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Influence of Gold Nanoparticles Deposition on Porous Silicon Properties

Meddeb HOSNY, Dimassi WISSEM, Haddadi IKBEL and Ezzaouia HATEM
Photovoltaic Laboratory Research and Technology Centre of Energy, Borj-Cedria Science Technology Park, BP 95, 2050 Hammam-Lif, Tunisia
Tel.: +216 94 340 886
E-mail: hosny_neuron@yahoo.fr

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Abstract: Gold nanoparticles (GNP) with different sizes from commercially available colloids were deposited based on destabilization using HF acid onto porous silicon (PS) substrate formed by an electrochemical process. We studied the controlling factors and conditions of the size, morphology and distribution, further, the influence of gold colloid on porous silicon characteristics have been investigated. The variation of the surfaces' roughness and morphology after noble metal modification was exhibited by atomic force microscopy (AFM), while, Fourier Transform Infrared (FTIR) characterization techniques proved the oxidation of porous silicon substrate, hence, the passivation of the surface states. It was also observed that the reflectivity decreased due to the deposition process according to the size and the quantity of gold colloid solution. Moreover, the photoluminescence (PL) spectroscopy revealed that the intensity strongly depend on gold nanoparticles deposition. These are attributed to metal nanoparticles with narrow particle-size distribution uniformly coated on the surface, thus, the substrate efficiency is strictly related to their dispersion, which could yield to local surface plasmons (LSP). .

Keywords: Porous silicon, Gold colloids, Morphology, Passivation, Surface Plasmons resonance.

1. Introduction

Porous silicon, a sponge-like network of crystalline silicon with pillars and nodules of nanometer dimensions has in recent years provided a very interesting ground for interdisciplinary basic and applied research. The extremely large surface to volume ratio of porous silicon, the ease of its formation and its compatibility to silicon technology make it a very attractive material [1]. In contrast to its optical properties, porous silicon has widely been investigated as a potential platform for photonic and sensor applications [2-5]. However, the use of as-grown porous silicon for device applications is limited due to the lack of reliability mainly because of material instability. The large density of s surfaces states is responsible for the of PS surface [6].

But, the major barrier preventing commercial applications of PS is the instability of its native surface/interface with a metastable Si–Hx termination [7]. The metastable hydro-silicon can undergo spontaneous oxidation in ambient atmosphere and results in the degradation of the surface structures. This also creates a problem for making good electrical contact on PS. So there is a need to modify the PS surface in order to passivate the large density

of defect states and a post formation treatment is necessary to stabilize its surface property [8]. Therefore, the passivation of the surface is necessary to fabricate a stable porous silicon based devices. The substitution of the surface hydrogen by another chemical species appears to be desirable for this purpose [9-11]. Surface passivation by chemical treatment with noble metal ions is also a potential and an economic alternative method [12]. Metals like Cu, Ag, In, etc. were also used to modify the porous silicon surface to develop the stable photoluminescence properties [12-13]. In the present investigation we prepared nanoporous silicon with the same porosity by anodization of p-Si and modified the PS surface with a treatment by gold metal ions using a simple, reliable and low cost chemical method to stabilize the material. Commercially available, citrate-stabilized gold nanoparticles are attractive engineering materials for a variety of applications given their unique and tuneable properties [14]. The resulting nanoparticles are stabilized by the presence of negatively charged citrate ions at the nanoparticle surface [15]. However, the negative surface charge prevents the nanoparticles from readily adhering to a hydrogen-terminated silicon surface [16]. It has been demonstrated that gold nanoparticles can be deposited onto a silicon substrate without the use of a linker by lowering the pH of the colloid solution to destabilize the colloid and favor the precipitation of the nanoparticles [16]. With the addition of hydrofluoric acid (HF) or hydrochloric acid (HCl) to lower the pH of the solution below 3.1, the citrate ions are converted to neutral citric acid [16]. The neutralization of the gold nanoparticle surface charge allows for adhesion onto the silicon substrate [17]. Here, we present and study a simple bench-top technique to deposit gold nanoparticles onto a hydrogen-terminated porous silicon wafer using gold colloids without the use of a linker. After modification, the surface was thoroughly investigated using AFM microscopy, FTIR, then, UV-VIS and PL spectroscopies. AFM studies were conducted to verify the change in the structural and morphological qualities of both the untreated and treated surfaces. FTIR spectroscopy was used to study the nature of the chemical bonding before and after surface modification, while UV-VIS enabled to investigate the reflectivity change due the gold colloids deposition. As for PL technique, it concerns the photoluminescence properties of our samples.

