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Dependence of Spin Density on the PL Properties of Ultra Thin Porous Silicon Layers

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ABSTRACT: Photoluminescence (PL) study of electrochemically grown porous silicon (PS) layers has been correlated with the Fourier Transform Infrared Spectroscopy (FTIR) and electron paramagnetic resonance (EPR) studies. PS layers have been grown electrochemically on CZ silicon wafers using a solution of HF and C₂H₅OH at room temperature for etching duration from 40s to 20min. PL intensity of PS layers increases with etching time and shows highest value for 10 minute and then decreases with further increase in etching time. In FTIR transmittance spectra, the absorption peak at ~856, corresponds to O-Si-H wragging mode, which is due to dangling bonds, follows the same trend as PL intensity. The spin density of silicon wafers with PS layers also starts increasing from its initial value of 8.64×10^{14} per gram for etching time 40s to a maximal value of 3.91×10^{15} per gram for the etching time 10 min then starts decreasing for further increase in etching time. Our experimental results confirm that the spin density/dangling bond density of the PS samples are correlated with PL intensity for PS layers of lower thickness (29-142 nm) which confirms that photoluminescence in thin PS layers is due to O-Si-H bond.

KEYWORDS: Porous silicon, Electrochemical etching, Photoluminescence, Electron spin density, Dangling bonds;

I. INTRODUCTION

Porous Silicon (PS) was discovered in 1956 at bell laboratory USA by A. Uhler [1]. It is formed using two different approaches viz. electrochemical etching and stain etching [2,3]. Canham [7] has observed strong visible photoluminescence (PL) properties of PS at room temperature in 1990. Different hypothesis and models have been proposed for PL emission in porous silicon. Unique optical and electronic properties have made porous silicon (PS) highly attractive for realization of single electron devices [6], chemical sensors [7], cold cathode field emission displays [8], optical sensors and filters [9, 10], photonic devices [11], nanobiotechnology developments [12], continuous wave Si laser [13] and biomedical applications [14]. In recent years great efforts have been made to fabricate porous silicon and its optical, physical and electronic properties are studied [15-20]. Chang and Chen [8] proposed that the PL emission in PS contained two components. One is correlated to the absorption of O-Si-H bonds. Other component of PL is shown to be sensitive to the strength of the Si-O-Si bond related absorption. Whereas, some other models: quantum confinement (QC) and quantum confinement luminescence centre (QCLC) [9, 10] have also been reported in literature. According to QC model PL emission of PS is due to the band to band transition and it depends on the Si crystallites size. However, QCLC model is based on radiative recombination of different luminescent centers in oxidized PS layers.

In literature PL intensity of PS has been reported as related with the bonding between Si, O and H by some authors [11-13] shown via the interrelation between PL and Fourier transform infrared spectroscopy (FTIR) characteristics. Many researchers [14,21,25] have tried to relate PL emission with the Electron Paramagnetic Resonance (EPR) study but no concrete dependence of PL on EPR study has been reported in case of PS layers having the thickness of nanometer range.

In this work, we have investigated dependence of PL intensity of PS layers on the spin densities using EPR technique. PS layers have been formed for various etching durations. The films are characterized by using Scanning Electron Microscopy (SEM), FTIR and EPR. A correlation between EPR signal and PL intensity is observed and

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supported by FTIR data. Striking observation is that both the PL emission intensity and dangling bond density are maximum for the PS layer grown for the etching duration of 10 min.

II.EXPERIMENTAL

Single crystal CZ grown silicon wafers of p-type (B-doped) conductivity, <100> orientation and 1-5 Ω -cm resistivity, 50 mm diameter and 300 μ m thickness were used in this study. The wafers were mechanically lapped on both sides and then chemically polished in solution of HF: CH₃COOH: HNO₃ (1:1:5). Back contact was made with thermal evaporation of Al metal under a vacuum of 2×10^{-6} mbar followed by sintering at 400°C in hydrogen ambient. Porous silicon was grown on the front surface of the polished silicon wafers by anodic etching in HF (48%): C₂H₅OH ::1:2 mixture (by volume) for different etching durations varying from 40 s to 20 min at a constant anodization current density of 20 mA/ cm². The electrochemical anodization was performed in a Teflon cell using a two electrode arrangement where the sample was held in a vertical position and Pt wire was used as a counter electrode. The details about the samples S1-S5 used in this study are given in the table 1.

