Structural properties of AuNPs/PSi nanostructure

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Nanostructure porous silicon (NPSi) was achieved by electrochemical etching. A p-type silicon of resistivity (0.1-0.02 Ω.cm) and n-type silicon of resistivity (1.5-4 Ω.cm) were immersed in 25% HF at etching time of 15 min and fixed current density 20mA/cm^2. Moreover. A gold nanoparticles were produced by laser ablation of energy (250, 350 and 450 mJ). The AuNPs were deposited on PSi layer ending up with a AuNPs/PSi.The structural, morphology and Raman properties of the AuNPs/PSi were all investigated. X-ray diffraction showed that the Au nanoparticles revealed a polycrystalline face-centered cubic structure (FCC). Furthermore, FESEM images displayed that the AuNPs have entered inside the pores with uniform sizes. Additionally, Raman spectrum showed shifting on the broadening peak below 520 cm^{-1} when laser energy is increased in p-type silicon. AuNPs plays crucial role and very effective to enhance this property.

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Keywords: Porous silicon, Au nanoparticles, Laser ablation, XRD, SEM, Raman spectroscopy

1. Introduction

Laser ablation (LAL) technique is one of the most effective method for nanoparticles material production recently due to its simplicity and low cost [1]. This method involves using high power with short pulsed duration laser beam to irradiated the solid target material immersed in liquid [2]. When the laser pulse interacts with the matter, the ablated material converted to a plasma phase, then formation of NPs. Nanoparticles materials showed a diverse of the unique characteristics that were not be observed in bulk materials[3,4]. The most crucial property of these materials is that their behaver becomes highly depends on the particle's size [5,6] . By controlling some laser ablation parameters such as, laser energy, wavelength, pulse duration, repletion rate, etc, it is possible to modify the nanoparticles size, hence, manipulating their properties[7]. Gold nanoparticles (AuNPs) showed extraordinary efficiency for absorbing and scattering light [8,9]. They strongly interact with light due to the conduction electrons on the metal surface which suffer a collective oscillation when irritated by certain wavelengths [10]. This oscillation termed a surface plasmon resonance (SPR). In this work, the Au nanoparticles were produced by laser ablation in liquid and deposited on PSi substrate layer prepared by electrochemical etching technique [11,12]. The structural properties of the AuNPs/PSi were characterized by XRD , FESEM and Raman spectroscopy.

2. Experimental part

The gold nanoparticles were formed by laser ablation technique. A high purity gold was immersed in an ionized water. A Q-swished Nd:YAG solid state laser emission at 1064nm was used to irradiate the gold target with different energy (250, 350, and 450 mJ). The laser produces short pulses in the order of nanosecond, we ablated the target for 200 pulses. A 12cm focal length lens was used to foci the laser beam as it shown in Fig. 1. On the other hand, the p-type silicon oriented towards <111> with resistivity (1.5-4 Ω.cm) and n-type silicon oriented towards <100>

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with resistivity (0.01-0.02 Ω.cm) were fabricated using electrochemical etching technique as it shows in Fig. 2.

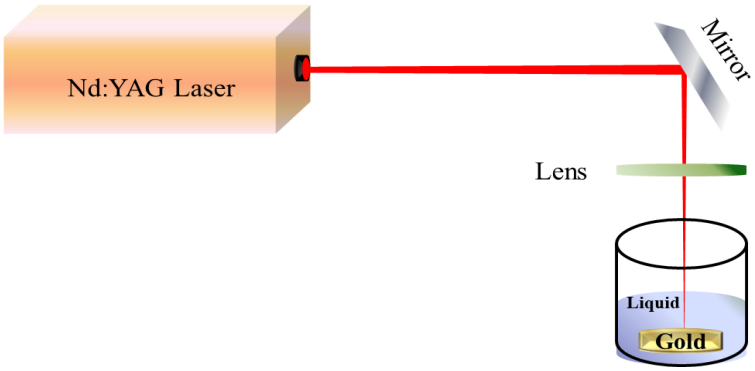

Fig. 1. Setup of laser ablation in Liquid.

