

# Selective Area Laser Deposition from Titanium Tetrachloride

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## Abstract

Selective Area Laser Deposition (SALD) has demonstrated the ability to deposit controlled shapes of silicon carbide and silicon nitride by using a laser beam to decompose a precursor gas. The goal of the work here is to include titanium among the list of SALD materials, although this goal has not yet been reached. This paper describes the selection of precursors and the results of some SALD experiments using the first precursor explored, titanium tetrachloride. The results of precursor gas mixture, pressure, and laser power on deposition composition and rates are discussed.

## Introduction

Selective Area Laser Deposition (SALD) is a gas based solid free-form technique that shares much in common with laser enhanced chemical vapor deposition in that both use a laser beam to decompose a precursor gas in a defined pattern. SALD, however, seeks to build bulk shapes by varying the laser scanning pattern as shape thickness increases. Previous and current work on SALD of ceramics such as carbon<sup>1,2</sup>, silicon carbide, and silicon nitride<sup>3</sup> shows promise in forming bulk shapes, but little work on SALD of metals has been published.<sup>4</sup> The goal of the work presented in this paper is to bring metals to the SALD process with deposition of titanium.

Included here are a description of the selection process for choosing a metallic precursor, a quick overview of a SALD system, and the results of preliminary titanium tetrachloride deposition experiments.

## Precursor Selection

The first key step in engineering a means of metal SALD is the selection of a suitable precursor. The term "suitable" is defined by establishing the following criteria for the selected precursor:

- 1) Capability to deposit a metal in pure form with preference given to the more widely used metals,
- 2) Availability as a gas or low boiling point liquid to ease handling ,
- 3) Lack of excessive air or water sensitivity,
- 4) Low toxicity.

A wide range of precursors and the decomposition reactions involved were examined with these criteria in mind. Table I summarizes the primary groups of precursors evaluated. Many of these precursors were first investigated by microelectronics researchers seeking new methods of forming interconnects and other structures for computer chip manufacture; therefore a large body of literature exists and several reviews are available.<sup>5-8</sup>

Table I  
Precursor Groups Under Consideration for SALD<sup>9</sup>

Precursor Group	CVD Elements	Advantages	Disadvantages
Halides			
Fluorides	W	- Gaseous	- Toxic - Corrosive (HF) - Limited Previous Work
Chlorides	Al, B, Cr, Hf, In, Mo, Nb, Si, Ta, Ti, V, W, Zr	- Extensive Previous Work - Readily Obtainable	- Toxic - Corrosive (HCl) - Low Vapor Pressure
Iodides & Bromides	Al, B, Hf, Ta, Tl, Zr	- Moderate Previous Work	- Toxic - Corrosive (HBr, HI) - Less Readily Available / More Expensive
Carbonyls	Co, Cr, Fe, Mn, Mo, Ni, W	- Gaseous	- Highly Toxic - Pyrophoric
Metallocenes	Co, Cr, Fe, Mn, Ni, Ru, V	- Low Deposition Temperature	- Most are Toxic - Low Vapor Pressure - Not Air Stable
Acetylacetonates	Au, Co, Cu, Pt	- Low Deposition Temperature	- Highly Toxic - Low Vapor Pressure

Based on the data of Table I and the criteria described above, the halide group, particularly the chlorides were chosen to provide the precursor for use with SALD. The features of the halides which are prominent include:

- 1) A wide range of metallic elements are accessible,
- 2) Several halides exist as a room temperature gas or low boiling point liquid,
- 3) Although air and water sensitive, most halides are not pyrophoric or extremely hygroscopic,
- 4) The toxicity for most is moderate and lower than most other precursors.

From the list of halides, titanium tetrachloride shows the most favorable aspects for use in SALD as summarized in Table II.

With a precursor selected, the chemical process to be used in implementing SALD could be defined. A direct decomposition, reaction (1),



is much more difficult to achieve (i.e. requires a higher temperature) than a hydrogen reduction reaction, reaction (2)



Figure 1 shows the free energy curves for these two reactions indicating that reaction (2) is the energetically more favorable. This situation exists in general for the metal chlorides. For this reason reaction (2) was selected for the SALD process.

