# Optical and Photoelectrical Characterizations of Wide-gap Nanocrystalline Silicon Layers

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## 1. Introduction

Quantum-sized nanocrystalline silicon (nc-Si) layer fabricated by electrochemical etching has drawn hot attention as a new material for potential applications such as optoelectronic devices, electron emitter, ultrasound emitter, and bio-sensing devices. Due to its blue-emissive and wide- gap properties  $^{1,2)}$ , this material is also attractive for photovoltaic applications.

To confirm the availability of an nc-Si material to use as a top cell for silicon-based multijunction solar cells, the optical and photoelectrical characteristics of self-standing nc-Si layer are presented here, including the fabrication process.

## 2. Experiments

Self-standing nc-Si layers were prepared by electrochemical process on different type of single-crystal (100) oriented silicon wafers: p-type (Boron doped, 2.4~3.6  $\Omega$ .cm), n-type (Phosphorus doped, 0.008-0.02  $\Omega$ .cm), p+ (Boron doped, < 0.01 $\Omega$ .cm) as well as p-type layer on n-type bulk (n-type bulk of 0.01~0.02  $\Omega$ .cm with ion implanted 3.0E<sup>+19</sup> boron doped p-type layer of 1 µm at the top) and n-type layer on p-type bulk (p-type bulk of 0.01~0.02  $\Omega$ .cm with ion implanted 3.0E<sup>+19</sup> phosphorus doped n-type layer of 1 µm at the top).

The nc-Si layers are fabricated by wet processing called "anodization". The silicon wafer surface is electrochemically etched in a solution containing HF and ethanol (usually in proportion 55% HF: Ethanol = 1:1 for p-type and 55% HF: Ethanol = 11:29 for n-type) under a moderate current density in order to produce a uniform layer composed of quantum-size nc-Si dots. Once the desired layer thickness is achieved by adjusting the anodization time, the current density is rapidly increased to a level of electropolishing (> 250 mA/cm<sup>2</sup>) where silicon at the dissolution front is completely dissolved leading to the separation of the nanocrystalline layer from the substrate.

Semitransparent contact with the self-standing layer were made by thin Au film deposition with a thin Al film pad on both side of the sample as shown in **Figure 1**. The sample was attached on an experimental frame with a bonding and electrical contact system.

The optical characterizations of the prepared samples were done by transmission and reflectance spectra measurements using a spectrophotometer (Hitachi U-4100).

Photoluminescence (PL) spectra were measured at room temperature using a 325 nm He–Cd laser as an excitation source. Photoelectrical properties were evaluated in terms of photoconduction and photovoltaic effects under illumination of a 150 W Xe lamp using a Source Measure Unit (Keithley 238).

## 3. Results and Discussion

#### - Photoluminescence

**Figure 2** shows the PL spectra of a self-standing nc-Si layer separated from a PN type substrate. The result of a simple nc-Si layer from p-type wafer is also shown for reference. Optical excitation was done from the top side of the sample (n-type) as well as from the bottom of the sample (p-type). Two kinds of PL peaks are clearly observed from the both sides, confirming that the fabricated layer contains two different band-gap nc-Si structures expected from the anodization conditions. These nc-Si layers are available for additional oxidation and annealing treatments to shift the PL peak toward the blue band and to render the fast blue PL phosphorescent with a decay time of few seconds as reported previously<sup>2</sup>.

#### - Photoconduction

An example of the photoconduction characteristics is shown in **Figure 3** for a 50 $\mu$ m thick NP self-standing nc-Si layer. Apparent photocurrent can be seen in positive and negative bias regions, though the dark current should be suppressed by control of the anodization parameters and subsequent surface oxidation. The results of spectroscopic analyses are consistent with the PL spectra. One possible way to enhance the sensitivity is to use of the field-induced multiplication effect of photo-carriers as observed in a dry-processed nc-Si diode<sup>3</sup>.

#### - Photovoltaic characteristics

As the first step of exploring the photovoltaic effect, the nc-Si samples were prepared by anodization without peeling out from the wafer. **Figure 4** shows the I-V characteristics under illumination for three bulk PN samples PN1, PN2 and PN3 in which the surfaces were anodized to form an nc-Si layer with thicknesses of 2.4  $\mu$ m, 1.2  $\mu$ m and 0.6  $\mu$ m, respectively.

Since the depth of the P doped layer is about 1  $\mu$ m, the formation of a 2.4  $\mu$ m thick nc-Si layer on the sample PN1

should affect upon the original junction property. So the open circuit voltage  $V_{\rm oc}$ , short-circuit current  $I_{\rm sc}$ , and fill-factor device remains relatively low values. The samples with thinner nc-Si layers, in contrast, show a significant fill-factor of about 60 % for both NP2 and NP3 with increased  $V_{\rm oc}$  (0.51 V) and  $I_{\rm sc}$  (2.5 mA), respectively.

The detected photovoltaic conversion suggests that the anodized nc-Si layer works not only as simple optical trapping component, but also as a medium for efficient carrier separation possibly by tunneling effect. Further enhancements of the photovoltaic efficiency may be attained by the structural and band gap control of the nc-Si layer. Appropriate combination of anodization, oxidation, and annealing are required, including the fabrication of self-standing nc-Si devices and their spectroscopic analyses.

#### 4. Conclusion

The wide-gap self-standing nc-Si layers exhibit the photoconductive and photovoltaic activities besides the visible luminescence. The quantum confinement effect looks not contradictory to either carrier separation or transport. Detailed investigations of photovoltaic properties of nc-Si will be pursued toward its application to a top cell for multijunction devices.

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#### References

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**Fig. 1.** Schematic experimental configuration for photoconduction measurements of the Au/nc-Si/Au diode structure. The top-left shows photograph of a 50µm thick NP self-standing nc-Si layer.



**Fig. 2.** PL spectra of a NP self-standing nc-Si layer measured under excitation from top and back side. The result of a simple nc-Si layer separated from p-type wafer is also shown for reference.



**Fig. 3.** Photoconduction characteristics of a NP as-prepared self-standing nc-Si diode under illumination of a 150-W Xe lamp.



**Fig. 4.** Photovoltaic characteristics of three PN bulk samples in which nc-Si layers were formed on the surface with a thickness of  $2.4 \mu m$  for NP1,  $1.2 \mu m$  for NP2 and  $0.6 \mu m$  for NP3.