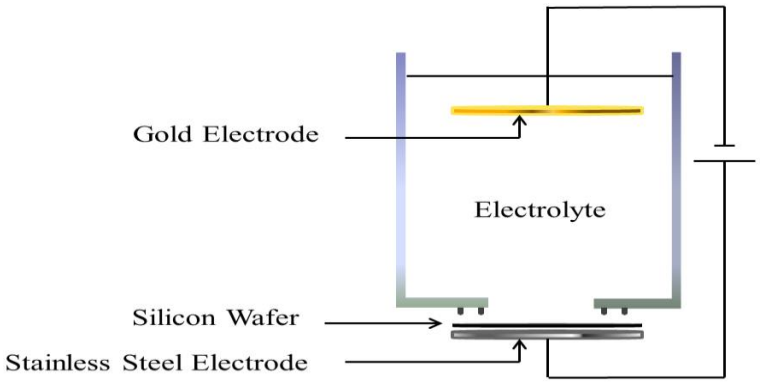

Fig. 2. Electrochemical etching setup.

The samples under consideration were studied through X-ray diffraction (XRD), Raman spectroscopy and Scan electron microscopy (FSEM). The X-ray source is Bruker./D9 by Cu K emission (λ = 1.5418 Å), the diffraction angles were measured of 25 to 110 at 0.03± sec^{-1}. The surface substrate was studied by a (FESEM) type (JEUMA-JSMI-6754H) turn on at 10 keV. Raman spectrum investigated type (GM SER No 87325 - Germany). The emitted wavelength by the helium - neon laser in the experiment is at 633 nm. The Raman spectroscopic consists of the aforementioned laser, which generates an excitation beam whose beam passes through a microscope, which is in the vicinity and very close to the sample. The intensity of the back scattered light was measured as a function of the frequency shift in the sample.

3. Results and discussion

3.1. X-ray diffraction

Fig. 3 and Fig. 4 show The XRD spectroscopies of Au nanoparticles grown into n-type and p-type PSi for different laser ablation energies (250,350 and 450 mJ). The diffraction pattern was recorded for a range of 2θ from 20° to 80°. The highest peak of n-type observed at 68.2° for Si (400) whereas for p-type it observed at 28.3° for Si (111). Furthermore, the diffraction peaks of Au NPs/PSi structure were observed at 38.14°, 44.06°, 64.92° and 77.7°, representing the index as (111), (200), (220) and (311), respectively. This confirmed the polycrystalline face-centered cubic structure of Au nanoparticles, according to (JCPDS) [13].

Additionally, the mean crystalline size can be evaluated according to the Debye-Scherrer equation [14] .

$$L = \frac{k\lambda}{B\cos\theta} \qquad (1)$$

where L is crystallites size (nm) and B is FWHM and k is a constant (k=0.892). Moreover, it is found that the size of crystalline decreases with increasing laser ablation energy which could be mainly due to quantum size effects arises from AuNPs[15]. In addition, it is confirmed that the AuNPs/PSi structure keeps in the phase of crystalline ,but it is very little shifted towards small angles with laser ablation energy for both n-type and p-type PSi[16]. This result is attributed to effect of tensile strain that formation due to the lattice mismatch between the nanoparticles and the substrate causing a shift in PSi peak towards small diffraction angle. Furthermore, formed gold atoms bond breaks by laser pulses, then, the occurrence of the recombination process [17]. Several Au atoms recombine with O atoms in the liquid ,thus , Au oxides atoms were formed . Table 1 shows the values crystalline size , FWHM, inter-plane distance (d), of NPsAu/ n-type and p-type PSi .

