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

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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

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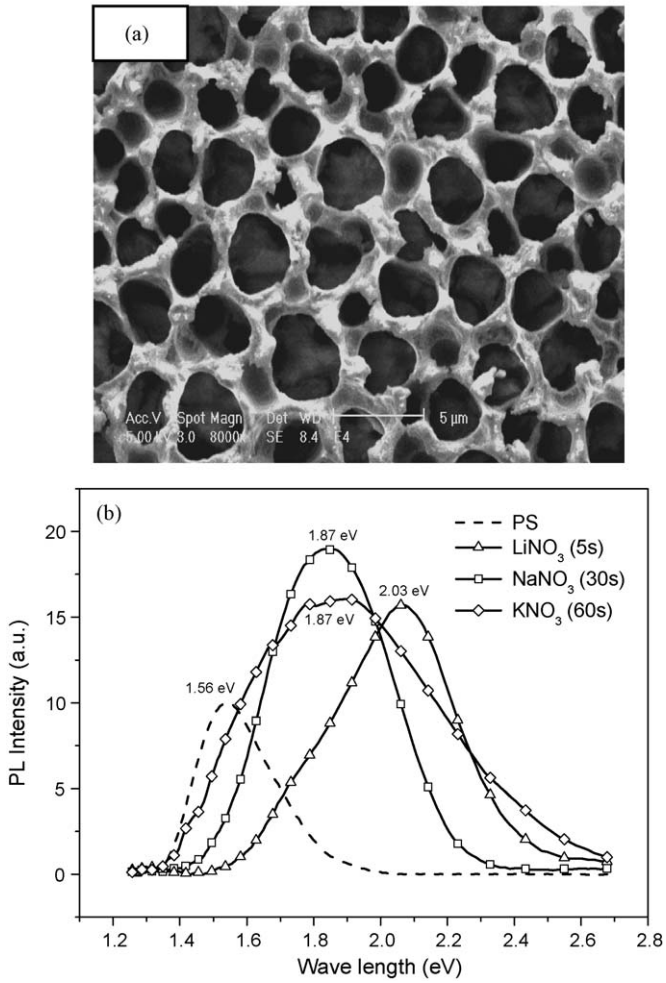

Fig. 1. (a) SEM image of porous silicon showing a uniform sponge-like structure. (b) The alkali metallization effect on PL properties of PS for Na, K and Li metallization for various times. Dashed line shows PL spectrum of freshly prepared PS for comparison of metallization effects.

