INVESTIGACIÓN REVISTA MEXICANA DE FÍSICA **53** (6) 431–435 DICIEMBRE 2007

FTIR and photoluminescence studies of porous silicon layers oxidized in controlled water vapor conditions

M.A. Vásquez-A.[a], G. Águila Rodríguez[a], G. García-Salgado[b], G. Romero-Paredes[a], and R. Peña-Sierra[a]
[a]Departamento de Ingeniería Eléctrica, SEES, CINVESTAV-IPN,
Av. IPN 2805, Col. Zacatenco, 07000, México, D.F.,
e-mail: rpsierra@cinvestav.mx,
[b]Centro de Investigación en Dispositivos Semiconductores, BUAP,
Puebla, Pue. 14 Sur y Av. San Claudio C.U., 72570,
e-mail:godgarcia@yahoo.com

Recibido el 29 de noviembre de 2006; aceptado el 28 de noviembre de 2007

A study is presented on the evolution of the FTIR features and the changes in the photoluminescence (PL) spectra of chemically oxidized porous silicon layers (PSLs) successively aged under controlled conditions. The PSLs were prepared by the electrochemical method to guarantee uniformity over extended areas. Just after the silicon porification process, the FTIR spectra of the PSLs show silicon-hydrogen bands related to the hydrogen terminated porous silicon surface. As the PSLs oxidized, various vibrational modes were modified. The new observed vibrational frequencies are related to the defective silicon oxide formed at the porous silicon surface. The room temperature PL spectra of freshly prepared PSLs show a characteristic peak located at $\sim$700 nm. The intensity of the PL signal on chemically oxidized samples increased by an order of magnitude; afterwards, when the samples were aged in saturated water vapor conditions, the PL spectra were strongly modified. These changes indicated that the PSL structure is modified by the oxidization processes applied. Analysis of the FTIR data and the behavior of the PL signal enable us to interrelate the quantum size related effects and the formation of some kind of defect in the silicon oxide film over the PSLs. The characteristics of the PSLs reported in this paper are perfectly reproducible in the conditions used for the sample preparation; therefore, these films can be used in different applications.

Keywords: Porous silicon; FTIR spectra; photoluminescence; silicon oxide; structure defects.

Se presenta un estudio de la evolución de las características de los espectros de FTIR y la respuesta de fotoluminiscencia (PL) en películas de silicio poroso (PSL) oxidadas químicamente y envejecidas en condiciones controladas. Las PSL se obtuvieron por el método electroquímico para obtener buena uniformidad en grandes áreas. Las mediciones de FTIR en las PSL recién preparadas manifiestan bandas de silicio-hidrogeno asociadas con la terminación en hidrogeno de superficie de silicio poroso justo después del proceso de porificación. Al oxidar las películas, los distintos modos de vibración se modifican. Esos modos de vibración se relacionan con los defectos en el oxido de silicio que recubre la superficie del silicio poroso. Los espectros de PL en muestras recién preparadas presentan un máximo en $\sim$700 nm. El espectro de PL en las PSL oxidadas químicamente y luego envejecidas, en condición de vapor de agua saturado, se modifica fuertemente con respecto a las muestras recién obtenidas. Estas variaciones están asociadas con los cambios en la estructura de las PSL inducidos por los procesos de oxidación. Los datos de FTIR y el comportamiento de la señal de PL nos permiten relacionar estas señales con los efectos de cuantización por pequeñas dimensiones e indicar que las transiciones a altas energías las produce algún centro de defecto en la película de óxido de silicio que se forma en su superficie. Las características de las PSL reportadas en este trabajo son perfectamente reproducibles en las condiciones que se utilizaron para prepararlas; por ello, las películas pueden usarse en distintas aplicaciones.

Descriptores: Silicio poroso; FTIR; fotoluminiscencia; oxido de silicio; defectos de estructura.

PACS: 81.05.Cy, 78.30.-j, 78.55.Mb, 68.47.Gh, 68.55.Ln

1. Introduction

The remarkable characteristics of visible photoluminescence (PL) in porous silicon layers (PSLs) at room temperature have given great impulse to material studies due to the vast possibilities for technological applications [1,2]. In order to attain visible PL with controllable characteristics, a variety of methods and procedures have been tried to date, based on the pioneer work done by Canham [3]. The studies on PSLs have aimed at greater stability in the PL over long periods of time [4]. Initial research into PSLs was directed mainly at establishing the origin of the radiative recombination mechanisms. The use of PSLs in specific applications could be expanded if their characteristics can be controlled with confidence; this work is directed could controlling these characteristics.

