Development of a novel cathodic plasma/electrolytic deposition technique
Part 2: Physico-chemical analysis of the plasma discharge

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Abstract

A novel plasma system has been developed recently for the deposition of carbon and titanium thin films on metal and metal alloy substrates. Unlike other deposition techniques, the process occurs in liquid precursors and a plasma discharge is created and confined around the cathode in a superheated vapour sheath surrounded by the liquid phase. This paper presents a detailed analysis of the physico-chemical mechanisms underlying this process. A correlation has then been carried out between the voltage/current characteristics and the consecutive physical phenomena occurring during the process (vapour phase formation, plasma discharge initiation and evolution). The structure and composition of the produced TiO₂ films have been compared with the composition and physical characteristics of the plasma discharge. This analysis allowed the construction of a first dissociation and deposition mechanism for this new plasma system.

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1. Introduction

Thin film deposition as a modern material fabrication technique is one of the key technologies in various industrial sectors such as micro-electronics, optical coatings, magnetic and optical data storage devices, anti-static coating, hard-surface coating and more recently solar cells and photo-catalytic sensors [1–5]. A wide range of surface engineering techniques have therefore been developed over the past decades to achieve the demanding technological specifications required in the engineering sector. Current advanced surface engineering methods can be separated into two main categories according to the phase used during the process: the liquid or semi-liquid phase methods and the gaseous or vapour phase methods [6]. The generation of plasma, much used in arc or glow discharge condition, is usually carried out under high vacuum which increases significantly the manufacturing costs. However, the glow discharge technique is often used to assist Chemical Vapour Deposition (CVD) and possesses the advantage of working either at low temperature or at high temperature, achieving then more flexibility for the structure and morphology of the produced film.

A new plasma electrolytic deposition technique has been developed during the past few years in anodic and cathodic configuration [7–16]. This technology is based on contact glow discharge electrolysis phenomena, thoroughly developed and studied by several authors over the past 40 years [17–21]. Operating at atmospheric pressure, the film deposition is activated on the smaller electrode by the formation of a plasma glow discharge within a gaseous sheath produced in an electrolytic bath around this electrode. Hence, this process combines different deposition mechanisms, which may include mechanisms found in CVD, PECVD, electrophoresis, cataphoresis, ion implantation and sputtering. Used in anodic configuration, this plasma electrolytic technique, also called ‘plasma electrolytic oxidation’, allows the production of adherent oxide, alumina, silica or titania based films [7,9].

In cathodic configuration, this plasma process allowed the production of nitride, carbon, titanium, molybdenum, zinc and zinc-aluminium based coatings on metal substrate [8,11–16]. Nano-crystalline graphite films have been deposited by the authors on a Ti, Al or Cu cathodic substrate from solutions composed of ethanol, potassium chloride and phosphate buffer [13]. The high field emission observed with these graphite films...
could have application for the manufacturing of high field emission electrodes for plasma devices such as microwave reactors. Highly crystalline titanium dioxide films, composed mainly of anatase and rutile, have been also produced with this technique using a solution composed of titanium tetra-isopro-

toxide (TTIP) and ethanol [12,13,22]. The nano-structure of these films, composed of nano-rods and nano-fibrils, and their composition are very promising for applications in photocatalysis and dye-sensitised solar cells. An interesting feature for these films is that it is possible to adjust their crystallinity and
morphology by adjusting the working voltage, and hence the intensity of the plasma discharge.

The production and technology of such a plasma discharge in a vapour phase surrounded by a liquid electrolytic phase is very new and the observation and understanding of this process has been necessary to enhance the potential development of this technique for the production of new advanced materials. This paper presents therefore a thorough investigation of the implied physico-chemical mechanisms in parallel with the voltage/current characteristics of this process. The formation and evolution of the vapour sheath and the plasma discharge have been analysed using a high speed camera. The plasma composition and electron temperature have moreover been evaluated by emission spectroscopy and correlated with the structure observed in the titanium dioxide films, allowing the construction of a first dissociation and deposition model.

2. Experimental set-up

The basic principles of the cathodic plasma electrolytic process as well as the reactor itself have already been described in the first part of this work [22]. For the voltage/current analysis and the study on the basic physical mechanisms (vapour sheath and plasma discharge), the solution was composed of absolute ethanol (96% vol.), phosphate buffer (4% vol.) and potassium chloride (0.2 mol dm$^{-3}$). The reason is that this solution remains clear for a
sufficiently long time to analyse the physical phenomena occurring during the different voltage/current stages.

