

## FTIR STUDY OF PHOTOLUMINESCENCE QUENCHING IN STAIN ETCHED POROUS SILICON CAUSED BY IMMERSION PLATING DEPOSITION OF Cu AND Ag

F.A. RUSTAMOV, N.H. DARVISHOV, M.Z. MAMEDOV, E.Y. BOBROVA,  
H.O. ASKEROVA

*Condensed Matter Physics Division, Institute for Physical Problems,  
Baku State University, Baku AZ 1148, Azerbaijan*

*E-mail: [farhad.rustamov@bsu.edu.az](mailto:farhad.rustamov@bsu.edu.az)*

The effect of immersion plating deposition of Cu and Ag metals onto a thin layer of stain etched porous silicon on its photoluminescent properties has been investigated. FTIR and photoluminescence spectra of samples before and after deposition were analyzed. It was found that the deposition of these metals leads to quenching of the photoluminescence, which is not restored even after removal of these metals by acid etching. FTIR analysis shows that the quenching of the photoluminescence correlates with the disappearance of the absorption band in the 2000-2300  $\text{cm}^{-1}$  range corresponding to hydrogen vibrations, and the appearance of a new absorption peak at 1221  $\text{cm}^{-1}$ , that is not typical for porous silicon. It was found that this absorption peak appears under the influence of the deposited metal, although the metal itself does not participate in the corresponding bonds, since this peak remains even after the removal of the deposited metal by acid etching. The ability of porous silicon to instantly dissolve in dilute HF after metal deposition, as well as the proximity of the peak at 1221  $\text{cm}^{-1}$  to the stretching vibrations Si-O-Si at 1172  $\text{cm}^{-1}$ , suggests a relationship between this peak and oxygen vibrations. The correlation of photoluminescence quenching with the occurrence of an absorption peak at 1221  $\text{cm}^{-1}$  indicates the deformed nature of these oxygen bonds. The deformed bonds lead to the formation of nonradiative recombination centers, which cause the quenching of photoluminescence.

**Keywords:** porous silicon; metal deposition; photoluminescence; FTIR, hydrogen bonds; oxygen bonds

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### 1. INTRODUCTION

The discovery of photo- and electroluminescence in porous silicon (PS) has stimulated research aimed both at the practical application of these materials and at clarifying the nature of the phenomenon itself [1-3]. For the practical realization of potential applications in micro- and optoelectronics, a detailed study of the deposition of various metals on porous silicon is essential. Various metal deposition techniques, such as vapor deposition, sputtering, electrodeposition, and immersion plating, can be used on porous silicon [4-7]. Immersion or electroless plating of soluble metal ions on PS does not require voltage application, and therefore, electrodes are not necessary. In this case, deposition occurs both on the surface of PS and inside the pores. By this method, Cu, Ag and Au metals can be precipitated from aqueous solutions of their salts [6, 7]. These metals are positioned in the electrochemical series of metal activity after hydrogen and have positive electrochemical potentials. The effect of these metal films on photoluminescence (PL) is complex. There are data on the quenching of PL [6-8], the PL restoration after treatment in some acids [8], the appearance of a weak blue emission [9] or near infrared emission [10], and an increase of PL [11,12]. Moreover, it is known that the immersion plating deposition of Cu and Ag metals leads to significant oxidation of PS [6-8, 13,14]. The identification of oxygen vibrations associated with this oxidation and their role in PL can be carried out through FTIR analysis.

In all of the studies mentioned above, PS films were obtained through electrochemical etching and had a thickness of more than 1  $\mu\text{m}$ . The penetration depth

of metal ions into the PS is approximately 200–300 nm and follows a gradient pattern [6, 8]. In these studies, the PS is essentially composed of two layers: the upper layer, which is exposed to the penetrating metal, and the lower layer, which remains unaffected by the metal. Therefore, when interpreting the effects of the deposited metal on PL, this fact must be taken into account. The influence of the deposited metal on the PL in its pure form may be noticeable only in the thin surface layer of PS, where the metal has penetrated to its full depth. Stain-etched PS is an example of such a material [15-17]. Films of stain etched PS are very thin (~100–200 nm), have high porosity, and, without further processing, exhibit intense visible PL.

The results of the FTIR study of the photoluminescence behavior of stain-etched porous silicon, induced by immersion plating deposition of Cu and Ag metals, are presented in this work.