Table II  
Titanium Tetrachloride Properties<sup>10,11</sup>

Chemical Formula	TiCl <sub>4</sub>
Molecular Weight	189.7 g / mole
Bond Type	Ionic
Room Temperature Appearance	Colorless Liquid
Room Temperature Vapor Pressure	~ 10 Torr
Boiling Point	136°C (409 K)
Toxicity	Moderate, danger from inhalation and liberation of HCl
Current Uses	In Kroll process (Mg reduction) used to produce ~100,000 tons / year of titanium

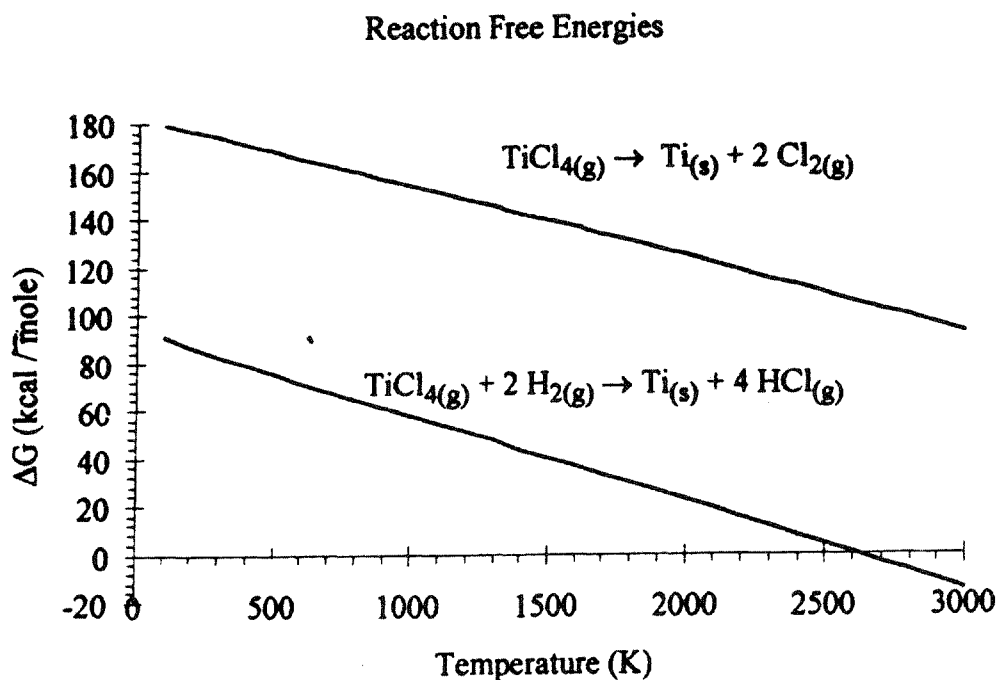


Figure 1 Reaction Free Energies for Decomposition and Hydrogen Reduction of TiCl<sub>4</sub><sup>12</sup>

## SALD System Design

The definition of a precursor and chemical process allow the design of a customized SALD deposition system. The most serious design concern for a system for SALD by hydrogen reduction of a metal chloride is the presence of highly corrosive hydrogen chloride. Even stainless steel is not immune to hydrogen chloride, so corrosion of the vacuum chamber and vacuum pump becomes an acute concern.

Several designs were considered including a predominantly glass vacuum chamber, but the practical advantages of a stainless steel vacuum chamber in the areas of durability and attachment of ancillary equipment were greater. A routine of careful purging through a chemical scrubber, however, then becomes important in limiting corrosion. Figure 2 schematically depicts the SALD system designed, assembled, and used in the experiments described below.

