

TiO₂ Thin Films by Atmospheric Pressure Chemical Vapor Deposition for Rear Surface Passivation of p-PERT Solar Cells

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Received: December 11, 2023; Revised: March 11, 2024; Accepted: March 13, 2024

The aim of this paper was to analyze the passivation of the rear face of silicon solar cells by TiO₂ thin films produced by atmospheric pressure chemical vapor deposition (APCVD). A compact high-throughput APCVD system was employed to deposit the TiO₂ films. Silicon solar cells with a n⁺pp⁺ PERT (passivated emitter rear totally-diffused) structure were produced and characterized. The use of TiO₂ on the rear face resulted in a 0.5 mA/cm² increase in short-circuit current density and a 0.5% absolute improvement in efficiency compared to devices without a passivation layer. Analyzing the internal quantum efficiency of the devices, we concluded that this economically technique provides passivation on the p⁺ surface, doped with boron, similar to that obtained with thermally grown silicon oxide films.

Keywords: Silicon solar cells, titanium dioxide, APCVD, surface passivation.

1. Introduction

Passivated emitter and rear cells (PERC) have become the most extensively employed technology in the production of photovoltaic modules in recent years^{1,2}. The primary reason for using this structure was its higher efficiency compared to Al-BSF (aluminum-back surface field) devices³, owing to the introduction of dielectric layers on the rear face to minimize the recombination of minority charge carriers. Al₂O₃ layers deposited by atomic layer deposition (ALD) have been implemented to passivate p-type surfaces on account of the negative charges produced. This process effectively reduces the concentration of minority charge carriers (electrons) near the surface². In addition to PERC solar cells, industries and laboratories have also dedicated efforts to TOPCon structure, with surfaces passivated with polysilicon films and tunnel oxides⁴.

Solar cells with boron or another p-type dopant diffused into the whole rear face are called PERT (passivated emitter, rear totally-diffused)². If manufactured on n-type silicon wafers, these solar cells are potential candidates for bifacial devices, exhibiting a high bifaciality coefficient. This coefficient is defined as the ratio of lower efficiency in relation to the higher efficiency subject to the same irradiance and measured independently^{5,6}. Bifacial cells can take advantage of solar radiation reflected by the surroundings, reaching the rear face of the cell. According to International Technology Roadmap for Photovoltaic (ITRPV)¹, currently, 65% of the world's production of solar cells are bifacial and it is expected that by 2033 this percentage will grow to 90%. Not all bifacial cells are used in bifacial PV modules, but by 2033 it is predicted that 70% of photovoltaic modules will be bifacial¹. Studies have been carried out to optimize

the passivation of the rear surface of solar cells, aiming to utilize them in bifacial devices. Wei et al.⁷ investigated the influence of SiN_x and SiO_xN_y as rear-side passivation of PERC+ devices, that is, PERC cells with an Al finger grid instead of the full-area Al rear surface used in monofacial devices. For instance, due to the lower parasitic absorption and better rear-side passivation, the sample with SiN_x/SiO_xN_y/SiN_x stacks showed an enhancement of conversion efficiency by 0.09% when compared to the sample passivated with a single 80 nm thick SiN_x film. Fan et al.⁸ analyzed an Al₂O₃/SiN_x rear side stacked passivation layer obtained by plasma enhanced chemical vapor deposition (PECVD) for multicrystalline PERC solar cells. The results indicated that the most effective passivation was achieved with a 10.8 nm thick Al₂O₃ layer and a 120 nm thick SiN_x layer. If the thickness of Al₂O₃ was decreased to 6.8 nm or increased to 16 nm, the efficiency was reduced by 0.05% and 0.10%, respectively. If the film thickness of SiN_x was reduced to 100 nm or increased to 150 nm, the efficiency decreases by 0.05% and 0.09%, respectively⁸.

TiO₂ thin films present high refractive index that is optimal for reducing reflection losses of glass-encapsulated solar cells, low extinction factor, high thermal stability and high chemical resistance^{9,10}. Atomic layer deposition is the most studied technique for obtaining TiO₂ films because it achieves higher surface passivation. However, it requires a long processing time and high-cost equipment¹¹. High vacuum evaporation, used to obtain antireflection TiO₂ films and slight surface passivation of the n⁺ emitter, was reported by Model et al.¹². The atmospheric pressure chemical vapor deposition (APCVD) was also used to obtain antireflection TiO₂ films and to passivate boron doped (p⁺) surfaces¹³. The passivation was attributed to significant levels of

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negative charges existing in the films after the deposition and subsequent irradiation with a halogen lamp¹³. Although low surface recombination velocities have been reported (in the order of 30 cm/s) in silicon wafers with p⁺ regions of 200 ohms/sq (lightly doped), no results were presented for solar cells manufactured with TiO₂ films¹³. Currently, TiO_x films have also been studied to be used as selective contacts, i.e., to reduce recombination under metallized regions and maintain a low contact resistivity^{14,15}. For example, for n-type regions in p⁺n solar cells, TiO_x films (obtained by ALD), LiF and Al were deposited on the rear face and high effective minority carrier lifetimes were achieved, in the order of 3 ms in n-type (100)-oriented FZ (float zone) silicon wafers¹⁴.

