Light induced chemical vapour deposition of titanium oxide thin films at room temperature

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Abstract

High resolution patterned deposition of titania is achieved by light induced chemical vapour deposition (LICVD), by imaging a mask onto a glass substrate. A long pulse XeCl Excimer laser (308 nm) provides, by perpendicular irradiation, the energy to convert titanium tetraisopropoxide (TTIP) vapour into titanium dioxide films, in an oxygen atmosphere, on unheated glass substrates. The amorphous titania deposits contain about 6% carbon contamination according to X-ray photoelectron spectroscopy (XPS) measurements. The deposition rate increases with increasing laser fluence until a maximum value is reached, then remains constant over a wide range, and finally decreases with further fluence increase due to titania ablation or thermal effects. The film thickness increases linearly with the number of pulses after a nucleation period. The strong influence of the laser pulse repetition rate on the growth rate and the thickness profile are reported. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

TiO₂ thin films are important for several applications, including optical coatings [1], protective coatings [2], microelectronic applications [3], and photochemically active layers [4]. Chemical vapour deposition (CVD) methods [5] have been extensively studied for thin film deposition, and are widely used industrially. Mainly thermal CVD [6] and, more recently, plasma-assisted CVD methods [7,8] are applied. Light induced deposition processes have already been studied for different oxides: SiO₂ [9,10], ZrO₂ [11], PbO [11], ZnO [12], Al₂O₃ [13] and Ta₂O₅ [14,15]. Ta₂O₅ is investigated as a competitor with titania for future low leakage insulator materials in microelectronics and storage devices. TiO₂ pyrolytic laser CVD was first carried out for localised deposition using an IR laser beam, which locally heated the substrate [16]. To improve the homogeneity and the selectivity of the deposition, surface photolytic processes applying UV-light were proposed [17,18]. Titania UV-light induced chemical vapour deposition (LICVD) has been reported in the literature applying either lamps [13,19] or lasers.
[11,13,20] and using different precursors. Titanium tetraisopropoxide (TTIP) is a classical CVD precursor exhibiting a high volatility (1 mbar at 40°C [21]). In LICVD, the strong Ti–O bond of TTIP (444 kJ/mol [22]) should not be broken by irradiation of wavelength higher than 270 nm. The addition of light irradiation to thermal CVD processes significantly increases the TiO₂ growth rate [11,19]. The correct combination of precursor and light source appears to be a crucial point: first, the optical absorption of the precursor at the wavelength used should be sufficient [11,13,23] and, secondly, the light source should not be so energetic as to induce complete decomposition of the precursor ligands, which would increase the carbon contamination [13]. LICVD enables very localised deposits in the irradiated area. Patterned deposits have been reported by directly inserting a mask in the laser beam pathway [11], but diffraction effects limited the resolution. Based on these results, we decided to study mask imaging deposition of titania with a mask projection set-up, using TTIP as the precursor, and an excimer laser at 308 nm, which is a longer wavelength than those reported in the literature.

2. Experimental

The optical absorption cross section (ε) of TTIP was determined in an isopropanol solution (UV-transparent) by UV-vis photospectrometry (Perkin Elmer Lambda 19): $\varepsilon = 1.6 \times 10^6$ cm²/mol.

The LICVD experiments were carried out with the installation shown schematically in Fig. 1. The TTIP was kept in an isothermal bath at 25°C, and was introduced into the reactor chamber through a heated line (60°C) by a 30 sccm controlled oxygen flow. The glass substrate was left at room temperature (RT) and its temperature was measured by a thermocouple. It was irradiated perpendicularly through a quartz window and purged by a 60 sccm controlled nitrogen flow. A long pulse (250 ns) XeCl (308 nm) laser was used as a light source. The beam size was adapted to the size of a free standing molybdenum mask (1 × 1 cm²) by an afocal telescope and the mask was imaged on the substrate by a quartz lens with a 1:2.8 reduction factor. The gases were pumped by a two-stage rotary pump through a liquid nitrogen vapour trap. The base pressure in the
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Fig. 3. Deposited thickness versus laser fluence on a glass substrate \((N = 1800, f = 1 \text{ Hz})\).

