Advanced Nano– and Micro– materials for Photovoltaics: future and emerging technologies

Chapter 11: “Multifunctional Optical Coatings and Light Management for Photovoltaics”

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Abstract (100-150 words) <Non-print Item>

In this chapter, we present a discussion of three main topics in coatings and light management for PV. First we will cover the basic principles behind light management and broadly discuss approaches that can be used to mitigate reflective losses. We build further on this topic by exploring the specific anti-reflection techniques used by PV glass and module manufacturers. Next, we explore anti-soiling coatings, a relatively understudied area until recently. We comment on the distinctly different approaches to anti-soiling coatings currently being explored by the PV community and the pros and cons of each. Additionally, anti-soiling coatings can also serve as anti-reflective coatings, providing a route to multifunctional coatings. We comment briefly on possible rich areas for new research efforts that we believe will provide a meaningful impact on solar module efficiency, reliability, and durability.

Key Words (5-10 words) <Non-print Item>

Photovoltaic, anti-soiling, anti-reflective, functional coatings, light management

1. Introduction

The most important aspect of solar energy generation is light. Light generated by the sun must travel through our atmosphere to eventually arrive at a solar module located perhaps on a roof or solar farm. Regardless of the location, if this light is unable to end its journey at the solar absorber, which is located below many layers of material in a solar module, the light will not generate power. For this reason, solar module manufacturers and researchers have strong interest in coatings and approaches that ensure the light arrives at the solar absorber with minimal losses. In this chapter we focus on two main areas for addressing this challenge: coatings, and light management, with focus on losses associated with light reflections, and soiling.

In figure 1, we provide a schematic illustration of the main components in a solar module. The cell consists of an absorber layer, which is the photoactive material responsible for generating electrical charge, and a number of electron and hole transport layers, which are responsible for charge collection. The absorber can be made from a number of materials. The most common commercial absorbers are silicon and thin film CdTe; however, earth abundant, easy to process, high efficiency materials continue to be an area of active research.[1–3] The cell is topped with an anti-reflection coating as well as electrical contacts for collecting current. The cell is laminated with a top encapsulant, the most common being ethylene vinyl acetate (EVA), and a layered backsheet material. The front “sunny” side is topped with solar glass, which is low in iron to reduce absorption losses, and can be coated with functional materials.

In solar modules, optical loss can occur when light reflects off the module components instead of being absorbed and converted into electricity. Figure 2a, illustrates the optical losses associated with absorption and reflection of light in solar module materials.[4] Reflection is a significant problem for solar modules since optical losses associated with reflection reduce the light intensity that reaches the solar absorber. With less light reaching the cell, less photocurrent is generated, reducing the overall efficiency of the solar module. Light can reflect off either the glass/air interface or the cell-encapsulant interface. In the case of silicon solar modules, polished silicon absorbers have a shiny mirror-like surface that is especially problematic. If unaddressed, reflection from the silicon and glass interfaces can decrease module efficiency by a large amount.[4–8] In figure 2a, the first bar, labelled baseline, shows how severe reflective losses can be in modules without any anti-reflection efforts; the orange sections show the total generated current in the module and the other colored sections illustrate the current losses associated with various reflections (cyan, black, and grey) and absorptions (dark blues). Added together these correspond to a relative current loss of over 9% (right axis) of the total possible current generated. The additional three bars illustrate modules that have used different anti-reflection approaches, decreasing the relative current loss to below 6% in the best case. The anti-reflective sample has an anti-reflective coating (ARC) applied to the airside of the top glass to reduce reflection at the air/glass interface; the physics of this approach will be discussed in detail below. The thin glass (TG) sample uses a thinner solar glass to reduce absorption, and the polyvinyl butyral (PVB) reduces absorption in the encapsulant, both increasing the amount of light that can reach the solar absorber (see figure 2). This shows how important anti-reflection coatings and light management are to producing devices with optimized efficiencies.

Another challenge for light absorption in solar modules is the accumulation of material (dirt, sand, etc.) onto the surface of solar cells, known as soiling. The origin and chemical composition of this soil can vary dramatically based on the location of the module. This soiling can reduce module performance in excess of 30%.[8–11] A demonstration of this reduction is shown in figure 2b. Here the energy output of two solar modules is shown over the course of a year.[12] One module (blue) was periodically cleaned, showing a recovery of the energy output. The other module (gray) was left dirty, resulting in a severe reduction in energy output (cross hatched region). Another challenge is that soiled cells can be difficult or impossible to clean when dirt begins to bind or cement onto the surface of the module. In addition, the labor and water resources used to clean PV modules are costly. The burden is especially large in desert regions where sands storms are frequent and water resources are minimal. Anti-soiling coatings (ASCs) may provide a solution; however, designing anti-soiling coatings is a challenge because many factors such as heat, light, moisture, and soil composition can influence soiling mechanisms.[13–15] Additionally, the durability of the coatings can be a challenge, as these thin film materials must be resistant to abrasion associated with cleaning the modules.

In this chapter, we present a discussion of three main topics in coatings and light management for PV. First we will cover the basic principles behind light management and broadly discuss approaches that can be used to mitigate reflective losses. We build further on this topic by exploring the specific anti-reflection techniques used by PV glass and module manufacturers. Next, we explore anti-soiling coatings, a relatively understudied area until recently. We comment on the distinctly different approaches currently being explored by the PV community and the pros and cons of each. Additionally, anti-soiling coatings can also serve as anti-reflective coatings, providing a route to multifunctional coatings. We comment briefly on possible rich areas for new research efforts that we believe could provide a meaningful impact on solar module efficiency, reliability, and durability.