The formation of the vapour sheath, the physical characteristics of the plasma discharge and their evolution with the applied voltage have been studied using a high speed camera (Photron 512 PCI FastCam-X) shot at 2000 frames/s (shutter: 1/2500 s).

The measurements on electric conductivity of the liquid solution have been performed using a TPS Model 2100 (TPS Pty. Ltd., Brisbane, Australia). It was used in conjunction with a $K=1$ sensor (the distance between the electrodes is 1 cm).

In situ optical emission spectroscopy (OES) was carried out on the plasma discharge using a S2000-UV–VIS Miniature Fibre Optic Spectrometer (Ocean Optics Inc.) with 200–850 nm wavelength range. The spectrometer was connected to a PC through a RS232 connection for the control of the spectrometer and the data acquisition. The acquisition time used during the measurements was 10 s. A special reactor was set-up in order to get the fibre optics as close as possible to the plasma discharge without immersing the fibre in the liquid solution. A glass hollow finger, where the fibre optics was introduced, was inserted into a glass reaction flask to place the fibre at around 5 mm from the axis centre, where the cathode was located (Fig. 1). For the emission spectroscopy study, we used a solution composed of 40% vol. of distilled titanium tetraisopropoxide.

<table>
<thead>
<tr>
<th>Voltage (V)</th>
<th>Current (mA)</th>
<th>Bubble radius (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>470</td>
<td>412</td>
<td>1</td>
</tr>
<tr>
<td>500</td>
<td>372</td>
<td>2</td>
</tr>
<tr>
<td>600</td>
<td>350</td>
<td>3</td>
</tr>
<tr>
<td>700</td>
<td>290</td>
<td>5</td>
</tr>
</tbody>
</table>

Fig. 5. Evolution of the vapour sheath with the applied voltage for an ethanol solution.
(TTIP, Ti(OC3H7)4, Sigma-Aldrich, 97%), 59.8% vol. of absolute ethanol and 0.2% vol. of hydrochloric acid (HCl) (concentration: 31.5% w/w).

3. Results and discussion

3.1. The bubble sheath formation

Fig. 2 shows the evolution of the voltage and current, as well as representations of the different physical phenomena occurring at each step of the process. In a first stage (A–B in Fig. 2), the solution is heated by the Joule effect. Fig. 3 shows the evolution of the liquid temperature in the vicinity of the anode (20 mm from the cathode). We observe that the bulk temperature of the solution increases with the current, up to the vaporisation temperature of the solution at 351 K. The overall solution is thus rapidly heated with the increasing current.

In a first approximation, the electric field $E$ between the two electrodes can be written in a cylindrical coordinate system:

$$E = \frac{V_2 - V_1}{\ln \left( \frac{r}{r'} \right)} \times \frac{1}{r} \hat{u}_r$$  \hspace{1cm} (1)

where $V_2$ and $V_1$ are the electric potentials at the anode and the cathode, $r_2$ and $r_1$ the anode and cathode radii, $r$ the point radius and $\hat{u}_r$ the radial vector in cylindrical configuration. The Joule heating flux, given by $\Phi = \sigma \times E^2$, is then concentrated around the cathode. During this stage, the solution is subject to strong and rapid heating, which is especially intense at the surface of the cathode. Some small bubbles are intensively emitted at the tip of the cathode where the electric field is the highest.

From Fig. 2 it can be seen that the current actually shows a super-linear evolution. This characteristic is due to the increase of the electric conductivity of the solution with temperature. Assuming that the temperature increase is uniform throughout the entire solution volume, we can estimate the evolution of the current in this region by calculating the temperature increase $\Delta T$ in the interval $t$ to $t + \Delta t$ from the power input $\Delta Q(t)$ in this time and the heat capacity of the solution $C$:

$$\Delta T(t) = \frac{\Delta Q(t)}{\nu \times \rho \times C}$$

where $\Delta Q(t) = \int_{t}^{t+\Delta t} V(t') \times I(t') dt'$, $\nu$ is the volume between the two electrodes and $\rho$ the density of the solution.

