

# Excimer laser direct writing of titanium lines on lithium niobate

R. Izquierdo, C. Lavoie, and M. Meunier

*Ecole Polytechnique de Montréal, Groupe des Couches Minces and Département de Génie Physique,  
C. P. 6079 Succ. "A" Montréal, Québec H3C 3A7, Canada*

(Received 16 February 1990; accepted for publication 4 June 1990)

We have investigated the deposition of titanium lines from titanium tetrachloride ( $\text{TiCl}_4$ ) onto lithium niobate ( $\text{LiNbO}_3$ ). The deposition is induced using a KrF excimer laser ( $\lambda = 248 \text{ nm}$ ). Our objective is the formation of titanium indiffused  $\text{LiNbO}_3$  optical waveguides. The titanium lines contain little chlorine ( $[\text{Cl}] < 2 \text{ at. \%}$ ) and are typically 20–100 nm thick, and 3–20  $\mu\text{m}$  wide. We find that the process is controlled by photochemistry of  $\text{TiCl}_4$ . However it is difficult, at this point, to determine whether the gas or the adsorbed layer is the primary source of thin-film growth.

There is a technological interest in the development of processing techniques for titanium (Ti) thin films on lithium niobate ( $\text{LiNbO}_3$ ) for the fabrication of titanium indiffused  $\text{LiNbO}_3$  ( $\text{Ti}:\text{LiNbO}_3$ ) optical waveguides.<sup>1</sup> Compared to the standard evaporation technique, the laser direct writing method eliminates the time consuming and critical photolithography steps, and also allows the deposition of a titanium thin film with variable thickness, permitting the production of  $\text{Ti}:\text{LiNbO}_3$  optical waveguides with novel properties. Tsao *et al.*<sup>2</sup> were the first to report the formation of a titanium thin film by laser direct writing, using a frequency-doubled  $\text{Ar}^+$  laser ( $\lambda = 257 \text{ nm}$ ). Other laser processing techniques on  $\text{LiNbO}_3$ , such as ablation<sup>3,4</sup> and etching<sup>5</sup> have also recently been reported. In this letter, we report on a preliminary study of KrF excimer laser deposition of Ti lines from  $\text{TiCl}_4$ , with a special emphasis on the description and characterization of the process.

Figure 1 is a schematic of the deposition system, based on a KrF excimer laser ( $\lambda = 248 \text{ nm}$ ) with a maximum pulse energy of 100 mJ and a repetition rate of 5 Hz. After the laser beam passes through two filters ( $F1$  and  $F2$ ), which decreases the intensity to avoid damaging the  $\text{LiNbO}_3$  substrate, the beam is focused to a 20  $\mu\text{m}$  spot with a reflection objective (Ealing X15; NA 0.28), which offers the long work distance and low aberrations needed for our system. A microscope is used to observe the sample before and after the process. Pattern formation is achieved by moving the substrate under the static beam, using two computer-controlled translation stages mounted in an  $x$ - $y$  configuration. A manually controlled  $z$  axis is used to set the focal point. The programmable stages have a resolution of 0.1  $\mu\text{m}$ . Their maximum speed is 100  $\mu\text{m/s}$ . The Ti lines are processed at scan speeds ranging from 0.2 to 5  $\mu\text{m/s}$ . The window of the reaction chamber is made of fused silica (suprasil 2). After we reach the basic vacuum of  $10^{-3}$  Torr, the cell is purged with argon before the deposition process. The reactive gas is  $\text{TiCl}_4$  (99.999% Alpha products) which, at room temperature is a liquid, with a vapor pressure of around 10 Torr. To prevent powder formation, the  $\text{TiCl}_4$  pressure has to be kept below 0.5 Torr. Any

unconsumed  $\text{TiCl}_4$  is condensed in a cryogenic trap to avoid any damage to the pump.

The substrates used are  $\text{LiNbO}_3$  or  $\text{LiNbO}_3$  covered with a thin layer of titanium (10 nm), used to check if the nucleation of the initial layer influences the process. Deposition has also been successfully performed with glass and silicon.<sup>6</sup> Before deposition, all substrates are washed in organic solvents, rinsed in de-ionized water, and heated to 120 °C in a vacuum oven for an hour, to eliminate any trace of water, which could react with  $\text{TiCl}_4$ .

