

## Large Area Excimer Laser Induced Deposition of Titanium from Titanium Tetrachloride

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**Abstract.** Large area excimer laser induced deposition of titanium on fused silica from  $\text{TiCl}_4$  is studied with an emphasis on process modeling. We show that several  $\text{TiCl}_4$  monolayers can be adsorbed if the surface is adequately prepared and that the Ti thin film growth occurs through the photodecomposition of this adsorbed  $\text{TiCl}_4$  layer. We propose two growth regimes. During an initiation phase, up to 3 nm in thickness, the adsorbed layer is photochemically decomposed giving a growth rate of  $\sim 0.015$  nm/pulse. In a second phase, the deposition rate increases to between 2 and 7 nm/pulse due to the laser heating of the preceding photochemically deposited titanium film. Between consecutive pulses,  $\text{TiCl}_4$  molecules primarily from the adsorbed layer diffuse to the reaction zone leading to a new adsorbed layer ready to be transformed to solid titanium.

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We recently reported [1] the development of a laser direct writing system for the production of titanium lines from titanium tetrachloride ( $\text{TiCl}_4$ ). Instead of a frequency doubled  $\text{Ar}^+$  laser used by Tsao et al. [2], we use here a KrF excimer laser with  $\lambda = 248$  nm. Both studies were done on the deposition of Ti on lithium niobate ( $\text{LiNbO}_3$ ) since there is a technological interest in the fabrication of Ti lines on such substrates for the production of new and more efficient Ti: $\text{LiNbO}_3$  optical waveguides. We also recently reported a detailed study of the line profile [3,4] as well as the fabrication and characterization of Ti: $\text{LiNbO}_3$  optical waveguides made from laser deposits [3,5].

In this paper, we present a study of the large area excimer laser induced deposition of Ti on fused silica from  $\text{TiCl}_4$  with an emphasis on process modeling. These experiments and analysis were done in order to obtain a better understanding of the growth mechanism. We investigated the  $\text{TiCl}_4$  adsorption phenomena and we show that several  $\text{TiCl}_4$  monolayers could be adsorbed on the surface if the reaction chamber is prepared adequately. With an unfocused beam, we have induced Ti deposition on the fused silica cell windows. From our analysis, we show that the radicals produced in the gas phase are not the primary source for the deposition and that the growth occurs through the photodecomposition of the

$\text{TiCl}_4$  adsorbed layers. Furthermore, from the transmissions analysis, we suggest two growth regimes.

### 1. $\text{TiCl}_4$ Adsorption Phenomena

Titanium tetrachloride ( $\text{TiCl}_4$ ) is a liquid with a vapor pressure of about 10 Torr at the operation temperature of 20°C [6]. When the reaction cell is exposed to a certain pressure of  $\text{TiCl}_4$ , adsorption takes place on all internal walls including the windows. It is expected that the ad-

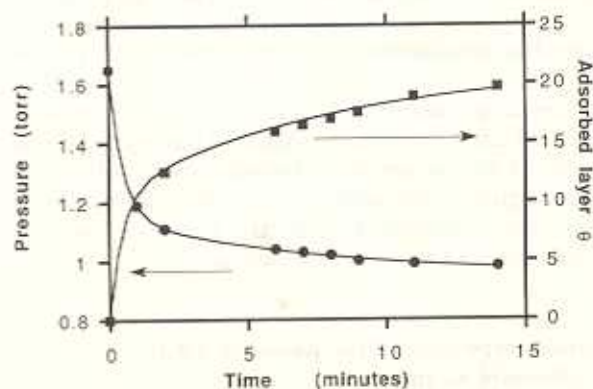


Fig. 1. Pressure variation and mean number of adsorbed layers  $\theta$  as deduced from the quartz crystal microbalance (QCM) measurements as a function of time after having isolated the cell

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sorbed layer thickness will be strongly affected by the cell preparation such as the cell heating temperature and time. As will be seen later, the adsorbed layer thickness is critical in this process because the growth occurs through the photodecomposition of this adsorbed  $\text{TiCl}_4$ .