Considering the importance of passivation in obtaining high-efficiency solar cells, the aim of this paper is to analyze the surface passivation of the rear face of n⁺pp⁺ PERT silicon solar cells with TiO₂ deposited by APCVD. The APCVD system was specially developed by the Institute of Microelectronic Technology at the University of the Basque Country to optimize cleanroom space in laboratories or industries while simultaneously achieving high throughput. Solar cells were manufactured and characterized and the TiO₂ films were analyzed by spectral reflectance and internal quantum efficiency of the devices.

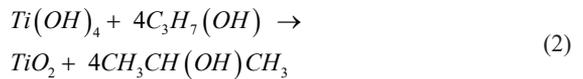
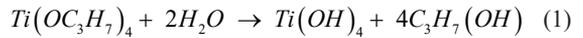
2. Materials and Methods

2.1. Solar cell fabrication process

Solar-grade silicon wafers grown by the Czochralski technique, p-type, boron doped with a diameter of 100 mm were used. Baseline process to produce n⁺pp⁺ PERT solar cells was presented elsewhere¹². The steps of the solar cell fabrication process were: texture etching, RCA cleaning, boron spin-coating, boron diffusion and oxide growth, RCA cleaning, phosphorus diffusion (POCl₃ as source of phosphorus), RCA cleaning, deposition of TiO₂ on the front and rear faces, metal paste screen-printing (Ag/Al and Ag on the rear and front face, respectively), metallization paste firing and laser edge isolation. Figure 1 presents a diagram of the solar cells. Devices with and without titanium oxide films on the rear face were produced to assess the passivation effect.

In chemical vapor deposition at atmospheric pressure, the TiO₂ liquid precursor was tetra isopropyl titanium (TPT). For deposition temperatures of 150 to 450 °C, TPT can

react via a two-step hydrolysis reaction¹⁶, as shown by the Equation 1 and Equation 2:



Deposition temperatures (T_{dep}) below 300 °C result in amorphous thin TiO₂ films, while T_{dep} from 300 °C to 450 °C favor the formation of polycrystalline TiO₂ films of the anatase phase¹⁷.

Figure 2a presents the equipment – bubblers with TPT and H₂O, and the injectors of the vapors – developed by the Institute of Microelectronic Technology at the University of Basque Country, requiring minimal space in the laboratory. The dimensions of the compact equipment are as follows: length of 1.5 m, width of 0.6 m and height of 1.3 m. For comparison, commercial CVD equipments have lengths on the order of 3.0 m to 5.3 m.

To produce a TiO₂ film, one linear nozzle injects water vapor and the other injects TPT vapor that react to form a film on the surface of the silicon wafer. The conditions for thin film formation are established by adjusting the following parameters: temperature of the injectors, conveyor belt temperature under the injectors, belt speed, temperature of dionized water, temperature of TPT, and the flow of N₂ through the deionized water/TPT bubblers.

Figure 2b presents a diagram of the equipment and its main parts. In the equipment for the deposition of titanium oxide films, TPT was maintained between 80 °C and 90 °C in a heater/bubbler (5). The TPT vapor is conducted via heated gas lines (7) to a stainless-steel linear injector (8) located in the chamber. A bubbler containing deionized water (6) is maintained at a temperature between 60 °C and 70 °C, serving as a water vapor supply that feeds the other injector. The flow rates were controlled by pneumatic valves (2), which release the N₂ (carrier gas), and by digital mass flow controllers (3). The silicon wafer is moved under the linear injectors by a conveyor belt (9) heated by a baseplate (10) at 200 °C. The conveyor belt speed was maintained in the range of 60 – 70 cm/min.

The silicon wafers with TiO₂ films were thermally processed in a standard infrared belt furnace, with three heating zones, a laboratory furnace currently used to dry and firing screen printed metal grids. Clean dry air was used in the process. The peak temperature was set to 860 °C¹², and belt speed was 300 cm/min.