reactor was \(10^{-2}\) mbar. The overall pressure was measured using a Baratron pressure gauge and regulated to 10 mbar via a controlled butterfly valve. The chamber could be moved perpendicularly to the laser beam such that several deposits could be obtained in a series of experiments. The gas flows were allowed to stabilise for 15 min prior to each irradiation. After deposition, samples were rinsed first with 2% HCl solutions (to remove traces of unreacted precursor), then with deionised water and dried in air. Adhesion was tested as follows: Scotch tape was vigorously rubbed onto the deposit with a pencil and rapidly pulled off. Scanning electron microscopy (SEM) (Philips XL 30), X-ray photoelectron spectroscopy (XPS) (Perkin Elmer PHI 5500 ESCA System), X-ray diffraction (XRD) and stylus profilometry (Tencor Instrument-Alpha step 200, tip curvature: 1.5 \(\mu\)m) were used to characterise the samples. Film thicknesses reported are average heights of all data points taken along a line traversing the deposit.

Results presented in this paper were obtained keeping constant the pressure and flow parameters chosen after preliminary tests and given in this section. We varied the laser irradiation parameters: fluence \((F)\), number of pulses \((N)\) and repetition rate \((f)\).

3. Results

The adhesion test showed the Scotch tape was removed without peeling off of the deposit from the substrate.

3.1. Chemical structure of the deposits

XRD measurements of selected samples proved that the deposits were amorphous. XPS measurements on as-deposited films show the presence of Ti and O at the correct binding energy values for TiO\(_2\) [24]: Ti2p3/2, Ti2p1/2, and O1s at 459, 465, and 530 eV, respectively. By applying sensitivity factors, the stoichiometry was found to be close to TiO\(_2\). The surface contamination with carbon (peak around 286 eV) of about 20% decreased to a constant value of about 6% in the bulk after the first of several ion sputtering cycles. This quantitative composition should not be overinterpreted, as it is known that ion sputtering can induce a modification of TiO\(_2\) stoichiometry [25].

3.2. Localised deposition

Image projection of the 50-\(\mu\)m thick molybdenum mask (see Fig. 2a) onto the glass substrate resulted in

Fig. 4. Thickness of individual titania deposits on glass substrates as a function of the number of laser pulses \((F = 250 \text{ mJ/cm}^2, f = 2 \text{ Hz})\).
highly resolved deposits, as shown in Fig. 2b. In this example, the 100-μm wide diagonal bar of the mask resulted in a 43-μm wide uncoated line on the glass substrate.

3.3. Deposited thickness vs. fluence

In Fig. 3, the deposited thickness, \( D \), is shown as a function of the laser fluence \( F \). The number of pulses, \( N \), and the repetition rate, \( f \), were held constant at \( N = 1800 \) and \( f = 1 \) Hz. For fluences below the deposition threshold value (\( F_{th} \approx 80 \) mJ/cm\(^2\)), the films did not adhere to the substrate. Increasing the laser fluence above \( F_{th} \) resulted in a large increase of \( D \) with \( F \), approaching asymptotically a thickness of 1.3 μm at 400 mJ/cm\(^2\). Further increase of the fluence resulted in a decrease of the titania deposited thickness. The titania ablation threshold was measured on oxidised titanium and found to be 650 mJ/cm\(^2\).

3.4. Deposited thickness vs. number of pulses

For constant fluence (\( F = 250 \) mJ/cm\(^2\)) and repetition rate (\( f = 2 \) Hz), the thickness of the deposition increased with the number of pulses, \( N \) (Fig. 4). A slow growth rate was observed for small \( N \) and then the deposited thickness increased linearly with increasing \( N \). The average growth rate in this linear part was 1.7 nm/pulse.

3.5. Influence of the repetition rate

3.5.1. Influence on the deposit profile

Concave deposits were obtained when working with repetition rates higher than 1 Hz. Fig. 5 shows two deposits obtained at \( f = 2 \) Hz (a) and \( f = 10 \) Hz (b), respectively, for \( F = 330 \) mJ/cm\(^2\) and after 30 min of deposition. The ratio of the edge height to the centre height of the deposit increased from 1.3 to 3.

3.5.2. Influence on the growth rate

Fig. 6 shows the average film thickness obtained for four different repetition rates \( f \), with \( N = 1000 \) and \( F = 190 \) mJ/cm\(^2\). A maximum deposited thickness was observed around \( f_{max} = 0.3 \) Hz.

