

Excimer laser direct writing of titanium lines on lithium niobate

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We have investigated the deposition of titanium lines from titanium tetrachloride (TiCl_4) onto lithium niobate (LiNbO_3). The deposition is induced using a KrF excimer laser ($\lambda = 248 \text{ nm}$). Our objective is the formation of titanium indiffused 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 μm wide. We find that the process is controlled by photochemistry of 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 (LiNbO_3) for the fabrication of titanium indiffused LiNbO_3 ($\text{Ti}:\text{LiNbO}_3$) optical waveguides.¹ 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.*² were the first to report the formation of a titanium thin film by laser direct writing, using a frequency-doubled Ar^+ laser ($\lambda = 257 \text{ nm}$). Other laser processing techniques on LiNbO_3 , such as ablation^{3,4} and etching⁵ have also recently been reported. In this letter, we report on a preliminary study of KrF excimer laser deposition of Ti lines from 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 LiNbO_3 substrate, the beam is focused to a 20 μm 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 μm . 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 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 TiCl_4 pressure has to be kept below 0.5 Torr. Any

unconsumed TiCl_4 is condensed in a cryogenic trap to avoid any damage to the pump.

The substrates used are LiNbO_3 or 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.⁶ 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 TiCl_4 .

Since 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 LiNbO_3 at energy pulses higher than 100 nJ, which corresponds to a threshold density of approximately 3 MW/cm^2 . When we cover 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 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 μm . This

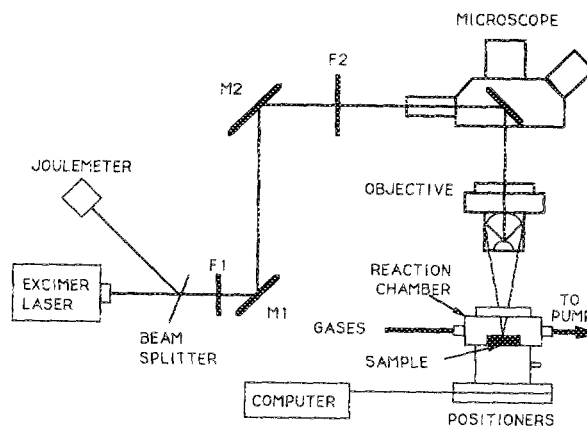


FIG. 1. Schematic drawing of the deposition system. $F1$ and $F2$ are filters while $M1$ and $M2$ are mirrors.

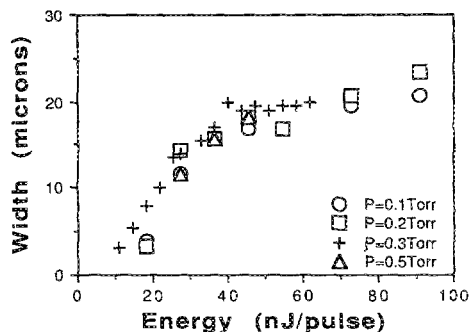


FIG. 2. Titanium linewidth variation as a function of the pulse energy and TiCl_4 pressure. The displacement speed is $0.2 \mu\text{m/s}$ and the laser frequency is 2 Hz.

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 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 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 TiCl_4 pressure conditions. Typical thicknesses vary from 20 to 70 nm for Ti lines deposited on 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 Ti:LiNbO_3 optical waveguides, as one wants to control the Ti thickness variation along the lines. As-

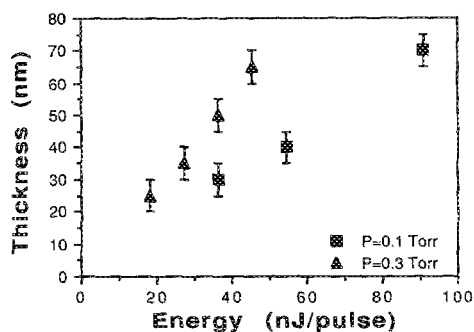

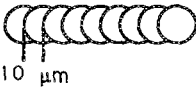
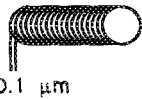


FIG. 3. Thickness variation of Ti deposited on LiNbO_3 as a function of pulse energy and pressure.

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 μm	$\pm 17 \%$	$\pm 19 \%$
 10 μm	$\pm 0.1 \%$	$\pm 2.5 \%$
 0.1 μm	$< 10^{-5} \%$	$\pm 0.5 \%$

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 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°C) necessary to thermally dissociate the TiCl_4 .⁷ If such temperature elevation was produced by a short pulse (10 ns), severe thermal damage would certainly occur, because LiNbO_3 is well known to be extremely fragile. Moreover, Tsao *et al.*² showed that visible photons ($\lambda = 514 \text{ nm}$) from the Ar^+ laser focused on LiNbO_3 in the presence of TiCl_4 lead to severe damage before deposition takes place. Due to the low gas absorptivity,⁸ 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.⁹ 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:LiNbO₃ optical waveguides.

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