Further assuming a linear relationship between conductivity and temperature ($\sigma(T + \Delta T) = \sigma(T) + \sigma_T \times \Delta T$), with $\sigma_T$ a constant over the temperature range involved (270–350 K), we can determine the evolution of the current. We have performed this calculation from the data in Fig. 2, and obtained the resultant $I - t$ curve shown in Fig. 4, for an initial conductivity $\sigma_0 = 265 \, \mu S/cm$ and $\alpha_T = 18 \, \mu S/cm$. The constant $\alpha_T$ has been adjusted to fit the theoretical data with the experimental ones. We can see from Fig. 4 that the two curves match very closely up to the vaporisation point. This simplified model, which does not take into account the spatial variation in temperature in the electrolyte and heat transfer processes, nevertheless clearly demonstrates the dominant contribution to the origin of the superlinear current evolution.

When the bulk temperature reaches the vaporisation one, the saturation temperature necessary to initiate the nucleation and formation of bubbles is attained at the vicinity of the cathode. The temperature gradient in the solution and the thermal fluctuations at the surface of the cathode may play as well a significant role in the nucleation of the bubbles. The thermal gradient can indeed delay the bubbles nucleation once the vaporisation temperature is reached in the bulk. These parameters are however difficult to assess since the time difference between the two moments (vaporisation temperature in the bulk and vaporisation at the cathode surface) is very low (less than 1 s). Thermal fluctuations can especially affect the shape of the ignited bubbles and its growth. But the differences remain at a microscopic level and cannot be observed in our experimental facility. The nucleation of bubbles all along the surface starts actually at point B (Fig. 2). It is initiated at this point, starting at the tip and moving to the end of the cathode. The transition from point B to point C (Fig. 2) corresponds to the displacement of the bubble front from the tip to the end of the cathode. At point C, the cathode is then completely covered by a vapour sheath, composed of a cluster of bubbles, which eventually isolates totally the electrode from the liquid electrolyte. This vapour sheath is formed very quickly, in a few milliseconds. It is not continuous and can be considered as a
composite of gas and liquid phases (Fig. 5). The effective conductivity \( \sigma_{\text{eff}} \) of the gas–liquid composite can be approximated by the Bruggeman relation, which is usually referred to in the electrochemical literature [23,24]:

\[
\sigma_{\text{eff}} = \sigma_L \times (1 - \alpha)^{3/2}
\]

where \( \sigma_L \) is the electrical conductivity of the liquid solution without bubbles and \( \alpha \) the volume fraction of bubbles.

Once the vapour sheath is formed, the electric conductivity of this overheated layer decreases leading to an increase of the total electric resistance of the liquid-vapour system and thus to a quasi instantaneous current fall (region BC in Fig. 2). We can notice in Fig. 5 that the gas phase fraction of the bubble sheath as well as the vapour thickness rise with the increasing applied voltage (region CD in Fig. 2). In other terms, as the voltage increases, the electric resistance of the composite vapour phase significantly soars up resulting in a decrease of the current intensity.

The increase of the vapour thickness is due to the two physical phenomena: coalescence and electrostatic pressure effect. We have indeed observed the coalescence of the bubbles at the cathode surface forming a discrete, then a long vapour column (or vapour mushrooms) along or perpendicular to the surface (see Fig. 5, especially at 600 V). Two kinds of coalescence processes have to be distinguished: lateral coalescence and longitudinal coalescence [25,26]. Lateral coalescence corresponds to the coalescence of bubbles growing on the surface at neighbouring nucleation sites. Coalescence in the direction normal to the surface of bubbles originating from the same nucleation site is called longitudinal coalescence. In this case, the growth speed of the second bubble is higher than the bulk speed of the first bubble, which leads to the impact between the two bubbles and to their coalescence. These two types of bubbles coalescence have both been observed during the transition stage (region CD in Fig. 2).

Furthermore, once initiated, the bubbles are subject to different internal and external pressures due to the electric field, exerted respectively in the gas and the liquid phase. As the effective resistance of the vapour sheath increases, the inner resistance of the vapour sheath increases, the inner resistance of the liquid-vapour system and thus to a quasi instantaneous current fall (region BC in Fig. 2). We can notice in Fig. 5 that the gas phase fraction of the bubble sheath as well as the vapour thickness rise with the increasing applied voltage (region CD in Fig. 2). In other terms, as the voltage increases, the electric resistance of the composite vapour phase significantly soars up resulting in a decrease of the current intensity.

