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Optimization of physicochemical and optical properties of nanocrystalline TiO\(_2\) deposited on porous silicon by metal-organic chemical vapor deposition (MOCVD)

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Abstract

Titanium dioxide (TiO\(_2\)) is very employed in solar cells due to its interesting physicochemical and optical properties allowing high device performances. Considering the extension of applications in nanotechnologies, nanocrystalline TiO\(_2\) is very promising for nanoscale components. In this work, nanocrystalline TiO\(_2\) thin films were successfully deposited on porous silicon (PSi) by metal organic chemical vapor deposition (MOCVD) technique at temperature of 550 °C for different periods of times: 5, 10 and 15 min. The objective was to optimize the physicochemical and optical properties of the TiO\(_2\)/PSi films dedicated for photovoltaic application. The structural, morphological and optical properties of the elaborated TiO\(_2\)/PSi samples were analyzed by means of x-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive x-ray spectroscopy (EDX), atomic force microscopy (AFM), photoluminescence (PL) and UV-Visible absorption spectroscopy methods. The effect of deposition time on the microstructural properties which influences the optical characteristics of the obtained samples was also examined. The XRD analysis confirms the nanocrystalline structure of the deposited TiO\(_2\) composed only by anatase phase. The SEM characterization evidenced an increase in the TiO\(_2\) film thickness showing more uniform surfaces as the deposition time rises. Correspondingly, the surface roughness increases with the particle size and film thickness as indicated by AFM studies. The TiO\(_2\)/PSi/Si sandwich structure evidenced by cross-sectional SEM confirms the good adherence of the TiO\(_2\) nanocrystalline film on the porous silicon forming with silicon a composite material. The UV-Vis measurements showed a considerable enhancement in optical absorption of porous silicon after the deposition of TiO\(_2\) films. Indeed, the TiO\(_2\) coatings deposited on PSi for 15 min with thickness of 200 nm have the best structure quality and exhibit, consequently, the highest absorption. From these interesting results, we demonstrate the viability of the use of the MOCVD as reproducible process for the elaboration of high-quality TiO\(_2\)/PSi films.

1. Introduction

Porous silicon and TiO\(_2\) are important materials which are extensively employed in many applications especially solar cells [1, 2]. In fact, Porous silicon is characterized notably by large specific surface area, good absorbance, direct and large band gap (2.2 eV) which favors its utilization as an antireflection coating (ARC) in solar cells.
In addition to the potential application of TiO₂ as a double antireflection coating, this material has distinct advantages comparatively to other transparent conducting oxides (TCO) (ZnO, SnO₂, TTO) such as: good stability of physicochemical properties, excellent transmittance, high refractive index and abundance in nature. In fact, the application of TiO₂ as antireflection coating permits to reduce the reflection losses and thus to increase the conversion efficiency of solar cells [5]. Moreover, TiO₂ exhibits generally a n-type conductivity [6] and can be used for the fabrication of heterojunction diode when deposited on p-type silicon.

Considering its crystallographic structure, TiO₂ exists on three phases called: anatase (tetragonal), rutile (tetragonal) and brookite (orthorhombic); among them, the anatase TiO₂ is known as the most efficient crystalline phase for application as ARC in solar cells comparatively to rutile form owing to its larger band gap [7] (3.23 eV for anatase and 3.05 for rutile) and higher electron mobility [8].

Nowadays, with the extension of applications in nanotechnologies, the development of TiO₂ nanostructured TiO₂ becomes more and more required. For this purpose, several synthesis techniques can be used [9–15]. Among them, metal-organic chemical vapor deposition (MOCVD) offers a notable advantage of easy and high control degree of the crystalline structure, crystallites size at the nanoscale dimension, porosity, thickness and film stoichiometry [16]. Moreover, due to its large throughput, high deposition rate and relatively low deposition temperature, suitability to large area [16], MOCVD becomes competitive method for industrial production. The MOCVD offers a good compromise between film quality and fabrication cost; highly pure precursors are commercially available at low cost [17]. Further important advantage of the MOCVD method is its ability to produce new composite materials as well as multilayers with controlled thicknesses by multiple injection sources attached to the same reactor [16].

A large variety of TiO₂ nanostructures with different morphologies and shapes were elaborated by researchers at the ICB laboratory [10, 18, 19]. The MOCVD is developed as a simple and stable technique which permits a perfect control of all growth parameters and ensures thus an excellent reproducibility of any form of deposition.

