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Effect of Different Chemical Environment on Porous Silicon

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ABSTRACT

Properties of porous silicon (PS) are found to be sensitive towards different chemical environment. Because of its large surface area, it is highly reactive and can adsorb chemical vapours. The present study shows that photoconductivity and photoluminescence (PL) properties are changed significantly in the presence of acetone, ammonia and steam vapours and can be used to identify and sense these chemical environment. These results also suggest that the molecules adsorbed on the pores change the transport mechanism of carriers in PS, leading to increase or decrease in conductivity. On the other hand, surface states on the enormous PS surface are modified under different chemical environment, leading to change in visible PL.

1. INTRODUCTION

Porous silicon (PS) is a new material which has attracted attention for use in silicon-based optoelectronic devices[1]. Efforts are going on worldwide to exploit its unique properties of visible photoluminescence (PL) and electroluminescence (EL) for new applications. An important property of PS, which needs to be studied in detail, is its high reactivity with chemicals due to its large surface area and surface defects. The surface area per unit volume in this material can range from a few m^2/cm^3 to 200 m^2/cm^3, depending on the fabrication conditions. The surface can adsorb gases, liquids or chemical vapours, resulting in drastic changes in its properties.

Studies on PS properties for various applications have been undertaken by many researchers[1,2]. The fact that efficient EL is observed when liquid contacts are used suggests that electrical properties are affected by the presence of liquids[3,4]. Another interesting aspect is the remarkable electronic passivation of silicon surfaces achieved using various techniques[5]. Very low values of surface recombination velocities[5] have been achieved by simple immersion of bulk silicon in hydrogen fluoride (*HF*), leading to surface recombination centres $< 10^8$ cm^{-2}. This has been ascribed mainly to complete hydrogen termination of surface with no dangling bonds. Studies of Canham[6], *et al.* showed that atmospheric impregnation of PS at room temperature can alter its properties. The impurity content and optical and electrical properties of PS are sensitive not only to anodisation conditions but also to duration and subsequent storage under atmospheric conditions.

Thermally oxidised PS shows a marked change in its PL properties with shift in PL peak and intensity[7]. Various techniques, e.g. rapid thermal annealing in ammonia and vapour-phase silation in hexamethyldisilazene (HMDS) or

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trimethylchlorosilane (TMCS), have been used to passivate PS surface against room temperature oxidation and to control the wetting properties of the surface[8,9]. These results suggest that electronic states on the surface play an important role in determining the properties of PS. These PS surface states can be modified easily in the presence of a chemical environment. Therefore, a detailed study of chemical vapours on PS luminescence is of interest not only to understand the physics behind its properties but also to use it as a chemical sensor. A detailed study on the effects of chemical vapours, viz., steam, ammonia and acetone on PS luminescence and infrared (IR) absorption has been carried out. Also, in making any practical device electrical properties are important. Therefore, changes in photoconductivity and I-V characteristics have been assessed under different chemical environment and the results are presented in this paper.

2. EXPERIMENTAL TECHNIQUES & RESULTS

2.1 Sample Preparation

Samples of PS were prepared by anodisation of silicon wafers (*p*-type, 100 orientation, 1 ohm-cm resistivity) in an electrochemical cell using *HF*:ethanol (1:1) solution. Silicon wafer was made the anode and a platinum foil served as the cathode. Back of the silicon wafer was coated with aluminium in a vacuum coating unit at 10^{-6} torr to give a good ohmic contact. During anodisation, back of the wafer was protected by epizone wax and the current was kept at 30 mA/cm^2 to get a good smooth surface. For measurements, PS samples (5 mm × 7 mm) were used. Aluminium strips were evaporated at a distance of 2-3 mm to take electrical contacts from the top surface of the PS for measurement of photoconductivity. For measuring I-V characteristics, aluminium dots of 1 mm diameter were evaporated on top of the porous layer for the front contact. Back contact was taken by evaporating aluminium at the back of the silicon wafer.

