

Research Article

Mohammad Jobayer Hossain*, Mengdi Sun, Gregory Doerk, Pieter G. Kik and Kristopher O. Davis*

Self-assembled multifunctional nanostructures for surface passivation and photon management in silicon photovoltaics

<https://doi.org/10.1515/nanoph-2021-0472>

Received August 22, 2021; accepted October 9, 2021;

published online November 2, 2021

Keywords: atomic layer deposition; multifunctional materials; nanostructures; photon management; self-assembly; solar cells; surface passivation.

Abstract: This work reports the fabrication and characterization of multifunctional, nanostructured passivation layers formed using a self-assembly process that provide both surface passivation and improved light trapping in crystalline silicon photovoltaic (PV) cells. Scalable block copolymer self-assembly and vapor phase infiltration processes are used to form arrays of aluminum oxide nanostructures (Al_2O_3) on crystalline silicon without substrate etching. The Al_2O_3 nanostructures are characterized using scanning electron microscopy (SEM), transmission electron microscopy (TEM), and spectroscopic ellipsometry. Injection-level dependent photoconductance measurements are used to determine the effective carrier lifetime of the samples to confirm the nanostructures successfully passivate the Si surface. Finite element method simulations and reflectance measurement show that the nanostructures increase the internal rear reflectance of the PV cell by suppressing the parasitic optical losses in the metal contact. An optimized morphology of the structures is identified for their potential use in PV cells as multifunctional materials providing surface passivation, photon management, and carrier transport pathways.

Present address: Mohammad Jobayer Hossain, 4304 Scorpius St, Orlando, FL 32816, USA.

*Corresponding authors: Mohammad Jobayer Hossain, College of Optics and Photonics (CREOL), University of Central Florida, Orlando, FL 32816, USA, E-mail: jobayer@knights.ucf.edu. <https://orcid.org/0000-0002-9908-5512>; and Kristopher O. Davis, College of Optics and Photonics (CREOL), University of Central Florida, Orlando, FL 32816, USA; and Department of Material Science and Engineering, University of Central Florida, Orlando, FL 32816, USA, E-mail: kristopher.davis@ucf.edu

Mengdi Sun and Pieter G. Kik, College of Optics and Photonics (CREOL), University of Central Florida, Orlando, FL 32816, USA

Gregory Doerk, Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton 11973, NY, USA

1 Introduction

With silicon solar cell efficiency values approaching their theoretical limit, the elimination of remaining energy conversion losses becomes more challenging. Energy conversion losses [1, 2] commonly take the form of either optical losses (e.g., reflection, parasitic optical absorption, and quantum defect) or electrical losses (e.g., carrier recombination losses, carrier selectivity losses, resistive losses). A persistent obstacle to this goal is the fact that many approaches that help lower one form of loss tend to increase another. Metal contact grids are required to deliver current to the external circuit with minimal voltage drop, limiting the resistive losses of solar cells. However, having metal in direct contact with silicon leads to increased recombination loss, and when the metal grid is placed on the front of the cell it blocks light from getting into the absorber (i.e., front reflection loss). Also, when placed on the rear side of the cell, it causes parasitic optical loss [3–6]. The current record holding silicon solar cell (26.7% efficient under standard test conditions) uses a passivating, carrier-selective contact structure to limit recombination and an all rear contacted configuration to avoid the optical shading of the front contact grid [7]. However, this cell architecture is very complex to manufacture, and it is unclear if it will gain significant market share.

Currently, passivated emitter and rear contact (PERC) cells [8–10] are the primary type of photovoltaic (PV) cell manufactured around the world [11]. These cells feature dielectric thin films covering most of the front and rear surfaces, along with local metal contacts (i.e., partially covering the surface) to extract carriers and deliver current to the external circuit. These dielectric thin films are

multifunctional, in that they both passivate the surfaces and help lower optical losses. On the front side of the cell, the thin film(s) act as single or multilayer antireflection coatings (ARC) [12]; on the rear side of the cell, the thin film(s) help increase the internal rear reflectance, thereby assisting light trapping for photons with energies near the band edge (i.e., 900–1280 nm) [13]. Together, the mitigation of surface recombination and optical losses help maximize both the short-circuit current density (J_{sc}) and the open-circuit voltage (V_{oc}) of c-Si PV cells [14]. Since the dielectric films are insulating, local contacts are required to extract charge carriers. For the rear contacts of PERC cells, these are formed using laser ablation to remove the dielectric and then screen-printing Al contacts to form a local aluminum–silicon (Al–Si) alloy back surface field (BSF) [15, 16]. This approach of forming local contacts has several limitations. Firstly, it damages the silicon surface. With an Al contact that can be fired at a high temperature, this issue is somewhat avoided by the formation of a local Al-BSF. However, this is not compatible with other contact materials, including various passivating, carrier-selective contact technologies under development [17, 18]. Another issue is the fact that the combination of laser ablation and screen-printing leads to a typical contact pitch (i.e., distance between contacts) on the order of mm. This introduces spreading resistance as carriers must travel further through the base of the wafer which in turn requires higher levels of doping in the wafer.

