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Deposition of TiO_2 thin films by atmospheric plasma post-discharge assisted injection MOCVD

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Abstract

TiO_2 thin films have been deposited at low temperature using a new atmospheric pressure deposition process, which combines remote Atmospheric Pressure (AP) Plasma with Pulsed Injection Metallorganic Chemical Vapour Deposition (PIMOCVD). The effects of post-discharge plasma and deposition parameters have been studied with respect to the deposition kinetics, morphology, and microstructure of TiO_2 films. It is shown that well-crystallised TiO_2 anatase films can be obtained at a temperature of only 275°C.

Introduction

MOCVD route offers several potential advantages including close control of film stoichiometric, crystallinity and uniformity, versatile control of composition, ability to coat complex shapes and large surfaces. Our laboratory has developed Pulsed Injection MOCVD [1] method, based on a liquid delivery system controlled by a high speed precision micro electro-valve which injects a very small volume of precursors into an evaporator at high temperature (150-300°C). This method allows to extend the precursor choice to non-volatile compounds [2]. An important feature of PIMOCVD is that the thermal exchange between gas and droplet ensures the total evaporation of precursors even at atmospheric pressure.

Axcys Technologies has commercialized a new dielectric barrier discharge (DBD) plasma system producing low temperature plasma at atmospheric pressure. The post-discharge is sent away from electrodes confinement [3]. In this work, we have combined these two systems working at atmospheric pressure to study the feasibility of low temperature deposition of TiO_2 in order to add an alternative and reliable method, PIMOCVD, to the innovative research line AP-PECVD [4,5].

Experimental

The PIMOCVD experimental set-up has been detailed in previous articles that also report on the deposition of a large variety of precursors [1, 2]. Precursors used in this study were $Ti(OiPr)_2(thd)_2$, dissolved in octane, and Titanium (IV) oxide acetylacetonate, $TiO[CH_3COCH=C(O-)CH_3]_2$, dissolved in butanol at concentrations ranging from 0.02 to 0.1 mol/l. The precursor solution was injected in the evaporator with a frequency of 4 Hz and

opening time of 3 ms, yielding droplet sizes of ca.3 µl. Evaporation temperature was 280°C. The precursor vapours were transported by the carrier gas (3.5 to 5 l/min of 20%O_2 in N_2) through a heated line to the post discharge zone and mixed with the active species from the plasma. We have used a cylindrical coaxial DBD plasma with an self-regulated frequency of around 100 KHz and electrical power of 600 watt. The internal electrode was 60 mm in length and 28 mm in diameter. The gap between electrodes was 1mm and the plasma outlet is 2mm width [3]. Plasma was created with air reconstituted (20% of O_2 in N_2) at total gas flow rates of 15 l/min. Few experiments were also performed with the same flow rate but with lower oxygen concentration in plasma gas to determine the plasma activity. Species activated in the plasma were mixed with the precursors in the post-discharge zone and reached the heated substrate placed at 90 mm of the plasma outlet, which yield the deposition of a thin solid film. The depositions were performed on 2" silicon substrates heated at temperatures ranging from 200°C and 300°C. The evacuation was ensured by an extracting motor.

The film thickness and refractive index were measured by ellipsometry with at a 632.8nm wavelength and 70º incidence angle. X-ray Photoelectron Spectroscopy (XPS) were performed in a Vacuum Generator using a Mg line and at two incidence angles (90° and 30°). Ti 2p, O 1s, C 1s and N 1 peaks were scanned and analysed. Rutherford Backscattering (RBS) and Nuclear Reaction Analysis (NRA) were simultaneously performed on the sample using deuteron particles at 870 keV. RBS detection was done at a dispersion angle of 165° and titanium content was calculated using a bismuth thin film as reference. Oxygen, carbon and nitrogen quantifications were obtained from the reactions $^{12}C(d,p)^{13}C$ and $^{16}O(d,p)^{17}O$ with deuteron particles at 870 keV at and $^{14}N(d,\alpha)^{13}C$ at 1400 keV. In all cases, the detection angle was 150º and a Mylar filter of 13 µm was used.

Fourier Transform Infrared (FTIR) spectra were monitored between 250 and 4000 cm^{-1} using a Bio-Rad FTS165 spectrometer (200 scans at 20Hz, 4cm^{-1} resolution). Raman excitation was performed with a green laser of 514.5 nm in a LabRam spectrometer (Jobin-Yvon). X-Ray Diffraction (XRD) was preformed at grazing incidence with λCu= 1.5406 Å. Film cross-sections were prepared using a Precision Ion Polishing System (PIPS)-GATAN at low angle (6°) and low voltage (2.5-3 kV) and subsequently studied by Transmission Electron Microscopy (TEM) using a JEOL-2010 instrument with an electron beam energy of 200keV. Surface morphology was analyzed by Scanning Electron Microscopy (SEM) in a SEM-FEG Hitachi 4500 and by Atomic Force Microscopy (AFM) in a Nanoscope II of Digital Instrument in contact mode.