2. Experimental Study

2.1. Porous Silicon Formation

In these experiments, Porous silicon was fabricated from a 400 μm thick p-type (boron-doped) single-crystal Czochralski (Cz) solar grade Si wafers, with a resistivity ranged between 0.5 and 2 Ω/cm by anodic etching method. The Si wafer was cut into small samples having dimension of 2 cm x 2 cm. Both sides of the Si wafers were etched with a (HF: 16 % / HNO_3: 64 % / CH_3COOH: 20 %) based solution; in order to remove saw damages and then to obtain cleaned surfaces. this step enables to remove about 15 mm from both sides. Then, these wafers were rinsed in de-ionized water and dried. After cleaning, samples are subjected to PS formation by anodic etching in a home-made all-Teflon electrolytic cell. Si was used as the anode and a platinum electrode was used as the cathode. The solution used for anodization was composed of HF (48 %) and ethanol (C_2H_5OH) in 7:3 ratios by volume. Added ethanol removes hydrogen bubbles evolving during the reaction and reduces the interfacial tension and decreases the inhomogeneity of the PS layer [18]. The wafer was etched at a current density of 5 mA/ cm^2 for 10 min, according to recommendations mentioned in literature [19]. After the etching process, the samples were rinsed thoroughly in DI water, classified in seven sets.

2.2. Surface Treatment

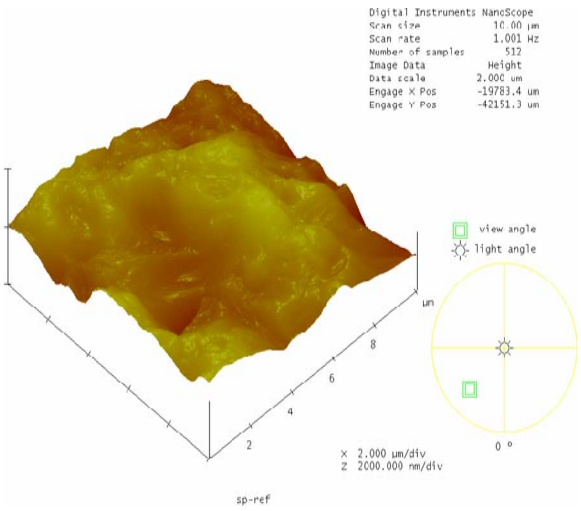
Gold colloids were obtained from British Biocell in three sizes, 20 nm, 50 nm and 100 nm with concentrations of approx. 9 × 1010 particles/mL. The HF dip removed the silicon native oxide and provided the hydrogen-terminated surface. Gold colloid, 100 μL, was dropped onto the silicon wafer followed by 33 μL of HF. The mixture was left on the substrate for a given time, specified in the study, and then rinsed with DI water. Surfaces of porous silicon surfaces were chemically treated with the ionic solution of gold nanoparticles, in which they undergo deposition of gold colloids by destabilization with HF. For each available size of colloids (20, 50 and 100 nm), we made two kinds of depositions by varying the amount: a first sample of 100 μL 300 μL and the other of the colloidal solution. The surface morphology and composition of samples were examined by atomic force microscopy (AFM) in tapping mode. Absorption FTIR spectra of the samples were measured using Bruker spectrometer for a domain of wave numbers ranged from 500 to 2500 cm^{-1}, in order to investigate the physico-chemical composition. The optical properties were studied using UV-visible spectrometer, while, photoluminescence spectra were dispersed by a double monochrometer SPEX system (0.8 m focal length), model 1404.