Alternative approaches to forming passivated surfaces with nanoscale local contacts have been demonstrated, but these approaches typically rely on random processes that limit the ability to engineer their optical and electrical properties. One such example was implemented using blistering in aluminum oxide (Al_2O_3) passivation layers produced by atomic layer deposition (ALD) [19]; blistering occurs through the gaseous desorption in the Al_2O_3 layer upon thermal treatments above a critical temperature. Another example is the POLO (polycrystalline silicon on oxide) process developed recently, which relies on the breakdown of the oxide layer at very high temperatures. In this process polycrystalline Si (poly-Si) penetrates the passivating oxide layer, resulting in the formation of randomly distributed pinhole contacts [20–23]. In this work, we fabricate the ordered arrays of Al_2O_3 nanostructures with various shapes (lamellae, nanoholes, and nanopillars) using the self-assembly of diblock copolymers without any lithography or substrate etching. The patterns and the sizes of the nanostructures can be controlled by chemical composition of the materials, spin coating speed, and annealing temperature in the synthesis process [24, 25].

The simultaneous need for high-quality passivation, low optical loss, and small spreading resistance suggests that optimal cell performance may be achieved using a densely spaced array of local metal contacts, surrounded by passivating dielectric material. In order to achieve such high-density metal contacts without the need for high resolution lithography, here we utilize a combination of self-assembly, atomic layer deposition, and metal thermal evaporation to fabricate nanostructured metal–dielectric networks that function simultaneously as a metallic contact, a high-quality optical reflector, and a passivating surface. These structures also exhibit great potential for engineering carrier transport properties.

2 Formation of nanostructured passivation layers using self-assembly

The PV research community has developed numerous passivation materials [26], but only a few have been adopted by industry. Hydrogenated amorphous silicon nitride (SiN_x or $a-SiN_x:H$) is one such material that provides surface passivation [27–29] and can act as an excellent ARC. Thermally grown silicon oxide (SiO_2) has also been used for many years, more so in research environments than in industry. More recently, Al_2O_3 has emerged as a preferred passivation material for solar cells [29–32] for several reasons. Firstly, Al_2O_3 was shown to provide very low interface defect density and excellent field-effect passivation by negative fixed charge [33]. Secondly, high-quality and ultrathin Al_2O_3 can be easily fabricated using atomic layer deposition (ALD) today. Thirdly, it demonstrates very good stability during processing [29] and can be used to passivate both the front and the rear side of the cell [34].

Ordered arrays of Al_2O_3 nanostructures with various shapes (lamellae, nanoholes, and nanopillars) are fabricated using the self-assembly of diblock copolymers without any lithography or substrate etching. This process relies on the selective vapor phase infiltration of precursors into one of the polymer blocks during the Al_2O_3 ALD process (details in the Experimental section). Scanning electron microscopy (SEM), transmission electron microscopy (TEM), and spectroscopic ellipsometry measurements were carried out to characterize the morphology of these structures. The SEM images of the nanostructures are shown in Figure 1(a)–(c). The width of the lamellae (Figure 1(a)) was found to be approximately 15 nm. Both the Al_2O_3 nanopillars (Figure 1(b)) and nanoholes (Figure 1(c)) self-assemble with hexagonal ordering. The diameter of the pillars and

