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Influence of alkali metallization (Li, Na and K) on photoluminescence properties of porous silicon

Kadir Esmer [a], Ersin Kayahan [b,*]

[a] Marmara University, Faculty of Science and Arts, Department of Physics, 34722 Kadıköy, Istanbul, Turkey
[b] Kocaeli University, Gebze MYO, 41410 Çayırova, Kocaeli, Turkey

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ABSTRACT

We present results for alkali metallization effects on photoluminescence (PL) properties of porous silicon (PS). The metallization of PS was realized by immersion plating in solutions containing 3 mM $LiNO_3$, KNO_3 and $NaNO_3$ metal salts. The surface bond configuration of PS was monitored by Fourier transmission infrared spectroscopy (FTIR) and it was found that the PS surface was oxidized after metallization. Surface properties of PS were investigated by field emission scanning electron microscopy (FE-SEM) and it was found that the PS surface was covered by alkali metals for short immersion times. The PL intensity increased for critical immersion times and PL spectrum shifted to high energy region with the metallization. The experimental results suggest a possibility that the metallization provides a relatively easy way to achieve an increase in the PL intensity and oxidation of the PS surface.

1. Introduction

In recent years, numerous experimental and theoretical studies have been reported in the literature in order to realize optical devices and biosensors with porous silicon (PS). However, inefficiency, photoluminescence (PL) stability and the origin of the luminescence of PS still remain unclear and controversial [1]. In addition, an extremely complex PL property of the PS depends on fabrication and storage conditions [2]. Several studies have addressed the problem of enhancement and stabilization of PS luminescence with different surface treatments as it is known that PS luminescence is strongly related with spaces on the surface. Hence, efforts to obtain stable surface species have led to the discovery of several chemical methods to functionalize Si surfaces [3–10]. However, there is still a pressing need for further investigation such as surface modification of the PS surface with some metal atoms leading to a definitive explanation of the origin of the PL and to more chemically stable PS surfaces.

It is important to deposit metals and change chemical composition of the PS surface with metal atoms to form a good electrical contact for microelectronics and photo electronics [3]. Metals can be deposited onto the PS surface by various methods such as sputtering or chemical vapour deposition. Furthermore, metals can also be deposited onto the PS surface in a more practical way by using wet processes such as electroplating, electrolyses plating and immersing plating. The wet processes have advantages of good throwing power and low costs due to simplicity of the equipment used. The immersion plating is more practical than others [4]. Various metals are deposited onto the PS surface by immersion plating by dipping the surface into a solution containing metal ions such as Ag [5], Cu [4,6], Ni [7], Fe [8,9] and Pd [10]. The PL properties such as intensity and stability of porous silicon were thus enhanced in various studies reported in the literature [4–9]. However, surface modification of the PS with metals such as Li, K and Na and effects that metallization processes have on the luminescence of the PS have not been reported in literature. This would be a rather interesting study for the PL properties as well as having the potential of being an alternative route for PS applications.

This paper presents results on the effects that surface modification has on the luminescence of the PS by adsorption of the alkali metals (alkali metallization) using immersion plating method. The effects of alkali metallization on PS photoluminescence are discussed and results of the spectral studies (PL, FTIR, and SEM) as well as spectral responses are reported.

2. Experimental

Porous silicon with (1 1 1) orientation and 10.5–19.5 Ω cm p-type silicon wafers by anodisation in a HF (48%) was formed in C_2H_5OH (98%) = 1:1 (by volume) mixture solutions with 10 mA cm^{-1} current density for 30 min. etching time. After the etching, PS is formed as shown in Fig. 1a. The PS samples which were dried in vacuum were coated with alkali metals by

* Corresponding author. Tel.: +90 262 742 32 90; fax: +90 262 742 40 91.
E-mail address: kayahan@kocaeli.edu.tr (E. Kayahan).