2.2. Characterization of solar cells and TiO₂ coatings

To characterize the TiO₂ thin films in terms of thickness and reflectance, hemispherical reflectance was measured at five points on the wafers using a spectrophotometer with an integrating sphere after the deposition and firing processes. Firing of solar cell metal contacts in infrared conveyor furnaces is an industry standard, and this thermal process can modify the TiO₂ film thickness and/or refraction index.

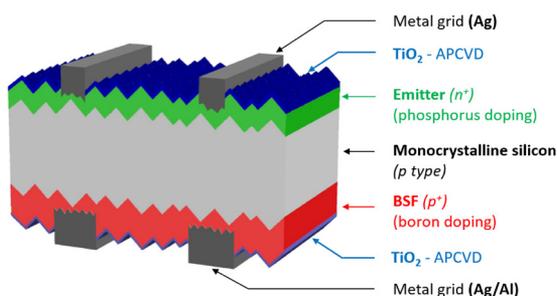


Figure 1. Solar cell structure with TiO₂ deposited by APCVD on both the front and rear faces.

Solar cells were characterized under standard conditions (100 mW/cm², AM1.5G and 25 °C) in a solar simulator calibrated with a silicon solar cell previously measured at CalLab - FhG-ISE (*Fraunhofer-Institut für Solare Energiesysteme*), Germany. The short-circuit current density (J_{sc}), the open circuit voltage (V_{oc}) and the efficiency (η) were determined from the I-V curve. The spectral response and hemispherical reflectance were measured to obtain the internal quantum efficiency (IQE).

3. Results and Discussion

Figure 3 presents a textured silicon wafer coated by TiO₂ and the hemispherical reflectance measured in five regions. Table 1 depicts the wavelength values for minimum reflectance (λ_{min}) and the estimated thickness of the TiO₂ film (d_{TiO_2}) deposited in two silicon wafers, before and after the thermal process of metallization paste firing. For the minimum reflectance, the product of refractive index (n)

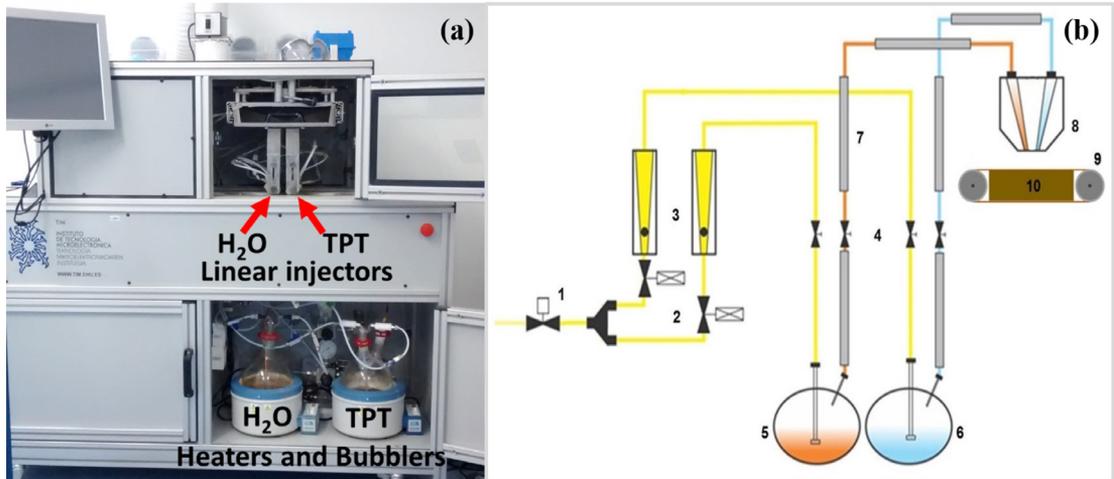


Figure 2. (a) TiO₂ film deposition equipment and (b) simplified diagram of the main components.

