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Porous silicon photoluminescence modification by colloidal gold nanoparticles: Plasmonic, surface and porosity roles

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ABSTRACT

Metal nanoparticles on semiconductors are of interest because of the tunable effect of the surface plasmon resonance on the physical properties of the semiconductor. In this work, colloidal gold nanoparticles obtained by two different methods, with an average size of 6.1 ± 2.0 nm and 5.0 ± 2.0 nm, were added to luminescent porous silicon by drop casting. The gold nanoparticles interact with porous silicon by modifying its optical properties such as photoluminescence. That being said, plasmon effects are not the only to be taken into account; as shown in this work, surface chemical modification and porosity also play a key role in the final performance of photoluminescence of a porous silicon–gold nanoparticle hybrid system.

1. Introduction

Porous silicon (pSi) has been extensively studied because of its unique properties such as visible luminescence at room temperature [1], high surface area and biocompatibility [2]. In recent years, the addition of gold nanoparticles (AuNPs) to pSi has been studied as a tool for improving its sensing [3–5] and luminescent [6] properties. Additionally, synthesis methods [7–10] and promising applications [3–6,11,12] of pSi–AuNPs hybrid systems have been reported. The possibility to modify the optical response of pSi with gold nanoparticles is related to the effect of the strong localized electric fields near the surface of nanostructured metals [13]. This behavior is due to the collective excitations in the metal called surface plasmons (SPs) [14]. SPs allow introducing new radiative recombination channels, which can help to overcome the low radiative decay typical in porous silicon [6]. In spite of previous reports, the interaction mechanisms between pSi and AuNPs, which influence the optical behavior of pSi, are not well understood yet. Existing work has been mainly focused on plasmonic effects [6,12,15]. Here, we present an analysis of three mechanisms that influence the final performance of PL in a pSi–AuNPs hybrid system: plasmonics, surface chemical modification, and porosity roles. Finally, we explore the viability of using the porosity of the pSi host matrix for tuning the optical response of the pSi–AuNPs plasmonic hybrid material.

2. Material and methods

2.1. Porous silicon fabrication

The pSi monolayers were fabricated by electrochemical etching of boron-doped crystalline silicon wafers, with orientation (1 0 0), and electrical resistivity of 1–2 Ω-cm. An electrolyte composed of hydrogen fluoride (HF, J.T. Baker 48%), ethanol (J.T. Baker), and glycerol (J.T. Baker) was used to anodize the silicon substrate, in a volume ratio of 5:7:2, respectively. In order to study the effect of the porosity on the PL of the pSi–AuNPs hybrid material, two different kinds of sam Prod. Type: FTPples were prepared, one with low porosity (LP), and other with high porosity (HP); both with the same thickness of 500 nm, approximately. The LP and HP samples were obtained by applying current densities of 5 and 30 mA/cm^2, respectively. Then, the samples were passivated by partial oxidation at 100 °C in air atmosphere for 20 min, to stabilize its surface area. The pSi porosity was determined by gravimetric analysis. This method is based upon the definition of porosity (P) as the ratio of the volume of the pores to the total apparent volume of the film: $P = V_{\text{pores}}/V_{\text{total}} = (m_1 - m_2)/(m_1 - m_3)$,

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where m_1 is the weight of the sample before etching in HF solution, m_2 is the weight after etching, and finally m_3 is the weight after chemical dissolution of the porous layer [16].

2.2. *Colloidal gold synthesis*

Colloidal gold nanoparticles (AuNPs) were fabricated by the citrate reduction method [17]. Citrate coated AuNPs are easy to prepare, and the parameters to control the particle size and the optical properties are very well known. Sodium citrate is also a widely available nontoxic stabilizer/reducing agent that does not affect drastically most proteins [17].

Chloroauric acid ($HAuCl_4$, Sigma Aldrich 99.9%), sodium citrate ($Na_3C_6H_5O_7 \cdot 2H_2O$, Sigma-Aldrich 99.9%), and sodium borohydride ($NaBH_4$, Sigma-Aldrich 99.9%) were employed as reactives. All chemical reagents were used as received without further purification. A colloidal gold solution was synthesized by adding subsequently 0.5 ml of 6.25×10^{-4} M $HAuCl_4$ and 0.5 ml of 1.25×10^{-3} M sodium borohydride solutions to a glass vial with 8.5 ml deionized water and 0.5 ml of 1×10^{-3} M sodium citrate solution. Ultrapure deionized water was used for all solution preparations. The final solution was stirred vigorously for 2 h.

As a second approach to improve the homogeneity in the AuNPs deposition, a new colloidal solution was prepared, this time by using toluene as solvent. The dispersion of AuNPs in a low surface energy solvent, such as toluene, can lead to a more homogeneous deposition [18]. This method is described as follows: 10 ml of colloidal gold solution was prepared as described just above, and then a solution of 20 ml of toluene, with 0.4 mg of a thiol-containing polyhedral oligomeric silsesquioxane (POSS-thiol) was added. The solution was stirred vigorously for 30 min. Due to the strong affinity of thiols to gold [17], some of the AuNPs were transferred to the toluene solution, forming a two phase solution.

