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Antireflection and SiO_2 Surface Passivation by Liquid-Phase Chemistry for Efficient Black Silicon Solar Cells

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Abstract — **We report solar cells with both black Si antireflection and SiO_2 surface passivation provided by inexpensive liquid-phase chemistry, rather than by conventional vacuum-based techniques. Preliminary cell efficiency has reached 16.4%. Nanoporous black Si antireflection on crystalline Si by aqueous etching promises low surface reflection for high photon utilization, together with lower manufacturing cost compared to vacuum-based antireflection coating. Ag-nanoparticle-assisted black Si etching and post-etching chemical treatment recently developed at NREL enables excellent control over the pore diameter and pore separation. Performance of black Si solar cells, including open-circuit voltage, short-circuit current density, and blue response, has benefited from these improvements. Prior to this study, our black Si solar cells were all passivated by thermal SiO_2 produced in tube furnaces. Although this passivation is effective, it is not yet ideal for ultra-low-cost manufacturing. In this study, we report, for the first time, the integration of black Si with a proprietary liquid-phase deposition (LPD) passivation from Natcore Technology. The Natcore LPD forms a layer of <10-nm SiO_2 on top of the black Si surface in a relatively mild chemical bath at room temperature. We demonstrate black Si solar cells with LPD SiO_2 with a spectrum-weighted average reflection lower than 5%, similar to the more costly thermally grown SiO_2 approach. However, LPD SiO_2 provides somewhat better surface-passivation quality according to the lifetime analysis by the photo-conductivity decay measurement. Moreover, black Si solar cells with LPD SiO_2 passivation exhibit higher spectral response at short wavelength compared to those passivated by thermally grown SiO_2. With further optimization, the combination of aqueous black Si etching and LPD could provide a pathway for low-cost, high-efficiency crystalline Si solar cells.**

Index Terms — **black silicon, metal-assisted porous silicon etching, antireflection, liquid-phase deposition, surface passivation, photovoltaic cells.**

I. INTRODUCTION

Nanoporous black Si by metal-assisted wet-chemical etching has demonstrated the potential of being a viable alternative to conventional vacuum-based antireflection coatings [1,2]. The nanoporous structure has feature sizes less than the wavelength of the incident light, and it creates a density-graded surface that suppresses photon reflection by eliminating any abrupt change of index of refraction at the interface [3,4]. The early development described in Refs. 1 and 2 used Au-assisted nanoporous etching to create a black Si surface with pore diameter of ~50 nm. The corresponding black Si solar cells have averaged surface reflection lower than 3%, but exhibit poor spectral response at short wavelength (blue response), which limits the short-circuit current density (J_{SC}). High surface area of the nanoporous structure is one of the major factors that attributes to the poor blue response.

To better control the nanoporous feature size and reduce the cost of the catalytic etching, we recently developed Ag-assisted black Si etching and a subsequent chemical surface treatment at NREL [5]. The pore diameter can be 50 to 100 nm or beyond, and the blue response improves accordingly.

High-quality surface passivation is essential for good blue response. A thin layer of 10- to 20-nm thermally grown SiO_2 has been used at NREL to passivate the front surface of black Si solar cells. Thermally grown SiO_2 conformally covers the Si nanostructure [6] and provides decent passivation quality [1,2]. However, this step often takes a separated high-temperature oxidation and could erode the cost benefit of the liquid-phase black Si antireflection. A proprietary liquid-phase deposition (LPD) currently being commercialized by Natcore Technology, on the other hand, deposits a layer of SiO_2 on the candidate substrate in a reactive chemical solution, and it represents a promising low-cost route to manufacturing black Si photovoltaics. Here, we report on promising characteristics of the LPD-SiO_2-passivated black Si solar cells, including their surface reflectance, photo-conductivity decay (PCD) lifetime, spectral response, and solar cell performance.

II. EXPERIMENT

The Si substrate is double-sided polished boron-doped p-type Si (100) float zone (FZ) with resistivity of ~2.8 Ω-cm and thickness of ~300 μm. During Ag-assisted black etch, the backside of the Si is protected with photoresist so that black Si etching forms porous black Si only on the front side. The etching consists of two steps; first, the Ag nanoparticles are electrolessly deposited on the Si substrate from $AgNO_3$ and HF solutions, and second, preferential nanoporous etching is performed by immersing the Ag-nanoparticle decorated Si in a diluted HF and H_2O_2 mixture. The duration of Ag deposition and the subsequent porous Si etching determine the diameter, separation, and depth of the nanopores. This two-step Ag-assisted etching creates porous Si with feature sizes well below the wavelength of incident light that a Si photovoltaic cell is able to use. The random pore depth results in a near-linear density-graded Si surface that suppresses the reflection.

