

Photovoltaic effect in organically surface-modified nanocrystalline porous silicon layers

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Abstract

The photovoltaic properties of electrochemically prepared nanocrystalline porous silicon free-standing membranes were investigated. A definitive photovoltaic effect with high open-circuit voltage in excess of 0.8 V has been observed. Current investigations are focusing on the surface passivation of the material through chemical modification with organic molecules and their impact on the photoconductive properties of the material.

1. Introduction

As previously reported [1,2], visible luminescent nanocrystalline porous silicon (nc-PSi), prepared through electrochemical etching process, exhibits intrinsic photovoltaic (PV) activity in the short wavelength region corresponding to the widened band gap. The PV property of nc-PSi cells is characterized by a significantly large open-circuit voltage V_{OC} , though the conversion efficiency is relatively low because of a poor short-circuit current density J_{SC} . To enhance the PV efficiency, it is important to clarify the limiting factor for the photo-carriers transport in nc-PSi layers. Especially the appropriate control of surface-sensitive electrical conduction is a critical issue. Here we report the effect of surface modification of nc-PSi membranes with organic molecules on their PV performance and stability.

2. Experiments

The nc-PSi free-standing layers were fabricated using a top down approach involving the nano-structuration of bulk silicon in an acidic HF solution under galvanostatic conditions. The physical properties of the resulting material are controlled during formation by the solution electrolyte type, HF content and the galvanostatic current among others parameters. Right after formation of the nc-PSi layer, injection of a high current ($\geq 250 \text{ mA/cm}^2$) allows for the separation of the freshly formed upper nc-PSi layer from the host bulk Si substrate in a controlled manner.

The resulting "free-standing" layers were then chemically modified in organic solution through thermal hydrosilylation [3] of the original hydrogen terminated sur-

face by various organic molecules including alkene and aldehyde groups. Typical modifications were conducted in neat organic solution at a temperature of 100°C during 3 hours. All the layers were contacted in sandwich configuration with metal or transparent conductive oxide for photo-electrical characterization. For photovoltaic application the starting material employed here was a pn type substrate doped in advance, in parallel single doped p and n type material were used for comparison as well. Photovoltaic and light induced degradation characterizations were conducted under simulated AM1.5G – 1 sun illumination from a solar simulator under regulated temperature. The surface chemistry modification was investigated through FTIR measurements in transmission mode.

3. Results and Discussion

A schematic representation of a pn type free-standing nc-PSi device with its corresponding PL and PV spectra is shown in Fig. 1. The PL emission originated from the nanoporous n type layer located under the upper non luminescent p type layer. A photovoltaic effect featuring high V_{OC} with a maximum recorded at 0.875V was observed only in pn type devices with a corresponding spectral response peaking at 450 nm. The relationship between the PV and PL spectra is similar to that between the photoconduction and PL spectra previously observed in luminescent nc-PSi samples [4]. The implication is that photo-excited carriers suffer significant losses in the transport process. Comparatively, devices made from single doped p or n type material only show a limited $V_{OC} < 0.3\text{V}$ with a sensitivity mostly in the UV range, suggesting a Schottky diode behavior for such devices.

In our previous report [2], we have also demonstrated that the rectifying behavior observed in pn type devices originated from the pn junction itself still active in the porosified material and that the contact had negligible effects. Furthermore, the effect of post-fabrication etching in HF solution as well as anneal in inert atmosphere clearly related the device performances and large inter-sample variation to the quality of the surface passivation.

To further investigate such involvement of the surface, the original hydrogen terminated surface was replaced by or-

organic molecules from the alkene (dodecene, decene) and aldehyde (decanal, octanal) groups through a simple thermal hydrosilation process as described in Fig. 2. The IR transmittance spectra for samples modified with decanal and dodecene clearly shows the presence of the organic molecules through absorption peak related to CH_x located at 2860, 2925 and 2960 cm^{-1} . The absence of both $\text{C}=\text{C}$ (1640 cm^{-1}) in alkene and $\text{C}=\text{O}$ (1729 cm^{-1}) in aldehyde modified devices shows that the molecules are present through covalent bonding and not simply physical adsorption. As seen in Fig 3(a), an increase in stability was obtained for most of the organic species starting with the aldehyde decanal up to higher stabilization with alkene dodecene and dodecene. The corresponding PV parameters are shown in Fig. 3(b) compare to the as prepared material. It is clear from both the PV parameters and the current time variation under illumination that the material properties are strongly dependent on the type of bonded molecules, with a better stabilization with alkene group (Si-C bonding) but slight decrease in conversion performance while aldehyde group (Si-O bonding) features a lower stabilization but a notable increase in the photo-generated current. The slight decrease in V_{OC} visible in modified samples could be related to the undesired partial oxidation of Si surface during the treatment. The technique is still largely opened to improvements to reduce the oxide content and further enhance the stabilization of the material.