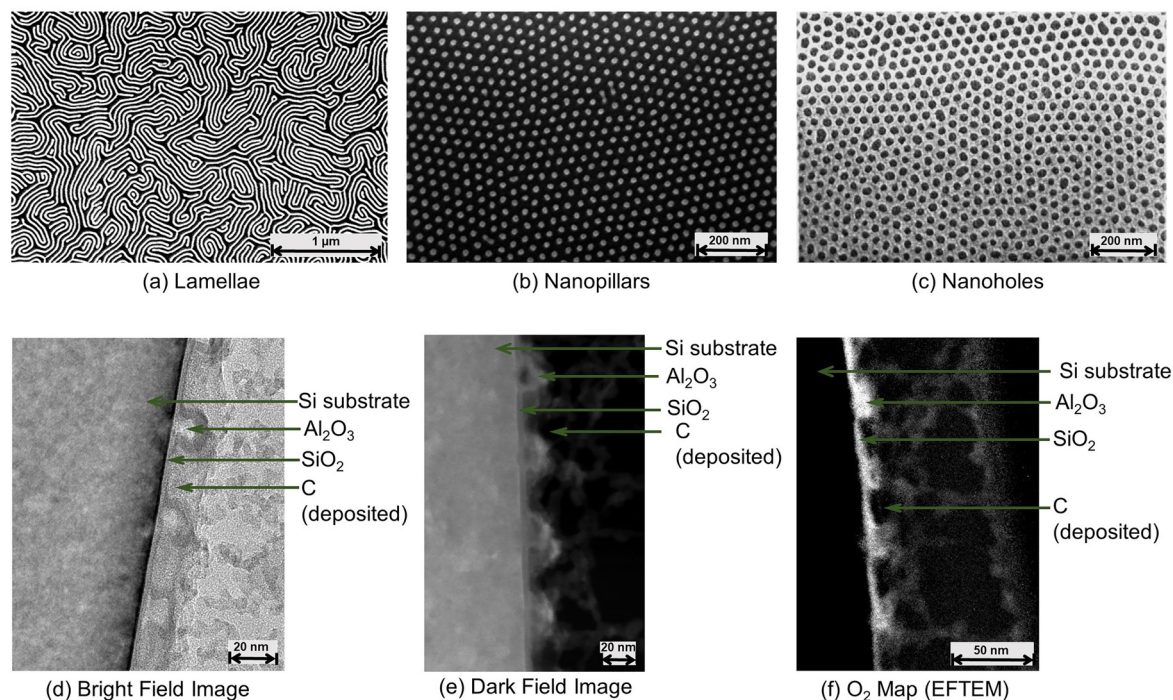


Figure 1: (a)–(c) Scanning electron microscopy image of three different nanostructures (the white regions are Al₂O₃) grown using block copolymer self-assembly assisted atomic layer deposition. (d)–(f) Transmission electron microscopy images (cross-section) of the Al₂O₃ lamellae nanostructure grown on Si substrate. The sample was carbon coated to protect it from damage at the time of imaging (d) bright field image (e) dark field image (f) O₂ map using energy filtered transmission electron microscopy.

their center to center distance were 16 and 36 nm, respectively. Similarly, the diameter of the holes and their center to center distance were 17 and 38 nm, respectively. The area fractions of Al₂O₃ in the lamellae, nanopillar, and nanohole patterns are 48, 28, and 67%, respectively.

TEM imaging was conducted at the Al₂O₃ nanostructure and Si interface. Figure 1(d)–(f) illustrates the bright field image, dark field image, and the EFTEM (energy-filtered TEM) image of the interface where Si is on the left side. A periodic structure indicative of the cross-section of different lamellae is readily apparent. The width of the lamellae is found to be approximately 20 nm which matches with the value from SEM images; the height is approximately 10 nm. The right side of the images is carbon which is deposited to protect the sample from damage at the time of imaging.

Ellipsometry was also conducted to complement the morphological characterization by SEM and TEM. To fit the measured data with the material model, Bruggeman approximation and the area fraction obtained from SEM are used. The presence of an SiO₂ layer was also assumed. The height of the structures was recorded for the best fit cases. The SiO₂ layer thickness was approximately 2.8 nm for all the samples. The height of the lamellae, pillar, and hole

structures, as obtained from the fit were approximately 9.2, 10.7, and 13.0 nm, respectively. The morphological data of all the structures are summarized in Table 1.

The Al₂O₃ nanostructured passivation layers were formed on both sides of a Si wafer. Then, photoconductance-based effective carrier lifetime measurements were carried out to assess the surface passivation quality achieved with each of these structures. For an unpassivated sample, the lifetime value was below the measurement threshold (5 μs). Table 1 lists the lifetime obtained with the nanostructures. In the cases of surface passivation with lamellae, nanopillars, and nanoholes, the lifetime values were 115, 119, and 147 μs, respectively. The corresponding dark saturation current density (J_0) values are also listed in Table 1.

3 Photon management

Silicon is an indirect bandgap material and it cannot absorb all the incident photons using practical cell thicknesses, especially when the wavelengths approach the band edge. This motivates the use of an efficient photon management technique on the rear side to provide the cell with additional opportunities to absorb photons, thus

Table 1: Morphology of the nanostructures and their surface passivation properties.

Nanostructure	Al ₂ O ₃ area fraction ^a	Al ₂ O ₃ height (nm) ^b	Lifetime (μs) ^c	<i>J</i> ₀ (A/cm ²) ^c
Lamellae	48%	9.2 ± 0.06	115	2.55 × 10 ⁻¹²
Nanopillars	28%	10.7 ± 0.01	119	2.18 × 10 ⁻¹²
Nanoholes	67%	13.0 ± 0.01	147	1.73 × 10 ⁻¹²

^aSEM image, ^bellipsometer measurement (with effective medium approx.), ^cphotoconductance measurement.

increasing the overall J_{SC} . A rear side with a high internal reflectance is needed to provide the cell with additional chance(s) for absorption. In the presence of a thick rear metal contact, the transmission is zero; therefore what fraction of the photons incident to the rear side are reflected back to silicon is dictated by the absorption loss in the metal. Unfortunately, a significant portion of these incident photons are lost through parasitic absorption loss in the metal [3, 35], even for a high conductivity metal like silver [35–37]. A dielectric layer between silicon and the metal resolves this problem by reducing the number of long wavelength photons reaching the metal [37–39]. Thus a rear passivation scheme may also improve the rear side internal reflectance of a cell [35].

