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TiO_2 thin layers with controlled morphology for ETA (extremely thin absorber) solar cells

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Abstract

The paper presents the synthesis process of dense and nanoporous TiO_2 anatase films obtained via Spray Pyrolysis Deposition (SPD). The deposition of dense and nanostructured TiO_2 films uses ethanol solutions of titaniumtetraisopropoxid and acetilacetonate. The influence of the precursor's concentration and deposition parameters (temperature, pressure of the carrier gas and distance of spraying) in tailoring the TiO_2 morphology is presented. The films are tested via X-ray Diffraction and Scanning Electron Microscopy. The photoelectrical properties are tested by current–voltage ($I-V$) experiments in dark, at room temperature. According to the results, SPD proves to be a reliable technique in obtaining thin layers of TiO_2 with controlled morphology.

Keywords: TiO_2 anatase films; Morphology; Spray pyrolysis deposition; ETA solar cells

1. Introduction

Extremely thin absorber layers solar cells (ETA cells) represent a follow up to the new generation of non-silicon based PVs, in the trend firstly stated by Graetzel (1991), [1]. The ETA cells represent solid-state solar cells with an extremely thin absorber layer and with the general structure: transparent n-type semiconductor/n or p-type absorber/transparent p-type semiconductor. In the ETA cell, the light absorber is embedded in a porous and transparent structure enhancing the path of the light through the material and limiting the losses at interface.

The n-type semiconductor investigated in our work is TiO_2 (anatase) semiconductor. Many applications of TiO_2 are based on thin films. Thin films of TiO_2 used as optical coatings, integrate circuits, solar cell and electro-chromic windows capacitor dielectrics, heat reflecting layers and waveguides show good corrosion resistance to corrosive and mechanical attack and stability over long time periods. TiO_2 has received a great deal of attention due to its chemical stability, non-toxicity, and low cost. TiO_2 exists as three polymorphs: anatase, rutile and brookite. The semiconductor properties of the first two polymorphs are presented in Table 1.

To avoid shunts at the front contact interface, the n-type TiO_2 semiconductor is formed out of two layers with different morphologies: a dense thin layer with low flexibility and the nanoporous matrix able to be infiltrated with the p-type absorber semiconductor, used as electron conductor in the cell. The dense films generally have superior mechanical, optical and electrical (charge transport) properties. The porous films are used when a large specific surface area is important as needed in the ETA solar cells, [3], Fig. 1.

Table 1
Properties of TiO_2

Properties	Anatase	Rutile
Bandgap (eV)	3.26	3.05
Density (g/cm^3)	3.90	4.27
Dielectric constant	55	170 E//c; 86E//a*
Refractive index	2.49–2.55	2.61–2.90
Heat of formation $\Delta H^\circ_{f,298.15}$ (kcal/mol)	−218.1	−255.5
Absolute entropy $S^\circ_{298.15}$ (cal/deg/mol)	11.93	12.01
Melting point (°C)	Phase transition to rutile before melting	1855
Hardness (Mohs scale)	5.5–6.0	7.0–7.5

* E//c: electrical field parallel to c-axis of unit cell. E//a: electrical field parallel to a-axis, [2].

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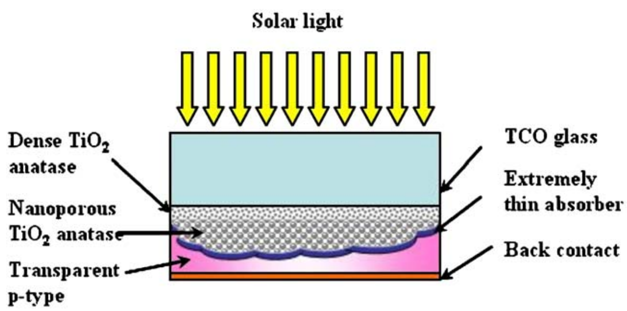

Fig. 1. The structure of ETA solar cell.

The deposition of thin films with specific properties is a challenge for the researchers. Many deposition techniques were used in obtaining TiO_2 anatase layers: Chemical Vapor Deposition (CVD), [4] doctor blade, [5], Spray Pyrolysis Deposition (SPD), [6,7], etc.

The aim of our research is to develop both dense and nanoporous layers by SPD. SPD is a low cost deposition method for large area thin films and it is economically more attractive than other techniques that have been used until this moment being also suitable for up-scaling. The SPD technique was proven to by suitable for the deposition of the dense TiO_2 films, but literature references on the deposition of the nanoporous films is scarce, [8].

In tailoring the thin films morphology two important factors must be considered: the nucleation and the particles' growth. For dense layers the nucleation rate must be higher than the growth rate while in the nanoporous layers growth, these must be reversed.