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3.2. The plasma discharge characteristics

At point D in Fig. 2, the voltage in the gas phase has been evaluated numerically equal to 694 V for a total applied voltage of 790 V. In this calculation, we have assumed that no deposit has been formed during the bubble stage and for the first seconds after the initiation of the plasma discharge. This assumption has been confirmed by the analysis of the samples after treatment. It is therefore possible by using the electric field...
conductivities calculated in Section 3.1 to evaluate the voltage in the gas phase during these two stages and the electric power delivered in the discharge just after its initiation. These calculations can give some information on the plasma discharge itself (glow discharge or arc discharge).

At the end of the transition stage, the voltage within the vapour sheath exceeds significantly the voltage in the liquid phase. As the liquid phase conductivity is much higher than the vapour sheath conductivity, the vapour phase-liquid interface acts as the anode: the effective distance between the anode and the cathode is then equal to 0.1–5 mm (bubble diameter) at point D. The breakdown voltage $V_b$ of a gas, which is critical in the initiation of a discharge, strongly depends on the product of pressure and distance $p \times d$ [27]:

$$V_b = \frac{B(p \times d)}{\ln[A(p \times d)] - \ln[\ln(1 + 1/\gamma_{se})]}$$

(3)

A and B are constants found experimentally and $\gamma_{se}$ is the secondary electron emission coefficient of the cathode. For
values of $p \times d$ higher than 10 (in Torr cm), the breakdown voltage increases rapidly with the inter-electrode gap at constant pressure. $V_b$ is usually lower than 1000 V for $p \times d$ lower than 10 [27]. We have been able to show, by high speed camera measurements, that the plasma discharges are actually initiated in very small bubbles presenting a diameter equal to around 0.1 mm. In our experiment, the tests are carried out at atmospheric pressure (760 Torr) and at voltages lower than 1200 V. In a very small diameter bubble (around 0.1 mm), the effective $p \times d$ product will be sufficiently low (equal to 7.6 Torr cm for a bubble diameter of 0.1 mm) to ensure a low breakdown voltage and initiate the formation of a plasma discharge within the small bubble.

If we increase the voltage again beyond the breakdown point, we observe an increase of the current (region DE in Fig. 2), explained by the increasing cathode surface area treated by the plasma discharge, as we can see in Fig. 6. At point E (Fig. 2), the plasma discharge blankets the entire cathode surface.

For a voltage equal to or above 900 V, the cathode surface is entirely covered by the plasma glow discharge, as seen in Fig. 6B. This figure shows that the plasma system is actually composed of a superposition of several small discharges along the substrate. Moreover, these plasma discharges remain in a diffuse or glow form.

The conductivity of the plasma discharge is much higher than the conductivity of the surrounding vapour phase, owing to the ionisation of the vapour. Therefore the current measured between the two electrodes corresponds to the total current in all the multiple micro-plasma discharges. The vapour layer surrounding the plasma discharge acts like an insulating component and does not contribute to the electric current. Fig. 7 shows the evolution of the current with the applied voltage for the same electrolyte, but with the voltage held constant beyond point E (see Fig. 2) at three different voltages — 900 V, 1000 V and 1200 V. The current increases with the applied voltage once the plasma discharge is established across the cathode. The mean current at 900, 1000 and 1200 V is equal to 268, 300 and 350 mA respectively for a total surface area equal to 1.07 cm$^2$. It is then possible to calculate the voltage and power in the plasma discharge for each applied voltage (Table 1). Once the surface is totally covered by the plasma discharge, increasing the voltage implies extracting more electrons per unit surface area, leading to an increase of the current density and the discharge power density. At the same time, the luminous intensity of the plasma discharge increases significantly. Moreover, we can notice (Fig. 8) that the maximum intensity for the luminosity is located at the vicinity of the cathode (the area close to the bubble surface, considered to be the anode, remaining dark) which is characteristic of a glow discharge [27].