In this work, we investigate the potential of the Al₂O₃ passivating nanostructures for photon management when applied to the rear side of a silicon solar cell. A 100 nm thick Ni film is grown on the nanostructured passivation layers, the film representing a nanoscale contact structure shown in Figure 2(a). The front side of all the samples is the same, so their total reflectance is correlated to the rear internal reflectance. Figure 2 illustrates the experimental geometry for reflectance measurement and shows both the simulated and experimental results. For the simulation, the rear internal reflectance was first calculated using frequency

domain finite-element method (FEM) simulation by CST Microwave Studio software. The results were then included in ray tracing simulations of the total reflectance using Sun-Solve [40]. The experimental results clearly follow the same trend as the simulated results; higher Al₂O₃ area fraction gives higher reflectance. The sample with nanoholes has the highest Al₂O₃ area fraction (67%) among all the nanostructures, so it shows the highest total reflectance. The bare Si shows comparable reflectance as the lamellae structure and more than the nanopillars. This is due to higher light absorption in the Ni–Al₂O₃ effective medium formed by the contacts at lower Al₂O₃ area fractions. However, as the Al₂O₃ area fraction increases, the complex refractive index of that effective medium becomes more and more similar to the full area Al₂O₃ layer, which opposes light reaching into Ni; the reflectance increases as a result. The simulated reflectance of the wafer with and without lamellae Al₂O₃ is comparable, but the experimental results are different. This could be because, the Ni in the FEM simulation was more absorptive than the actual Ni used in the experiment. The difference it made was more evident in case of 100% Ni coating (wafer without lamellae or any nanostructure), than 33% Ni coating (wafer with lamellae). The fact that all the simulated reflectance is lower than the corresponding experimental reflectance supports this point. It should

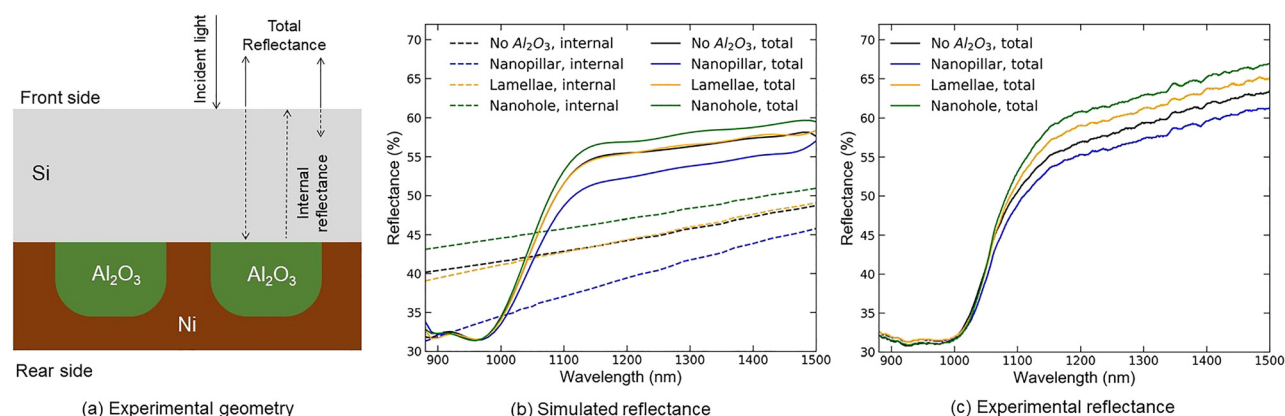


Figure 2: Optical behavior of the nanostructured passivation layers at normal incidence of light (a) experimental setup to measure the total reflectance as a function of the variation in the rear side structure, the front side of all the samples being the same (b) simulated results; the internal reflectance was calculated using the finite element method simulation of the rear side and then it was used for calculating the total reflectance using ray tracing simulation of the wafer (c) experimental validation: measured total reflectance.

also be noted here that because the nanostructures are sub-wavelength in size, area fraction has more of an impact on the optical properties of these materials than the shape.

The opening in these nanostructured passivation layers facilitates nanoscale contact formation for current collection, and because this is an additive manufacturing process that does not require ablation or etching, it is broadly applicable to virtually any contacting scheme. In this study, we considered four possible contact structures, as illustrated in Figure 3: (a) Al; (b) Al–Si; (c) Ni–Cu; and (d) poly–Si. A SiO_2 layer of 2 nm that formed during processing is assumed in all the contact structures. FEM simulation was conducted to calculate the internal back reflectance corresponding to each of these contact structures for varying thickness (0–100 nm) and area fraction (67–100%) of Al_2O_3 .

In a Si solar cell with subwavelength black Si front side or a tandem cell featuring Si bottom cell, the nonabsorbed light comes to the rear side at normal incidence. However, most of the commercial solar cells have a typical

random pyramid structure on the front side to enhance light trapping. In such a cell, 76.4% of the non-absorbed light comes to the rear side at an angle of 41.4° , the rest being incident at other angles including the normal direction [3, 41, 42]. Acknowledging the fact that most of the literature describes reflectance characteristics for normal incidence, we divide our study into two parts: normal incidence (popular case) and oblique incidence (41.4° , the dominant case). Keeping in mind that sunlight is randomly polarized, we still calculate the internal reflectance at first for TE and TM sources separately, to clearly understand the influence of different factors involved. Also, considering the typical cell thickness of about $170\text{ }\mu\text{m}$, most of the shorter wavelength photons get absorbed before they reach the rear side of the cell. Therefore, we consider only longer wavelength photons.

