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Structuraland Optical Properties of Gold Nanoparticles Coated on Porous Silicon Thin film

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Abstract:
Porous Silicon (PSi) samples were prepared by chemical etching (stain etching) of boron doped p-type silicon wafers. The gold nanoparticles (Au) were deposited on PS surface by Au-sputtered by Physical Vapor Deposition (PVD) technique. The Au/Psi composites get incorporated into the pores of PSi so that Au/PSi composites formed. The surface morphological studies of PSi and Au/PSi composites were studied by Scanning Electron Microscopy (SEM). Photoluminescence (PL) measurements have been carried out to investigate the surface modification and optical properties of PSi and Au coated samples. In the case of Au/PSi structure, this peak is blue shifted with a reduction in the peak intensity, indicating modification at the interface of Au/PSi. The absorption coefficient and the thickness of the Au/PSi composites were calculated from the interference of transmittance spectra. Optical constants such as the refractive index (n) and extinction coefficient ($_k$) and film thickness (t) have been determined from the transmittance spectrum in the UV-VIS-NIR regions using the envelope method. The thicknesses of the Au/PSi composite are strongly influences the optical constants. These results suggest that the Au/PSi could be a potential candidate for device applications.

Keywords*: Porous Silicon, Au, SEM, PL, Envelop method and Optical constants.*

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I. INTRODUCTION

Porous silicon (PSi), 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 [38]. In contrast to its optical properties, PSi has widely been investigated as a potential platform for photonic and sensor applications [39]. However, the use of as-grown PSi 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 PSi surface. But, the major barrier preventing commercial applications of PSi is the instability of its native surface/interface with a metastable Si–H_x termination [40]. 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 PSi. So there is a need to modify the PSi surface in order to passivate the large density of defect states and a post formation treatment is necessary to stabilize its surface property [41]. 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 [42,43].

Surface passivation by chemical treatment with noble metal ions is also a potential and an economic alternative method [44]. Metals like Cu, Ag, In, etc. were also used to modify the PSi surface to develop the stable photoluminescence properties [45,46]. In the present investigation, we prepared porous silicon sample by chemical etching of p-type crystalline silicon (c-Si) and modified the PSi surface with a treatment by gold nanoparticle (Au) using a Physical Vapor Deposition (PVD) method. Gold nanoparticles are attractive engineering materials for a variety of applications given their unique and tunable properties [47]. There are a few papers on the Au/PSi by using electrochemical method, but there is no report on the Au/PSi thin film by using chemical (strain) etching method. Therefore, in this paper, the structural and optical properties of Au/PSi thin film have been studied for the first time.

II. EXPERIMENTAL

Porous Silicon (Psi) layers were prepared by chemical (stain) etching of boron doped p-type silicon wafers (100) orientation having a resistivity of 0.5-3.0 ohm-cm, and a thickness of 250±0.5. Chemical etching was performed in a mixture of HF and ethanol (volume ratio 1:2) solution with constant etching time of 30 minutes. Prior to etching, the samples were placed in the etching solution for 1 minute to remove the native oxide. The prepared PSi substrate and the atomically flat Si wafer surface were Au-sputtered by Physical Vapor Deposition (PVD) technique [48] and herein this study, the sputtering procedure was done as per protocol described in the literature with minor modifications [49]. A layer of Au thin film was therefore coated onto PSi by PVD of pure gold (99.9999%, Sigma-Aldrich, USA) using LJUHV E-400 electron-beam (e-beam) technology.

The Au deposition was accomplished by maintaining a vacuum level of 10^{-7}torr with deposition rate 0.6 Å per second and an argon flow equal to 50 sccm. Au nanofilm of 100 nm thickness onto PSi surface was therefore achieved by regulating the deposition time. The SEM micrographs of all the samples have been obtained using a scanning electron microscope (Hitachi) model S-3000N with an accelerating voltage of the electron beam of 20 kV was employed. The surface morphology and composition of samples were examined by atomic force microscopy (AFM) in tapping mode. Atomic Force Microscopy (AFM) images were recorded by using AMBIOS Technology (Q-Scope Nomad TM model). The PL spectra have been recorded using a Perkin Elmer Luminescence Spectrometer LS55 in the emission wavelength range of 300-800 nm, keeping the excitation wavelength fixed at 450 nm. The optical measurements of the Au/PSi thin films were carried out at room temperature using Shimadzu UV-VIS-NIR 3150 spectrophotometer in the wavelength range from 100 to 1000 nm.