It is clear however that once the carbon or TiO$_2$ coating is formed, the resistance of the system could be modified by the possible barrier discharge formed around the electrode. On the other hand, the average electric current does not show any significant decrease during all the discharge stage and the coating production. This observation means that the resistance of the system has not evolved dramatically and that the influence of the coating on the evaluation of the gas voltage and electric power in the discharge remains negligible. This phenomenon can be first explained by the fact that the produced carbon and TiO$_2$ coatings present a large amount of crevices and cracks [22] that can lead to an important decrease of their resistivity [28]. The composition of the TiO$_2$ coatings can affect as well their electric conductivity: we have indeed noticed that the deposited coatings contain a large quantity of carbon (up to 17%) which may induce a strong increase of the electric conductivity in regard of pure TiO$_2$ coatings. Using an ethanol solution, the produced film is mainly composed of graphite [11–14] which is highly conductive. As a consequence, the produced coatings (carbon or TiO$_2$/C coatings), by their relatively low resistivity, do not disturb significantly the properties of the discharge.

Hence, the values calculated on the discharge power (Table 1), the current/voltage characteristics, the range of the current (hundreds of mA/cm$^2$), and the physical shape of the discharge are all akin to the features of an abnormal glow discharge [27,29].

The temporal evolution of the plasma discharge has been studied using a sharp tip cathode in order to obtain the best picture quality and to observe accurately the evolution of the plasma.
discharge. Fig. 8 illustrates the temporal evolution of the plasma discharge: the plasma discharge is initiated within bubbles with very small diameter (around 0.1 mm). The high electric field within this very small bubble is sufficiently high (around 100 kV cm\(^{-1}\)) to induce the breakdown of the gas leading to a plasma discharge. We propose that the relatively high temperature of the initial discharge induces a dramatic increase of the vaporisation rate of the electrolyte liquid solution around the bubble. Due to this high vaporisation rate, the bubble diameter and the plasma discharge enlarge rapidly, in a few milliseconds, as we can see in Fig. 8. The expansion of the bubble is caused as well by the plasma pressure exerted at the surface of the bubble. This plasma pressure is expressed by the relation:

\[
P_p = \sum_k n_e kT_e = n_e kT_e + n_i kT_i + n_0 kT_0
\]

with \(n_e\): electron density, \(n_i\): ion density, \(n_0\): neutral particle density, \(T_e\): electron temperature, \(T_i\): ion temperature, \(T_0\): neutral temperature.

The total force is the sum of the plasma pressure acting inside the bubble and the electrostatic pressure acting outside the bubble (in the liquid phase). As the voltage within the vapour sheath is high comparing to the voltage in the liquid phase, the electric field within the liquid solution is very low: we therefore believe that the electrostatic pressure in the liquid phase is negligible compared to the inner plasma pressure. The total electrostatic pressure thus tends to expand the bubble and the plasma discharge.

Once the bubble volume is sufficiently large, the buoyancy force will overcome the plasma pressure within the bubble. The bubble then moves upward until the discharge subsides, as observed in Fig. 8 (time 27.5 ms). Another discharge is then initiated in a very small diameter bubble. We can then observe the succession of several abnormal glow discharges formed within the gas phase.

Using a TTIP liquid solution, the electron temperature has been calculated at 700 and 1000 V from the emission spectra measured on the plasma discharges (Fig. 9). The plasma discharge is mainly composed of Ti radicals, coming from the dissociation of the TTIP solution, oxygen species, hydrogen and water molecules. Three titanium lines, whose parameters are measured on the plasma discharges (Fig. 9). The plasma discharge is initiated within bubbles with very small diameter (around 0.1 mm). The high electric field comparing to the voltage in the liquid phase, the electric field within the liquid solution is very low: we therefore believe that the plasma discharge by four different processes: the photon-dissociation, the electron impact dissociation, the ion impact dissociation and the thermal impact dissociation [31]. We can assume that the thermal dissociative processes play a significant role in the deposition mechanism: we have indeed demonstrated previously that the plasma discharge produced in our experimental conditions is an abnormal glow discharge. This basically means that the temperature of neutral and ionised species is relatively high (500 K or higher) due to the high energy exchange by collision between the electrons and the molecules and ions of the gas [27]. The degree of ionisation caused by the generated electrons remains however relatively low making the electron impact dissociation process negligible in regard of the thermal one. Submitted to the high plasma temperatures, the surface of the cathode is strongly heated and vaporised TTIP is then thermally dissociated at the surface of the cathode. Cho et al. [32] have studied the thermal decomposition mechanisms of TTIP. They have used the intensity ratio measurements between line 1 and 3 and between line 2 and 3 (see Table 2). The spectral transmission of the glass and liquid solution is approximately continuous in the spectral range covered by these three titanium lines. The electron temperature is relatively the same for the two studied voltages, equal to 1 eV. This temperature level is a physical characteristic of a plasma glow discharge and is relatively low compared to hot plasma and arc discharges where the electron temperature can reach 2 to 3 eV. The main difference between the two applied voltages may lie in the electron density which should increase with the voltage. Due to the confinement of the plasma discharge and the liquid medium surrounding the discharge, the evaluation of this density remains however a very tedious operation.