Al is a very common contact material that can be applied to a wide range of Si PV cells [43–47]. Figure 3(a)

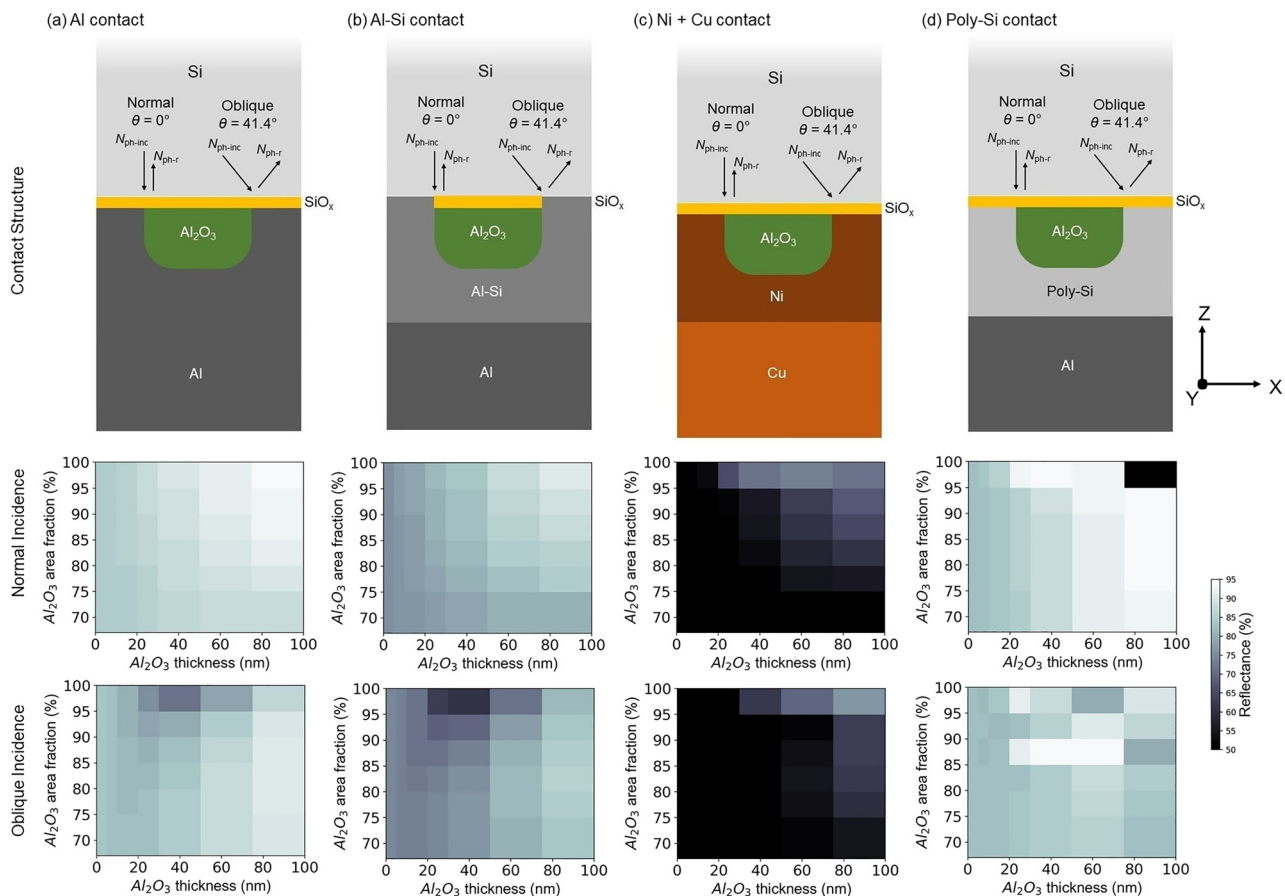


Figure 3: Different rear side contact structures featuring the self-assembled nanohole structures and their corresponding rear internal reflectance as a function of passivation area fraction and the nanostructure thickness (calculated for unpolarized light of 1000 nm wavelength). Both normal and oblique incidence angles of light at the rear surface are considered based on how different front side surface morphologies (e.g., random pyramids and subwavelength black Si) redirect light into the Si absorber.

demonstrates the average reflectance in terms of nanostructure thickness and passivation area fraction, calculated for 1000 nm wavelength. For the Al contact, the normal incidence demonstrates the expected trend i.e. increasing Al_2O_3 area fraction and thickness increases the reflectance. However, the reflectance is minimized at oblique incidence for a thickness around 25 nm, with 95% area passivated. This is attributable to the TM polarization contribution (50% of the incident light), in which increasing the Al_2O_3 thickness initially reduces the reflectance, then increases it, as illustrated in the Supplementary material (Figure 7); the arrangement here is similar to prism coupling in the Otto geometry [48], where optimum coupling occurs at a certain thickness of the dielectric between the medium of incidence (Si in our case) and the metal. Overall, a thickness and area passivation fraction greater than 85 nm and 95%, respectively, ensure a high reflectance (>90%) from the rear side of the cell.

