Controllable synthesization of Au nanoparticles by laser enhanced wet KOH etching process

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Abstract. In Si substrate, anisotropic KOH etchants are mainly utilized to form pyramids like on the Si surface. However, this process is not well controlled way owing to the different and random etching pathway. In this work, we applied laser radiation during the anisotropic KOH wet etching process to modifies the topographical properties of Si substrate, as an efficient, simple and low cost texturing process for Si substrate. This approach employs different laser wavelength to modify the topographical features from a crater like structures to Si nanocrystallites in the form of pillars like structures on the Si surface. In order to investigate the formation of plasmonics species, gold nanoparticles was incorporated into Si surfaces by simple ion reduction process. The Si topographical features was studied with atomic scanning microscopy (AFM) images of Si before and after laser irradiation process. The irradiation with 405 laser wavelength, show the formation of thin and high density of Si nano pillars-like structures compared with more thick depther Si nano pillars like structures layer.

1. Introduction

Wet chemical etching is an essential procedure in formation of rough Si surface, which more benefit for solar cells application. For etching process of Si in KOH solutions is largely used [1], like Sana et al. examined the anisotropy of Si substrate through the wet (KOH) chemical etching. The resulted silicon nano-structures, like hillocks, or pyramids, were typical size in micrometer/nanometric. since its can form textured Si layer with random pyramids or craters like structures and hence, increased the advantages of it's in different application such as light sensing, solar cells and chemical sensing applications. In the Si etching procedure with alkaline solutions, the wafers is isotropically and hence creating round shaped textures in all Si surface. This etching process is difficult to regulate and disposal of the chemical waste is expensive. To minimize these difficulties with excellent controlling of the topographical properties Si wafers, laser assisted the texturing in KOH solutions was proposed. The rough Si layer in the form of Si nano pillars-like structures, contains a high density of gold ions reduction centers Si dangling bonds Si-Hx (nucleation sites) [2]. The formation of gold nanoparticles by immersion process of rough Si layer in ionic solution of Gold ions through the reduction process of ion by utilizing the dangling bonds of rough Si surface is very useful technique to synthesize specific plasmonics nanoparticle [3,4].
Topographical features play an essential role in the activity of rough silicon (Si) based surface enhanced Raman scattering (SERS) sensor as it modifies the formation of plasmonics nanoparticles. To maximize density of nucleation sites of tough Si surface and thus enhance both of the density of Raman active sites, the Si substrate must be well textured. In Si substrate, anisotropic KOH etchants are mainly utilized to form pyramids like on the Si surface. However, this process is not well controlled way owing to the different and random etching pathway [5-8].

In this work, the effect of laser illumination process during the KOH wet etching process was investigated extensively to reconstruction the topographical properties of Si surface to an optimum feature for the SERS sensing performance. The main goal was to synthesize an active Si nanopillars layer for nanophotonic applications.

2. Experimental work

n-type mirror like Si wafer of resistivity 10 Ω·cm, 500 µm thick with (100) orientation was used. The substrate was cutting into 2 × 2 cm², after cleaning process with very dilute 10% Hydrofluoric acid, the wet KOH texturizing process was carried out at 3M KOH concentrations. The irradiation process of Si substrate during the wet etching process was performed by using two laser wavelength of about 405 nm and 650 nm at fixed power density of about 150 mW/cm². The laser spot area was expanded in order to cover all the Si surface area. The irradiation and hence the wet etching process period of all the substrate is about 2 min, and the effects of the laser wavelength on surface topography was investigated. The topographical features (dimensions of Si nanopillars and shape of textured surface, roughness of the surface and the depth of Si nanopillars) were calculated by using scanning probe microscopy (SPM); contact mode type SPM-AA 3000 system. Moreover; The spectral features of the Si substrates (PL) spectra were investigated.; after using CW 325nm, 300mW He_Cd laser of photoluminescence system.

The most important point for modifying the properties of gold nanoparticles is to change the topographical features of the resulting rough Si surface to Si nanopillars layer. The plasmonic topographies of gold nanoparticles modifies with nanopillars dimensions, the density and shape, and surface roughness at fixed immersion condition. The gold nanoparticles/Si nanopillars layers were created through passivation of the gold ions on silicon nanopillars or rough Si surface by the decrease of gold ions to gold nanoparticles by simple and fast dipping process.