Results

a) General features

Films deposited from Ti $(OiPr)_2(thd)_2$ or from Titanium (IV) oxide acetylacetonate behaved similarly. Films were deposited in remote mode with a plasma outlet-to-substrate distance of 90 mm. With this configuration, the deposition rate is only of 0.4µm/h, and the deposition is isotropic, i.e. vapors reach even the chamber walls. No other publication has shown deposition at so high distance. On the other hand, it means that 3D pieces could be covered under these conditions. Nevertheless, a convergent flow can be created with a nozzle to improve the deposition yield if needed.

Calibration of substrate temperature, using a thermocouple in intimate contact with a silicon substrate, showed that the temperature at the substrate surface was lower (of 40°C at 300°C and of 25°C at 200°C) than inside the substrate holder. It is due to the cooling effect of the high flow rates used for plasma generation, which can not be balanced by the interaction of

the active particles with the substrate. In next parts of this article, we will specify the temperature measured inside the substrate holder.

Keeping constant air oxygen proportion (20%) in the evaporator, oxygen concentration in the plasma discharge varied between 0 and 20%. Firstly, no film could be grown with plasma of pure nitrogen, while a low oxygen proportion (3.3%) was sufficient to produce TiO_2 films. Furthermore, films were grown at temperatures as low as 200°C. By thermal CVD at the same deposition conditions, depositions starts at 400°C. It should be mentioned that 200°C is lower than the evaporation temperature (280°C). However, XPS and FTIR measurements showed that the deposited film did not ensue form a precursor condensation. Stability of films was tested by annealing at 500°C in air for 1 h. All films stood this treatment, which provokes crystallization in anatase phase and a film thickness shrinking evidenced by a colour change, mainly for the lowest temperature film, due to densification. A plasma treatment at 300°C on films deposited at 200°C did not induce any change. It is then inferred that the plasma acts differently when used during deposition or during post-deposition annealing.

a) Effect of deposition temperature

Samples were grown at 200, 225, 250, 275 and 300°C from $Ti(OiPr)_2(thd)_2$. Final thickness was 100nm at all temperatures for the same injected volume. The refractive index was 2.4 for deposition at 300°C and 2.3 for lower temperatures; to be compared to 2.55 for the bulk TiO_2 anatase value. Films are very smooth, with rms roughness values of around 1nm and mean grain size of 20 nm independently of deposition temperature.

For all samples, FTIR spectra show the absorbing bands at 440 cm^{-1} and 260 cm^{-1} associated to TO mode of TiO_2 anatase [6] any additional band corresponding to contamination from organics products could not be evidenced. Increasing deposition temperature induces the film crystallization, reflected by a decreasing width of the IR bands. The anatase phase was detected at deposition 275°C or higher temperatures by Raman spectroscopy (peaks at 143 and 392 cm^{-1}, Fig. 1 [6]) and grazing XRD (reflections are (101), (103) (004) (112) (200)). Films deposited at lower temperatures were amorphous. In TEM observation, anatase formation was confirmed at 300°C by indexing of electron diffraction patterns in Fig 2a by comparison with the simulated diffraction spectrum (TiO_2 anatase a= 3.78520Å, c= 9.51390Å, space group I41/amd). High resolution pictures show small crystals where different lattice planes could be clearly resolved (see (101) plane; d= 0.352nm in Fig. 2b)

RBS and NRA studies indicated that the films were mainly contaminated by nitrogen and carbon species, films deposited at 200°C showing a higher contamination level: 4.5% C and 3.7 % N to be compared with 3% C and 1% N for films deposited at higher temperatures. The O/Ti ratio was slightly higher than 2 without influence of deposition temperature. XPS was performed on the same samples without any surface preparation. De-convolution of the Ti, C and O peaks was performed considering the components summarized in Table 1 [7]. O 1s peaks were fitted by a main Ti-O contribution (more than 50% for all temperatures) followed by a Ti-OH contribution. The effect of deposition temperature is to increase the Ti-O contribution and to decrease the Ti-OH contribution (Fig 3) for the two angles of measurement. Ti 2p peaks were fitted by only one contribution at 458.5 eV with a FWHM of 1.5 eV which corresponds to Ti^{+4}. N 1s peak was very small with only one contribution at 399.4 eV.

