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Laser writing of semiconductor nanoparticles and quantum dots

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Silica aerogels were patterned with CdS using a photolithographic technique based on local heating with infrared (IR) light. The solvent of silica hydrogels was exchanged with an aqueous solution of the precursors CdNO₃ and NH₄OH, all precooled to a temperature of 5 °C. Half of the bathing solution was then replaced by a thiourea solution. After thiourea diffused into the hydrogels, the samples were exposed to a focused IR beam from a continuous wave, Nd-YAG laser. The precursors reacted in the spots heated by the IR beam to form CdS nanoparticles. We lithographed features with a diameter of about 40 μm, which extended inside the monoliths for up to 4 mm. Samples were characterized with transmission electron microscopy and optical absorption, photoluminescence, and Raman spectroscopies. Spots illuminated by the IR beam were made up by CdS nanoparticles dispersed in a silica matrix. The CdS nanoparticles had a diameter in the 4–6 nm range in samples exposed for 4 min to the IR beam, and of up to 100 nm in samples exposed for 10 min. © 2004 American Institute of Physics. [DOI: 10.1063/1.1836000]

Photolithographic patterning of sol-gel materials is becoming increasingly important for optical and electronic applications, and for data storage and encryption. Surface patterning can be employed to realize electrical contacts,¹ and diffraction gratings.^{2,3} Patterning can also have a more three-dimensional character, and the lithographed features can extend from the surface deep into the bulk of the materials.⁴ “True” three-dimensional patterning, i.e., formation of patterns in the bulk of the materials but not on their surface, is achieved with multiphoton ionization techniques.^{5,6}

Patterning with these techniques is attained in two simple steps, impregnation of the matrices with a solution of metal ions followed by photoreduction. However, patterns can be produced only out of materials accessible to photoreduction, usually noble and semi-noble metals. Patterning of sol-gel materials with electronically active components like semiconductors and magnetic materials usually requires multiple steps. The (preformed) active phase is added during gelification of the matrix,^{7–9} or synthesized by calcination of precursors.^{10–13} The resulting composites are homogeneously loaded with the active phase, and patterning is achieved by etching.

We report here a photolithographic technique that allows patterning of porous materials with electronically active materials. In our technique, the porous matrix is washed with a

solution of the precursors, which react to form nanoparticles in the spots heated by an IR laser. The experiments described here focus on photolithography of CdS nanoparticles inside a silica hydrogel. The mean size of the CdS nanoparticles can be increased from a few nanometers to about 100 nm by increasing the exposure to the IR beam. The hydrogel is subsequently dried in supercritical CO₂ to form an aerogel. Our technique, however, is more general. It can produce patterns of metals and magnetic materials, and can be probably extended to other porous matrices. For example, we have successfully patterned silica aerogels with Ag by irradiating solutions of AgNO₃ and formaldehyde, and with Fe (and Fe oxides) by irradiating solutions of Fe-triethanolamine complexes and hydrazine.¹⁴ These results will be reported in a forthcoming publication.¹⁵

Silica hydrogels were prepared with a conventional base-catalyzed route.^{4,16} The hydrogels were then washed in methanol and in water, and placed in a refrigerator kept at 5 °C. CdS was synthesized by hydrolyzing thiourea in basic solution.^{17–21} Hydrogels were bathed in a precooled aqueous solution of CdNO₃ (1 mol·l⁻¹) and NH₄OH (4 mol·l⁻¹). After about 2 h, half of the bathing solution was removed from the vial, and was replaced by a 1 mol·l⁻¹ thiourea solution. The samples were left in the refrigerator for an additional hour to let thiourea diffuse inside the monoliths. Cooling was necessary, since hydrogels loaded with the precursors turned pale yellow within about 1 h when kept at room temperature. The monoliths did not appreciably change their color when refrigerated. The samples were then rapidly removed from the refrigerator, placed in a glass cuvette, and exposed to the

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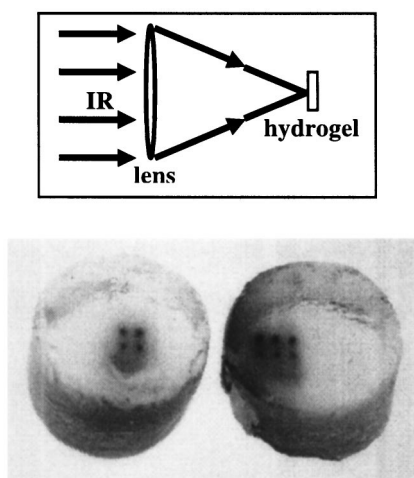


