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Low-temperature deposition of TiO_2 by atmospheric pressure PECVD towards photoanode elaboration for perovskite and solid-state dye-sensitized solar cells

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Abstract. An original low-temperature atmospheric pressure plasma-enhanced chemical vapor deposition process was used to deposit titanium dioxide thin films. The parametric study in dynamic mode deposition aimed at growing an ideal columnar film composed of aligned anatase monocrystals as solar cell photoanode, previously obtained on silicon wafers in static mode deposition. A process parameters optimization was necessary to deposit onto thermally sensitive glass/FTO substrates. In this paper, the morphology, crystallinity and optical transmission of the coatings have been studied. The coatings display a columnar cauliflower-like structure, composed of TiO_2 amorphous particles assembly. After deposition, the light transmission properties of the substrate were reduced. As a solution, an ultrasound bath cleaning was set up to enhance the transmitted light through the photoanode.

Keywords: Atmospheric pressure / plasma-enhanced chemical vapor deposition / microwave plasma torch / Titanium dioxide / perovskite solar cells

1 Introduction

The surface modification or thin film deposition are of great interest for many applications and could help the development of renewable energy technologies which are a challenge nowadays. Solar energy is particularly interesting considering that each day the earth receives almost 10 000 times the energy consumed by humankind [1]. Several photovoltaic cells generations were developed, but among the third generation, the perovskite solar cells are recording a fast development lately [1,2]. Their multilayer structure is inspired by those of solid-state dye sensitized solar cells where the dye is replaced by a hybrid perovskite absorber. In this device structure, photogenerated electron-hole pairs are separated by electron transfer from the dye to an electron transporting layer (ETL) while the dye is regenerated by a hole transporting layer (HTL). The efficient solar energy conversion into electric current is thus mainly governed by the interface area between the dye and the ETL, and the dye and the HTL. Consequently, mesoporous ETL structure have proven to both insure good interface area with the dye and good electron transport to the anode provided an intimate penetration of the dye into the pores. Titanium dioxide is usually used as the mesoporous layer deposited most of the time by sol-gel techniques [3–5]. However, other processes are more and more tested to obtain an ideal structure enhancing electron mobility. A 100 nm thick columnar crystallized microstructure with an intercolumnar porosity allowing the dye impregnation seems the most suitable [1,6]. The layer could be deposited by reactive sputtering [7,8] or plasma enhanced chemical vapor deposition (PECVD) [9,10], but these processes use pumping systems and thus are relatively expensive.

To elaborate the photoanode composed of thermally sensitive materials, low-temperature atmospheric plasma processes could be used and were developed a lot to improve PECVD systems [11–13]. Atmospheric pressure PECVD systems were widely investigated in the past few years to deposit titania thin films. Most of the time, the as-deposited coating is amorphous and needs annealing treatment to be crystallized [11–15]. The substrate is also sometimes heated to improve the film microstructure [16].

In this work, an original atmospheric pressure PECVD process using an axial injection torch with a microwave excitation is studied for the deposition of TiO_2 thin films on silicon wafers and glass substrates. It was demonstrated

