

Three-dimensional mapping of photoluminescence and Raman spectra

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Abstract The mapping system, *Nanofinder*[®], has been developed, which allows to achieve simultaneously a high time, space and spectral resolution and allows the measurements on a single particle or region-of-interest, which is selected after a pre-scan. All this is available in real three-dimensional (3D) measurement due to confocal scheme.

1 Introduction

3D resolution added to a standard spectral characterization is prospective for the measurements on living organisms, also can be applied for a property characterization of photonic crystals and solid state materials.

2 Experimental

For a presented confocal microscope detection scheme the lateral, L , and axial, A , resolutions are given by: $L = 0.44\bar{\lambda}/NA$ and $A = 0.75\bar{\lambda}/(n - \sqrt{n^2 - NA^2})$ (at FWHM), where $\bar{\lambda} = \sqrt{2}\lambda_{EX}\lambda_{EM}/\sqrt{\lambda_{EX}^2 + \lambda_{EM}^2}$ is the mean wavelength of excitation, λ_{EX} , and emission, λ_{EM} [1]; n is the refractive index at the focus, and NA is the numerical aperture of the focusing optics. The values of *Lateral* and *Axial* resolutions are 186 nm and 436 nm, respectively, for optics with $NA = 0.95$ and GaN-based LED laser operating at 400 nm.

2.1 Resolutions

The modular system of *Nanofinder*[®] is based on a continuous wave or pulsed laser as an excitation light source (standard optical setup is transmittive from 380 nm up to near-infrared spectral region), confocal far-field optical microscope, XYZ-piezo-stage and spectrometer. The optional equipment such as CCD, photo-multiplier tube with single photon counting facilities, a set of notch filters and polarizers entitles to expand the functionality towards a 3D mapping of Raman and photoluminescence (PL) intensity (with a possible discrimination in polarization) as well as a photoluminescence decay-time-constant mapping. High spectral (1 cm^{-1}), spatial ($200 \times 200 \times 500\text{ nm}^3$) and time (35 ps) scanning resolutions and high signal throughput 15-30% are achieved in the accessible spectral region of 330-1100 nm. Up to 20 spectral regions-of-interest can be selected and scanned simultaneously. Combining mathematical processing and mapping data, the sensitivity close to a single nanocrystal

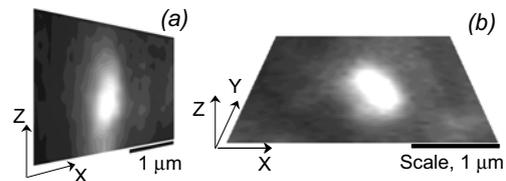


Fig. 1 Axial (a) and lateral (b) maps of PL at 520 nm excited by 400 nm illumination from cluster of CdS colloids. Scanning step was 100 nm and numerical aperture of objective lens $NA = 0.95$.

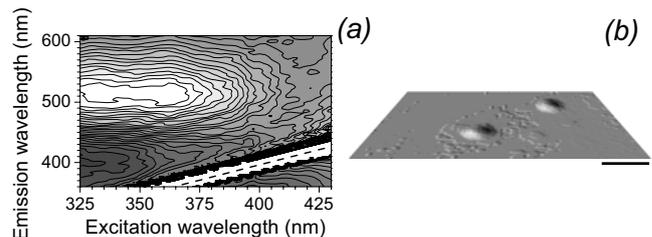


Fig. 2 (a) PL excitation spectra of CdS colloids with absorption maximum at 385 nm immobilized in PMMA film. Dashed line marks the 1st order of excitation diffraction. (b) Lateral PL map from the most small detectable clusters of CdS colloids. Excitation-registration conditions are same as in Fig.1. Scanning step was 100 nm and numerical aperture of objective lens $NA = 0.95$. Scale bar, 1 μm .

tal with radii ca. 5 nm detection is achieved. The real size of luminous particle is calculated from the wavelength of the absorption peak.

2.2 Samples

Colloidal particles of CdS were prepared from 2.5 mmol N,N -dimethylformamide (DMF) solution of cadmium acetate and thiourea. Mixture was kept for a fixed duration of 3-5 s in microwave oven at 200 W to obtain CdS particles, which have distinct absorption band at 370-385 nm, respectively. Colloids were immobilized into PMMA film by casting 0.4-0.7 mm thick film with final CdS concentration of 17 wt%.

For Raman mapping we used chemical vapor deposition (CVD) grown diamond array [2]. Diamond-like material was deposited inside SiO_2 pits of few- μm in diameter (specified where it applies) on Pt (200 nm), which

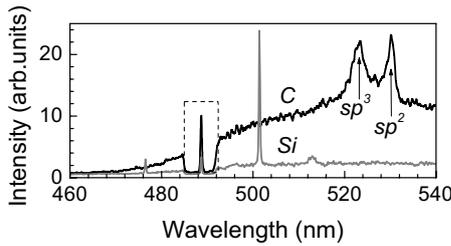


Fig. 3 Raman spectrum of CVD-grown diamond|graphite island [2]. The diamond-like line at 1332 cm^{-1} (at ca. 522 nm) is marked as sp^3 . Graphite-like line is marked as sp^2 ; Raman shift for Stokes and anti-Stokes lines of Si is 520 cm^{-1} . Excitation was at 488 nm (laser line and notch filter profile are enclosed in dashed box).

