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Photovoltaic Property of Wide-Gap Nanocrystalline Silicon Layers

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1. Introduction

Nanocrystalline silicon (nc-Si) material fabricated by electrochemical wet etching has been under investigation as a new material for potential applications in photonics, electronics, acoustics, and bio-sensing devices. Due to its blue-emissive and wide-gap properties [1,2], this material is also attractive in photosensing and photovoltaic applications[3] in the visible region.

To confirm the availability of nc-Si material for practical use as a top cell for silicon-based multi-junction solar cells, optical and photoelectrical characteristics of free-standing nc-Si layers are presented in this paper.

2. Experiments

The experimental nc-Si layers were fabricated by electrochemical dissolution of single-crystalline silicon wafers in an ethanoic HF acidic solution, a technique termed "anodization". The structures and properties of the resulting nc-Si material are controlled by the formation parameters such as the solution type and content as well as the current density (in a usual range of 10–100 mA/cm^2). Current density can be controlled during anodization to realize different structures by varying the porosity such as linearly graded band-gap profile or multi-layer structures.

When the desired thickness for the nc-Si layer is obtained, the layer can be separated from the original substrate by applying either a high current step (>250 mA/cm^2) leading to electro-polishing at the dissolution front or by creating a strong porosity variation at the nc-Si/substrate interface. The resulting layers, called free-standing nc-Si membranes, were successfully fabricated in varying thicknesses from around 15 µm up to 100 µm. The active area of membranes was 1-5 cm in diameter.

After anodization, the layers were dried using the super critical rinsing and drying method (drying under super critical fluid CO_2). The dried samples are then available for further passivation treatment including oxidation by RTO (rapid thermal oxidation) and HWA (high pressure water vapor annealing) as well as surface derivatization by organic molecules.

The prepared samples were optically characterized by transmission and reflection spectra measurements using a spectrophotometer (Hitachi U-4100). Photoelectric properties were evaluated both in terms of photoconduction and PV effects under AM 1.5 illumination of 1 sun (100mW/cm^2) through a class A solar simulator.

3. Results and Discussion

- Absorption characteristics

The fabrication of free-standing layers of nc-Si allows for the assessment of absorption by measurement of transmission and reflection spectra. In the case of nc-Si, the absorption spectra contain important information about the bang-gap widening in the materials as seen in **Figure 1**.

Spectra of as-prepared and RTO/HWA oxidized p-type and n-type layers are plotted together with bulk silicon as a reference. A shift of the absorption edge toward higher energies is clearly observed, from 1.5 eV for low porosity as-prepared n-type samples up to 2.4 eV for highly oxidized and high porosity p-type nc-Si, confirming that the effective band-gap of the material can be controlled in the useful range for application as a top cell in multi-junction solar cells.

On the other hand, heavily oxidized (by combination of RTO and HWA) samples showed characteristic luminescent properties such as stable and efficient blue emission (450 nm) as well as long lived phosphorescence as reported in a previous paper[2].

- Photovoltaic characteristics

Nc-Si effect on PV characteristics was evaluated first by fabricating thin graded layer of nc-Si at the top of a pn junction substrate, resulting in a metal/nc-Si/Si hetero-structure. Characterization of several graded layers in function of their thickness shows that the formation of a relatively thin nc-Si layer is useful to improve the overall characteristics without affecting the original junction properties. Nc-Si layer shows a PV activity and the quantum efficiency is slightly enhanced in the short-wavelength region.

In order to investigate photoconduction effect of nc-Si material itself, measurements were also conducted on free-standing layers of nc-Si layers without contribution of the heterojunction nc-Si/substrate. Photovoltaic characteristics of three different free-standing pn-junction devices with a metal/nc-Si/metal structure (thickness of around 30 µm) are shown in **Figure 2**. All three devices have a different porosity profile, the device number 1 as its porosity constant all along the thickness while devices number 2 and 3 features a graded band, a decrease of porosity along the thickness of the membranes.

Despite a short-circuit photocurrent density J_{SC} remaining small because of a limited conductivity, the device shows a significant increase in the open-circuit photo-voltage V_{OC} over 0.7V. Such a high V_{OC} has not been observed in nc-Si on substrate samples or in n-type free-standing layers as seen in **Figure 3**. The spectral response of the quantum efficiency is clearly shifted toward the higher energy side confirming that nc-Si may indeed act as a wide-gap absorber. Improvement in performance such as increase of the shortcut current density J_{SC} will be pursued by optimization of the band gap profile and the interfacial passivation as well as the establishment of a built-in field.

4. Conclusion

The wide-gap free-standing nc-Si layers exhibit photoconductive and photovoltaic effects with a relatively large open-circuit voltage. As further control of the built-in field and interfacial passivation are needed for practical application in multijunction solar cells, investigation will be conducted toward the enhancement of PV performances and understanding of conduction phenomena in nc-Si material.

