

Dielectric coatings: agents for passivation and anti-reflection

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ABSTRACT

The key to delivering highly efficient solar cells is to absorb as much light as possible from the solar spectrum and convert it effectively into electrical energy. Anti-reflective coatings have served as agents for reducing reflective losses and improving bulk and surface passivation thus enhancing both of the parameters – short circuit current and open circuit voltage of a solar cell. Simulation studies show that an SiN/MgF₂ dual-layer anti-reflective coating is best for a bare cell. This paper takes a closer look at how this coating can reduce the reflectance for a broad range of wavelengths and thus enhance the quantum efficiency of the cell in the blue and red region of the solar spectrum.

Introduction

Bare silicon surface reflects more than 30% of incident sunlight for wavelengths corresponding to energy greater than the band gap of silicon [1]. Minimizing reflection losses is crucial in order to produce high efficiency silicon solar cells. Single-crystal silicon (sc-Si) cells commonly use anisotropic etches to form a textured surface to reduce surface reflectance. These anisotropic etches are less effective with mc-Si-substrates because the grains have random crystal orientations [2]. Several methods have been investigated to texture mc-Si to reduce reflectance losses, including: isotropic chemical etches with masks [3]; scribing the surface with a laser [3]; mechanically texturing the surface with a dicing wheel or saw [4]; and chemically texturing the surface with anodic HF porous-silicon etchants [5].

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Mitsubishi Electric achieved an 18.9% conversion efficiency rate by introducing: 1) A 26% improved efficiency in utilizing infrared rays with a newly developed rear surface reflection structure, and 2) A low-reflective honeycomb-textured front surface to absorb more sunlight at the front surface [6]. Future highly efficient cell technologies are evolving towards methodologies of utilizing the full solar spectrum. A common thread in all these systems is the tradeoff between efficient light absorption and charge collection. Cells engineered to absorb as much light as possible exhibit decreased efficiency, because increased path lengths strongly

increase energy losses by recombination of oppositely charged electrical carriers. Photovoltaics engineered to exhibit less recombination absorb little light.

An antireflection (AR) coating is a type of coating applied to the surface of a material to reduce light reflection and to increase light transmission. An AR coating plays a significant role in reducing these reflective losses in crystalline silicon substrates even after surface texturization using acidic or alkaline solutions. The coating can improve solar collection efficiency and, therefore, the overall light-to-electricity conversion efficiency. As solar radiation is broadband, the AR coating needs to be effective over the entire solar spectrum from ultraviolet and visible to IR wavelengths. A single layer of quarter-wave AR coating can give zero reflection at a specific wavelength [7]. However, it is effective only for a small wavelength range. A double-layer AR coating has also been proposed to extend the wavelength range between 450–700nm [8]. Double-layer anti-reflective coatings work on the principle of creating two reflectance minima fairly close together and keeping the interconnecting maximum as low as possible. An alternative approach to increase the bandwidth is to create an artificially modified surface structure. For example, a periodic sub-wavelength surface structure was shown to suppress reflection in the visible and near-IR wavelength regime [9]. It has been reported that a random silicon nano-tip structure can give a total reflectance of less than 1% for the wavelength regime of 200–2500nm [10].

Anti-reflection properties are dependent on the composition and thickness of the encapsulation material. Some of these ARCs serve as good agents for bulk/surface passivation, which lead to improvement in open circuit voltage (V_{oc}) of the solar cells. In this paper we review some of the best electrical results reported based on the design of an ARC and its passivation properties. The most efficient ARC in

practice is the zinc sulphide/magnesium fluoride (ZnS: MgF₂) double layer, with an effective reflectance of 3.3% [11]. A very high V_{oc} of 649mV was reported for a solar cell passivated with SiN at the front and rear surface (all-SiN cells) by Hubner et al. [12]. Duerinckx et al. has reported a V_{oc} of 621mV and a very impressive efficiency of 17.1% for a variety of multicrystalline substrates with resistivity in the range 0.5–1Ωcm and a cell area of 12.5cm by 12.5cm [13]. These cells were given an isotropic acidic texturing and a double-layer anti-reflection coating of SiN and MgF₂.