### 2. EXPERIMENT

The porous silicon layers were prepared by stain etching on monocrystalline p-type wafers with a resistivity of 40  $\Omega\cdot\text{cm}$  and (100) orientation. The reaction was performed in a Teflon cell on a limited surface area of ~ 1  $\text{cm}^2$ . To degrease the surface and remove organic impurities, the wafers were first immersed in acetone for 50 minutes. Next, to remove the oxide layer, the Si wafers were treated in a 10% aqueous HF solution and then washed in bidistilled water. The PS layer was formed at room temperature and under natural light in a solution of HF (50%):  $\text{HNO}_3$  (65%):  $\text{CH}_3\text{COOH}$  (glacial) in a volume ratio of 1200:1:800 [16]. The incubation time was 2 minutes,

and the PS formation reaction lasted for 9 minutes. The resulting films had a thickness of about 150 nm and a porosity of over 70%. After etching, the samples were washed in bidistilled water and isopropyl alcohol, then dried with a nitrogen jet. Cu or Ag metals were then deposited from aqueous solutions of CuCl<sub>2</sub>, CuSO<sub>4</sub>, or AgNO<sub>3</sub> (10<sup>-3</sup> M) via wet chemical deposition, i.e., electroless immersion plating, for 1 minute. After deposition, the samples were washed again in bidistilled water and isopropyl alcohol and then dried with a nitrogen jet.

The PL spectra were measured at room temperature. The PL was excited by a Xenon lamp (DKSL-1000) transmitted through monochromators

(SPM-2 and IKS-12). In the PL measurements, the excitation wavelength was 320 nm. The surface chemical bonds on the PS were analyzed using a Fourier transform infrared spectrophotometer (Varian 3600).

### 3. RESULTS

Fig. 1 shows the PL spectra of stain-etched porous silicon. This spectrum is quite stable and does not change upon exposure to air [16, 18, 19]. The maximum of the spectrum is located at 620 nm.

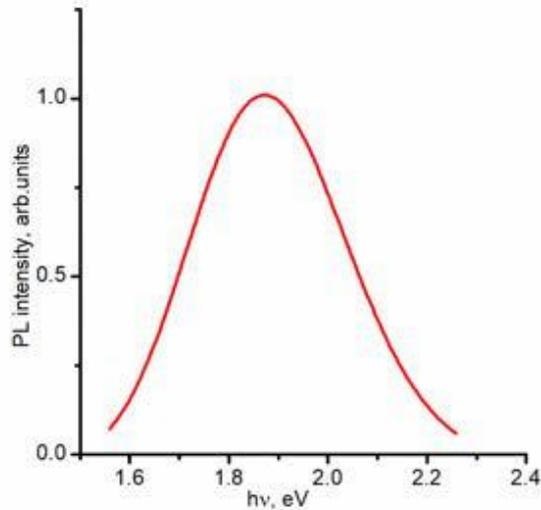


Fig. 1. PL spectra of stain etched PS before immersion plating of Cu or Ag.

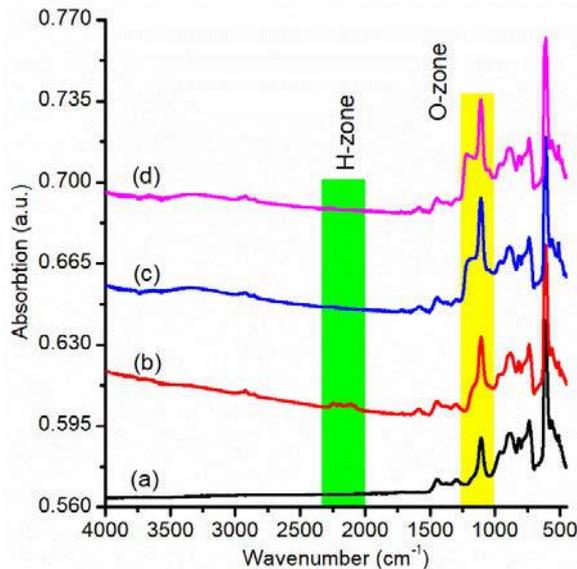


Fig. 2. FTIR spectra of silicon wafer (a), stain etched PS (b), PS after immersion plating of Cu (c), and PS after removal of Cu by HNO<sub>3</sub> (d)

Precipitation of metals from the above-mentioned aqueous solutions within 1 minute leads to the complete quenching of this PL. To investigate the role of the deposited metals in PL quenching, some samples were etched in HNO<sub>3</sub> for 1-60 minutes after deposition. Such

acid treatment was expected to remove the deposited metal from the PS surface. Despite the etching of the deposited metal, no PL recovery was observed. To clarify the role of various bonds on the PS surface, FTIR spectra of the obtained samples were analyzed.