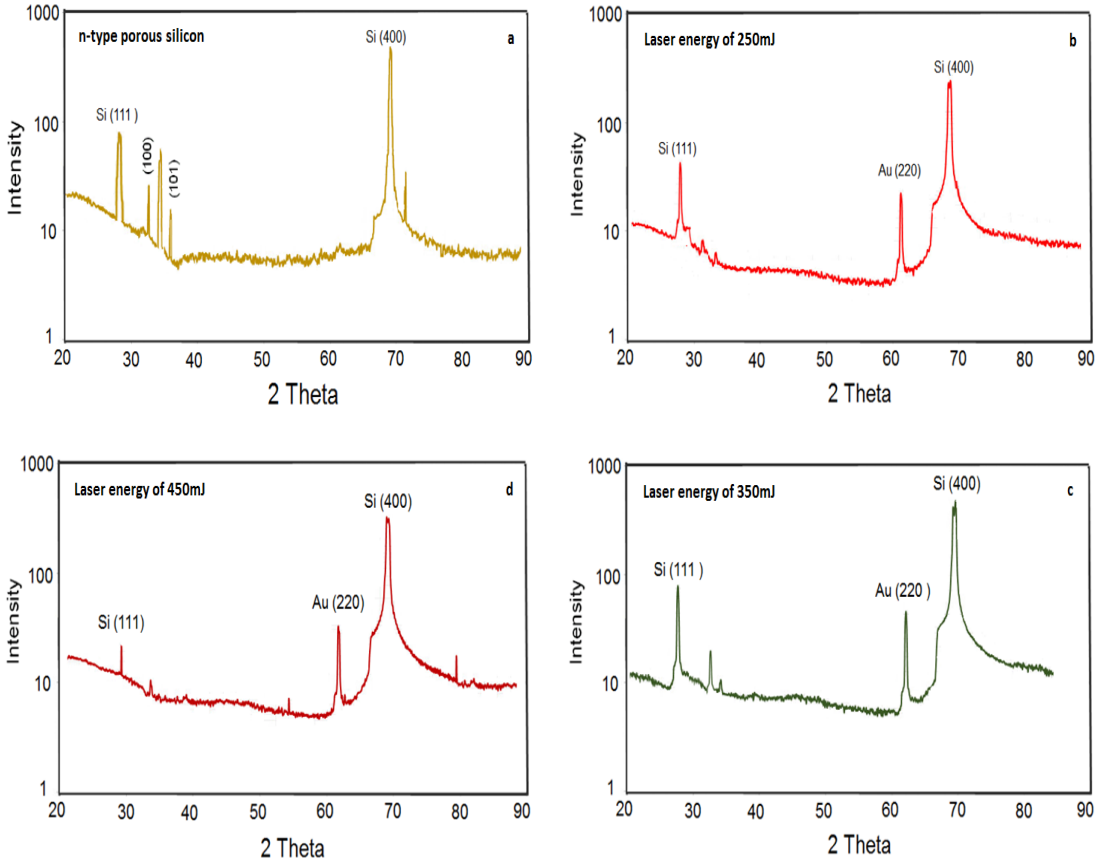

Fig. 3. XRD of n-type porous silicon (a) PSi (b) 250 mJ , (c) 350mJ and(d) 450mJ.