3. Results and Discussions

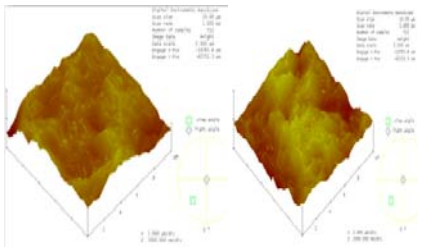
3.1. Atomic Force Microscopy

The AFM images shown in Fig. 1 show 3D topographies for the seven samples of porous silicon

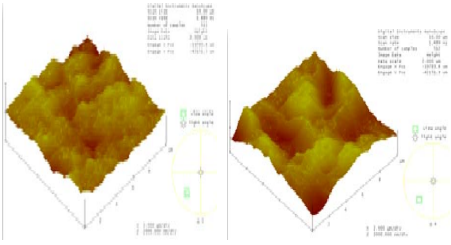
all prepared with a fixed current density J = 5 mA for 10 minutes: one reference with no surface treatment, while others are assigned to each diameter of the nanoparticles 20.50 and 100 for two different amounts of colloids 100 µL and 300 µL for one minute.



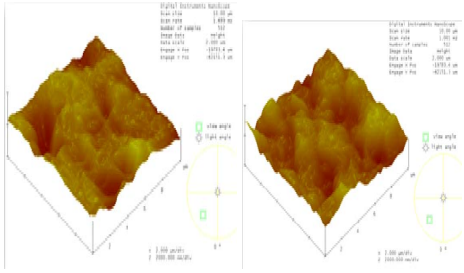
Reference porous silicon (5 mA/cm^3-10 min).



Deposition of 100 µL (Left) and 300 µL (right) from 20 nm gold colloids solution



Deposition of 100 µL (Left) and 300 µL (right) from 50 nm gold colloids solution



Deposition of 100 µL (Left) and 300 µL (right) from 100 nm gold colloids solution

Fig. 1. AFM 3D topographies of SP layer after GNP depositions with different diameter sizes (20 nm, 50 nm, 100 nm) for 100 µL et 300 µL from colloid solution.

Topographies exhibit a remarkable difference in the surface morphology after formation of porous silicon proved by spongy nanostructures with different nanometer sizes. It clearly can be seen that the pore size expands when the diameter of the colloids is larger; the morphology of substrates which have undergone a deposition of gold nanoparticles of 100 nm size present pores larger and deeper than 50 nm and 20 nm. We note also that the colloids quantity affects the size and the depth of the pores: the greater the amount of deposited colloids, larger and deeper pores will be. These observations are well supported by the values of average surface roughness which increases with the size and quantity of aggregates deposited colloids, illustrated in Table 1.

Table 1. Roughness (Rms) values attributed to samples before and after AU deposition for different sizes and quantities.

Sample	PS without colloid	20 nm	50 nm	100 nm
Rms 100µl (nm)	152.62	226.81	258.56	303.96
Rms 300 µl (nm)	152.62	339.67	386.06	392.72

Moreover, porous silicon is less noble than the metal nanoparticles; hence, substrate surface can act as a reducing agent which allows the spontaneous deposition of gold nanoparticles, preferably located in the porous part, (Fig. 2) more specifically on the walls of the pores (b) or inside the pores (a) according to the diameter of the nanoparticles compared to that of the pores. The sites are physically limited, allowing selective metal deposition positions [20].

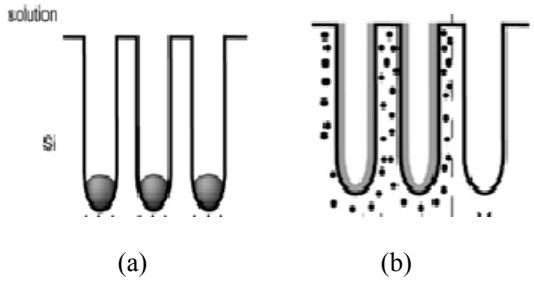


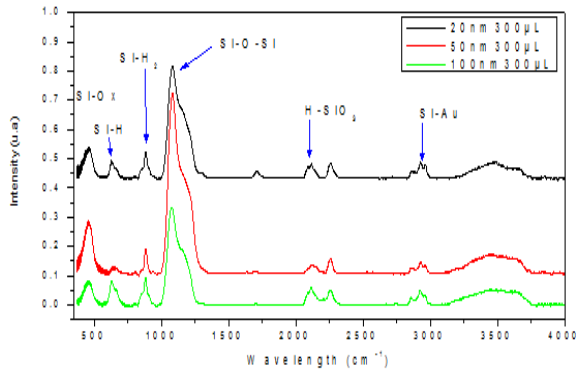
Fig. 2. Illustration of preferential sites of Au deposition into PS (a) metal fill inside Si macropores (b) Localisation of Au nanoparticles in pores wall interface.