2.3. *Porous silicon–gold nanoparticles (pSi–AuNPs) hybrid material*

In order to deposit the AuNPs on the pSi samples, one drop of 10 μL of the gold colloidal solution was casted on their surface. Samples were analyzed by EDS and SEM to confirm the presence of gold on the pSi and to investigate its distribution on it. The low-porosity pSi–AuNPs hybrid sample will be denoted hereafter as “HLP”, whereas the high-porosity one will be denoted as “HHP”.

Once obtained, the toluene transferred NPs were deposited on pSi substrates by drop casting in an analogous way as described before. As with the previous set of samples, in this case the low-porosity pSi–AuNPs hybrid sample will be denoted hereafter as “HLPT”, whereas the high-porosity one will be denoted as “HHPT”.

3. Experimental

Once the pSi–AuNPs hybrid samples were obtained, their PL was measured, as well as that of the LP and HP monolayers. Around 20 samples of each type were fabricated. In order to have comparative results, in general, a set, formed by one of each type of sample, was measured the same day, under the same aging and illumination conditions. As the excitation source, a tunable pulsed laser system (PL2143A+OPG401/SH EKSPLA, ~30 ps) was used, focused to a 0.4 cm diameter spot. To detect the light, an optical fiber was used (P1000-2-UV–vis, Ocean Optics). The optical fiber was connected to a spectrophotometer controlled by computer (USB 2000+, Ocean Optics). Since the samples remained attached to the crystalline silicon substrate, the emitted light was collected from the top of the sample surface, being necessary to filter the reflection of the incident light used to excite the pSi (the setup is shown in Fig. 1a). The PL excited at 250 nm was studied to analyze how the hybrid material behaved, that is when the nanowires emitters were excited and they interacted with the AuNPs. Additionally, to study the excitation power dependence, a pulsed laser (PL2143A EKSPLA, $\lambda_{exc}=355$ nm, 26 ps) was used, which let us increase the power of the incident light by several times. In order to complete these studies, the FTIR spectrum (FTIR Perkin-Elmer) and the decay times (PMT module H10721-20) of the PL of all the samples (the setup is shown in Fig. 1b) were measured.

4. Results and discussion

4.1. *Materials characterization*

Regarding the pSi monolayers, porosity values of 56±7% for the LP samples and of 82±12% for the HP ones were obtained. The effective refractive index of the pSi monolayers on the crystalline silicon substrate, determined through reflectance measurements, were s_{LP}: 1.9±0.4, and η_{HP}: 1.3±0.4, respectively. The morphology of the pSi samples is shown in Fig. 2, LP (Fig. 2a) and HP (Fig. 2c). The SEM images of the cross-section of both samples exhibit the characteristic sponge-like structure of pSi produced from high resistivity substrates. Atomic force microscopy (AFM) images are shown in Fig. 2b and d. The image analysis shows pore diameters of 11.0±0.7 nm for the LP samples, and of 59.00±15.12 nm for the HP ones. A broad pore size distribution is observed in the HP samples.

Regarding the colloidal gold nanoparticles, the citrate colloidal solution reached a typical ruby-red color. Gold nanoparticles (AuNPs) with an average diameter value of 6.1±2.0 nm were obtained. In Fig. 3, the TEM images at different amplification

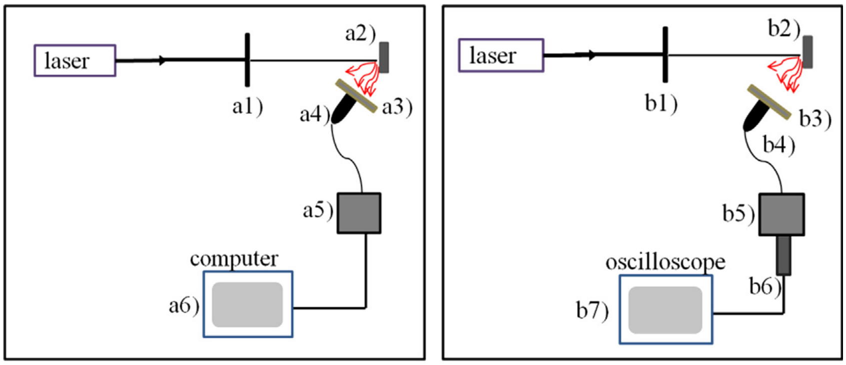

Fig. 1. Experimental setup for PL and PL-time-resolved measurements. A tunable pulsed laser was used to irradiate the samples through a 4 mm diameter diaphragm (a1 and b1). The signal from the sample (a2 and b2) was filtered by a band pass filter (a3 and b3), and collected by an optical fiber (a4 and b4) to decompose it, in the first case, at the spectrophotometer (a5), and then be analyzed with the computer (a6). In the second case, it was sent to a spectroscopic system (monochromator (b5) and photomultiplier (b6)), and then analyzed at the oscilloscope (b7).