b) Effect of titanium to oxygen (Ti/O) reaction ratio

The Ti/O reaction ratio was varied by changing $TiO(acac)_2$ concentration in solution and oxygen concentrations in plasma flow at a deposition temperature of 300°C. Fig 4 shows that the deposition rate increases with increasing the Ti concentration in the solution. The deposition rate follows a same behaviour with the oxygen content in plasma for all Ti concentrations. It initially increases with the oxygen concentration in plasma and saturates for values higher than 8%. FTIR spectra of Fig 5 also show that, for film deposited with a same deposition rate, increasing the oxygen content favours an enhancement of the crystallization degree, as depicted by a decrease in width of bands at 440 cm^{-1} and 260 cm^{-1}. Accordingly, films deposited at 6.66% and 20% of oxygen have the same deposition rate, but the decrease of Ti/O reaction ratio enhances the anatase formation. Besides, if the oxygen concentration in plasma is kept constant at 13%, anatase is more easily detected as films are deposited with lower precursor concentration in the solution, i.e. at lower Ti/O reaction ratio. Similar effect was found in [8] when using a plasma formed by hydrogen in helium.

Discussion

Results presented in this work established that plasma generated from oxygen-containing atmosphere does assist the deposition and plays a dual role: it enhances titanium oxide formation and decreases the energy needed for crystallisation in anatase phase

On the one hand, plasma assistance on the oxide formation is clearly evidenced by a non-dependence in temperature of the deposition rate within the whole investigated thermal range. Moreover, oxygen concentration in plasma discharge seems to be crucial for the deposition process since no deposition could be obtained without oxygen uptake in the plasma. Finally, films grown at low temperature (200°C) consist of TiO_2 with relatively low carbon content (3%). This result could not be reproduced by thermal CVD.

On the other hand, two main parameters are involved in anatase formation and enhancement of the crystallization degree, namely the substrate temperature (anatase is detected after deposition at 275°C) and Ti/O reaction ratio. Our results show that anatase formation is enhanced by increasing the temperature deposition for a constant Ti/O reaction ratio and, for a fixed temperature, by decreasing the Ti/O reaction ratio.

Other characteristic aspects of our plasma system can be analyzed as follows. Films were deposited using artificial air for plasma generation, which implies a rather high O_2 concentration. Few groups use air as plasma gas [9] and, in plasma generated with oxygen, only very low O_2 concentrations are used [10]. Furthermore, we used a plasma outlet-substrate distance greater than any other mentioned in literature. Remote PECVD is strongly dependent on electrode-wafer spacing, which is always kept smaller than15 mm [11].

In our conditions, anatase formation started at T=275°C which was lower than for CVD at atmospheric pressure ($T \geq 400$°C) [12] or AP-PECVD (T = 350°C) [8]. Only one technique working at low pressure was reported to promote anatase formation at lower temperature (210°C), which used an excimer lamp to activate the process (Photo CVD) [13].

Conclusions

We have studied the deposition of TiO_2 thin films using a new Injection MOCVD process working at atmospheric pressure and combined with remote Atmospheric Plasma. TiO_2 films could be deposited at very low temperature (200°C), even lower than the evaporation

temperature. When using oxygen concentration in air (20%) for the plasma gas flow, TiO_2 films crystallized in anatase phase from temperatures as low as 275°C. Oxygen in plasma has a dual role: it enhances TiO_2 deposition rates and it provokes its crystallization. No film was deposited when using oxygen-free plasma.

Acknowledgements

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Table 1. Contributions and energies for the XPS peaks de-convolution.

Element	Contributions and energies from [7]			
C1s	C-H/C-C at 285eV	C-O at 286.4 eV	C=O/O-C-O at 287.9 eV	O-C=O at 289.0 eV
O1s	C-O, C=O at 532.6 eV	M-OH at 531.5 eV	M-O at 530.1 eV	
Ti 2p3/2	Ti-O at 458.5 eV			
N 1s	N at 399.4 eV			