2. Light management

As discussed in the introduction, solar modules are made of many different materials, layers, and interfaces. Unfortunately, each of these have the potential to reflect light away from the module, resulting in decreased module efficiencies. In order to mitigate the losses associated with light reflection, it is important to understand a few basic fundamentals of the way light behaves when it encounters an interface, in particular, the reflection and refraction (or transmission) of light at these interfaces. For solar modules there are a number of interfaces to consider: air/glass, glass/encapsulant, encapsulant/cell, etc. and these interfaces can vary depending on module and manufacturers. In the later sections of this chapter we will explore how light management can be implemented at a number of these interfaces and show how some interfaces are better suited for different approaches such as texturing or multilayer coatings.

In this section, we will focus on a fundamental understanding of the interaction of light at interfaces by discussing two simplified case studies for understanding reflection. First we will discuss how light interacts with a single interface (air/glass, figure 3a). Next we add another layer to create a two interface system (air/glass/silicon, figure 3b) and discuss which factors are most important to consider when designing anti-reflective layers and coatings. Finally, we discuss how materials properties of the layers can be tuned to reduce reflections. Note that multiple interfaces are a straight forward, but messy extrapolation from two interfaces, due to the number of mathematical terms needed to describe all of the layers. To simplify these calculations Demir and Elsherbeni have developed a GUI for use with MATLAB (program package available at http://www.aces-society.org/software.php).[16]

As light propagates through a material and eventually encounters an interface, the behavior of light is dictated by the index of refraction (*n*) of the two materials. To understand this phenomenon one can draw a simple picture (figure 3a), here the incident light meets the interface and some fraction of light is reflected (*R*) and the remaining light is refracted or transmitted (*T*), which leads us to $R = 1-T$. For solar modules the reflected light (*R*) needs to be minimized, as every photon reflected is not absorbed by the cell resulting in a decrease in efficiency. Note, the approach described in this section ignores other optical effects such as scattering and absorption. The Fresnel equations are used to calculate the reflectivity at an interface (*r*) which is related to the total intensity of reflection (*R*) by $R = r^2$. The Fresnel equations are dependent on the complex refractive index for each layer ($n + ik$) and the incidence angle of the light (θ_i), which determines the angle of refracted light (θ_g), given by Snell's law ($n_{air}*\sin\theta_i = n_g*\sin\theta_g$). For simplicity, here we consider $k = 0$; including more realistic absorption is straightforward. The reflectivity is dependent on the light polarization – either parallel (*s*) or perpendicular (*p*) orientation of the electric field with respect to the plane of incidence on the sample. The equations describing the reflection at the interface in figure 2a are:

$$r_p = \frac{n_{air}cos\theta_i - n_g cos\theta_g}{n_g cos\theta_i + n_{air}cos\theta_g}\ ; r_s = \frac{n_g cos\theta_i - n_{air}cos\theta_g}{n_g cos\theta_i + n_{air}cos\theta_g} \quad \text{(equation 1)}$$

Adding another interface to this picture brings into focus the basis for anti-reflection. Figure 3b, illustrates a material with two interfaces, consisting of the air/glass interface that would be on the top or "sunny" side of the module and the glass-silicon interface between the cell and the top glass. Note, this picture is a simplification of the solar module; however, the general concepts can also be applied to more complex systems. The two interfaces in figure 3b result in two reflected waves r_1 *and* r_2 from each interface, with the total reflected intensity equal to R_{Total}. In order to reduce reflection (minimize R_{Total}) r_1 and r_2 should interfere out of phase. The condition for this interference with the layers illustrated in figure 3b is given by:

$$2n_g d * \cos\theta_g = \left(m - \frac{1}{2}\right)\lambda \text{ (equation 2),}$$

where n_g is the index of refraction of the intermediate layer, in this case glass of thickness d, θ_g is the angle of refracted light in the glass, m is an integer, and λ is the wavelength of incident light. Taking into consideration equation 2, it is clear that the anti-reflective properties of a coating are dependent on the wavelength of light and the incidence angle onto the solar module. Since solar radiation consists of a wide range of wavelengths and can reach the module surface at a variety of angles, anti-reflection coatings must be carefully optimized. The strategy for this optimization will be discussed in section 3.2.

To further understand how the materials properties influence reflection, we will explore reflectance under one set of conditions, where the reflected waves are out of phase and destructively interfere:

1. The optical thickness of the glass meets the "quarter-wave" film conditions, $n_g*d = \lambda/4$ and
2. The light strikes the surface at normal incidence, $\theta_i = 0$; therefore, the refracted angle $\theta_g = 0$.