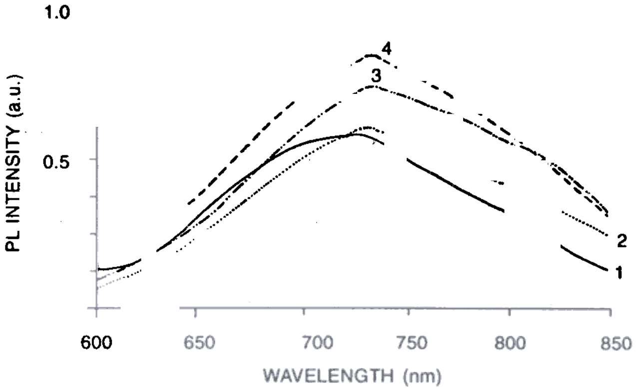

Figure 1. PL spectra of porous silicon: (a) as prepared, (b) after exposure in steam for (1) 5 min, (2) 20 min, and (3) 60 min.

2.2 Photoluminescence

Samples prepared above gave strong red PL under ultraviolet lamp. To obtain PL spectrum, the sample was mounted on a brass fixture and an argon ion laser source at 488 nm was used for excitation. Measurements were carried out using a grating monochromator and a *GaAs* PMT. The sample was treated with steam and the PL spectrum was measured after treatment for 5, 20 and 60 min. It is seen from Fig.1 that the intensity of PL increases with increase in duration of steam treatment. There is no significant shift in the peak position. However, the peak appears to become sharper with

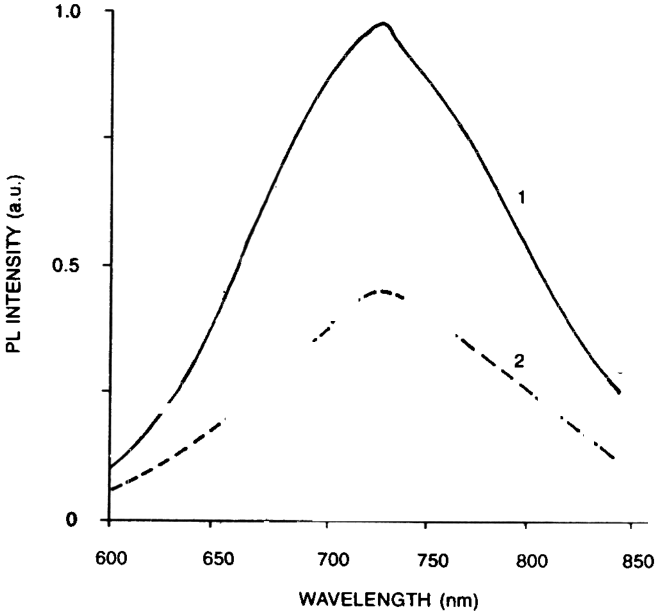

Figure 2. PL spectra of porous silicon: (a) as prepared, (b) after exposure to acetone vapours.

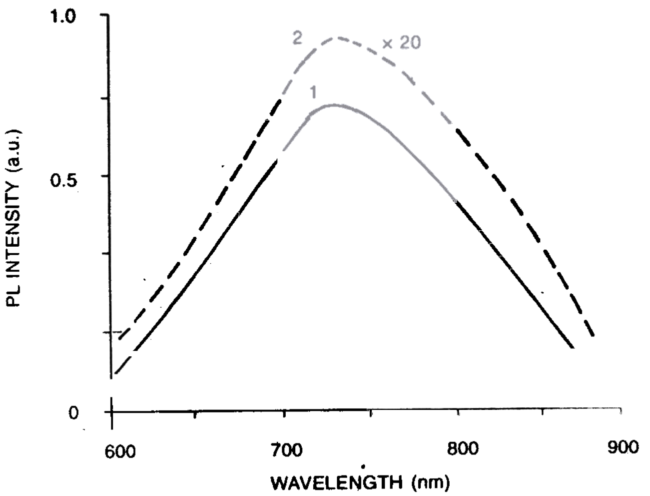

Figure 3. PL: (a) before, and (b) after exposure to ammonia vapours.

time. After 1 hr treatment, the sample appears to get saturated and no further increase in PL with further exposure to steam was observed.