As mentioned previously, it is crucial to minimize the surface recombination to obtain high conversion efficiency. Here, we intentionally reduce the surface area of the pore structure by immersing the black Si sample in TMAH solution, which etches Si and widens the pores. Two different TMAH treatments, Treatments I and II, are performed. The primary purpose of the treatment is to reduce the surface area of the porous black Si. Treatments I and II differ on the duration of the TMAH etching and when it is performed during the solar cell fabrication.

An n-type emitter is formed by $POCl_3$ diffusion at 850°C with a sheet resistance of ~80 Ω/□. After stripping the PSG layer in dilute HF, the surface of black Si samples is either passivated by LPD or thermal SiO_2. LPD is performed in a reactive solution containing H_2SiF_6, SiO_2 powder, and H_2O. As the reaction progresses, SiO_2 deposits on the black Si surface and we control the thickness of the LPD SiO_2 to be less than 10 nm in this study. At this moment, we have found that the LPD SiO_2 needs to be annealed in an oxygen-containing ambient followed by forming gas annealing to achieve the best surface-passivation quality. The control samples, on the other hand, have the black Si passivated by a thicker thermal SiO_2 (25–30 nm) separately grown at 850°C in dry O_2 ambient.

A full-area Al-BSF and lithographically patterned metal grid finishes the back and front contact of the solar cells, respectively. The cell area is ~1 cm^2. There is no additional antireflection coating on either type of nanostructured solar cell under study.

The reflectance is measured by a Varian Cary 6000i spectrophotometer with an integrating sphere, and the PCD lifetime is measured by a Sinton WCT-120 lifetime tester. Current density-voltage (J-V) characteristics are measured by a calibrated XT-10 1-sun solar simulator.

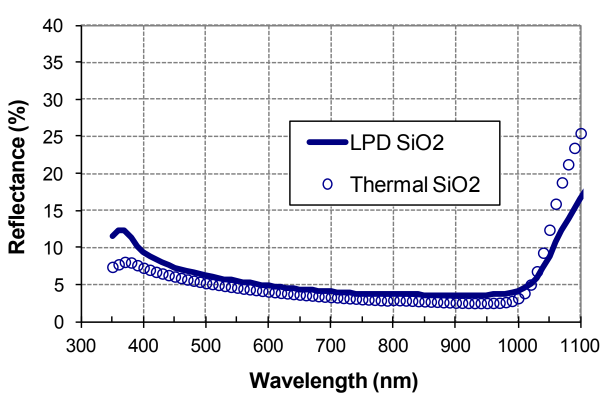

Fig. 1: Reflectance of black Si solar cells passivated by LPD and thermally grown SiO_2.

III. RESULT

Figure 1 shows the reflectance of black Si solar cells: LPD-SiO_2 passivated and control (thermal SiO_2), with TMAH Treatment II. Both the thermal SiO_2 control and the LPD sample have similarly low reflectance, indicating that the LPD does not interfere with the antireflection of the black Si surface. Minor difference in the reflectivity spectrum is likely the result of slight variation of black Si etching. Solar spectrum-weighted average reflectance from 350–1000-nm wavelength is 5% and 4% for LPD and thermal SiO_2 black Si, respectively. The LPD black Si solar cell with Treatment I has spectrum-weighted average reflectance of 4%, again similar to the control. Figure 2 presents the implied open-circuit voltage (V_{OC}) obtained from PCD-lifetime measurement of the passivated, one-sided, black Si samples with an n-type emitter on both front and back surfaces. LPD SiO_2 demonstrates better passivation quality than the thermal SiO_2 in both treatments.

Emitter dark-saturation current density (J_{oe}) extracted from the PCD-lifetime measurement is 370 and 180 fA/cm^2 for LPD black Si samples that have undergone Treatments I and II, respectively. They are about five times higher than the reported J_{oe} on SiO_2-passivated $POCl_3$-diffused Si surface with similar emitter sheet resistance [7]. The higher J_{oe} reflects the intrinsic surface passivation quality, as well as the inevitable impact of the large surface area of nanoporous black Si. Nevertheless, we believe that a further optimization of black Si etching, TMAH treatment, and LPD passivation can provide both excellent antireflection and solar cell performance.

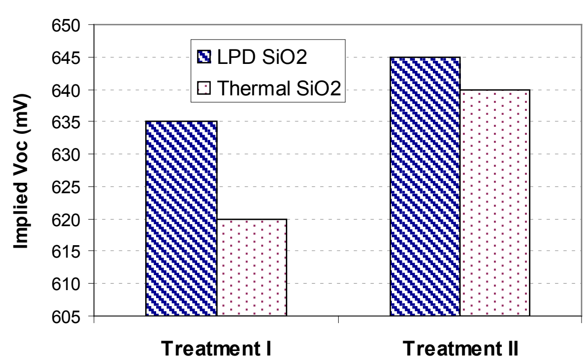

Fig. 2: Implied V_{OC} of passivated one-sided black Si samples.

