Study of porous silicon structure by Raman scattering

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ABSTRACT

In this paper, the effect of etching time on light emitting porous silicon has been studied by using Raman scattering. Enhancement of Raman intensity by increasing the porosity is observed. Also there is a red shift, about $4 \, cm^{-1}$, from the Raman peak of crystalline silicon to that of porous silicon. The phonon confinement model suggests the existence of spherical nanocrystalline silicon with diameter around 7 nm. But SEM images show that the samples have a sheetlike structure that confines phonons in one dimension. This should not cause any shift in their Raman spectra. It is suggested that the observed Raman peak shift is due to the spherical nanocrystals on the surface of these sheets.

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1. Introduction

Discovery of light emission of porous silicon (PS) at room temperature has been stimulated a lot of attempts to lead this material into optoelectronic industry. For this purpose, structural investigation of PS is essential. The most common method for making porous silicon is electrochemical method which prepares PS in a low cost [1,2]. But the problem in this method is, a lot of parameters interfere and affect PS structure that make the PS structure somehow unpredictable and thus structural study of PS samples is always needed.

Among variety of tools, Raman spectroscopy is a nondestructive tool that can give us a lot of information about the structure of solids [3]. For strongly absorbing materials such as many semiconductors Raman scattering is a perfect tool for studying their structural characters like stress, strain, and also disorders [4]. Raman peaks of well-defined phonons in single crystal semiconductors are very sharp. Finite-size effects in nano porous materials cause in peak broadening and a shift to lower frequencies in their Raman spectra [5]. There have been several reports and analysis on Raman spectra of PS [6]. The first-order Raman peak shift of c-Si is at $520.5 \, cm^{-1}$ [7]. It is reported to be symmetric and sharp with an FWHM of $3 \, cm^{-1}$ [7]. Also the Raman spectrum of amorphous silicon (a-Si) shows a broad peak near $480 \, cm^{-1}$ [7]. Because of massive surface area to volume ratio in PS structure, it is expected to see an interface of crystalline silicon with its oxides. It is proved that silicon oxides in PS form far more rapidly than in crystalline silicon

[8]. Thus an amorphous phase might be seen in Raman spectra of PS. It has been observed in PS that the peak shift relative to c-Si increases as nanocrystal size decreases [9]. Some studies have determined the local structure of PS is more like a sphere than a rod and polarization Raman measurements suggest that the structure does not consist of a series of parallel columns [9,10]. The shift is the result of phonon confinement that happens by the phonons whose wave vectors extend out of the Brillouin zone. This happens for crystal sizes less than $100 \, \text{Å}$ [11]. Using phonon confinement model, Richter et al. and Campbell et al. have theoretically studied the effect of crystal size on Raman spectra [4,5].

In this study, we report our results on PS Raman spectra with different etching times. Most researches have included analysis of peak shift and line width of spectra, but less considered on intensity changes. We tried to give our analysis by paying more attention on Raman spectra intensities. Speaking about Raman intensity of PS requires knowing about the porosity amounts, thus they also have been measured. Then, we confirmed our results with the help of SEM images from our samples. Finally, we speak about silicon nanocrystal sizes of our samples by calculations done by using phonon confinement model.

2. Experimental details

Porous silicon films are prepared on p-type, (1 0 0) oriented silicon wafers with sheet resistance of $600 \, \Omega/\square$, by electrochemical etching method in a HF (38–40%) = ethanol (1:1) etchant. Current density of $10 \, mA/cm^2$ is kept constant during etching time. Raman spectra of samples are measured using NICOLET, Almega Dispersive Raman system consists of a laser source with 532 nm light beam wavelength. Fig. 1 shows the Raman spectra of PS samples that

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Table 1
Experimental detail and porosity measurement of PS samples.

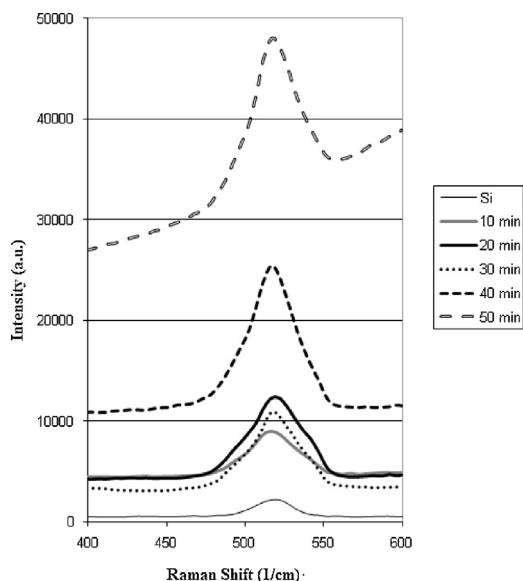| Sample	Current Density (mA/cm²)	Etching Time (min)	HF:Ethanol Concentration	Porosity by Gravimetric (%)	Porosity from SEM Image (%)	Peak shift (cm⁻¹)
1	10	10	1:1	31	52	4
2	10	20	1:1	67	58	2
3	10	30	1:1	22	12	4
4	10	40	1:1	56	44	4
5	10	50	1:1	71	64	3

Fig. 1. Raman spectra of crystalline silicon and PS samples with 10, 20, 30, 40, and 50 min etching time.

are etched electrochemically for 10, 20, 30, 40 and 50 min. Raman spectrum of crystalline silicon is also shown for comparison.