TABLE1:

Sample name	S1	S2	S3	S4	S5
Etching time (s)	40s	120s	480s	600s	1200s

The as prepared PS layers were subjected for various characterizations. The thickness of the PS layers was estimated by ellipsometer (Gaertner, model 117) at wavelength of 632.8 nm using He-Ne laser light source. Detailed photoluminescence (PL) measurements of the PS layers were carried out at room temperature using 405 nm wavelength light as excitation source. The morphology of the PS layers was examined by LEO 440 VP scanning electron microscope (SEM). FTIR spectra of PS layers were recorded in transmission mode at room temperature with a spectrophotometer, Perkin-Elmer Model BX2 in the wave number range 400–4000 cm⁻¹. EPR study is carried out using a Bruker ER200D-X band spectrometer operating at a nominal microwave frequency of 9.65 GHz. Magnetic field modulation at 100KHz and phase sensitive detection were used to record the derivative of the absorbed microwave power. Samples S₁-S₆ were prepared and characterized at room temperature.

III.RESULTS AND DISCUSSION

Figure 1 shows the variation of the PS layers (S₁-S₅) thickness with etching time (t_e) formed by electrochemical etching of polished silicon wafers. It is seen that the thickness of the PS layers increases with t_e and acquires a maximum thickness of 142 nm for the PS layer S₄. The thickness starts decreasing for $t_e > 10$ min. The thickness of PS layer in sample S₅ is found to be 118 nm for $t_e = 20$ min. The same observation has been made by Verma et al. [23]. Reduced thickness for longer etching indicates that a part of the silicon skeleton from top might have been fallen in the solution after a certain etching time ($t_e > 10$ min). This may possibly be due to the fact that the PS layer consists of silicon nanowire like structures which in our electrochemical cell grow horizontally as cantilevers held at the vertically placed Si wafer. A cantilever may break and fall in the solution after attaining the sustainably large length [24].

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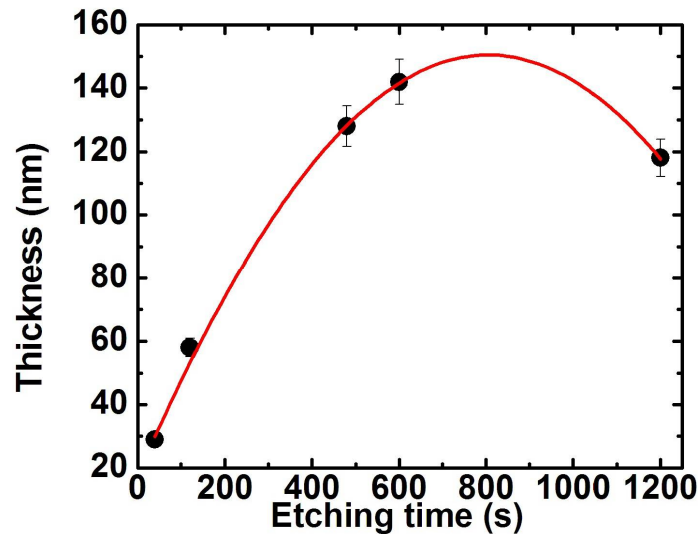


Fig. 1 Dependence of thickness of PS layers on etching time (t_e) from 40s to 20min.

Detailed information about surface morphology of the PS layer is obtained from SEM. Front and cross sectional views is shown in Fig.2 (a), (b), (c). Fig. 2(a) shows the front view of the PS layer (S_4) grown for $t_e = 10$ min etching duration and Fig. 2(b) and (c) show the cross sectional view of PS layer respectively. It is clearly visible from Fig.2(a) that the PS layers consists of 100-250 nm sized features over the PS grown regions which are responsible for the PL emission.

