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X-RAY LITHOGRAPHY OF METAL AND SEMICONDUCTOR NANOPARTICLES

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In the last few years, a considerable amount of research has focused on the three-dimensional fabrication of contacts and electronic devices. Most techniques, however, are essentially based on photoreduction, and are limited to noble- and semi-noble metals. We present here a general method that allows patterning of porous matrices in 3D with metal, but also with semiconductor nanoparticles which is of potential relevance for microfabrication applications.

Our method possesses several attractive features. Sample preparation is very simple; the technique has a bottom-up character; it allows access to a wide number of materials, such as noble metals and II-VI semiconductor precursors. The bathing solution contained Cd(NO3)2 or Pb(NO3)2 in a concentration of 0.1 M. Precursors diffuse inside the gels in 1-2 hours, and prevent unreacted precursors from reaching the surface of the monoliths. The patterns have the same resolution than the masks, i.e., around 10 µm, and extend into the bulk of the monoliths for up to a depth of 12 mm.

The mechanism of Ag pattern formation is closely related to the gamma radiolysis process. In gamma radiolysis, reduction of metal ions to form homo- and heteronuclear clusters of transition metals is initiated by formation of solvated electrons, \( e_{aq} \) (eq 1), which reduce metal ions \( M^{n+} \) to metal atoms (eqs 2, 3). Metal atoms eventually form aggregates, \( M_n \) (eq 4).

\[ H_2O \rightarrow e_{aq}, H^+, OH^- \]  
\[ Pb^{2+} + 2e_{aq} \rightarrow Pb \]  
\[ Mn \rightarrow M_n \]  

In previous publications we showed that noble metal nanoparticles formed inside hydrogel monoliths irradiated with gamma- or X-rays. In the experiments with gamma rays, masking was clearly impossible, and hydrogels were obtained which were homogeneously loaded with metal particles. In our preliminary experiments with X-rays, relative primitive patterns were obtained by translating a monolith in front of a small beam-defining aperture. Figure 1 shows, instead, that patterns of any complexity could be obtained by masking; the patterns are transferred faithfully to the hydrogels and were seen to penetrate inside the monoliths for up to 12 mm. Patterns were formed readily with X-ray lithography. Typically, an exposure to 85 mA · minute was sufficient to generate clearly visible patterns. This exposure is very low when compared to more conventional X-ray lithography processes such as LIGA. These processes are usually based on radiation-induced cross-linking of polymers like poly(methyl metacrylate) (PMMA) which require extremely lengthy exposures. On our apparatus, PMMA structures were obtained after exposures on the order of 40000 mA · minute.

For chalcogendie formation, the mechanism is probably of indirect nature. The chalcogenide precursors were aliphatic alcohols carrying a thiol group such as 2-mercaptoethanol. These compounds are dissociated and liberate SH when they react with the solvated electrons and the radicals produced when water is ionized by X-rays. The overall reaction is reported in Eqs. (5-7). Reduction of the metal ions by solvated electrons, Eq. (8), was prevented by working in excess RSH, typically 10-100 times the metal ions concentration.

\[ H_2O \rightarrow e_{aq}, H^+, OH^- \]  
\[ HOCH2CH2SH + e_{aq} \rightarrow SH^- + CH3CH2OH \]  
\[ SH^- + Pb^{2+} \rightarrow PbS + H^+ \]  
[PHb] 2+ + 2e_{aq} \rightarrow Pb0 (8)

The composites were characterized in our previous reports with techniques such as Raman spectroscopy, transmission electron microscopy, X-Ray diffraction, and X-Ray photoelectron spectroscopy. All these techniques showed that the nanoparticles were free of contamination, and that they had a bulk crystalline structure. In this work we characterized the nanoparticles with Raman spectroscopy, and the results were in agreement with our previous research.
X-Ray lithography. A peak at 303 cm⁻¹ was measured for CdS. This frequency is in good agreement with previous measurements of CdS/silica composites, and corresponds to the first-order longitudinal optical (LO) phonon. The interpretation of the Raman results for PbS is more complex. The LO phonon of crystalline PbS at ~205 cm⁻¹ in normal Raman scattering is forbidden. However, by using an excitation source close to the intergap energies allows the forbidden Raman bands through the Fröhlich interaction mechanism. The Raman spectrum of bulk PbS contains mainly three peaks at 154, 204, and 454 cm⁻¹. The 154 cm⁻¹ peak is a combination of a transverse acoustic (TA) and a transverse optic (TO) phonon; the 204 peak is the first-order LO phonon and the 450 is the first overtone of the LO phonon (2LO). Our Raman measurements from a PbS powder show the first-order LO phonon at 200 cm⁻¹ and a peak at 143 cm⁻¹ which probably arises due to a combination of TA and TO phonons. The Raman spectrum from monoliths patterned with PbS shows the second and the third order LO phonons peaks at 440 and 610 cm⁻¹, respectively. Observation of overtones which are not detected in the bulk appears to be a common phenomenon in nanocrystals, and has been reported for PbS nanoparticles with a mean size of 1.5 nm. We notice that a shoulder around 240 cm⁻¹ is evident also in the spectra of the PbS powder.

Figure 2. Room temperature Raman spectra of PbS and CdS produced by X-ray lithography in silica hydrogels. The Raman spectrum of a PbS powder is also shown for reference.

Conclusions

In conclusion, we have shown that metal and chalcogenide nanoparticles can be produced by X-ray lithography in the bulk of porous sol-gel materials such as silica hydrogels. The features lithographed on the surface and in the bulk of the hydrogels reproduce faithfully those of the masks, and penetrate inside the bulk of the monoliths for up to 12 mm. The technique is very simple and robust, and does not present issues typically encountered in X-ray lithographic processes, such as polymer foaming. Therefore, with additional developments, the technique might be employed to complement X-ray lithographic techniques such as LIGA.

References


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