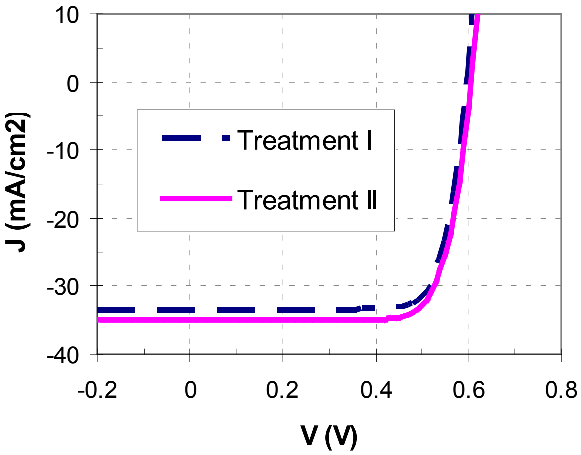

Fig. 3: J-V curves of LPD black Si solar cells.

Figure 3 presents J-V curves of LPD black Si solar cells measured under simulated 1-sun conditions at 25°C. The LPD black Si solar cell with Treatment II has higher energy conversion efficiency than the solar cell with Treatment I, mainly due to the better surface-passivation quality seen in Fig. 2. The best LPD black Si solar cell (Treatment II) has a V_{OC} of 607.4 mV, J_{SC} of 34.9 mA/cm^2, FF of 77.2%, and efficiency of 16.4%. Its J_{SC} and FF are comparable to the thermal SiO_2 black Si counterpart. However, the V_{OC} of the LPD cell is about 20 mV below the thermal SiO_2 control, even though the implied V_{OC} is slightly higher than the thermal SiO_2 (Fig. 2).

Internal quantum efficiency (IQE) shown in Fig. 4 compares the spectral response of LPD- and thermal-SiO_2 black Si solar cells with Treatments I and II, respectively. The variation in IQE in the near-infrared (IR) region is still under investigation, but most likely related to the Al-BSF formation. We believe it is the poor near-IR response that contributes to low V_{OC} of the LPD black Si solar cell by Treatment II, as mentioned previously. Nonetheless, the superior blue response of the LPD black Si solar cell in both cases indicates better passivation quality by LPD SiO_2.

IV. CONCLUSION

Nanoporous black Si solar cells integrated with low-cost, solution-based LPD SiO_2 passivation are reported for the first time. The combination demonstrates promising results; the LPD solar cells 1) retain low reflectivity of the black Si surface, and 2) provide better surface-passivation quality compared with the thermally grown SiO_2, as seen by PCD-lifetime and spectral response measurements. Further optimization of the key processing steps—such as black Si formation, LPD, and TMAH treatment—could promise an extremely low-cost and high-efficiency black Si solar cell.

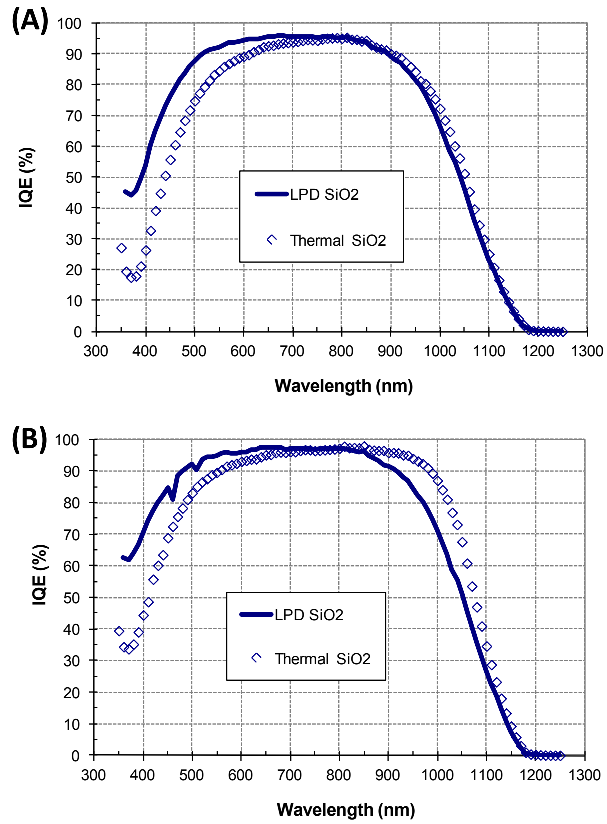

Fig. 4: Intrinsic quantum efficiency of LPD and thermal SiO_2 black Si solar cells treated by (A) Treatment I, and (B) Treatment II.

ACKNOWLEDGMENT

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