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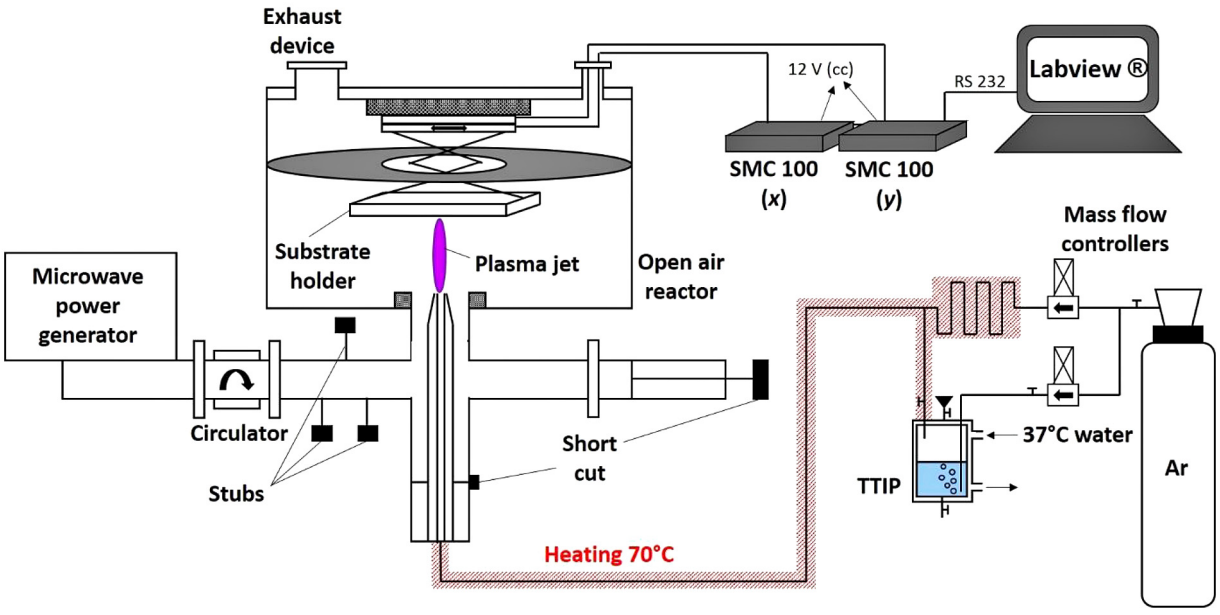

Fig. 1. Schematic representation of the AP-PECVD microwave plasma torch.

that the as-deposited coating were fully crystallized under the anatase phase, as a columnar layer composed of aligned monocrystals [17]. Moreover, the intercolumnar porosity of the coating make it suitable for the dye impregnation and thus for the integration into photovoltaic cells. This paper relates the process parameters optimization from a static mode deposition, i.e. the substrate is motionless during deposition, to a dynamic mode deposition, i.e. with a moving substrate during deposition. The coating is no longer localized, and a square centimeter surface can be covered by a titania film. Then, the first parameters adjustments were carried out to transfer the ideal columnar microstructure on glass substrates covered by fluorine-doped tin oxide layer, as the solar cells photoanodes.

2 Experimental

2.1 Plasma enhanced CVD process at atmospheric pressure

The atmospheric pressure plasma-enhanced CVD (AP-PECVD) system used in this study is an axial injection torch (AIT), represented in Figure 1. Microwaves are provided by a SAIREM 1200 KED generator (2,45 GHz) and transported by a rectangular waveguide to supply the cylindrical outer conductor of the coaxial guide. The nozzle, with a 2 mm inner diameter, is placed on the top of the coaxial conductor in a large cylindrical open-air reactor. An exhaust device removes gas or particles produced during the deposition. The substrate holder faces the plasma jet and can be moved along the x and y-axis using a Labview® program. The substrate-nozzle distance can be modified manually.

Argon (AirLiquide Alphagaz I, purity >99.999%) was used as plasma gas. Oxygen required to form titania films was provided by the ambient air, which was well incorporated into the discharge according to the previous optical emission spectroscopy studies [18,19]. The titanium tetraisopropoxide (TTIP), organometallic precursor (Alfa Aesar, Ti(OC3H7)4, purity >97%) was kept into a 300 mL container under argon atmosphere, heated at a constant temperature of 37 °C. Argon gas bubbled into the container and went out saturated with TTIP into the stainless steel gas lines, maintained at a temperature of 70 °C to avoid the precursor liquefaction during the transport. The argon flowrate bubbling into the container, called later "TTIP flow rate" as a misuse of language, fixed the TTIP quantity injected in the gas phase. The plasma gas and the carrier gas were mixed in the lines and carried through the inner conductor of the coaxial line to reach the nozzle. In this study, all the coatings were elaborated in dynamic mode, meaning that the substrate holder is moving at a speed of 1 mm/s during the deposition. All the films were elaborated by doing 10 coating lines of 8 passes set side by side.

The films were deposited on silicon wafer (100) pieces for the process parameters optimization and then, on 1 cm^2 glass pieces with a thickness of 3 mm to elaborate photoanodes. They were covered by a 350 nm-thick fluorine-doped tin oxide film (FTO), a transparent electrode suitable for solar cell application. But it has to be noted that the phase transition from a conductive behavior to an insulating behavior happening at around 450 °C has to be avoided. Before deposition, each substrate is cleaned with an optical paper and ethanol.