For having a more visual discussion, SEM images of our samples are taken with scale bar of 3 μm (Fig. 2). Then, every claim about Raman spectroscopy discussion can be compared with the SEM images. Besides, porosity can be estimated from SEM images. Table 1 shows the experimental details and porosity measurements of each sample by gravimetric method [1] and by using SEM images.

3. Results and discussions

Fig. 1 shows the Raman spectra of crystalline silicon and PS samples with different etching times. Comparing these Raman spectra, one can observe the Raman variation of porous silicon after different etching times. All the Raman spectra in Fig. 1, has symmetric peak with the same FWHMs about $30 \, cm^{-1}$. A very weak bump
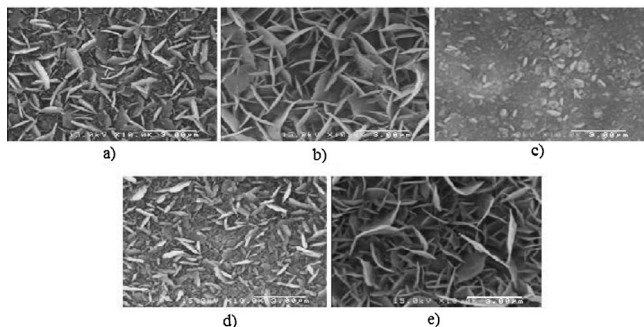

Fig. 2. SEM images of PS samples produced after (a) 10, (b) 20, (c) 30, (d) 40, and (e) 50 min of etching time.

in lower frequencies of the peak position, at $480 \, cm^{-1}$ is seen for some samples. This shows the existence of amorphous silicon (a-Si) phase on the sample surface.

Peak position, intensity, and width and Raman spectra background are features that differ with bulk silicon. The origin of these differences is the porous structure of the samples. These structural changes can be followed from Fig. 2. Fig. 2a and b shows SEM images of samples 1 and 2 that are etched electrochemically for 10 and 20 min. By comparing them with each other it is clear that porosity has been raised in sample 2 in a special manner that ends in a sheetlike structure. A non-completed form of this structure also exists in sample 1. Different agents may cause such a structure in PS samples. Silicon wafer resistance or the characteristic of Al layer coated on the Si wafer surface can be two possible reasons. The structure has been disappeared in Fig. 2c. It seems that porous silicon structure has been ruined between 20 and 30 min of etching. This happens when chemical etching makes the sheets narrower and finally ruins them.

After 30 min, porous silicon layer starts forming again and the structures in samples 2 and 3 is seen in samples 4 and 5 repeatedly. In fact after the slump of PS layer, anodization forms the porous structure again. The estimated amount of samples porosities are presented in Table 1.

Porosity measurements also were done by gravimetric method as described by Canham [1]. The porosity percentage of Table 1 also shows the porosity growth by increasing the etching time and porosity drop in sample 3. There is a good agreement between porosity percentages obtained by both methods. Porosity measurement from SEM image seems not to be a reliable method, because SEM images can just show the surface of the porous silicon. However, the thickness of the porous silicon layer and variation of the hole diameter in deep points will change the porosity.

Likewise, gravimetric method faces several errors because it includes 3 times of gravity measurements. Another important problem in this method arises from the dissolution of porous layer in KOH solution that does not finish at an exact and accurate time. The expression used in this method assumes a homogenous structure in porous layer with exactly the same thickness in all points. These conditions rarely are achievable experimentally.

For all these reasons the result come from both methods cannot be so exact. On the other hand Raman intensity is so sensitive to porosity and it can measure the local porosity of the sample. The only error in this method is the systematic error.

Raman peak intensity is proportional to Si density and photon penetration length in the material [12]. When the porosity increases these two factors together cause in enhancement of the peak intensity. In fact when a light beam collides with a PS surface a portion of it scatters from the silicon crystallites and the rest of photons enter the material and will scatter by the inner silicon atoms. But some may be trapped in pores inside the PS structure and encounter successive scattering, while this mechanism will just happen on the surface of crystalline silicon. As the porosity increases in PS structure, the probability of successive scattering increases and then Raman intensity raises up. Raman intensity in Fig. 1 increases from sample 1 to 2 and then after shows a drop from sample 3 to 5. Peak intensity variations correspond