The LMP Process: Layered Metal Prototyping of Titanium from Condensed Thin-Films for Microelectromechanical Devices

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Layered prototyping of three-dimensional titanium micromechanical components was demonstrated using selected area laser photolysis of liquid-phase organo-metallic and metal halide thin films. Scanning KrF and XeF excimer lasers were employed at 248 and 351 nm, respectively, generating solid titanium traces from condensed precursor films. Multiple layers were patterned to produce high-aspect ratio titanium lines. Laser pulse repetition rate, scan rate, pulse energy, and layer thickness were related to the resulting layer topography. This process is a first step toward layered metal rapid prototyping of electronic packaging microstructures and microelectromechanical systems.

I. Introduction

Surface micromachining has been the primary means of fabricating microelectromechanical systems (MEMS) for over 15 years.[1] this process employs photolithography and selective chemical etching to obtain desired micromechanical forms from thin films. The purpose of this work was to demonstrate a method of selective deposition which performs the function of surface micromachining, but which also possesses all the advantages of a solid freeform fabrication tool. A process was desired which would allow electronic materials to be deposited, both metals and dielectrics, with a single instrument. In this way, rapid prototyping and complete integration of MEMS and supporting electronic packaging would be possible.

II. Background

Several alternatives to lithographic methods have been developed in the literature, which employ laser-induced deposition, and thus do not require a mask to obtain selective growth. Three-dimensional microstereolithography of photosensitive resins has been demonstrated by several authors.[2] Techniques which can be used to deposit metals were developed for the custom metallization and soldering of interconnects in microelectronics. Laser-induced electroplating,[3] for example, may be used to selectively plate metal onto a semi-conductive surface from a liquid electrolyte. Laser-induced electroless plating has also been demonstrated on metals and insulators.[4] Finally, lasers have been used to heat and decompose a variety of spun-on inks and liquid films.[5]

In this paper we will demonstrate the prototyping of titanium from thin liquid films of titanium tetrachloride. Since the bond energies of the $TiCl_4$ molecule correspond closely with the wavelength of the KrF laser (248 nm),[6] titanium tetrachloride can be dissociated directly by the laser light; this is termed photolysis. $TiCl_4$ can also be thermally decomposed, yielding solid titanium, according to the overall reaction:

$$TiCl_{4(1)} \longrightarrow Ti_{(s)} + 2Cl_{2(g)}. \tag{1}$$
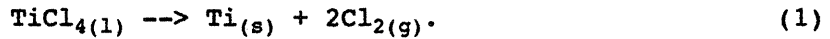
TiCl$_4$ has been explored previously as a gas-phase precursor for excimer laser-induced chemical vapor deposition (LCVD); Alexandrescu *et al.* recently demonstrated that the mechanism through which vapor phase Ti growth occurs,[7] is: first, *adsorption* of the vapor-phase TiCl$_4$ onto the growth surface; second, photolysis of the TiCl$_4$ to nuclei of Ti and adsorbed TiCl$_3$; and third, the thermal decomposition of additional TiCl$_4$ and TiCl$_3$ adsorbate by heating of the Ti nuclei. Thus, *gas-phase* photolysis of TiCl$_4$ contributes little to deposition of Ti during excimer-laser induced vapor deposition. This is borne out by other authors.[8,9] However, Meunier *et al.* proposed that photolysis of *adsorbed* TiCl$_4$ was the dominant growth mechanism for Ti films[10] during the initial stages of growth; while for Ti deposit thicknesses greater than 3 nm, laser heating became the dominant mechanism, yielding much greater growth rates (on the order of 2-7 nm/s). Mochizuki *et al.* additionally reported that the rate limiting step in the LCVD of Ti is not the adsorption of the TiCl$_4$, but the desorption of Cl$_2$.[11] For this reason, it is common practice to use hydrogen reduction of TiCl$_4$ to eliminate build-up of Cl$_2$ at the growth surface. Kubat *et al.* also showed that high UV laser fluences and the use of hydrogen reduction, favored the growth of pure Ti from TiCl$_4$ --again implying a pyrolytic growth mechanism.[12]