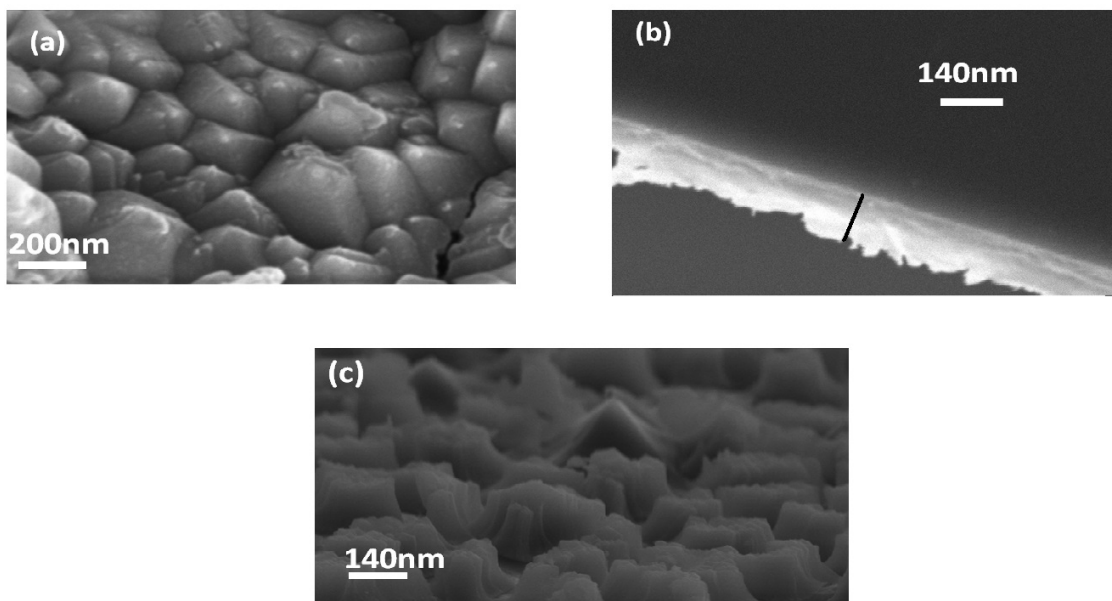


Fig.2 SEM micrograph of PS layer S_4 (a) top front view (b) cross sectional view and (c) lateral cross- sectional view.

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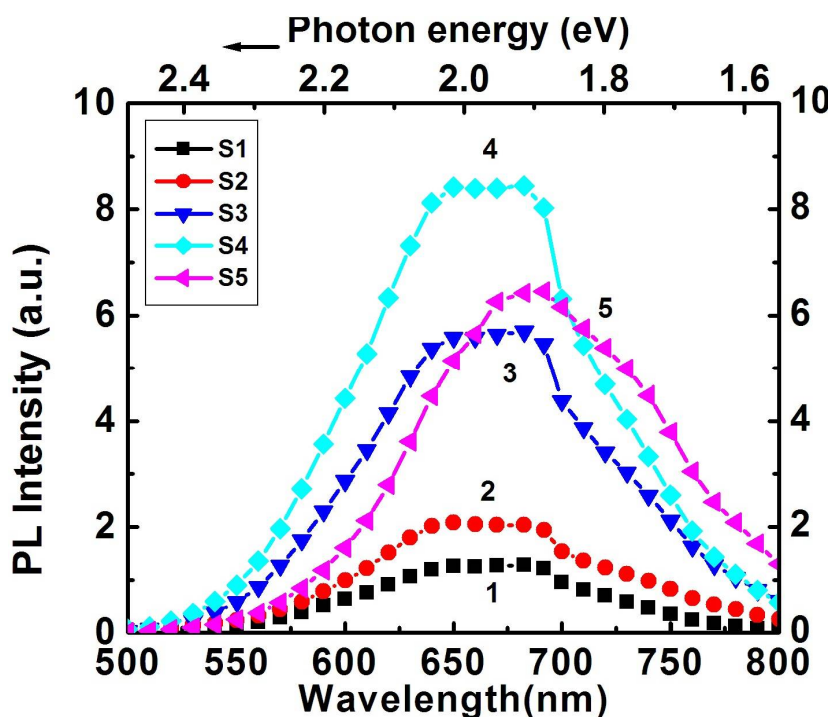


Fig. 3 Photoluminescence emission spectra of different PS layers grown electrochemically for different time durations varying from 40s to 20 min at constant current density of 20mA/cm².

Figure 3 shows the broad PL emission spectra [23] (ranging from 500-800nm wavelength) of electrochemically etched PS layers S₁-S₅. The PL intensity of PS layers increases with t_e and attains a maximum value for $t_e = 10$ min (Sample S₄) and thereafter it decreases. The PL peak of maximum intensity corresponds to $t_e = 10$ min lies at $\lambda = 650$ nm. As t_e increases further, the PL peak position shows the red shift. Chang and Chen [8] observed that the PL emission in PS layers may be originated from the absorption of O-Si-H bonds.