FIG. 1. Top: Schematic representation of the illumination arrangement. Bottom: digital camera image showing arrays of CdS spots photolithographed in two aerogel monoliths. The diameter of the aerogel monoliths was about 7 mm, and the diameter of the circular spots was about 400 μm .

light of a continuous wave Nd-YAG laser. The IR power on the sample was typically 1.8 W. Nanoparticle formation was monitored with transmission electron microscopy (TEM) and by observing the coloration of the illuminated spots. Nanoparticles started forming and the spots started becoming yellow after an irradiation time of about 4 min. The spots kept becoming darker (and the particles somewhat larger, and more densely distributed) for another 6 min. We did not notice any relevant changes afterwards. We then compared this reaction time with the reaction time of hydrogels that were loaded with the precursors and placed in a constant temperature bath. The reaction time was about 10 min at temperatures below 35°C, and of a few seconds at temperatures higher than 60°C. We thus estimated that the local temperature was between 35 and 60°C. After exposure, the samples were immediately washed several times in cold distilled water to quench any further reaction of the precursors. To produce aerogels, the hydrogels were washed in methanol and in acetone, and were then dried in supercritical CO₂.

Arrays of circular spots photolithographed with our technique are shown in Fig. 1. By varying the focal length of the lens and the distance between the hydrogel surface and the lens focus, the diameter of the spots could be varied between 40 and 400 μm , and the penetration depth from a few microns to a few millimeters. The size and color of the spots did not change upon washing and supercritical drying, indicating that CdS was neither chemically altered nor removed by the washings, in agreement with our previous patterning experiments.⁴ After drying, regions lithographed with CdS were carved out of the matrix and crushed. The powder was analyzed with TEM. Typical micrographs of samples ex-

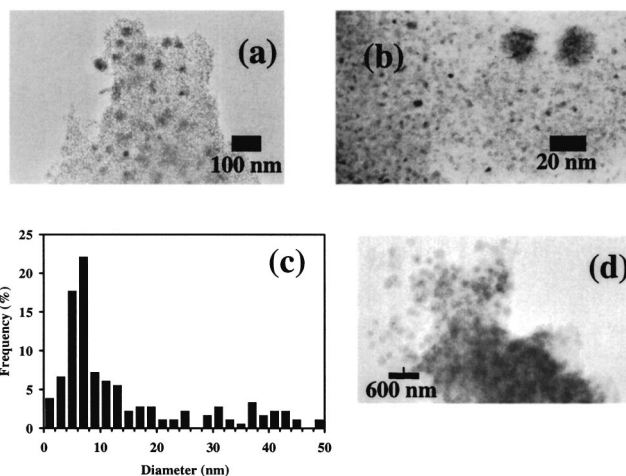


FIG. 2. (a), (b) Bright field micrographs of CdS-patterned silica aerogels. IR exposure was 4 min. (c) Corresponding size distribution histogram. (d) Same as above, for an IR exposure of 10 min.

posed for 4 min to the IR beam are reported in Figs. 2(a) and 2(b). CdS nanoparticles appeared as dark spots, and were fairly uniformly distributed within the silica matrix. Energy-dispersive x-ray chemical analysis showed that the composition of the particles was 55% Cd–45% S, comparable to the composition of the bathing solution. High magnification micrographs [Fig. 2(b)] showed that particles with a typical diameter of 20 nm coexisted with a large number of particles with a diameter of a few nanometers. A size distribution histogram is reported in Fig. 2(c). The mean particle size was around 7 nm. With increasing exposure to the IR beam, the nanoparticles became larger (~100 nm) and more densely packed, as shown in Fig. 2(d). This indicated that growth of preformed particles prevailed on nucleation of new particles, consistent with our previous findings on the synthesis of Ag nanoparticles in silica aerogels.¹⁶ Preliminary results show that the size of the nanoparticles did not depend strongly on laser power within the range accessible to our instrument (1–7 W, measured at the sample). A complete investigation of the factors affecting nanoparticle size will be reported in a separate publication.¹⁵