These conditions are relevant to operation of the solar module because the light arriving at normal incidence to the module produces the highest power output. Because of this, minimizing reflections at normal incidence will improve the efficiency of the module. Additionally, at normal incidence the Fresnel equations (1) simplify (*s* and *p* polarization are the same). Solving for the total reflected intensity R_{Total} for the top interface, we arrive at:

$$R_{Total}(1) = \left[\frac{n_{air} - n_g}{n_{air} + n_g}\right]^2 \text{, for 1 interface (equation 3)}$$

$$\text{and } R_{Total}(2) = \left[\frac{n_{air}n_{Si} - n_g^2}{n_{air}n_{Si} + n_g^2}\right]^2 \text{, for 2 interfaces (equation 4)}$$

Where, n_{air}, n_g, and n_{Si} are the refractive indices for air, glass, and silicon respectively. Using these equations and the index of refraction of air (1), glass (1.5), and silicon (3.8) at λ = 680 nm, we calculate the reflection intensity at the first interface (glass/air) to be 4 %. When we determine the reflection intensity for the stack illustrated in figure 3b, we see the reflection from the silicon/glass interface is much worse (18.8%) than the air/glass interface (4%), resulting in a 6.5 % total reflection for the full stack. This observation leads us to an important relationship to consider when determining which materials should be used to minimize reflections. If we take R_{Total} = 0, which would be completely anti-reflection, and solve equation 5 for the index of refraction of the glass (n_g), we find a relationship that identifies the ideal scenario for the materials indices of refraction, at normal incidence (θ = 0) and quarter wave conditions ($n_g*d = \lambda/4$):

$$n_g = \sqrt{n_{air} * n_{Si}} \text{ (equation 5)}$$

The important conclusion from this is that the material between two layers should be intermediate in index of refraction of the two outer layers.

Using these principles one can design materials to reduce reflection from surfaces. One approach is to create multilayers with varying indices of refraction between each layer. Another approach is to create a rough surface to change the incident angle of the incoming light. Each of these approaches will be discussed in further detail in the following sections.

3. Anti-reflection Coatings

Anti-reflection coatings (ARCs) are found at two interfaces in PV modules: the silicon/encapsulant interface and the top air/glass interface. Though coatings can be designed for both interfaces, using the principles described above, anti-reflection coatings are only common in current industry standard PV modules at the silicon/encapsulant interface. Top-surface, air/glass interface coatings are more challenging to design because the anti-reflection coating must be stable in the face of direct sunlight and environmental exposure. In addition, as calculated above, the reflection at the glass/air interface is minimal (only 4%) as compared to the reflection losses at the silicon/encapsulant interface, which is approximately 19% when using EVA (n=1.495) as the encapsulant.[17] Therefore, the PV industry focuses on reducing reflection at the silicon/encapsulant interface. Reducing reflection at this internal interface is achieved with a two-pronged approach. The first aspect is to add a planar anti-reflection coating on top of the silicon. The second aspect is to change the surface morphology of the silicon. These two tactics to combat reflection losses at the silicon/encapsulant interface will be the initial focus of this section. Multi-interface approaches combating reflection at both the air/glass and silicon/encapsulant interfaces will be discussed in sections 4 and 5 of this chapter.

3.1 Planar anti-reflection layer at the silicon/encapsulant interface

As mentioned in section 2, the reflected light lost from the silicon/encapsulant interface of a PV module is significant (19%). As such, in the PV industry it is standard procedure to reduce the reflection from the silicon wafers by depositing a layer of silicon nitride (Si_3N_4) on the top surface of the wafers. The incident light interacts with the Si_3N_4 layer in the same way as the glass layer in figure 3b. Like figure 3b there are three layers creating 2 interfaces, but instead of the layers consisting of air/glass/silicon, they consist of encapsulant/Si_3N_4/silicon (see figure 1). The Si_3N_4 coating functions as a “quarter-wave film”, causing reflected rays of light from the encapsulant/Si_3N_4 interface and the Si_3N_4/silicon interface to destructively interfere. As the name “quarter-wave” suggests, the optical thickness of the Si_3N_4 layer needs to be ¼ the wavelength of the incident light, $n_{Si3N4}*d = \lambda/4$ (see section 2) (n_{Si3N4} is the Si_3N_4 index of refraction). For PV applications, the incident light is generated by the sun and is described by range of wavelengths, known as the solar spectrum. Since the quarter-wave anti-reflection coating can only optimize the transmission of light for one wavelength (see equation 2), manufacturers typically choose the wavelength where solar cell quantum efficiency peaks. The solar quantum efficiency describes how efficiently the absorber layer converts sunlight into electricity at a given wavelength. For commercial modules with a silicon absorber layer the peak in the solar quantum efficiency occurs at a wavelength of 550nm. Therefore, the Si_3N_4 anti-reflection coating is typically designed to optimize the transmission of 550 nm light.[18]

In most commercial PV modules, the Si_3N_4 layer is grown via plasma-enhanced chemical vapor deposition. Other coating materials, such as TiO_2 and SiO_2, have been explored as anti-reflection coatings, but the Si_3N_4 improves other areas of cell performance and hence is widely used.[5] For example, the Si_3N_4 also provides a surface well-suited to creating good Ohmic contact between the metal contacts (figure 1) and the silicon absorber layer. Also, during the heating cycle, which is necessary for contact formation, the contact material is able to etch through the Si_3N_4 anti-reflection layer and interface directly with the silicon absorber layer.[5,19] Potentially the most important role of the Si_3N_4, is that it effectively passivates the silicon surface. By passivating the silicon surface, the Si_3N_4 decreases the recombination of photogenerated electrons and holes, thereby improving cell quantum efficiency.