Since the adsorbed layer was shown to be the dominant source of reactants during LCVD, and the normal spectral reflectance of TiCl$_4$ at 248 nm is only 0.05, thick condensed films of TiCl$_4$ should be readily pyrolyzed--and should exhibit Ti growth rates greater than those obtained from vapor-phase diffusion during LCVD. In addition, the use of a KrF excimer laser at 248 nm, should provide the best means of initiating the reaction, and may also enhance the growth rate through photolytic decomposition of TiCl$_4$ into TiCl$_3$ --and subsequently to Ti.
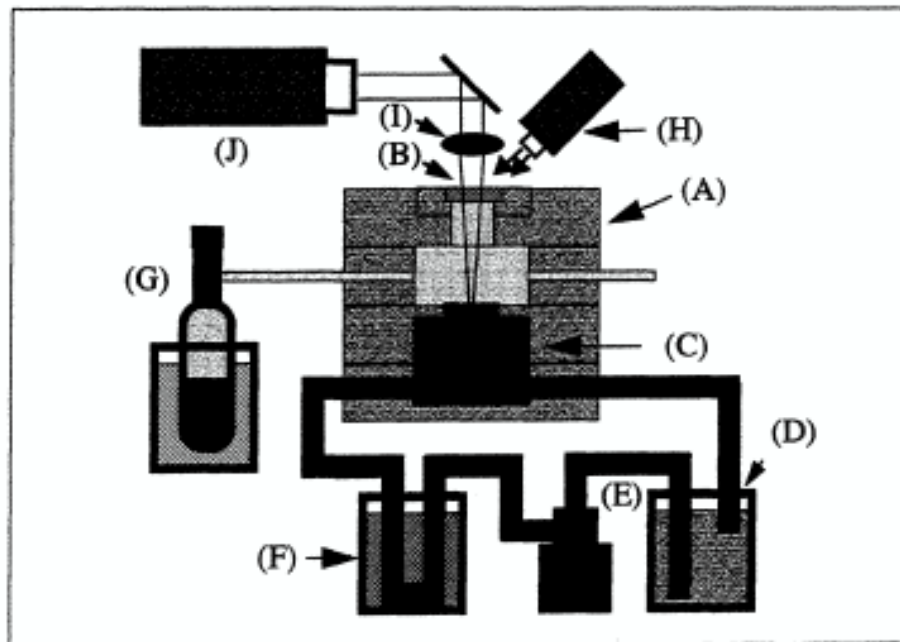

Fig. 1: Apparatus for Moderate Pressure Experiments

III. Experimental

While several methods were devised to disperse the $TiCl_4$ as a thin liquid film, practical difficulties in handling the chemical, e.g. its reactivity with atmospheric water vapor, high room-temperature vapor pressure, etc., required a closed delivery system. $TiCl_4$ also readily adsorbs and decomposes on quartz and glass windows, making it necessary to remove the windows from the vicinity of the laser focus. This also eliminated the possibility of merely sandwiching the liquid between the window and the sample. For simplicity the titanium tetrachloride was merely evaporated from a source container, and allowed to recondense as a liquid coating on the target substrate. In this way, a highly-uniform film of sub-micron thickness could be obtained, and the liquid film could be grown continuously--even while it is being patterned by the laser.

For the LMP experiments, a simple apparatus was constructed, consisting of a reaction chamber, cooling apparatus, and precursor source, as shown in Fig. 1. The reactor (A) was made from two 1-1/3" Conflat flanges, sealed by a viton gasket. The upper flange had a 0.75" diameter sapphire window attached (B), while the lower flange had two machined recesses, one to hold the target substrate, and the another behind the substrate which acted as a cooling reservoir (C). The gap between the substrate and this reservoir was minimized to obtain effective cooling. A recessed aluminum base plate with two 1/8" outlets formed the other half of the cooling reservoir. In this way, a high vacuum could be maintained in the chamber, while chilling the sample from outside the chamber.

