

Role of surface substances in excitation of porous silicon photoluminescence*

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Photoluminescence (PL) and photoluminescence excitation (PLE) spectra studies as well as SIMS and FTIR methods were used for investigation of PL excitation mechanism of porous silicon (PS). It is shown that there are two types of PS PLE spectra, which consist of either two bands (visible and ultraviolet) or only ultraviolet one. The different dependencies of intensity of each PLE band upon anodization regimes as well as during aging and thermal treatment were observed. Two excitation channels have been shown to be present in PS. The visible PLE band at 300 K has been attributed to light absorption of some species on Si wire surface.

Keywords: porous silicon, photoluminescence, photoluminescence excitation, absorption center, emission center

1. Introduction

In spite of numerous investigations on the photoluminescence (PL) of porous silicon (PS) the origin of visible emission (silicon wires or substances on their surface) and the mechanisms of its excitation are still unknown.

PL and PL excitation (PLE) spectra research as well as SIMS and FTIR methods were used for investigation of PS PL excitation mechanism in this paper. Three approaches have been used for investigation of role of surface substances in PS PL:

- (i) study of PL, PLE spectra, and SIMS dependencies on the anodization regimes;
- (ii) the thermal treatment effect on PL, PLE, and FTIR spectra;
- (iii) investigation of the aging phenomena in air and vacuum by PL and, especially, PLE methods.

It should be noted that the systematic research of the PLE spectra dependence upon the preparation regimes and aging conditions have not been fulfilled so far.

2. Experimental results and discussion

The PS samples were prepared from p-type B-doped, (100) oriented silicon wafers with the resistivity of 4.5 Ω cm by anodization in solution HF:H₂O:C₂H₅OH = 1:1:2. The anodized current density (I_a) and time (t_a) were 25, 50, 100 mA/cm² and 2, 8, 15 min respectively. PL measurements were carried out under a xenon lamp with an MDR-23 monochromator excitation. SIMS studies have been performed by using LAS 2000 (RIBER) spectrometer in the range of mass 1–100 m.u.

The luminescence band parameters of as-prepared samples depend on excitation light wavelength and anodization regimes (Fig. 1). This dependence shows that the PL band is complex. The PLE spectrum is complex too. It exhibits the wide band in the visible range (400–500 nm) and sharp rise (or maximum) in ultraviolet (UV) one (250–350 nm) (see Fig. 2). The dependencies of the PL band parameters on the preparation regimes measured under various excitation light wavelength are different.

The intensity W_V of the luminescence band excited by visible light (430 nm) increases and peak po-

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sition shifts to the lower photon energy region with t_a rise. The intensity W_{UV} and position of luminescence band excited by UV light change with t_a insignificantly.

When I_a rises up to $I_a = 50 \text{ mA/cm}^2$ W_{UV} and W_V values change slightly. At the higher I_a , W_V and W_{UV} drop, W_V decreases faster than W_{UV} . At the same time when the I_a arises both bands shift to high-energy region (see Fig. 1).

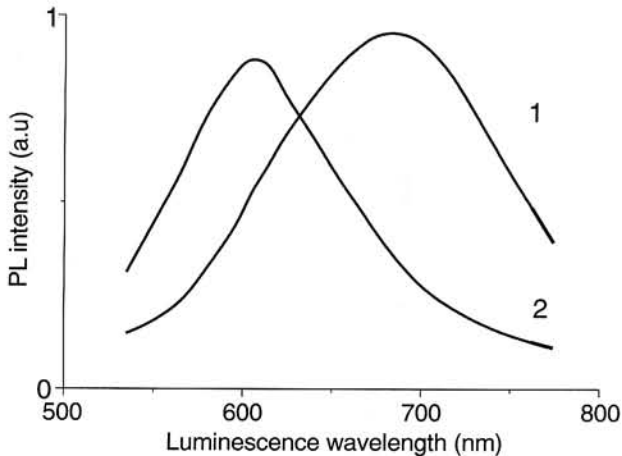


Fig. 1. PL spectra of PS samples prepared at current densities $I_a = 25$ (1) and 50 (2) mA/cm^2 and the same time $t_a = 8$ min. PL was excited by 430 nm light wavelength.