3.2 Complex architectures

As discussed in section 3.1 above and equation 2, a single anti-reflection layer, like the Si_3N_4 layer, is optimized for a single wavelength of light, with an incident angle of zero. One approach to broadening the wavelengths where there is minimal light reflection is to expand from a single layer (figure 4a) to multiple anti-reflection layers (figure 4b). Using multiple layers, each with a different index of refraction, increases the number of interfaces where rays of light interact. The improvement of multi-layer ARCs over a single layer can be seen in figure 4e. While a ray tracing computation for a single wavelength of light and a single layer of material is simple(section 2), the optimization of thickness and refractive index for multi-layer coatings for broadband anti-reflection is often done computationally.[16] With good control over both refractive index and layer thickness in a multilayer coating, broad-band ARCs can be achieved.[5,20] One approach to multi-layer ARCs is to create a stepwise gradient in the refractive index between the encapsulant/silicon interface. This can be achieved by varying the layer composition so that each subsequent layer has a refractive index progressively closer to that of the substrate (figure 4b). An effective example of this approach is seen in in the work of Kuo et al.[20] (figure 5), who used 7 layers with various compositions of silica and titania to create a multi-layer ARC on the surface of silicon wafers. This multi-layer coating out performs the single film approach at most wavelengths, including the important 550nm, but especially in the 800-1000nm range (figure 5b).

Looking to nature, we see a different approach to anti-reflection which depends not on layers, but on microstructure. The eyeballs of a moth are made up of sub-wavelength (~100nm) parabolic structures, see figure 4d. These parabolic structures reduce reflection almost perfectly across the full spectrum of visible light (figure 4e).[21] The key to the functionality of the moth's eyeball comes from the parabolic structures which 1) create a parabolic gradient in the refractive index (figure 4d) and 2) create a patterned surface texture that enables multiple internal reflections (figure 6b, see section 3.2.2). While the complexity in the microstructure of the moth's eyeball prohibits the PV field from copying the blueprint of nature, the governing properties of the moth's eyeball can be used to inspire ARC design.

3.2.1. Gradient in the refractive index

Creating a refractive index gradient removes abrupt interfaces where light can reflect. Instead, as first described by Rayleigh, a smooth gradient in the refractive index encourages light to bend rather than reflect (e.g., basically continuous refraction, see figure 6a). Because gradient ARCs lack abrupt interfaces, their exact thickness is less important than in quarter-wave ARCs. In addition, they can be more broadband than quarter-wave ARCs.

Multiple approaches to achieving gradient interfaces have been explored for PV applications. As mentioned in the discussion of multi-layer ARCs above (section 3.2), the group from Rensselaer Polytechnic Institute used a seven layer stack, with various compositions, to create an approximate gradient-like ARC for a silicon PV device (figure 5).[20] This approach demonstrated good broadband transmission. However, for light to fully bend rather than reflect, a much larger number of layers would be needed to achieve a uniform gradient. Furthermore, even depositing seven layers is likely cost-prohibitive for the larger PV module industry.

Another approach to creating a gradient in the refractive index of a film is to tune the microstructure. The key is to make the features that define the morphology of the film, such as pyramids (figure 4c) or parabolas (figure 4d), smaller than the wavelength of the incident light. When light is incident upon features which are small enough, such as the parabolas of a moth's eyeball, the refractive index experienced by the light is a linear combination of the parabolas and the surrounding air. The parabolic shape results in a quadratic increase in the average density of the eyeball as a function of depth. In turn, there is a parabolic increase in the refractive index (figure 4d). In the case of simpler pyramid structures, the change in the average density is linear with depth, and thus the average refractive index is linear with depth (figure 4c).

In commercial PV modules, silicon wafers are etched after they are cut from a larger single crystal (figure 7a). This etching process leaves behind pyramid structures (see figures 7a and b).[22] The tips of these pyramids creates a refractive index gradient at the interface and reduces the tendency of light to reflect from the silicon/encapsulant interface. The average size of these pyramids is close in size to the wavelengths of sunlight so while the smaller pyramids and the tips of the pyramids will be experienced as gradients by the longer wavelengths, the majority of light will likely scatter off of the pyramids. The larger role of these pyramids is to act as a rough interface which increases internal reflections, as we expand below in section 3.2.2.

The final approach to creating a coating with a refractive index gradient is to slowly changing the porosity or packing density of the coating. This approach shows promise for reducing reflection at the glass/air interface. Silica colloids can be packed to form a density gradient at the glass surface. This approach is especially promising for glass/air interface ARC on PV modules because silica colloids are stable in the face of most weather-related stressors.[18]

3.2.2. Patterned/rough interfaces

In the previous section, we considered the situation where the microstructure feature sizes were small (e.g., <100 nm) compared to the wavelength of light and so the refractive index was well approximated by an average of the microstructure index and the surrounding air. Below we consider the opposite situation, where the microstructure sizes are much larger than wavelength of light. Here light is treated as rays that both reflect and refract as they interact with a microstructure. The important (and perhaps more relevant) case is where the wavelength of light and the microstructure feature sizes are similar. This regime is more complicated and cannot be accurately described by either of these approximations. Advanced computational methods can assist in designing and understanding these types of structures, see Sec 5.

