

XPS study of palladium sensitized nano porous silicon thin film

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Abstract. Nano porous silicon (PS) was formed on *p*-type monocrystalline silicon of 2–5 Ω cm resistivity and (100) orientation by electrochemical anodization method using HF and ethanol as the electrolytes. High density of surface states, arising due to its nano structure, is responsible for the uncontrolled oxidation in air and for the deterioration of the PS surface with time. To stabilize the material PS surface was modified by a simple and low cost chemical method using PdCl₂ solution at room temperature. X-ray photoelectron spectroscopy (XPS) was performed to reveal the chemical composition and the relative concentration of palladium on the nanoporous silicon thin films. An increase of SiO₂ formation was observed after PdCl₂ treatment and presence of palladium was also detected on the modified surface. *I–V* characteristics of Al/PS junction were studied using two lateral Al contacts and a linear relationship was obtained for Pd modified PS surface. Stability of the contact was studied for a time period of around 30 days and no significant ageing effect could be observed.

Keywords. Porous silicon; passivation; palladium; oxidation; XPS.

1. Introduction

Porous silicon (PS) is an attractive material due to its extremely large surface to volume ratio, the ease of formation, control of the surface morphology through variation of the formation parameters and its compatibility to silicon IC technology. It has a wide range of applications in photonics and optoelectronics, quantum electronics, silicon-on insulator technology and recently in sensors (Dimitrov 1995; Pavesi and Dubos 1997; Tsamis *et al* 2002). In spite of all advantages the major barrier against the commercial applications of PS is the temporal degradation of its surface property in oxygen or moisture containing environment and the difficulty in obtaining reliable ohmic contacts (Barillaro *et al* 2003).

A great deal of research has been focused on the improvement of the quality of PS surface. The high density of dangling bonds and other defect states arising due to its nano structure is mainly responsible for the material instability (Stievenard and Deresmes 1995). Therefore, passivation of the PS surface by some post anodization treatment is necessary (Jeske *et al* 1995). The need for a stable termination of dangling bonds on the surface of PS has naturally led to the studies of SiO₂ as a surface passivation layer. Several groups have reported successful stabilization of the material by furnace oxidation (Tsybeskov *et al* 1995) or rapid thermal oxidation of PS (Gullis *et al* 1994; Kanemitsu *et al* 1994). Though these

processes provide higher quality oxides on the surface with fewer defects but at the same time these high temperature processes may break the PS structure as well. Tomioka *et al* (2007) reported that the addition of oxidant H₂O₂ in HF solution results in a stable formation of PS layers in a short time. Chen *et al* (2007) developed an oxidizing technique with ozone for the passivation of PS at room temperature. They achieved a complete replacement of Si–H_x coverage with Si–O_x film and Si–alkyl film. PS prepared with the aid of ozone shows better stability against aging in air.

Controlled oxidation, nitridation, halogenation and polymerization (Lavine *et al* 1993; Hirschman 1996; Mrazzani 1996; Mandal *et al* 2006) are a few other methods that have been reported to passivate PS surface. There are reports on coating the surface of PS by the electroless deposition of metals to provide improved stability (Ansager *et al* 1994).

In the present investigation, we prepared porous silicon by anodization of *p*-Si and modified the surface by a noble metal like Pd using a simple, reliable and low cost chemical method to passivate the defect states. Further, this is a room temperature process and hence the porous structure does not get damaged. The samples were thoroughly characterized by X-ray photoelectron spectroscopy (XPS) to reveal the chemical composition and the relative concentration of palladium on the nanoporous silicon thin films. Current–voltage measurements were carried out to study the stability of the metal contact to PS after Pd sensitization.

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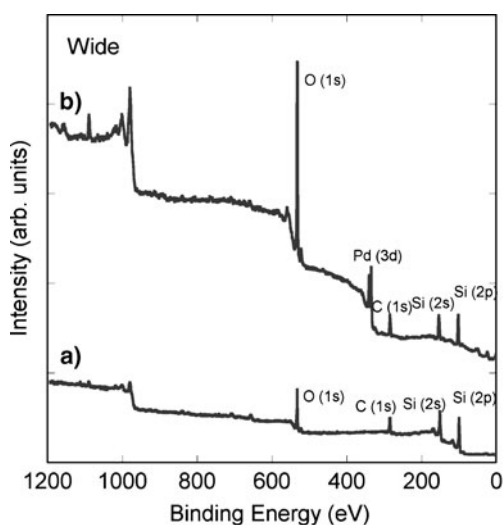


Figure 1. Wide scan XPS spectra of the films: (a) unmodified porous silicon film and (b) palladium modified porous silicon film.

