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Full Length Article

Growth and properties of nanostructured titanium dioxide deposited by supersonic plasma jet deposition

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ABSTRACT

Titanium dioxide (TiO_2) is a wide gap semiconductor suitable for many applications. In this work, TiO_2 nanostructured thin films are deposited by a plasma assisted supersonic deposition technique on silicon and on conductive glass substrates. Optical Emission Spectroscopy (OES) is used to monitor plasma conditions and precursor dissociation reactions. The influence of deposition parameters on TiO_2 structure, uniformity, grain size, and optical properties are investigated by atomic force microscopy (AFM), mechanical profilometer, scanning electron microscopy (SEM) and spectroscopic ellipsometry (SE). Experimental results show how employed technique allows obtaining uniform films, with a tunable deposition range. Grains size could be chosen varying precursor flux during the deposition process. Films nanostructure and porosity result to be affected by grains size. Substrate roughness results to affect film morphology.

1. Introduction

In the last years, great attention has been paid to nanostructured metal oxide semiconductors, a class of materials with unique structural characteristics making them different from the corresponding bulk materials and suitable for the development of many innovative chemical and physical properties [1]. Titanium dioxide (TiO_2) materials, like nanotubes, nanorods and mesoporous thin films, are widely used in a variety of applications in the environmental and energy fields, such as the fabrication of self-cleaning surfaces, of sensors [2–4], the hydrogen generation by water photo-electrolysis [5,6], and the photo-electrochemical conversion (e.g. DSSC and thin film solar cells) [5–11]. The nano-structure of a TiO_2 material influences many of its properties, such as its photo-catalytic performances, and also its surface area, adsorption capability, optical reflectance, adhesion, and carrier transport properties [12–18]. For this reason the study of TiO_2 morphology and structure has been very attractive [13,14]. In particular, columnar structures (e.g. nano-rods and nano-wire) have showed interesting features, since they offer some advantages in charge carriers transfer rate and in hole-electron recombination behavior. These effects are favorable for photo-catalytic reactions and solar cells efficiency [12,19].

Despite the relevance of this kind of materials, to date there are few available techniques for controlled deposition of nanostructured oxides. Currently, nanostructured metal oxides are usually synthesized by sol-gel methods or from colloidal solutions containing a dispersion of nanoparticles [20]. These methods, however, do not allow a proper control of the nanostructure, and they often exhibit problems of adhesion between the film and the substrate. Other deposition techniques, such as Chemical Vapor Deposition (CVD) and Physical Vapor Deposition (PVD), permit a higher control over the structure of the film, but they don't allow to obtain at the same time a good uniformity and high deposition rate, so they are ineffective in the growth of thin films on surface of large scale area [21].

The novelty of the technique denominated Plasma Assisted Supersonic Jet Deposition (PA-SJD) is the segmentation of the gas phase material synthesis in two separate steps: chemistry control in a reactive cold plasma environment; assembling control by means of a supersonic inseminated jet over a substrate [22–24]. Proposed technique is versatile; vaporizable and stable metalorganic precursors could be employed as the source of oxides, semiconductors or metals. The extraction of a supersonic plasma jet allows focusing the precursor flow on the substrate. Fast deposition rates could be reached using high plasma density and high precursor flux. Compared to conventional gas phase processes, the proposed technique allows control of the kinetic energy of clusters and control on their assembly arrangement on the substrate. Some of achievable

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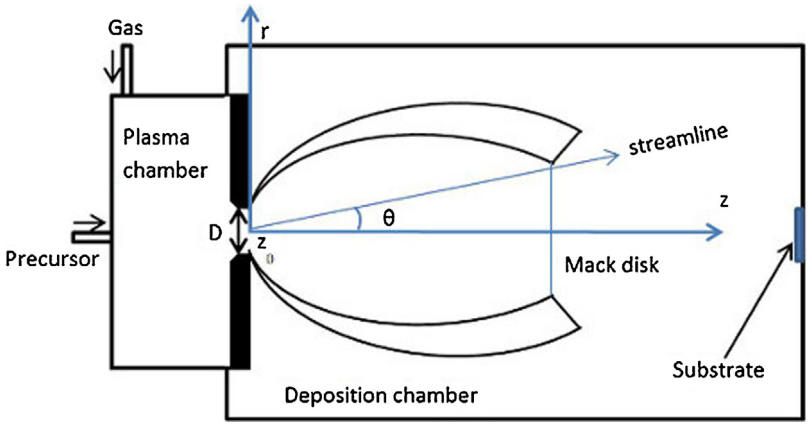

Fig. 1. A schematic representation of supersonic jet extraction from the plasma chamber. The jet expands along both the axial direction (z axis) and the radial one (r axis), until the Mach disk, where a transition to subsonic condition takes place. The substrate could be moved along both axes.

advantages are a good collimation and stability and the control of crystallinity. By changing the processing parameters, it is possible to change film thickness, porosity and nano-structure.

