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Excellent Passivation and Low Reflectivity Al_2O_3/TiO_2 Bilayer Coatings for n-Wafer Silicon Solar Cells

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***Abstract* — A bilayer coating of Al_2O_3 and TiO_2 is used to simultaneously achieve excellent passivation and low reflectivity on p-type silicon. This coating is targeted for achieving high efficiency n-wafer Si solar cells, where both passivation and anti-reflection (AR) are needed at the front-side p-type emitter. It could also be valuable for front-side passivation and AR of rear-emitter and interdigitated back contact p-wafer cells. We achieve high minority carrier lifetimes ~1 ms, as well as a nearly 2% decrease in absolute reflectivity, as compared to a standard silicon nitride AR coating.**

***Index Terms* — passivation, anti-reflection, n-wafer silicon, minority carrier lifetime, atomic layer deposition.**

I. Introduction

Advanced n-wafer Si solar cells are considered promising because of their greater tolerance for common impurities (e.g. Fe) and because they do not suffer from the boron-oxygen related light-induced degradation seen in p-wafer Czochralski (Cz) solar cells. In order to achieve high efficiency n-wafer cells, excellent passivation of the p-type emitter is crucial. Previous literature has demonstrated the efficacy of a thin Al_2O_3 coating as a surface passivant for p-type Si wafers [1-4] and also solar cells with p-emitters [5]. Minority carrier lifetimes in excess of 1 ms have been demonstrated, corresponding to surface recombination velocities below 10 cm/s. This has allowed the fabrication of solar cells with open circuit voltage V_{OC} ~ 700 mV and efficiency >20% [5], showing the potential of this technique for passivation.

However, since the coating is applied to the emitter, on the front side where light enters the cell, it is also important to consider its anti-reflection properties. Up to now, there has not been a concerted effort to improve the coating for reduced reflection. Unfortunately, Al_2O_3 has a low refractive index (n ~ 1.6) so it is not suitable by itself as an AR coating. Silicon nitride can be deposited on top as an AR layer [5], but is not ideal since it also has a relatively low refractive index (n ~ 2). Since practically all commercial Si solar cells are encapsulated under glass/ethylene-vinyl acetate (EVA), a higher refractive index AR layer (n ~ 2.3) is strongly preferred.

In this paper, we show that a bilayer coating of Al_2O_3/TiO_2 can function to simultaneously provide excellent passivation for p-type Si and significantly reduce reflectivity. We deposit the bilayer coating using atomic layer deposition (ALD). Other industrially-relevant, high-throughput techniques could be used to deposit the coating, including spatial-ALD, plasma-enhanced chemical vapor deposition (PECVD), sputtering, evaporation and spray-coating. Importantly, excellent passivation (lifetimes ~ 1 ms) with Al_2O_3 deposited by spatial-ALD [4] and PECVD [2] has already been demonstrated. It is well-known that TiO_2 can also be deposited by numerous rapid and inexpensive techniques.

II. Bilayer Coating

We design the bilayer coating to have as thin a layer of Al_2O_3 as possible. This is desirable, since Al_2O_3 has a low refractive index that will decrease the anti-reflection performance of the bilayer coating. Previous literature has shown that even ~10 nm of Al_2O_3 can be sufficient to achieve excellent passivation [1-4]. Using the optical transfer-matrix method to calculate reflectivities, we search for the optimal thicknesses for Al_2O_3 and TiO_2 layers. The aim is to achieve an anti-reflection coating optimized for the lowest solar-averaged reflectivity – the reflectivity averaged across the solar spectrum, as weighted by solar flux. We find that a bilayer stack of 10 nm Al_2O_3 followed by 50.5 nm of TiO_2 is optimal.

We use ALD to deposit this bilayer coating onto both sides of p-type Si wafers. Cz p-type Si wafers are used, boron-doped to a resistivity of 3 Ω-cm, and with a thickness of 400 µm. The native oxide layer on the wafers is removed in dilute HF. The thermal ALD deposition of the bilayer coating is performed in a Beneq P400A machine, which is capable of processing both single wafers for R&D purposes as well as large wafer batches. Al_2O_3 is deposited by using a Beneq proprietary modified O_3 process. Trimethylaluminium (TMA) is used as the aluminum precursor and the ALD cycle time is 4 s. TiO_2 is deposited from $TiCl_4$ and H_2O. The entire process is done at 200 °C, with nitrogen carrier gas at 2.5 SLM flow and 1 mbar process pressure.

After deposition, the coated wafers are annealed in an inert N_2 environment at 450 °C for 30 minutes. This is done to activate the surface passivation, as described in previous literature [1-4].