Three mechanisms have been thoroughly discussed in the literature as being responsible for the various PL features reported in PSLs [5,6,7]. The generally accepted PL mechanism is the quantum size effect (QSE), which is supported by the nanometric dimensions of the filaments constituting the PSLs [8]. A second mechanism is related to the siloxene-like film covering the porous silicon structured net [9]. Furthermore, the non-stable behavior of PL has been related to some kind of interfacial states located between the silicon filaments and the siloxene-like surface film [10]. For the use of PSLs in technological applications, the interaction between the phenomena mentioned must be taken into account.

PSLs prepared by several methods show different features in their PL spectra, but the works discussing the relative influence of the different mechanisms are limited [11]. For example, some authors have reported multiple peak PL spectra but have not precisely linked the PL spectrum structure to the aforementioned mechanisms [12,13]. Studies reporting multiple peak spectra have usually resulted from very low temperature PL measurements, or have arisen from the interpretation of combined PL and photoluminescence excitation studies on fresh samples. Other papers reporting multiple peak PL spectra, taken on very thin PSLs, have been associated with optical interference effects.

In other works, the multiple peak PL spectra have been discussed on the basis of the presence of silicon nanocrystallites on the exposed filament surface [14]. Undoubtedly, a combined analysis of FTIR spectroscopy and PL spectra could be useful in identifying the interrelation between the aforementioned effects in the PSLs.

In a previous work, we reported morphological and optical studies on anodic prepared PSLs [15]. Coinciding with us, numerous authors have reported changes in the PL spectra resulting from post-preparation treatments applied to the PSLs. In this work, we report the behavior of FTIR features and PL spectra on PSL as a result of the controlled oxidation process. When the PSLs were oxidized, various vibrational modes of the FTIR were modified. We have followed the PL signal evolution of samples oxidized under a two-step process; the first step includes a slight oxidization just after the films were anodized, and the second one was a very slow oxidization process under controlled humidity conditions. These vibrational frequencies observed in the oxidized samples are related to defective silicon oxide at the extended surface of the PSLs. The main aim of this work is to demonstrate the interrelation between PL and FTIR characteristics, and to contribute toward clarifying the origin of the unstable properties of PSLs. Furthermore, in this work we demonstrate that PSLs could be produced with specific characteristics, either as fresh samples with a high PL signal or as completely oxidized, dense films with a relatively low PL response.

2. Experiments

The PSLs were prepared by anodic etching in a home-made all-Teflon electrolytic cell. (100) silicon wafers (1.0-2.0 Ohm-cm), n- and p-type, were used as substrates. Before the anodic etching, the wafers were cleaned using the MOS cleaning procedure.

The anodizing solutions were formed with HF (48%), ethanol and de-ionized (DI) water in a 4:3:3 volume proportion. All the samples were anodized using a constant current of 10 mA/cm^2 for 10 minutes. After the etching process, the samples were rinsed thoroughly in DI water, classified in five sets, and processed as described in the following paragraphs.

Three sets of samples were immersed in different silicon oxidizing agents for a period of 15 minutes. One of the sets was oxidized in sulphuric acid (H_2SO_4), another in hydrogen peroxide (H_2O_2), and the third set in a mixture of H_2SO_4 and H_2O_2. After this process, the samples were rinsed thoroughly with DI water and dried with nitrogen gas. Those three sets of samples were conserved at all times in contact with the normal laboratory atmosphere.

The two additional sets of samples prepared under the same conditions, including the oxidizing process with H_2SO_4, were kept in sealed vessels with different atmosphere conditions. One of these was kept as a control set of samples in a strictly dry atmosphere, using a vacuum vessel desiccators with activated silica gel in it. The second set was kept at all time in a vessel containing DI water (18 M-Ohm); these samples were not submerged in the water, but only the saturated water vapor was in contact with the PSL surface. The samples of the last two sets were taken from the vessels only for the time necessary to make the corresponding characterization.

Absorption FTIR spectra of the PSLs were measured using a double beam Perkin-Elmer 850 spectrometer. Photoluminescence spectra were dispersed by a double monochrometer SPEX system (0.8 m focal length), model 1404. The PL system was equipped with an S1 photomultiplier tube. The PL was excited with the 488 nm line of a 4W Argon laser. The PL measurements were taken at 300 and 10 K. For PL measurements at 10 K, a Janis He-closed cycle cryostat was used. All the PL spectra reported in this work were not corrected with respect to the detector response. The measurements were usually taken with a power density of $\sim$100 W/cm^2. The PL measurements were taken systematically in order to follow the time evolution of the different signals.