PL spectrum on exposure to acetone vapours for 20 min is shown in Fig. 2. It is seen that the PL intensity is reduced. Figure 3 shows that ammonia environment quenches the PL intensity by an order of magnitude. Although a few samples showed some sign of recovery after removal of the chemical environment, the original PL was not obtained in any case.

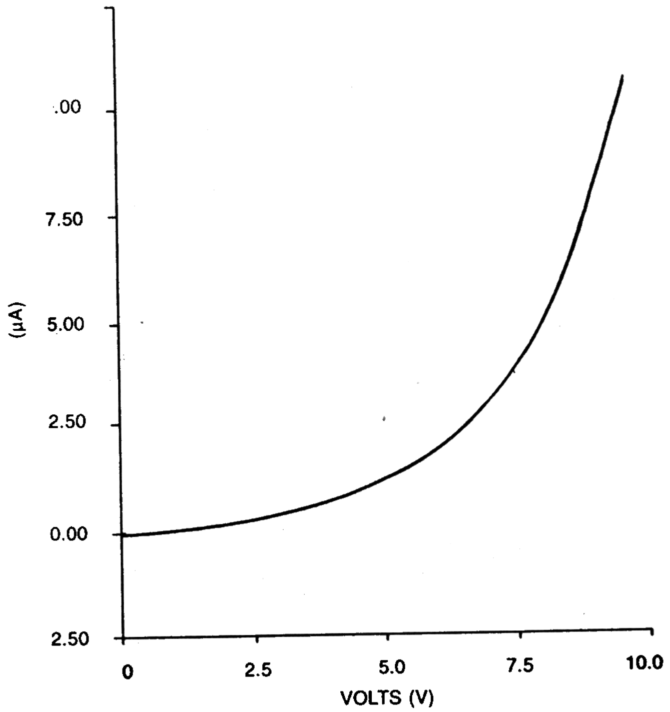

Figure 4. I-V characteristics of PS between two top contacts

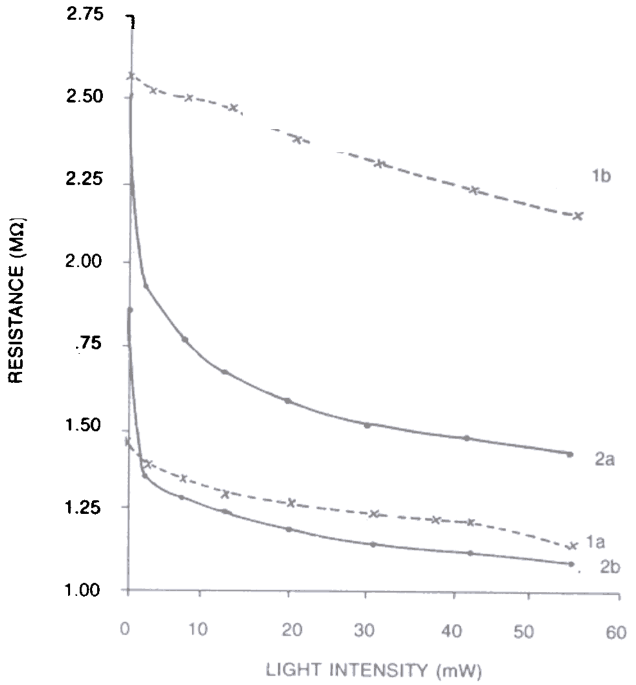

Figure 5. Change in resistance of PS (1a), as prepare (2a), after passing steam (1b), and after passing ammonia (2b).

