



THE EFFECTS OF SURFACE TREATMENT ON OPTICAL AND VIBRATIONAL PROPERTIES OF STAIN-ETCHED SILICON

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Abstract - *The effects of surface treatment on optical and vibrational properties of porous silicon (por-Si) layers grown on p-type Si wafers by electroless etching technique were studied by FTIR spectroscopy and photoluminescence (PL). The results indicate a correlation between the PL intensity and the strength of the absorption bands induced by multihydride complexes (SiH_n , $n \geq 2$). However, similar correlation was also established for monohydride species as evidenced from the layers containing no multihydrides. Furthermore, a new band is observed at 710 cm^{-1} and assigned to multihydrides suggesting a new local bonding environment in these layers.*

Visible light emission from electrochemically modified surfaces of Si wafers has stimulated research since there are ample possibilities of applications (1). It was demonstrated that the stain etching (electroless) in HF solutions also yield the por-Si layers at Si surfaces (2). Recent studies have suggested several reasons such as quantum size effect (1), chemical quantum confinement in siloxene-like structures (3) and hydride excitation (4) as possible explanation for light emission. Despite extensive studies, the precise physical origin of the observed luminescence is not well understood and numerous investigations are still being made in order to bring more insight into the mechanism of the light emission.

Si wafers (p-type) with both (100) (2-20 $\Omega\cdot\text{cm}$) and (111) (10.5-19.5 $\Omega\cdot\text{cm}$) orientations have been subjected to stain etching in HF:HNO₃:H₂O. Combinations of different type of surface cleaning, etching and post-treatment were used which resulted in layer thicknesses of about 0.3 μm as evidenced from cross-sectional SEM micrographs. The saturation in thickness may be attributed to low energy carriers generated during etching in the absence of external fields. Information about hydrogenation and the presence of different species at the surfaces has been obtained from FTIR measurements. PL was excited by an unfocused Ar-ion laser using both 488 nm and 514 nm lines at 300 K using standard detection system which was calibrated to the spectral response of detector.

The results of the PL measurements are summarized in Table 1 for a variety of samples. As it is shown in this table, the emission band is located around 650 nm with approximately 400 meV bandwidth (ΔE). This PL energy would corresponds to a cluster size of 20 Å - 30 Å in diameter (mesoporous region), if the size effects are considered in quantum dots. A slight red or blue shift of the peak position occurs depending on the preparation conditions. The blue shift in PL is also confirmed by the shift at the optical absorption edge with respect to crystalline silicon. The PL degradation is observed due

to strong laser irradiation (≥ 100 mW). But, the PL intensity only decreases without any shift in the spectra after exposure to laser light, suggesting probably that the intrinsic properties are not disturbed due to local heating. Prolonged etching and ultrasonic treatment yielded a slight red shift in PL peak position, a narrowing in PL band and an increase in PL intensity regardless of doping and crystal orientation [except slight blue shift in (111) oriented samples]. In Table 1, the characteristics of PL spectrum of a por-Si taken after 75 minutes in 25 % HF (sample no. # 12) is shown. This pore widening experiment resulted in a blueshifted weak emission which is in contradiction with the previous report (4). The weak emission in this case can be attributed to excessive removal of oxides which probably leads to an abundant non-radiative recombination centers around nanocrystalline structures.

Typical FTIR vibrational spectra are shown in Figure 1 for layers grown in different electroless etching solutions as function of time and concentration. FTIR bands are located at around $2300 - 2000 \text{ cm}^{-1}$ (stretching modes), $1000 - 800 \text{ cm}^{-1}$ (bending modes), $750 - 600 \text{ cm}^{-1}$ (wagging modes) associated with Si-H_n ($n \geq 1$) bondings. In addition to these vibrations there is a large band at 1070 cm^{-1} with a shoulder at 1140 cm^{-1} due to heavy oxidation (Si-O-Si stretching vibrations). TO modes are located at energies lower than 600 cm^{-1} . In our layers, the band at 2200 cm^{-1} is the most important and dominant feature among others in this region unlike previous observations made for both anodic and non-anodic por-Si. This vibration is likely associated with multihydride species with one or more oxygen atoms backbonded to Si from analysis based on earlier studies (5). We find that the band at 870 cm^{-1} together with the shoulder at 840 cm^{-1} is the most important band and assigned to multihydrides (Si-H_2) (5). We always observe an intense band at 630 cm^{-1} and a shoulder at 665 cm^{-1} , which are assigned to Si-H and Si-H_2 wagging-bending vibrations. In addition, a new band at 710 cm^{-1} was observed whose strength increases with etching time and dominates this region with increasing HNO_3 concentration [Figure 1(b)]. To our knowledge, this is the first observation of the band at 710 cm^{-1} in por-Si. The correlation in strength between this band and those at 840 , 870 and 2200 cm^{-1} suggests that it is associated with multihydrides. The broad absorption band around 460 cm^{-1} is attributable to TO phonon modes of silicon and