III. Passivation Results

The minority carrier lifetime is measured using a Sinton Instruments WCT-100 lifetime tester. Both transient photoconductance decay (PCD) and quasi-steady-state photoconductance (QSSPC) measurements are done to determine the minority carrier lifetime as a function of injected photocarrier density. We see that for injection levels up to 10^{16} cm^{-3}, the Auger-corrected effective lifetime is approx. 1 ms (Fig. 1).

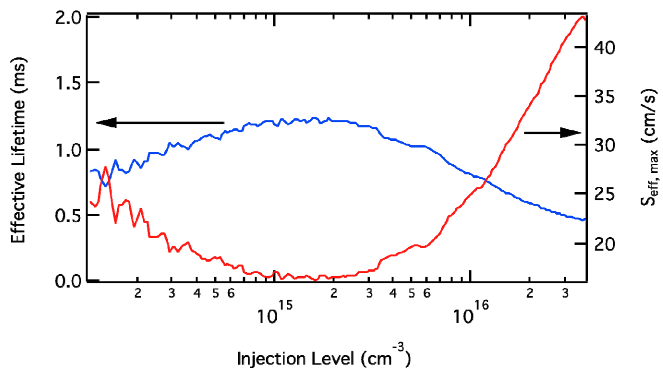

Fig. 1. Effective minority carrier lifetime (left axis) and maximum surface recombination velocity (right axis) as a function of injection level.

Assuming an infinite lifetime in the bulk, we can calculate the maximum surface recombination velocity $S_{eff,max}$ according to:

$$S_{eff,\max} = W/(2\tau_{eff}) \qquad (1)$$

Here, W is the wafer thickness and τ_{eff} is the effective minority carrier lifetime. Thus, we find that the maximum surface recombination velocity is below 25 cm/s for injection levels up to 10^{16} cm^{-3} (Fig. 1). So, for injection levels corresponding to 0-1 sun illumination, we see that the minority carrier lifetime (alternatively the surface recombination velocity) is excellent.

The implied open-circuit voltage may also be calculated from the effective minority carrier lifetime [6]. At 1-sun intensity, we see that the implied V_{OC} is ~700 mV (Fig. 2).

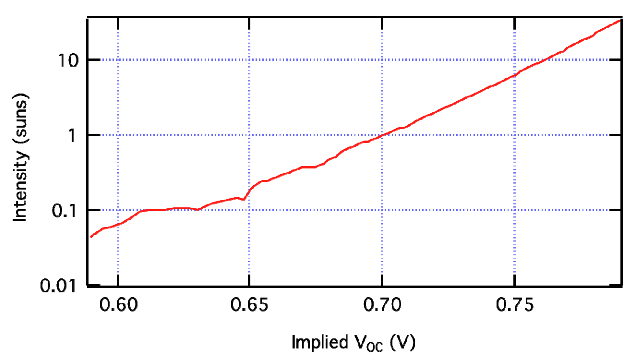

Fig. 2. Implied open circuit voltage V_{oc} for a solar cell with the bilayer surface passivation. Near 1-sun intensity, the implied V_{oc} is ~700 mV.

Therefore, we can assert that the Al_2O_3/TiO_2 bilayer coating achieves excellent passivation, approaching the best results for passivation of p-doped Si in the literature [1-4].

IV. Optical Properties

We use spectroscopic ellipsometry to measure the dielectric functions of the coating. First, we measure the dielectric functions of separate films of Al_2O_3 and TiO_2 deposited under the same ALD conditions. These are single-layer films deposited on Si wafer. We then measure the bilayer coating. We confirm that the dielectric functions of Al_2O_3 and TiO_2 are basically identical in the bilayer stack, compared to those of the separate single-layer films. The dielectric functions determined from ellipsometry are shown in Fig. 3. Importantly, the (complex) refractive index ($n = \varepsilon^{1/2}$) of TiO_2 is high, in the range of n ~ 2.4 in the visible and near-infrared. This is beneficial for achieving a good anti-reflection coating for Si, encapsulated under glass/EVA.

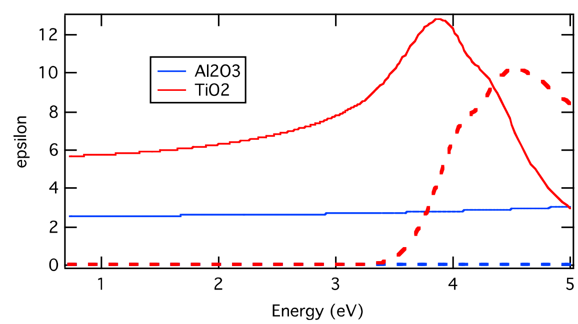

Fig. 3. Dielectric functions of Al_2O_3 and TiO_2 films deposited by ALD on Si wafer. Solid lines denote the real part of epsilon and dashed lines the imaginary part.