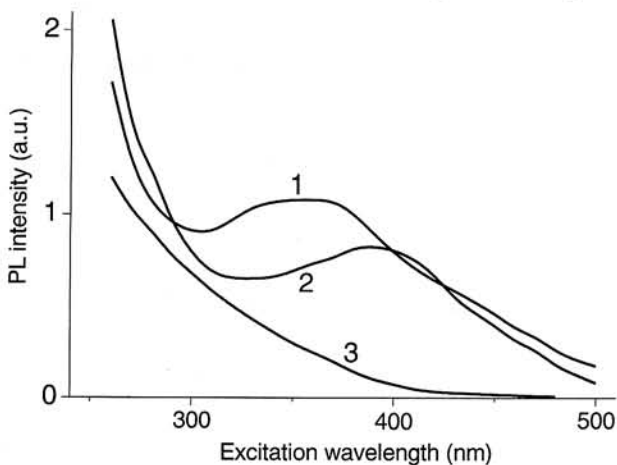


Fig. 2. PLE spectra detected at luminescence peak energy for PS samples prepared at current densities $I_a = 25$ (1), 50 (2) and 100 (3) mA/cm^2 and the same $t_a = 8$ min.

According to the above mentioned results in PLE spectra, the visible excitation band increases with t_a and decreases with I_a rise. At the large I_a the visible PLE band disappears (Fig. 2, curve 3). Thus there are two types of PLE spectra; with and without visible excitation band. In PLE spectra the UV excitation changes insignificantly with t_a and decreases with I_a rise.

The existence of two PLE bands (visible and UV) and their different dependencies upon the preparation regimes allows to suppose that there are two different channels of the PS luminescence excitation. This conclusion is confirmed by different behavior of PL intensity at visible and UV excitation during aging process.

The variation of the PL intensity during aging of PS samples in the air at room temperature is characterized by two stages. At the first one, W_V decreases whereas W_{UV} changes slightly. At the second stage, only W_{UV} significantly increases and W_V practically does not change [1].

Keeping the PS samples in the vacuum leads to the reduction of both W_V and W_{UV} intensities and their shifting to short wavelength. After sample displacement to the air, W_V does practically not change, but W_{UV} recovers and then rises. So, the increase of W_{UV} during aging could be attributed to oxidation. The visible band behaviour during aging at the air and in vacuum indicates that W_V decreases due to desorption of some species from the silicon wire surface.

For the surface substance analysis we use SIMS and FTIR investigations. The SIMS spectra of the PS layer were studied for negative and positive type ions. The O^- , H^- , OH^- , F^- , SiO^- and SiO_2^- ions have the highest concentrations.

Figure 3 represents the depth distribution of the above mentioned ions for two PS samples prepared with the same current density $I_a = 50 \text{ mA/cm}^2$ and different time $t_a = 2$ and 15 min. As follows from Fig. 3, the quantity of H^- , OH^- and F^- ions in PS layer increases with t_a rise. It is obvious that this effect correlates with the visible PLE band intensity increase.

Taking into account that visible PLE band intensity increases with t_a we could suppose that this band is connected with OH^- and H^- atoms on Si wire surface. This conclusion is confirmed by FTIR studies of as-prepared and thermally treated PS samples. The infrared absorption spectrum of as-prepared PS exhibits a number of features which can be assigned to the Si-H ($800\text{--}900 \text{ cm}^{-1}$, $2090\text{--}2140 \text{ cm}^{-1}$), Si-O ($1050\text{--}1170 \text{ cm}^{-1}$), O-Si-H ($2200\text{--}2240 \text{ cm}^{-1}$), C-H ($2850\text{--}2930 \text{ cm}^{-1}$) and O-H (1620 cm^{-1} , $3300\text{--}3600 \text{ cm}^{-1}$) bonds (Fig. 4). The appearance of the C-H related band is evidently connected with electrolyte component, namely, ethanol. Figure 4 (curve 2) shows the FTIR spectra of PS sample after thermal treatment at 370 K for 1 h . The bands attributed to O-H and C-H bonds decrease. At the same time, the Si-H, Si-O and O-Si-H related bands change insignificantly.