2. Experimental

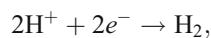
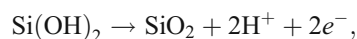
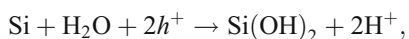
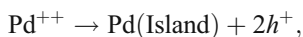
2.1 Porous silicon formation

Porous silicon layer was formed by electrochemical anodization of a *p*-type monocrystalline silicon (100) wafer of resistivity 2–5 Ω cm using a mixture of HF and ethanol (7:3) as electrolyte. The back of the sample was coated and fired with aluminium paste for making the anodic contact. We applied an etching current density of 10 mA/cm² for 40 min. The porosity and thickness of around 55% and 5 μ m, respectively were measured gravimetrically (Kanungo *et al* 2006, 2009) using a precision semi-microbalance (290–9842/K, PAG OERLIKONAG CH-DIETKON, Switzerland).

2.2 Modification of porous silicon surface

PS samples were dipped into 10% HF solution for 10 s to remove the native oxide layer to a large extent and were immediately dipped into aqueous 0.01 M PdCl₂ solution (containing 2–3 drops HCl) for 5 s. Subsequently, the samples were rinsed gently by DI water, dried and annealed in air at 110°C inside an electric oven for 10 min.

The chemical modification steps are cited as follows:



Pd⁺⁺ formed by decomposition of PdCl₂ in an aqueous acidic solution is reduced to Pd metal islands by a chemical reduction process (Jeske *et al* 1995; Kanungo *et al* 2009) and two holes released. The *h*⁺ oxidizes the PS surface to SiO₂.

The XPS measurement was performed on a VG microlab Auger/XPS Spectrometer with a 310-F analyser. The measurements were carried out with Al K α photons (1486.6 eV) with a base pressure of around 2×10^{-8} mbar during measurement. Resolution was determined from the full width at half maximum (FWHM) of the Au (4*f*_{7/2}) line in a reference sample and was around 1.5 eV using pass energy of 50 eV. The binding energy scale was aligned through the C1s peak at 285 eV.

3. Results

3.1 XPS study

The wide scan XPS spectra for porous Si and Pd modified porous Si are presented in figure 1. Similar line shape of the carbon peaks in both the samples as shown in figures 1 and 2 implies proper calibration of the instrument.

A strong signal from Pd is obtained for the Pd modified porous Si, detected as a spin orbit doublet with Pd (3*d*) peak

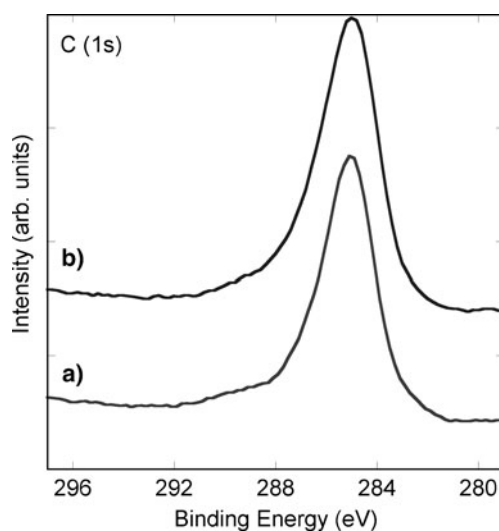


Figure 2. C(1s) XPS core level spectra of the films: (a) unmodified porous silicon film and (b) palladium modified porous silicon film.

positioned at about 335 eV and 340 eV, respectively as shown in figure 3. No palladium was detected on the porous silicon sample prior to surface modification, as expected.

The O1s spectra in figure 4 clearly indicates that there is a much higher contribution of oxygen in the sample with palladium modified porous silicon, compared to the unmodified one. The Si/O ratio is about 0.6 for the palladium modified surface whereas the pure porous silicon surface prior to surface modification has a Si/O ratio of ~ 3.4 .