Since  $\text{LiNbO}_3$  is highly absorbant at  $\lambda = 248 \text{ nm}$ , the short laser pulse of 10 ns might give a high local temperature rise, which can cause severe damage to the sample. By visual inspection using both a differential interference contrast microscope and a scanning electron microscope, we observed damage on  $\text{LiNbO}_3$  at energy pulses higher than 100 nJ, which corresponds to a threshold density of approximately 3  $\text{MW/cm}^2$ . When we cover  $\text{LiNbO}_3$  with a 10 nm layer of Ti, this threshold increases to 250 nJ/pulse, probably due to the higher reflectivity of Ti compared to that of the  $\text{LiNbO}_3$  surface. All lines have been made at energies below 100 nJ/pulse, under various pressure conditions. Depositions were made at different energies and pressures and on all the types of substrates. The composition of the lines was measured by micro-Auger electron spectroscopy, with a spatial resolution of 0.1  $\mu\text{m}$ . This

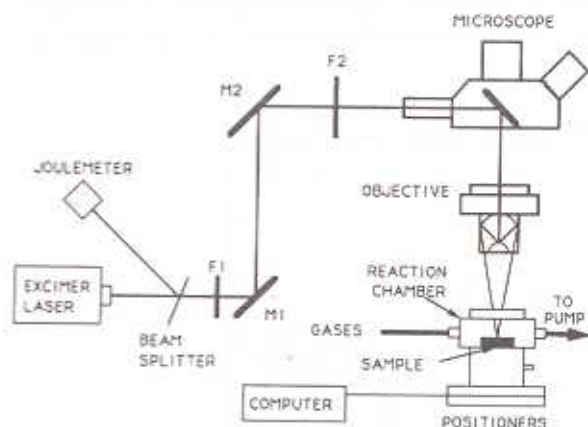


FIG. 1. Schematic drawing of the deposition system.  $F1$  and  $F2$  are filters while  $M1$  and  $M2$  are mirrors.



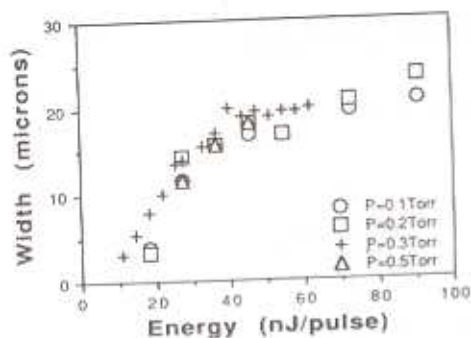


FIG. 2. Titanium linewidth variation as a function of the pulse energy and  $\text{TiCl}_4$  pressure. The displacement speed is  $0.2 \mu\text{m/s}$  and the laser frequency is 2 Hz.

shows that all Ti films are oxidized, due to air exposure, and that they all contain a very low Cl concentration ( $[\text{Cl}] < 2 \text{ at. } \%$ ).

Figure 2 shows the linewidth,  $W$ , as a function of pulse laser energy,  $E$ , for films made on  $\text{LiNbO}_3$  at different pressures and at a speed of  $0.2 \mu\text{m/s}$  with a repetition rate of 2 Hz. We find that  $W$  is independent of  $\text{TiCl}_4$  pressure, and increases monotonically with  $E$ . Assuming a threshold energy to obtain a deposition, an increase in energy will increase  $W$ . This variation will depend on the actual beam shape.

Figure 3 shows the Ti line thickness as measured by a profilometer (Dektak, Sloan) as a function of laser energy at two different  $\text{TiCl}_4$  pressure conditions. Typical thicknesses vary from 20 to 70 nm for Ti lines deposited on  $\text{LiNbO}_3$  at a speed of  $0.2 \mu\text{m/s}$ . As the pressure increases, more molecules in the gas, as well as on the adsorbed layer, can react, leading to a thicker film. Also as the energy increases, more photons arrive in the reaction zone, leading again to a thicker film.

The fact that excimer lasers are pulsed could result in thickness variation along the lines due to two different causes. The first is the pulse-to-pulse energy variation. Second, depositing step by step will cause a regular thickness oscillation which will increase as the pulses become more widely separated. This point is critical, especially for the fabrication of  $\text{Ti:LiNbO}_3$  optical waveguides, as one wants to control the Ti thickness variation along the lines. As-

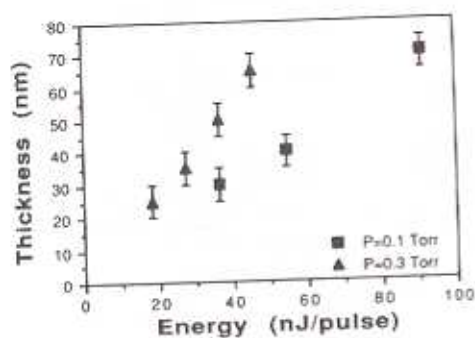





FIG. 3. Thickness variation of Ti deposited on  $\text{LiNbO}_3$  as a function of pulse energy and pressure.

TABLE I. Numerical simulation of the thickness variations with pulse-to-pulse energy variation and beam displacement between pulses. The beam diameter is assumed to be  $20 \mu\text{m}$ .