The Si nanopillars and the rough Si surface were immersed in 5x10⁻³ M concentration of (HAuCl4) solution with a several drops of diluted 3 M of HF at a room temperature immersing period of 3 min. In the gold immersing corroboration, the synthesis of gold nanoparticles on Si nan pillars surfaces or rough surfaces takes place via the Volmer-Weber growth mechanism[9]. Once a Si substrate is immersed in the HAuCl4 solution, gold-nanostructures is synthesized through gold ion reduction by the dangling bonds existing on the Si nanocrystallites. The amount of these dangling bonds (nucleation sites) vary strongly with the nature of surface and has a huge populace at Si nanopillars. The synthesis gold nanoparticles occur according to the following equations [8,9].

As a result of these reactions, gold nuclei and henceforth; the nanoparticles growth process, take place at the Si surfaces progressively. The aggregated process of gold nanoparticles at fixed immersing conditions is affected by several notably parameters like amount, type and surface locations of nucleation sites Si–Hₓ bonds. The plasmonic features of gold nanoparticles/Si surface were inspected using (MIRA3 TESICAN) scanning electron microscopy SEM in addition to X-ray diffraction (XRD-6000, Shemadzuie), Where as Image_J program was used to study gold nanoparticle size and hotspot histogram from SEM images.
3. Results and discussion

3.1 Surface characterization of Si

Figures 2a, 2b and 2c illustrate the SPM micro images of the substrates of rough Si surface and Si surface with nanocrystallites in the form of nano pillars like structures respectively. The 3D micro image of figure 2a without laser illumination, displays that the surface of the Si of rough structure contains silicon Carter-like morphologies with different sizes and forms. These silicon carters are distributed in random way with different dimensions. For the laser illuminated substrates of wavelengths 405 nm and 650 nm figure 2b and 2c respectively, the Si nanocrystallites were converted from the Carter-like structure shape to nano pillars-like structure. The topographical features of the Si surface was found to have Si nano pillars with high tendency to be very well-organized and more uniformly distributed especially for the case of 405 nm illumination process. While for the case of 650 nm illumination process, the 3-D micro image of the substrate revealed a low uniformity in nano pillars aligned within the Si surface.
Figure 2. present the SPM micro images of Si nanocrystallites of non illuminated (2a) and laser illuminated substrates with wavelengths: (2b) 405nm and (2c) 650nm.

These dramatic changes in the surface topographies of the silicon nanocrystallites with the laser illumination process during the wet etching process are strongly connected with the photons absorption process and hence, the increasing of the temperature locally within the irradiated region. This increasing of the temperature will enhance the Si dissolution process and hence reduce the dimensions of the Carter in x and y directions and this behaviors will increase the probability of converting the Si morphologies from Carter shape to pillars shape. As the laser wavelength decreases the absorption of laser photons will occur in the surface of Si surface. The increasing of laser wavelength, will increase the probability of absorption the photons deeply within the Si layer and this will lead to increase the depth of resulting nanocrystallites (absorption in a z direction). Based on the suggested explanation that stated above, application of laser radiation during the wet KOH etching the process can enhance the Si engraving rate thus; Si solving process locally.

The absorption depth (the depth at which the laser power drops to (1/e) from its initial value) of the laser photons varies with the laser wavelength. The value of this depth is about (44.47 nm) and (41.40 nm) for the laser wavelength 650 nm and 405 nm respectively [10], which indicates an effective heating process within this depth.

In addition, for low laser wavelength, the Carter heating increases and this will lead to an increase in the temperature inside the Carter matrix. The very low thermal conductivity 0.75 W/mK of silicon
nanocrystallite of dimensions (100 to 300) nm as compared with that of bulk Si 160 W/m K [11-14], will lead to improving the probability of melting the Silicon Carter owing to the heat accumulation inside the nano Carter. This will enhance the likelihood of the dissolution process amongst the Si nano Carter.

The histogram for Si nano pillars and Carter sizes without and with laser illumination process is shown in Figure 3a-c. For Si substrate without illumination, Figure 3a, the nano Carter dimension is ranging from (20 to 80) nm with an average value of 70 nm. For substrate of illumination wavelength 405 nm, the nano pillars dimension is ranging from (30 to 105) nm with an average value of 45nm, Figure 3b. By increasing the laser wavelength to 650nm, Figure 3c, the nanopillars exposed a dimension ranging from (50 to 110) nm with an average value of 60 nm.