3. Experimental results and discussion

The FTIR absorption spectrum on freshly prepared PSLs from 400 to 4000 cm^{-1} is shown in Fig. 1. The different vibrational modes are detected described in Table I. As can be seen from Fig. 1, the freshly prepared PSLs showed well-defined silicon-hydrogen absorption bands at 905-910 and 2087-2106 cm^{-1}. These modes are related to groups adsorbed at the extended porous silicon surface. As the PSLs were slightly oxidized in wet solutions, the initial spectrum remains almost identical, but the most relevant changes are produced near the frequencies related to silicon-oxygen bonds, 900 to 1400 cm^{-1}. Figure 2 shows a portion of the FTIR spectra where the most important changes are observed, the relevant vibrational modes are centered at 1065, 1105 and 1150 cm^{-1}. The signal at 1065 cm^{-1} corresponds to the stretching modes of the Si-O-Si bridges in SiO_x [16]. The peak at 1105 cm^{-1} is generated by the asymmetrical stretching of Si-O-Si bridges in stoichiometric SiO_2. As this peak does not underego important changes when the samples are processed, it can be argued than this mode is related to the silicon substrate. Otherwise, as the modes at 1065 and 1150 cm^{-1} appear only in PSLs with some oxidation degree, these frequencies can be related to the highly stressed SiO_2-Si interface or defective silicon oxide at the porous silicon surface. These modes are the symmetrical and antisymmetrical vibrational modes of the Si-O-Si bridges [17,18].

TABLE I. Identification of the IR modes observed in the PSLs.

Frequency (cm^{-1})	Associated Species	Reference
611	Si - Si (Bonds)	[12]
905	SiH_2 scissor	[13]
910	SiH_2 scissor	[13]
1105	Si-O-Si asymmetric stretching	[14]
1150	Si-O-Si asymmetric stretching	[14]
2087	SiH stretching	[15,16]
2106	SiH_2 stretching	[15,16]
2330-2360	SiH_x	[17]
2860	CH_2 symmetric stretching	[18]
2921	CH_2 asymmetric stretching	[18]
2960	CH_3 asymmetric stretching	[18]

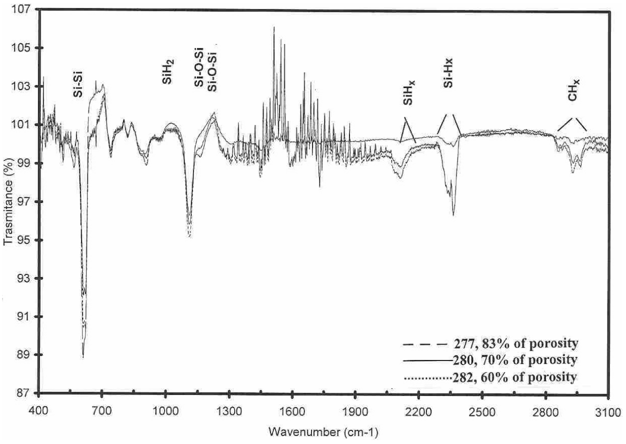

FIGURE 1. FTIR absorption spectra on freshly porous silicon layers (PSL).

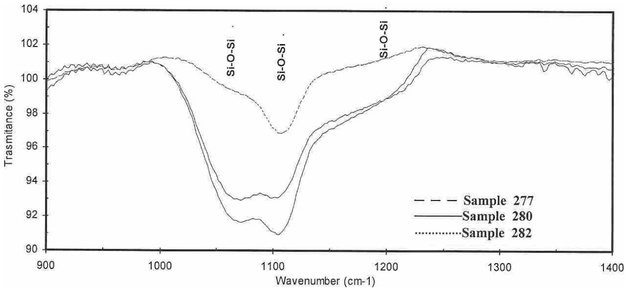

FIGURE 2. Section of the FTIR absorption spectra on wet oxidized PSL.

In order to obtain a point of reference, PL spectra were taken from freshly prepared PSLs. The PL at room temperature (300 K) was intense, with a characteristic Gaussian-like spectrum. The maximum of the main PL peak is located between 620 and 780 nm, depending on the anodizing parameters used. The PL spectrum possesses similar characteristics to those usually reported in the literature, with a full width at half maximum (FWHM) of $\sim$320 meV [19,20].

