



Review

Influence of LiBr on photoluminescence properties of porous silicon

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ABSTRACT

A new method has been developed to improve the photoluminescence intensity of porous silicon (PS), which is first time that LiBr is used for passivation of PS. Immersion of the PS in a LiBr solution, followed by a thermal treatment at 100 °C for 30 min under nitrogen, leads to a nine fold increase in the intensity of the photoluminescence. The atomic force microscope (AFM) shows an increase of the nanoparticle dimension compared to the initial dimension of the PS nanostructure. The LiBr covers the nanoparticles of silicon without changing the wavelength distribution of the optical excitation and emission spectra. Moreover, a significant decrease of reflectivity was observed for the wavelength in the range of 350–500 nm.

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1. Introduction

PS is considered to be a promising engineered material for silicon based devices due to its nanostructure and visible (600–800 nm) light emission properties [1,2]. The photoluminescence (PL) of PS has attracted much attention, especially to enhance and stabilize its emission [3–6]. However, there are many problems before that the PS can be put into applications, such as its insufficient light emission efficiency due to the indirect energy gap of bulk Si and the degradation of the emission characteristics due to the H-terminated surface and the atmospheric oxidation [7].

To improve the electro and the PL intensity of PS, several passivation methods have been proposed. Many materials such as silver (Ag) [8], gold [9] and the transparent conducting oxides such as indium tin oxide [10], were tested and proved their ability to improve the PS properties. Various metals are deposited onto the PS surface by immersion plating or by dipping the surface into a solution

containing metal ions such as Ag [5], Cu [4,6], Ni [10], and Pd [4]. Rahmani et al. [11] have impregnated PS in ferric nitrate aqueous solution, to introduce Fe ions into the pores. They have found a strong PL intensity and the PL peak energy is centered at about 1.71 eV. The PL enhancement after Fe doping is due to the iron-passivation of nc-Si and demonstrated that Si–H bonds can be substituted by Si–Fe ones.

Esmer et al. [12] have studied the effect of deposition of some alkali metals onto the PS surface by immersion plating in XNO₃ solutions where X(=Li, Na, K) was investigated. They found that after alkali metallization the PL intensity increased for critical immersion times and PL spectrum shifted to high energy region.

Fujiwara et al. [13] studied the luminescence properties of LiBr crystals cleaved at 6 K and demonstrated that the holes in LiBr are mobile and migrate to impurities to recombine with electrons there, emitting the 5.4 eV luminescence.

Zhao and White [14] fawnd that an inorganic salt, LiBr, doped into an electroluminescent polymer, and fabricated into a single layer polymer light-emitting diodes structure, exhibits dramatically improved performance compared to an undoped polymer. LiBr doping does not alter the wavelength distribution of the optical excitation and emission spectra.

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In this article, inspired by the works of Rahmani et al. [11], Esmer and Kayahan [12] and the LiBr properties presented by Fujiwara et al. [13] Zhao and White [14], we present a study of the possibility to enhance the PS photoluminescence intensity using LiBr aqueous solution deep-coating. The influence of LiBr concentration on the PL was discussed.

2. Experimental

The initial material was p-type, B-doped, (1 0 0) oriented Si wafers with a resistivity of $1\text{--}12\ \Omega\text{ cm}^{-1}$. Six PS samples were prepared by the electrochemical anodisation in a solution of HF (40%)/C₂H₅OH (1:1), and the current density being 20 mA/cm^2 for 20 min. One Sample was used as a control for comparison, did not undergo any treatment. five samples were dipped in five LiBr aqueous solution with different concentration S/2, S/2.5, S/4, S/10 and S/100, ($S=1.66\text{ g/ml}$ is the solubility of LiBr in water at $26\text{ }^\circ\text{C}$). A thermal treatment at $100\text{ }^\circ\text{C}$ of the samples was realized in an infrared furnace under nitrogen for 30 min. The samples were rinsed in deionized water, blown dry with nitrogen stream.

PL spectroscopic analyses of PS and the LiBr-deposited PS samples were performed at ambient temperature with 4765 Å laser. Typical Fourier Transform Infrared (FTIR) using Nicolet MAGNA-IR 560 spectrometer between 300 and 2500 cm^{-1} spectra was achieved to assess the chemical change associated with LiBr coating. The morphology of the PS surface before and after LiBr treatment was investigated by atomic force microscopy (AFM) with a tapping mode. The reflectivity spectra were realized using LAMBDA 950 UV/Vis/NIR Spectrophotometer equipped with an integrating sphere.

3. Results and discussion

Fig. 1 shows typical FTIR absorption spectra of freshly prepared PS, oxidized porous silicon (ox-PS) performed under a dry oxygen flux (10 l/min) at $100\text{ }^\circ\text{C}$ for 30 min and PS treated by the low LiBr

concentration (S/100) aqueous solution. The oxidized PS is prepared to identify and to study the oxide vibration bonds after LiBr treatment.

