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Photovoltaic Property of Nanocrystalline Silicon Membranes Cells

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1. Introduction

Optical properties of quantum-sized nanocrystalline silicon (nc-Si) fabricated by electrochemical process has attracted much attentions since the discovery of its efficient visible photoluminescence (PL) as well as possible applications as an electroluminescent devices based on a strong confinement effect. While efforts were mostly focusing on the luminescent properties and silicon based optoelectronics, early as well as more recent studies[1)] showed the photoconducting and photovoltaic activities of nc-Si leading to the potential application in solar cells with a wide-gap feature. With the interest in the development of nc-Si solar cells, we are presenting our results on the optical and photoelectrical properties of free-standing nc-Si layers for applications to a top cell in silicon-based multi-junction solar cells.

2. Experiments

The fabrication process of nc-Si is based on a top-down approach were bulk crystalline silicon (c-Si) is electrochemically etched in ethanoic HF solution, a technique referred here as "anodization". The properties of the resulting nc-Si material can be controlled during the formation by matching the conduction type of substrates with both the content of the solution (HF to solvent ratio) and the current density in order to produce a material with a wide range of the porosity from 40% to 80%.

The starting material used in this study was a pn junction substrate. A 1μm-thick boron-implanted p-type layer was formed on an n-type (100) silicon substrate of resistivity 0.01-0.02 Ω.cm. The anodization current density was modulated such that a graded band gap profile is built-in along the nc-Si layer in the p-type region in the same way as that reported previously.[1)] Once the desired thickness for the nc-Si layer is obtained, the layer can be separated from the remaining bulk silicon substrate by applying a high current step (≥250 mA/cm^2) leading to electro-polishing at the nc-Si/c-Si interface, separating the nc-Si layer in a controlled way. The resulting layers, called free-standing nc-Si membranes, were successfully fabricated in different thicknesses from around 15 μm up to 100 μm. The resulting layers were then dried under super critical condition (drying under super critical fluid CO_2) and are then available for direct characterization (as-anodized samples) or further treatments of thermal oxidation, surface modification, and/or sensitization.

The samples were contacted by vacuum deposition of a semi-transparent 5 nm thick Au layer at the top and an Al layer at the back as shown in **Fig. 1(a)**. Photovoltaic properties were measured under an AM1.5-1 sun (100mW/cm^2) illumination from a Class A solar simulator under a regulated temperature of 25°C. The spectral response was acquired under monochromatic illumination from a Xe lamp coupled with a monochromator and corrected with a silicon detector reference in the range 350-1100 nm.

In parallel to the photovoltaic evaluation, optical characterization of prepared nc-Si membranes was conducted by transmission and reflection spectra measurements using a spectrophotometer Hitachi U-4100. The possibility of fabricating large area membranes with a diameter of up to 8 cm was also demonstrated as seen in **Fig. 1(b)**.

3. Results and Discussion

The fabrication of free-standing layers allows the study of optical and electrical properties of the nc-PSi material itself without any contribution from the Si substrate. The PL spectra shown in **Fig. 2**, measured both from the top surface (p-side) and the back surface (n-side) at room temperature confirms the presence of quantum-sized nc-Si dots in the material. Confirmation of the blue shift of the absorption edge has also been reported in a previous paper[2)].

Current-voltage measurements under AM 1.5 - 1 sun illumination of pn type nc-Si layers show a definite PV effect with the relatively large open circuit voltage V_{oc}, the highest V_{oc} value measured at 0.84 V as seen in **Fig. 3**. Such high V_{oc} value has not yet been reported in structure involving nc-Si where the values previously reported are in the usual range of 0.15-0.36 V[3-5)]. The low value of photo-generated current can be explained by the high resistivity of the as anodized material and the thickness of the layers (around 30 μm in this study). While there is still no agreement and definite explanation for observed conduction phenomena in nc-Si material, it is expected to include both conduction through the nc-Si dot chain interconnected with tunnel oxides and the surface conduction along the nanometric silicon skeleton structure passivated with hydrogen or oxide.

The spectral response of pn type membranes, as seen in the inset of **Fig. 3**, also shows a sensitivity with a peak at around 450-460 nm, clearly shifted compare to the response of bulk crystalline Silicon which contribution in the lower energy (low energy part of visible and NIR) disappears in the case of free-standing nc-Si layers.

For comparison PV characteristics of free-standing p type and n type only layers as well as on-substrate nc-Si layer (nc-Si/c-Si heterojunction) are shown together in **Fig. 4**. All fabricated samples involving only rectifying metal/nc-Si junction features extremely low V_{oc} compare to samples made from pn substrate. Further investigation are under way in both term of performance and stability improvement, including the reduction of membrane thickness, more complete interfacial passivation, and the impregnation with conductive materials.

4. Conclusion

Investigation on free-standing nc-Si layers made from electrochemically etched c-Si in a pn diode configuration shows a definite photovoltaic activity with large open circuit voltage in excess of 0.8V, indicating the possibility that the material may act as a wide gap absorber. Further studies are necessary for clarifying conduction phenomena and improvement of conversion performances for practical applications in solar cells.

