Profile of titanium lines produced by excimer laser direct writing on lithium niobate

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The profile of titanium (Ti) lines produced by KrF excimer laser direct writing on lithium niobate ($LiNbO_3$) has been investigated in detail since it is critical in the fabrication of Ti in-diffused $LiNbO_3$ optical waveguides. Lines written at speeds varying from 0.5 to 10 μm/s have typical thicknesses and linewidths varying from 10 to 185 nm and from 2 to 24 μm, respectively. At a low power density E, the maximum thickness t is proportional to the number of photons or the power density. Increasing E allows a sufficient heating, which leads to the diffusion of Ti into $LiNbO_3$, resulting in a sharp decrease of the thickness in the middle of the deposited line.

I. INTRODUCTION

We recently[1,2] reported the development of a laser direct writing system for the production of titanium (Ti) lines from titanium tetrachloride ($TiCl_4$). Instead of a frequency-doubled Ar^+ laser used by Tsao *et al.*,[3] we use here a KrF excimer laser with $\lambda = 248$ nm. Laser direct writing of Ti on lithium niobate ($LiNbO_3$) is interesting for the production of new and more efficient Ti in-diffused $LiNbO_3$ (Ti:$LiNbO_3$) optical waveguides. Compared to the conventional evaporation technique, this system has the advantage of avoiding the critical photolithography steps as well as giving the possibility of varying the Ti thickness and width along the line leading to better quality optical waveguides. We have recently reported the fabrication and characterization of Ti:$LiNbO_3$ optical waveguides.[4]

We recently performed[5] a detailed analysis of unfocused laser-beam-induced deposition of Ti from $TiCl_4$ with an emphasis on growth modeling. We showed that many $TiCl_4$ monolayers (up to 50 in some cases) can be adsorbed on the substrate and that films having a few μm in thickness can be deposited from these adsorbed layers. We concluded that the growth occurs through the photodecomposition of the $TiCl_4$ adsorbed layer and that the gas-phase chemistry is not important in the process. After an initiation phase, during which a growth of 0.015 nm/pulse occurs through the photochemistry of the adsorbed layer, the decomposition speeds up to between 2 and 7 nm/pulse as the laser beam heats the already deposited titanium. Between pulses, adsorbed $TiCl_4$ diffuses to the reaction zone, leading to a freshly by adsorbed layer ready to be transformed into solid titanium at the next pulse.

For the fabrication of Ti:$LiNbO_3$ optical waveguides, the line profile is critical since it determines and controls the propagating optical modes. In this paper, we present a detailed study of the line profile as a function of the most important process parameters: $TiCl_4$ pressure P (Torr), laser power density E (MW/cm^2), laser repetition rate R (s^{-1}), and the writing speed v (μm/s). We propose that at low fluence, Ti thickness is proportional to the laser power, while Ti diffuses into the $LiNbO_3$ substrate as the energy is increased.

II. EXCIMER LASER DIRECT WRITING OF Ti ON $LiNbO_3$

The excimer laser direct writing system of Ti on $LiNbO_3$ has been described previously.[1,2] Very briefly, a KrF excimer laser is focused with a reflective objective (15×, numerical aperture = 0.28) onto a $LiNbO_3$ substrate placed in a chamber whose position is controlled by a XY electronic positioner with a 0.1-μm resolution. To avoid damages to the brittle $LiNbO_3$, the laser energy has to be kept below the damage threshold of 17 nJ/pulse. This corresponds to a power density E=4.4 MW/cm^2 when a pulse length of 10 ns and a beam spot of 7 μm diameter is used. When a 10-nm-thick Ti film is deposited onto the $LiNbO_3$ by e-beam evaporation, damage threshold goes up to 11 MW/cm^2, probably due to higher reflectivity of Ti,[1] indicating that during the Ti deposition, the critical damage step occurs when no Ti is present on the surface. Even though we have shown that deposition occurs through the photodecomposition of the adsorbed $TiCl_4$ on the surface and that gas-phase chemistry is not important for the growth,[5] all our experiments were performed in a chamber with a certain $TiCl_4$ pressure and a small flow rate of 0.5 sccm in order to maintain steady-state conditions of the adsorbed layer during the growth period. Also, the $TiCl_4$ pressure has to be kept below 0.5 Torr in order to prevent powder formation or deposition on the reaction cell windows.