For the PS spectra, the principal recorded vibration bands at 2114 and 2087 cm^{-1} are Si–H₂ and Si–H stretching modes, respectively. The peak at 907 cm^{-1} is attributed to scissors mode of Si–H₂. The vibration absorption band at 629 cm^{-1} which is a mixture of stretching wagging mode Si–Si and wagging mode Si–H_n ($n=1$ and 2). Vibration bonds around 1111 cm^{-1} correspond to the stretching mode of Si–O–Si. After oxidation (ox-PS) and LiBr S/100 treatments, we observe a total disappearance of the vibrations modes relative to Si–H_n bands. The peak observed at 460 cm^{-1} was assigned to Si–O–Si bending vibration. The vibration band at 1077 cm^{-1} was assigned to asymmetric stretching vibrations of the three-dimensional Si–O–Si network [15]. This peak can be attributed to the oxidation accompanying the deposition of alkali metals from the solutions. A weaker peak seen at approximately 800 cm^{-1} corresponding to the symmetric stretching vibration of the Si–O–Si network [16].

Fig. 2 shows typical FTIR absorption spectra of S/4, S/10 and S/100 prepared samples for all spectra's, it is clearly seen the disappearance of the peaks at 629 , 907 , 2114 and 2087 cm^{-1} attributed to Si–H_n bonds. Compared to PS, ox-PS and S/100 spectra, after the immersing of PS in the S/10 and S/4 solution, new peaks at 850 , 733 , 610 and 518 cm^{-1} was observed. Metal-oxygen stretches generally occur well below 1000 cm^{-1} with most metal-oxygen bonds vibrating in the $700\text{--}300\text{ cm}^{-1}$ range. Therefore, the peaks observed at 516 , 607 and 850 cm^{-1} can be assigned to the formation of new metal-oxygen bonds [17]. The weak band around $900\text{--}940\text{ cm}^{-1}$ region may be attributed to the stretching of Si–O– of non-bridging oxygen associated with the Li⁺ ion [17].

For the S/4 and S/10 spectra, we can also see the disappearance of the peaks at 460 and 800 cm^{-1} , respectively, and the decrease of the intensity of the peak at 1070 cm^{-1} assigned to the Si–O–Si vibration modes. These results assume that Si–O–Si bonds are substituted by Lithium-Si and (Lithium-oxygen)-Si.

Fig. 3 shows the PL spectra of the PS (used as a reference) and the LiBr-porous silicon samples. An enhancement of the PL is obtained for all LiBr used concentration. The maximum intensity of PL is obtained for the S/4 LiBr concentration solution. The peak intensity increases

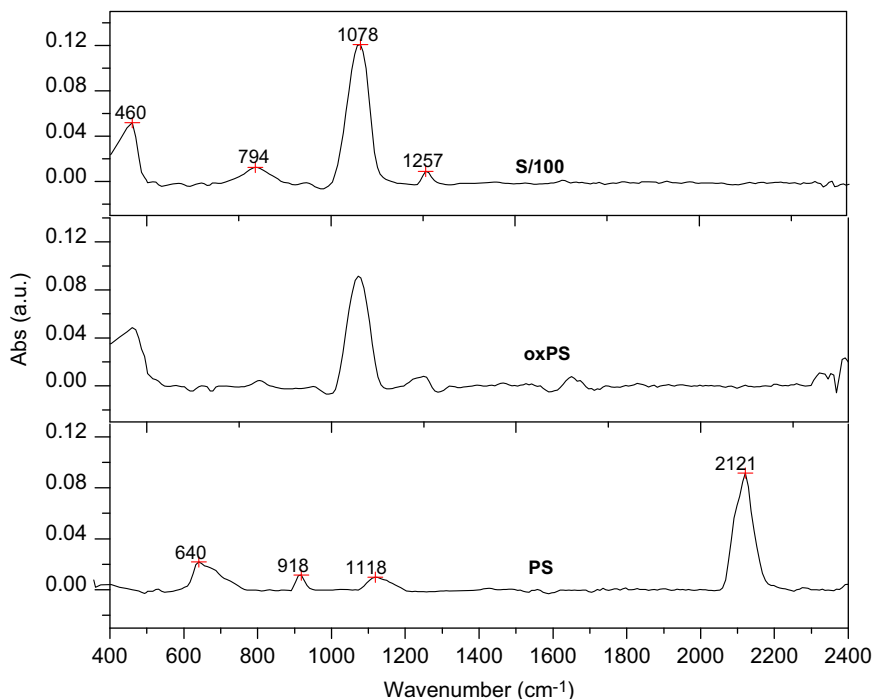


Fig. 1. FTIR absorption spectra of freshly prepared porous silicon (PS), oxidized porous silicon (ox-PS) and PS treated by the LiBr concentration (S/100) aqueous solution.

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