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

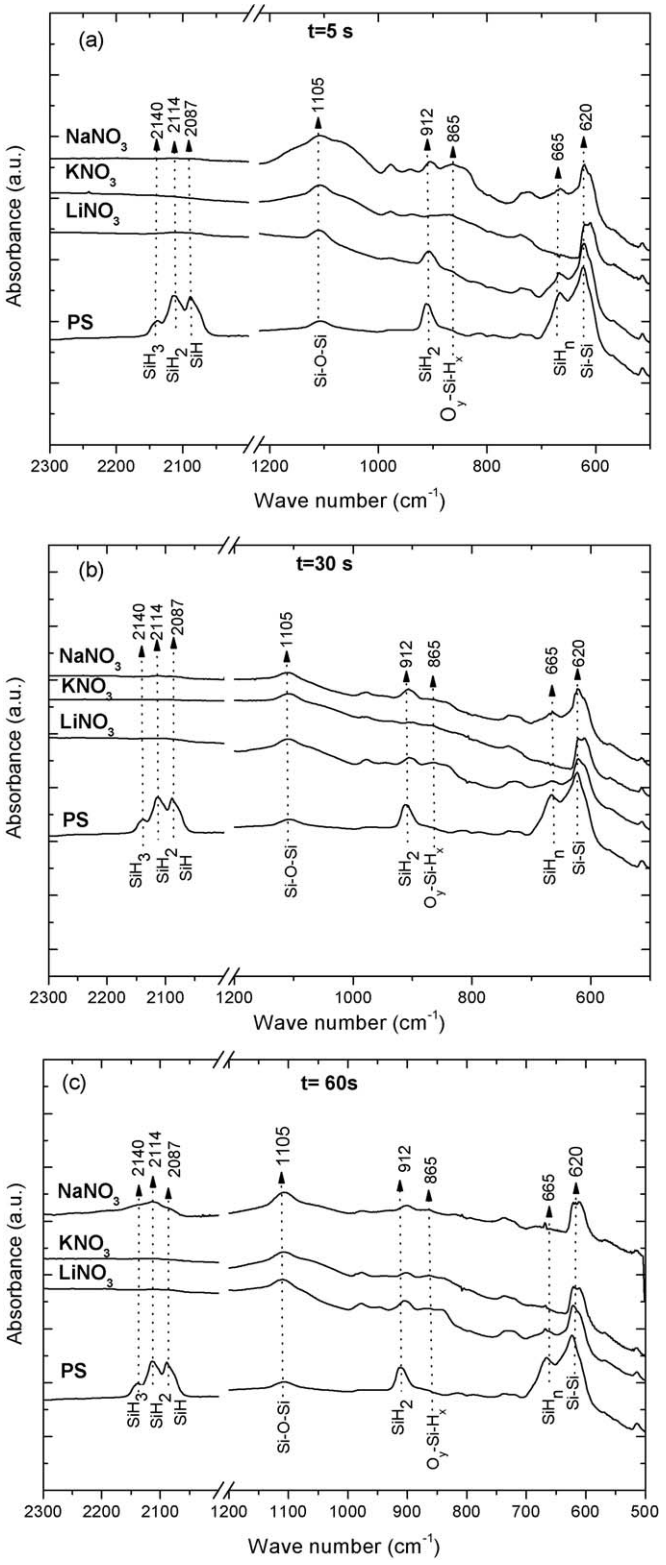

Fig. 2. Infrared absorption spectra of freshly prepared and metallized PS in $LiNO_3$, $NaNO_3$ and KNO_3 solutions for various immersion times (a) 5 s (b) 30 s and (c) 60 s.

three absorption peaks at 2140, 2114 and 2087 are Si–H_3, Si–H_2 and Si–H stretching modes, respectively. The peaks shown in Fig. 2 are in good agreement with the data reported in the literature [2,4,7,9,11,12].

It can be seen from Fig. 2 that a marked change in the spectra was observed following the immersion of PS into the alkali metal containing aqueous solution for various immersion times. An absorption peak centred around 1105 cm^{-1} is due to Si–O–Si stretching mode being partly extended and increased with increased immersion times of the PS in solutions. The extension of Si–O–Si can be attributed to the oxidation accompanying the deposition of alkali metals from the solutions. Moreover, the peaks of Si–H_n at 2087, 2114 and 2140 cm^{-1} have disappeared in the alkali metallized samples as the metallization time proceeds from 5 to 60 s. Furthermore, other Si–H_n (n = 1 and 2) related peaks at 912 and 624–667 cm^{-1} have also decreased or disappeared for all metallized samples. The extension and increase in the Si–O–Si stretch band at 1105 $cm^{-1}$and decrease or diminish of Si–H related peaks are due to the replacement of the hydrogen atoms by the oxygen and/or oxygen-metal atoms.

Fig. 2a shows Na metallized spectra for 5 s. It can be seen that the width and intensity of the Si–O–Si stretch peak observed at 1105 cm^{-1} has increased. However, for 60 s metallization time, the intensity of the peak decreased with increased metallization times as shown in Fig. 2b and c. A similar behaviour is also present for 865 cm^{-1} O_y–Si–H_x deformation peak. This means that free Na metal ions in the solution combine with the oxygen ions leaving from the PS surface. Furthermore, it is seen that for 60 s Na metallization, new peaks are being formed in 2050–2150 cm^{-1} Si–H_n stretch peak region. This can be explained by hydrogen atoms getting bound to the PS surface again.

Similarly, the decrease and diminish in the intensity with respect to the metallization times in the Si–H_n bands at 630–680, 912 and 2090–2150 cm^{-1} have been reported by Harraz et al. [7] and Sasano et al. [4] via immersion plating of the PS in Ni ions containing NH_4F solution and in Cu ions in H_2SO_4 solution, respectively. The theoretical studies of Wei et al. [13] report a strong interaction between the Ag atoms and surface Si atoms in their work on Ag adsorption to the Si surface. They conclude that this is due to the adsorption of the Ag atoms on the surface because of dangling bonds of the surface atoms being partially saturated by the adsorbed Ag atoms. In addition, in our previous study [5], adsorbed Ag atoms to PS surface by immersion platting effects show an enhancement of PL intensity and electrical conductivity. A blue shift was observed in PL spectra by Ag metallization. Similar to the above, we show in this study that Si–H_n related peaks diminished and/or decreased and oxygen related peaks increased. Similar results were reported by Rahmani et al. [9] where they used ferric nitrate aqueous solution for immersion plating.