Two methods were used to cool the substrate. In the first case, liquid nitrogen was passed directly through the cooling reservoir; this yielded high cooling rates, but was difficult to maintain over long periods due to moisture freezing in the cooling line. The second, more flexible method employed a closed-loop system which recirculated ethylene glycol from a large heated storage reservoir (D), through pump (E), past a liquid-nitrogen cooled copper coil (F), and finally through the cooling reservoir (C). The advantage of this method is that the temperature could be maintained precisely within 1-2 degrees, and varied according to the pumping rate.

Precursor gases were released into the reactor from a heated sample cylinder (G), and thereafter condensed on the cooled substrate. The sapphire window was heated by
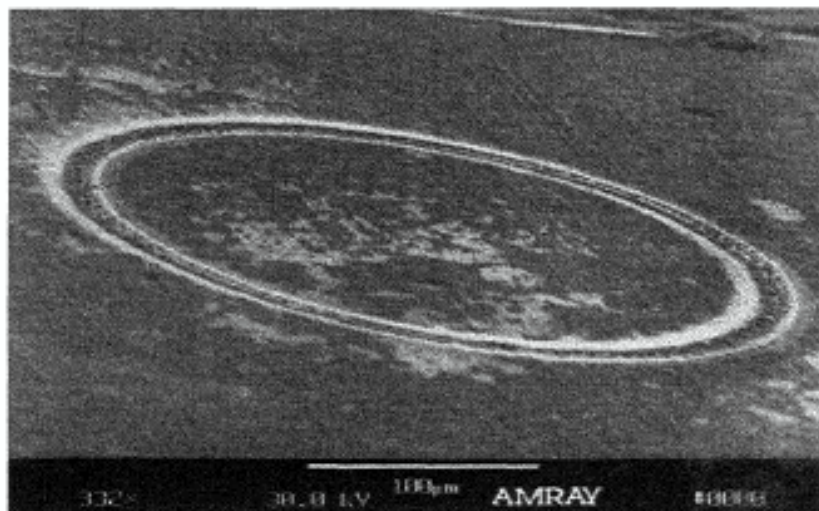

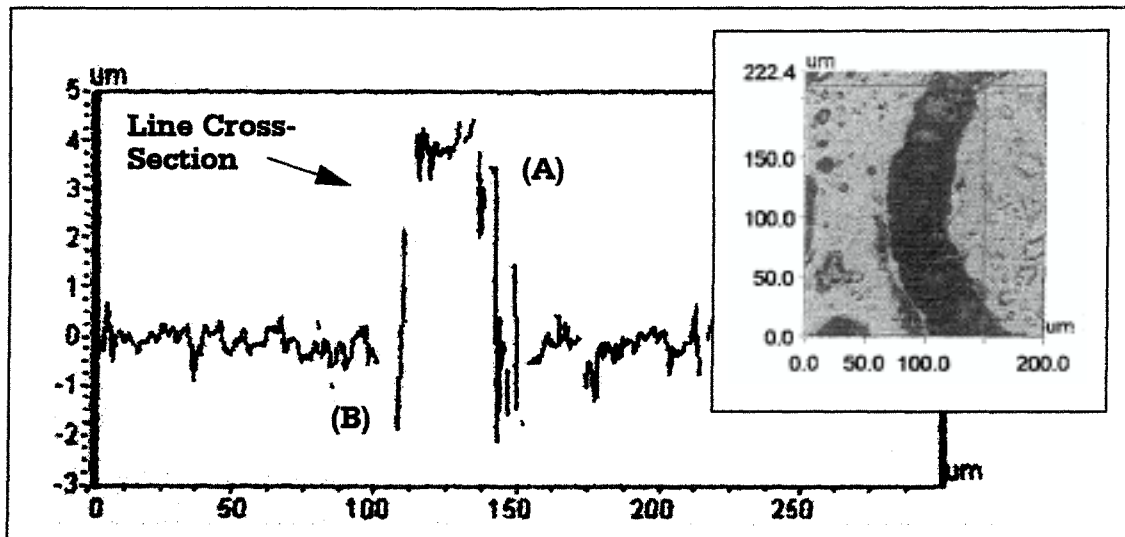**Fig. 2: Titanium Circular Line Traces**