The composition of the Ti lines has been determined by Auger electron spectroscopy (AES). In addition to Ti, samples contain oxygen throughout. This is probably because they were exposed to air before performing AES.

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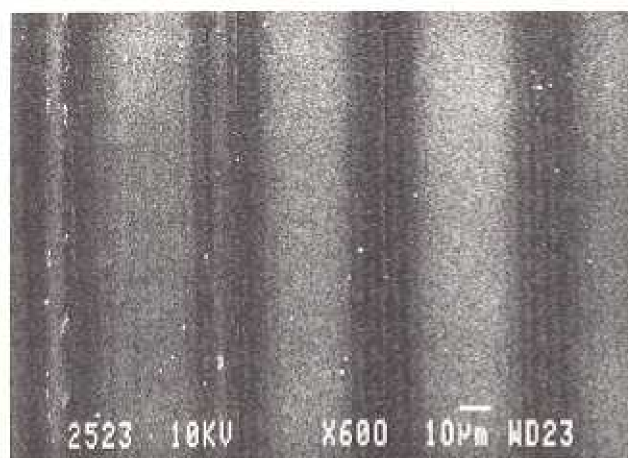
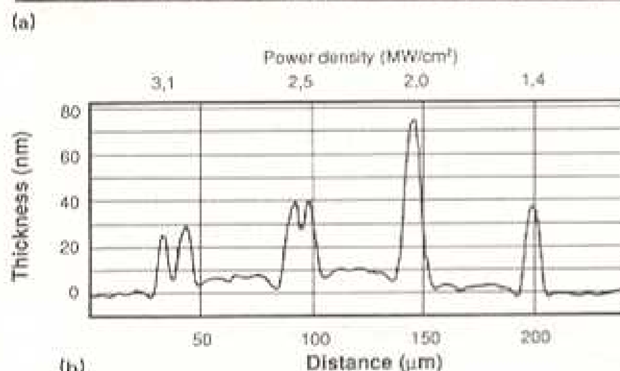


(a)



(b)

FIG. 1. Scanning electron micrograph of four ~1-mm-long Ti lines written on $LiNbO_3$ at 5 μm/s. The profile is also shown for each line. The $TiCl_4$ pressure is 0.5 Torr.

Within the limits of the system, no chlorine was detected thus suggesting that [Cl] < 2 at. %. Note that the presence of oxygen in the film does not affect the Ti in-diffused $LiNbO_3$ optical waveguide properties since, during fabrication, the Ti will be oxidized in a wet O_2 atmosphere at 1025 °C during diffusion.[6]

III. Ti LINE PROFILE

Figure 1 shows a scanning electron micrograph of four ~1-mm-long lines written on $LiNbO_3$ at a speed of $v=5$ μm/s with laser power density of $E=1.4$, 2.0, 2.5, and 3.1 MW/cm^2, respectively. The profile is also shown for each line and will be discussed in detail later. Along a 1-mm-long line, thickness and line area vary by less than 10% (approaching 3% in certain cases). This is acceptable for waveguide fabrication.

Figure 2 shows the line cross-section area A (μm^2), the maximum thickness t (nm), and the width $W_{1/e}$ (μm) at $1/e$ of t as a function of power density E for lines made at pressures of 0.5 and 0.3 Torr of $TiCl_4$ and at a speed of 2 μm/s. For $E \leqslant 2$ MW/cm^2 at $P=0.5$ Torr and for $E \leqslant 1.1$ MW/cm^2 at $P=0.3$ Torr, t and A are proportional to E. Since the growth occurs through the photodecomposition of the adsorbed layer, the overall proposed reaction is