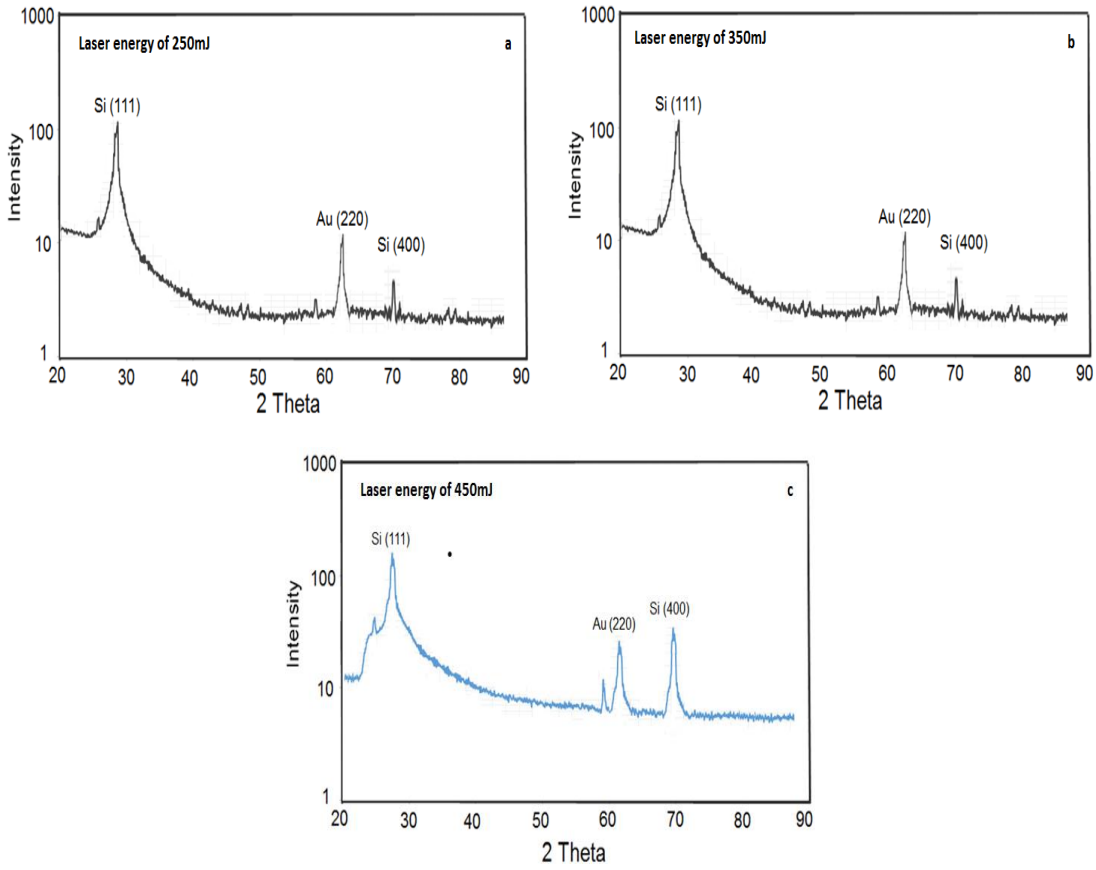

Fig. 4. XRD of p-type porous silicon (a) 250 mJ , (b) 350mJ and (c) 450mJ.

Table 1. Crystalline size, FWHM, inter-plane distance (d) of n-type and p-type porous silicon.

Sample	Laser energy (mJ)	*L* (nm)	FWHM (deg)	d (A^o)
n-type porous silicon	-	33.47	0.421	0.195
	250	16.34	0.834	1.733
AuNPs/PSi (n-type)	350		0.723	1.634
	450	17.83	0.672	1.532
AuNPs/PSi (p-type)	250		0.941	1. 81
	350		0.812	1.788
	450	19.43	0.782	1.774
		12.63		
		13.65		
		14.89		

3.2. Topographic structure (FESEM)

The surface morphology of the crystal is strongly depended on fabrication conditions. Fig. 5 and Fig. 6 illustrate FESEM images of AuNPs for both n-type and p-type PSi substrate before and after laser ablation respectively. The surface morphology reveals the existence of pore sponge like structure due to extra holes on the surface of the PSi as it is evident in Figure 5a and Figure 6a. The pore sizes produced are with an average diameter of 31.53 nm of n-type and 27.54 nm of p-type porous silicon. The mean pore size appears in good matching with expected value for a meso -porous layer [18,19]. The morphology of Au nanoparticles on porous silicon substrate was changed remarkably with laser energy (250,350 and 450 mJ). Most of gold nano particles are formed at pores walls and the Au nanoparticles are penetrated inside the pores with uniform sizes.

These images showed that the pores are occupied by gold nanoparticles. The surface of the sample at 450 mJ exhibited larger pore compared with at 250 mJ and 350 mJ . Where the mean particle size was increased from 56.77 nm , 63.76 nm to 76.91 nm at 250 mJ, 350 mJ and 450 mJ of n-type porous silicon respectively .However, the average particle size of p-type porous silicon was 46.14 nm, 57.16 nm and 59.81 nm at 250 mJ , 350 nm and 450 mJ respectively . This indicates that increasing of laser energy leads to an increase in the particle size [20]. This can be attributed to by the formation of a small fraction of AuNPs scattered on every side in a solution, the nanoparticle grows by the attraction of these small fragments and the increasing of laser energy leads to increase the fragmentation process [21,22].