![Histogram](image)

**Figure 3.** Display the histogram of Si nanocrystallites dimensions of non illuminated 3(a) and laser illuminated substrates with wavelengths: (3 b) 405 nm and (3c) 650 nm.
Can expose average surface roughness and depth of Silicon nanocrystallites (pillars and Carter like structures), substrates as in the table 1. The average surface roughness varies with laser illumination process, the surface roughness reaches a larger value of about 11.4 nm for etched substrate with 405 nm and a smaller value of about 4.76 nm for the etched substrate without illumination.

**Table 1.** Topographical features of textured Si substrates (a) without illumination, (b) 650 nm and (c) 405 nm.

|                | Avg hillocks height (nm) | Roughness (nm) | Si nano size (nm) |
|----------------|--------------------------|----------------|------------------|
| (a) Without illumination | 37.74                    | 4.76           | 70               |
| (b) 405 nm     | 44.47                    | 7.51           | 60               |
| (c) 650 nm     | 41.40                    | 11.4           | 45               |

The changes of the depth of Si nanocrystallites showed a highest value of nano pillars depth 44.47 nm was achieved for etched substrate with 650 nm, while the lowest value 37.74 nm has obtained from etched substrate without laser illumination. The main goal behind this performance could be owing to the lower etching rate of the Si surface in the Z directions compared to the rate in the x and y for the case of 405nm illumination process and in Z-direction through the Si layer for the case of 650nm laser illumination.

The PL spectra of the Si nanocrystallites substrates with and without laser illumination of KOH wet etching process is shown in Figure 4.

**Figure 4.** show the PL spectra of Si nanocrystallites of non illuminated (4a) and laser illuminated substrates with wavelengths: (4b) 650 nm and (4c) 405 nm.
For the case without illumination, the etched substrate the peak position of PL spectrum is located at 790 nm with an intensity of 1020 au. On the wavelength peak position and intensity of the PL peaks, the effects of laser illumination on the PL spectrum are clearly visible. The effect of change from a traditional wet KOH etching process to a laser-assisted wet KOH etching process has resulted in a blue shift in the PL peak position and an increase in PL intensity. For the case of laser illuminated with 650 nm and 405 nm wavelength, the PL peak position is 730 and 612 nm respectively, with their PL intensity of about 3630 and 4250 au. The etched substrate without illumination process, showed the minimum value of $E_g=1.65$ eV and the maximum value of energy band gap of about 1.98 eV was achieved for substrate in which Si nanopillars have lower Silicon nano dimensions. The quantum confinement effect of confined charged carriers within the matrix of Si nanocrystallites is well aligned with the dependence of the PL bands of Si nanocrystallites on the dimensions of Si nanocrystallites. The rising of PL intensity is connected to the density of Si nanocrystallites owing to the irradiative recombination process among electron and holes within each crystallites. The increase in the PL intensity is a fingerprint for the density of nanocrystallites. The dependence of the dimension of nanocrystallites (looks like nanowire).

where $E_g$ (eV) represents the energy of Si nanocrystallites and the energy gap of native Si before the etching $E_g=1.1$ eV, $h=4.14\times10^{-15}$ eV s is Planck’s constant, $m^*_{e}=0.19\, m_0$, $m^*_{h}=0.16m_0$ are the effective mass of electrons and holes corresponding, and $m_0=9.1\times10^{-31}$ kg, $d(x)$ and $d(y)$ are the dimensions of Si nanocrystallites. The absorbed laser power part that converts to heating $Q_h$ inside the Si nanocrystallites is given by [15].

$$Q_h = m C_v \Delta T \quad (1)$$

Where; $\Delta T$ is the temperature rise and $Q_h$ is the input heating energy $= (1 -$ quantum efficiency of Si $) \times$ (laser power) $\times$ illumination period.

Heating a mass within the Si nanocrystallites $M_h$ is expressed as [15].

$$M_h = d \text{ Si nanocrystallites} \times A \times \rho \quad (2)$$

Where $A$ is the etched area, $\rho$ is the density and $d$ Si nanocrystallites is the depth of Si nanocrystallites.

