Using multilayer silicon nanostructures to enhanced Raman spectroscopy

Muna S. Mohammed Jawad
Laser and Optoelectronics Engineering Department, University of Technology, Baghdad, IRAQ
Mona2004sss@yahoo.com@yahoo.com
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الخلاصة

تم تحضير سيليكون النانوي متعدد الطبقات باستعمال طريقة التنميش الضوئي-الكيميائي لشرائح السيليكون نوع n باوقات تنميش مختلفة (10، 20، 30، 40) دقيقة مع شدة إضاءة مختلفة من (10، 15، 20، 25) ملي واط/سم^2 هذه الشدات أدت إلى تشكيل أنظمة السيليكون باحجام تتروح من(2.85- 4.02) نانومتر. وأظهرت الصور الماسح الالكتروني سطح طبقة مسامية باحجام وابعاد مختلفة المسامية. وبينت قياس تشتت رامان في السيليكون المسامي ازاحة طيفية حمراء التي زادت مع زيادة وقت التنميش وشدة الإضاءة

ABSTRSCT

Porous silicon multi layer has been prepared by photo-chemical etching of n-type silicon wafer at different etching time (10, 20, 30, 40)min with different illumination intensities of (10, 15, 20, 25) mW/cm^2. These intensities lead to form porous silicon systems of size in the range (2.85-4.02)nm. SEM images indicated that the surface of the etched layer has pore-like structure with different pore sizes and porosities. The measurement of Raman scattering in porous silicon showed a red shift of the phonon frequency which increased with increasing the etching time and illumination intensity.
Keywords: Silicon nanostructures, Raman spectroscopy, Photochemical etching.

INTRODUCTION

Silicon nanostructures device is expected to have significant applications in nano-laser systems and light emitting devices. PS were first reported by [1] from electro-chemical etching process of silicon wafer in (HF) solution. Among many physical and chemical analyses, photoluminescence and Raman plays an important role in the identification and structural characterization of semiconductors [2].

The Raman Effect in silicon is more than 10,000 times stronger than in glass fiber, making silicon an advantageous material. Instead of kilometers of fiber, only centimeters of silicon are required. However, 'Raman amplification' is a small effect, and to build a laser with it you need very high power intensity and very low absorption losses [3]. Such conditions have already been achieved in optical devices made in silica (SiO_2), whereas, in silicon on insulator structure, Raman amplification was limited to very short pulses of a few nanoseconds at most [4]. The problem is that an unwanted nonlinear side effect -two photon absorption- creates pairs of electrons and holes that remain for a long time in the

sample and absorb both the pump and light and signal light and so quickly turn off the Raman amplification [5], solve this problem by embedding the silicon waveguide within a reverse-biased p-i-n junction diode, designed to extract electrons and holes away from the waveguide. With this design, they demonstrate a silicon laser with continuous operation. However spectral limitation of the Raman Effect in silicon is unavoidable in the Silicon on insulator (SOI) plat form.

In this paper, an approach based on Raman scattering in porous silicon is discussed [6]. These approaches present some advantages:

- Spectral broadening of spontaneous Raman scattering with respect to silicon is achieved.
- Infiltrating liquids in porous silicon a tuning of the Stokes shift is achieved.
- Raman gain coefficient can be enhanced and due to quantum confinement the two photon absorption can be eliminate.

In the present work, the effects of etching time with laser illumination intensity during electrochemical etching process on the spectroscopy of PS and the properties of PS were studied, based on the SEM investigation and Raman scattering method [7].

THEORTICAL CONSTRACTIONS

The porosity of the quantum wire system is one of important parameters of the nano wire system and is defined as the fraction of void within the nano silicon layer. The porosity is measured by using gravimetric measurements: first; the weight of the virgin wafer is measured before anodization (M_1) , then after anodization (M_2) , and finally after removing of the porous silicon layer (M_3) in a 1 molar solution of sodium hydroxide (NaOH). After determining these values , the porosity is given by the following equation(1) [1] :

$$Porosity\ \% = \frac{M_1 - M_2}{M_1 - M_3} \qquad \text{---------- (1)}$$

etching process depends on the photo-generation of electron- hole pairs (G) in the silicon wafer and is given as:

$$G = Q_E \frac{P}{h\upsilon} \qquad \text{……(2)}$$

Where P is the power of the laser, hν is the energy of the incident photons and Q_E is the quantum efficiency.