Figure 4 shows the electric field distribution (complex amplitude $|E|$, including all field components) across the Al contact (67% area passivated) TM polarization cases: (a) normal incidence, 10 nm thickness (b) oblique incidence, 10 nm thickness (c) normal incidence, and 50 nm thickness (d) oblique incidence, 50 nm thickness, calculated for 1000 nm wavelength and all shown on the same scale ($\max|E| = 6 \times 10^8$ V/m). The TE cases are less interesting and are not shown in the figure since there are no surface normal incident fields for any angle, so the fields near the contact are similar to the TM normal incidence case. There is a notable difference between 4(a) and (c): larger fields at the top of the patterned layer, and the position of the interference maximum (horizontal bright band) is closer to the surface in (c) with the patterned layer acting similar to a magnetic mirror (i.e. large field at the surface of the reflector). That suggests we'll get more dissipation i.e. lower reflectance for the thick-film case, for TM polarization. Also, the lack of a dark horizontal band in (b) and (d) is because loosely speaking, the reflection flips the horizontal component of the field, but not the vertical component. As a result, for

inclined illumination the position of destructive interference for E_x and E_z shows up at different heights, preventing the formation of a deep interference minimum. For normal incidence illumination there's no reflected E_z , so there's a well-defined height for destructive interference in the standing wave.

Other contact types were also investigated. An Al–Si alloy is included in Figure 3(b) based on its use for both full area Al–BSF cells and at the local contacts of PERC cells [49]. The Al–Si contact demonstrates similar characteristics as the Al contact, but with lower overall reflectance. Ni is another metal of interest; though it is a very lossy metal, it is a common seed layer used when plating Cu [50]. Ni also has a relatively high work function and does not oxidize as readily as Al, so has been used to contact hole-selective materials [51]. The Ni contact in Figure 3(c) also shows that increasing passivation area fraction and thickness increases internal reflectance. Finally, poly-Si (Figure 3(d)) is considered because poly-Si passivating contacts have gained significant traction within the PV industry due to their ability to dramatically limit contact recombination [52–57]. The poly-Si exhibits complicated reflectance characteristics unlike the other 3 contacts studied, including a region with low reflectance at high film thicknesses and passivation area fractions. This is due to the emergence of waveguiding effects as Al_2O_3 thickness is increased, as discussed in the Supplementary material (Figure 6).

Simulations were carried out using SunSolve to quantify the gain in J_{SC} due to photon management properties of the contacts featuring the nanostructured passivation layer. A random pyramid textured front side with a 75 nm SiN_x ARC and a 170 μm thick Si solar cell was assumed here. For Al contact, the reflectance of the unpassivated surface is around 83% at oblique incidence (dominant case). This gives a J_{SC} of around 38.6 mA/cm² (Figure 8 in Supplementary material). For any passivated area fraction greater than 67% and Al_2O_3 thickness greater than 80 nm, the internal reflectance climbs above 97% which gives a J_{SC} of around 39.5 mA/cm², a gain of 0.9 mA/cm². For a

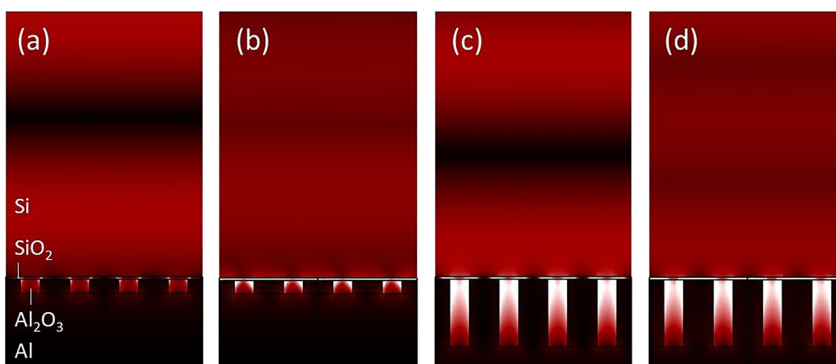


Figure 4: Electric field distribution (complex magnitude $|E|$) in Al contact (67% area passivated) in the rear side of a Si solar cell for two different Al_2O_3 nanostructure thickness, and two angles of incidence, calculated for 1000 nm wavelength and TM polarization (a) normal incidence, 10 nm thickness (b) oblique incidence, 10 nm thickness (c) normal incidence, and 50 nm thickness (d) oblique incidence, 50 nm thickness.

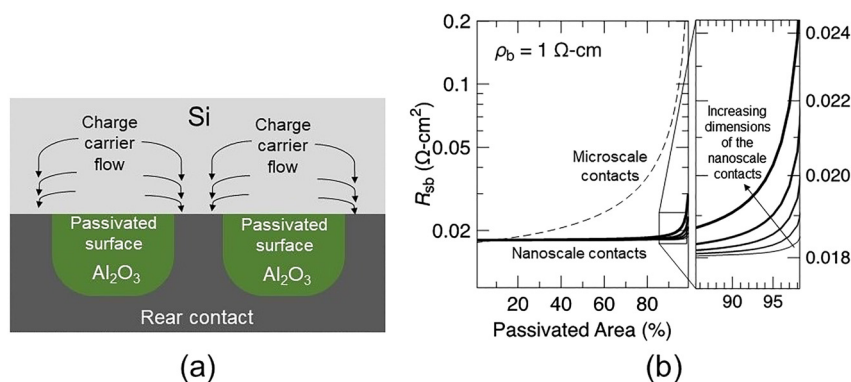


Figure 5: Charge carrier transport characteristics in nanostructured contacts (a) charge carrier transport mechanism in the rear side of a silicon solar cell featuring nanoscale passivated contacts (b) spreading resistance, R_{sb} in the bulk of the wafer for different contact diameters, nanoscale: 20, 50, 100, 200, 500 nm, and microscale: 50 μm .