This work aims, particularly, to improve the light absorption in porous silicon with the deposition of nanocrystalline TiO₂ films by MOCVD technique. The optical absorption depends on the film thickness. Since the MOCVD allows a control of thickness by the deposition time, a series of TiO₂ films were deposited at 5, 10 and 15 min for the optimization of TiO₂ film thickness with the goal to achieve higher absorption.

The good absorption of TiO₂/PSi sample is interesting for its use as an active material for the elaboration of highly efficient solar cells. In fact, the improvement of light absorption in the semiconductor increases the electron–hole carriers, leading to an enhancement of the photogenerated current and thus the conversion efficiency of the photovoltaic cell.

To our best of knowledge, there are no reports in the literature about the study of TiO₂/PSi structures. For this study, a various characterization techniques were used to analyze the physicochemical and optical properties of the produced TiO₂/PSi films dedicated for photovoltaic application.

2. Experimental procedure

2.1. Fabrication of TiO₂/PSi films

The elaboration of TiO₂/PSi samples consisted on two steps:

2.1.1. Preparation of porous silicon by Stain etching

A porous silicon layer was formed on (100) p-type monocrystalline silicon (Si) wafers with thickness of 340 μm by Stain etching method using the solution based on HF/HNO₃/H₂O for 12 s at room temperature, following the same procedure reported in our previous studies [20].

2.1.2. TiO₂ deposition on PSi substrates by MOCVD

A range of TiO₂ films were deposited on PSi substrates at 550 °C using a cold wall low pressure MOCVD system for different periods of times. The MOCVD installation scheme is previously presented with detailed description by A. Crispasian in [19]. This MOCVD system is mainly composed of a horizontal reactor with 50 mm diameter and 600 mm a length, precursor supply system, a metal catalyst supply system, a gas supply system, a water bath, and a vacuum pump.

Titanium tetraisopropoxide (TTIP) with chemical formula of Ti(OC₃H₇)₄ (99.999% - Sigma Aldrich) and Ferrocene (Fe(C₅H₅)₂) (98% - Sigma Aldrich) are used as TiO₂ precursor and metal catalyst, respectively. The PSi substrate was placed on a graphite substrate heated by magnetic induction and positioned at the center of the tubular reactor.

The organometallic precursor, placed in a water bath, was vaporized. The TTIP vapor was transported into the reactor (deposition chamber) by carrier gas of pure nitrogen (N₂) where the thermal decomposition leads to
the formation of TiO\(_2\) onto the PSi surface following the main reaction:

\[
\text{Ti(OC}_2\text{H}_4\text{)}_4 \rightarrow \text{TiO}_2 + 4\text{C}_2\text{H}_6 + 2\text{H}_2\text{O}
\]

More details about the TiO\(_2\) growth could be found in [10]. The experimental conditions given in table 1 were used for all the deposits in order to investigate only the influence of the variation of deposition time on the properties of the material.

The produced TiO\(_2\)/PSi samples were then removed from the reactor and characterized, without any further treatment, in order to explore their physicochemical and optical properties.

### 2.2. Characterization of TiO\(_2\)/PSi samples

The crystalline phase composition and orientation of the elaborated samples were examined using x-ray diffractometer (D8 Discover BRUKER) using Cu-K\(\alpha\) radiation (\(\lambda = 1.5406 \text{ Å}\)).

Scanning Electron Microscope (SEM - HITACHI SU8230) was used to observe the surface morphology of the final products and to determine the TiO\(_2\) films thicknesses. The elemental composition of TiO\(_2\)/PSi was further studied by an Energy Dispersive X-ray Spectroscopy (EDX) probe coupled to the SEM. The Atomic Force Microscope (Ando model—HS-AFM 1.0 with PID feedback 2.0) was used to evaluate the surface roughness of the deposited films. The optical properties were characterized by photoluminescence using a fluorescence spectrometer (Andor Shamrock SR-i, Detector: Camera Andor Newton 920) and by absorption measurements using an OL 750 automated spectro-radiometric measurement system.

### 3. Results and discussion

#### 3.1. Structural characterization: XRD measurements

From the XRD patterns (figure 1), all the TiO\(_2\) films deposited on PSi, at different periods of time, are anatase phase nanocrystalline layers. This is revealed by the characteristic peak located at 2\(\theta = 25.3^\circ\) corresponding to (101) crystal plane (reference PDF card No.: 00-021-1272). Whereas the intense diffraction peak centered at 2\(\theta = 56.12^\circ\) is assigned to porous silicon (reference PDF card No.: 00-027-1402) which confirms that the PSi keeps the same crystallographic orientation (100) as monocrystalline silicon substrate.
3.2. Morphological characterization