3.1. Surface Morphological Studies (SEM)

Figure 1(a) – (d) illustrates the surface morphology (magnifications: 500 and 2000) of as-formed Porous Silicon (PSi) and gold coated PSi substrates like pore size and pore shape are investigated by analysis of scanning electron microscopy (SEM) images. This analysis based on the SEM images of PSi substrates showed that the surface of the porous layer looks like pore-like structure consists sting of two types of pores shape rectangular and gambling forms with randomly distributed over the surface, the average pore diameter of the PSi is 7.06 nm. The major value of the pore sizes may possibly attribute to accumulative of electron-hole pairs inside the porous layer, which improve the silicon dissolution process between the nearest-neighbor pores [50].
The SEM images of gold nanoparticles coated porous silicon showed that its shape was mostly rounded with average pore diameter is 7.22 nm. The porosity of PSi was defined as the quantity of silicon removed during anodization compared with the silicon concentration before anodization evaluated in the same volume. The porosity can also be defined as a function of geometrical parameters is written as [49],

$$P = \left(\frac{\pi}{2} * 1.732\right)\left(\frac{1}{1+\frac{m}{d}}\right)^2$$

where d is the average pore size and m is the distance between pores. Using the above equation, we have estimated the porosity of our PSi and Au/PSi are 76 % and 57%. The average pore diameter was calculated using the following Equation [49].

$$E(eV) = Eg + \frac{h^2}{8d^2}\left[\frac{1}{m^*_e} + \frac{1}{m^*_h}\right]$$

where E(*eV*) is the energy band gap of PSi and Au/PSi obtained from the PL peak (Fig.3). The energy band gap of c-Si is 1.12 eV, h is Planck's constant = 4.13×10^{-15}eVs, d is the diameter of the pore and m^*_e and m^*_h are the electron and hole effective mass, respectively (at 300 K, $m^*_e = 0.19m_o$, $m^*_h = 0.16m_o$ and $m_o = 9.109\times10^{-31}$kg). Average pore diameter of PSi and Au/PSi are found to be 7.06 nm and 7.22 nm.

3.2. Atomic Force Microscopy (AFM) studies

Figure 2(a) and 2 (b) represents a typical AFM image of the PSi and Au/PSi substrates. Generally, the surface of PSi layers show nano-pyramid like pillars which are perpendicular to c-Si wafer and it consist of nanoscale pores, circular micropores and microstructural islands. AFM images visually evidenced that the gold nanoparticles coated porous silicon has a significant effect on the size and shape of the pores. In 100 nm gold nanoparticles deposited on porous silicon, the appearances of high magnitude of flat pyramid pillars are due to

the c-Si among the more pore channels. The circular micropores are related to the sites with deposition range of gold nanoparticles. The results indicated that the Au/PSi showed high roughness owing to high pore-filling effect as confirmed their gold nanoparticles fraction values. The AFM analysis, parallely coincides with SEM analysis. It is important to note that the RMS roughness values of PSi and Au/PSi are found to be 256 nm and 560 nm.

3.3. Photoluminescence (PL) studies

Figure 3 illustrate the photoluminescence spectra of PSi layers before and after deposition of gold nanoparticles (100 nm). PL spectra exhibit a peak centered at 746 nm (PSi) whose intensity and width seem to be enhanced significantly due to Au deposition (757 nm). Not to mention that, PSi 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. 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 PSi and develop more stable photoluminescence properties [51]. 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. From the PL spectrum, the energy band gap of the PSi and Au/PS were evaluated as 1.659 eV and 1.635 eV respectively.