From the FTIR spectroscopy results, it is clear that silicon bonds with oxygen or oxygen metal pairs replaced those with hydrogen with alkali metallization. It was further illustrated from the comparison of the FTIR spectra between metallized and non-metallized PS surfaces that surface oxidation takes place rather quickly.

Scanning electron microscopy micrographs of alkali metallized PS surfaces are shown in Fig. 3. Fig. 3a, d and g are due to metallization in $LiNO_3$, Fig. 3b, e and h are due to $NaNO_3$ and Fig. 3c, f and i are due to metallization in KNO_3 solutions respectively. When compared to the SEM image of freshly prepared PS samples shown in Fig. 1, it is clear that there is a continuous distribution of pore sizes ranging from 1 to 2 μm. After alkali metallization process by immersion plating, the PS surface is coated with different alkali metals and the coating is as fast as 5 s.

It can be seen from Fig. 3 that the PS surface can be coated in a rather fast fashion. However, the coating for K is different from

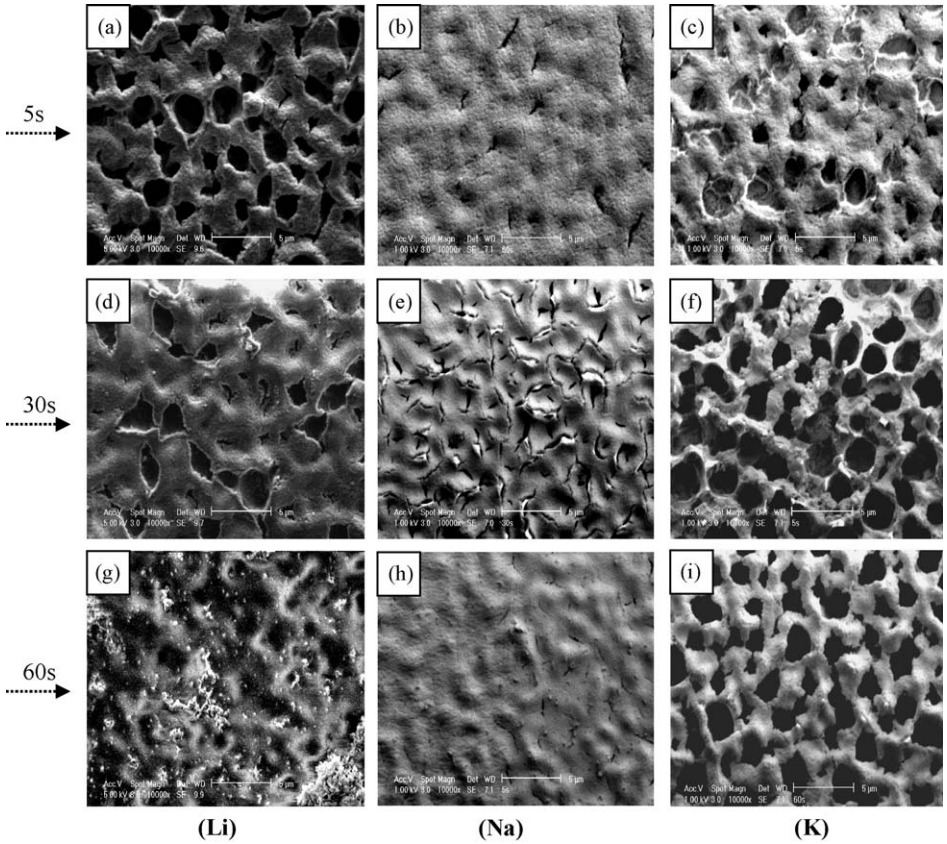

Fig. 3. Planar SEM images of metallized PS surface with Li,Na and K by immersion platting in theirs nitrate solutions for various times; 5 s (a–c), 30 s (d–f) and 60 s (g–i).

the other coatings. The *K* coating takes place in the pores as can be seen from Fig. 3f and i. It is seen that *K* metal goes through dissolution on the PS surface. This can be due to the fact that free oxygen atoms in the solution combine with *K* atoms on the surface. A similar result was also reported by Sasono et al. [4] where they report that Cu leaves the PS surface when it was deposited onto the surface via immersion plating after a certain immersion time. Fig. 3a–h shows that Li and Na atoms coat the PS surface rather fast. Contrary to K coating, following Li and Na coating, the pores were filled by Li and Na metals as seen in Fig. 3a–h. From the SEM images, it was shown that it is possible to obtain thinner and more uniform coatings on the PS surface with Li and Na with increasing metallization times.