Anti-reflective coatings

Single-layer ARC is far from being the most efficient system because it allows a reduction in reflectance only in a narrow wavelength domain of the solar spectrum. As a result of this, the effective reflectance still represents about 11% of the incident photon flux [14]. At normal incidence, a quarter wavelength-thick single ARC layer effectively reduces the reflection to a minimum. The optimal single-layer thickness for minimum reflection at wavelength λ is defined by the equation:

$$d_{SL} = \lambda / (4n_{SL}) \quad (1)$$

where n_{SL} is the refractive index of the single layer AR coating (SLARC). The zero reflection condition requires that the refractive index of the single layer be the geometric mean of the refractive indices of the adjacent layers and the light be at normal incidence. For a $\lambda/4$ thick coating on Si, the reflectance is given by the general equation:

$$R = ((n_0 n_{Si} - n_{SL}^2) / (n_0 n_{Si} + n_{SL}^2))^2 \quad (2)$$

Therefore, the reflectance is zero, if

$$n_{SL}^2 = n_0 n_{Si} \quad (3)$$

For the air/SLARC/Si system (considering $n_0=1$ for air and $n_{Si}=3.87$

at 640nm, for Si), the ideal values of n_{SL} and d_{SL} are 1.97 and 81nm respectively. Considering the glass/SLARC/Si system with encapsulating glass refractive index of $n_g = 1.55$, the optimum values change to 2.45 and 65nm respectively.

Studies on double layer ARCs (DLARC) have been reported. The most stable configuration with respect to variations in film thicknesses have been found to be designs with a high refractive index (n) on the substrate and a low n towards the ambient [14]. Explanations of minima and maxima in double layers are more complex than for single layers. Two-quarter wavelength coatings of optimized indices can effectively reduce the reflectance at two wavelengths. The required refractive indices for the top and bottom layers of the dual layer ARC coating are given by the equations:

$$\begin{aligned} R_1 &= ((n_0 n_2 - n_1^2)/(n_0 n_2 + n_1^2))^2 \text{ and} \\ R_2 &= ((n_1 n_{Si} - n_2^2)/(n_1 n_{Si} + n_2^2))^2 \end{aligned} \quad (4)$$

Where R_1 is the reflectance of the top layer, R_2 is reflectance of the bottom layer adjacent to Si and n_1 and n_2 are the refractive indices of the top and bottom layers respectively. For zero reflectance at normal incidence, these equations reduce to:

$$n_1^2 = n_0 n_2 \text{ and } n_2^2 = n_1 n_{Si} \quad (5)$$

The optimal thickness for each layer in terms of their refractive indices can be obtained using relation 1. For the air/Layer1/Layer2/Si component system, the ideal values for n_1 and d_1 are 1.57 and 102nm whereas the bottom layer parameters are 2.46 and 65nm respectively. For the glass/Layer1/Layer2/Si system, the optimum values change to 1.96/81nm for the top layer and 2.76/58nm for the bottom layer respectively. Among the various possible combinations of DLARC, combinations such as $\text{SiO}_2/\text{TiO}_2$, MgF_2/ZnS , $\text{MgF}_2/\text{TiO}_2$, $\text{SiO}_2/\text{SiN}_x$, and $\text{MgF}_2/\text{CeO}_2$ have already been reported [15, 16]. Both magnesium fluoride/zinc sulphide (MgF_2/ZnS) double layers deposited by electron beam sputtering [17] and titanium oxide (TiO_2) double layers deposited by Atmospheric Pressure Chemical Vapour Deposition [18] show very low reflectance over a broad wavelength range. However, both techniques require a separately thermally grown silicon oxide (SiO_2) layer for surface passivation.

Takato et al. demonstrated use of textured antireflection coatings for mc-Si solar cells. They showed an improvement of current and long-wavelength spectral response compared to a planar SLAR c-Si cell, which they attributed to optical confinement in the textured ZnO coating [14]. The textured-dielectric coating works optically with the module

encapsulation to promote optical confinement of rays inside the module encapsulation structure, which reduces the net reflectance of the photovoltaic module. The advantage of the approach was that deposition of a textured dielectric film may be less costly and less intrusive on the cell manufacturing process than texturing multicrystalline-silicon substrates. Suitable materials for the textured dielectric coating include ZnO, TiO_2 , and SnO_2 ; these materials have large refractive indices (~ 2) and have been deposited with textured surfaces and with low-cost technologies [19].

Porous silicon (PS) has been extensively investigated over the past 10 years for solar cell applications due to several advantages, including light trapping, antireflection properties, variable refractive index and solar light conversion from ultraviolet to red wavelengths [20,21]. The PS morphology depends critically on the metal type and thickness, silicon doping type and level and etching solution concentration. The resulting nano-scale texturing markedly reduces the reflectivity of the multi-crystalline silicon surface to below 6% in the spectral range 350-1000nm [22, 23].