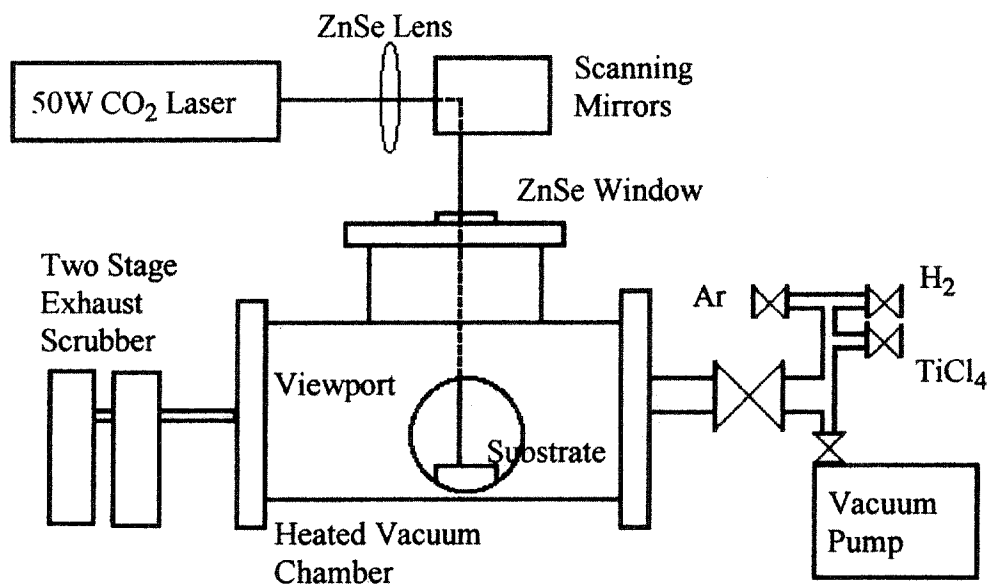


Figure 2 Schematic of Metal Halide SALD System

## Preliminary Experiment Results and Discussion

To date only preliminary experimentation at the proof of concept stage has been conducted using a limited range of variables to produce deposits from titanium tetrachloride. Additional experiments will include using a more comprehensive range of laser power and precursor pressure in addition to incorporating laser scanning for bulk shape forming.

Macroscopic rods of titanium oxide have been deposited using the system described above. Table III summarizes the deposition parameters of the rod shown in Figure 3. Total length of the rod is 5.75 mm with a diameter close to the laser beam size of 0.5 mm. Figure 4 gives the EDS spectrum and chemical analysis of the tip of the rod shown in Figure 3. EDS of