2.3 Resistance & Photoconductivity

Resistance of the porous layer measured between two metal contacts (Section 2.1) is very high and can be in the range of a few mega-ohms. The changes in current at different applied voltages between the top two metal electrodes under dark conditions are shown in Fig. 4. However, under illumination from a tungsten halogen lamp, the resistance decreases rapidly with increase in light intensity, showing increase in conductivity of PS. The dark resistance as well as photoconductivity under dynamic conditions, i.e. in the presence of various vapours, are shown in Figs 5 and 6. All observations were recorded after chemical treatment for 20 min. In the presence of steam, the resistance was found to increase (Fig. 5), whereas the resistance decreased in the presence of ammonia. Acetone vapours also increased the

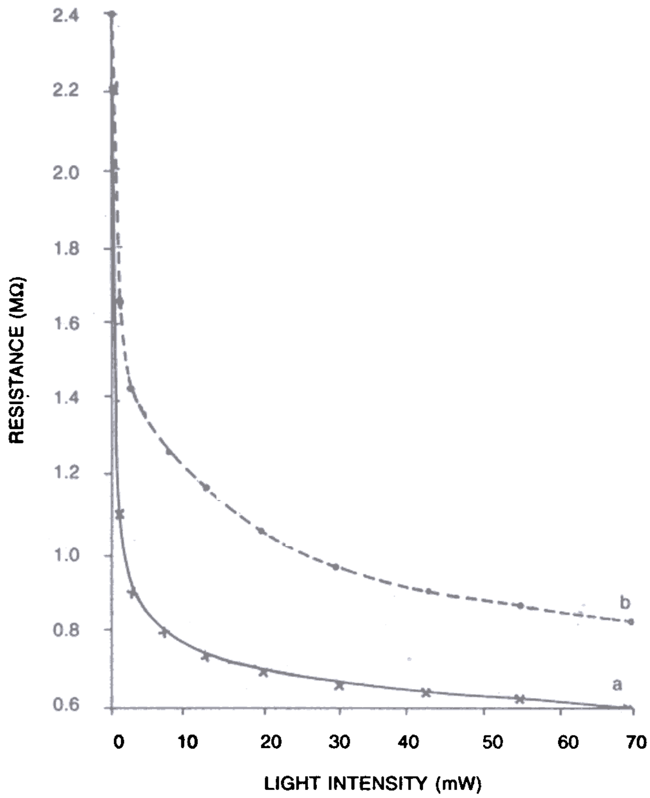

Figure 6. Resistance of PS: (a) as prepared, and (b) in acetone environment.

resistance (Fig. 6). Benzene and nitrogen were found to have no effect on the electrical properties.

2.4 I-V Characteristics

PS forms a heterojunction with the crystalline silicon on which it is formed because of the different band gaps[1] [e.g. of PS = 2.5 eV]. I-V characteristics of the samples were measured between the top *Al* contact and the bottom aluminium electrode and are shown in Figs 7 and 8. I-V characteristics in air show diode behaviour, but the shape is seen to change on exposure to different chemicals. In the case of steam, the diode becomes leaky. In the case of ammonia, shape characteristic is drastically changed and the rectifying behaviour is lost. Acetone and benzene were found to have no effect on these characteristics.

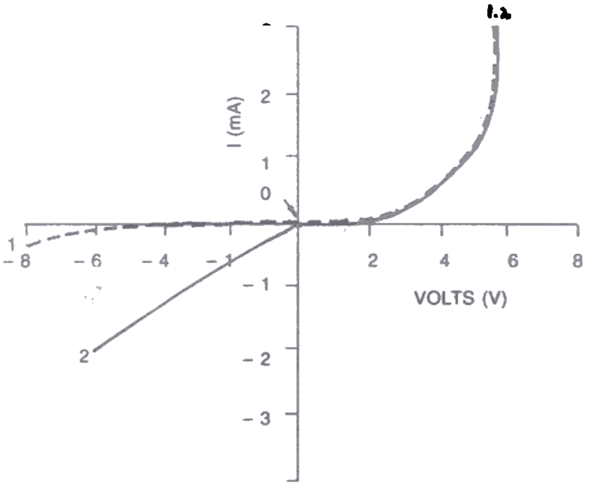

Figure 7. I-V characteristics: (a) as prepared, and (b) after steam treatment.