Here we consider an additional functionality of the structure of a moth's eye ball. In addition to creating a gradient in the refractive index, the parabolic structures of a moth eyeball also facilitate light trapping by creating multiple reflections within the interior structure (figure 6b). Light reflected off the sides of the parabolas will, on average, reflect further into the eye, trapping the light and decreasing overall reflection (figure 6b). While the patterned parabolic structures of the moth's eye are especially effective at light-trapping, even a random rough surface will increase the average number of times an incoming beam reflects before it escapes. In the case of a pyramidal surface (figure 7c), light which approaches at normal incidence angle (θ_i = 0) will reflect off the first pyramid and into the second pyramid. Thus, light has increased opportunities to be absorbed when incident on rough surfaces.

As seen in equation 2, section 2, reflection is dependent on the angle of the incident light (θ_i). Grazing angles, where θ_i is greater than 45°, tend to reflect light more strongly. This means that for a flat solar absorber layer (figure 7c, top), the transmitted or refracted light (blue dashed arrows) is less when the incident sunlight approaches at a shallow angle. In a rough or patterned surface, like the pyramids of an etched silicon wafer (figure 7c, bottom), light that approaches the solar module plane (black line) at a grazing angle becomes roughly orthogonal to pyramid surface. Therefore, grazing incidence light is reflected less on rough surfaces.

The PV industry's current state-of-the-art in commercial modules uses roughness to further increase light-absorption in the silicon active layer. The roughening of the silicon surface is induced by etching the wafers with NaOH or KOH (figure 7a).[22] Initially when the wafers are cut, the flat (100) plane is exposed but, because the etch-rate is crystal plane-dependent, the {111} planes of silicon become the top surface after the wafer is exposed to the etchant. Because the {111} planes run at an angle to the (100) planes, when they are exposed, a surface of pyramids is created (figure 6a). As with the Si_3N_4 layer, the etching step provides a dual purpose; etching also works to clean up the silicon wafer after it has been sawed from the bool.

3.3. Synthesis challenge

If the moth's eyeball morphology was easy to synthesize, a near perfect ARC could be made. However, nano-scale parabolas are quite difficult to replicate. For commercial applications, synthesis needs to be as simple and inexpensive as possible. A challenge for researchers is to capture as much of the functionality, described in the sections above, as possible without needing a laborious synthesis process. The current synthetic approaches to ARCs can be divided into top-down and bottom-up methodologies.

Top down methods create microstructure by taking away material. This can be done either with a chemical medium, which etches away the surface, or with lithography, which uses stamping or lasing, to pattern the surface.[5] The **bottom up** method changes the surface by growing a new materials on top of the surface. The bottom up approach is primarily used for the simpler one layer quarter-wave ARC which can be deposited as a film. Films can be deposited through a solution based method, such as spin- or dip-coating or by a physical vapor deposition method like sputtering.[5,23]

4. Anti-soiling

As discussed in the introduction of this chapter, the deposition of dust and other particulates onto solar modules, known as soiling, can result in substantial efficiency losses over the lifetime of a module. In this section, we will focus on the mechanisms behind soil adhesion, and define the different layers of dirt that form. We will also present the different approaches currently being explored to mitigate the impact of soiling on PV module performance. The approaches used to prevent soiling vary widely and there is little agreement in the current literature about the best approaches. However, the composition of dirt and other soiling material is significantly different across geographies and climates where PV modules are deployed. For this reason, different approaches to anti-soiling are needed in different parts of the world. Thus, we present a broad look at efforts to combat soiling of PV modules.

It is important to note that most anti-soiling coatings are multifunctional and provide some level of both anti-soiling and reduction in reflection at the air/glass interface. As discussed above, the reflectivity loss at the glass/air interface is small when compared to the loss at the silicon/encapsulant interface and thus, most commercial PV modules today do not employ top surface ARCs. However, multifunctional coatings, which provides both anti-soiling and anti-reflection functionality, can further increase the value of a glass-surface coating.

4.1. Adhesion Mechanisms

Electrostatic and Van der Waals forces, as well as chemical bonding, all play a role in soiling. [14] Electrostatic forces are long-range interactions that increase the amount of soil which adheres to the module surface by attracting soil from the air.[24–26] As soil is carried on the wind, it becomes charged. In addition, PV modules operate at high voltage, and thus the module surface can also be charged. The interaction between charged soil and the charged PV module attracts soil from the air onto the module surface. Electrostatic attraction continues to play a role in the adhesion of soil until it is dissipated or screened by other species on the module surface.[27] After soil deposits onto the top of the modules, van der Waals forces and chemical bonding become important. Van der Waals forces bind physisorbed soil particles.[14] These are the weakest forces that significantly influence soil dynamics and they require that particles are very close to the binding surface. Once there is physical contact with soil particles, the strongest sticking force, chemical bonding, begins to occur. Chemical bonding is increased by the presence of light and heat. These energy inputs are inherent in PV operating conditions and as such, chemically bonded dirt is a significant problem for PV modules.