### 3.3. The dissociation mechanisms

From the previous experimental analysis on the plasma discharge and the analysis on the produced TiO\(_2\) coatings [22], we have tried to deduce the dissociation and deposition mechanisms leading to the formation of this coating. In a first step, we can assert that the plasma discharge is directly responsible of the formation of the titanium dioxide coating since no deposits have been observed without the presence of the plasma discharge. The TTIP solution needs therefore to be heated, vapourised around the cathode and treated by the plasma discharge. It is thus wise to say that the deposition mechanisms are mainly ruled by the plasma processes.

We have found out from the emission spectroscopy on the plasma that TTIP is entirely decomposed in the plasma discharge into titanium radicals. The TTIP can be dissociated within the plasma discharge by four different processes: the photo-dissociation, the electron impact dissociation, the ion impact dissociation and the thermal impact dissociation [31]. We can assume that the thermal dissociative processes play a significant role in the deposition mechanism: we have indeed demonstrated previously that the plasma discharge produced in our experimental conditions is an abnormal glow discharge. This basically means that the temperature of neutral and ionised species is relatively high (500 K or higher) due to the high energy exchange by collision between the electrons and the molecules and ions of the gas [27]. The degree of ionisation caused by the generated electrons remains however relatively low making the electron impact dissociation process negligible in regard of the thermal one. Submitted to the high plasma temperatures, the surface of the cathode is strongly heated and vaporised TTIP is then thermally dissociated at the surface of the cathode. Cho et al. [32] have studied the thermal decomposition mechanisms of TTIP. They

### Table 2

Theoretical titanium line parameters used for the determination of electron temperature

<table>
<thead>
<tr>
<th>Line</th>
<th>(\lambda) (nm)</th>
<th>Transition</th>
<th>(E) (eV)</th>
<th>(g)</th>
<th>(A) ((10^8 \text{s}^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>501</td>
<td>5F–5G*</td>
<td>3.31</td>
<td>11</td>
<td>6.43 \times 10^2</td>
</tr>
<tr>
<td>2</td>
<td>517</td>
<td>3F–3F*</td>
<td>2.39</td>
<td>5</td>
<td>3.81 \times 10^2</td>
</tr>
<tr>
<td>3</td>
<td>625.8</td>
<td>3F–3G*</td>
<td>3.42</td>
<td>9</td>
<td>8.36 \times 10^2</td>
</tr>
</tbody>
</table>

* an excited state of the specified level.
have demonstrated that TTIP can be adsorbed at the surface of a heated substrate and then dissociated according to the scheme:

\[
\begin{align*}
\text{Ti(OC}_3\text{H}_7\text{)}_4 & \rightarrow \text{Ti(OC}_3\text{H}_7\text{)}_4^* \\
\text{Ti(OC}_3\text{H}_7\text{)}_4^* & \rightarrow \text{Ti(OC}_3\text{H}_7\text{)}_4 - x^* + x(\text{OC}_3\text{H}_7)^* \\
\text{Ti-O-C}_3\text{H}_7^* & \rightarrow \text{Ti-OH+C}_3\text{H}_6 \\
2\text{Ti-O-C}_3\text{H}_7^* & \rightarrow 2\text{Ti}^* + \text{HOC}_3\text{H}_7+\text{OC}_3\text{H}_6 \\
\text{Ti-O-C}_3\text{H}_7^* & \rightarrow \text{Ti}^* + \text{OC}_3\text{H}_6+1/2\text{H}_2 \\
\text{OC}_3\text{H}_7^* & \rightarrow \text{C}_3\text{H}_6\text{O}+\text{H}^* \\
-\text{R-C}_3\text{H}_2^* & \rightarrow \text{R}^*+\text{C}^*+3\text{H}^*
\end{align*}
\]

This model is in good agreement with the observation carried out on the plasma discharge by emission spectroscopy. In accordance with this model, we have indeed observed a high concentration of Ti radicals and the presence of hydrogen (H alpha line). Furthermore, the analyses of the produced coatings have revealed the presence of graphite coming, according to this model, from the thermal dissociation of the volatile hydrocarbons, products of the TTIP decomposition.