2.2 Optimization methodology for the titania layer deposition

At atmospheric pressure, more collisions are generated between reactive species in the plasma phase. Before reaching the substrate, they can react and create clusters by homogeneous reactions. These powders are transported

to the substrate and can interfere with the film growth and be embedded in the layer. This phenomenon is amplified when precursor partial pressure and/or plasma power are increased [20]. Atmospheric pressure also causes plasma contraction. The AIT plasma is composed of two different zones: (i) the central zone called the core at the plasma basis, the most reactive area of the flame, and (ii) the peripheral zone called the plume, characterized by a low electron density. For an incident power of 420 W, the AIT plasma has a 2 mm diameter and a length of 16 mm, comprising the dart and the plume. This plasma shape is defined by temperature and composition gradients from the plasma basis to the plasma plume.

The process parameters of the AIT were studied to understand how each one of them limit the homogeneous nucleation in the gas phase and affect the coating morphology and crystallinity [17,18,21]. As mentioned, the microwave power must be limited to avoid homogeneous nucleation, but enough to decompose the gaseous precursor properly for the deposition. The distance between the nozzle and the substrate can be adjusted between 10 and 30 mm to optimize the residence time of the species into the plasma to avoid the formation of powder in the gas phase. When this distance is increased, the microstructure is affected due to particles embedded into the coating, and the coating becomes amorphous. For example, the titania film is amorphous beyond a distance of 15 mm for a plasma excited with an incident microwave power of 420 W. The gas flow rates appeared to have a strong influence on the coating growth and the particles formation in the plasma. The argon plasma flow rate ensures the discharge stability and the precursor dilution in the plasma phase. It must be sufficient to obtain a stable jet and promote the film growth instead of the formation of non-adherent powder. The TTIP flow rate is determinant for the thin film growth. For a TTIP flow rate under 0.2 slpm, the growth by surface reactions is promoted, and the homogeneous nucleation is drastically limited in the plasma.

Adjustments were, then, necessary to preserve the FTO layer electrical conductivity. The thermal conductivity of the glass is much lower than that of silicon, thus heat is more accumulated into the substrate and could lead to its breakage. The nozzle-substrate distance needed to be increased to take the substrate away from the hotter zone of the plasma. However, to limit homogeneous nucleation, this distance had to be minimized. The microwave power was then decreased to reduce the plasma length. A compromise was mandatory to choose the right parameters to preserve the substrate properties.

2.3 Thin film characterization

First, the morphologies of the titania films were observed using a field emission scanning electron microscope (FESEM) Quanta 450 FEG FEI with an operating range of 15 kV. A 5 nm platinum coating covered the analyzed surfaces before observations. X-ray diffraction (XRD) was used to determine the crystallinity of the films. The apparatus is a D8 Advance from Bruker, with a θ–2θ configuration using the Cu K_α filtered radiation (0.154 nm). The measurements were performed between 20° and 60°, and the sample was spinned at 15 rpm. The optical properties of the photoanodes were measured with a Cary 500 UV-Vis-NIR spectrophotometer, between 200 and 1000 nm, in transmission mode.

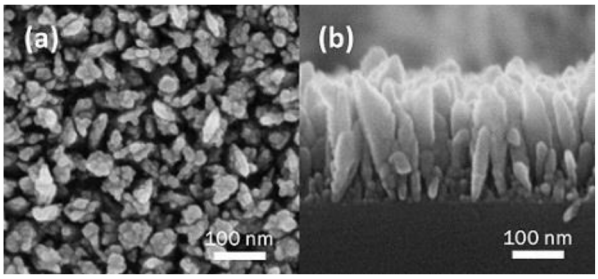

Fig. 2. FESEM images of the optimized TiO_2 thin film on a silicon wafer, (a) top view and (b) cross-section.

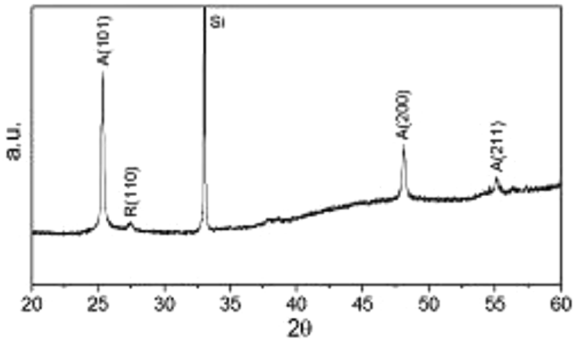

Fig. 3. XRD pattern of the titania film elaborated in the optimized conditions.