lower cell thickness, for example 50 μm , this gain could be around 1.0 mA/cm^2 . For the Ni–Cu contact, the reflectance of an unpassivated surface is very low, about 41%. Using a 100 nm thick nanostructured passivation layer with 97% area coverage shows 83% reflectance, which gives a gain of 2.9 and 2.1 mA/cm^2 over the unpassivated surface for 50 and 170 μm cell thicknesses, respectively. These values show the potential of our nanostructured passivation layers for improving the J_{sc} of a cell substantially.

4 Charge carrier transport

In most PV cells, photogenerated carriers (electrons and holes) are collected both at the front and rear side of the cell. For passivated surface with partial contacts (e.g., PERC), the carriers have to travel a lateral distance before they can be collected (Figure 5(a)), leading to spreading resistance (R_{sb}). The first PERC cells had contact area fractions of about 1% with a contact pitch of 1 mm [8–10]. In recent years, the contact pitches of PERC cells have ranged from 1 μm to 1 mm with typical contact fractions of 1.5–5% [58, 59]. By forming nanoscale contacts, our nanostructured passivation layer can minimize the distances required for lateral carrier transport.

Figure 5(b) shows the R_{sb} versus passivation area fraction calculated using the analytical 2D carrier transport model outlined in [60] and [61]. A bulk resistivity of 1 $\Omega\text{ cm}$ was assumed for this study. For microscale contacts, representative of current PERC cells, the R_{sb} climbs rapidly as we increase passivation area fraction; for 50 μm contact diameter the R_{sb} value reaches around 0.25 $\Omega\text{ cm}^2$ at 98% passivated area fraction. In contrast, R_{sb} is far less sensitive to the passivated area fraction for nanoscale contacts: nanoscale contacts with diameters ranging from 20 to 500 nm achieve more than an order-of-magnitude reduction in R_{sb} ($\approx 0.02\text{ }\Omega\text{ cm}^2$) compared to microscale contacts for 98% area passivation. These calculations highlight the

great potential our nanostructured passivation layer holds for a new generation of partially rear contacted cells.

5 Conclusions

Multifunctional, nanostructured passivation layers were fabricated in this work using a block copolymer self-assembly method resulting in three different shapes with different Al_2O_3 area fractions: a lamellae structure (48% Al_2O_3 area fraction); nanopillars (28%); and nanoholes (67%). This approach is an additive manufacturing process that does not require etching or laser ablation. Optoelectronic and optical measurements of these structures demonstrate that both surface passivation and improved photon management can be achieved for Si PV cells. Effective carrier lifetimes in the range of 115–147 μs are obtained on Si wafers with the nanostructured passivation layers, compared to less than 5 μs for unpassivated Si wafers. The highest lifetimes are achieved with the nanoholes, since they feature the largest Al_2O_3 area fraction (67%). There is still room to improve the passivation performance in the future by further increasing the Al_2O_3 area fraction and/or modifying the infiltration process to produce hydrogen rich Al_2O_3 [62].

Thicker Al_2O_3 structures with a larger area fraction yield a higher rear internal reflectance and are therefore better equipped to minimize optical losses. This is confirmed both by optical simulations and experimental reflectance measurements, wherein the nanoholes yield the highest internal rear reflectance. Simulations using the experimentally validated model were carried out on four types of contacts: Al; an Al–Si alloy; Ni–Cu; and poly-Si. These simulations confirm that, thicker Al_2O_3 structures with a larger coverage area provide the largest increase in the rear internal reflectance. Various scenarios predict potential increases in the J_{sc} of ≈ 0.9 –1.0 mA/cm^2 for Al rear contacts on Si PV cells with 170 and 50 μm

thick absorbers, respectively, and show increases of 2.1–2.9 mA/cm² for Ni–Cu rear contacts.

Future work will aim at the integration of these nanostructures into Si PV cells. Ultimately, the ability to engineer the structure of passivation layers at the nanoscale using scalable self-assembly processes offers the potential to significantly reduce the optical, recombination, and resistivity losses of not only Si PV cells, but other types of PV cells and optoelectronic devices [63].

6 Experimental procedure

6.1 Fabrication: block copolymer self-assembly-assisted oxide nanostructure formation

Self-assembled block copolymer (BCP) Al₂O₃ nanostructures were synthesized on both sides of p-type silicon float zone (FZ) wafers, with a $\approx$ 2 nm native SiO₂ on it. The thickness and the base resistivity of the wafer were 300 μ m and 85–115 Ω cm, respectively.