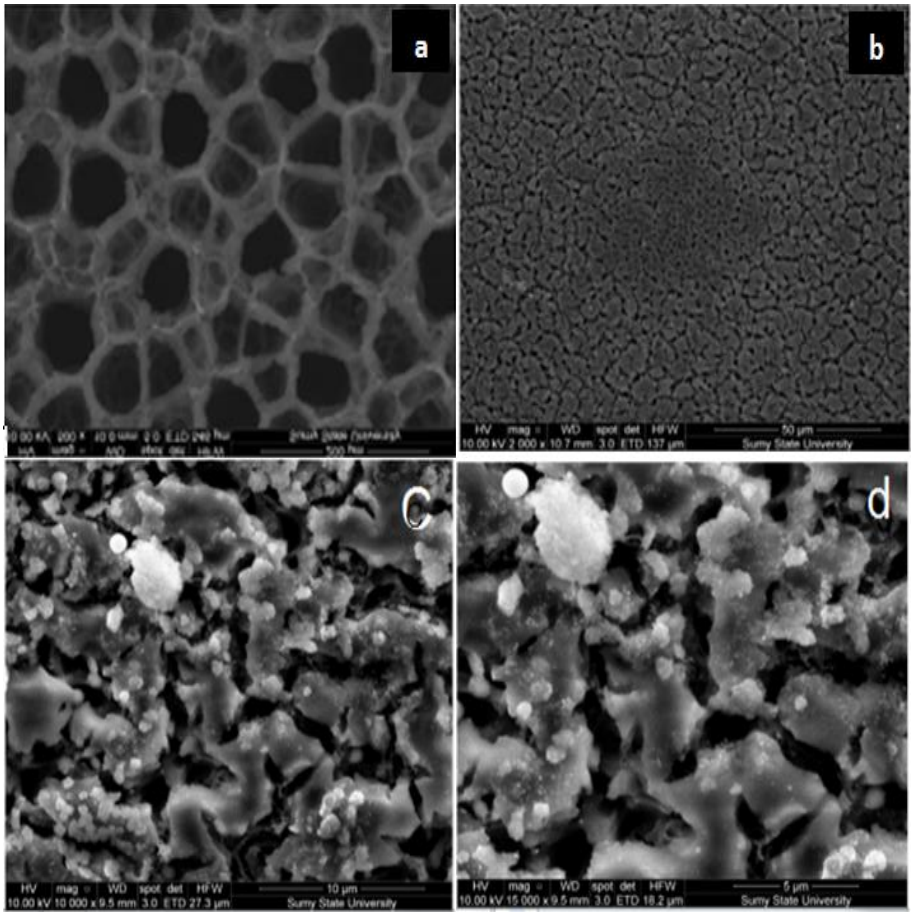

Fig. 5. FESEM of n-type porous silicon (a) Porous silicon , (b) 250mJ, (c) 350 mJ , (d) 450 mJ

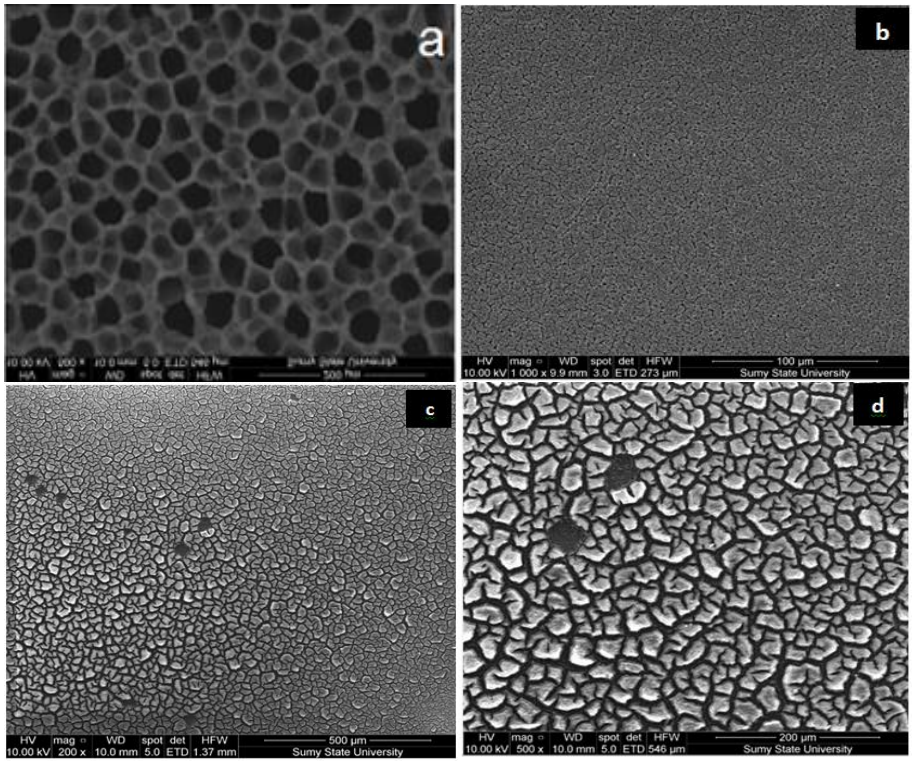

Fig. 6. FESEM of p-type porous silicon (a) Porous silicon , (b) 250mJ, (c) 350 mJ , (d) 450 mJ.