Fig. 3: RST Profile of a Titanium Line

a hot air gun (H) to prevent condensation inside (or outside) the window, and a heater tape was placed around the upper flange to maximize condensation on the substrate. Temperatures from -55°C to 0°C were readily attained at the substrate, while the upper portion of the chamber was maintained at 50-90°C.

A 25 mm f.l. plano-convex, fused-silica lens (I) was used to focus the incident beam on the substrate, yielding spot sizes of roughly 30 microns. A KrF or XeF excimer laser (J) could be interchanged at will, yielding 60-70 ns pulses of 87 μJ at 248 nm or 20 μJ at 351 nm, respectively.

IV. Results

To deposit titanium films, the chamber (A) in Fig. 1 was first evacuated using a roughing and turbomolecular pump, then the substrate was cooled as described previously. When a stable temperature of approximately -4 to -12°C was attained, the valve on the source chamber (G) was opened, releasing $TiCl_4$ vapor into the reactor, and the roughing valve was closed. The precursor was allowed to condense for a prescribed amount of time (with the source valve continually open), and then the laser was scanned once over a prescribed pattern. This procedure was then repeated for a designated number of times, allowing the precursor to condense for a given interval prior to each laser scan. For all experiments, the laser scan speed was a constant 167 μm/s.

Preliminary results in the deposition of Ti from condensed $TiCl_4$ thin films were encouraging. High-aspect ratio lines were patterned with thickness up to 15 microns. A typical pattern is shown in Fig. 2. Note the raised titanium circular film, straddled on either side by thinly-ablated rings on the Ti substrate. Excellent film uniformity was obtained at thicknesses up to 5 microns, with grain structure and surface roughness on the order of 1 micron or smaller. This is illustrated in Fig. 3, where a profile of a 4 μm-thick Ti line was scanned using a Wyko phase-shifting interferometer. Note that the upper surface of the film is relatively flat and exhibits a roughness similar to that of the substrate--which was not polished. Also, note the ablation trenches to either side of the deposited line, which sharply define the deposited region. While the focused beam
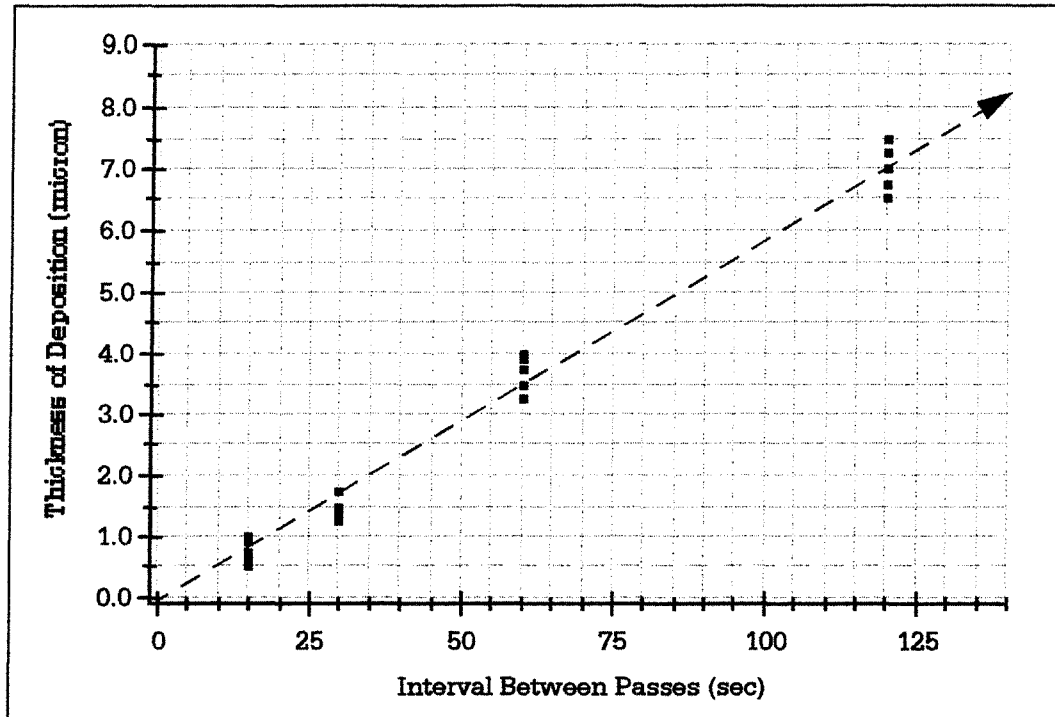
Fig. 4: Deposit Thickness [μm] vs. Condensation Interval [s]