Another method of increasing solar energy conversion is through surface plasmons, i.e., collective surface oscillations of conducting electrons in metal nanostructures that tend to trap optical waves near their surface. They enhance optical absorption, allowing for development of solar cells that circumvent the tradeoff between optical thickness and carrier transport [24,25]. Yet, because strong recombination can occur at metal surfaces in contact with the active layer of a solar cell, attempts at this approach have not been very successful, except for some cases where they were used deliberately as recombination sites. These issues have recently been circumvented by employing buffer layers between the plasmonically active material and the active layer of the solar cell [26,27]. A hybrid approach has been employed, where plasmonic effects potentially enable third generation solar-energy conversion [28].

Anti-reflective and passivation properties of multi-layer stacks

Historically, silicon dioxide films, thermally grown into the silicon surface at high temperatures, have been the preferred means used for surface passivation. Indeed, the use of silicon oxide for passivating non-diffused surfaces resulted in the first solar cells with efficiencies $>21\%$ [29,30]. The surface passivation properties of SiO_2 are excellent, but it does not passivate the bulk defects in multicrystalline silicon. Furthermore, oxidation requires high temperatures creating additional defects within multicrystalline silicon and reducing equipment throughput.

Stacks of amorphous silicon and silicon oxide – both deposited applying a PECVD system – were successfully used to passivate crystalline silicon solar cells' rear surfaces and led to a maximum cell efficiency of 21.7% on p-type (boron-doped) float zone silicon substrates with a thickness of 250 μm [31].

It has been observed that the refractive index of TiO_2 can be increased from 1.9, directly after an APCVD process, to a more optimal value for encapsulation of 2.3 if a thermal treatment at temperatures above 700°C is applied. However, TiO_2 has no surface or bulk passivation properties. Solar cells fabricated using the firing through PECVD SiN_x delivers cells which are 2.5% more efficient than the firing through APCVD TiO_2 ARC processed cells [32].

“As solar radiation is broadband, the AR coating needs to be effective over the entire solar spectrum from ultraviolet and visible to IR wavelengths.”

Lauinger et al. [33,34] have shown that the quality of the surface passivation obtained for 1.5 Ωcm p-type silicon is strongly affected by the deposition parameters used, as well as by the mode of PECVD deposition. They concluded that films fabricated using either remote or high frequency direct PECVD result in a lower surface recombination velocity than films prepared using low-frequency direct PECVD. Lauinger et al. also showed there is a clear correlation between the refractive index of the SiN films and their ability to passivate the silicon surface. They demonstrated that the surface passivation is maximized when SiN films with a refractive index greater than 2.3 were used, that is silicon-rich SiN films [34]. These films bring about several issues which limit their applicability to solar cells in production lines: (i) the etch rates of the films are extremely low, hindering the local opening of the SiN by means of photolithography and chemical etching; (ii) the films show a considerable absorption in the UV range of the sun spectrum, leading to a reduction of the short-circuit current; and (iii) the films are very poor insulators and cannot be used at point-contacted rears of solar cells. PECVD SiN contains between 15 to 20 at.% hydrogen [35,36] due to the high hydrogen content in the precursor gases. During the high temperature process of contact firing, the hydrogen will be released from the silicon nitride and diffuse into the silicon and passivate recombination sites in the bulk [37].

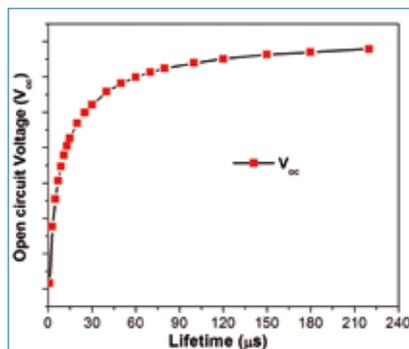


Figure 1. Effect of bulk lifetime on the open circuit voltage.

Simulation studies

Gettering and hydrogen passivation improve the minority carrier lifetime in $\mu\text{-Si}$ wafers. Bulk passivation can lead to increase in minority carrier lifetime (τ) and in effect lead to increase in open circuit voltage (V_{oc}) of the solar cell. Fig. 1 shows the effect of bulk lifetime τ on the V_{oc} based on PC1D simulation. For typical industrial phosphorus diffusions with sheet resistances in the vicinity of $50\Omega/\text{sq}$, there is minimal difference in the passivation quality obtained with PECVD SiN compared to any of the oxides or the oxide/nitride stacks. Conventional forming gas anneals of the finished cells are known to improve carrier lifetime up to 90 μs .