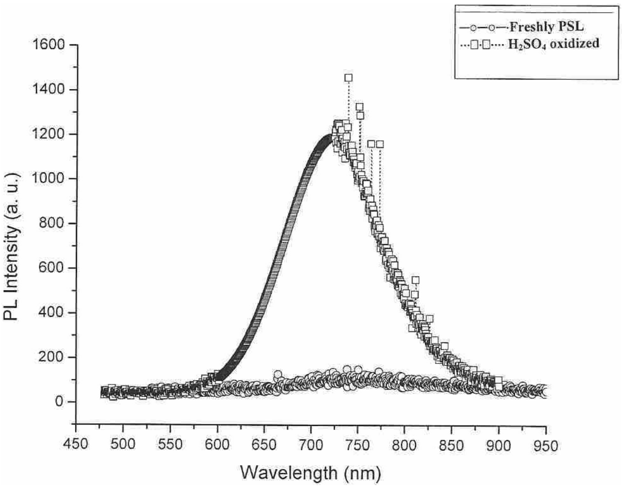

FIGURE 3. 300 K PL signal for a freshly prepared PSL (S283I) and the same sample but slightly oxidized by immersion in sulphuric acid for fifteen minutes (S283II).

When the samples were treated with the chemical oxidizing agents, the PL signal increased in intensity. When the samples were soaked in H_2SO_4 for periods of fifteen minute, the PL signal intensity increased by an order of magnitude. Similar processing in H_2O_2 and in the mixture of H_2SO_4 and H_2O_2 only result in a slight increment of the PL signal. With the oxidation process in H_2SO_4, the PL spectra that appeared weak in freshly prepared samples were now intense and clearly distinguishable. Furthermore, the maximum of the main peak was displaced by approximately 40-50 meV towards the high energy region, as is shown in Fig. 3. Therefore, the H_2SO_4 treatment was adopted as an essential part of the process to prepare PSL samples with the best PL response.

The increase in PL intensity is the result of surface passivation by the chemical oxidizing treatment [21,22]. However, it must be noted that any oxidation process acts to reduce the diameter of the filaments constituting the PSL. Hence, the observed increase and blue shifting of the PL could be related to the QSE due to the thinning of filaments by the oxidation process [5], and the passivation by a thin silicon oxide film formed at the PSL surface.

Otherwise, the intensity of PL spectra taken at 10 K on the chemically oxidized PSLs increased by about one order of magnitude. The PL now appeared shifted towards the blue by about $\sim$100 meV as compared to the 300 K spectra, as is shown in Fig. 4. The energy shifting was greater than the crystalline silicon gap widening produced by the measurement at low temperatures, and retains the same positive coefficient. These increments of PL intensity are related to the reduction in the dispersion mechanisms by the low measurement temperature [23].

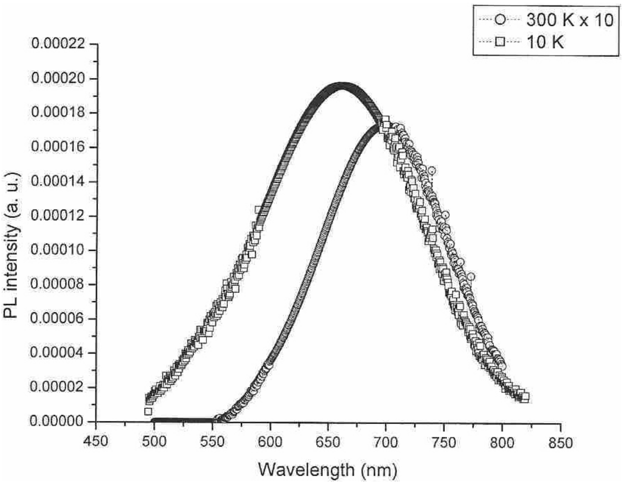

FIGURE 4. Typical PL spectra at room temperature and at 10K on reference porous silicon layers.

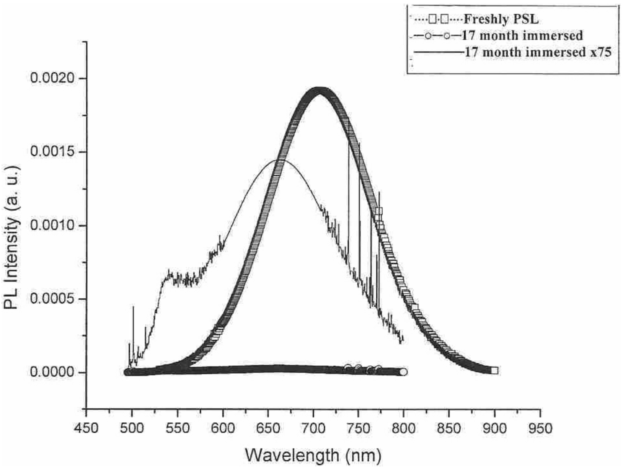

FIGURE 5. PL spectra taken at 10 K for sample S4 at different oxidation degrees. Spectrum 1 for a freshly PSL and spectrum 2 for a sample keep for 17 months in saturated vapor water conditions.