was approximately Gaussian in profile, the Ti film exhibits nearly vertical side-walls and a flat top--clear advantages for continued high-aspect ratio growth.

To optimize the LMP process, a series of experiments were carried out, varying the condensation time, beam pulse repetition rate, exposure time, and focal position. Fig. 4 shows the thickness of the deposited Ti films for varying intervals between scans. The purpose of this experiment was to see if the $TiCl_4$ condensed layer would increase without bound, or if an optimal adsorbed layer thickness exists. During the experiment, the pulse repetition rate was held constant at 200 Hz, and each pattern was scanned a total of 40 times, with the given interval between passes. The substrate was held at a constant temperature of -4°C, while the source chamber was maintained at a moderate temperature of 28°C, providing a $TiCl_4$ vapor pressure of about 13 mbar. Note that there appears to be no limit to the condensed layer which can be converted to Ti--up to a nominal $TiCl_4$ thickness of at least 175 nm/scan.

The slope of the line in Fig. 4 provides a measure of the Ti film growth rate, which was approximately 1.4 nm/s. However, this rate was set by the $TiCl_4$ condensation rate, which was by no means optimal; if the source temperature were instead 145°C, and the vapor pressure within the source cylinder 1300 mbar, then $TiCl_4$ transport to the substrate could be increased by nearly two orders of magnitude. The substrate could also be cooled to lower temperatures and the conductance of the flow path from source to sample improved. Thus, the ultimate limit of this process will not be the rate of $TiCl_4$ transport, but rather the pulse repetition rate of the excimer laser!

To observe the effects of varying exposure, the pulse repetition rate was varied between 150-225 Hz, while the interval between scans was held constant (at 30 s/scan). As can be seen in Fig. 5., two competing processes were found to occur; first, at low repetition rates, the adsorbed layer is incompletely converted to Ti, and the growth rate
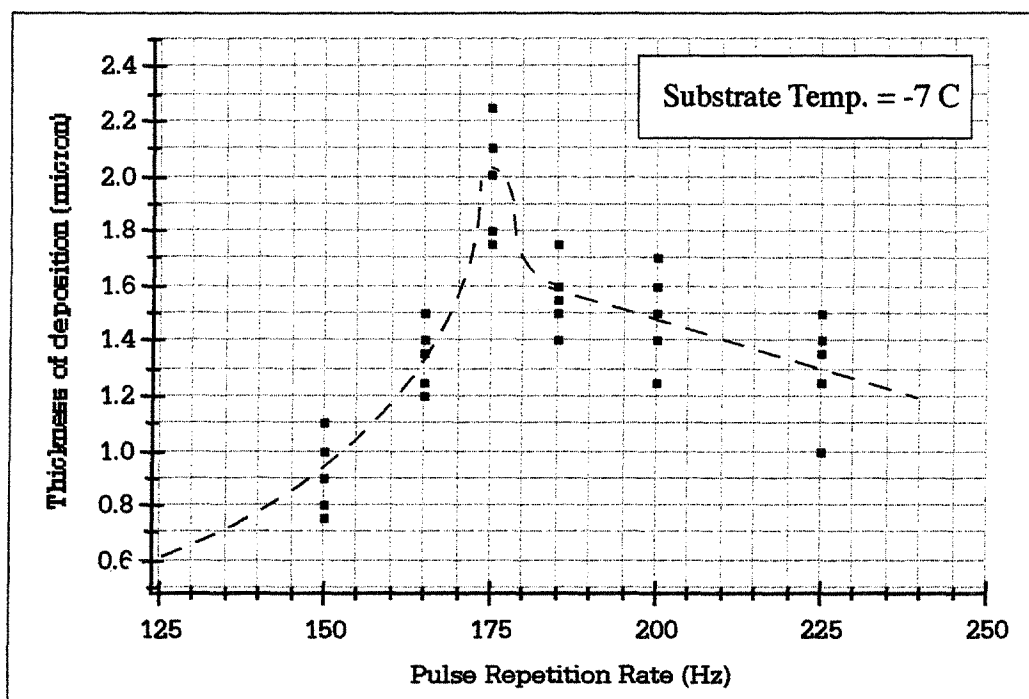
Fig. 5: Deposit Thickness [μm] vs. Laser Pulse Repetition Rate