### 3.2 Morphological features of plasmonic gold nanoparticles/Si nanocrystallites

Figure 5a–c, presents the synthesized gold nanoparticles; due to the gold ion reduction process by incomes of the nucleation sites Si–Hx bonds of Si nanocrystallites. Figure 5a, of substrate without illumination process, presents a morphology Above the Si nano Carter like structure is a semi continuous gold coat; resulting from semi homogeneous growth, where the smaller values of surface roughness, and the depth of Si-nano Carter indicates to gold ion reduction process above Si-rich with extra ordinary amount of (Si–H1) bonds. The existence of isolated semi-spherical gold nanoparticles above Si nano pillars structure is obviously exposed in Fig. 5b of the substrate synthesis with 405nm illumination wavelength. This shape of nano-particles reflects a formation with a very low aggregation rate manners between the nanoparticles and the forming combined gold nano layer for being just one layer. This manner, may be in general, attributed to the position of surface ions reduction centers Si–H1 bonds over the apex of the forming pillars. Figure 5c is for the substrate synthesized with 650nm illumination wavelength at which the surface roughness and the depth of Si pillars reached to higher value. It is evident that the gold nucleation process was dependent on Weber-Vomer mechanism.
Figure 5. present the SPM micro images of Si nanocrystallites of non illuminated (5a) and laser illuminated substrates with wavelengths (5b) 405nm and (5c) 650nm.

The shape of the formed nanoparticles is semi-spherical too but with high degree of agglomeration between the gold nano-particles. This behavior might, in overall, be very linked to the existence of high degree nucleation sites Si–Hx (x=2, 3) groups over the peak Si nano pillars. The structural features of Si-nanocrystallites greatly affect with the morphology of plasmonic gold nanoparticles. It is difficult to recognize the size of the forming gold nanoparticles for non-illuminated substrate; Figure 5a, as the gold nanoparticles spread above the Si nano Carter structure. The histogram of the gold nanoparticles without illumination process Figure 6a, ranges from (40 to 100)nm, with highest value at 90nm. After the illumination with 405 nm, Figure 6b, the histogram decreased in dimensions to a minimum amount.
fluctuating from (45 to 140) nm, with a highest value at 75nm. The increasing of illumination wavelength to 650 nm; Figure 6c, the gold nanoparticles sizes continue to increase, but with dimensions histogram fluctuating from (10 to 75) nm, with a peak located 75nm.

Figure 6. show the histogram of gold nanoparticles dimensions of non-illuminated (6a) and laser illuminated substrates with wavelengths ; (6b) 405nm and (6c) 650nm.

The dimensions of aggregated gold nanoparticles and therefore; the scopes and amount of hot-spot regions between the synthesized nanoparticles changes with the structural features. Figure 7, show the hot spot region without illumination substrate and laser illuminated substrates. According to SEM images of non-illumination substrate, the effective hot spot vacancies is inattentive. This is due to the plasmonic gold nanoparticles Synthesized are presented as a semi coating layer with very low density of vacancies owing to the lower value of the surface roughness [15]. The formed hot spot region, for
substrate with 405 nm illumination wavelength, Figure 7a, the vacancies density in the formed plasmonic gold nanoparticles was located within the range 25 to 235 nm with its peak value positioned at 80 nm. These hotspot vacancies are just hot-spot Vacancies. For substrate with 650nm illumination wavelength, Figure 7b, the dimensions of the hot spot Vacancies plasmonic gold nanoparticles are within the range from 230 to 1030 nm and the peak value is at 400 nm. Based to these values, this vacancies is a collection of hot and cold nano vacancies. The obtained results infer that the plasmonic gold nanoparticles sizes can be understood as a touch of the features of Si-nanocrystallites (surface roughness and depth), wherever the largest gold nucleation sites were located at the high energy points such the sharp nanopillars region[16, 17].

Figure 7. show the histogram of hot spot vacancies within the the Si nanocrystallites/ gold nanoparticles layer of laser illuminated substrates with wavelengths : (7a) 405nm and (7b) 650nm.