6.1.1 Materials

A hydroxyl-terminated polystyrene-poly(methyl methacrylate) (PS-*r*-PMMA-OH) random copolymer [60 mol% styrene, determined by ¹³C NMR, M_n = 9.2 kg/mol, PDI = 1.35 (determined by gel permeation chromatography relative to PS standards)] [13] was obtained as a sample from Dow chemical already dissolved in propylene glycol monomethyl ether acetate (PGMEA) and diluted with additional PGMEA to a 1% (w/w) concentration before use. Lamellae-forming 75 kg/mol polystyrene-*block*-poly(methyl methacrylate) (PS-*b*-PMMA; (M_n = 38–37 kg/mol; PDI = 1.08), PMMA cylinder-forming 67 kg/mol PS-*b*-PMMA (M_n = 46.1–21 kg/mol; PDI = 1.09), and PS cylinder-forming 71 kg/mol PS-*b*-PMMA (M_n = 20–51 kg/mol; PDI = 1.07) BCPs were purchased from Polymer Source and used as received. Upon self-assembly, these BCPs form morphologies corresponding to lamellae, nanopillar and nanohole structures, respectively. For film casting, all BCPs were dissolved in toluene at a concentration of 1% (w/w).

6.1.2 BCP thin film self-assembly

The BCP assembly process was conducted according to previously described methods [24]. Briefly, to promote

vertical domain orientation, substrates were grafted with the PS-*r*-PMMA-OH random copolymer, which minimizes preferential substrate wetting between the two blocks. First, a random copolymer films were spin-casted onto the substrates at 1500 rpm for 30 s. Polymer grafting to the substrates was achieved by baking on a hot plate for 5 min at 250 °C under continuous N₂ gas purging using a Wenesco hot plate. The excess ungrafted random copolymer was then removed by spin-rinsing the sample with PGMEA at 3000 rpm for 30 s. BCP was then spin-coated at a speed of 3000 rpm and thermally annealed for 5 min at 250 °C under continuous N₂ gas purging to achieve self-assembly.

6.1.3 Formation of oxide nanostructures

The Al₂O₃ nanostructures were synthesized by vapor phase infiltration approach described previously [64, 65]. Briefly, vapor phase infiltration was performed using four cycles of exposure to trimethylaluminum and water vapor (100 s each) at 85 °C in a commercial atomic layer deposition tool (Cambridge Ultratech Savannah S100) with a base pressure of <3 Torr. The chemical selectivity of Al₂O₃ deposition for PMMA moieties means that it is deposited almost exclusively within the PMMA domains. After infiltration, the polymer template was removed by O₂ plasma ashing (March Plasma CS1701F, 100 mTorr, 20 W, 300 s) to reveal alumina replicas of the self-assembled PMMA domain structure.

6.1.4 Metal deposition

To form the contacts, 100 nm thick Ni was deposited on the samples using a Temescal FC-2000 evaporation system.

6.2 Characterization

6.2.1 Lifetime measurements using photoconductance coil

The samples were annealed at 400 °C for 15 min to activate the passivation. As a note, the optimal annealing temperature is 350–450 °C [66]. The quasi-steady state photoconductance method (Sinton WCT-120) was then used for the measurement of effective carrier lifetime at the excess carrier concentration (Δn) of 10¹⁵ cm^{−3}.

6.2.2 Scanning electron microscopy (SEM)

A Hitachi 4800 SEM was used for SEM imaging on the samples. It provided the 2D morphology of the nanostructures.

6.2.3 Transmission electron microscopy

The samples were coated with carbon to protect it from any damage from the focused ion beam. STEM was used for TEM images and FTEM for the elemental maps (O_2 , SiO_2 , Si, and Al).

6.2.4 Ellipsometry

A Woollam M2000 Spectroscopic Ellipsometer was used to estimate the area fraction of Al_2O_3 and thickness utilizing an effective medium approximation. The measurement was carried out from 240 to 1685 nm wavelength at five different angles of incidence: 50° , 55° , 60° , 65° , and 70° . The acquisition time was 20 s which ensured a very high signal to noise ratio. The acquired data was fitted into optical model to estimate the area fraction using CompleteEASE software.

6.2.5 Reflectance measurement

A reflectance probe based measurement system from StellarNet is used for measuring specular reflectance. The system features a halogen lamp, and Si (shorter wavelength) and InGaAs (longer wavelength) detectors. An aluminum based mirror was used for calibration purpose and the measured data is processed using the actual reflectance data of the mirror found in the data-sheet.

Author contribution: All the authors have accepted responsibility for the entire content of this submitted manuscript and approved submission.

Research funding: This work is supported by the U.S. Department of Energy's Solar Energy Technologies Office under award number DE-EE-0007533. A portion of this research was carried out at the Center for Functional Nanomaterials, Brookhaven National Laboratory, which is supported by the U.S. Department of Energy Office of Science under Contract DE-SC0012704. This work is also supported by the National Science Foundation (NSF ECCS-1650002). Article processing charges were provided in part by the UCF College of Graduate Studies Open Access Publishing Fund.

Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

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Supplementary Material: The online version of this article offers supplementary material (<https://doi.org/10.1515/nanoph-2021-0472>).