In order to evaluate the adsorption layer thickness, we performed pressure ( $P$ ) and quartz crystal microbalance (QCM) measurements. The chamber is prepared by heating it to  $80^\circ\text{C}$  under Ar flow for 30–45 min. Figure 1 shows  $P$  measured by a capacitance gauge as a function of time following a rapid introduction of 1.65 torr of  $\text{TiCl}_4$  and isolating the chamber from the pump. A 0.65 torr decrease of the pressure is observed. It was verified that this decrease is due to the  $\text{TiCl}_4$  adsorption on surfaces by the following desorption test. After reaching equilibrium, the system was pumped rapidly (few seconds) to evacuate all the residual gas molecules in the cell and the chamber was then isolated from the pump. The observed pressure increase corresponded to the previous pressure decrease.

Figure 1 also shows the coverage  $\theta$  as deduced from the QCM measurements. Note that there is good correspondence between both the  $P$  and the QCM measurements. Assuming that the adsorption layer is in the liquid phase, and using the  $\text{TiCl}_4$  liquid density of  $1.727\text{ g/cm}^3$  [6], the calculated surface site density for a monolayer is  $3.1 \times 10^{14}$  sites/cm<sup>2</sup>. For our cell, where the total internal surface is  $400\text{ cm}^2$  and the volume is  $130\text{ cm}^3$ , we estimate that at  $20^\circ\text{C}$ , a pressure of 0.03 Torr corresponds to a full  $\text{TiCl}_4$  monolayer. Using this calculation, it was possible to calibrate the QCM signal and deduce  $\theta$ .

Depending on the initial pressure, pressure variations  $\Delta P$  range from 0.5 to 1.5 Torr leading to a  $\text{TiCl}_4$  adsorbed layer average thickness of  $\theta \sim 16$ –50 layers. This is a large number of adsorbed layers which cannot be explained by the BET model which predicts a coverage of approximately one monolayer at 10% of the vapor pressure. It is also larger than the monolayer measured by Tsao et al. [2]. However, when the cell is heated at  $150^\circ\text{C}$  for 12 h, before doing the adsorption experiment, the adsorbed layer goes down to  $\sim 1$  monolayer when the exposure pressure is 0.5 Torr. This strongly suggests that the adsorption is activated by the presence of  $\text{H}_2\text{O}$  on the surfaces. It is therefore suspected that some  $\text{TiCl}_4$  reacts with the very few  $\text{H}_2\text{O}$  molecules present on the surface and forms nucleation centers which give rise to a more pronounced adsorption process. Due to the low initial  $\text{H}_2\text{O}$  concentration in the adsorbed layer, the titanium oxide concentration should be relatively low. As will be seen later, this phenomenon gives higher deposition rates, which is important from a technological point of view. Note that when Ti is deposited on  $\text{LiNbO}_3$  for optical waveguide fabrication, the presence of oxygen in the films is not important because the Ti will diffuse into the  $\text{LiNbO}_3$  in an oxidizing atmosphere.

## 2. Photodecomposition of the Adsorbed $\text{TiCl}_4$ by an Unfocused Beam

Large area Ti deposition was performed using an unfocused KrF excimer laser,  $\lambda = 248\text{ nm}$ . In these ex-

periments, the laser beam passes through a cell, with front and rear fused silica windows, on which the deposition takes place. After purging the chamber with Ar for 30 min,  $\text{TiCl}_4$  is introduced in the cell up to a determined pressure  $P_i$ . After 10 min, the cell is pumped down to below  $0.02 \pm 0.01$  torr essentially leaving an adsorbed layer on all internal surfaces including the two windows. While pumping on the cell, the windows were exposed to the unfocused beam having an energy of 15–20 mJ/pulse over a  $1\text{ cm}^2$  area and at a pulse frequency of 2 Hz. During a typical experiment, 1000–2000 pulses are delivered into the cell.

Since the adsorbed layer is expected to be a few tens of nanometers thick before pumping, it is expected that a deposit with a thickness on the same order of magnitude will be produced. Surprisingly, the Ti thin films produced on both windows have considerably higher thicknesses, reaching a few micrometers in most experiments. Since the deposit dimension follows the laser beam shape and since almost no powder is found surrounding the deposit,