$$TiCl_4 \text{ (adsorbed)} \xrightarrow{h\nu} Ti(s) + 2Cl_2(g). \qquad (1)$$

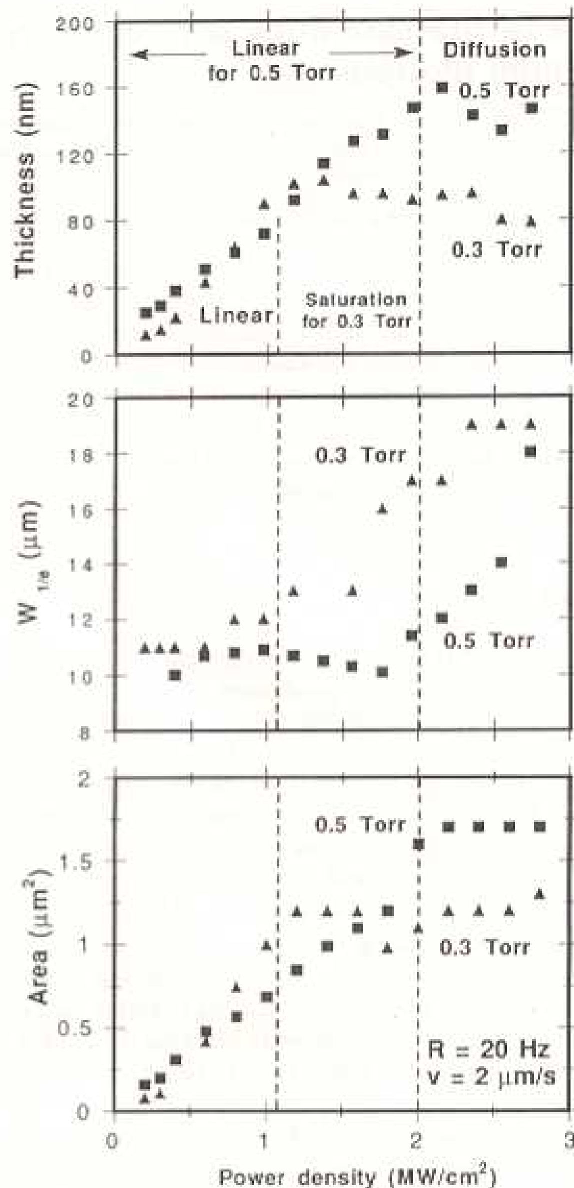


FIG. 2. Maximum thickness (t), width ($W_{1/e}$ at $1/e$ of t), and area (A), as a function of power density. The pressure is 0.3 and 0.5 Torr and the writing speed is 2 μm/s.

At low power densities, since t is proportional to E or to the number of photons $n_{h\nu}$, the overall reaction (1) is a first-order reaction in $n_{h\nu}$. Furthermore, since at low E the line thickness does not depend on the pressure and therefore on the adsorbed layer thickness, we suggest that the existing adsorbed layer is not completely transformed with one laser pulse. Between pulses, the adsorbed layer is renewed by fresh $TiCl_4$ diffusing from outside the reaction zone.[5]

When $E > 2$ MW/cm^2 at $P=0.5$ Torr and when $E > 1.1$ MW/cm^2 at $P=0.3$ Torr, a saturation and even a decrease in t is observed. The pressure dependence of this phenomena suggests that it is not related to photoablation of the Ti deposited. Using reaction (1), we expect a saturation due to the final thickness of the $TiCl_4$ adsorbed layer