Samples were additionally characterized with optical absorption, photoluminescence and Raman spectroscopies. Room temperature absorption and photoluminescence (PL) spectra are reported in Fig. 3(a). The absorption spectrum exhibited an excitonic shoulder at about 440 nm, characteristic of CdS nanoparticles with a diameter in the 4–4.5 nm range.²² PL spectra exhibited a peak around 475 nm and a shoulder around 520 nm. A peak around 475 nm has been found in CdS/silica composites with a CdS nanoparticle diameter between 4 and 5 nm.^{23–25} The shoulder at 520 nm was probably due to particles with a larger diameter,²⁴ but

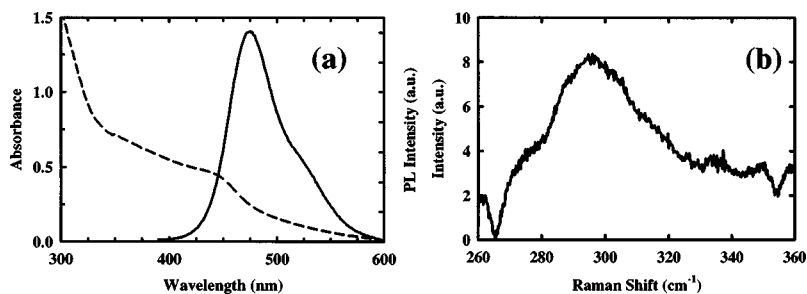


FIG. 3. (a) Room temperature absorption (dashed line) and photoluminescence (solid line) of silica aerogel samples patterned with CdS. PL was excited at 350 nm. (b) Room temperature Raman spectra of silica aerogel samples patterned with CdS. IR exposure was 4 min for all samples.

may also be due to recombination at surface defects.^{23,25} Formation of defects at the surface of CdS nanoparticles is not surprising, since the nanoparticles are probably nucleated at and remain in contact with the pore walls.^{26,27} Spots exposed for long times to the IR beam were optically dense, and their absorption spectrum could not be measured. PL intensity from these samples was absent or below the detection limit of our instrumentation. Raman spectra, shown in Fig. 3(b), exhibited a peak at 298 cm^{-1} . This frequency was in good agreement with previous Raman measurements of CdS/silica composites,²⁸ and corresponded to the first-order LO phonon frequency of CdS. The full width at half maximum of the Raman peak was 36 cm^{-1} , which was found to correspond to a mean particle size of about 3 nm in CdS/silicon dioxide films.²⁹

Optical characterization confirmed the chemical identity of the CdS nanoparticles. It also showed that a relevant fraction of nanoparticles exhibited quantum confinement effects in samples exposed for a short time to the IR beam. The mean particle size determined with linear optical spectroscopies was between 3 and 5 nm. The difference with the TEM mean size ($\sim 7\text{ nm}$) is not irreconcilable, since the TEM size determination procedure was probably skewed toward large sizes. Small CdS particles could hardly be distinguished from the silica matrix, and we counted only particles with regular shapes which showed a large contrast. Mean sizes determined with optical spectroscopies also have a fairly large indetermination, the main sources of error being polydispersity and surface defects.^{25,30}

In conclusion, we have shown a simple method to pattern silica aerogels with CdS. Our method is quite general, and can be extended to other semiconductors, to magnetic materials, to metals, and also to other porous matrices. Size control is reasonable, and can probably be improved by adding surfactants to the bathing solution, or by employing matrices with a uniform pore size like MCM-41¹³ or porous anodized alumina.²⁸ The main challenge of our technique concerns the choice of the precursors. These must not react rapidly at room temperature, otherwise the composites will be uniformly loaded with the active phase. The reaction cannot require too high temperatures, because these need high laser powers, which can damage the host matrix. In the experiments described here, the reaction rate is tuned by varying the NH_4OH concentration. When the concentration of NH_4OH is too low, most of the Cd precipitates as $\text{Cd}(\text{OH})_2$, and does not diffuse inside the hydrogel. $\text{Cd}(\text{OH})_2$ also catalyzes hydrolysis of thiourea, and CdS forms rapidly even in cold samples. At high NH_4OH concentrations, $\text{Cd}(\text{NH}_3)_4^{2+}$ complexes are formed. These complexes are water soluble, and they diffuse inside the matrix. They also do not catalyze hydrolysis of thiourea as strongly as $\text{Cd}(\text{OH})_2$. Temperatures

of the order of $35\text{--}60^\circ\text{C}$ are required to hydrolyze thiourea at an appreciable rate,¹⁷ and these temperatures are easily reached with IR irradiation.

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