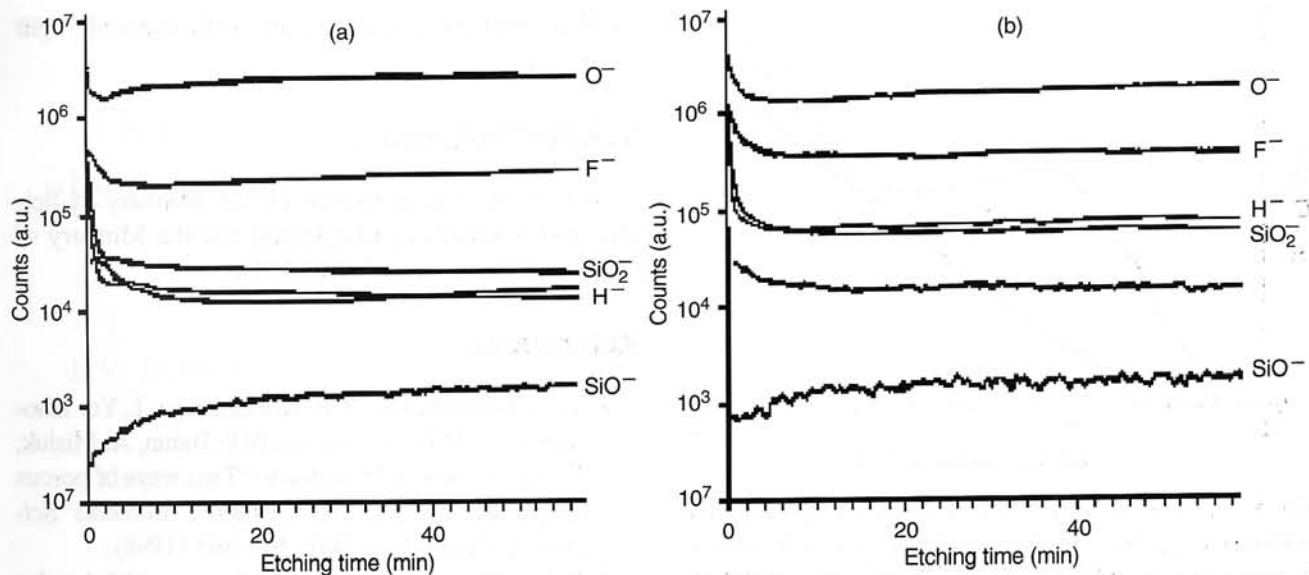


Fig. 3. Dependence of different ion depth distribution upon PS preparation regime parameters; current density $I_a = 50 \text{ mA/cm}^2$, time $t_a = 2 \text{ min}$ (a) and 15 min (b).

It is known that water molecules have not light absorption band in visible spectral region. But it is known that water molecule complexes containing some impurities (Li, Na, K, H, CH_3 , etc.) exhibit the photoluminescence in 350–500 nm region [2]. Thus we can conclude that the visible PL excitation may be connected with the water complexes with some impurities, for example, H, CH_3 and, possibly, F and B.

It should be noted that the PL excitation of PS as a rule is attributed to light absorption in Si wires [3,4]. This conclusion is often based on analysis of PLE spectra that were like spectra shown in Fig. 2 (curve 3). This analysis is based on the assumption that the PLE signal is proportional to the absorption in the

limit of optically thin sample, if the quantum efficiency is independent of the exciting photon energy. In this case the dependence of PLE signal on excitation photon energy in low energy region followed the dependence

$$\sqrt{\alpha_{\text{PLE}} h\nu} \sim (h\nu - E_e) \quad (1)$$

and was attributed to two indirect light absorption transitions in Si. The shifts of absorption edges to higher energy in comparison with one for bulk silicon were ascribed to quantum confinement effect [4]. We applied such analysis to both types of the PLE spectra of our PS samples (Fig. 2, curves 1 and 3).