Acknowledgements

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References

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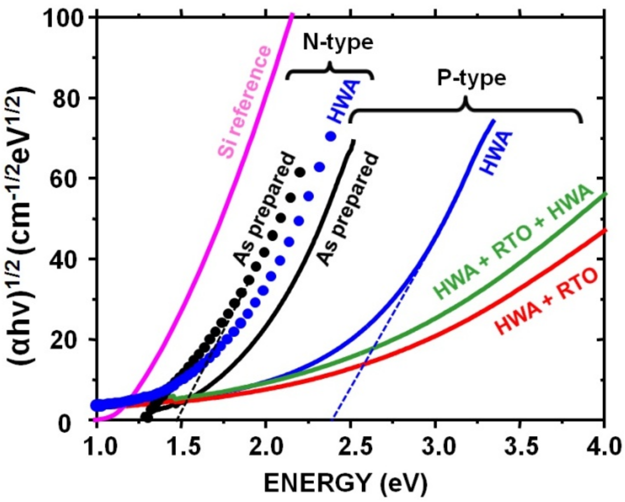

Fig. 1. Tauc plots of the absorption coefficient of nc-Si layers made from p-doped and n-doped substrates. After oxidation treatments, the effective band-gap indicates a significant blue shift, meeting the requirements for application as a top cell.

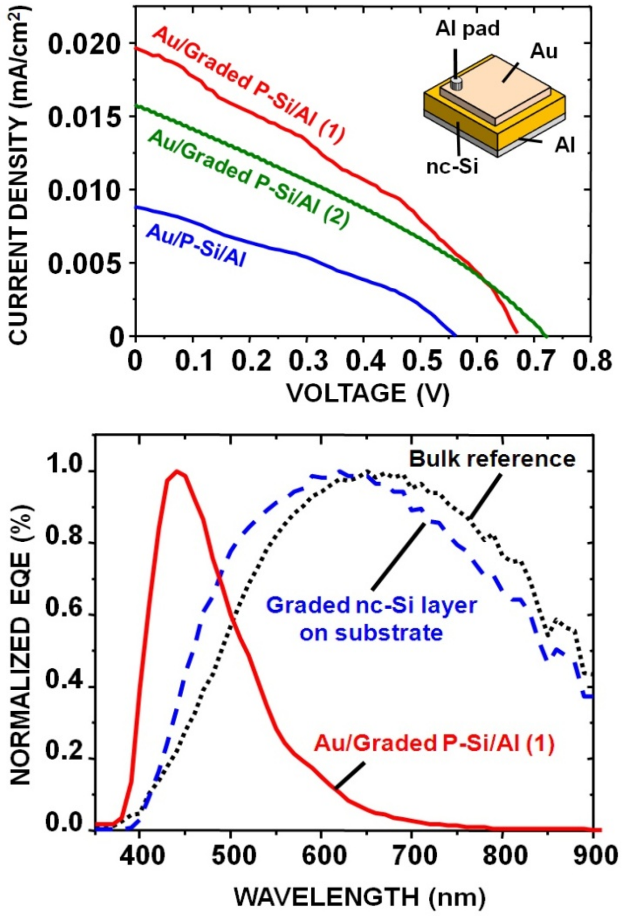

Fig. 2. Top graph shows photovoltaic characteristics of free-standing nc-Si devices with different band grading. The bottom graph displays the normalized EQE of graded sample (1) against those of nc-Si layers on pn substrate and bulk pn junction.

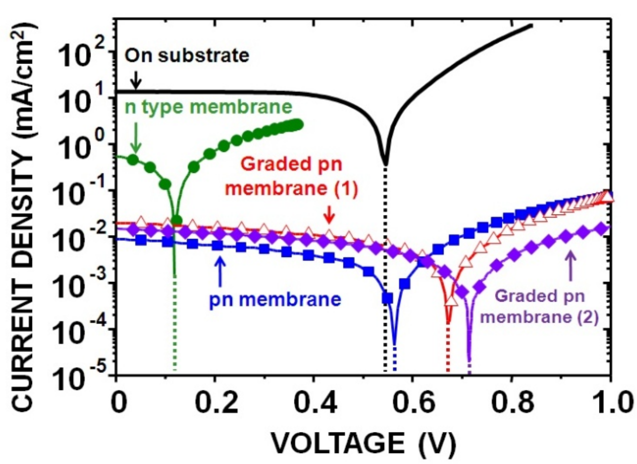

Fig. 3. Comparison of PV characteristics under 1 sun illumination for nc-Si layer on substrate (straight line), n type nc-Si membrane (dot line), pn nc-Si membrane (square line), and finally two graded pn nc-Si membrane (1) and (2) (triangle and lozenge line).