In figure 5a the main Si (2p) peak consists of a spin-orbit coupled doublet (Si 2p_{3/2} and Si 2p_{1/2}). The Si 2p_{3/2} binding energy peak position is found at 100 eV. The split is ~ 1 eV. The peak position indicates that the film consists mainly of pure silicon. There is also one less pronounced binding energy peak at 103 eV, consisting of a spin-orbit coupled

doublet Si 2p_{3/2} and Si 2p_{1/2} corresponding to SiO₂. In figure 5b, the main peak in the spectrum of Pd modified porous Si is a strong doublet at around 103 eV in good agreement with SiO₂. A small doublet at around 100 eV corresponding to pure silicon is also observed. It indicates that the formation of SiO₂ is very much enhanced in presence of Pd corresponding to the reactions shown above. The Si/SiO₂ ratio on the palladium modified surface is 0.06 and on the porous silicon surface is 5.2, which means that there is around 85 times more SiO₂ on the palladium modified surface than on the unmodified porous silicon surface. This is consistent with the observation shown earlier that palladium modified PS surface has been shown to be more oxidized than pristine porous silicon surface.

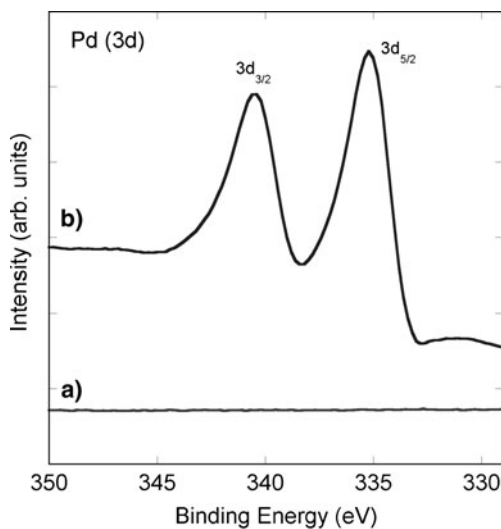


Figure 3. Pd(3d) XPS core level spectra of the films: (a) unmodified porous silicon film and (b) palladium modified porous silicon film.

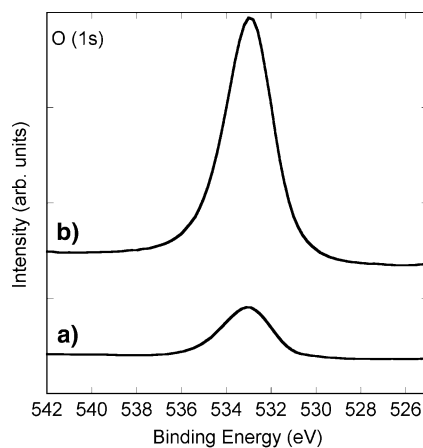


Figure 4. O(1s) XPS core level spectra of the films: (a) unmodified porous silicon film and (b) palladium modified porous silicon film.

3.2 Study of metal/PS contact

The $I-V$ characteristics were studied using Al lateral contacts (contacts 1 and 2) of dimension 2×2 mm to PS

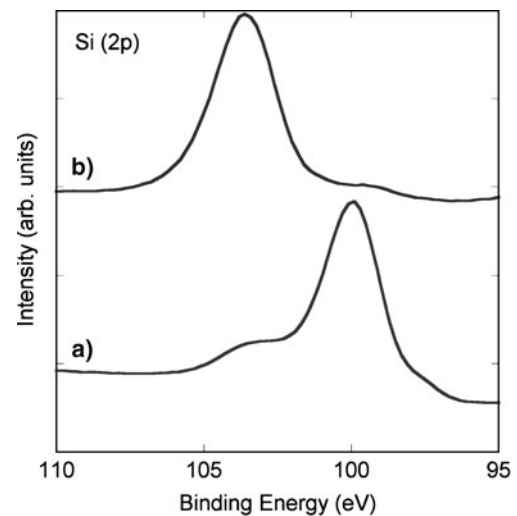


Figure 5. Si(2p) XPS core level spectra of the films: (a) unmodified porous silicon film and (b) palladium modified porous silicon film.

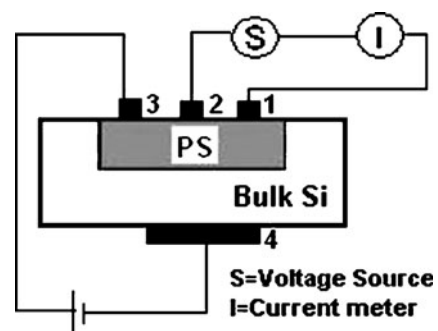


Figure 6. Schematic circuit diagram for $I-V$ measurements.