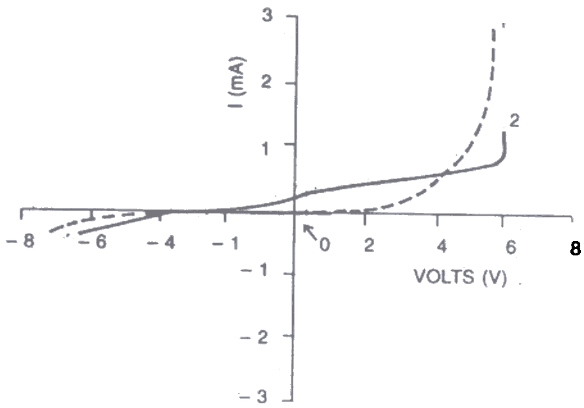

Figure 8. I-V characteristics: (a) as prepared, and (b) after exposure to ammonia vapours.

2.5 Infrared Absorption

To determine the change in the chemical species present on PS surface after exposure to chemical vapours, IR absorption measurements were carried out using FTIR. For these experiments, the samples were first saturated with the vapours for 20 min and then measurements were carried out under static conditions. Infrared absorption results

Table 1. Results of various chemical treatments on porous silicon characteristics

Chemical environment	Photo-luminescence	Resistance	I-V characteristics
Steam			Leaky diodes
Ammonia			Diode characteristics are lost
Acetone	Decreases slightly	Increases slightly	No change

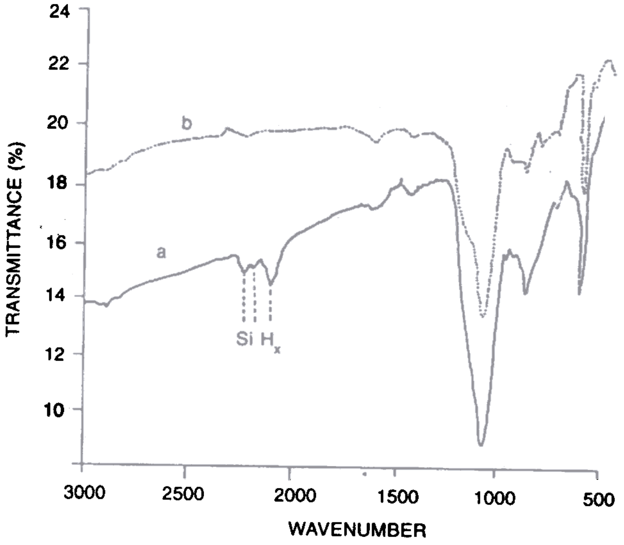

Figure 9. FTIR transmission spectra of PS: (a) as prepared, and (b) after exposure to ammonia vapours.

for PS before and after exposure to ammonia vapours are presented in Fig. 9. It is seen that silicon hydride-related peaks disappeared on treatment with ammonia. A similar effect was observed with steam. No change was found in the case of acetone and benzene. The results of these measurements are summarised in Table 1.

3. DISCUSSION

The experimental results obtained in the present study have shown that different chemical environment have different effects on the optical and electrical properties of PS.