We can note also that the porous silicon can act both as a reducing agent for ions $AuCl_4$-gold complexes and as substrate, since it has been proved in literature that any system of aqueous metal ions with a standard reduction potential greater than zero may be effectively reduced by porous silicon. [21] It is also observed according (AFM) images, a

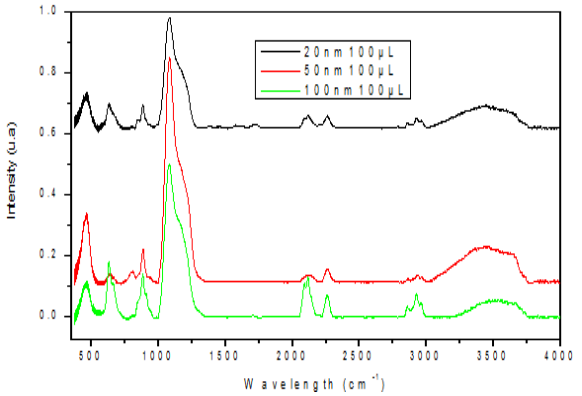
discontinuous dispersion of gold aggregates (Volmer-Weber layer) which appear preferentially deposited near to the pores on the surface, where there is a considerable density of energetic sites (i.e. dangling bonds). Note to mention that, despite the modification of the silicon surface, its porous nature is verified [22].

3.2. Fourier Transform Infrared

In order to study the chemical composition of the samples, we resorted to FTIR spectroscopy technique which assigns the predominance of elements such as hydrogen, oxygen and gold in the structure due to the deposition of gold colloids on PS. Fig. 3 shows the evolution FTIR spectra in absorption mode for three available sizes of nanoparticles diameters (20.50 and 100 nm) for two different deposited amounts (100 µL 300 µL and) on the surface of PS.



(a)



(b)

Fig. 3. FTIR spectra des SP after GNP depositions with different diameter sizes (20 nm, 50 nm, 100 nm) for two quantity of colloids (a) 100 µL (b) 300 µL.

The peaks presented in those spectra respectively corresponded to: Si-O-Si located at 460 cm^{-1}, 640 cm^{-1} for Si-H in Bending mode, another peak centered near vicinity to 870 cm^{-1} attributed to the $Si-H_2$ scissors mode and a large band between 1040 cm^{-1} and 1270 cm^{-1} is assigned to local vibration of Si-O-Si in stretching mode [23]. Otherwise, there is a band around 2100 cm^{-1} attributed to $Si-H-O_3$ bond and particularly a characteristic band of the Si-Au around about 3000 cm^{-1}. It clearly can be seen that the intensity of the Si-O band is broad and intense in stretching mode, while the $H-Si-O_3$ is deformed. While colloids deposited amount increase, the oxide peak presents a significant enhancement, which proves the formation of gold islands followed by a formation of oxide layer. Thus, the network consists of a mixture of silicon chains interconnected by oxygen bonds. It appears also a Si-Au band as a result of the combination of gold atoms with dangling bonds of silicon.

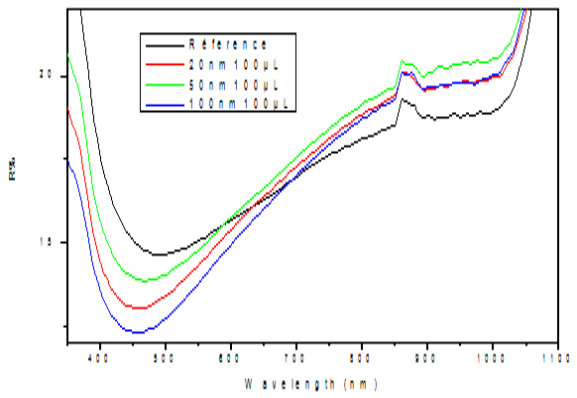
Porous silicon layer is easily oxidized under ambient conditions to form a non-conductive oxide layer on the surface.