Fig. 2 shows the FTIR spectra of a silicon wafer, porous silicon, porous silicon with deposited Cu, and porous silicon after removal of the metal by HNO<sub>3</sub>.

Since the precipitation of Cu or Ag leads to similar results, the following data will be presented only for Cu. As can be seen from the figure, the main

changes occur in the regions of 1000–1300 cm<sup>-1</sup> (O - zone) and 2000–2300 cm<sup>-1</sup> (H - zone), which are associated with oxygen and hydrogen bonds, respectively. These regions are extracted and shown separately in Fig. 3.

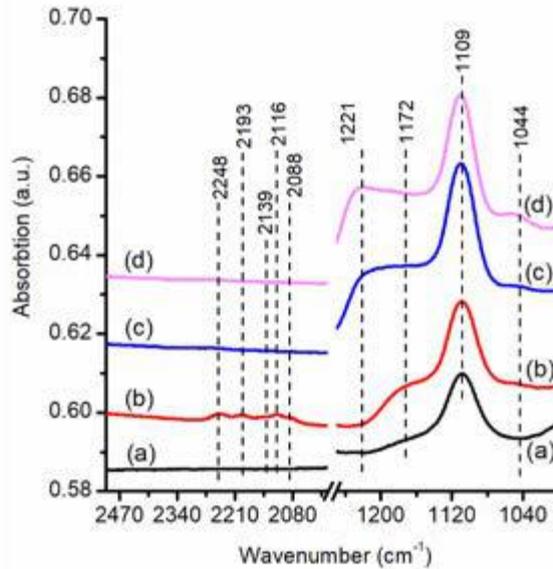


Fig. 3. Changes in the FTIR spectral regions. H-zone - hydrogen bonds, O-zone - oxygen bonds. (a) Si, (b) stain etched PS, (c) PS after immersion plating of Cu, (d) PS after removal of Cu by HNO<sub>3</sub>

As seen in Fig.3a and Fig.3b, the formation of PS on the surface of a silicon wafer leads to a change in the spectra. In the region of 2000–2300 cm<sup>-1</sup>, absorption peaks associated with SiH<sub>n</sub> vibrations, and in the region of 1000–1300 cm<sup>-1</sup>, absorption peaks associated with Si–O–Si vibrations arise [15, 18-24]. Upon Cu deposition, absorption peaks in the 2000–2300 cm<sup>-1</sup> region completely disappear, and a new absorption peak appears in the 1200 cm<sup>-1</sup> region (Fig. 3c). When Cu is removed by etching in HNO<sub>3</sub>, the absorption

spectrum remains almost unchanged (Fig. 3d). To precisely analyze and identify these peaks, baseline correction of the FTIR spectra was performed using OriginPro (Fig. 4 and Fig. 5). Fig. 4 shows absorption peaks in PS at 2088 cm<sup>-1</sup>, 2116 cm<sup>-1</sup>, and 2139 cm<sup>-1</sup> corresponding to stretching modes of SiH, SiH<sub>2</sub>, and SiH<sub>3</sub>, respectively, a peak at 2193 cm<sup>-1</sup> corresponding to the structural group SiH–SiO<sub>2</sub>, and a peak at 2248 cm<sup>-1</sup> corresponding to the stretching mode O<sub>3</sub>–Si–H.

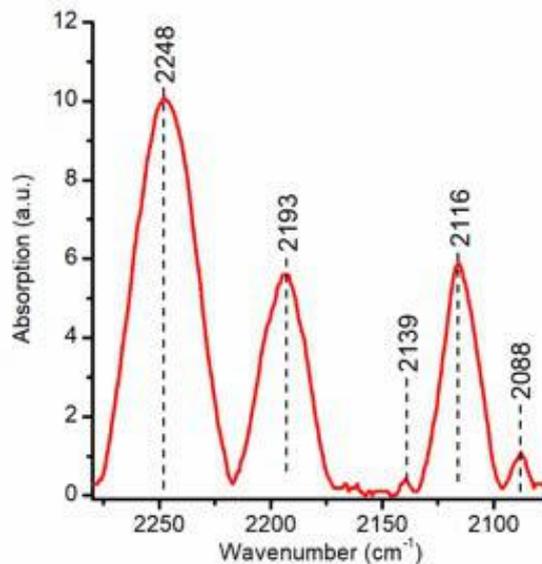


Fig. 4. Absorption peaks corresponding to hydrogen bonds after baseline correction of the FTIR spectra of PS (H-zone in Fig.2 and Fig.3 (b))

Upon metal deposition, these peaks completely disappear (Fig. 3c). These absorption peaks are also absent in the spectra after metal removal by acid (Fig. 3d). Fig. 5a shows an absorption peak at  $1109\text{ cm}^{-1}$

corresponding to Si–O–Si asymmetric stretching of interstitial oxygen in Si, which is observed both on untreated Si wafers and on PS layers.