These two rates and, consequently, the size of the particles formed and the morphology of the resulting films are strongly dependent on the precursors (especially the complexation agents), the substrate temperature, the pressure of the carrier gas, the time between the sprayed layers, and the spraying distance.

2. Experimental

The precursors' solutions for the TiO_2 layers deposition are obtained using absolute ethanol, EtOH (J.T. Baker) solutions of titanium(IV)isopropoxid, TTIP (99.99%, Sigma-Aldrich), and acetilacetonate, AcAc (2,4 pentadione 99+%, Aldrich) used as complexation agent.

The dens TiO_2 layer was deposited via SPD, [4] on the top of a *TCO glass* (transparent conducting oxide, F doped SnO_2 coated glass, Libbey Owens Ford-TEC 20/2.5 mm) using absolute ethanol solutions of TTIP and AcAc in a volumetric ratio of 22.5 : 1 : 1.5. The TCO substrate was cleaned before using by successive immersion in ethanol and acetone in an ultrasonic bath and dried in a nitrogen flow. The deposition is

Table 2
The parameters varied in the deposition of nanoporous TiO_2 layers by SPD

Tests	Temperature (°C)	TTIP : AcAc : EtOH	Substrate	H_{SPD} (cm)	$P_{carrier\ gas}$ (bar)
1 (A)	400*	1.3 : 1 : 20.8	TCO	25, 30, 35	1.2
2 (A)			TCO	30	0.8, 1.0, 1.2, 1.4
3 (B)			TCO/dense TiO_2 anatase	30	1.2

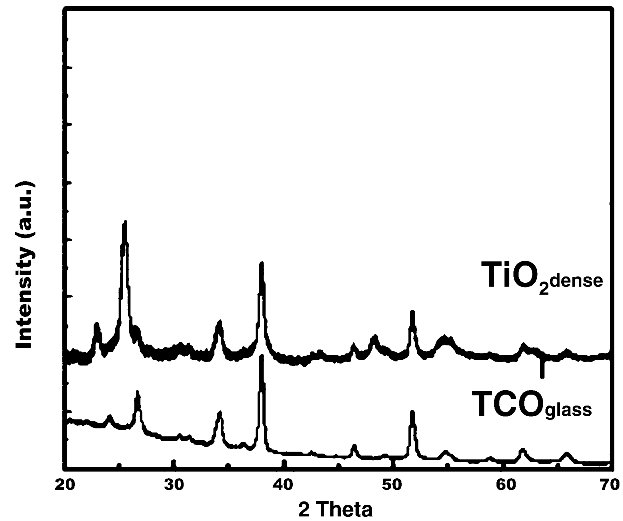

Fig. 2. X-ray Diffraction of dense TiO_2 (anatase) film.

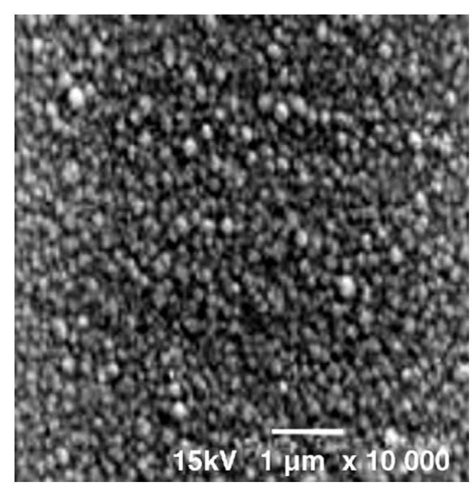

Fig. 3. SEM picture of dense and homogenous anatase TiO_2.

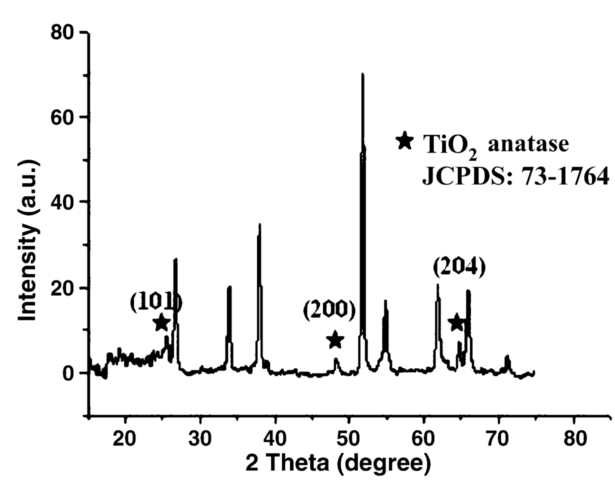

Fig. 4. X-ray diffraction of nanoporous TiO_2 (anatase) film. The other peaks represent the TCO substrate.