The spectrum of Raman scattering is composed of a few characteristic peaks corresponding to all the Raman-visible phonon modes. The location of each Raman characteristic peak is mostly determined by the vibration energy of its phonon mode, but it may vary more or less when the crystal lattice of the material deforms, leading to an energy variation in lattice vibration. Raman spectroscopy plays an important role in the identification and structural characterization of molecules [8]. Although Raman spectroscopy shows extremely low scattering cross sections as compared to fluorescence, the surface enhanced Raman scattering effect can provide cross sections with several orders of magnitude higher than normal Raman spectroscopy and does not suffer from photo bleaching effects [9]. Raman enhancement can be explained in terms of electromagnetic and chemical enhancement in the presence of metallic nanostructures such as silver, gold, copper and aluminum [10]. The most accredited theory predicts that the electromagnetic enhancement mechanism is largely responsible for the enhancement of Raman scattering. The magnitude of electromagnetic enhancement is determined by the localized optical properties of surface features at nanoscales. It is the intricate relationship between the surface structure and optical characteristics that determines the signal intensity. The oscillation of conduction electrons in metal nanoparticles can be driven by incident light. This electron oscillation, also known as the localized surface plasmon resonance, generates an electromagnetic field that is localized near the surface of a metal nanoparticle [5]. This large electromagnetic field induces a dipole in nearby molecules, thus enhancing Raman scattering from adsorbed molecules. A Raman spectrum of PS is important to check the crystalline property of the prepared material [11, 12]. Raman spectroscopy is an efficient technique to evaluate quantitatively measurements of stress, presence of nanocrystals and homogeneity [13].

MATERIALS AND METHODS

Silicon nanostructures were fabricated from n-type silicon wafer of (111) orientation and (20 Ω.cm) resistivity. The silicon samples were $(1.5\times1.5)cm^2$. The etching process was carried out using photochemical

etching process which employed 530nm diode laser at different illumination intensities (10,15,20,25) mW/cm^2. The irradiated area was about 1cm^2 and different etching time (10, 20 30, 40)min. The etching process was materialized in specially designed cell. Cell made from Teflon to synthesize nanostructures layer at the top of silicon wafer. The experiment was conducted in room temperature and is shown in the figure (1). The cell has been provided a porous silicon layer of uniform cross sectional area. This uniformity is recommended for the application of porous silicon and photovoltaic cells. The cross section of cell is shown in figure (1). The Raman spectra were recorded using 1000 micro-Raman spectrometer (Horiba Jobin Yvon LabRAM HR800UV Raman spectrometer) is used. at room temperature, together with an excitation light from a He-Ne laser (632.8 nm). Raman measurements and the SEM measurements were carried out in Indian Institute of Technology Madras Chennai, India

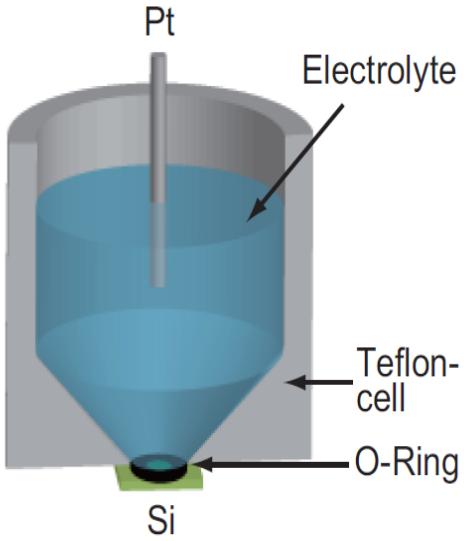

Figure 1: Schematic diagram of the etching system used in this work.

RESULTS AND DISCUSSION

The porosity increased gradually with increasing laser illumination intensity. This behavior is attributed to the increase of the number and diameter of pores which lie between the silicon nanowires. The latter SEM, images confirm this view. This behavior of the porosity has led to a large variation in refractive index as compare to the crystalline bulk silicon. The refractive index decreased to (2.693) at laser illumination

intensity of 10mW/cm^2 and to (2.551) when the laser illumination intensity increased to 20 mW/cm^2 . The minimum value of refractive index (1.91) in PS was obtained at 25mW/cm^2. These low values of refractive index make the PS acts as an antireflecting coating layer. Figure (2) shows the SEM micrograph of the PS at illumination intensities of (10)mW/cm^2 and (25)mW/cm^2 .

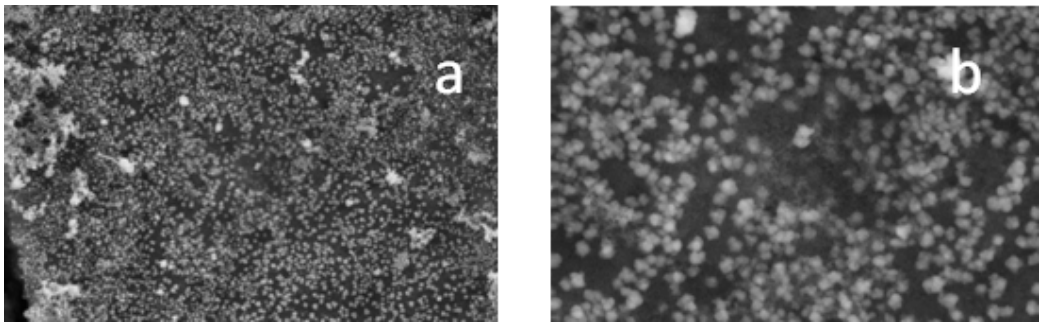

Figure 2: Scanning Electron Microscope (SEM) image of the PS at different illumination intensity (a)10 mW/cm^2, (b) 25mW/cm^2

Increasing the laser illumination intensity will form a complex silicon nanowire matrix system of different size and the morphological nature of the etched surfaces show a different pores, trenches size and shapes. These pores and trenches are aligned in random direction and the pores widths are increased with increasing the laser illumination intensity.
The Raman curves of PS at different illumination laser intensities are shown in figure (3).