It is conceivable that the agglomerates of gold nanoparticles are in good contact with the non-oxidized substrate deeper into the layer and then have a metal signal. Generated defects in porous silicon during its formation by electrochemical anodization are primarily responsible for the instability state. The deposition of noble metals on the porous silicon is performed to passivate the surface defects due to the formation of a thin oxide layer. Porous silicon is characterized by instability of the surface due to $Si-H_x$ metastable terminal which can undergo spontaneous oxidation by generating a deterioration of the surface structure, where the passivation is needed to achieve stable porous silicon. Thus, there is a substitution of hydrogenated surface by another chemical species that is none than gold colloids. So, we can then prove that the oxidation of porous silicon occurs during gold colloids deposition thanks to formation of gold islands on the surface of porous silicon which contributes to the formation of a thin layer of SiO_2 located between the aggregates of nanoparticles of gold. Thereby, the deposition of gold colloids in porous silicon plays a double role: On the one hand, it contributes to the passivation of surface atoms of gold; on the other hand, it promotes the oxidation of substrate.

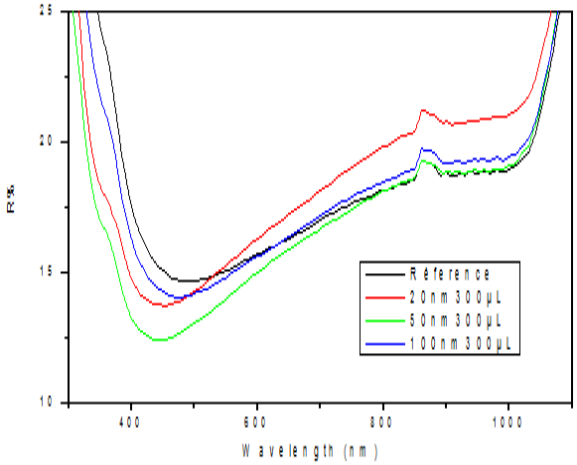
2.3. Reflectivity

In Fig. 4, we presented the reflectivity spectra of porous silicon before (reference) and after gold colloids deposition of two quantities about (100 µL and 300 µL) for three different sizes of nanoparticles (20, 50 and 100 nm) on the surface of PS.

We can clearly notice a minimum between 400 nm and 500 nm of the reflectivity for all samples prepared by anodizing for a period of 10 minutes at a current density (J = 5 mA/cm^3), a minimum between 400 and 500 nm, which prove that it is a true monolayer.



(a)



(b)

Fig. 4. Reflectivity spectra for untreated PS layer (reference) compared to treated samples after GNP deposition with different diameter sizes (20 nm, 50 nm, 100 nm) for two quantity of colloids (a) 100 µL (b) 300 µL.

For the range of wavelengths of visible light ($300 \leq \lambda \leq 600$ nm), these spectra show that there is a remarkable decrease in the reflectivity of the samples that have undergone a deposition of gold colloids compared to reference one. This decrease from almost 15 to 12 is mainly due to the increase in the surface roughness of porous silicon after deposition, which is in agreement with the AFM topography (Fig. 1 and Table 1) Optical improvements that occur during deposition of gold colloids on PS are related to the morphology and distribution of GNP, which generate local surface plasmons coupled to other neighboring particles and also interactions in short distances, while also increasing the surface roughness. It is worth noting the surface plasmon excitation leads to an improvement of the local electromagnetic field near to metal surfaces [24].

Surface plasmons are electromagnetic waves which propagate in a direction parallel to the metal-dielectric interface (or metal / vacuum). Since the wave is located at the boundary between the metal and the external medium (air or water, for example), these oscillations are very sensitive to any change in this limit, such as the adsorption of molecules on the surface of the metal [25]. Moreover, PS substrate provides a large surface area for adsorption of the particles, which contributes to improving the reflectivity [26]. But, beyond the visible light range, the effect of surface plasmons disappears, which explains the increase in reflectivity samples that have undergone a deposition of gold colloids compared to reference one.