4.2. Soil Layers

Soil which has built up on a surface can be roughly classified into three layers.[27,28] Figure 8a shows a schematic approximating these three layers. Note that this model of soiling is an oversimplification; ordinarily, soiling layers build up over time, with continual deposition, and not as completely uniform layers. However, this schematic is a good conceptual model for discussing the complex soiling process. Since the presence of all three layers at any one point on a module surface is not guaranteed, the layers in figure 8a have been drawn with only partial coverage. Note that no layer contains particles with a diameter greater than 50 µm, since bonding strength with particles that large is weak, compared to gravity, and they easily roll off the tilted PV module surface and/or are removed by wind.[25] In figure 8a, layer A, is the green layer closest to the blue module surface and forms as a result of chemical reactions with the surface and, as such, is described as the chemisorbed layer. Chemical bonding is the strongest force at play in soiling and thus layer A has the strongest attachment of the layers.[14] It can only be removed by abrasive scrubbing, which can damage the module surface. Layer B, the purple middle layer in figure 8a, is bonded to green layer A and has a highly organized packing structure. Adhesion of layer B is governed by electrostatic forces. The bonding strength within layer B is strongest closer to layer A, and decreases continuously until it is fully screened and the final type of soiling, layer C begins. Since smaller particles have a higher surface to volume ratio, and therefore greater surface charge, they are more quickly pulled to the surface by electrostatic forces, resulting in a particle size gradient in layer B. The smallest light purple particles are located closer to the green layer A, with a gradual increase in size closer to the orange layer C. Layer B can be organized in this way because it forms during the process known as cementation, which is described in more detail below. Layer B is resistant to rain but can be removed by washing or adhesive tape. Lastly, the orange layer C has the weakest bonding to the surface; it is chemically inert and is only attached by van der Waals forces because electrostatic forces are screened by layer B. Layer C can be removed naturally by rain. It is also important to note that even though layer C has the weakest bonding to the surface, the van der Waals forces are strong enough that even layer C is resistant to removal by wind. Even hurricane force winds are not strong enough to remove this soil.[15]

4.3 Cementation

We explain here why Layer B (figure 8a, purple) is a key contributor to PV related soiling losses. Above we described that the organization of particles in this layer occurs through the process known as cementation. A diagram of this process is shown in figure 8b.[11] Soil particles are composed of both soluble and insoluble, as well as organic and inorganic components.[25] The organic components, often organic molecules, primarily make up the chemisorbed layer A. When water interacts with soil particles on a surface, the soluble components dissolve in the water and a salt solution is created, with insoluble particles suspended in this solution. Each time the water evaporates, the soluble salt is also left behind and anchors the insoluble particles to the surface. Because the insoluble particles can move freely during this suspension process, a mature cementation layer can be highly organized. Each time the module is exposed to water, the insoluble particles are suspended in solution and can move within the layer. During this suspension, electrostatic forces come in to play, pulling the smaller particles closer to the surface than the larger particles. This is because smaller particles have a larger surface to volume ratio and so they have more surface charge per volume. Thus, smaller insoluble dirt particles are more strongly attracted to the charged module surface. After multiple cycles of moisture exposure, a mature cementation layer resembles the one depicted in figure 8, where the average size of the light purple particles is smaller close to the blue module surface.[13,27] The group of Ilse, et al., found that, following cementation, insoluble soil particles are connected to their glass substrates by small, needle-like salt structures.[13] As the cycling of dissolution and evaporation happens, more and more over time, a layer of tightly packed and tightly bound particles forms on the surface. This cement-like layer is very difficult to remove from the solar module surface after it has formed. Preventing this detrimental cementation is a strong motivator for the design of effective anti-soiling coatings.

4.4 Coating Design Rules

While soiled PV modules can often be manually cleaned and some types of soiling (section 4.2, layer C) can be washed off with rain, soiling is still a significant problem.[27] Anti-soiling coatings, on the top-surface of solar modules, are being developed as a solution to the problem. However, as sections 4.1-4.3 outlined, soiling is a complex process with many forces at play. Here we outline current approaches to developing anti-soiling coatings that address the problem from several angles.

4.4.1 Microstructure

Current research often focuses on how the microstructuring of a coating can influence soil deposition. Microstructuring can be a very effective tool to combat soiling since it limits the area available for intimate particle/coating contact. The value of morphology in preventing soiling is seen in nature; leaves, most famously the lotus leaf, avoid soiling by growing microstructurally rough surfaces.[18] The lotus leaf surface is covered with micron sized bumps, which are in turn covered with nanometer-sized bumps (figure 9a).[29,30] This morphology can discourage the formation of layer C-type soiling because dirt particles perch on the peaks of the microstructure and have very little direct contact with the coating and thus the van der Waals attractive force to the coating is weak. Indeed, work by Glaubitt et al found that coatings with two-tiers of microstructure made the most effective ASCs.[18]

In addition to limiting van der Waals bonding, the lotus leaf morphology also makes the surface hydrophobic. The detailed, two-tiered microstructure causes water to bead up into droplets. In turn, water has almost no contact with a lotus leaf's surface. Hydrophobic surfaces can also be made by controlling the chemistry of a film. Coating surface chemistry plays an important role in soil accumulation. There are several schools of thought and it is under debate as to which surface chemistry is best for ASC development, as discussed below.

4.4.2. Low Surface Energy

One approach to anti-soiling coatings is to create materials with low surface energy, i.e. hydrophobic. The goal is to reduce soil-to-surface interaction strength. If the surface energy of a coating is low, then the interaction with soil particles will be weak. As a result, only particles with very high bonding strength will stick (either through chemical bonds or strong electrostatic interactions) to the surface.[31] Low surface energy coatings are also described as self-cleaning. Because these coatings are hydrophobic, water droplets on the surface form ball-like structures that are mobile. Most often solar panels are tilted, and thus rain can bead up and easily roll down the hydrophobic surface, collecting dirt, and rolling off the solar module (figure 9a). Researchers at Arizona State University tested the role of tilt angle in self-cleaning by comparing modules that were consistently cleaned or untouched, each at various tilt angles, over a 3-month period.[31] The most significant effect was seen in the panel tilted to 40°: only 0.69% loss in efficiency was recorded vs. a 2.02% loss in efficiency of the module held horizontally. This suggests that a greater tilt angle can be combined with a hydrophobic coating to improve the self-cleaning effect.