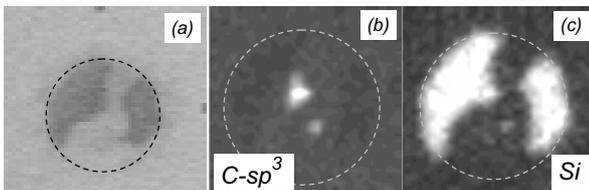


Fig. 4 Raman mapping of diamond CVD-grown on Pt in a $6\text{ }\mu\text{m}$ -diameter hole (shown by dashed circles) made in SiO_2 . (a) Optical reflection image of the deposition pit. The darkest regions are those where Pt was removed and a Si substrate became exposed. (b) Mapping was carried out at 1332 cm^{-1} line (522 nm in Fig. 3). (c) Map recorded at Si Raman line of 520 cm^{-1} (501 nm in Fig. 3).

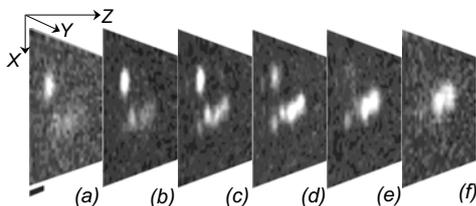


Fig. 5 Raman mapping of diamond CVD-grown on Pt in a $2\text{ }\mu\text{m}$ -diameter hole. Mapping was carried out at 1332 cm^{-1} line. The images (a-f) are each separated by $0.4\text{ }\mu\text{m}$. Scale bar, $1\text{ }\mu\text{m}$.

was coated over Si substrate. Diamond was formed preferentially inside the pits due to a large, ca. 10^6 times, difference in a nucleation rate on Pt and SiO_2 .

3 Results and Discussion

Two perpendicular cross-sections of PL from a cluster of CdS colloids is presented in Fig. 1. The colloidal solution had a distinct absorption band centered at 385 nm . Corresponding PL excitation spectra (Fig. 2(a)) shows that an excitation shorter than ca. 390 nm is necessary to observe the PL with its maximum at 515 nm . This PL band was used for mapping. An example of detectable CdS colloids cluster is given in Fig. 2(b). Particles as small as 200 nm were observed (FWHM measure of PL intensity profile). Real size of luminous CdS nanocrystal (nc) can be calculated from the bandgap energy E_g , which is dependent on the radius of nc and in the case

of CdS reads [3]:

$$E_g = E_{bulk} + \frac{\pi^2 \hbar^2}{2r^2} \left(\frac{1}{m_e^*} + \frac{1}{m_h^*} \right) - 1.8 \frac{e^2}{\epsilon r}, \quad (1)$$

here $E_{bulk} = 2.489\text{ eV}$ is the bandgap energy of bulk CdS at room temperature, $m_{e,h}^*$ are effective masses of electrons and holes respectively, e is the electron charge, ϵ and r are dielectric susceptibility and nc-radius, respectively. For $r[\text{nm}]$, the eqn. 1 is $E_g = 2.489 + 2.45/r^2 - 0.45/r$. Then the absorption at 385 nm corresponds to the nc-CdS of 2.15 nm , the size, which is smaller than Bohr radius of 2.8 nm in bulk CdS, and, consequently, the strong optical nonlinearities are expected [4]. How many colloidal particles were forming the luminous object, which was optically unresolved by direct observation, is uncertain. Segregation of nc-CdS was observed taking place on the hourly time scale in colloidal suspension. The nc - CdS containing PMMA films were prepared in 1-2 min, but still the real size of nc-CdS clusters and their size distribution inside samples is unknown. However, we think that the availability of real 3D PL mapping with actual sensitivity of PL registration down to 1 photon out of 15 will prove helpful in characterization of nc particles.

Mapping at a selected Raman scattering line was achieved on a Si substrate coated by Pt (200 nm) and SiO_2 . The carbon was deposited by CVD into the pits dry-etched in a top SiO_2 layer. Two forms of carbon were found: diamond-like with sp^3 electronic structure and graphite-like with sp^2 shell. Diamond was recognized by its Raman line at 1332 cm^{-1} . Si Raman line at 520 cm^{-1} was also observed from the locations where dry etching was removing the inner Pt layer as well as an outer SiO_2 (Fig. 3). Fig. 4 shows an optical image and Raman maps recorded at corresponding diamond and Si scattering lines. Locations of deposition of different materials are clearly distinguished (Fig. 4). This approach allowed us to obtain sectioning of the C deposition site at different depths (Fig. 5).

4 Conclusions

A versatile setup (realized in *Nanofinder*[®]) in demonstrated, which allows extended optical characterization of different samples with combined high spatial (ca. $< 200\text{ nm}$), spectral (width of Raman line), and time (down to fewtens-of-ps) resolutions.

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