We input the actual, experimental dielectric functions of Al_2O_3, TiO_2 and Si into a transfer-matrix calculation, to determine the reflectivity of the bilayer coating on silicon. We assume that the light is initially incident on the bilayer coating from glass/EVA with refractive index n = 1.5.

We find that the bilayer behaves as an excellent AR coating. The calculated solar-averaged reflectivity of a coated, flat Si wafer is only 4.7% under glass/EVA. By comparison, a standard silicon nitride AR coating on flat wafer has 6.5% solar-averaged reflectivity under glass/EVA. The lower reflectivity of the Al_2O_3/TiO_2 coating can be clearly seen in Fig. 4. Notably, if we attempt to combine Al_2O_3 passivation with silicon nitride for anti-reflection, we will have solar-averaged reflectivity even above 6.5%.

High efficiency solar cells made from mono-crystalline Si wafers are typically textured by KOH etching, to further reduce reflectivity. However, even on textured wafers, there will still be a significant benefit with the Al_2O_3/TiO_2 bilayer coating. We estimate a ~1% decrease in absolute reflectivity compared to standard silicon nitride. This translates to an additional ~0.4 mA/cm^2 in current, or several tenths of a percentage point in efficiency. Therefore, we see that the bilayer stack can be an improved anti-reflection coating for high-efficiency cells, in addition to providing excellent surface passivation.

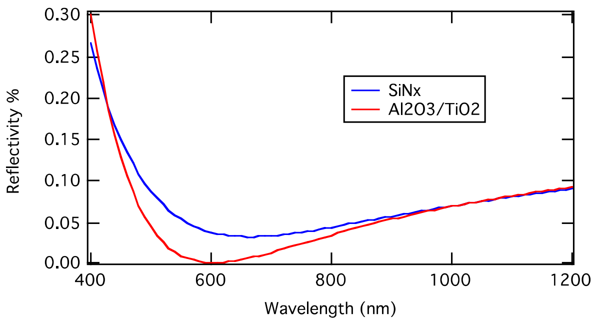

Fig. 4. Reflectivity of the bilayer coating, as compared to a standard silicon nitride AR coating. Calculated assuming that the initial medium is glass/EVA (n = 1.5) and the final medium is silicon.

V. Conclusion

We simultaneously achieve low reflectivity and excellent passivation of p-type Si with an ALD-deposited bilayer coating consisting of 10 nm Al_2O_3 followed by 50.5 nm TiO_2. A high minority carrier lifetime ~1 ms is measured in a wafer coated with the bilayer stack. This is equivalent to a low surface recombination velocity below 25 cm/s, or an implied V_{oc} ~ 700 mV for a solar cell. The high refractive index of the TiO_2 (n ~ 2.4) is beneficial for decreased reflectivity. We calculate the solar-averaged reflectivity of a flat, coated Si wafer under glass/EVA to be only 4.7%. This is nearly 2% less in absolute reflectivity than with a standard silicon nitride AR coating.

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References

[1] B. Hoex et al., "Excellent passivation of highly doped p-type Si surfaces by the negative-charge-dielectric Al_2O_3," *Appl. Phys. Lett*. **91**, 112107 (2007).

[2] P. Saint-Cast et al., "Very low surface recombination velocity on p-type c-Si by high-rate plasma-deposited aluminum oxide," *Appl. Phys. Lett*. **95**, 151502 (2009).

[3] G. Dingemans et al., "Silicon surface passivation by ultrathin Al2O3 films synthesized by thermal and plasma atomic layer deposition," *Phys. Status Solidi RRL* **4**, 10-12 (2010).

[4] F. Werner et al., "Very low surface recombination velocities on p- and n-type c-Si by ultrafast spatial atomic layer deposition of aluminum oxide," *Appl. Phys. Lett*. **97**, 162103 (2010).

[5] J. Benick et al., "High efficiency n-type Si solar cells on Al_2O_3-passivated boron emitters," *Appl. Phys. Lett*. **92**, 253504 (2008).

[6] R.A. Sinton and A. Cuevas, "Contactless determination of current–voltage characteristics and minority□carrier lifetimes in semiconductors from quasi□steady□state photoconductance data," *Appl. Phys. Lett*. **69**, 2510 (1996).