Beam displacement	Pulse-to-pulse E variation	
	0 %	$\pm 6 \%$
 20 $\mu\text{m}$	$\pm 17 \%$	$\pm 19 \%$
 10 $\mu\text{m}$	$\pm 0.1 \%$	$\pm 2.5 \%$
 0.1 $\mu\text{m}$	$< 10^{-5} \%$	$\pm 0.5 \%$

suming a Gaussian beam of  $20 \mu\text{m}$  diameter, Table I gives the result of a numerical simulation of the thickness variation along the line as a function of beam displacement when there is no pulse-to-pulse energy variation as well as when this variation is  $\pm 6\%$ , which corresponds to our conditions. To obtain a film thickness varying less than a few percent, a beam displacement smaller than the spot radius is necessary. In our case, in order to have line thicknesses ranging from 20 to 100 nm, a beam displacement of  $0.1 \mu\text{m}$  has been chosen. This should give a thickness variation of  $\pm 0.5\%$ . This value only takes into account the thickness variation induced by the beam parameters (energy variation and exposition discontinuity), and it shows that the excimer laser is a possible alternative ultraviolet source to the cw, frequency-doubled  $\text{Ar}^+$  laser. Since the experimental error in thickness measurements is between 8 and 10% for 70-nm-thick line and since the thickness variation along a line is approximately that value, we cannot come to a conclusion about the real thickness variation.

In principle, the deposition process could be either thermal or photolytic, or possibly both. However, in this case it is not a thermal process, because of the high temperature (more than  $600^\circ\text{C}$ ) necessary to thermally dissociate the  $\text{TiCl}_4$ .<sup>7</sup> If such temperature elevation was produced by a short pulse (10 ns), severe thermal damage would certainly occur, because  $\text{LiNbO}_3$  is well known to be extremely fragile. Moreover, Tsao *et al.*<sup>2</sup> showed that visible photons ( $\lambda = 514 \text{ nm}$ ) from the  $\text{Ar}^+$  laser focused on  $\text{LiNbO}_3$  in the presence of  $\text{TiCl}_4$  lead to severe damage before deposition takes place. Due to the low gas absorptivity,<sup>8</sup> thermal reaction is not expected to occur in the gas. Thus the process is not controlled by thermal reaction, but is based on photochemical reactions. A photon energy of 4.98 eV at  $\lambda = 248 \text{ nm}$  is certainly enough to break a Ti—Cl bond of 4.47 eV bonding energy.<sup>9</sup> However, it is difficult at this point to say whether the gas or the adsorbed layer is the primary source of thin-film growth. The presence of powder at pressure higher than 0.5 Torr suggests that gas phase reaction occurs, but at lower pres-

sures the absence of powder as well as the pressure independence of linewidth (Fig. 3) suggest that the adsorbed layer is probably the primary source of thin-film growth. More experiments are necessary to distinguish between the two processes. Work is in progress to model the process and to use this technique in the fabrication of Ti:LiNbO<sub>3</sub> optical waveguides.

The authors would like to thank M. Moreau and J. P. Lévesque for their technical assistance and S. Boivin, J. R. Simard, and I. Najafi for valuable discussions on Ti:LiNbO<sub>3</sub> optical waveguide technology. We also acknowledge the National Science and Engineering Research Council of Canada (NSERC) for its financial assistance.

<sup>1</sup>M. N. Armenise, IEEE Proc. 135, 85 (1988).

<sup>2</sup>J. Y. Tsao, R. A. Becker, D. J. Ehrlich, and F. J. Leonberger, Appl. Phys. Lett. 42, 559 (1983).

<sup>3</sup>M. Eyett and D. Bäuerle, Appl. Phys. Lett. 51, 2054 (1987).

<sup>4</sup>D. C. Ferranti, Microelectronic Manufacturing and Testing April, 18 (1989).

<sup>5</sup>K. W. Beeson and N. S. Clements, in *Laser- and Particle-Beam Chemical Process on Surfaces*, MRS Symposium Proceedings, edited by A. W. Johnson, G. L. Loper, and T. W. Sigmon (MRS, Pittsburgh, 1989), Vol. 129, p. 321.

<sup>6</sup>R. Izquierdo, C. Lavoie, and M. Meunier, Proceedings of the MRS fall 1989 Symposium B In-Situ Patterning: Selective Area Deposition and Etching, (to be published).

<sup>7</sup>A. Chretien and W. Freundlich, *Nouveau Traité de Chimie Minérale* (Masson et Cie, Paris, 1963), p. 1.

<sup>8</sup>M. Rothschild, in *Laser Microfabrication Thin Film Process and Lithography*, edited by D. J. Ehrlich and J. Y. Tsao (Academic, San Diego, 1989), p. 163.

<sup>9</sup>R. T. Sanderson, *Chemical Bonds and Bond Energy*, 2nd ed. (Academic, New York, 1976), p. 52.