It has also been demonstrated [33,34] that TTIP can be thermally decomposed in the gas phase to form particles of TiO2 according to the following reactions:

\[
\begin{align*}
\text{Ti(OC}_3\text{H}_7\text{)}_4 & \rightarrow \text{TiO}_2 + 2\text{C}_3\text{H}_6 + 2\text{HOC}_3\text{H}_7 & \text{for } T<673 \text{ K} \\
\text{Ti(OC}_3\text{H}_7\text{)}_4 & \rightarrow \text{TiO}_2 + 4\text{C}_3\text{H}_6 + 2\text{H}_2\text{O} & \text{for } T\geq673 \text{ K}
\end{align*}
\]

(7)

In our case, we have demonstrated [22] that the temperature of the plasma discharge is sufficiently high (around 623 K or higher) to produce a mixture of anatase and rutile at the surface of the cathode. This temperature allows the dissociation of the vaporized TTIP according to reactions Eq. (7) and form crystallized nano-particles that are then chemically adsorbed at the surface of the cathode.

For temperature above 623 K, we can see that reaction Eq. (7) leads to the formation of water in the gas phase. Several studies on contact glow discharge electrolysis [18,20,35] have shown that water molecules can interact with the plasma discharge to produce O2, H2 and H2O.

\[
\begin{align*}
\text{H}_2\text{O} & \rightarrow \text{H}^*+\text{OH}^* \\
\text{H}^*+\text{H}^* & \rightarrow \text{H}_2 \\
\text{OH}^*+\text{OH}^* & \rightarrow \text{H}_2\text{O}+1/2\text{O}_2 \\
\text{OH}^*+\text{H}_2 & \rightarrow \text{H}_2\text{O} \\
\text{OH}^*+\text{H}_2\text{O} & \rightarrow \text{H}_2\text{O}+\text{H}_2\text{O} \\
\text{OH}^*+\text{HO}_2^* & \rightarrow \text{H}_2\text{O}+\text{O}_2
\end{align*}
\]

(8)

The presence of O2 at the cathode within the plasma discharge has indeed been detected by emission spectroscopy. This oxygen will rapidly react in the vapour sheath with the titanium radicals produced from reactions Eq. (4) and adsorbed at the surface to produce TiO2.

The reaction scheme described here should be completed by the possible photon or ion impact dissociation process. A future comprehensive analysis of the plasma discharge, of the liquid solution and the gas phase, is however necessary to achieve this task.

4. Summary and conclusion

This paper presents an analysis of the physico-chemical mechanisms underlying a novel plasma electrolytic system which has been developed over the past few years to deposit thin films on a cathodically-biased substrate. As for any film deposition technique, the control and adjustment of the quality and structure of the produced films requires a good understanding on the plasma phenomena occurring during the deposition.

In this paper, we have been able to demonstrate that the vapour sheath, the result of the vapourisation of the adjacent liquid layer around the cathode, is submitted to a strong ionisation process leading to the initiation of a plasma discharge within this gas phase. The physical characteristics of this plasma discharge (shape, electron temperature, current density, plasma power, current/voltage characteristics) are the signature of an abnormal glow discharge. Due to the high temperature involved within this type of plasma, the vaporised titanium isopropoxide or ethanol solutions are submitted to a significant plasma chemical dissociation at the surface of the plasma-heated cathode. These processes induce the formation of nano-structured crystalline titanium dioxide or graphite coatings at the surface of the electrode.

The advantage of this plasma electrolytic discharge for film deposition is that we can obtain novel and different structures and crystallinities by adjusting the electric operating parameter of the system. The high deposition kinetic, the operation at atmospheric pressure (without any supply of additional oxygen), the direct production of crystalline coatings without further post-deposition annealing make this technique very efficient, cheap compared to the other more conventional techniques and thus the technique is industrially very attractive.

This study provides a foundation for future optimisation and control of this process. Further studies are necessary to get a comprehensive understanding on the plasma chemical dissociation processes including the photon, electron and ion impact dissociation phenomena. This step implies a complete experimental characterisation of the entire system (analysis and evolution of the liquid, gas and plasma composition) and the development of a theoretical model describing the overall plasma deposition mechanisms.

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References