4. Conclusion

Free-standing pn type nc-PSi layers prepared by electrochemical wet etching show a definite photovoltaic activity with large V_{OC} up to 0.87 V, indicating the possibility that the material acts as a wide gap absorber. Modification of the original hydrogenated surface by organic molecules shows the possibility to better stabilize the material and even moderately improve the performance of the devices. Further investigations are underway to clarify the observed photoconduction phenomena and further enhance the performance keeping a high V_{OC} toward practical applications.

Acknowledgements

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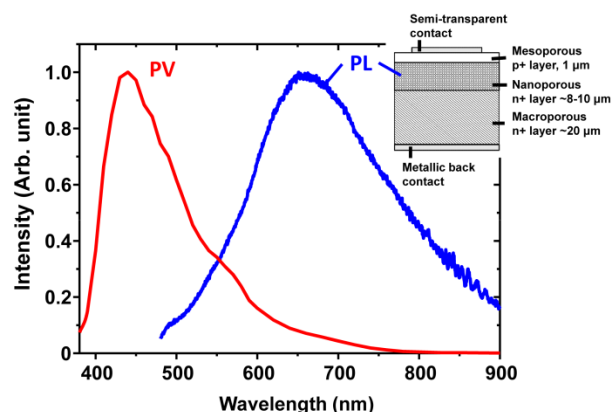


Fig. 1. PL and PV response spectra measured from a pn type nc-Si layers at room temperature. The corresponding device structure is shown in the inset.

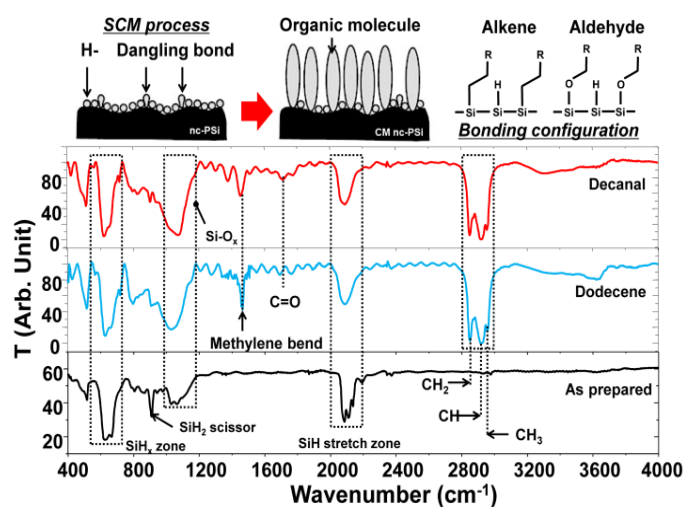


Fig. 2. Schematic of the surface chemical modification of nc-PSi layers with the corresponding IR transmittance spectra showing the presence or the organic molecules from alkene and aldehyde groups.

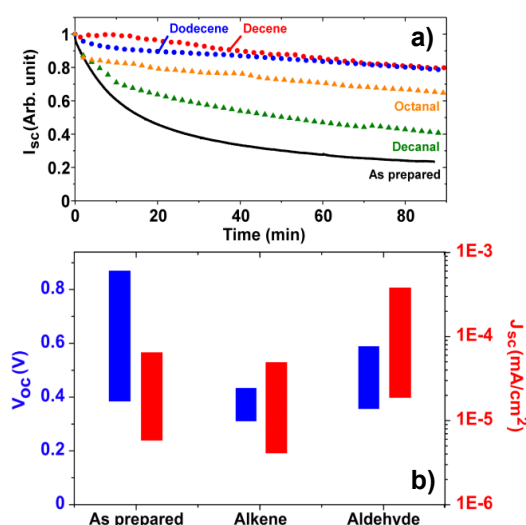


Fig. 3. (a) Time variation of the photocurrent of pn type devices before and after surface chemical modification, (b) corresponding range of PV parameters observed on as prepared and organically modified devices.