TABLE 1

Summary of the photoluminescence measurements in por-Si layers grown by electroless etching in a variety of solutions. λ_p : PL peak position, ΔE : full width at half maximum.

Sample	λ_p (nm)	ΔE (meV)	Solution (HF:HNO ₃ :H ₂ O)	Intensity (a.u)	Etch Time (min)
# 2 (100)	647	444	(4:1:5)	990	5
# 3 (100)	657	386	(4:1:5)	9750	10
# 12 (100)	632	366	(4:1:5)	1300	5
# 15 (111)	653	419	(4:1:5)	600	2
# 17 (111)	645	400	(4:1:5)	5400	10
# 18 (111)	662	416	(4:2:5)	725	2
# 20 (111)	659	450	(4:2:5)	5900	10
# 21 (111)	666	413	(2:1:5)	1025	2
# 23 (111)	657	383	(2:1:5)	1775	10

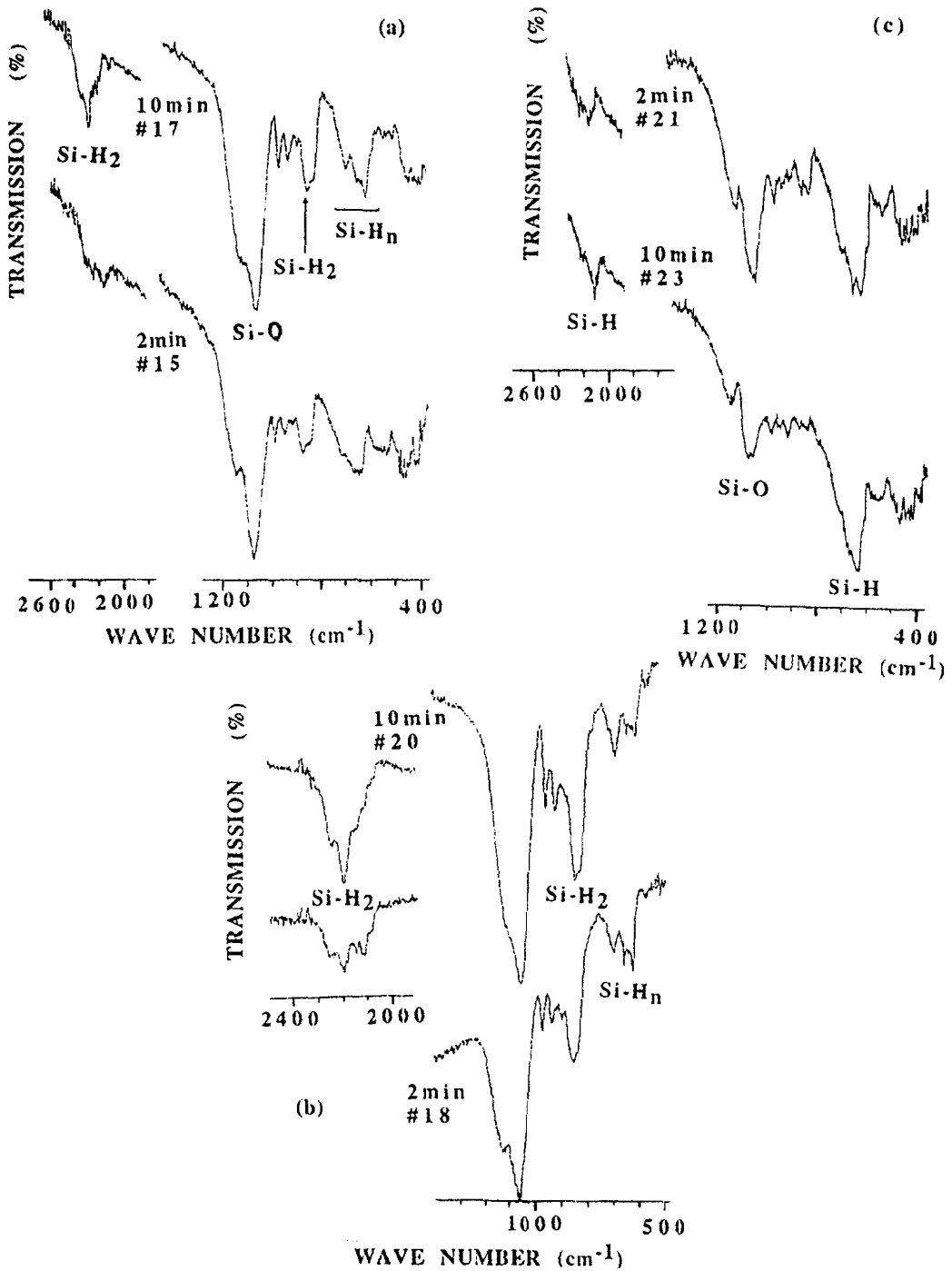


Figure 1. Time evolution of FTIR transmission spectra of por-Si layers grown by stain-etching on Si. (a) 4:1:5 (# 15, #17), (b) 4:2:5 (#18, # 20) and (c) 2:1:5 (#21, #23).

Si-O-Si bending vibrations.

Upon close examination of FTIR spectra [Figure 1(a) and Figure 1(b)] and PL data (Table 1), one finds a good correlation between the PL intensity and the strength of multihydride related bands. The layers grown in both etching solutions (4:1:5 and 4:2:5), the modes (2200 , 870 and 710 cm^{-1}) associated with the multihydrides dominate the spectral regions of interest. We see also that the predominance of these bands over others increases further with the etching time. This evolution in FTIR bands is followed by an increase in the PL intensity. This situation may be indicative of an increased number of luminescent chemical species or an increased number of Si nano-clusters. The vibrational properties of the layers grown in 2:1:5 solution indicate somewhat different behavior [Figure 1(c)]. For these layers, the monohydride related vibrations dominate spectral regions of interest (2120 and 630 cm^{-1}). There is a weak multihydride absorption band at 870 cm^{-1} which disappears almost completely with the etching and the strength of the monohydride related bands increases at 630 and 2120 cm^{-1} . Also, in the spectra of these