe nanocrystals size at about 3.1 nm, the large

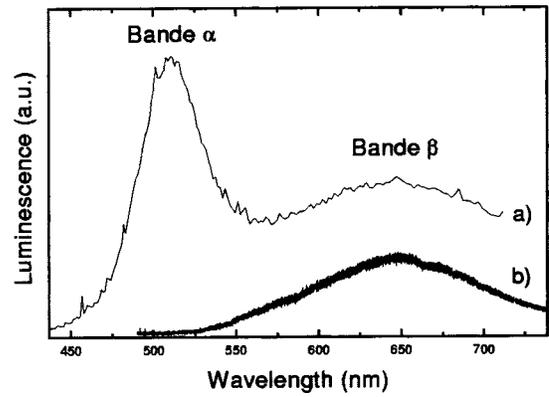


FIG. 9. Luminescence spectra of CdSe nanocrystals embedded in a bulk SiO₂ matrix (a) and of sample B (b).

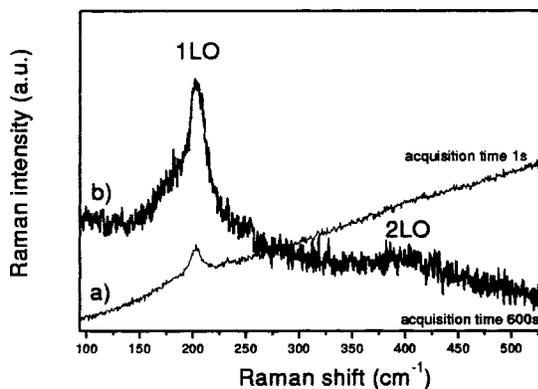


FIG. 8. Raman spectra obtained at 514.5 nm of CdSe nanocrystals embedded in a bulk SiO₂ matrix (a) and of sample A (b).

surface–volume ratio explains the high luminescence dependence on the nanocrystals surface defects. In sample A, surface defect luminescence dominates the “intrinsic” one. These surface defects are due to the strong reactivity between silver and selenium which induces formation of AgSe and Ag₂Se compounds.

In the thinner sample A (thickness 19.1 nm), no luminescence signal has been observed. For such a sample in this case, the CdSe nanocrystals are very close to the metallic layer, creating new nonradiative decay channels. As a consequence, radiative CdSe nanocrystal emission is quenched.¹⁸

CONCLUSION

In this work, Raman scattering of around 5000 CdSe nanocrystals included in a very thin SiO₂ film has been investigated by surface plasmon resonance in a resonant Raman spectroscopy experiment. By comparison with Raman spectroscopy study of a bulk sample, we show that our specific experimental configuration can avoid the luminescence background signal and then improve Raman scattering measurements. In such resonance configuration, Raman bands from CdSe nanocrystals have been clearly observed and assigned. This configuration is well adapted when studying a small amount of doped material and following effects of interactions between nanocrystals and the surrounding matrix. The luminescence has been measured and examined. Its dependence on the separation distance between the metal layer and CdSe nanocrystals is analyzed, showing the great sensitivity of the luminescence emission due to surface defects.

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