3 Results and discussion

3.1 Optimized TiO_2 thin films obtained on silicon wafers

Optimized process parameters were determined to obtain a columnar microstructure and avoid homogeneous nucleation in the gas phase. The microwave power was set to 420 W to ensure plasma stability. The nozzle-substrate distance was fixed at 10 mm to limit homogeneous nucleation and to promote the film crystallinity. The main argon flow rate was settled to 17 slpm to ensure plasma stability and precursor dilution in the gas phase. The TTIP flow rate was then fixed to 0.2 slpm to avoid homogeneous nucleation and promote a film growth by surface reaction.

Figure 2 shows the FESEM images of the TiO_2 film deposited on Si. Its surface (Fig. 2a) displays a rice-like structure composed of facetted grains. The cross-section (Fig. 2b) reveals a columnar structure composed of aligned facetted columns exhibiting an intercolumnar porosity. The XRD pattern in Figure 3 shows that the film is polycrystalline, following the JCPDF 00-021-1272.

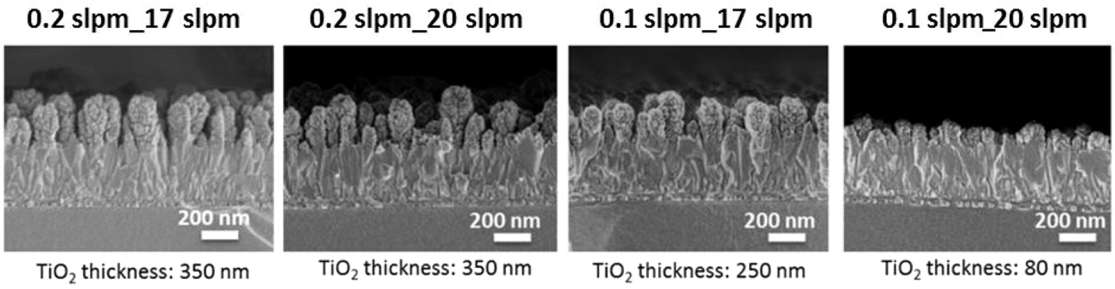

Fig. 4. FESEM images of films elaborated with the different gas flow rates combinations ([TTIP flow rate]_[Ar plasma flow rate]) on glass/FTO substrates, from the plasma phase with the higher TTIP proportion (left) to the lower proportion.

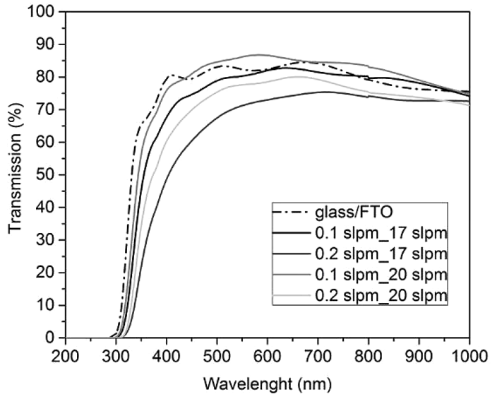

Fig. 5. UV-Visible transmission results.

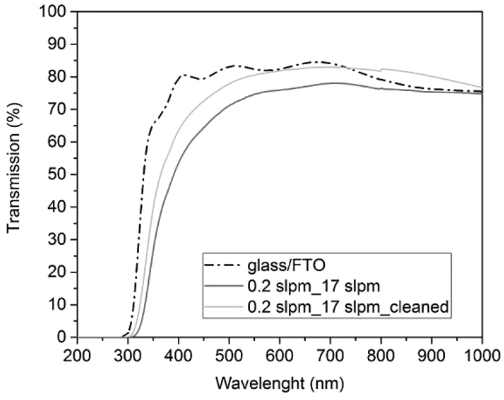

Fig. 6. UV-Visible transmission results after cleaning the 0.2 slpm_17 slpm titania film.