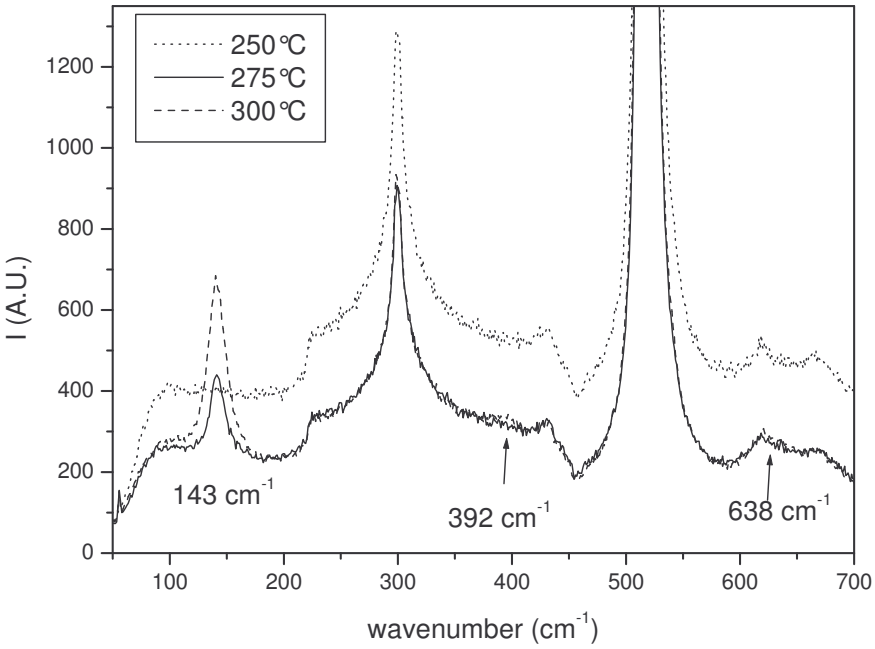

Figure 1 Raman spectra of TiO_2 samples deposited from $Ti(OiPr)_2(thd)_2$. Peaks associated to anatase are indicated

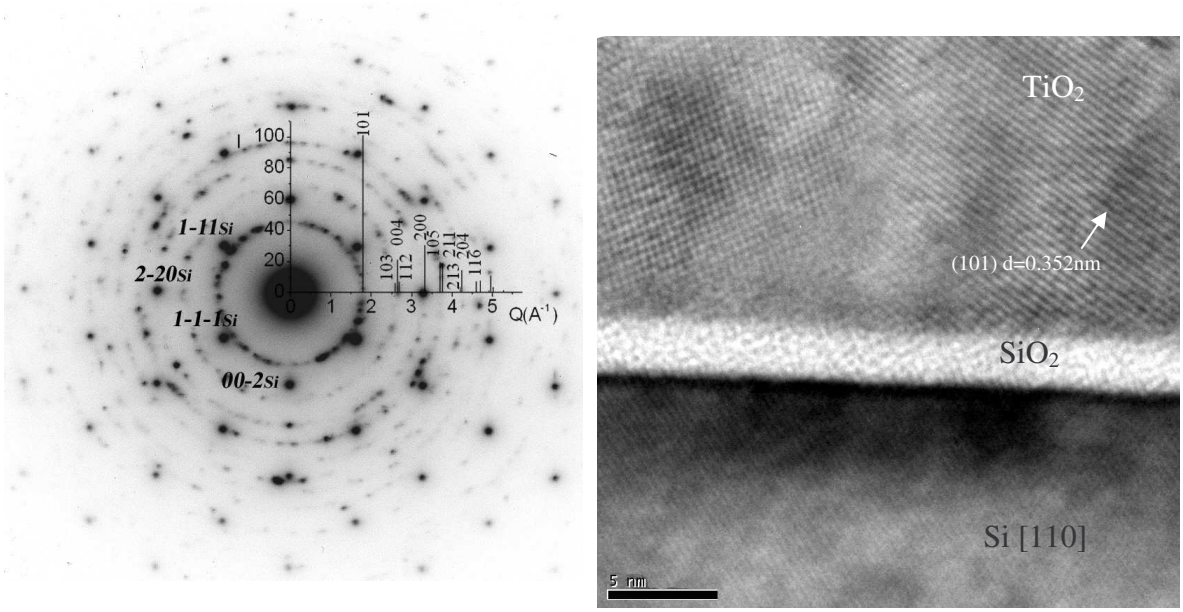

Figure 2 a) Indexation of the electron diffraction pattern of the layer TiO_2 interface where the Si substrate is oriented along a [110] zone axis. B) High resolution image of the layer cross