increases steadily with exposure; second, following the optimal exposure, the Ti thickness drops linearly due to evaporation of the condensed layer and/or ablation of the titanium deposit. Desorption of an adsorbed precursor film due to excessive exposure has been noted by other authors.[13] At this time, however, it is not known whether it is the adsorbed $TiCl_4$ layer or the titanium itself which is removed.

Fig. 6 shows the Ti deposit thickness vs. the cumulative number of laser scans, for a constant scan interval of 8 s. The pulse repetition rate was maintained at 200 Hz throughout the experiment. Observe the similarity of this plot to Fig. 5; however, in this case, the cumulative effects of continuous scanning at constant repeated exposures are represented--rather than the effects of varying exposure (e.g. in Fig. 5). Since the time between scans is large, while the time for the titanium film to cool after exposure is short (generally less than 1 ms), no cumulative heating of the Ti film should occur *between* scans; the deposit height should rise linearly, since each scan adds to the preceding deposit. As expected, linear growth is observed up to 60 cumulative scans, with a growth slope of abt. 11 nm/pass. Surprisingly, the deposit height drops dramatically above a peak at 70 passes--at a rate of 30 nm/pass! The mechanism for this *continual etching* is unknown. If a self-limiting deposit height were reached, the growth would merely cease--leaving a constant film thickness above 70 scans.

