KrF EXCIMER LASER DEPOSITION OF TITANIUM FROM $TiCl_4$

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ABSTRACT

We have investigated the deposition of titanium lines from $TiCl_4$ induced by KrF excimer laser (248 nm). Substrates are primarily $LiNbO_3$, for the possible formation of Ti:$LiNbO_3$ optical waveguides, as well as silicon and glass. Titanium lines contain [Cl] < 2 at% and are typically 200 to 1000 Angstroms thick with a width ranging from 3 to 20 μm. Results suggest that the process is controlled by photochemistry of $TiCl_4$ but it is difficult at this point to assert which of the gas or adsorbed layer is the primary source of thin film growth.

INTRODUCTION

There is a technological interest in development of processing technique of titanium (Ti) thin film for optoelectronic applications (Ti:$LiNbO_3$ optical waveguides[1]) as well as for microelectronic applications (contacts for silicon devices [2]). 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 a variable thickness permitting the production of Ti:$LiNbO_3$ optical waveguides with novel properties. Tsao et al. [3] were the first to report the formation of titanium thin film by laser direct writing using a frequency doubled Ar^+ laser. In this paper, we report 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.

DEPOSITION SYSTEM

Figure 1 describes schematically the experimental set up consisting of a KrF excimer laser (λ=248nm) 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 decrease the intensity to avoid damaging the substrate, the beam is focalized with a reflection objective (X15; NA 0.28) which offers the advantages of long work distance and low aberrations needed for our system. The microscope is also used to observe

Figure 1: Deposition system

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 a 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 and the maximum speed is 100 µm/s. The Ti lines are processed at scan speeds ranging from 0.2 µm/s to 5 µm/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 is a liquid at room temperature with a vapor pressure of around 10 Torr. To prevent powder formation, $TiCl_4$ pressure has to be kept below 500 mTorr. After the process the $TiCl_4$ is condensed in a cryogenic trap to avoid any damage to the pump. Every month, we neutralize the used $TiCl_4$ with a basic solution of NaOH.

The subtrates used are $LiNbO_3$, glass, crystalline silicon (c-Si). We have also investigated the use of $LiNbO_3$ covered by a thin layer of titanium (100 Å) to check if the nucleation of initial layer influences the thickness. Before deposition, all substrates are washed in organic solvants, rinsed in deionized water and heated at 120 °C in a vacuum oven for an hour to eliminate any trace of water which could react with $TiCl_4$.

Compared to the cw frequency doubled Ar^+ laser, excimer laser is a possible alternative UV source which presents many possible UV wavelengths at a reasonnable price. However, the fact that excimer lasers are pulsed might bring two different causes of thickness variation along the lines. In addition to the energy pulse variation, depositing step by step will cause a regular oscillation with thickness which will increase as the pulses become more distant from each other. Assuming a Gaussian beam of 10 µm diameter, Table 1 gives numerical simulation results of the thickness variation along the line as a function of beam displacement when there is no pulse energy variation as well as when this variation is ± 6%

which represents our conditions. To obtain a uniform film thickness of a few percent variation, a beam displacement smaller than the spot radius is necessary. In order to have thicknesses ranging from 200 to 1000 Å, a beam displacement of 0.1 µm has been chosen which assures us a thickness variation of ± 0,6%.

TABLE I
THICKNESS VARIATION WITH ENERGY VARIATION AND DISPLACEMENT

displacement \ E variation	0 %	± 6 %
10 µm	± 17 %	± 19 %
5 µm	± 0.1 %	± 2.5 %
0.1 µm	$<10^{-5}$ %	± 0.6 %

CHARACTERIZATION OF THE DEPOSITION PROCESS

All the subtrates used are opaque at λ=248 nm. Because of their low reflectivities, glass and $LiNbO_3$ are highly absorbant. The short laser pulse of 9 ns, might give a local temperature rise which can cause severe damage to the sample. We optically observed thermal damages on $LiNbO_3$ at energy pulse as low as 100 nJ which corresponds to a power density of several MW/cm^2. The glass is less sensitive with a damage threshold of 140 nJ. When we cover $LiNbO_3$ with a 100 Å layer of Ti we observe damages at around 250 nJ/pulse. For c-Si the threshold is much higher due to its high reflectivity and higher thermal diffusivity.

Figure 2 shows a typical titanium line on $LiNbO_3$ covered with a 100 Å titanium thin film. The choice of the substrates is justified by the fact that it enables us to take a scanning electron microscope picture without any charging effect. The scan speed is 0.5 um/s, the $TiCl_4$ pressure is 0.2 Torr and the laser repetition rate is 5 Hz.

Line composition made at different energies and pressures and on all type of substrates was measured by micro Auger electron spectroscopy with a spatial resolution of 0.1 µm. Results show that all Ti films are oxydized due to air exposition and they all contain a very low Cl concentration ([Cl] < 2 at%).