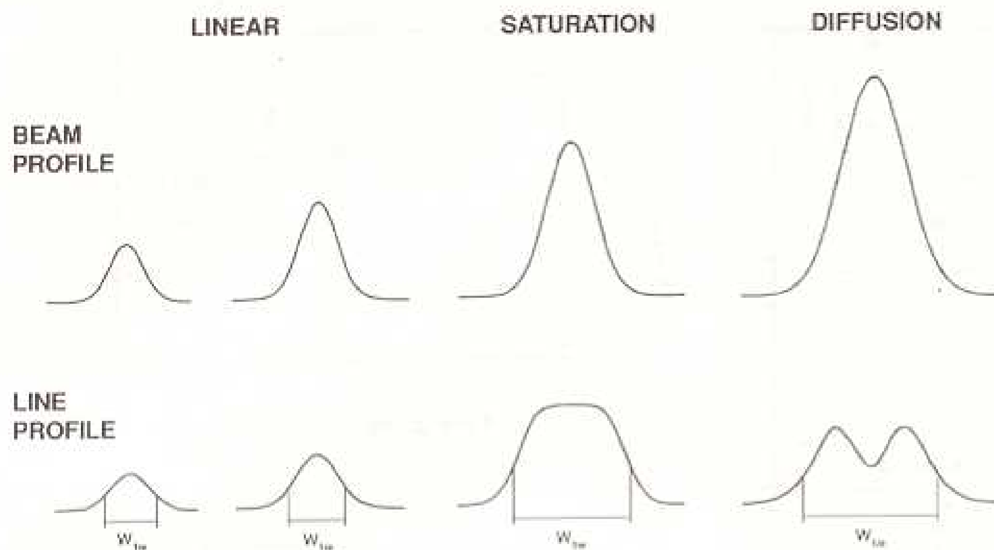


FIG. 3. Effects of the beam profile on the line profile in the linear regime and when diffusion becomes important.

that can be transformed to Ti by the laser beam. As mentioned in Ref. 5, the $TiCl_4$ adsorbed layer thickness depends on the $TiCl_4$ pressure. It can be seen from Fig. 2 that, as expected, t saturation for $P=0.3$ Torr occurs before the one for $P=0.5$ Torr.

For further increase in E, there is a decrease in t and a saturation in A. By looking at the profile of Fig. 1, we note a sharp decrease in the middle of the line for $E>2.2$ MW/cm^2. This suggests that, in addition to transforming adsorbed $TiCl_4$ into solid Ti, the laser energy arriving on the surface might be absorbed by the Ti layer and the substrate, leading to a local increase in temperature. This occurs between 2 and 2.5 MW/cm^2, which corresponds to approximately half of the power-density threshold for damage. This resulting heating, which could reach the Ti melting temperature of 1668 °C,[7] leads to a speedup of the growth, as discussed previously,[5] and to a combination of $TiCl_4$ desorption and Ti diffusion into the $LiNbO_3$. This laser heating might also melt the $LiNbO_3$, which has a fusion temperature of 1253 °C, leading to a Ti liquid-phase diffusion process. In a previous publication,[1] the decrease in thickness was primarily explained by desorption or ablation of the deposited film. We now propose that diffusion is probably the main explanation. Al-Chalabi and Goodall[8] reported that they were able to diffuse electron-beam-evaporated Ti thin film in $LiNbO_3$ by KrF excimer laser with power density comparable to the one used here. Moreover, for such Ti in-diffused $LiNbO_3$ waveguides, showing a depression in the middle of the line profile, the observed optical modes are similar to those of a waveguide done with a line having a Gaussian profile before the furnace diffusion.[4] This suggests that Ti is possibly diffused into the $LiNbO_3$ by the laser before performing the diffusion in the furnace.

The line profile is probably produced in the following way. Suppose that the laser beam with radius r moves at speed v in the x direction with a maximum energy at a time t_0 located at $x = x_0$. Assuming that the energy at $x = x_0 + r$ is sufficient to transform $TiCl_4$ into solid titanium, after few pulses, the maximum energy will arrive at $x = x_0 + r$, where some Ti(s) has already been deposited. The energy might then be sufficient to cause a local temperature increase and to diffuse the previously deposited Ti, leading to a line profile with a sharp depression in the middle. If desorption caused the thickness reduction, the low energy at the forefront of the beam would still give a deposit, but as the beam moved and the energy increased, the adsorbed layer would desorb, leading to a thickness saturation. Since there is a decrease in the middle of the line, we conclude that Ti diffusion into $LiNbO_3$ occurs at high energy.

Figure 3 summarizes schematically the effect of the laser-beam profile on the deposited Ti line profile. At low power density, a linear regime is observed and the line profile follows the beam profile. The thickness t and area A increase linearly with power, while $W_{1/e}$ remains constant. After saturation (where t and A become constant even if E increases), t decreases due to the diffusion of Ti into $LiNbO_3$. The width $W_{1/e}$ should therefore increase as shown in the figure due to the flattening out of the profile.