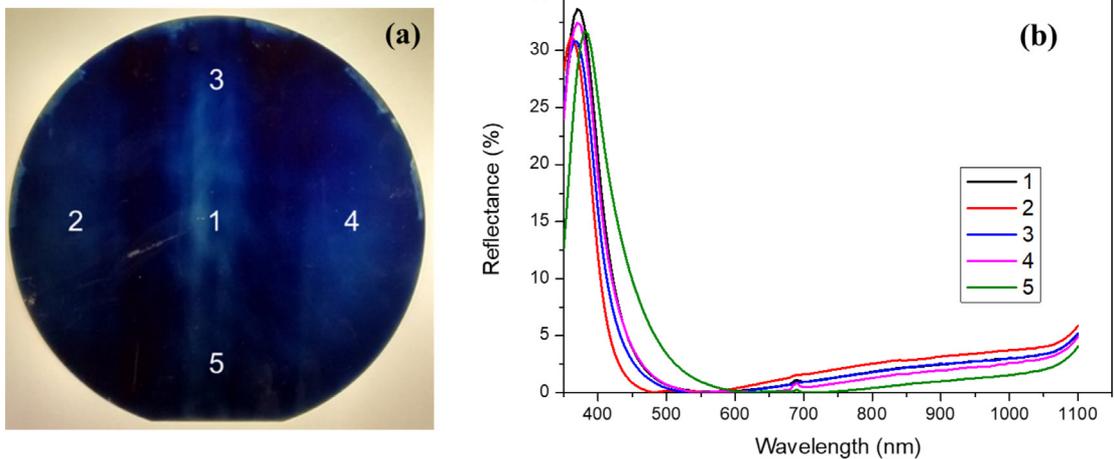


Figure 3. (a) Silicon wafer coated with TiO₂ deposited by APCVD and (b) reflectance for five regions of the wafers. Sample with TiO₂ film as-deposited (without firing).

Table 1. Average values of the wavelength for minimum reflectance (λ_{min}) and the estimated thickness of the deposited TiO₂ film (d_{TiO_2}).

Sample	Before firing		After firing	
	λ_{min} (nm)	d_{TiO_2} (nm)	λ_{min} (nm)	d_{TiO_2} (nm)
L05P84	678 ± 10	74 ± 1	560 ± 55	61 ± 6
L15P85	687 ± 55	75 ± 6	545 ± 30	59 ± 3

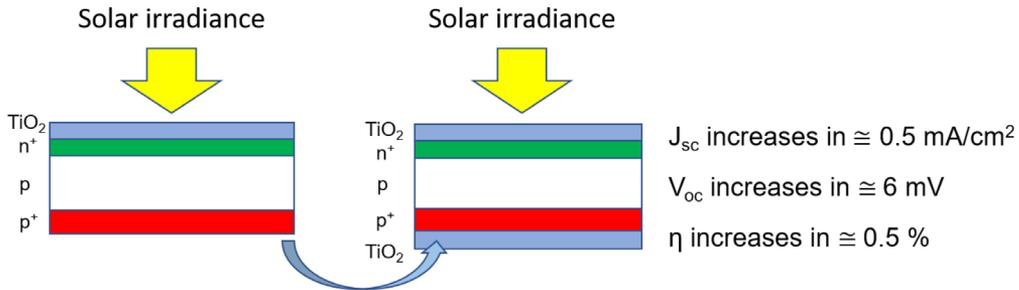


Figure 4. Deposition of TiO_2 by APCVD on the rear face increases the J_{sc} , V_{oc} and efficiency of the n^+pp^+ solar cells.

and layer thickness is equal to a quarter of the wavelength ($n \cdot d_{\text{TiO}_2} = \lambda_{\text{min}}/4$). To calculate the d_{TiO_2} , a refractive index of 2.25 was considered¹⁸. The thicknesses of the deposited films ranged from 71 nm to 82 nm. The average value of d_{TiO_2} was (74 ± 1) nm and (61 ± 6) nm before and after firing, respectively. In a second processed sample, a film thickness of (75 ± 6) nm and (59 ± 3) nm was estimated, before and after firing, respectively. For TiO_2 film deposited by electron beam evaporation and firing process at 860 °C, Model et al.¹² observed a wavelength shift of the minimum spectral reflectance ($\Delta\lambda_{\text{min}}$) of around 40 nm, value similar to that reported by Ly et al.¹⁹. On the contrary, an average $\Delta\lambda_{\text{min}}$ of 130 nm was observed for the TiO_2 films deposited by APCVD in this work. The physical mechanisms to explain this change is the reduction of the film thickness and/or the increase of refractive index¹⁷⁻¹⁹. Vallejo et al.¹⁷ analyzed TiO_2 films deposited by APCVD and explained the thickness reduction and refractive index increasing by a phase transition from amorphous to partially crystalline.

The deposition of the TiO_2 on the rear face of the n^+pp^+ PERT cells caused an increase of around 0.5 mA/cm² in the short-circuit current, 6 mV in the open circuit voltage and 0.5% (absolute) in the efficiency (see Figure 4). Although a 0.5% gain in efficiency may seem relatively small, the associated lower-cost process has an impact on the power of photovoltaic modules, especially considering the high yearly production of industrial lines of solar cell. The current industrial plants are capable of annually producing multi-gigawatts, with an hourly processing capacity of up to five thousand 210 mm x 210 mm silicon wafers^{1,20}. The throughput is limited by the deposition of SiN_x using plasma-enhanced chemical vapor deposition²⁰.

