

Short communication

# Photovoltaic effect with high open circuit voltage observed in electrochemically prepared nanocrystalline silicon membranes



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## ABSTRACT

We have investigated photovoltaic effect in electrochemically etched nanocrystalline porous silicon (nc-PSi) thin layer for potential application as a wide-gap absorber for solar cells. The free-standing nc-PSi layer with a pn junction structure shows a photovoltaic effect with a large open circuit voltage in excess of 0.87 V. Comparison with single doped material in different top contact configurations clearly indicates that the original junction remains in the porosified material and plays a major role in the observed photovoltaic effect, while the contributions from the contacts are negligible. The effects of additional processing of the material including chemical etching as well as annealing of the material in an inert atmosphere suggests a strong contribution from the hydrogenated surface in the observed photoconductive characteristics. Replacement of interfacial hydrogen by more stable organic molecules appears to be a promising approach toward stabilization of the material for practical application.

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## 1. Introduction

Silicon has been the leading material in commercial photovoltaics (PV) for the last decades and despite numerous developments of alternative materials and technologies, it is highly probable that Si will continue to dominate the photovoltaic industries for the decades to come. The recent and urging necessity of reducing the cost of PV has led to the emergence of new concepts and approaches [1], among them the concept of multi-junction solar cells with distributed gap absorbers and the use of new nano-materials as a way to enhance the overall efficiency of the cells [2]. Due to its wide availability, low cost and well developed processing technology, Si-based nano-materials are good candidates and can be fabricated either by forming the material at the dot/cluster level (bottom-up approach) or by nano-structuring high quality bulk silicon substrate (top-down approach) [3].

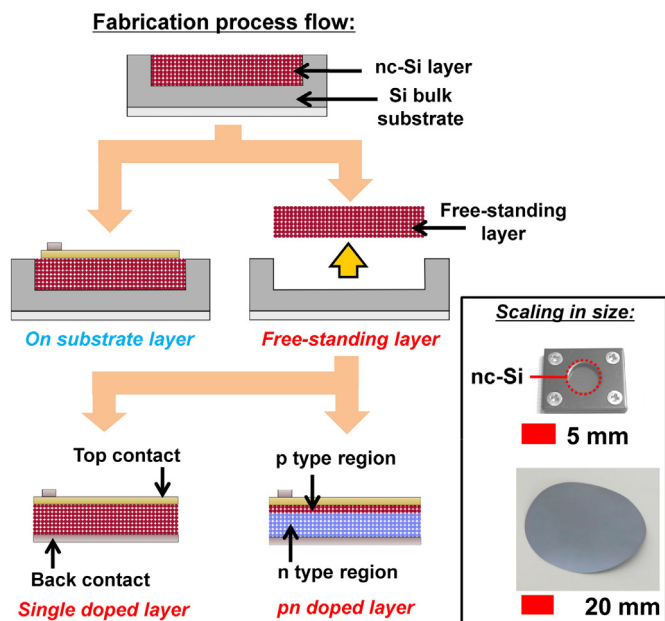
Nanocrystalline porous silicon (nc-PSi) fabricated by electrochemical wet etching belongs to the latest group and has attracted tremendous interest since the discovery of its visible luminescence at room temperature by Canham in the early 1990s [4]. The material has since been the subject of various investigations and reviews of its physical properties [5,6], including the nature of its

bandgap [7,8] and the presence of quantum confinement in the nanocrystallites contained in the material, for their potential applications in electroluminescent devices [9,10], photo-sensors [11,12], and photovoltaic devices. While a relatively large amount of studies involving the use of nc-PSi in solar cells as a passive element (anti-reflection coating, layer transfer process, etc.) are available [13–17], only a few reports actually focused on the possible wide gap absorber nature of the material and its application to solar cells as an active element [18]. Nc-PSi relative simplicity of fabrication as well as a strongly established relation between its observed optical properties and band gap widening model make the material a possible candidate for top cell material in next generation solar cells. In this paper, we report the fabrication of free-standing nc-PSi layers featuring a photovoltaic effect with large open circuit voltage in excess of 0.87 V and discuss the possible origin of the phenomenon, limitations of the material and ways for improvements toward practical applications in solar cells.

## 2. Experimental methods

Nc-PSi was produced by electrochemical dissolution of crystalline silicon (c-Si) wafers in an ethanoic HF acidic solution under galvanostatic condition, a method referred as “anodization”, the silicon material acting as an anode in the electrochemical circuit. The overall fabrication process is schematically represented in Fig. 1. The starting pn-doped substrate employed here was a

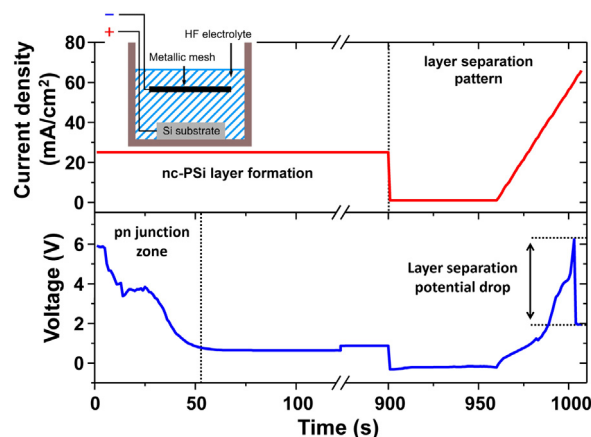
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**Fig. 1.** Schematic of the fabrication process of nc-PSi material with on-substrate and free-standing layer structures after the separation from the substrate. The right corner of the figure shows the possibility of scaling the free-standing layers from a few millimeters in size to near wafer dimensions as seen in the damage free separated layer of 8 cm in diameter.