In order to gain insight into the PSL properties, we studied the behavior of PL for the samples aged under controlled atmosphere conditions. For this study, all samples were slightly oxidized in order to achive the best PL response. All the PL spectra that will be used in the discussion were taken at 10 K.

For the oxidized samples that were stored in contact with the water vapor, the evolution of the PL spectra showed nonperceptible changes within the few days immediately after the samples were prepared. Two months after the samples were introduced into the wet atmosphere, the PL spectrum began to modify. As the aging time increased, a new signal appeared in the short wavelength region ($\sim$520 nm), as shown in Fig. 5.

By contrast, the control samples stored in dry media did not show any change in their PL spectra. The PL spectra taken on those samples during the time lapse of this study were similar to the most intense peak shown in Fig. 3. The observed behavior can be explained using the widely accepted model for PSLs made up of crystalline silicon filament cladding over a thin siloxene-like core. As a result of the chemical oxidizing step and the succeeding aging processes, a silicon oxide layer is produced [24]. This additional oxide layer grew at the expense of the silicon filaments, and its properties must depend on the aging conditions. The presence of this silicon oxide film is demonstrated in the FTIR spectra shown in Fig. 2 for the chemically oxidized PSLs.

According to the evolution of the PL spectra, a fresh PSL possesses a lot of PL killer centers. These non-radiative centers were considerably reduced with the initial chemical oxidation step. The PL intensity in the chemically treated samples was maintained without changes for several months after they were prepared.

On the other hand, with the ensuing aging processes in 100% humidity conditions, a silicon oxide film was formed and the PL related to QSE was reduced as the aging time progressed. New PL features were detected at 520 nm; this high energy peak can be related to the silicon defective oxide layer produced by the aging process in wet ambient conditions.

Certain authors have reported PL spectra in silicon oxide based materials with similar characteristics to those resulting in our samples. Some PL peaks at 600-620 nm are related to intrinsic defects such as the E'-center or due to native defect centers in silica [25,26]. The possible origin for those signals is related to defect centers due to post-preparation treatment [27]. Some other emissive centers have been reported in PSL at even greater energies, but with our experimental PL system we do not observe them.

When the PL features in the samples kept in wet media did not reveal any evolution with the aging time, we considered the oxidation process ended. Then the samples that were stored in the wet atmosphere were taken from the vessel, dried and annealed in air at 450°C for 24 hours. The PL spectra for those samples, taken before and after that step, were identical to that marked "17 months" in Fig. 5. This fact demonstrates that the final PL spectrum originate in the PSL converted to a silicon oxide layer by the two-step oxidation process. The remaining low-energy signal can be related to crystalline silicon islands embedded in the silicon oxide layer [28]. Studies on the optical properties of the resulting silicon oxide layers are now in progress in order to clarify the origin of the signals at about 520 nm.

4. Conclusions

A combined study of FTIR and PL was conducted on PSLs with different oxidation degrees. In freshly prepared PSL, the FTIR studies demonstrate the presence of silicon-hydrogen bonds, related to groups formed at the extended PSi surface. As the PSLs were aged, various silicon-oxygen vibrational modes became apparent. These frequencies are related to defective silicon oxide formed at the PSL surface.

On the other hand, the PL in PSLs slightly oxidized by chemical means was stable, reproducible and independent of the silicon conductivity type. The intensities of all PL spectra in fresh samples were enhanced by a factor of ten as compared to the PSLs just after the anodizing process.

The QSE related signal was located around 720 nm in fresh PSLs. This signal was shifted towards higher energies after the chemical oxidation process was applied. This behavior was interpreted as PS filament thinning.

The PL spectrum of the PSLs exposed for several months to 100% humidity conditions was markedly modified. The PL intensity decreased in time, and other PL features appeared on the high energy side.

The evolution of the different PL features as a function of the aging time enables us to recognize the signal at 520 nm as produced by a silicon oxide layer. This signal is possibly related to emissive centers existing in the defective silicon oxide layer grown by the oxidation process. The resulting characteristics of the PSLs were completely reproducible under the conditions used to synthesize the films.

Acknowledgements

This work is supported in part by CONACYT-México under contract 47104-Y The technical support of Benito Nepomuceno and M. Avendaño is acknowledged.

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