Additional information about the optical properties of the PS layers has been obtained from the FTIR measurements. Figure 4 shows the FTIR transmittance spectra of PS layers formed for samples S₁ to S₅. The FTIR transmittance spectra shows the absorption peaks at ~ 856 , ~ 1375 , ~ 1739 cm⁻¹ corresponding to O-Si-H wragging mode, C=O stretching mode, C=C bonding respectively [8, 26] and the absorption peaks intensity at 619 and 2100-2200 cm⁻¹ corresponding to Si-Si bonding and SiH_x stretching mode increases with etching time increase [8, 26]. C=O, C=C bonds are increasing with the etching time but these bonds are not responsible for the PL emission. Si-H_x, Si-Si bond intensity increases with the etching time. Therefore these bonds are also not responsible for the PL emission.

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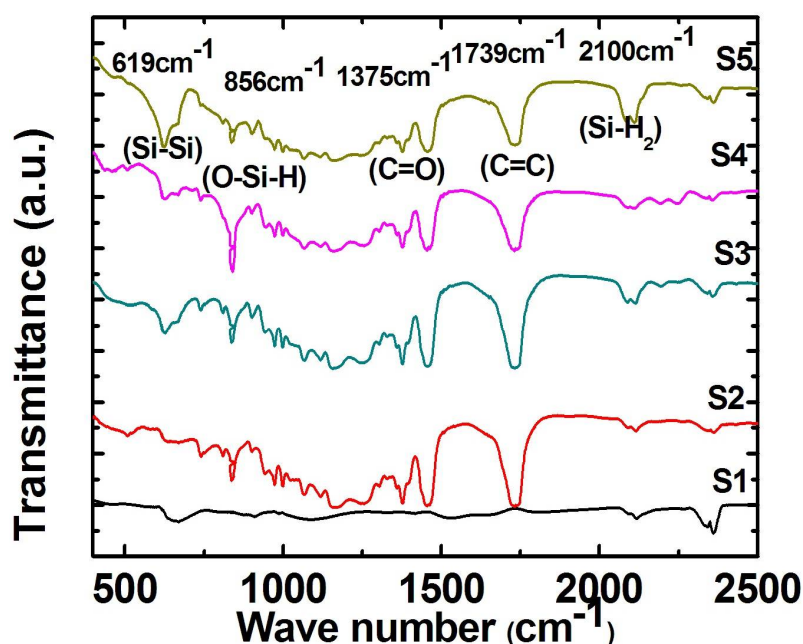


Fig. 4 FTIR transmission spectra of PS layers grown for etching time 40s to 20min

It is observed from the Fig. 4 that the O-Si-H bond intensity increases with t_e and is maximum for 10 min (S_4) and then decrease with increase in etching time. O-Si-H bond intensity follows the PL intensity trend. It shows that the PL intensity change is reflected in O-Si-H bond behavior so it may be due to the O-Si-H bond. Cheng et al [8] observed that the PL intensity below 1.7eV is due to the quantum confinement effect and greater than 1.7eV is due to the recombination at the surface states of the bond formation of O-Si-H at 856cm⁻¹. In our case since the PL position lies between 1.7-1.9 eV so this result can be better correlated by the FTIR data.

Figure 5 shows the EPR signals of PS layers grown for t_e varying from 40s to 20 min. It may be noted that the spike intensity of EPR signals increases with the increase in the t_e and obtained signals of maximum intensity for PS layers corresponding to $t_e = 10$ min and then shows a decrease with further increase in etching time. This behavior of EPR signal resembles with the PL intensity and the thickness of the PS layers. Since, the EPR signals are sharp and the dangling orbitals are well aligned with the tetrahedral directions of the Si wafer substrate, the luminescent PS layers must be crystalline on a lattice which is continuous with the substrate lattice despite the skeletal structure of the PS layer.

The electron spin density or dangling bond density is calculated using EPR signals. Figure 6 shows the variation of spin density and PL intensity of PS layers with t_e for the above mentioned t_e range. The Gaussian fit of the spin density is also shown in Fig. 6. The spin density of polished silicon wafer is found to be of the order of $\sim 10^{12}$ per gram. The spin density of silicon wafers with PS layers starts increasing from its initial value of 8.64×10^{14} per gram for etching time 40s to a maximal value of 3.91×10^{15} per gram for the $t_e = 10$ min then starts decreasing for $t_e > 10$ min. The spin density was found 1.44×10^{15} per gram for $t_e = 20$ min. Our experimental results show that the PL intensity has an excellent correlation with spin density of the PS layers as shown from the figure (plotted between the spin density vs. PL intensity) inserted in Fig. 6. Mao et al. [27] found no quantitative rule for the EPR and PL correlation which may be due to the thickness of PS layers. PS layer thickness in our samples are much less (28-142 nm) than the thickness of the PS layers of Mao et al (4-120 μ m) [27] and the EPR signals originates from the whole PS layer while the PL intensity is mainly coming from the top region of the PS layer [27].