Several possible explanations have been proposed to explain this phenomenon. The most likely is that chlorine in the reaction chamber builds up during the processing of each pattern, and that once a sufficient concentration is present, laser-induced etching of the freshly deposited titanium occurs. If so, the effect is merely an artifact of processing in a small, static reactor. Another possible explanation is that the $TiCl_4$ can no longer condense or migrate to the Ti film after an excessive number of scans--hence deposition slows or ceases, and ablation of the film becomes dominant. However, further investigations will be required to determine a precise cause.
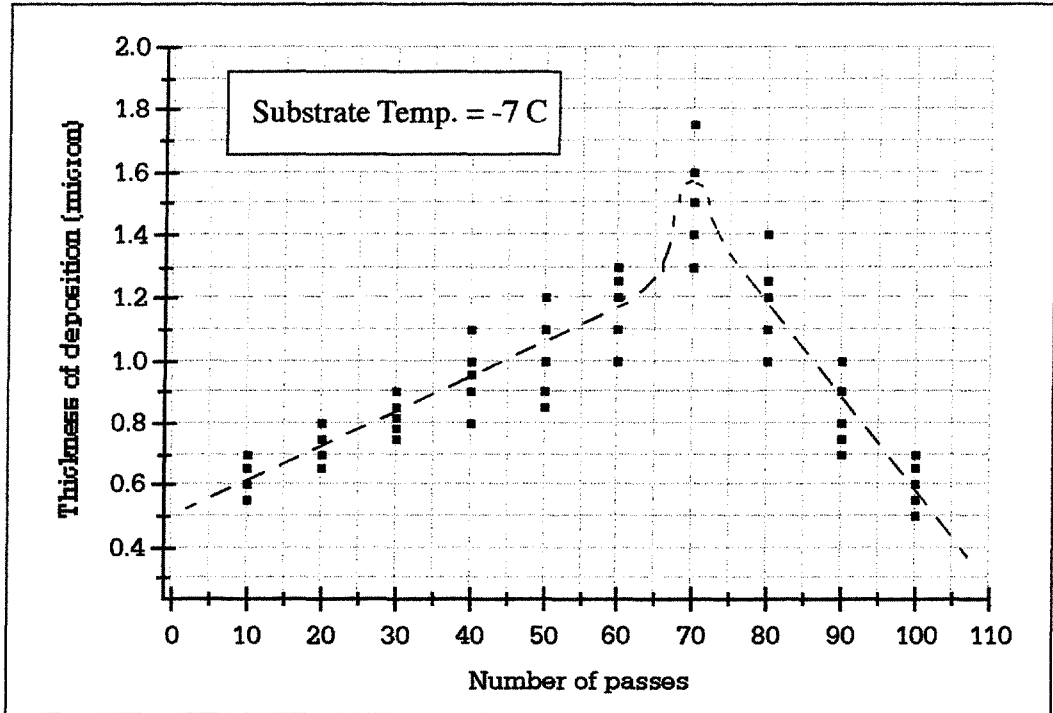
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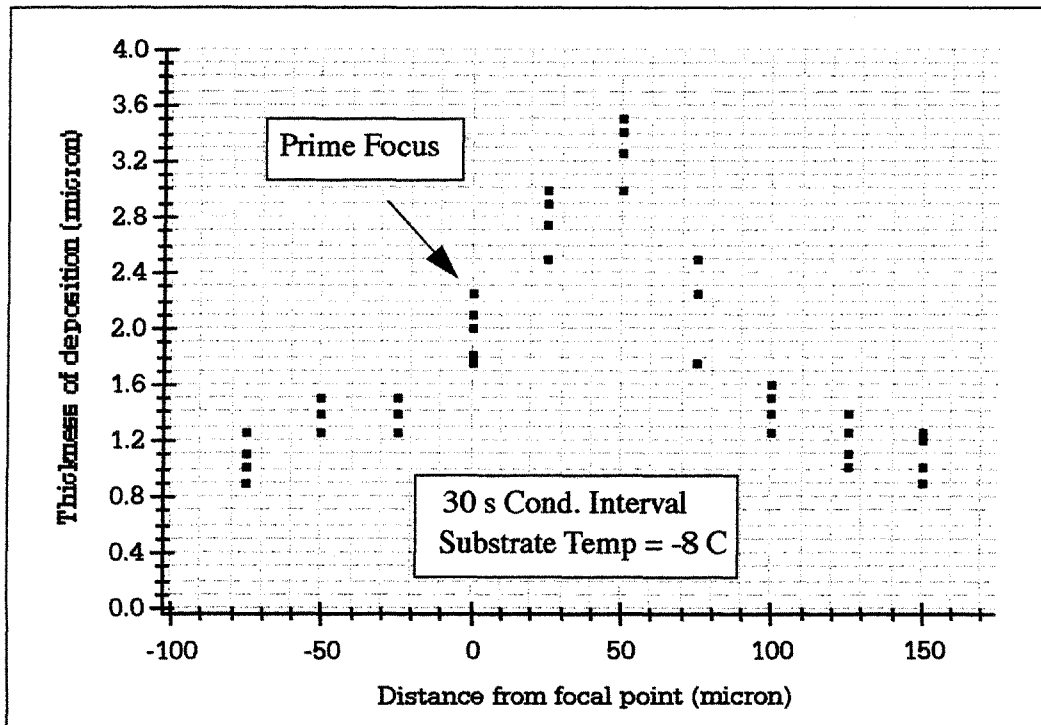**Fig. 6: Deposit Thickness [μm] vs. Number of Laser Scans**