Figure 4 shows the linewidth at $t=20$ nm, W_{20}, as a function of E when $P=0.3$ and 0.5 Torr. We choose W_{20} because this corresponds to the linewidth measured with an optical microscope. As previously mentioned,[1] W_{20} is essentially independent of pressure, indicating again that the deposition occurs through the photodecomposition of the adsorbed layers. This curve depends on the beam profile. As shown in Fig. 2, a thickness of 20 nm is always in the linear regime. This linearity can be used to determine the beam profile. Using the variable y as the direction perpendicular to the line and $f(y)$ as the beam profile, the power density to produce $t=20$ nm is $E_{20} = CE_f(W_{20}/2)$, where C is a proportionality constant. Since E_{20} is a constant, $f(y)$ is determined by plotting E^{-1} as a function of $W_{20}/2$. The result, shown in the inset of Fig. 4, is a Gaussian with a full width at half maximum of 7 μm. This value was used for the calculation of the power-density threshold for beam damage.

Using the deduced beam diameter of 7 μm and the distance of 0.1 μm between pulses, we calculated that ap-

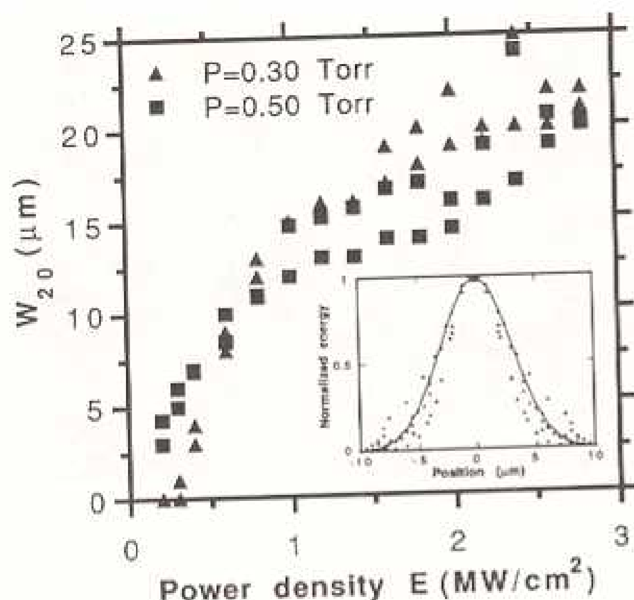


FIG. 4. Linewidth W_{20} at 20-nm thickness as a function of power density E when pressures are 0.3 and 0.5 Torr. The deduced beam profile is shown in the inset.

proximatively 74 pulses impinge on a specific point along the line. Since the line thickness typically varies from 10 to 185 nm, the growth rate ranges from 0.13 to 2.5 nm/pulse. This implies that between ~0.5 and up to 8 Ti layers are formed per pulse. This rate is in the same order of magnitude as the one obtained from large-area excimer-laser-induced deposition of Ti.[5]

Figure 5 shows the effect of the writing speed v on the line thickness t for 0.5 μm/s $< v < 10$ μm/s at a constant repetition rate R of 20 Hz. We observe that t is proportional to v^{β}, where $\beta = 0.8$. Since t is proportional to E (see Fig. 2) and since the number of photons impinging on a specific point is proportional to v^{-1} at a constant R, we

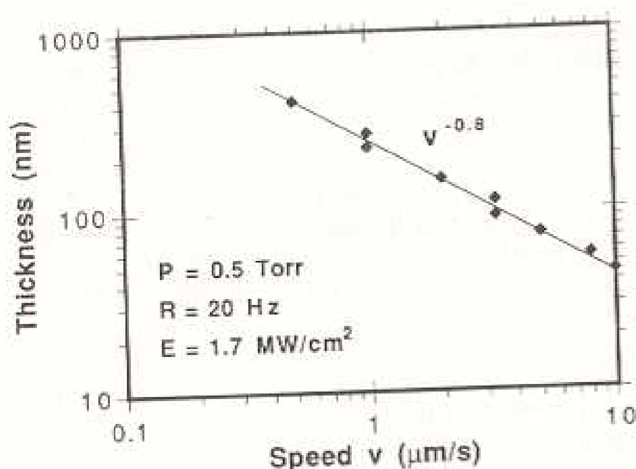


FIG. 5. Line maximum thickness t as a function of the speed v. The power density is 1.7 MW/cm^2, the pressure is 0.5 Torr, and the repetition rate is 20 Hz.