From the perspective of optimizing the reflective properties of the ARC coatings we present the results of the simulation studies done on different dielectric combinations. As seen in Fig. 2, single-layer AR coatings are out-performed by the multilayer AR coating in terms of the broad range of wavelengths for which the coatings are effective. The simulation clearly shows the advantage in lowering the reflectivity while using the SiN single layer compared to the SiO₂ single layer. The average weighted reflectance is lower for single-layer SiN compared to any single- or double-layer ARC; however it is limited by the bandwidth of the AR coating. The SiN/MgF combination appears to be the best in terms of flatness of the response achieved from the overlapping of the minima of the individual layers. The simulation is done assuming there are no absorption losses in the layers. The simulation also shows that a $\sim 2\text{mV}$ gain in V_{oc} can be delivered (provided all other cell parameters are unaltered) by the SiN/MgF stack compared to the single layer of SiN. Typically for the $12.5 \times 12.5\text{cm}^2$ Si solar cell, a 1mV gain in V_{oc} can deliver $\sim 0.024\%$ absolute increase in efficiency so that the 2mV gain can deliver a $\sim 0.048\%$ absolute increase in efficiency. The SiN/SiO₂ stack appears to be the best industrially feasible approach of improving the cell response both at the red and blue end of the spectrum.

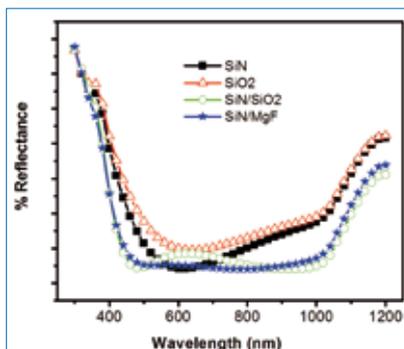


Figure 2. Relative reflectance plots based on PC1D simulation.

Another study we carried out was to quantify the gain attainable by improving the reflective properties based on PC1D simulation. We started with the assumption of a single-layer broad band SiN AR coating with average reflectance of 15% at the quarter-wave thickness for a $12.5 \times 12.5\text{cm}^2$ c-Si solar cell. Fixing all other cell parameters for the simulation and varying only the reflectance from 15% to 1%, the variation in electrical performance of the cells was studied. The cell efficiency as a function of the reflectance is plotted in Fig. 3. Increase in short circuit current I_{sc} with decrease in reflectance was the most evident contributor to improved cell efficiency. Our calculations show that for the $12.5 \times 12.5\text{cm}^2$ cell, and for a decrease in broadband reflectance from 15% to 1%, the short circuit current I_{sc} increases by $\sim 0.85\text{A}$. For the $12.5 \times 12.5\text{cm}^2$ Si solar cell, a 1mA increase in I_{sc} can deliver a $\sim 0.0028\%$ absolute increase in efficiency so that the 850mA increase in I_{sc} can deliver a $\sim 2.38\%$ absolute increase in efficiency.

Conclusions

Most of the commercially available cell technologies today use single-layer or dual coating with weighted average reflectance of $\sim 8\%$. AR coating technologies that can reduce average reflectance below 3% are much sought after. The limitation on actual production lines that are unable to tap these potential technologies is in the inability of the screen-printed contacts to fire through the AR coatings of dielectric multilayers and form proper front contacts. With the evolution of back contact cells and alternate paste, the possibility of implementing such multilayer stacks is being pursued widely. From an industry perspective, the most widely used AR coating today is the single- or dual-layer SiN based on the compromise between throughput, equipment availability and volume demands. The coming age presents a challenge to production lines on their ability to adapt to these new designs and find alternatives to complement minor snags put forth by such technological changes.

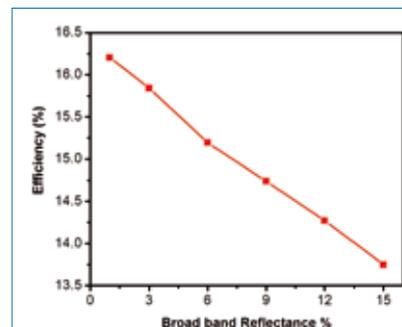


Figure 3. Cell efficiency as a function of reflectance of the single layer SiN AR coating.

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