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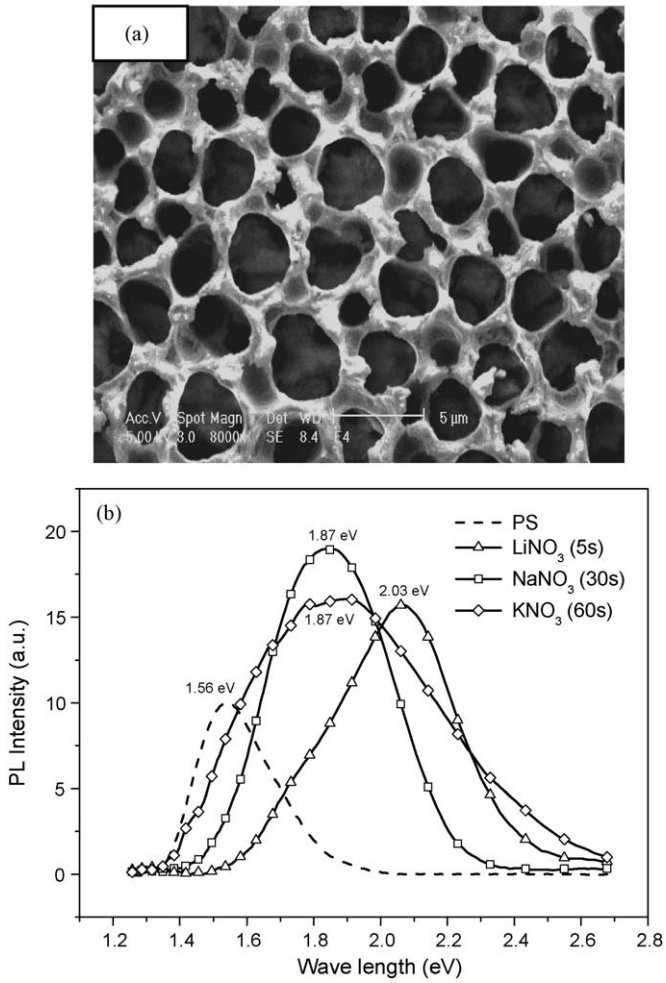

Fig. 1. (a) SEM image of porous silicon showing a uniform sponge-like structure. (b) The alkali metallization effect on PL properties of PS for Na, K and Li metallization for various times. Dashed line shows PL spectrum of freshly prepared PS for comparison of metallization effects.

immersion plating method in 3 mM $LiNO_3$, 3 mM $NaNO_3$ and 3 mM KNO_3, solutions each for 5, 30 and 60 s metallization times. For each metal salt, three metallized PS structures were also produced. All samples were rinsed with deionised water and dried under vacuum subsequently.

The surface morphology of the samples was studied by using a field emission scanning electron microscopy (FE-SEM) Philips 30XL SPEG. The infrared spectra were collected by a Shimadzu 8201/86601 PC spectrometer. The PL spectra were obtained using a PC controlled MMS spectrometer. PL excitation was taken by 366 nm light from a UV lamp (Konrad-Benda). All spectral measurements were taken at room temperature. The typical PL spectra of the freshly prepared PS and alkali metallized PS are shown in Fig. 1b.

3. Result and discussion

The PS surface modifications due to alkali metallization were monitored by Fourier transform infrared (FTIR) spectroscopy. Fig. 2 shows typical FTIR absorption spectra before and after adsorption of alkali metals on the PS surface by immersion plating in 3 mM alkali metal ($LiNO_3$ $NaNO_3$, and KNO_3) containing aqueous solution. The spectra (a), (b) and (c) show 5, 30 and 60 s metallization times of PS surface in different solutions, respectively. Vibration bonds around 1105 cm^{-1} correspond to the stretching mode of Si–O–Si while 910 cm^{-1} is attributed to scissors mode of $Si–H_2$. A large vibration absorption band at 610–660 cm^{-1} is a mixture of stretching mode of Si–Si and wagging mode of $Si–H_n$ (n = 1 and 2). The peak around 617 cm^{-1} corresponds to the Si–Si stretch mode and the peak at 624–667 cm^{-1} corresponds to $Si–H_n$ wagging mode. The peak observed at 870 cm^{-1} is for $O_y–Si–H_x$ deformation mode. In the high energy region of the spectra, the