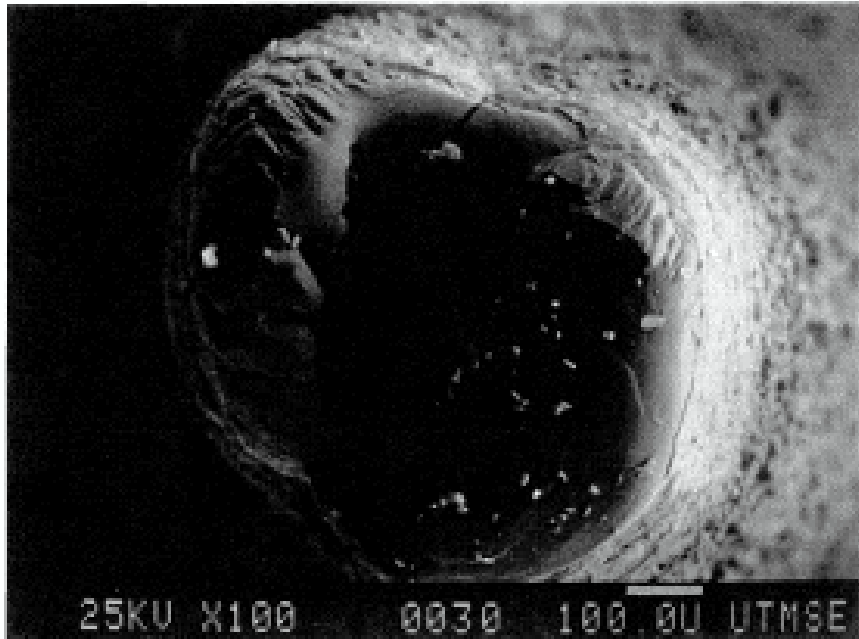


Figure 3 SEM Micrograph of Deposited Titanium Oxide Rod

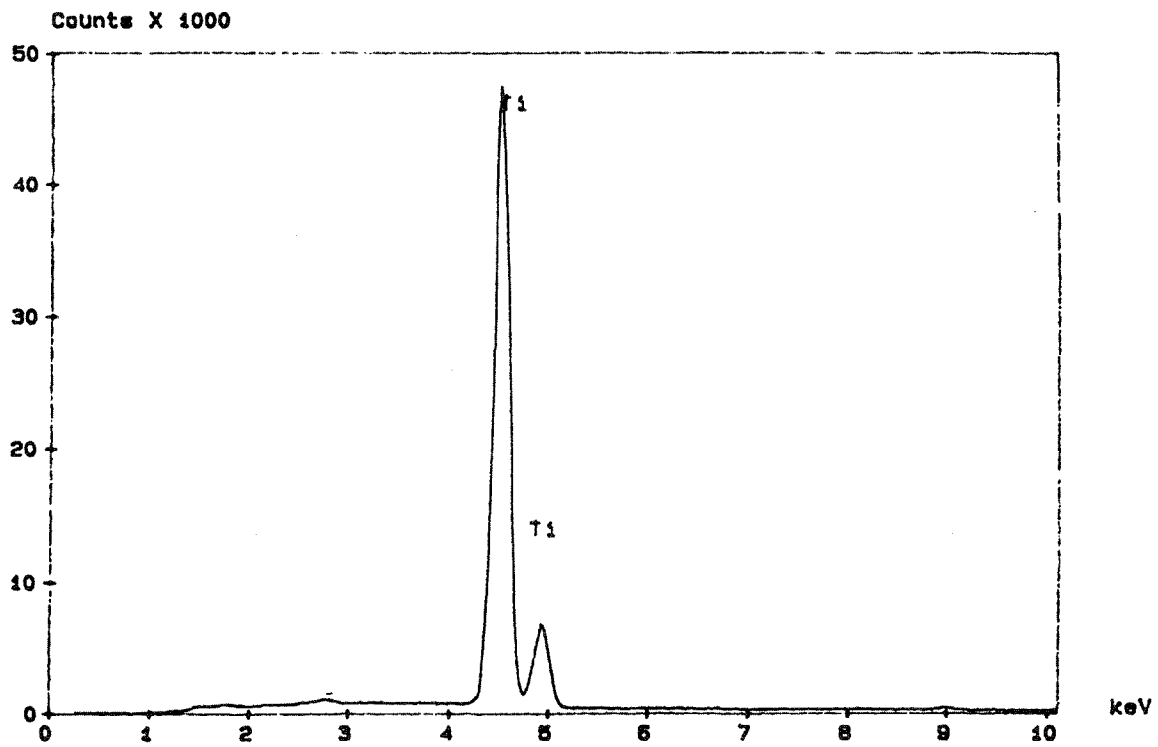


Figure 4 EDS Spectrum of the Area Shown in Figure 4

the deposit detected no chlorine, but x-ray diffraction shows the deposit to be primarily TiO<sub>2</sub> (rutile) with some TiN. This is likely the result of residual air remaining in the chamber due to the current limits of the vacuum system.

Table III  
Rod Growth Experiment Summary

Laser Parameters	14 W, ~ 0.5 mm beam diameter, 60 minute exposure time
Substrate	Tungsten Carbide powder 99.5% purity, -325 mesh + 10 μm particles
Gas Mixture	15 Torr TiCl <sub>4</sub> , 25 Torr Ar, 300 Torr H <sub>2</sub>
Rod Characteristics	5.75 mm long, hollow tip with 0.5 mm outer diameter with 0.2 mm inner diameter

A morphological and chemical analysis (by EDS) along the length and width of the deposit show three interesting features:

- 1) surface deposition but not rod growth occurs out to a radius of ~2.5 mm with chlorine: titanium ratios increasing with distance from the rod edge.
- 2) the rod tip is hollow with a “volcano” shape,
- 3) the rod tip appears as a smooth, “clean” deposit while most of the length of the rod has a rough, nodular surface,

These first two features are understandable in terms of temperature distribution and the partial decomposition of TiCl<sub>4</sub> to TiCl<sub>3</sub>, TiCl<sub>2</sub>, and TiCl. Figure 5 illustrates the temperature distribution / composition relationship. For this analysis, a Gaussian laser intensity profile and therefore a Gaussian temperature distribution are assumed. Also the reduction of TiCl<sub>4</sub> is taken to occur in steps by the removal of chlorine with the number of chlorine removal steps occurring being proportional to temperature. From this, the observed areas of deposition beyond the grown rod follow with thin, relatively high chlorine content deposition at the outer edge and thicker, lower chlorine content deposition near the base of the rod. At some critical temperature (T<sub>Cr1</sub>), decomposition of TiCl<sub>4</sub> is essentially complete and happens quickly enough for a rod to grow. At the center of the rod, however, growth is countered by several possible mechanisms including evaporation, a precursor sticking factor which decreases with temperature, or precursor depletion from slow mass transport.<sup>13</sup> The result is the “volcano” shape of the rod.