Fig. 7: Deposit Thickness [μm] vs. Focal Position [μm]

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To investigate the effects of beam intensity on the growth, it was not possible to vary the power per pulse of the excimer lasers. However, the position of the laser focus could be varied axially relative to the target substrate, lowering pulse intensities by up to two orders of magnitude above and below the prime focus. If the $TiCl_4$ were underexposed or at precisely the optimal exposure, one would expect the growth rate to drop symmetrically to either side of the prime focus. However, if the films were overexposed, ablation or etching would result, and the optimal growth would appear at some extra-focal location, where the pulse intensity is less. From Fig. 7 it is clear that the film is, in fact, over-exposed, confirming that ablation of the Ti and/or condensed $TiCl_4$ film is occurring. The optimal intensity is found approximately 50 microns below the prime focus, implying an optimal power/pulse as low as 0.27 μJ/pulse with a repetition rate of 175 Hz and scan rate of 10 μm/s.

V. Conclusions

The LMP process is a viable method for prototyping thin titanium films without the use of lithography. High-aspect ratio films may be grown with vertical sidewalls and flat-topped cross-sections. Two competing processes were observed during growth: (1) photolytically-enhanced pyrolysis of the condensed film, and (2) ablation of the Ti deposit or $TiCl_4$ adsorbed film. The process may be optimized for high speed growth by lowering the intensity per pulse of the excimer laser so that ablation of the Ti deposit or condensed film is minimized--and by heating the source vessel. Further studies will concentrate on optimizing the deposition speed and surface morphology of the Ti films, allowing the microfabrication of freestanding microstructures.

VI. Bibliography

1. Petersen, K., Proc. of the IEEE, Vol. 70, No. 5, (May 1982), Repinted in Microsensors, pp. 39-77.

2. Ikuta, K., Hirowatari, K., IEEE Micro Electro Mechanical Systems Proceedings, (1993), pp. 42-47.

3. Von Gutfeld, R. J., Gelchinski, M. H., Vigliotti, D. R., Romankiw, L. T., MRS Symp. Proc., Vol. 29, Laser-Controlled Chem. Processing of Surfaces, (1984), pp. 325-332.

4. Bali, K., Geretovszky, Zs., Tóth, A. L., Szörényi, T., Appl. Surf. Sci., Vol. 69, (1993), pp. 326-329.

5. Gupta, A., Jagannathan, R., MRS Symp. Proc., Vol. 101, (1988), pp.95-100.

6. Decleva, P., Fronzoni, G., Stener, M., Chem. Phys., Vol. 186, (1994), pp. 1-16.

7. Alexandrescu, R., Cireasa, R., Dragnea, B., Morjan, I., Voicu, I., Andrei, A., Vasiliu, F., Popescu, C., Adv. Materials for Optics and Electronics, Vol. 5, (1995), pp. 19-30.

8. Izquierdo, R., Lavoie, C, Meunier, M., MRS Symp., Vol. 158, (1993), pp. 141-146.

9. Lavoie, C., Meunier, M., Izquierdo, R., Boivin, S., Desjardins, P., Applied Physics A, Vol. A53, No. 5, (Oct. 1991), pp. 339-342.

10. Meunier, M., Lavoie, C., Boivin, S., Izquierdo, R, Desjardins, P., Applied Surface Science, Vol. 54, (1992), pp. 52-55.

11. Mochizuki, Y., Odamoto, Y., Ishitani, A., Hirose, K., Takada, T., Jpn. J. Appl. Phys., Vol. 34, (1995), pp. L326-L329.

12. Kubat, P., Engst, P., J. Photochem. Photobiol. A: Chem, Vol. 63, (1992), pp. 257-263.

13. Braichotte, D., Van Den Bergh, H., Appl. Phys. A., Vol. A49, (1989), p.189.