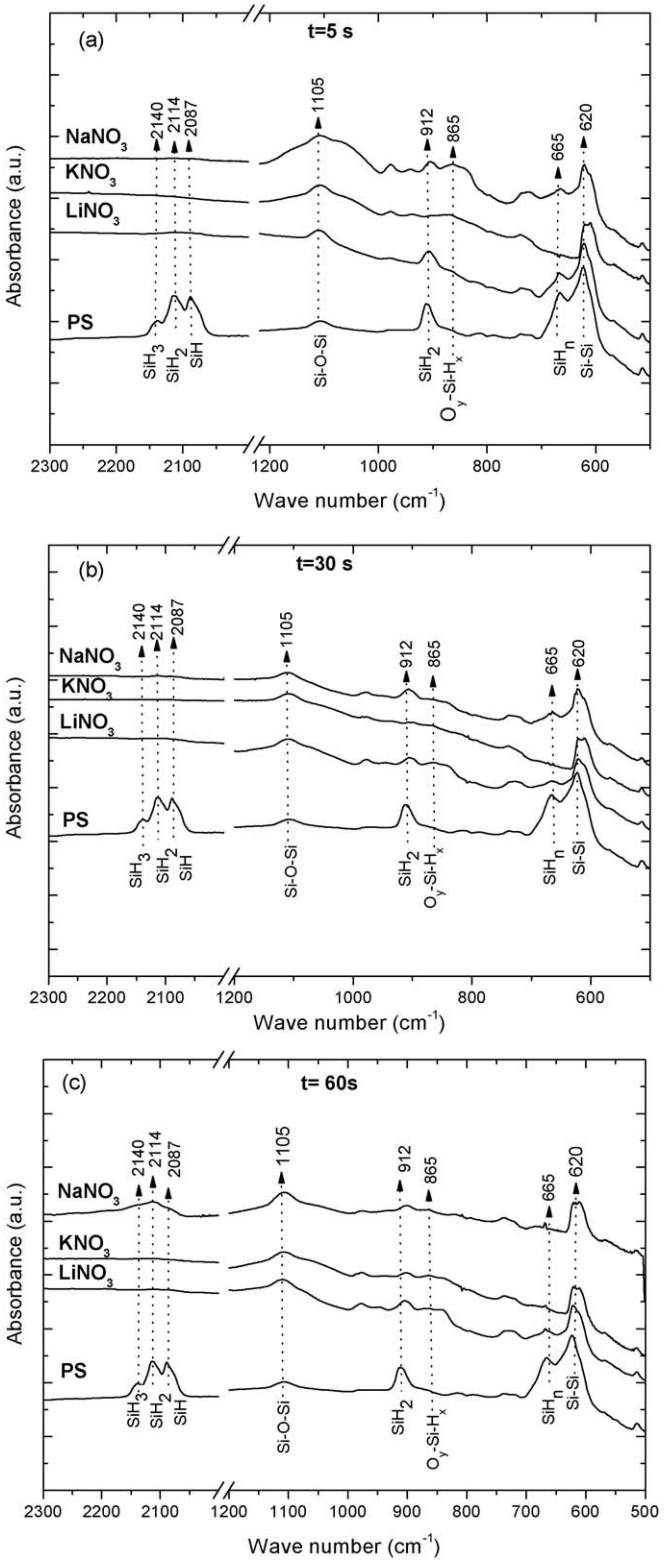

Fig. 2. Infrared absorption spectra of freshly prepared and metallized PS in $LiNO_3$, $NaNO_3$ and KNO_3 solutions for various immersion times (a) 5 s (b) 30 s and (c) 60 s.