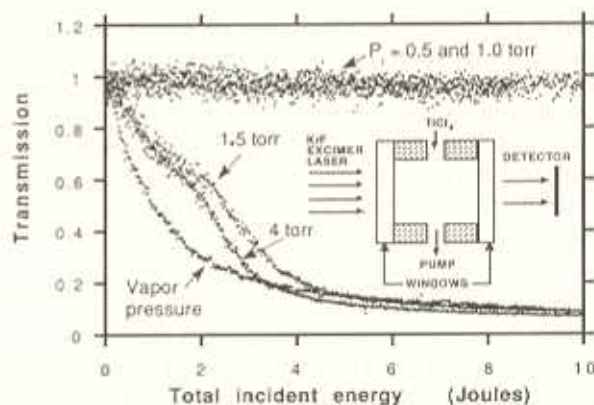


Fig. 2. Transmission as a function of the accumulated incident energy for various  $\text{TiCl}_4$  exposure pressures over 10 min. In all cases, pressures were below  $0.02 \pm 0.01$  Torr during the laser irradiation. A time scale can be found by using our average 20 mJ/pulse at 2 Hz.

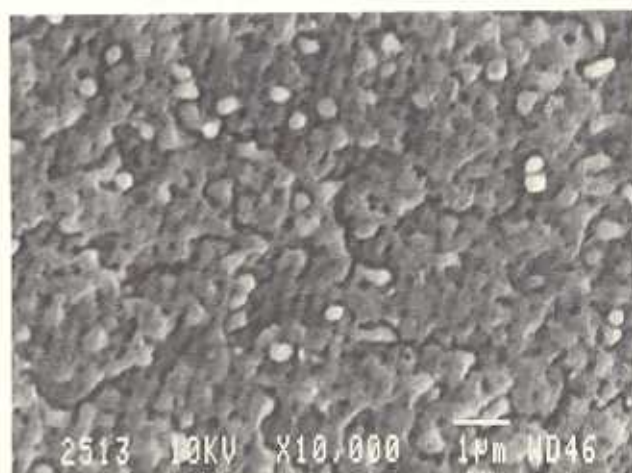


Fig. 3. Scanning electron micrograph of a Ti thin film produced by an unfocused KrF excimer laser beam on the front fused silica window. The cell was exposed to 1.5 torr of  $\text{TiCl}_4$  for 10 min. During the process, the pressure remained less than  $0.02 \pm 0.01$  torr.

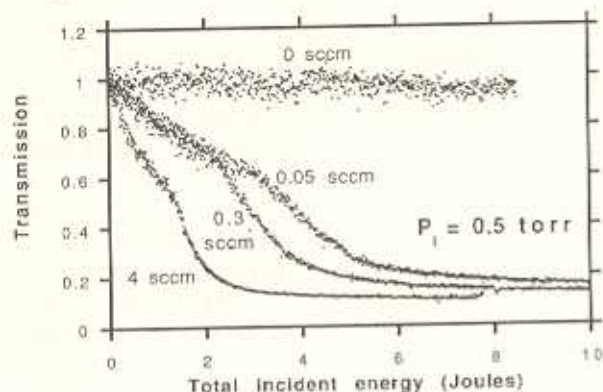


Fig. 4. Transmission as a function of the accumulated incident energy for various  $\text{TiCl}_4$  flow rates during preparation. In all cases, the pressure was 0.5 torr during preparation and was kept below  $0.02 \pm 0.01$  torr during the experiments

it is concluded that reactions occur primarily on the window surfaces and not in the gas phase whose pressure is kept below 0.02 torr. Indeed, at this pressure the number of gas molecules in the laser beam path is not sufficient to produce such an important deposit. To obtain such thick films from a thin adsorbed layer, freshly adsorbed  $\text{TiCl}_4$  coming from the surrounding region should diffuse to the growth region between each pulse. This will be discussed later.

Measuring the incident and transmitted energy, it was possible to monitor the transmission as a function of time. However, even though the time should affect the adsorption layer, we have opted to plot the transmission as a function of accumulated energy, since the deposition process should depend more strongly on the number of photons. Figure 2 shows these variations for various initial  $\text{TiCl}_4$  pressures  $P_1$  ranging from 0.5 torr to vapor pressure. For  $P_1 < 1$  torr, almost no transmission variations occur and the deposit is less than 10 nm thick. When the initial pressure is between 1 and 4 torr, few micrometer deposits are observed and the transmission decreases rapidly due to the growing of a metallic Ti film on the windows. However, as the transmission drops, less energy reaches the rear window and the Ti film final thickness at this window is lower, usually by a factor of 2. Figure 3 shows a scanning electron micrograph of a typical film made in these conditions. Grains ranging from 200 to 500 nm in dimension, probably related to a non-uniform growth are observed. When  $P_1$  is vapor pressure, the deposit is highly non-uniform showing volcanic and column-like protrusions extending from the film. Furthermore, these films peeled off from the windows when exposed to air, which indicates that some unreacted  $\text{TiCl}_4$  and subproducts are still in the film and react with  $\text{O}_2$  and  $\text{H}_2\text{O}$  when exposed to air.