3.4. Photoluminescence

Fig. 5 below illustrates the PL spectra of PS layers (5 mA/cm^2 – 10 min) before and after deposition of 300 µL of a colloidal solution of 100 nm size. Both spectra exhibit a peak centered at 625 nm whose intensity and width seem to be enhanced significantly due to GNP deposition.

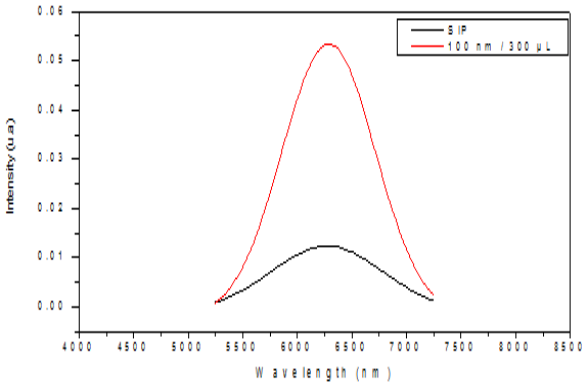


Fig. 5. Photoluminescence spectra for untreated PS layer (reference) compared to treated sample after GNP deposition with a size of 100 nm for a quantity 300 µL of colloids.

Not to mention that, PS luminescence is mainly due to radiative recombination in nanostructures with a diameter less than 20 Å, so that the optical phonon confinement in small crystallites sizes or also by dint of the Si-O-H bond [23]. The width modification is due to the uncontrolled substitution of hydrogen by the OH group which is in agreement with the results provided by FTIR. (Fig. 3) This phenomenon of visible light emission isn't, therefore, an intrinsic property of silicon, but it is highly dependent on chemical reactions of silicon with hydrogen and oxygen. Metals such as Cu, Ag, Au ... have also been used to modify the surface of porous silicon and develop more stable photoluminescence properties [27]. In addition, we proclaim that luminescent sites are independent; the proportion of carriers who jump from one site to another before recombining is negligible. Our results allow describing reality in a simple way PL mechanism is described as a local competition between radiative recombination of carriers and their escape to a non-radiative hole. Thus, carriers must be "isolated" from non-radiative recombination centers in well passivated wafer.

It is noteworthy that the intensity of the photoluminescence (PL) of porous silicon is very sensitive to changes in pH; it appears more intense in an acidic environment. In our case, the use of HF for the destabilization of colloidal gold has contributed to the improvement of PL. This phenomenon is explained by the competition between the adsorption of hydrogen and the oxidation process [28]. Also, the formation of Si-Au bond contributes in enhancement of PS photoluminescence. (Fig. 5), thus, gold nanoparticles (AuNPs) are characterized by localized surface plasmon resonance (LSPR), which yields to resonant coupling with electronic excitation of PS, and inhibits the process of non-radiative Auger recombination for high excitation powers. These results indicate that the effect plasmon (collective oscillation of the electrons in the conduction band at the surface of a metal particle) may be effective and gainful for the design of optoelectronic devices and of course photovoltaic cells [27]. After the introduction of gold nanoparticles, metal plasmons provide a new channel for relaxation and therefore can annihilate the Auger recombination rate. An interesting observation is that the increase is greatest in the visible region, which can be attributed in part to the reduction of emissions extraction efficiency due to the presence of gold nanoparticles. In summary, the plasmons of gold colloids can provide effective relaxation energy, thus, a considerable improvement of emission [27].

6. Conclusions

In our work, we proved that the deposition of gold colloids provoke a considerable variation in the morphological and structural properties of porous silicon, confirmed by FTIR and AFM investigations. This treatment allows an enhancement in the reflectivity and photoluminescence of the samples. To crop it all, we demonstrate that these improvements are due, on the one hand, to the increase of roughness following the incorporation of nanoparticles in the pores, and, on the other hand, to the surface passivation thanks to localized surface plasmons resonance.

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