Acknowledgements

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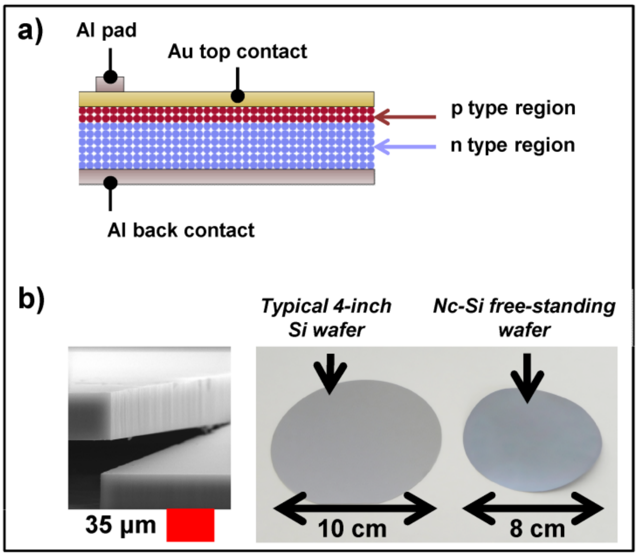

Fig. 1. (a) Schematic of the nc-Si devices with electric contact, (b) SEM imaging of the side of a free-standing layer (left) and optical picture of a large nc-Si membrane with a diameter of 8 cm (right).

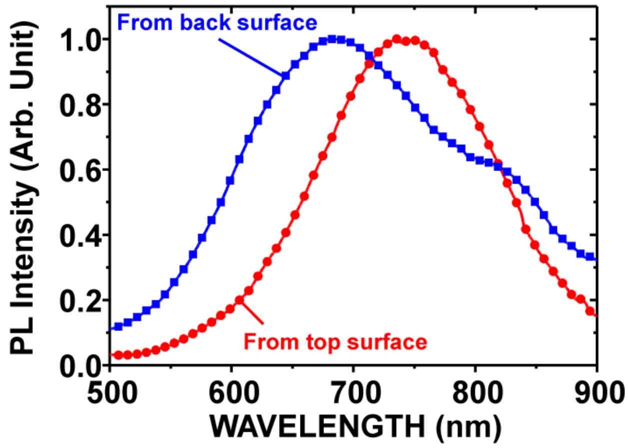

Fig. 2. Normalized PL spectra of a pn type nc-Si free-standing layer measured from the top (p-type) and bottom (n-type) with their respective peak at 740 nm and 680 nm.

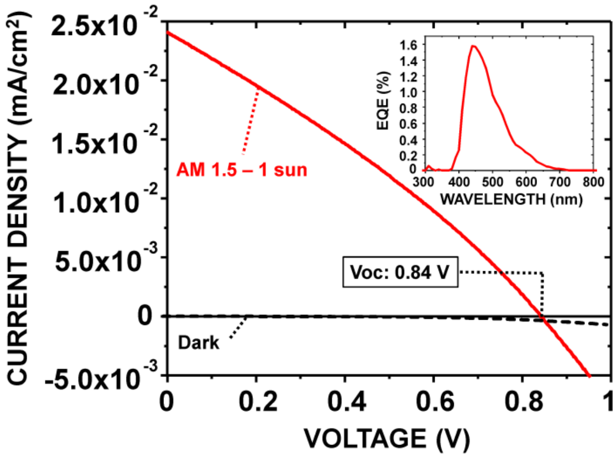

Fig. 3. Typical PV characteristic of pn type nc-Si layer featuring a large V_{oc} of 0.84 V. The inset shows the corresponding quantum efficiency of the device peaking at around 450 nm.

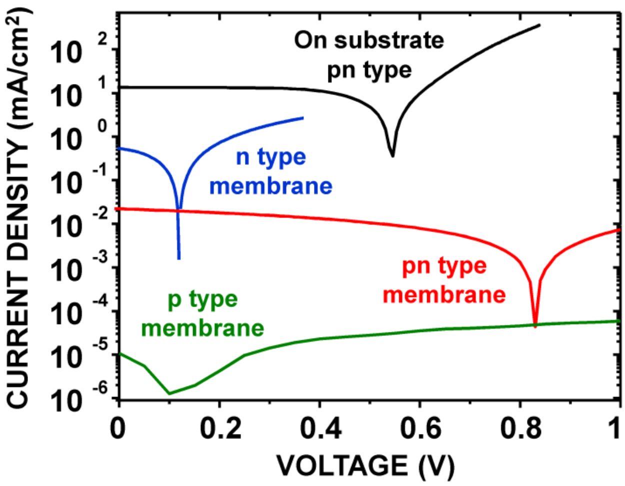

Fig. 4. Comparison of PV characteristics of different free-standing layers including pn type, p and n type only (no junction) and an on-substrate nc-Si thin layer.