It was also noticed that the  $\text{TiCl}_4$  flow during the adsorbed layer formation influences all the experiments. To clarify this, testing was done by maintaining the initial pressure at 0.5 Torr but by using different flows during the 10 min exposure. The cell is then pumped down below 0.02 Torr. Figure 4 shows the transmission as a function of the accumulated incident energy for various prepa-

ration flow rates. It is very surprising to see a strong dependence of the Ti thin film growth rate on the flow rate. Indeed, a comparison of Figs. 2 and 4, show that a flow rate of 4 sccm at 0.5 Torr leads to an even higher growth rate than 4 Torr and 0 sccm. These results suggest that the flow affects the  $\text{TiCl}_4$  adsorbed layer thickness.

### 3. Discussion

In Fig. 2, a drastic difference is observed between the curves for  $P_1 \leq 1.0$  torr and the curves for  $P_1 > 1.5$  torr, while there is almost no change between different curves for  $1.5 \leq P_1 \leq 4$  torr. A possible explanation involves the  $\text{TiCl}_4$  adsorption and desorption processes on the nucleation center discussed previously. As indicated in Fig. 1, the adsorption varies rapidly during the first minutes before slowing down. The adsorption is fast when  $\text{TiCl}_4$  drops are formed on a nucleation center because the adsorption surface is large. At a high enough pressure, these drops become so large that they join together to form a uniform film. This behavior seems to explain the situation below 1.0 torr where we propose that the pressure is not high enough to allow the formation of a uniform film. With continued pumping, drops that were formed rapidly will desorb rapidly, giving a thin adsorbed layer and a slow growth rate as indicated in the curves for  $P_1 \leq 1.0$  torr. However, if  $P_1 > 1.5$  torr, drops join together to form a uniform film which is more resistant to pumping due to the surface energy minimization. The presence of a significant adsorbed layer will give rise to a thin film growth and a large transmission variation. If  $P_1$  is greater than 1.5 torr, additional adsorbed layers on the uniform film are not as strongly bonded and may desorb easily, explaining the similar curves for  $1.5 \leq P_1 \leq 4$  torr. When the vapor pressure is reached, a large adsorbed layer is formed giving rise to a thick film which probably still contains  $\text{TiCl}_4$  which can react with  $\text{H}_2\text{O}$  when exposed to air.

Figure 4 suggests that increasing the flow rate will lead to a thicker  $\text{TiCl}_4$  adsorbed layer. The  $\text{TiCl}_4$  molecular thermal velocity is about 200 m/s and the average molecular velocity due to the flow rate is 0.1–6 m/s. Thus, the flow rate component does not seem to be significant when compared to the thermal velocity, except that it slightly increases the number of contacts on the substrate. However, its effect on the adsorbed layer is important. It is presently unclear how the preparation flow rate can influence the adsorbed layers.

Most curves in Fig. 2, 4 display a break, somewhat resembling a knee, at 60% of transmission. Below 60% transmission, the variation is low but then increases. By measuring the laser beam transmission through an electron-beam evaporated Ti thin film, the Ti film absorptivity was estimated to be  $5.4 \times 10^5 \text{ cm}^{-1}$ , in agreement with reported values [7]. Reflection coefficients are estimated to be  $\approx 0.17$  for pure Ti and approaching 0.05 if there were only liquid  $\text{TiCl}_4$ . Therefore, at 60% transmission, the average Ti thickness per window should be approximately 3 nm. In general, 200 pulses are needed to deposit this 3 nm, giving an average growth rate of