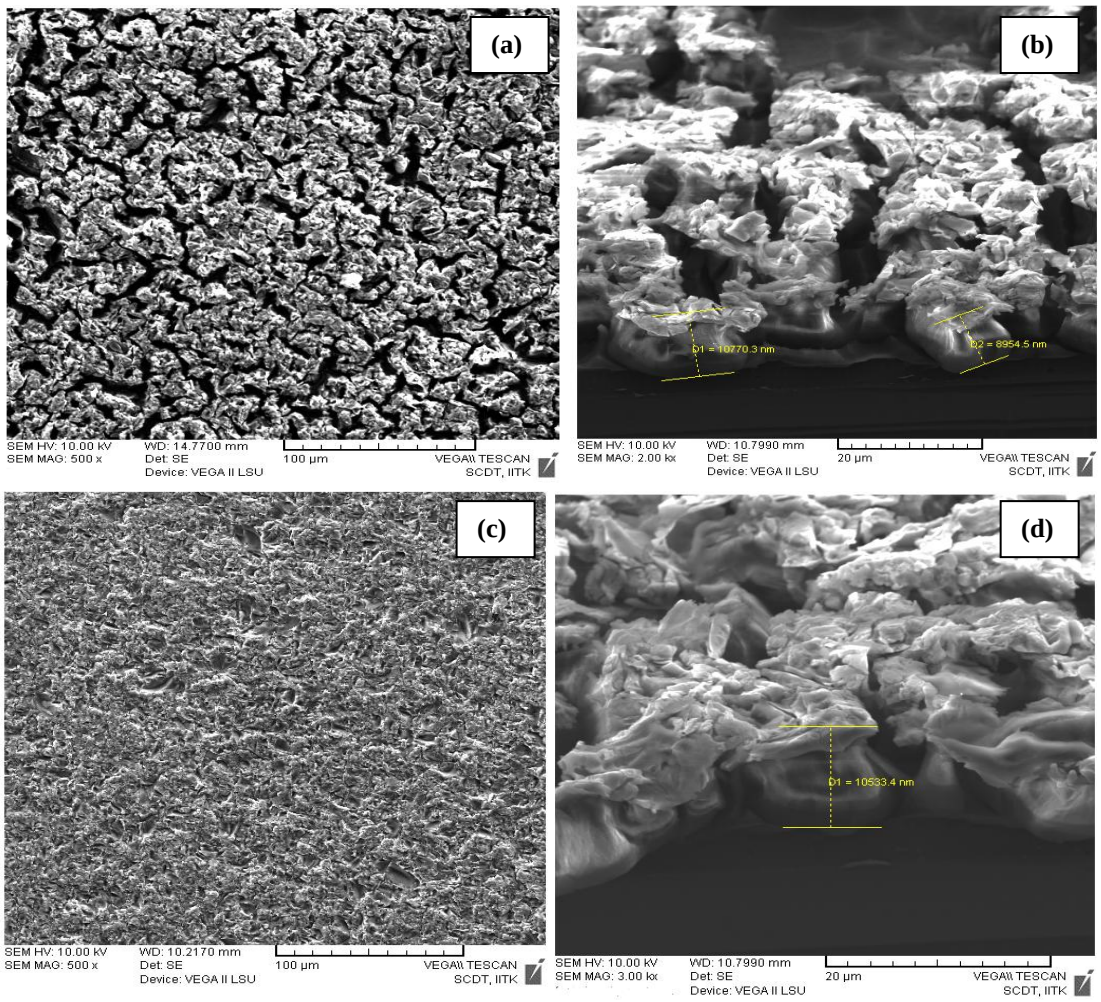

Figure 1.SEM images of (a) PSi (magnification: 500) (b) PSi (magnification: 2000) (c) Au/PSi (magnification: 500) and (d) Au/PSi (magnification: 2000)