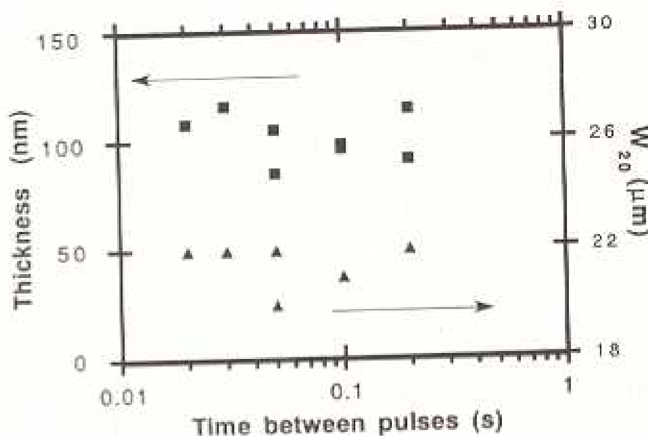


FIG. 6. Line maximum thickness t and linewidth W_{20} as a function of the time between consecutive pulses. The power density is 1.3 MW/cm^2 and the pressure is 0.5 Torr.

expect that t is proportional to v^{-1}. This gives relatively good agreement with our experimental results.

Since the number of photons arriving at a specific point between x and $x+\Delta x$ is $Rv^{-1}\Delta x$, maintaining the ratio R/v should result in similar line profiles. This is shown in Fig. 6, where t and W_{20} are plotted as a function of the time between pulses (R^{-1}) by keeping R/v constant for 5 Hz $< R <$ 50 Hz. The constant t and W_{20} values suggest again that the growth is proportional to the number of photons. Furthermore, we can also conclude that all reactions producing the films occur on time scale smaller than 20 ms. After the excimer laser pulses of ~10 ns, some adsorbed $TiCl_4$ will be transformed into Ti(s) and the Cl_2 reaction products will leave the film in less than 20 ms. Furthermore, new adsorbed $TiCl_4$ layer coming to the reaction zone by diffusion will be formed in less than 20 ms. These steps are all feasible on such time scale, but more experiments are required to determine which one is the rate-limiting step.

IV. CONCLUSION

Titanium lines with a controlled profile can be produced on $LiNbO_3$ by excimer laser direct writing. Lines are written at speeds ranging from 0.5 to 10 μm/s, giving maximum thicknesses between 10 and 185 nm and linewidths between 2 and 24 μm. At low power density, the line profile follows the laser-beam profile and the growth rate is proportional to the number of photons arriving on the $TiCl_4$ adsorbed layer. At higher power density, the additional energy is absorbed by both the Ti film already deposited and the substrate giving rise to a local heating and to Ti diffusion into $LiNbO_3$. This leads to a sharp decrease in the middle of the Ti line profile.

We have recently used this technique efficiently to fabricate Ti:$LiNbO_3$ optical waveguides.[4] This technique is limited by its small writing speed due to the low repetition rate of our excimer laser. However, there now exist KrF excimer waveguide lasers that could operate at a repetition rate of 2000 Hz.[9] If the surface diffusion of the $TiCl_4$ ad-

sorbed layers is high enough and if reaction products are evacuated quickly, writing speed could be increased up to 0.4 mm/s, rendering this process technologically interesting for high-throughput Ti:$LiNbO_3$ optical waveguide fabrication. Another technological interest is the possibility of producing Ti:$LiNbO_3$ optical waveguides by laser direct writing at an energy sufficiently high to ensure that Ti is diffused into the $LiNbO_3$ by the laser. This eliminates the furnace diffusion step. Experiments are underway to verify this.

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