In this study, we briefly describe the deposition technique and analyze plasma chemical species during the deposition process. Then we show the results obtained on a series of TiO_2 films in terms of morphology and properties using Atomic Force Microscopy (AFM), Scanning Electron Microscopy (SEM), Spectroscopic Ellipsometry (SE), and a mechanic profilometer.

2. Material and methods

The deposition technique set-up was exhaustively described previously [22]. Nanostructured thin film growth by PA-SJD is based on the separation of the deposition process into two steps: the precursor dissociation in a reactive plasma environment and the nanoparticles acceleration and assembly on a substrate by means of a supersonic jet (Fig. 1). The extraction of a supersonic plasma jet allows to focus the precursor flow on the substrate and to control atoms kinetic energy and clusters size. In the first stainless-steel cylindrical chamber (inner radius 62.5 mm, length 95 mm), a non-thermal inductively coupled plasma is generated by means of a three-loop copper antenna in a planar configuration, powered by a 13.56 MHz radiofrequency generator through a L-type matching box. The plasma chamber is connected to the second stainless-steel chamber by a circular converging nozzle, with a diameter D = 6.9 mm. The deposition chamber is cylindrical, it has an inner radius of 160 mm and the length is 200 mm. The deposition chamber is connected to the pumping system (Fig. 1). After the nozzle, the gas flows from the orifice into the deposition chamber, with an initial sonic velocity, forming an expanded free jet. Along the jet the gas pressure is initially greater than the background pressure and the gas expands radially and axially (Fig. 1). The radial velocity is smaller than the flow speed, while the axial one reaches quickly the limit value v_{limit} [25]. The expansion ends with a shock, called Mach disk, where a transition to a subsonic expansion takes place.

Titanium isopropoxide (TTIP) is used as metalorganic precursor. TTIP is stored in an aluminum container of a few tens of ml with a brass sealing. This system is connected to plasma chamber using a micrometric valve. A heater was put around the container and around the injection system, the apparatus is insulated and the temperature is controlled during all the deposition process by the use of thermocouples. The heating of the precursor allows to vaporize it and to introduce the precursor inside the plasma chamber. The precursor flux is adjusted by varying its temperature. TTIP is introduced inside the plasma chamber when the plasma discharged is ignited and it is stable.

The plasma discharge is ignited using an oxygen-argon feedstock gas mixture with controlled partial pressures. The pressure inside the plasma chamber is 8 Pa, and the gas is a 2:3 mixture of argon and oxygen. Under these conditions, the pressure ratio between the two chambers, here set to 28, determines the formation of a supersonic expanding jet.

The TTIP flux can be tuned from 0.3 g/h to 0.8 g/h by varying the temperature from 40 °C to 50 °C. The flux is calculated by the precursor consumption during the deposition process.

After TTIP injection, the total pressure inside plasma chamber increases until 11–13 Pa, depending on the TTIP flux. The plasma jet after the nozzle hits a substrate located at a given distance from the nozzle, which could be varied from 5 to 30 mm.

In this work two substrates are employed: small slabs of oxidized single crystal silicon and fluorine doped tin oxide (FTO) coated glass. Before the deposition, the substrates are cleaned using pure ethanol. During the deposition process, an aluminum mask is located on the substrate to define the deposition area (7 × 7 mm for samples A–G reported in Table 1).

After the deposition, the films are annealed at 500 °C for 20 min in order to remove organic impurities.

Table 1
Deposition parameters and properties of all the samples.

Sample	Substrate	RF power [W]	Precursor flux [g/h]	Working pressure [Pa]	Nozzle-substrate distance d [mm]	Deposition time [min]
01	Si	450	0.8	13	14	25
A	Si	450	0.8	13	7	2
B	Si	450	0.8	13	9	10
C	Si	450	0.8	13	14	15
D	Si	450	0.8	13	30	25
E	Si	450	0.3	11	14	15
F	FTO	450	0.8	13	14	15
G	FTO	450	0.8	13	7	55