This microstructure is typical of a growth by surface reaction, giving a coating composed of aligned TiO_2 monocrystals [17]. These as-deposited coatings display many advantages to be integrated in solar cells without any additional post-treatments. Their columnar structure, intercolumnar porosity and crystallinity seem ideal for the application. The next step is the deposition of these titania films on a suitable photoanode like glass substrates covered by an FTO layer.

3.2 Transfer of the TiO_2 layer on glass/FTO substrates

Distance/power couples were tested to find the right compromise to preserve the FTO electrical conductivity and avoid the glass breakage. A microwave power of 250 W associated with a nozzle-substrate distance of 19 mm were chosen for the following experiments. Different TTIP and main argon flow rates were tested to deposit a TiO_2 film on the photoanode: 0.1–0.2 slpm and 17–20 slpm, respectively. The aim is to dilute the TTIP precursor to avoid homogeneous nucleation in the plasma phase and thus preserve adequate light transmission through the photoanode.

Figure 4 shows the SEM images of the elaborated coatings. The titania films are columnar exhibiting a cauliflower-like structure. Each column is an assembly of nanoparticles and their growth seem to start on FTO grains. This morphology suggests that, as a consequence of the distance of deposition, titania powders were created in the plasma phase and were then glued with each other thanks to reactive species when reaching the substrate surface. The more the precursor was diluted in the gas phase, the thinner became the titania film. The DRX analyses permitted to conclude that all the films were amorphous.

The UV-visible transmission spectra (Fig. 5) display that the more is the precursor diluted into the plasma, the better is the optical transmission of the photoanode. It can be explained by the titania layer is thinness, for example the film elaborated at flow rates of argon and TTIP of 20 slpm and 0.1 slpm respectively, is only 80 nm thick. The transmission of the films elaborated at a plasma flow rate of 17 slpm with a 0.2 slpm flow rate of TTIP exhibits a reduced transmission as more particles were formed by homogeneous nucleation in the gas phase. A significant proportion of these particles leads to clusters polluting the substrate as non-adherent powders and thus affect the photoanode transparency. To improve the photoanode transmission, the film 0.2–17 slpm was cleaned after deposition in ethanol in an ultrasound bath for four hours. As depicted in Figure 6, the transmission was enhanced meaning that a part of the non-adherent clusters was successfully removed.

4 Conclusions

This work has demonstrated the versatility of the AIT to deposit titania thin films on different kind of substrates. On silicon wafers, the thin films presented an ideal columnar microstructure composed of aligned anatase crystals, with an interesting intercolumnar porosity. On glass/FTO substrates, the coatings were columnar and composed of cauliflower-like assembly, inducing a high specific surface area. This would allow a higher surface of contact with the perovskite layer or the dye, and thus more possibilities to create electron-hole pairs for the solar energy conversion. However, the coatings were amorphous. Indeed, for a nozzle-substrate distance of 19 mm, the substrate is out of the core of the plasma jet which is the hotter and the most reactive zone. The heat transferred from the plasma to the growing film should not be enough to crystallize it. However, this distance cannot be reduced to preserve the FTO layer electrical conductivity. On their pathway along the plasma jet, the titanium and oxygen reactive species would see many collisions allowing the formation of amorphous TiO_2 particles that then reach the substrate to grow the cauliflower columns. A post-treatment ultrasound cleaning was necessary to improve the photoanode optical transmission by removing these non-adherent particles. Further investigations are planned to study the plasma jet and then optimize the process parameters for the deposition of crystallized thin films on thermally sensitive substrates like glass/FTO. These investigations could allow to calculate the gas temperature and help to understand how the reactive species evolve along the jet. In the meantime, the titania layer composed of aligned anatase monocrystals deposited on silicon wafers will be operated to evaluate its performances. An original reverse perovskite device will be developed and tested to confirm the great interest of this microstructure.

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Author contribution statement

Amélie Perraudeau conceived the samples and carried out their characterization. Amélie Perraudeau, Christelle Dublanche-Tixier, Pascal Tristant and Christophe Chazelas developed the PECVD process and conducted its optimization. The UV-Visible experiments were done in collaboration with Sylvain Vedraine and Bernard Ratier. All the authors contributed to the writing of the article.

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