For low excitation energy the signal of the first type PLE spectra (Fig. 2, curve 3) follows the dependence (1) with two different slopes and two absorption edges $E_{e1} = 1.9\text{--}2.2 \text{ eV}$ and $E_{e2} = 2.4\text{--}2.7 \text{ eV}$ (Fig. 5, curve 1). At the same time for low excitation energy the signal of the second type PLE spectra (Fig. 2, curve 1) is also described by such dependence with only one slope and one absorption edge $E_{e1} = 1.9\text{--}2.2 \text{ eV}$. So we should conclude that the light absorption of some species on Si wire surface is also characterized by the dependence (1). This dependence is in agreement with the assumption that these species are the complexes (or clusters) contained in water. Thus, the dependence like (1) with the absorption edge $E_{e1} = 1.9\text{--}2.2 \text{ eV}$ could be due to light absorption not only in Si wires, but also in some complexes on their surface. So this light absorption dependence could not be considered as an evidence of Si wire absorption.

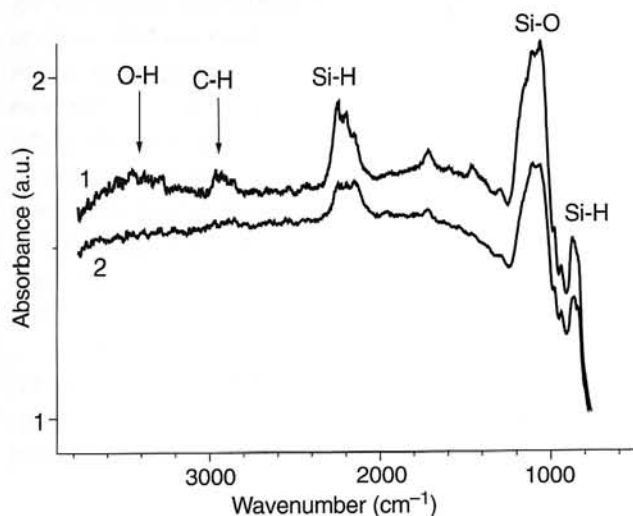


Fig. 4. FTIR spectra of as-prepared (1) and thermally treated at 370 K for 1 h (2) PS sample.

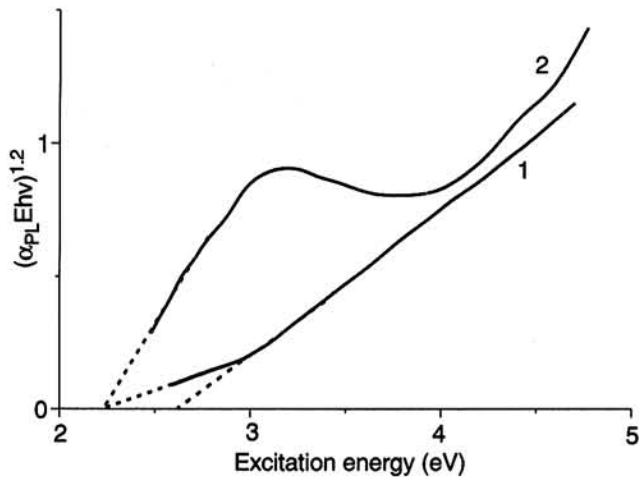


Fig. 5. The dependence of the PLE signal on the excitation photon energy for two PS samples prepared at current densities $I_a = 25 \text{ mA/cm}^2$ (1) and 100 mA/cm^2 (2) and the same time $t_a = 8 \text{ min}$.

3. Conclusions

There are two types of PLE spectra in PS containing two (visible and ultraviolet) or one (only ultraviolet) bands. We have shown that visible PLE band at 300 K is connected with some complexes (possibly water molecules with impurities) on Si wire surface. The nature of UV PLE band is not clear. This band

could be connected with Si wire or Si suboxide light absorption.

Acknowledgments

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