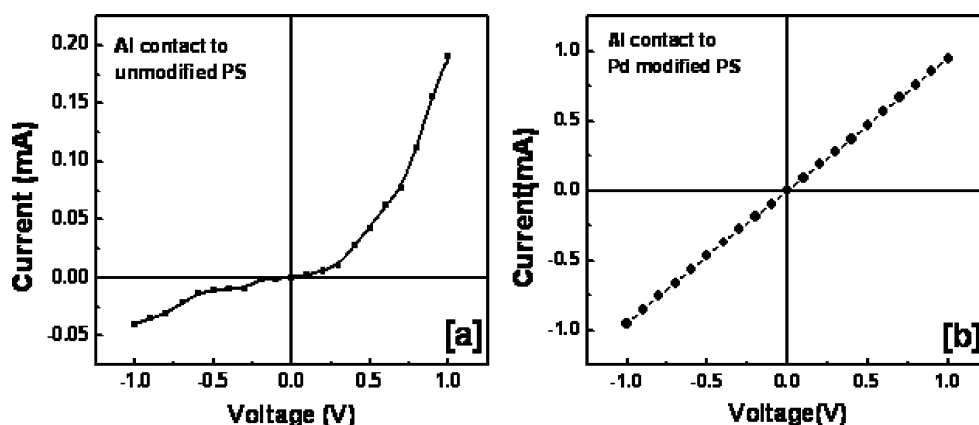


Figure 7 I - V characteristics of (a) unmodified and (b) palladium modified porous silicon using Al contact.

and separated by a distance of 2 mm (figure 6) for both unmodified and modified PS surfaces. Since there is a possibility of the current flowing partly through the bulk silicon because of the high resistance of PS, a reverse bias was applied at the PS/ p -Si junction (contacts 3 and 4) to keep the current lines confined within the porous silicon layer. All I - V measurements were taken when the PS/ p -Si junction was completely reverse biased. Detailed measurement condition is reported elsewhere (Kanungo *et al* 2009). Aluminium is supposed to form ohmic contact with p -type porous silicon. Figure 7 clearly demonstrates that the electrical response which is Schottky by nature for unmodified PS becomes ohmic after PdCl_2 treatment. This explains the role of Pd to form SiO_2 that passivates the defect states of porous silicon surface and reduces the barrier against the flow of free carriers.

3.3 Stability of contact

In order to verify the long-term stability of Al ohmic contact to PS after modifying the surface with Pd, I - V measurements were repeated at different intervals of time for a period of around 30 days (figure 8) and it was found that the linear I - V curves measured at different time intervals practically overlap signifying a stability of the contact.

4. Discussion

After Pd sensitization, as described in § 2.2, Pd clusters are formed on the PS layer, Si surface gets oxidized and a thin layer of SiO_2 is formed (Kanungo *et al* 2009). The PdCl_2 treatment enhances oxygen quantity and formation of SiO_2 is clearly visible from the XPS results. The Pd cluster and oxidation of PS surface improve the electrical property of Al/PS contact. The unreliable metal contact to PS is due to unstable porous silicon surface. The high density of surface states on porous silicon, arising due to its nano structure,

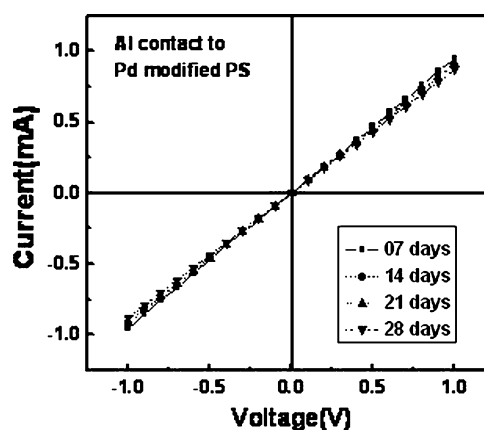


Figure 8. I - V characteristics of Pd modified porous silicon measured at different intervals of time up to 28 days.

disturbs the stability of the material. Our study indicates that Pd dispersed on the PS surface helps in two ways. The oxidized PS contains less defect states and hence the surface is more stable. Additionally, the dispersed Pd islands help to increase the conductivity as observed from the I - V characteristics of Pd modified PS samples. Electrical property of Pd modified PS is already reported in detail in our earlier communication (Kanungo *et al* 2009). Since the Pd modification process is carried out at room temperature the possibility of damage of the porous structure is minimized, unlike other methods like furnace oxidations which are already reported.

5. Conclusions

The XPS analysis of the Pd modified nano porous silicon surface clearly demonstrates a pronounced increase in the oxidation of porous silicon compared to the unmodified PS. Thin oxide layer protects the PS surface from further deterioration and stabilizes the Al/PS electrical contact as verified by the long-term stability of the current-voltage characteristics.

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