The solar cells with the front and rear faces coated with TiO_2 deposited by APCVD reached an efficiency of 15.6% (with $V_{oc} = 589.8$ mV and $J_{sc} = 34.9$ mA/cm²), a value 0.3% above than that achieved in previous studies with TiO_2 films deposited by electron beam evaporation¹². With this process, it is necessary to use high vacuum equipment, requiring longer running times and, thus, resulting in lower throughput. This way, the TiO_2 obtained by APCVD could be more cost-effective for an industrial line.

It is worth mentioning that there are PERT solar cells that achieve efficiencies above 20% with processes that use BBr_3 for boron diffusion, selective emitters on the front face and an advanced metal grid (20-30 μm wide fingers)²¹. These technologies were not used in the solar cells developed in

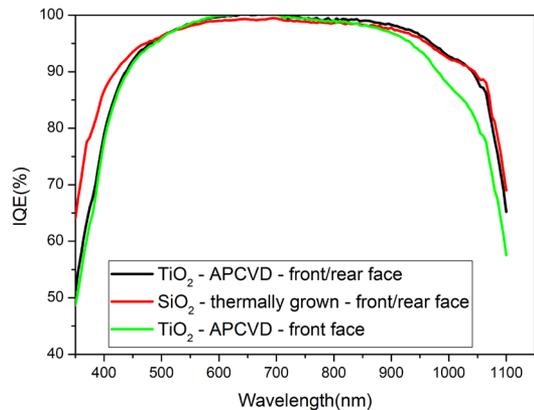


Figure 5. Internal quantum efficiency of solar cells with TiO_2 film deposited by APCVD on both faces and only on the front face. The IQE of a n^+pp^+ solar cell with surfaces passivated by thermally grown SiO_2 is also presented²².

this work. Passivation films, such as SiN_x and Al_2O_3 , are employed in high-efficiency PERT solar cells. However, TiO_2 deposited via APCVD offers a more cost-effective implementation and utilizes non-hazardous chemicals.

In the Figure 5, the internal quantum efficiencies of the solar cells developed with TiO_2 deposited by APCVD are presented. Additionally, the IQE of a similar device with both surfaces coated by a SiO_2 layer (10 nm thick), thermally grown at 800 °C in a quartz tube furnace, is shown²². The silicon dioxide is a well-known passivation layer from the microelectronic industry and experienced new applications on silicon solar cells²³. The use of TiO_2 on the boron-doped rear face increased the IQE for long wavelengths, highlighting its effectiveness in surface passivation. For instance, for $\lambda = 1000$ nm, an IQE of 93% was obtained for the solar cell with rear TiO_2 film. The device without rear passivation achieved an IQE of 88%. For $\lambda = 1000$ nm, the IQE of the solar cell with SiO_2 reached 92.3%. Compared to devices passivated with SiO_2 , TiO_2 films provide similar surface passivation on boron doped region. Conversely, regarding the phosphorus-doped emitter (n-type front surface), the deposited TiO_2 film is not as effective as the SiO_2 film in reducing surface recombination. At a wavelength of 400 nm, the device with SiO_2 achieved an IQE of approximately 88%,

while those with TiO₂ reached 78%. These results suggest that negative charges are generated during the formation of TiO₂, contributing to field-effect passivation in the p⁺ region while potentially increasing recombination in n⁺ surfaces^{2,13,24}.

4. Conclusions

The surface passivation provided by TiO₂ films deposited by APCVD was analyzed in n⁺pp⁺ PERT solar cells. The TiO₂ film on the boron-doped rear face increases the IQE of the solar cells in the infrared wavelength range when compared to devices without passivation layer on the p⁺ surface. The short-circuit current density was increased by 0.5 mA/cm² and the efficiency by 0.5% (absolute) with the use of TiO₂ on the rear face. This cost-effective technique provided passivation on the boron doped rear surface, similar to the result obtained with thermally grown silicon oxide films.

New studies are being carried out to analyze the homogeneity of the films as-deposited and after the thermal process of firing. Furthermore, TiO₂ thin films will also be analyzed on n-type silicon solar cells with a n⁺np⁺ structure.

5. Acknowledgments

The authors acknowledge the financial support provided by the Brazilian financing agencies FINEP, CNPq and CAPES and by the Brazilian utility Eletrosul Centrais Elétricas S. A.. They are also grateful for the development of TiO₂ film deposition equipment by the Institute of Microelectronic Technology, University of the Basque Country, particularly to Professors José Rubén Gutierrez and Juan Carlos Jimeno.

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