Given that solar panels are typically placed on a south facing incline to capture more of the sunlight at an incident angle orthogonal to the panel surface (see sections 2 and 3.2.2), low surface energy self-cleaning coatings, which shed rain and dirt, show strong promise.[12] Furthermore, low surface energy coatings may be effective even in areas without rain because strong chemisorbed bonds (layer A) will be difficult to form and cementation (layer B) will not form without rain.

4.4.3. High Surface Energy

The second major approach for anti-soiling coatings are those with a high surface energy, making them hydrophilic. A major benefit from a hydrophilic coating is an improved cleaning efficiency; water that is on the surface spreads easily to cover a large portion of the surface (figure 9b). This means that less water is needed to coat/wash a hydrophilic coating than a hydrophobic coating. This enhanced coverage provides greater water-to-soil contact per water droplet than a hydrophobic coating and thus limits the amount of water needed during cleaning.[24] As with the hydrophobic surfaces, cleaning is enhanced on a tilted surface.[12]

Additionally, in a humid environment a thin layer of water can form across the face of a hydrophilic coating (figure 8b). This creates a barrier, preventing soil from reaching the module surface and becoming bound. This water protection layer may be especially beneficial for reducing cementation. As described in section 4.3 and figure 8b, the precipitated salt solution sticks the insoluble particles to the module surface. If even a thin layer of water is maintained on the surface, the salt can dissolve above the ASC and will be unable to create a bridge between the module and the insoluble dirt particles.

The layer of water on the surface of hydrophilic ASCs also acts to delocalize the surface charge of the module (figure 8b). Water has a large dielectric constant and thus is highly effective at screening electrostatic charge. This means that there is less electrostatic attraction of dirt particles on PV modules with a hydrophilic anti-soiling coating and thus less dirt accumulates.[26] The effect of a hydrophilic ASC to screen electrostatic charge was demonstrated by a group at the University of Miyazaki.[26] The electrostatic potential of a bare substrate and a coated substrate was measured during a soiling study where silica particles were used as the soiling material. After soiling, the electrostatic potential of the uncoated substrate reached a maximum of 0.25kV while for the coated sample it was suppressed to 0.10kV. In addition, after soiling, the mass of sand attached to the uncoated substrate was more than two times that attached to the coated substrate.

4.4.4. Photocatalytic Coatings

It should be noted that low surface energy and high surface energy are mutually exclusive properties. In contrast, the introduction of a photocatalytic self-cleaning mechanism could be incorporated into either a low or a high surface energy coating. The photocatalytic effect takes advantage of the fact that coatings can be made semiconducting in order to absorb some of the incident light and use the resulting electrons/holes for breaking down bound organic soiling molecules which make up layer A (figure 8a). The most common material in photocatalytically active anti-soiling coatings is TiO_2.[32] Short wavelengths are absorbed by the coating and excite electrons into a higher energy state, leaving behind holes. Most of the time, electron-hole pairs simply recombine and don't result in any cleaning effect. However, electrons and holes can migrate to the surface of the coating. Once there, holes can oxidize organic soil on the surface (layer A) and electrons can interact with oxygen, creating an unstable radical. This radical can rapidly attack nearby organic molecules in soil layer A. The products of these reactions are typically carbon dioxide gas and water (with occasional heteroatoms from the reactants), which will not contribute to the soiling layer. One of the challenges to this approach is that the light which is harnessed to break down the organic soil molecules is not used by the solar cell. However, a photocatalytic coating could be a promising approach to ASC if the wavelength of light harnessed by the coating was in a range of wavelengths where the solar absorber layer had poor quantum efficiency.

5. Advanced Research Areas

In section 3, we focused on the anti-reflection coating techniques currently used in commercially produced silicon-based PV modules: application of a Si_3N_4 quarter-wave film and chemically-etched silicon pyramids. As the PV field continues to evolve and different module architectures, possibly involving different solar absorber layers, enter the field, light management techniques will also need to evolve. Below we describe some of the new and emerging approaches to light management.

5.1. Modeling

Highly-tuned materials such as multi-layer ARCs can reduce reflection effectively over a wide range of wavelengths[20] and patterned surfaces can create up to 15 times more internal reflections than a flat surface[33]; however, these materials have highly inhomogeneous surfaces. These inhomogeneities make precise calculation of refractive indices of materials in these complex ARCs extremely challenging and prevent using the simple approach for understanding reflections described in section 2. Therefore, computational modeling is often used to determine the optimal balance of refractive index, layer thickness, and pattern design. A common approach to dealing with these complex structures is the Effective Medium Theory (EMT) or Effective Medium Approximations (EMA). Two mathematical models are most commonly used in EMT to calculate the effective refractive index in complex ARCs: Maxwell-Garnett[34,35], and Bruggeman[36,37]. EMT is an approximation method; therefore, as new more complex ARCs are envisioned a more rigorous analysis may need to be developed. The rigorous coupled wave analysis (RCWA) has been demonstrated to be very successful at calculating the reflectance spectrum of complex structures similar to those shown in figure 6b.[38] Thus, as advances in manufacturing allow for more complex structures to be realized, the community can take advantage of computational modeling to predict better performing new ARCs.