$\sim 0.015$  nm/pulse. We associate this regime to an initiation phase where the UV laser beam induces a photochemical decomposition of the adsorbed  $\text{TiCl}_4$  layer to form a solid Ti film. This small growth rate phase can also be associated with an initiation phase where the critical density of radicals and species needed for the Ti deposition are formed. After the knee-like break, taking the average Ti thickness of the front window divided by the number of incident pulses, average growth rates are in the range 2–7 nm/pulse, depending on experimental conditions. We propose that, during that regime, photon absorption in the Ti deposited layer gives a temperature rise [8,9] which could exceed the  $600^\circ\text{C}$  necessary to thermally decompose the  $\text{TiCl}_4$  [10]. This could considerably speed up the  $\text{TiCl}_4$  decomposition into solid titanium. Therefore we propose two growth regimes: (i) an initiation phase during which photolysis of the adsorbed  $\text{TiCl}_4$  produces enough radicals to form a 3 nm thick Ti film; and (ii) a growth phase during which laser heating of the Ti film speeds up the chemistry therefore leading to a much higher growth rate.

Figures 2 and 4, show that the transmission does not have a sharp decrease according to a high average growth rate of 2–7 nm/pulse and that it does not go down to zero even after a long period (10000 pulses). Both phenomena are probably due to the effect of the initiation phase on the sides of the deposit. Indeed, on the border of the deposit, the accumulated energy is probably not high enough to initiate the growth phase and produce a thin film with significant thickness. Therefore, some light passes through the side of the deposit explaining the higher observed transmission values.

Using the average growth rate of 2–7 nm/pulse and the Ti density of  $4.5\text{ g/cm}^3$ , we estimate that the average deposit of Ti varies from 7 to 27 monolayers per pulse. To deposit this number of monolayers per pulse requires a constant renewal of the adsorbed layer between consecutive pulses. Since the pulse lasts only 10 ns, the renewal of the adsorbed layer is not achieved during this time but between pulses which are spaced 0.5 s in this experiment. Fresh  $\text{TiCl}_4$  possibly comes from the gas phase or from

the diffusion of the adsorbed layer to the reaction zone. To clarify the possible involvement of the residual  $\text{TiCl}_4$  gas, the experiment of Fig. 1 was repeated using an initial pressure of 0.03 torr and a very low flow rate in order to maintain this pressure. This simulates the conditions in which the experiment of Fig. 1 was performed except that a much thinner adsorbed layer is now expected due to the low pressure during the preparation step. Figure 5 presents the results of this experiment as well as a typical result of Fig. 1. Since the growth occurs much faster when the adsorbed layer is thicker, we conclude that the gas phase is not the primary source of renewal of adsorbed  $\text{TiCl}_4$ . Instead, between consecutive pulses, adsorbed  $\text{TiCl}_4$  diffuses to the reaction zone to renew the exposed layer to the beam.

#### 4. Conclusion

Excimer laser induced deposition of Ti from  $\text{TiCl}_4$  occurs through the photodecomposition of an adsorbed  $\text{TiCl}_4$  layer. In this process, the gas-phase chemistry is not involved in the deposition. After an initiation phase where the deposition takes place through the photochemical decomposition of the adsorbed layer with a slow growth rate of  $\sim 0.015$  nm/pulse (up to  $t = 3$  nm), the deposition process speeds up due to laser heating with a growth rate of 2–7 nm/pulse. Between consecutive pulses, adsorbed  $\text{TiCl}_4$  molecules diffuse to the reaction zone leading to a new adsorbed layer ready to be transformed into solid titanium.

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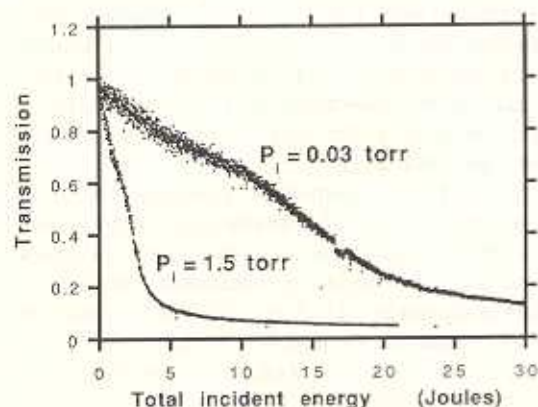


Fig. 5. Transmission as a function of the accumulated incident energy for (i)  $P_1 = 0.03$  torr and (ii)  $P_1 = 1.5$  torr. For (i) a small gas flow is present. The pressure was  $\sim 0.03$  torr during the experiment in both cases