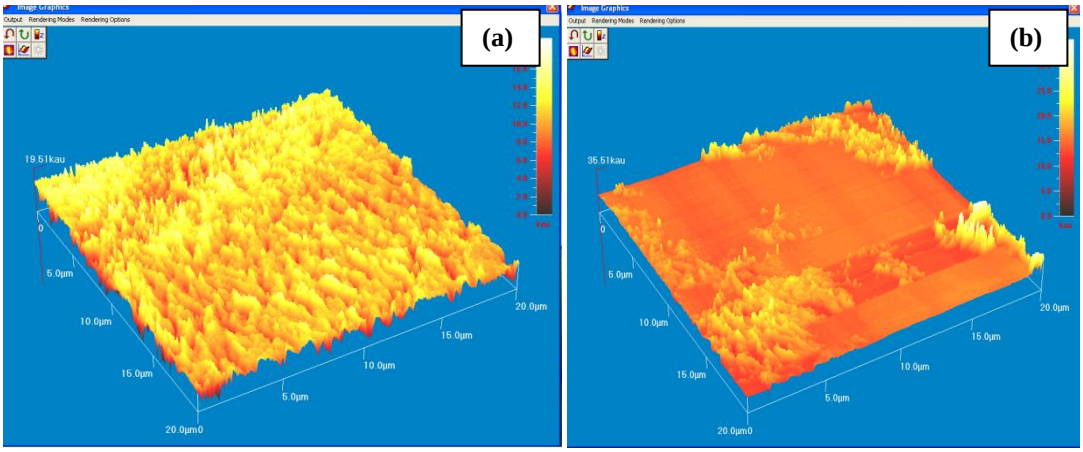

Figure 2.AFM images of (a) PSi and (b) Au/PSi

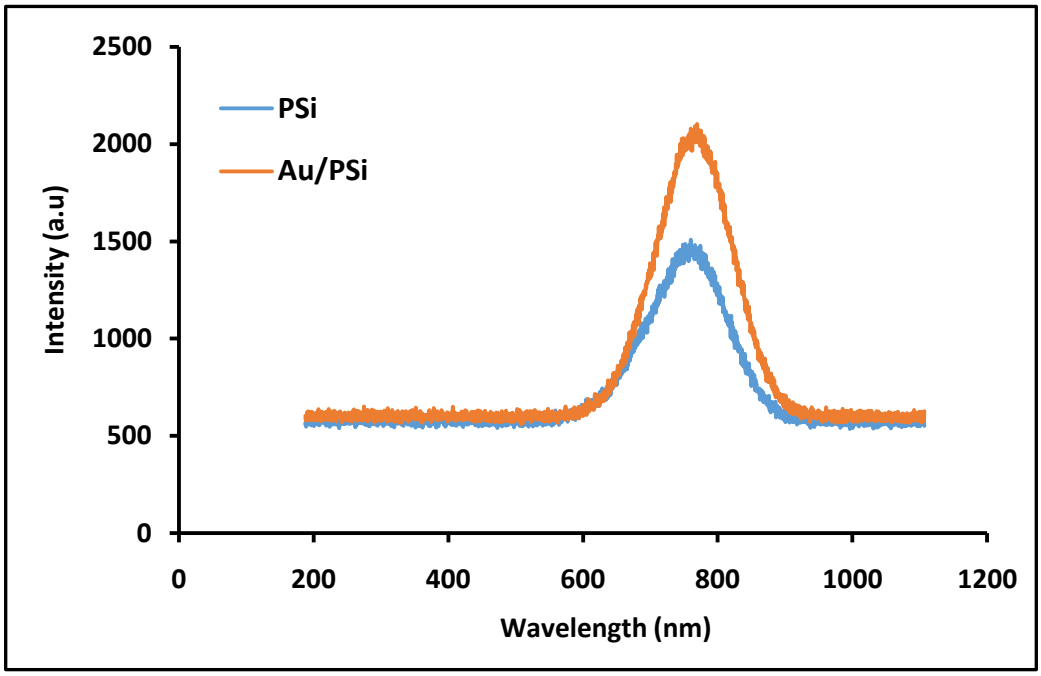

Figure 3. Photoluminescence (PL) Spectra of the PSi and Au/PSi

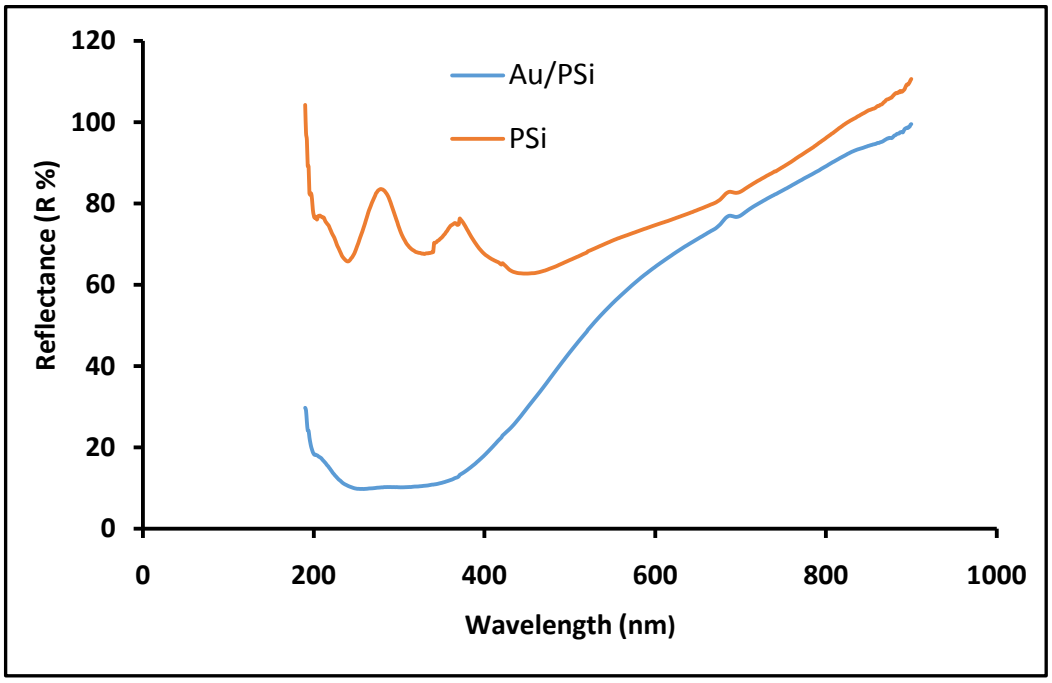

Figure 4. Transmittance Spectra of the PSi and Au/PSi

3.4. Optical (Reflectivity) studies

In Figure 4, we presented the reflectivity spectra of porous silicon before (reference) and after gold nanoparticles deposition by PVD techniques. For the range of wavelengths of visible light ($200 \leq \lambda \leq 500$ nm), these spectra show that there is a remarkable decrease in the reflectivity of the samples that have undergone a deposition of gold nanoparticles compared to reference one. This decrease from almost 30 to 15 is mainly due to the increase in the surface roughness of porous silicon after deposition, which is in agreement with the AFM topography (Fig. 2). Optical improvements that occur during deposition of gold nanoparticles on PSi are related to the morphology and distribution of gold nanoparticles, 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 [52]. 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 [53]. Moreover, PSi 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 nanoparticles compared to reference one.

IV. Conclusion

Porous Silicon (Psi) layers were successfully fabricated from p-type crystalline silicon (c-Si) wafer by the chemical etching (stain etching) method. The surface morphological and structural properties of PSi and Au/PSi thin films were studied by using SEM and AFM. The SEM micrographs shows uniformly distributed particle nature in PSi layer. The pores are covered with very thin layer of gold nanoparticles (100 nm) by using PVD technique. The PL studies shows that as-formed PSi has an intense and broad PL peak at 746 nm, on the other hand in the Au/PS thin films, this peak is blue shifted (757 nm) indicating modification at the interface of Au/PSi. The band gap energy values of the PSi and Au/PSi thin films were calculated from the PL spectrum. The structural properties of PSi and Au/PSi, confirmed by AFM investigations. This treatment allows an enhancement in the reflectivity and photoluminescence of the samples.

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