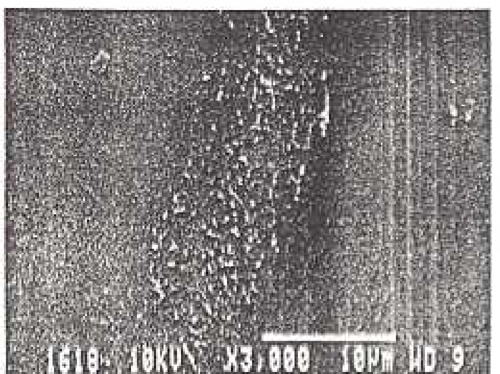

Fig. 2: Morphology of a Ti line written on $LiNbO_3$ covered by 100 Å Ti thin film.

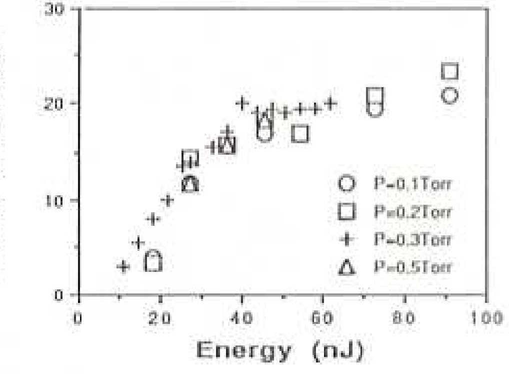

Fig. 3: Variation of linewidth as a function of pulse energy and $TiCl_4$ pressure.

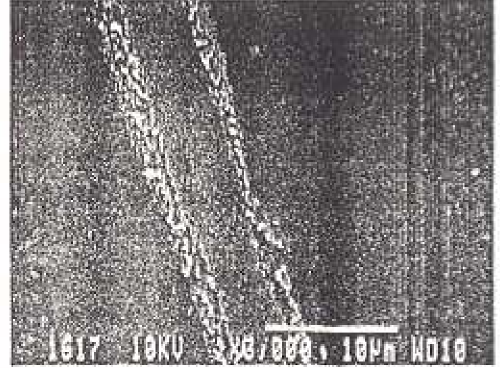

Fig. 4: Ti line written on silicon showing irregular deposition.

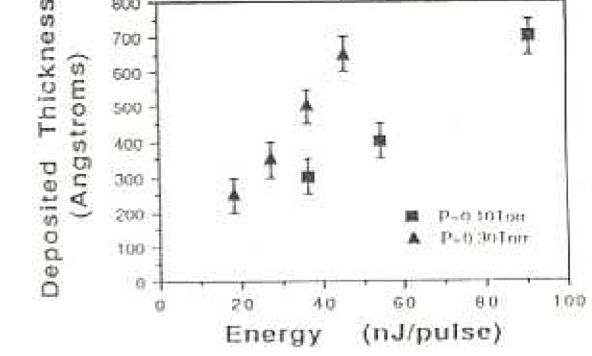

Fig. 5: Deposited thickness of Ti on $LiNbO_3$ as a function of energy pulse and pressure.

Figure 3 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 µm/s with a repetition rate of 2 Hz (to improve pulse stability). We notice that W is independent of $TiCl_4$ pressure and increases monotonically with E. Assuming a threshold energy to get a deposit, an increase in energy will increase W and this variation will depend on the beam shape.

Figure 4 shows a Ti line on silicon made at a $TiCl_4$ pressure of 0.3 Torr, laser energy of 36 nJ and at a speed of 0.2 µm/s. Notice the sudden thickness decrease near the middle of the line. This is probably due to either a $TiCl_4$ desorption due to substrate heating at high laser energy[4] or to an ablation of the film deposited. It is not clear which one is more important and more experiments are necessary to clarify this phenomenon.

Figure 5 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 200 to 700 Å for Ti lines deposited on $LiNbO_3$ at a speed of 0.2 µm/s. As the pressure increases, more molecules in the gas, as well as on the adsorbed layer, can react leading to a thicker film. As the energy increases, more photons arrive in the reaction zone leading again to a thicker film.

MODELING THE DEPOSITION PROCESS

In principle the process is either thermal or photolytic or possibly both. However, it is not a thermal process because of the high temperature (600 °C) necessary to thermally dissociate the $TiCl_4$ [5]. If this was due to the short pulse (10 ns), severe thermal damage would certainly occur because $LiNbO_3$ is well known to be extremely fragile. Tsao et al [3] did check that Ar^+ laser focalised on $LiNbO_3$ in presence of $TiCl_4$ lead to severe damage but no deposition. Due to the low gas absorptivity [6] thermal

reaction is not expected to occur in the gas. This process is certainly not controlled by thermal reaction.

The process is rather based on photochemical reaction. Photon energy of 4.98 eV at λ=248 nm is certainly enough to break a Ti-Cl bond of 4.47 eV bonding energy [7]. However, it is difficult at this point to say which of the gas or 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 pressures, the absence of powder as well as the pressure independence of linewidth (Figure 3) suggest the opposite,i.e. that the adsorbed layer is probably the primary source of thin film growth. More experiments are necessary to distinguish between the two processes.

CONCLUSION

We have deposited Ti lines by KrF excimer laser direct writing primarily on $LiNbO_3$ and also on silicon and glass. Titanium lines contain [Cl]< 2 at% and have linewidths between 3 to 20 µm with film thickness of 200 to 1000 Å. Work is under progress to model this process.

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