The third feature, the change in morphology of the rod along its length, is also describable using this temperature distribution model. At the very tip of the rod, where temperatures are highest, a clean deposit of titanium oxide occurs as all of the chlorine atoms are stripped from TiCl<sub>4</sub> and oxygen is added. Further down the grown rod, the temperature decreases but is still sufficient for the formation of titanium oxide. The very tip of the rod remains relatively “clean” when the laser is turned off because of it cools quickly passing through the temperature range of oxide formation in a short time limiting the amount of lateral growth that can occur. The formation of oxide beyond the immediate area of rod growth in the

regions of higher chlorine content are not expected because its formation can not take place until after all chlorine atoms have been stripped from  $\text{TiCl}_4$  and elevated temperatures are maintained.

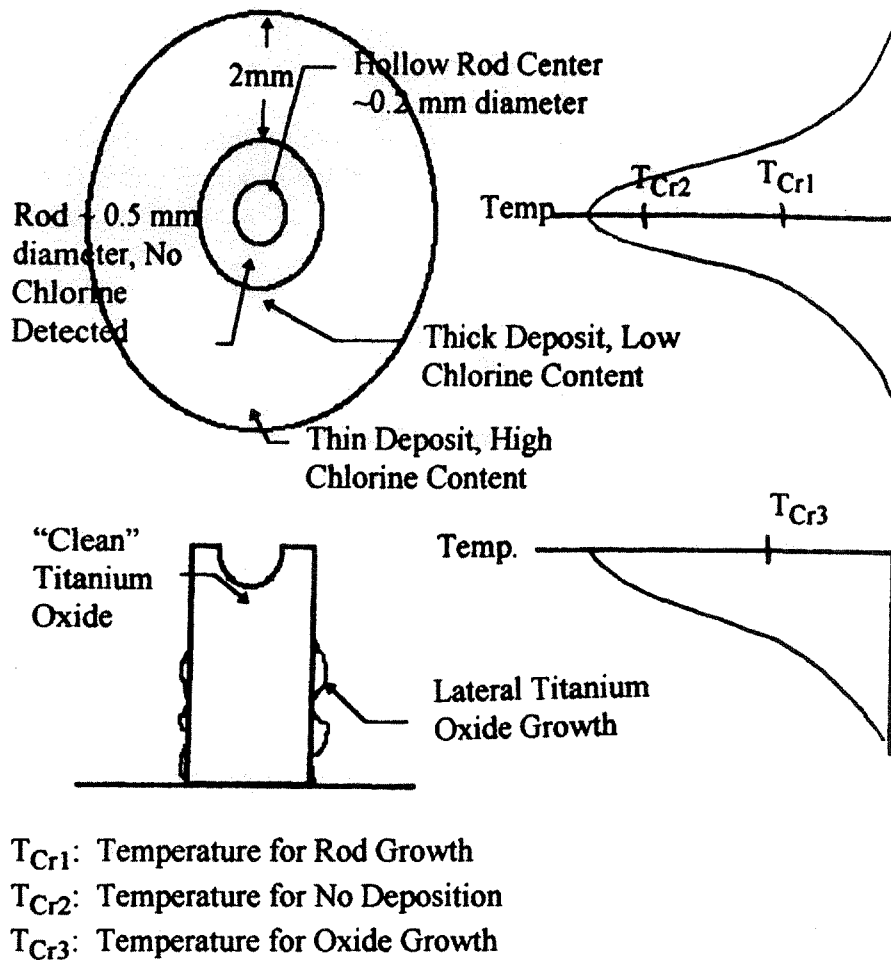


Figure 5 Schematic of Titanium Oxide Rod Composition and Laser Temperature Distribution

### Conclusions

The experiments described confirm that titanium oxide deposition from  $\text{TiCl}_4$  is possible by SALD. The goal of deposition of titanium metal has not yet been reached due to oxygen contamination of the vacuum chamber. Even with an improved vacuum system, a laser power beyond that currently available on the described system may be required to deposit titanium as indicated by the free energy curves.

Future work on rod growth and scanned laser shapes will address these problems. Further, deposition of titanium is considered only a first step in metal SALD. Since most useful metals are not pure metals but are alloys, co-deposition from multiple precursors is an important future goal. The next step in the research described here after viable titanium deposition is to

use a precursor gas mixture of  $\text{TiCl}_4$  and  $\text{SiCl}_4$  to form titanium silicide intermetallics. While a worthwhile goal, titanium silicides are themselves seen as primarily an instructive stepping stone to the complex process of SALD alloys and in situ formed metal matrix composites of high complexity.

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