4. Discussion

The combination of a 308-nm laser with the classical TTIP precursor proves to be valuable for obtaining well-adhering titania deposits with correct chemical composition. These results fill the gap reported in the literature between the successful depo-
sition at 248 nm ($\epsilon = 5.4 \times 10^6 \text{ cm}^2/\text{mol}$) and the unsuccessful at 351 nm ($\epsilon = 1.2 \times 10^6 \text{ cm}^2/\text{mol}$) due to variation of the TTIP optical cross section [11]. At RT, the deposits obtained are amorphous, suggesting the necessity for additional heating of the substrate to obtain crystalline deposits.

The possibility of obtaining highly resolved patterned deposits by mask projection is demonstrated. The theoretical resolution, product of size of the mask features by the projecting reduction factor, is not fully achieved. This could either be due to an uncertainty in the relative positioning of mask features by the projecting reduction factor, or due to an intrinsic effect (either thermal or optical) of the deposition process, that will be further investigated.

A threshold fluence value ($F_{\text{th}} \approx 80 \text{ mJ/cm}^2$) to obtain adhering deposits is observed. After a rapid increase above this value, the deposited thickness remains almost constant between 200 and 400 mJ/cm². At even higher fluences, the deposited thickness decreases. This could be due to a starting competition between the deposition and the ablation process. Another explanation could be that higher fluence results in laser heating of the substrate, inducing thermal desorption of precursor molecules.

LICVD processes with perpendicular irradiation consist in either photolytic or pyrolytic processes, or in a combination of both, depending on the precursor and substrate light absorption. Models have been proposed to estimate the temperature rise induced by a laser pulse [26–28]. To estimate the photothermal effect in our system, we calculated the temperature rise, $\Delta T$, after one pulse (308 nm, 250 ns, 200 mJ/cm²), both on glass substrate and titania, assuming no temperature dependence of the parameters, an infinite homogeneous substrate and a rectangular temporal laser pulse. In this calculation, the following values were taken, respectively for glass and titania: thermal conductivity: $K = 0.014$ and 0.089 W/cm K, thermal diffusivity: $D = 0.009$ and 0.031 cm²/s, optical penetration depth: $\alpha = 1129$ and 4.32 $\times 10^6 \text{ cm}^{-1}$, reflectivity: $R = 0.05$ and 0.25 [29–31]. We obtained $\Delta T(\text{glass}) = 133^\circ \text{C}$ and $\Delta T(\text{titania}) = 353^\circ \text{C}$.

This could explain as pure photothermal effects the discrepancy between the small growth rate observed in the initial nucleation step on glass and the much higher one observed on already deposited titania in the linear growth step. But a photocatalytic effect of electron-hole formation in titania under irradiation might be important as well. The linear behaviour of the deposited thickness with the number of pulses, together with the constant deposition rate per pulse over a relatively wide fluence range, allows the thickness of the deposits to be closely controlled.

The values of the growth rates observed are much higher than the calculated value of 0.1 nm/pulse for a monolayer by monolayer dissociation of the precursor (using Tokita’s equation [11]). This indicates that the amount of precursor decomposed during 1 pulse originates from several layers adsorbed since the previous laser pulse.

The repetition rate $f$ defines the time interval $\tau$ existing between two successive laser pulses: $\tau = 1/f$.

A variation of $\tau$ influences the deposition process in two different ways with the same observed result.

First, the smaller the $\tau$, the thinner the layer of precursor that can re-adsorb on the substrate after a laser pulse and be decomposed by the next laser pulse, and therefore the smaller the deposited thickness per pulse.

Secondly, the smaller the $\tau$, the less can the substrate cool completely between two laser pulses, and the more a temperature rise of the substrate can be expected. It could induce two thermal effects: a thermal desorption of the adsorbed precursor on the substrate and a densification of the deposit, both resulting in a decrease of the deposited thickness per pulse.

These two arguments compete to explain the results obtained by varying the repetition rate.

Concerning the shape of the deposits: the centre of the deposit can have a reduced layer of adsorbed precursor compared to the edges when increasing $f$ (if the precursor diffusivity to re-adsorb a layer is slow compared to $\tau$), or its temperature can be higher due to less efficient cooling.

Concerning the variation of the deposited thickness keeping the number of pulses constant: the first increase of the deposited thickness with the repetition rate could be attributed to an enhancement of the chemical reaction activation by a small thermal contribution, and the following decrease can be explained also by the two arguments mentioned above.
5. Conclusions

Amorphous well adherent titania deposits are obtained by LICVD without external heating of the glass substrate. High resolution localised titania deposition is demonstrated. Results of the influence of the irradiation parameters (fluence, number of pulses, repetition rate) on the growth process are presented for a selective and non optimised range of CVD parameters.

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