3.3. Raman Spectroscopy

Fig. 7 shows Raman spectra of AuNPs/PSi structure of n-type porous silicon and at different laser ablation energy. It can be seen the spectrum consist of one sharp peak and a broadening peak shifted below 520 cm^{-1} with increase laser energy (250,350 and 450mJ). The optical phonon peak shifts to toward lower frequency and becomes asymmetrically which indicates the presence of nanoscale features of the crystalline structures [23,24,25]. On the other hand, Fig. 8 illustrates more than one peaks of AuNPs/PSi structure of p-type porous silicon , this might be attributed to create a multiple scattering center which is proportional with stimulates the Au nanoparticles reduction [26,27] .Table 2 shows data of FWHM, Raman peak position & Asymmetry of Raman spectrum.

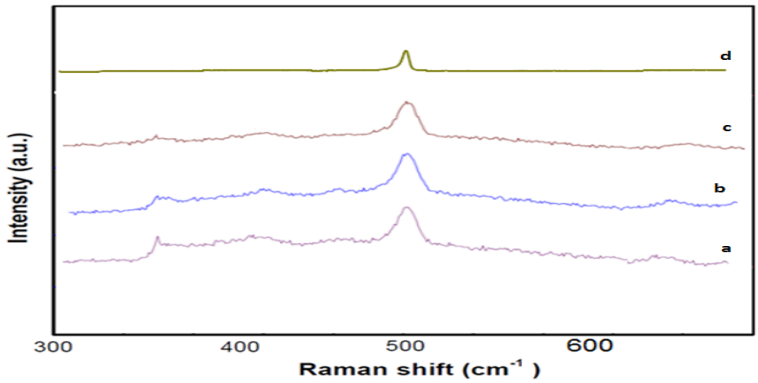

Fig. 7. Raman spectrum of AuNPs/PSi structure of n-type porous silicon (a) porous silicon (b) 250 mJ (c) 350 mJ (d) 450 mJ.

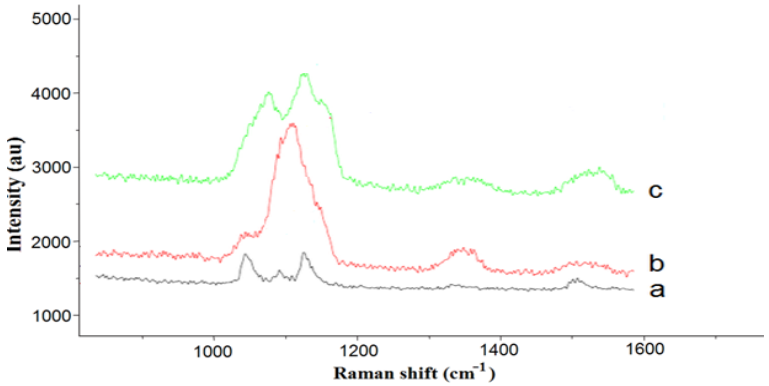

Fig. 8.. Raman spectrum of AuNPs/PSi structure of p-type porous silicon (a) 250 mJ (b) 350 mJ (c) 450 mJ.

Table 2. FWHM, Raman peak position and asymmetry of Raman spectrum.

PSi	Laser energy(m J)	First strong Peak position(cm^{-1})	Second strong Peak position(cm^{-1})	FWHM (cm^{-1})	Asymmetry
n-type porous silicon	250	519.41	-	12.97	1.08
	350	518.76	-	15.75	1.42
	450	519.19	-	24.87	1.56
p-type porous silicon	250	540.79	810.89	8.38	2.53
	350	780.31	-	8.68	2.64
	450	680.65	870.56	8.83	2.89

4. Conclusion

In summary, we produced a Gold nanoparticles using laser ablation in liquid technique at deferent pluses energies. The AuNPs were deposited on the n-type and p-type pore silicon substrate prepared by electrochemical etching. The result showed that the AuNPs as small as 12.63nm can be created at laser ablation energy of 250 mJ, and the AuNPs revealed a face center cubic (FCC) structure. Moreover, the SEM images revealed a spherical shape of the AuNPs with good homogenous surfaces. Raman measurement of AuNPs/Si p-type showed a significant shift of the strong peak position with increasing laser ablation energy with high crystal asymmetric with increasing laser ablation energy. We believe that by carful optimizing the conditions of laser ablation a high quality AuNPs /PSi can be prepared for medicine and industry applications.

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