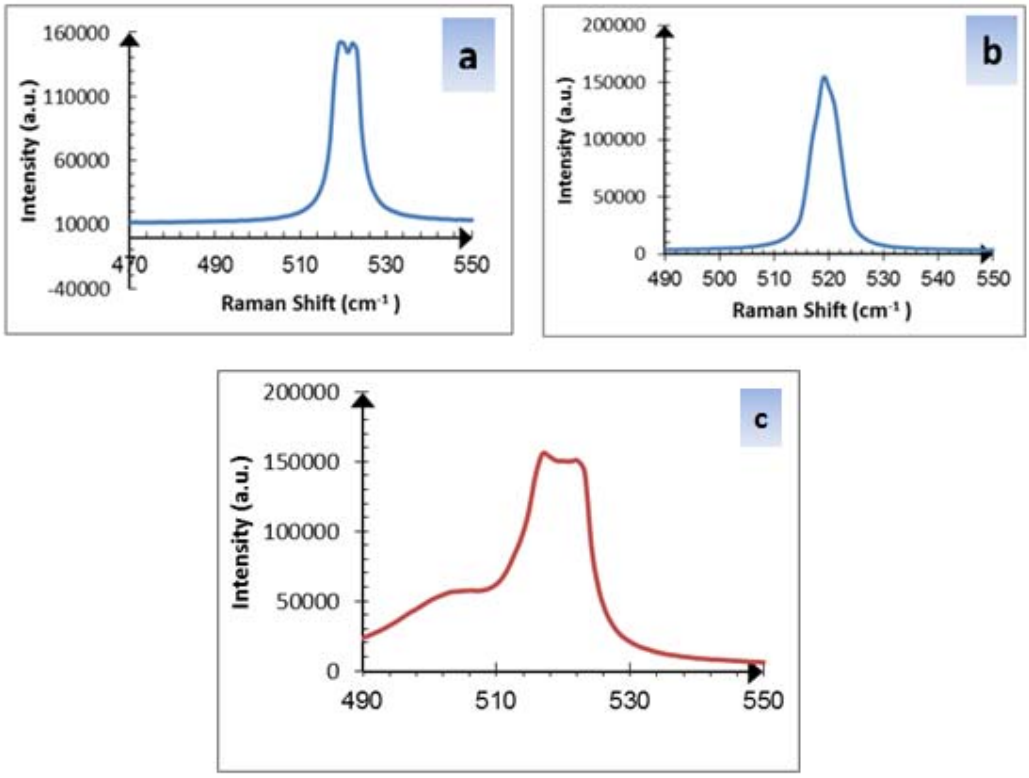

Figure 3: Raman spectra of PS prepared at different etching time (a) 10 min, (b)20 min, (c)25 min

Figure (3) shows Raman spectra of the PS with different porosities caused by different illumination intensities. Raman spectra, of PS indicate red shift and increasing broadening toward low energy when the porosities increase and this is a good agreement with [10]. For PS, the broadening and down shift of Raman peak towards lower energy indicates the presence of nano scale features in the crystalline silicon. As the size of the nano crystal deceases, the silicon optical phonon line shifts to lower frequency. The downshift towards lower energies is more sensitive and distinct for high porosity layer of PS. The presence of quantum size nano structures in PS relaxes the associated selection rule so that the Raman peak depends on the nanostructure shape and size parameters this is a good agreement with and this is a good agreement with [11, 12].

An important issue is whether Si nanoparticls are amorphous or crystalline, it has been assumed that the Si particles are amorphous. The obtained Raman spectrum is presented in figure (3) for different etching time (10, 20, 25) min. It clearly shows that the porous silicon material uniform film.

Si crystals have typical characteristics of strength emission and narrow band at (520 cm^{-1}), suggesting that it contain small amounts of

nanocrystalline silicon (nc-Si) because the phonon confinement in nc-Si should be different from that in amorphous Si , which corresponds to transverse acoustic mode in first order. However in the case of amorphous silicon, the lack of order induces modifications in the vibrational density of states and in this case the Raman spectrum is characterized by two faint and broad bands at (150 cm^{-1}) and (480 cm^{-1}).

CONCLUSIONS

PS have been prepared and characterized by laser radiation at different intensities. The SEM images investigation show increased porosity has resulted with laser intensity. Red shift of the Raman peak with the increase in broadening and peak intensity. The red shift in Raman and blue shift in photoluminescence spectra reveal the quantum confinement effect in PS samples. As the laser intensity increase these shift, increase due to a decrease in sizes.

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