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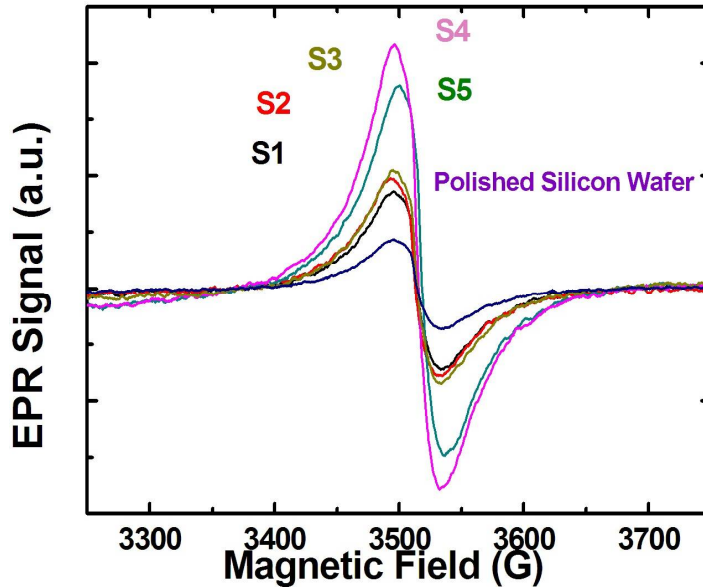


Fig.5 EPR signals of PS layers grown for etching time 40s to 20min.

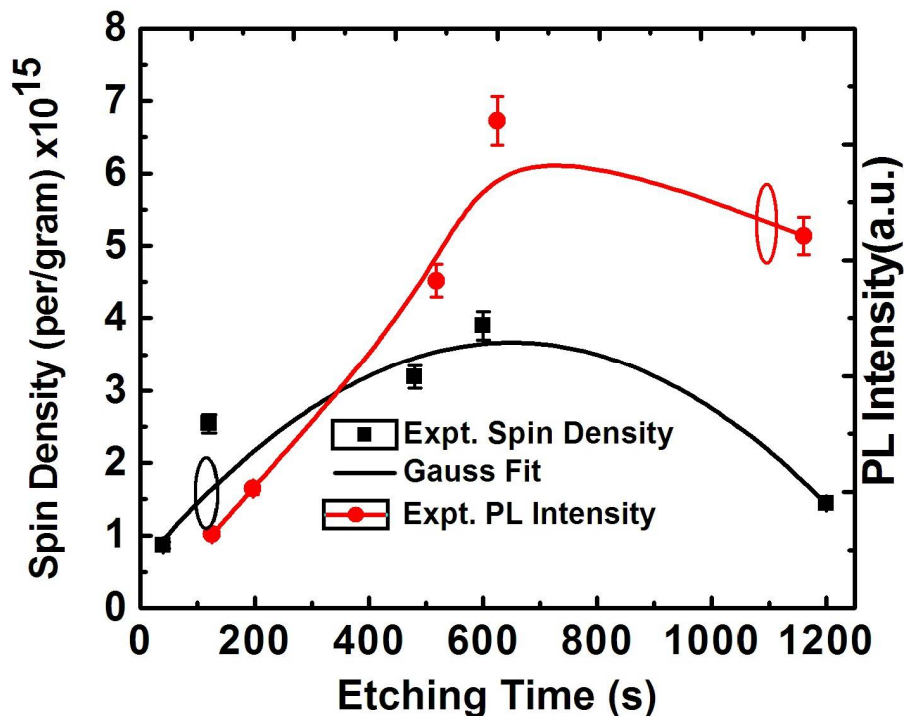


Fig. 6 Plot of electron spin density and PL intensity with etching time of PS layers from 40s to 20min.