The results show that PL increases in steam environment, but decreases in acetone and ammonia environment. The PL spectrum of PS contains two dominant bands–blue and red. This has been explained by the modified quantum confinement model[10] according to which absorption of light takes place in the core of silicon nanocrystallites formed on silicon surface during anodisation, whereas recombination takes place by two mechanisms: direct recombination in the core, leading to the blue PL and recombination via midgap surface states, leading to red PL. It has been observed[7] that blue PL dominates the spectrum when the sample contains a large amount of oxygen. Blue PL has been attributed to the core region of silicon crystallites and reduced size of silicon quantum wires due to oxidation. In contrast to the red band which decays in several microseconds, the blue band-exhibits a nanosecond decay. It has also been reported[8,9] that the *Si-H* species are present on *HF*-treated PS and silicon samples, which are responsible for chemical sensitivity of the material. Despite several studies, no direct correlation has been observed between PL and *Si-H* species present on the surface. The samples continue to show red PL under steam environment. Although the peak intensity increases significantly (by 40 per cent), no significant change in the spectrum was found. After 1 hr of exposure, no further increase in PL was observed, indicating saturation of the sample. These results can be explained by considering the role of surface states on the enormous PS surface.

It has been suggested[10,11] that surface states play a central role in the luminescence process. Specifically, surface states have been used to explain the energy shift between the absorption edge and the luminescence peak in PS. In the present experiments, temperature was not high enough for thermal oxidation to take place; therefore, reduction of crystallite size is ruled out, but it is possible that steam vapours are causing passivation of surface states, leading to enhanced radiative recombination in the visible region. Presence of SiO and SiO_x has been confirmed by IR absorption measurements. This thin layer of SiO formed around crystallites now acts as a barrier (as band gap of SiO is more than that of Si) and carriers are not able to migrate from one crystallite to the other, resulting in decrease in carrier conductivity and increase in the measured resistance. In the case of ammonia vapours, PL diminishes significantly, whereas resistance also decreases. This observation can also be explained as follows: the adsorption of ammonia molecules on the enormous surface of PS causes charge redistribution, reducing the barrier between crystallites. Now, easy migration of carriers is possible, which increases the conductivity. PL is quenched as NH_3 groups now attached to the surface modify the surface states in such a way that radiative recombination is reduced

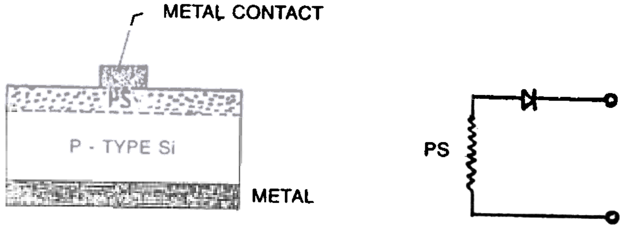

Figure 10. Model for the device

and carriers are able to migrate faster before recombining. Acetone adsorption also causes modification of surface states with increase in nonradiative centres instead of surface passivation as caused by steam. This decreases the PL. However, the chemical groups now attached at the surface do not help in the migration of carriers. Therefore, resistance was found to increase in this environment. FTIR measurements also showed the disappearance of hydride peaks in the case of steam/ammonia vapours, showing a change in the surface chemistry. However, no direct correlation with the changed properties was found.

The change in I-V characteristics is also different in each case. The system (Fig. 10) can be modelled as a resistor connected in series to a diode where the PS layer serves as the resistor and the top metallic contact with the porous layer as Schottky diode. In air, current flowing through the system is limited by Schottky contact and the system shows rectifying characteristics. Under steam environment, the Schottky diode becomes leaky, as increase in reverse current is obtained due to the moisture adsorbed on the surface and the porous layer below the metal contacts. In ammonia environment, ammonia molecules act as a dopant in the PS layer decreasing its resistance as also modifying the Schottky contact. This leads to change in I-V characteristics, which no longer show rectifying behaviour, as was the case in air environment, when current was limited by the contact barriers.

4. CONCLUSION

It has been shown that PS is sensitive to the chemical environment. A significant effect of steam, acetone and ammonia vapours on this material has been observed. The results also show that changes in electrical and optical properties of PS are different in different environment, showing selectivity. Moreover, chemicals like ammonia molecules are acting as dopants, decreasing the PS resistance. Detailed studies aimed at making a practical chemical sensor using this material, are in hand.

5. ACKNOWLEDGEMENTS

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