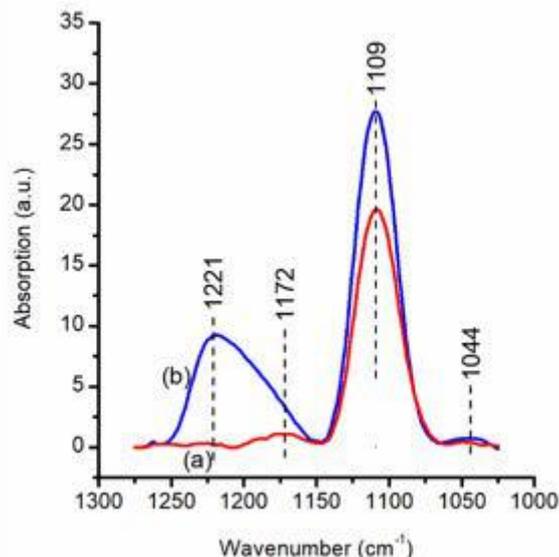


Fig. 5. Absorption peaks corresponding to oxygen bonds in (a) PS and (b) PS with immersion-deposited Cu after baseline correction of the FTIR spectra (O-zone in Fig. 2 and Fig. 3(b), (c))

Two new PS-specific peaks are also visible here: a peak at  $1172\text{ cm}^{-1}$  corresponding to the stretching mode (LO), and a peak at  $1044\text{ cm}^{-1}$  corresponding to the stretching mode (TO) of Si–O–Si. When Cu is deposited, a fairly intense and broad new absorption peak appears in the spectrum at  $1221\text{ cm}^{-1}$  (Fig.3c and Fig.5b). It is noteworthy that this peak is also observed after acid removal of the metal (Fig. 3d).

#### 4. DISCUSSION

The PL spectrum shown in Fig. 1 is typical for as-prepared stain-etched PS. Immersion plating deposition of Cu or Ag metals on PS results in the quenching of this photoluminescence. This may be due either to the absorption of excitation or emission light by films of these metals, or to a disruption of the PL mechanism caused by these metals. If the cause is light absorption, then luminescence quenching should occur regardless of the method of film deposition. However, it is known that with thermal sputtering of these metals, PL quenching does not occur [6]. This fact, coupled with the observation that at such low concentrations ( $10^{-3}\text{ M}$ ), the films of these metals are in the form of islands, rather than forming a uniform layer, suggests that the quenching of PL is not related to light absorption.

It is known that surface bonds, together with the quantum size effect of bandgap expansion with decreasing silicon crystallite size, also play a major role in the mechanism of visible PL. On the surface of silicon, there is always a large number of dangling bonds, which lead to the appearance of non-radiative recombination centers. Therefore, a decrease in crystallite size, accompanied by the broadening of the bandgap above 1.1 eV, does not, in itself, lead to visible

PL. For visible PL to occur, these dangling bonds must be compensated. From the comparison of the (a) and (b) curves in Fig. 2 and Fig. 3, it is evident that the formation of PS is accompanied by the appearance of absorption peaks at  $1000\text{--}1300\text{ cm}^{-1}$  (O - zone) and  $2000\text{--}2300\text{ cm}^{-1}$  (H - zone). These peaks, corresponding to Si–O–Si and SiH<sub>n</sub> vibrations, lead to the compensation of dangling bonds and the emergence of radiative recombination levels. As mentioned, immersion plating of Cu or Ag results in PL quenching. In the FTIR spectra (Fig. 2 and Fig. 3, (a) and (b)), this correlates with the complete disappearance of absorption bands in the  $2000\text{--}2300\text{ cm}^{-1}$  region and the appearance of a new absorption peak at  $1221\text{ cm}^{-1}$ .