The EDX result of the synthesized plasmonic gold nanoparticles; income Si nanocrystallites, are exposed in Figure 8a–c. These results confirms the formation of Au nanoparticles with the presence of Si element, without any extra elements. The peak value of the intensity of plasmonic gold nanoparticles of non-illumination substrate Due to the high ion reduction rate with groups of (Si–H1) nucleation sites, Figure 8a is higher than other substrates. The amount of synthesized gold nanoparticles for the substrates with laser illumination process, Figure 8b- c, have a comparable value due to the identical ion reduction rate.
3.3 XRD spectra of plasmonic gold nanoparticles/silicon nano crystallites

Figure 9a–c presents the results of XRD pattern of gold nanoparticles/Si nanocrystallites synthesized by integrating of gold nanoparticles on Si nanocrystallites substrates without and with laser illumination process.
Figure 9. display the XRD of Si nanocrystallites /gold nanoparticles layer of non-illuminated (9a) and laser illuminated substrates with wavelengths: (9b) 405nm and (9c) 650nm.

These figures present that the Si-nanocrystallites are still in crystalline phases along the 100 plane with 20 diffraction angle of about 31.12°, whereas the XRD of gold nanoparticles display specific Bragg’s reflections with 20 diffraction angles of about 38.37° and 44.45° for the crystalline planes 111 and 200. The application of laser illumination source during the wet KOH etching process leads to broadening the (FWHM) of the XRD peaks. This manner is really connected to the dimensions of the resulting gold nanoparticles. This little deflect in Bragg’s reflection peaks is owing to the presence of local interatomic space changes of the formed gold nanoparticles deposited on Si nanocrystallites [18]. As the sizes of the formed nanoparticles reduce, the (FWHM) is growing wider. As a result, the laser illumination process during wet KOH etching will alter the dimensions of Si nano crystallites and therefore; the synthesized nanoparticles. The grain sizes of deposited gold nanoparticles were calculated based on the XRD peak widening by using the Scherer’s equation [18, 19]. The specific surface area
(S.S.A.) is very important limiting parameter for the characterization. Table 2 lists the values of gold nanoparticles grain sizes, (FWHM) and (S.S.A.) for plasmonics nanoparticles with and without illumination process. From this table, the higher value of grain size of about 17.64 nm in the plane (111) for the substrate without illumination. The lower value of grain size is in the plane (111) is around 4.24 nm for the substrate with 405 nm laser illumination wavelength. The higher value of S.S.A for plasmonic nanoparticles of about 73.18 m²/g is achieved for the substrate with 405nm illumination whereas the lower value of about 18.72 m²/g is for the substrate without illumination. The lessing of plasmonic nanoparticles grain sizes and rise of S.S.A can be clarified based on the Si nano crystallites aspects mainly the surface roughness and the depth of base substrate.

| Peaks   | Grain Sizes (nm) | FWHM (deg) | S.S.A. (m²/g) |
|---------|------------------|------------|--------------|
| (a)     |                  |            |              |
| Without illumination | (100) | 25.61 | 0.31 | -------- |
|         | (111) | 17.64 | 0.45 | 18.72   |
|         | (200) | 16.54 | 0.59 | 19.97   |
| (b)     |                  |            |              |
| 405 nm  | (100) | 19.8  | 0.41 | -------- |
|         | (111) | 4.24  | 1.86 | 73.18   |
|         | (200) | 4.33  | 1.83 | 71.76   |
| (c)     |                  |            |              |
| 650 nm  | (100) | 24.81 | 0.29 | -------- |
|         | (111) | 14.48 | 0.54 | 22.68   |
|         | (200) | 9.05  | 0.87 | 36.30   |

Conclusions

In this study, we report for the modifications of surface topography of Si nanocrystallites synthesized by wet KOH etching process; using laser illumination process during the etching route was achieved. With different laser wavelength with fixed laser intensity, the surface roughness, depth and the shape of the Si nanocrystallites were performed. For an etching process without illumination process, the Si nanocrystallites were irregular Carter like structures with large average dimensions. The application of laser illumination process leads to covert the resulting nanocrystallites to well organize and uniformly Si nano pillars-like structures distributed with smaller dimensions.

The laser illumination during the procedure lead to an increase in the Si dissolution within the nano crystallites layer. Smaller dimensions and highest depth were obtained with 405 nm illumination wavelength. The application of laser illumination process leads to produced higher PL emission with blue-shifted intensity than that of non-illumination case. Simple, low cost, fast and well-controlled approach for formation plasmonic gold nanoparticles (dimension and S.S.A) on silicon nanocrystallites was obtained via applying laser illumination during the wet KOH etching process. The achieved results represent as an addition valuable to the domain of plasmonics gold nanoparticles.

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