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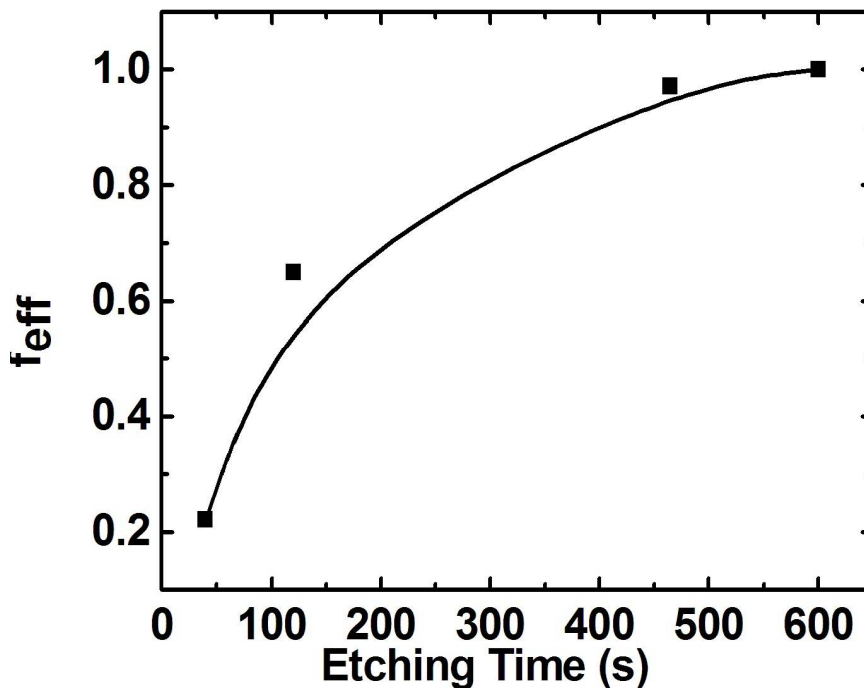


Fig.7 Effective factor f_{eff} vs. function of the etching time.

The spin density with etching time can be described approximately by an equation as following

$$S_{exp} = f_{eff} * S_{max} + (1-f_{eff}) * S_{min}$$

where S_{max} and S_{min} are the maximum and minimum spin density values for silicon and the parameter f_{eff} is a function of the etching time. Out of these two extreme values of the spin density, the later can be the spin density of a chemically polished silicon surface whereas the former may be the maximum value obtained experimentally and f_{eff} is a factor representing the combined effect of the enhanced silicon surface area and the surface states. It is referred that two limiting cases of $f_{eff} = 0$ and 1 represent the spin density of the polished silicon surface and spin density for the porous silicon layer in our experimental case. Fig.7 represents the effective factor f_{eff} as a function of the etching time. In the present study, we have used the value of $S_{min}=1 \times 10^{12}$ per gm for polished silicon surface (No etching) and $S_{max}=3.91 \times 10^{15}$ per gm for porous silicon layer etched for 10 min. From Fig. 7, it is clear that effective factor follows the same trend as is observed for PL intensity (Fig.6). It confirms that as the etching time is increased, the effectiveness of the spin density also increases and it is contributed by the enhancement in the surface area and the increased surface states which are confirmed by the FTIR study.

The PL peak intensity increases with etching time and attains a maximum value at $t_e = 10$ min and then decreases. The FTIR results shows that O-Si-H bond intensity follows the PL peak intensity trend whereas all other bonds show increase in bond intensity with etching time even after 10 min. EPR results and effective factor f_{eff} show that the spin density/ dangling bond density follow the similar trend as for the PL peak emission. It confirms that spin densities/dangling bonds density of the PS samples are responsible for PL intensity of PS layers of lower thicknesses (in the nm range). The FTIR results show enhancement in O-Si-H bond intensity with PL peak intensity and this bond

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correspond to dangling bonds. It confirms that the major contribution towards EPR signal change is due to the O-Si-H bonds in thin PS layers.

IV.CONCLUSIONS

Photoluminescence (PL) study of electrochemically grown porous silicon (PS) layers for different etching duration has been made on the basis of Fourier Transform Infrared Spectroscopy (FTIR) and electron paramagnetic resonance (EPR). The bond signature of FTIR spectra confirms that the absorption peak at $\sim 856\text{ cm}^{-1}$ is responsible for PL emission. A relation between the PL intensity and the electron spin density was found in PS layers due to their lower thicknesses. The PL emission origin is correlated with the dangling bond density and mainly O-Si-H bond.

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