The disappearance of absorption bands at  $2088\text{ cm}^{-1}$ ,  $2116\text{ cm}^{-1}$ ,  $2139\text{ cm}^{-1}$ ,  $2193\text{ cm}^{-1}$ , and  $2248\text{ cm}^{-1}$ , corresponding to SiH, SiH<sub>2</sub>, SiH<sub>3</sub>, SiH–SiO<sub>2</sub>, and O<sub>3</sub>–Si–H vibrations (Fig. 2 and Fig. 3, curves (b) and (c)) may be one of the reasons for the PL quenching, but it is not necessarily the cause. If, after the rupture of hydrogen bonds, uncompensated dangling bonds are formed, non-radiative recombination centers arise and PL quenching actually occurs [18]. However, such samples usually oxidize in air over time, the dangling bonds are compensated by oxygen, and PL is restored. The appearance of such oxygen bonds is manifested in FTIR spectra as absorption peaks at  $1172\text{ cm}^{-1}$  and  $1044\text{ cm}^{-1}$  (Fig. 2b and Fig. 3b), corresponding to Si–O–Si stretching LO and TO modes. In this case, only a transformation in the shape of the PL spectrum occurs. For example, during atmospheric oxidation of as-prepared PS, unstable hydrogen bonds are gradually replaced by more stable oxygen bonds. PL quenching does not occur, although the shape of the PL spectrum changes and its maximum shifts to the short-

wavelength region [18]. The same effect can occur during liquid oxidation of PS.

Another reason for the quenching of PL in PS may be the emergence of new bonds, leading to the formation of non-radiative recombination centers. The comparison of the (b) and (c) curves in the FTIR spectra in Fig. 2 and Fig. 3 shows that immersion plating deposition of Cu is accompanied by the appearance of a new intense absorption peak at  $1221\text{ cm}^{-1}$  (Fig.5). To identify this peak, FTIR analysis was also performed on samples after Cu removal with nitric acid. After removal of the Cu film, the PL is not restored, and, as can be seen from Fig.3d and Fig.5b, this peak remains unchanged even after the removal of the copper film with acid.

Thus, although the deposited Cu leads to the appearance of new bonds, it does not itself participate in these bonds. The proximity of this peak to the peak at  $1172\text{ cm}^{-1}$  (stretching mode Si–O–Si) indicates its relationship with oxygen vibrations. The occurrence of such deformed oxygen bonds, which differ from the oxygen bonds characteristic of conventional PS, is also manifested by the different response of the as-prepared PS and PS with deposited Cu to a dilute aqueous HF solution. As is known, ordinary stain-etched PS can be kept in a dilute HF solution for tens of minutes without any damage. However, PS with deposited Cu, even after its removal with acid, instantly and completely dissolves in dilute HF. In this case, the absence of PL indicates that the oxide produced by the metal has poor quality. These deformed oxygen bonds lead to the emergence of non-radiative recombination centers in the bandgap of PS, which quench the PL. This is similar to the quenching of PL during oxidation of PS with

dimethyl sulfoxide, which is also caused by the formation of deformed oxygen bonds [25].

## 5. CONCLUSIONS

The effect of immersion plating deposition of Cu and Ag metals on stain etched porous silicon on photoluminescence was studied. It was shown that such deposition leads to complete quenching of PL, which is not restored even after removal of the metal by acid. The thickness of the PS layers was approximately 150 nm, which allowed the metal ions to penetrate the entire thickness of the sample. FTIR spectra were analyzed before and after deposition, as well as after removal of the deposited metal by acid etching. It was found that the PL quenching upon deposition of Cu and Ag by immersion plating correlates with the disappearance of the absorption band at  $2000\text{--}2300\text{ cm}^{-1}$ , corresponding to hydrogen vibrations, and the appearance of a new absorption peak at  $1221\text{ cm}^{-1}$ . This peak is also observed after removal of the deposited metal. Thus, metal deposition leads to the formation of new bonds, which are manifested by the appearance of an absorption peak at  $1221\text{ cm}^{-1}$ , but the metal itself does not participate in these bonds. The proximity of this peak to the peak at  $1172\text{ cm}^{-1}$ , as well as the ability of PS to instantly dissolve in dilute HF after metal deposition, indicates its relation to oxygen vibrations. In contrast to absorption peaks characteristic of PS at  $1044\text{ cm}^{-1}$ ,  $1109\text{ cm}^{-1}$ , and  $1172\text{ cm}^{-1}$ , which correspond to oxygen bonds and appear in the presence of PL, these deformed oxygen bonds lead to the formation of non-radiative recombination centers, causing quenching of PL.

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