The PL spectra in Fig. 4 were obtained from the freshly prepared samples The metallized surfaces of PS with alkali metals of Li, Na and K are for different metallization times (5, 30 and 60 s). It is obvious that a blue-shift of the PL spectra is observed. The biggest shift is observed in Li metallization. The PL intensity is highest in 5 s Li metallization, in 30 s Na metallization and in 60 s K metallization times. FWHM of the PL spectra of metallized samples increased when compared to the freshly prepared PS samples. This means that PL mechanisms involved could be different. Looking at the FTIR results, it is shown that metal deposition onto the PS surface is accompanied by the oxidation of Si surface. The deposition of the metals depends on the concentration of metal ions and immersion times [7]. It is possible that hydrogen atoms leaving the PS surface might have formed new oxide related interface states with a surface modification. This oxygen or alkali oxide metal related electronic states should play an important role in the PL mechanism of the PS. The shifts of the PL spectra towards high energy region may be ascribed to the recombination of electrons trapped at the states due to Si=O bonds of PS leading to the quantum confinement effect [9].

Oxidation has also been carried out by using thermal annealing, electrochemical anodic oxidation and laser irradiation as reported in the literature. Similar to this study, an efficient and blue shifted luminescence was achieved from the oxidized PS surfaces [2,14,15]. Effects of the aging of the PS in air were observed in [16]. Kanemitsu et al. [17] have studied the PL spectra and dynamics of the surface-oxidized Si nanocrystals [17] and their results suggest that PL from oxide related interface states is very important. According to Mahmoudi et al. [1], observed blue shift of the PL spectra where CH_x modified PS was aged in air may be understood in terms of reduction in size of silicon wires resulting in an increase in the energy band gap of silicon. Taking these into consideration, we deduce that the blue shift of PL spectrum and enhancement in the PL intensity is a result of alkali metal oxidation of the PS surface by the metallization.

It can be shown from the FTIR results that metal deposition onto the PS surface after immersion plating is accompanied by the oxidation of Si surface. The oxidation reactions that take place in immersion plating are thought to proceed as follows [4].

$$M^{n+} + ne^- \rightarrow M$$

$$Si + 2H_2O \rightarrow SiO_2 + 4H^+ + 4e^-$$

The first reaction is the reduction of the metal and the second is the oxidation of Si. The oxidation of silicon to SiO_2 is necessary for the alkali metals deposition. Consequently, as a result of the formation of oxide layer on the surface, saturation for the alkali metallization is reached when the silicon on the surface is no longer in contact with the plating solutions. Under this condition, the displacement reaction between the alkali metals with silicon is stopped because silicon is completely oxidized and is not able to supply electrons for the reduction of the alkali metal ions (M^+) anymore.