layers, the oxygen band is very well resolved into two bands (1060 and 1150 cm^{-1}). The splitting was considered to be the consequence of the ordering of oxygen atoms which is responsible for the luminescence properties in planar siloxene structures (3). However, as it is shown in Table 1, PL intensity is relatively low in these layers. From the analysis of FTIR spectra, we find also that the amount of oxygen in the layers reaches a maximum after a certain time of etching and then decreases for all the samples except those grown in 4:2:5 solution where it increases and then remains constant for the time range explored. If we combine these trends of oxidation with the results of PL summarized in Table 1, we find that the broadening of PL band can be attributed to an increase in oxidation. However, we rule out the possibility of attributing the origin of these changes to the presence of a-Si:O:H like structural phases. Because, in this material, the high energy PL band is usually accompanied by a defect luminescence at around 1 eV, which we do not see in our layers. Previous studies report an effective opening of the band gap with H content regardless of the type of Si-H units (6). In our layers there is no significant change in PL peak position, despite an increase in hydride content. Hence, we suggest that the increase in hydride content might be the result of an increased hydrogenation around Si clusters or an increase in the number of Si nanocrystallines.

In conclusion, PL intensity in por-Si layers grown by electroless etching is correlated with the increase in intensity of the multihydride related vibrational modes. Nevertheless, PL persists in the layers containing no multihydride complexes. The FTIR spectrum provides evidence for the existence of a new vibrational mode at 710 cm^{-1} which might bring deeper insight into the understanding of the microstructure of por-Si layers.

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