5.2. Plasmon enhanced

In order to further increase the amount of light absorbed by the active layer of the PV module, recent work has explored the use of plasmonic structures. Plasmonic structures are typically nano-scale metal particles that can both concentrate and guide the light that interacts with them. By using plasmonic structures, light can be concentrated into optically thick, but physically thin, solar absorber layers. Work from the group of Martin Green has demonstrated the use of silver nanoparticles grown on the surface of thin film silicon absorber layers to improve light trapping and increase light absorption across the solar spectrum.[39] By tuning the size of the silver nanoparticles, light absorption was improved up to 16-fold at certain wavelengths. Work is also being done to not only concentrate light, but to guide incident light into travelling along a metal-nanoparticle/solar-absorber-layer interface.[40] Plasmonic structures provide a new approach to light management and may become especially important for application with very thin absorber layers, such as for light-weight PV modules.

6. Conclusions

Anti-reflection coatings are a crucial component to improving the efficiency of solar energy harvesting. While significant progress has been made in combating the reflection of light at the silicon/encapsulant interface, including commercially successful techniques, durable anti-reflection coatings at the air/glass interface still need to be developed and vetted. Most likely, a successful air/glass coating will combine both anti-reflection properties and anti-soiling properties. However, a deeper understanding of how coatings can inhibit soiling is needed. Furthermore, more research is needed to test the durability of top-surface coatings to guarantee their long-term functionality as both anti-soiling and anti-reflection coatings. As the demand for coatings that combine both anti-reflective and anti-soiling functionalities has increased, research to address these research challenges is still in progress and represents a potentially rich area for future innovation for the photovoltaics communities.

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Figure Captions:

Figure 1. Schematic illustration of a solar module. This simplified diagram ignores additional module components, such as edge seals, interconnects, etc.

Figure 2. a) Calculated generated photocurrent density and reflection and absorption losses for a series of PV modules (left axis). The right axis provides the relative current losses in percent. The baseline, anti-reflective coating (ARC), thin glass (TG), and polyvinyl butyral (PVB) cases are shown.[4] b) Energy output of solar modules with (blue) and without cleaning (gray), illustrating the potential losses associated with soil deposition onto solar modules.[12]

Figure 3. Schematic illustration of interface structures a) 1 interface between air and glass b) 2 interfaces air-glass, and glass-silicon. Where n is the index of refraction for the given layer, *d* is the layer spacing, R_1 or R_2 is the reflected light intensity, θ is the angle of light, and λ is the wavelength of light.

Figure 4. Illustrations of anti-reflection coating-morphologies alongside cartoon graphs of the resulting depth (*d*)-dependence of the index of refraction (*n*). (modified from [41]) a) single layer quarter-wave film b) multi-layer film c) pyramids d) moth's eye parabolas. The final panel e) illustrates the resulting transmission of light as a function of wavelength for each of the four structures illustrated above, as compared to uncoated silicon.

Figure 5. a) TEM image of multilayer ARC with step-wise gradient in the refractive index b) Measured total reflectance spectra for bare silicon (red), quarter wave film (green) and multi-layer ARC (blue)[20]

Figure 6. a) Illustration of how a gradient refractive index promotes light bending rather than light reflection b) Illustration of the parabolic structures, seen in the moth's eyeball, and how light (red arrows) participates in multiple internal reflections and is guided further into the eye by the parabolas. The multiple reflections essentially trap the light; very few rays are able to reflect up and out of the eye. (modified from [5])

Figure 7. a) Silicon single crystal wafers begin with the (100) face exposed. After the wafers are etched in a NaOH solution, the {111} planes become exposed and give the wafer the surface morphology seen in the SEM image in b).[22] c) Illustration of how roughness promotes increased absorption through light-trapping. In a flat surface, light which approaches at low-incident angles results in less transmitted light (thin blue arrow). In contrast, for a rough surface, when light approaches the PV module surface at low-incident angles, the light becomes orthogonal with the microstructure surface and can undergo multiple internal reflections (blue arrows). In addition, light which approaches at a normal incidence to the module (1, red arrow) reflects back into the microstructure (2, green arrow) and has a second opportunity to be absorbed.

Figure 8. a) Schematic of the three classes of soiling layers. Layer A (green) is chemisorbed to the module surface (blue). Layer B is a gradient of particles (light purple circles), with the smallest, most tightly bound particles closest to layer A. Layer B is held on by electrostatics. The end of layer B is defined by the point at which all electrostatic interactions are effectively screened and thus layer C (orange) is solely bound by Van der Waals forces. b) Illustration of the cementation process which results in the formation of layer B of figure a.[11,15]

Figure 9. a) Hydrophobic "self-cleaning" coating where water molecules roll off the surface collecting soil particles. In this example, the hydrophobicity is created with the two-tiered microstructure as is seen on a lotus leaf. The water droplet perches on the peaks of the microstructure and thus has very little contact with the coating itself. b) Hydrophilic "anti-soiling" coating where a spread out layer of

water forms over the surface and prevents soil particles from coming in contact with the surface and binding. (modified from [29]).

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