n-type (1 0 0) silicon wafer (resistivity: 0.01–0.02  $\Omega$  cm) on which an  $B^+$ -implanted layer was formed with a dose of  $3\text{--}5 \times 10^{15} \text{ cm}^{-3}$  and a final junction depth of approximately 1  $\mu\text{m}$  after annealing at high temperature. Single doped n- and p-type wafers with a similar doping level as the pn substrate were also used for comparison of their respective photo-electric characteristics. All substrates were anodized in a (55% HF:99.5% ethanol = 1:1) solution under a constant current in the range 5–50  $\text{mA}/\text{cm}^2$ . Photo-assistance from a tungsten lamp (500 W–5900 K) located at 20 cm from the substrate was employed in the case of pn substrate. The layers were then separated from their bulk host by switching to a higher current density ( $\geq 250 \text{ mA}/\text{cm}^2$ ) at the end of the anodization step, provoking an electrochemical polishing reaction at the dissolution front and separating the upper nc-PSi layer from the bulk substrate. Pn type layers with an area of 1.4 cm  $\times$  1.4 cm were successfully fabricated in a thickness range of 100  $\mu\text{m}$  down to 30  $\mu\text{m}$  using a slowly increasing current ramp as shown in Fig. 2. Additional enhancement in the separation process, involving a control of the viscosity of the electrolyte through chemical additive or better temperature control of the process, allowed for a preliminary reduction of the layer thickness down to 13  $\mu\text{m}$  and for the separation of larger circular layer up to 8 cm in diameter, showing the possibility to scale the nc-PSi free-standing layer fabrication process to near Si wafer dimension as demonstrated in Fig. 1. The separation process is still under active investigation to further reduce the thickness of the separated nc-PSi layers.

After separation, the free-standing nc-PSi layers were rinsed in pure ethanol during several minutes and kept as is in ethanol until transfer to a chamber where they were dried under supercritical condition with a  $\text{CO}_2$ /ethanol super critical fluid at 40  $^\circ\text{C}$ /14 MPa during 50 min. The supercritical rinsing method has the advantage of eliminating the surface tension effect of the rinsing solvent during natural evaporation, allowing for the drying of fragile and fine structures such as nc-PSi as well as large surface of the material without damage. Some layers were subsequently treated under a low temperature surface derivatization step where the samples were immersed into neat organic reagents such as decene



**Fig. 2.** Evolution of the anodization current and terminal voltage during galvanostatic processing of a pn type layer with front side illumination. The high voltage at the beginning of the graph confirms the presence of a pn junction near the surface of the material. The low current step followed by a rapid linear increase of the current starting at time 900 s allows for the separation of the nc-PSi layer without damage. The sharp drop of potential at the final stage is a confirmation of the successful separation of the upper layer. The schematic of a typical anodization cell is shown in the inset.

(alkene,  $\text{C}_{10}\text{H}_{20}$ ), decanal (aldehyde,  $\text{C}_9\text{H}_{19}\text{CHO}$ ) and undecylenic acid ( $\text{CH}_2\text{CH}(\text{CH}_2)_8\text{COOH}$ ) at a temperature in excess of 90  $^\circ\text{C}$  for a duration of 3 h under Ar gas sparging. The samples were then successively rinsed in 1,1,1-trichloroethane and heptane bathes before being allowed to dry in ambient atmosphere. After drying, the presence of the organic species on the surface of the material was detected through FTIR measurement in transmittance mode in ambient atmosphere.

The fabricated free-standing layers are then available for optical [19] and electrical characterization. Photoluminescence (PL) spectra were measured under 325 nm He-Cd continuous wave excitation and collected with a monochromator–CCD camera system at room temperature. In order to investigate both the photoconduction and the contribution of the contact/nc-PSi interface, samples were contacted in sandwich configurations with different material including vacuum evaporated 5 nm thin semi-transparent Au layer, a 300 nm Al layer, or a RF sputtered 70 nm ITO layer. The free-standing membranes were subsequently bonded onto metallic holders using electro-conductive Ag paste.

Photovoltaic properties were measured under an AM1.5G – 1 sun (100  $\text{mW}/\text{cm}^2$ ) illumination from a Class A solar simulator in a 25  $^\circ\text{C}$  temperature regulated environment. The aperture area of the cells under solar illumination was 0.36  $\text{cm}^2$ . The spectral response was acquired under monochromatic illumination from a set of a Xe lamp coupled with a monochromator and corrected with a silicon detector reference in the range 350–1100 nm.

### 3. Results and discussion

#### 3.1. Structure and photoluminescence

The presence of Si nanocrystals in the material was confirmed by the observation of a visible PL emission from the surface of an as-prepared pn type nc-PSi layer at room temperature, as shown in the lower part of Fig. 3. The depth dependent PL measurements were carried out after successive mechanical scraping of the upper part of the material. The results show that the PL originates directly from the underlying porous n type layer formed through the assistance of illumination during the electrochemical anodization, while the top p+ layer is non-luminescent. From the previous PL spectra together with scanning electron imaging of the device cross section, the structure of the device made from pn type starting material has

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