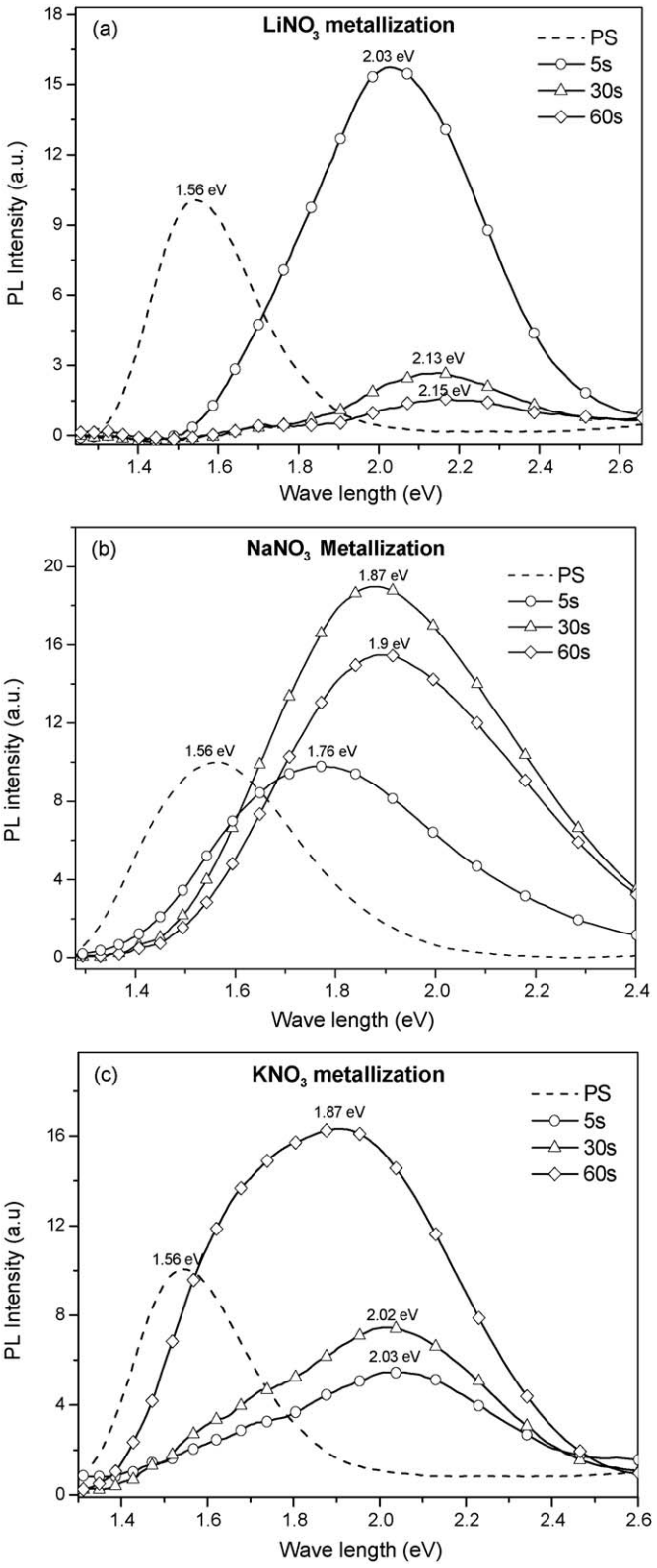

Fig. 4. PL spectra of PS metallized with different alkali metal solutions, $LiNO_3$ (a), $NaNO_3$ (b) and KNO_3 (c) for various metallization times. Dash line shows PL spectrum of freshly prepared PS.

It was reported that metal–oxygen–silicon bonding is expected between 300 and 700 cm^{-1} wave number region [18,19]. However, no new peak has been observed in this study in this region. This could be due to the fact that alkali metal atoms not bonding directly onto the silicon surface. However, the metallization might

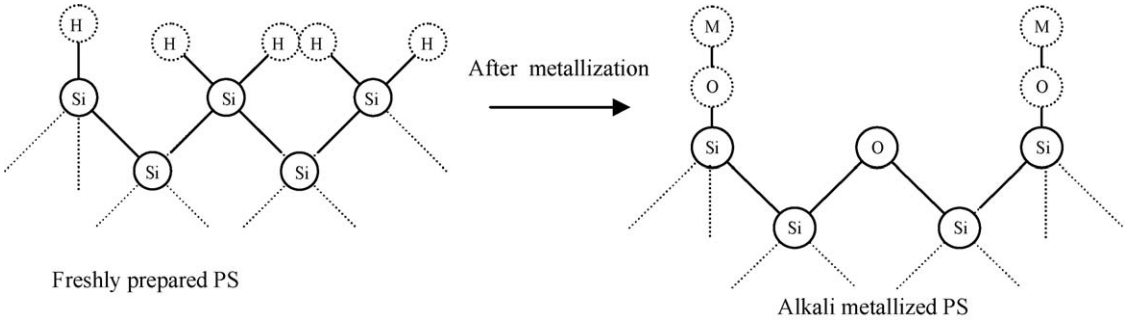

Fig. 5. Physical configuration of freshly prepared PS and alkali metallized PS. Where (M) is alkali metal (Na, K, Li) bonded to silicon over oxygen atoms.

be accompanied with the oxidation. Based on the results of FTIR and SEM, a possible physical configuration of alkali metallization of the PS surface can be illustrated as in Fig. 5.

4. Conclusions

The deposition of some alkali metals onto the PS surface by immersion plating in XNO_3 solutions where X(=Li, Na, K) was investigated. From the SEM images, it was shown that PS surface was coated with the alkali metals for short immersion times. Luminescence properties of the PS are very sensitive to the surface properties of PS and it might be enhanced by surface modification. Alkali metallization via immersion plating causes oxidation on the PS surface and increases PL intensity for critical metallization times. The FTIR spectroscopy results made it clear that the PS surface oxygen and/or alkali oxide metal pairs are pacified with immersion plating. Newly formed oxygen or alkali oxide metal related energy states give rise to a blue shift in the PL spectra.

The experimental results in this study suggest a possibility that surface modification with alkali metallization by immersion plating is a relatively easy way for the oxidation of the PS surface, leading to a stable and efficient luminescence from the PS. A model for PS termination was proposed to describe the passivation process.

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