3.2.1. SEM/EDX studies

Figure 2 shows SEM images of the prepared PSi and nanocrystalline TiO$_2$/PSi samples with different surface morphologies (b–d) depending on the deposition time. Figure 2(a) displays the sponge-like surface of porous silicon substrate which consists of many nano-pores and interconnected silicon nano-crystals. All the deposited TiO$_2$ films exhibit smooth surfaces, however TiO$_2$ deposited at 15 min shows better morphology. This result can be explained by the amelioration in crystallization quality due to the thermal effect favoured by the rise in deposition time (figures 2(b)–(d)). The TiO$_2$ films thicknesses are measured by cross-sectional SEM images and found to be 120, 170 and 200 nm for depositions times of 5, 10 and 15 min, respectively.

Figure 3 shows the sandwich structure TiO$_2$/PSi/Si. This figure shows the good adhesion of TiO$_2$ nanocrystals on porous silicon forming with silicon a composite material. Thus MOCVD is an appropriate technique for the deposition of nanocrystalline TiO$_2$ on porous substrates.

Furthermore, the corresponding EDX spectra (figures 4(b)–(d)) illustrate the presence of the Oxygen (O) and Titanium (Ti) elements. At 10 and 15 min, the Ti and O peaks seem more important than at 5 min. A layer of TiO$_2$ is therefore present on the PSi from the first deposition time. The appearance of the Carbone (C) peak is due to the use of metal-organic precursors in the MOCVD technique while the Aluminum (Al) peak is originated from crucible used during the silicon manufacture.

3.2.2. AFM analysis

The surface roughness increases with the particle size and film thickness as indicated by AFM and SEM results (table 2). The increase in surface roughness with TiO$_2$ film thickness is also observed by other studies [9]. However, the low values of RMS roughness confirm that the three deposited TiO$_2$ films are indeed smooth.
3.3. Optical characterization

3.3.1. Photoluminescence

The photoluminescence measurements were performed on TiO$_2$/PSi samples at the excitation wavelength of 325 nm corresponding to 3.8 eV which exceeds the band gap of titania (3.0–3.2 eV). As shown in figure 5, the porous silicon exhibits intensive photoluminescence intensity with a strong peak at 685 nm corresponding to

![Figure 3](image-url)

**Figure 3.** Cross-section SEM image of the sandwich structure TiO$_2$/PSi/Si obtained at 550 °C for 15 min time deposition.

![Figure 4](image-url)

**Figure 4.** Corresponding EDX spectra of (a) PSi; (b) TiO$_2$/PSi 5 min time deposition; (c) TiO$_2$/PSi 10 min time deposition; (d) TiO$_2$/PSi 15 min time deposition.
1.8 eV which reflects directly its band gap energy [4]. The decrease in the PL emission of PSi after the deposition of TiO2 films is indicative of a reduced carrier’s recombination activity. In addition to recombination of photo-induced electrons and holes, the PL spectrum of anatase TiO2 material can also result from oxygen vacancies and surface states, as reported by others studies [21].

### 3.3.2. Absorption studies

Figure 6 shows the variation of optical absorption of PSi and TiO2/PSi samples as a function of wavelength. The light absorption of porous silicon increases after the deposition of TiO2 films.

#### Table 2. Microstructural parameters of the deposited nanocrystalline TiO2 films.

| Deposition time | Mean grain size (nm) | RMS Roughness (nm) |
|-----------------|----------------------|--------------------|
| 5 min           | 20                   | 6.53               |
| 10 min          | 25                   | 6.92               |
| 15 min          | 30                   | 7.73               |

Figure 5. PL spectra of PSi and TiO2/PSi deposited by MOCVD for different periods of time deposition.

Figure 6. Comparative absorption of PSi and TiO2 deposited on PSi samples for different periods of time deposition.
Moreover, in the range of 500–900 nm, the rise of absorbance with the deposition time and hence, with the increase of TiO₂ thickness is evidenced indicating the best absorption characteristic for 200 nm thick TiO₂ films deposited during 15 min.

4. Conclusion

In this work, we have described the deposition of nanocrystalline TiO₂ films on porous silicon substrates by MOCVD technique with high control of structure and thickness via the variation of deposition time. A comparison was made for morphological and optical properties of TiO₂ films deposited at 5, 10 and 15 min. Based on characterization results, all the produced TiO₂ films are pure anatase and smooth. However, TiO₂ samples deposited at 15 min with thickness of 200 nm exhibit better microstructure resulting in higher optical absorption.

We can conclude that MOCVD, as a reproducible technique, is well adapted for the elaboration of high-quality TiO₂/PSi films with interesting properties for photovoltaic application.

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