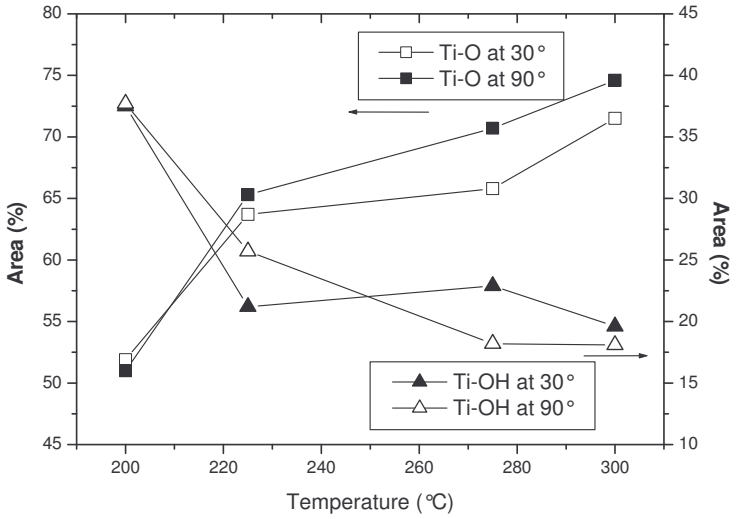

Figure 3 .Temperature dependence of the a) Ti-O and b) Ti-OH contributions from the O 1s peak de-convolution

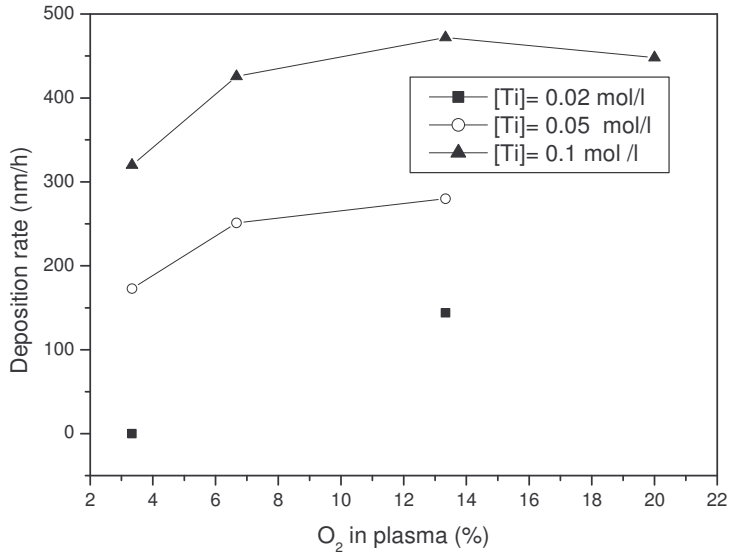

Figure 4. Variation of the deposition rate as a function of oxygen content in plasma for several Ti concentrations of $TiO(acac)_2$ in solution

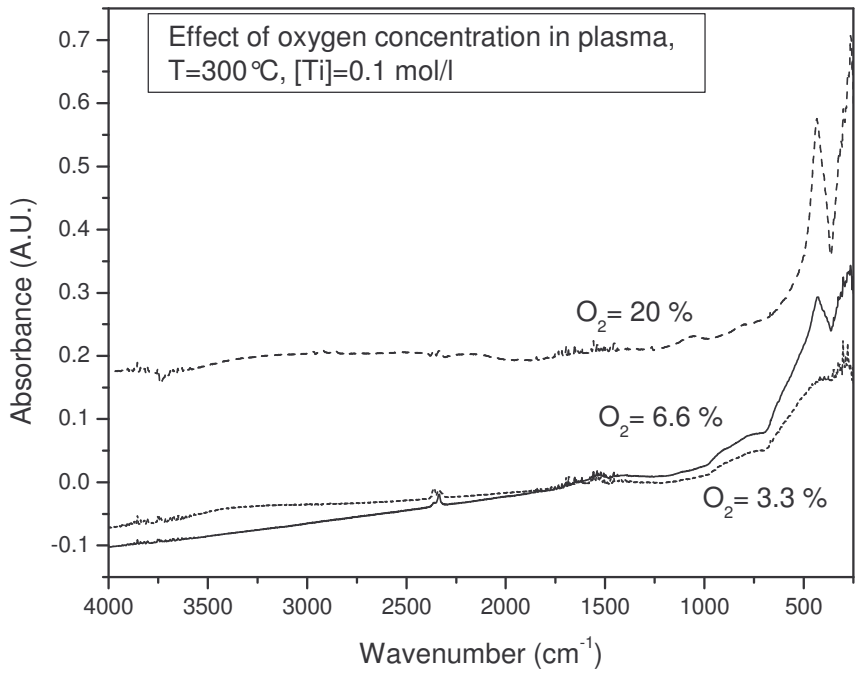

Figure 5 FTIR spectra of samples deposited from 0.1mol/l $TiO(acac)_2$ solution with different oxygen concentration in plasma