REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY (*Leave Blank*)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	1Aug97	Final 1Jan97 - 30Jun97

4. TITLE AND SUBTITLE

F04606-97-C-0025 Final Report

5. FUNDING NUMBERS

C

F04606-97-C-0025

6. AUTHOR(S)

Kenneth H. Church

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

CM Consulting
5202 N. Richmond Hill Campus
Stillwater, OK 74078-9011

8. PERFORMING ORGANIZATION REPORT NUMBER

Final OSD96

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

SM-ALC/PKLT
Joe St. Clair
5039 Dudley Blvd.
McClellan AFB, CA 95652-1027

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

CMS0005Z

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT

Approved for public release; distribution unlimited

12b. DISTRIBUTION CODE

13. ABSTRACT (*Maximum 200 words*)

Report developed under SBIR contract. Studied the feasibility of using Laser Chemical Vapor Deposition (LCVD) technology to repair electronic boards and to manufacture small lot microcircuit boards. An LCVD system was built and a gold organometallic gas was synthesized for the process. Gold patterns with line widths ranging from a few microns up to 200 microns were written. Various substrates (Alumina, Polyimide, Silicon Nitride) were written on to determine the diversity of the process. A larger system, capable of housing 2 feet in two directions, was designed on paper. The proposed system would be capable of removing unwanted metal, via ablation and laying down new metal in any desired area with sub-micron accuracy.

The LCVD technique parallels much of the current technology in laser ablation and trimming. Sub-micron accuracy, laser sources, vision systems and chemical vapor deposition are well developed areas. Integrating these areas to do LCVD specifically will be a straight forward task. The areas in this technology that will need to be improved is the write rates and resolution that is achievable using conventional lasers and optics. It is the opinion of this company that this technology can be used immediately in the hybrid microcircuit and older monolithic microcircuit arena and with further research will compete with photolithography in the semiconductor business.

14. SUBJECT TERMS

Laser
SBIR Report
Organometallic
Chemical Vapor Deposition
Microcircuits
Sub-Micron Accuracies

15. NUMBER OF PAGES
14

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	UL

NSN 7540-01-280-5500

REF D

Standard Form 298 (Rev. 2-89)
Prescribed by ANSI Std Z39-18
298-102

GENERAL INSTRUCTIONS FOR COMPLETING SF 298

The Report Documentation Page (RDP) is used in announcing and cataloging reports. It is important that this information be consistent with the rest of the report, particularly the cover and title page. Instructions for filling in each block of the form follow. It is important to stay within the lines to meet optical scanning requirements.

Block 1. Agency Use Only *(Leave blank).*

Block 2. Report Date. Full publication date including day, month, and year, if available (e.g. 1Jan88). Must cite at least the year.

Block 3. Type of Report and Dates Covered. State whether report is interim, final, etc. If applicable, enter inclusive report dates (e.g. 10Jan87 - 30Jun88).

Block 4. Title and Subtitle. A title is taken from the part of the report that provides the most meaningful and complete information. When a report is prepared in more than one volume, repeat the primary title, add volume number, and include subtitle for the specific volume. On classified documents enter the title classification in parentheses.

Block 5. Funding Numbers. To include contract and grant numbers; may include program element number(s), project number(s), task number(s), and work unit number(s). Use the following labels:

C - Contract
G - Grant
PE - Program Element
PR - Project
TA - Task
WU - Work Unit Accession No.

Block 6. Author(s). Name(s) of person(s) responsible for writing the report, performing the research, or credited with the content of the report. If editor or compiler, this should follow the name(s).

Block 7. Performing Organization Name(s) and Address(es). Self-explanatory.

Block 8. Performing Organization Report Number. Enter the unique alphanumeric report number(s) assigned by the organization performing the report.

Block 9. Sponsoring/Monitoring Agency Name(s) and Address(es). Self-explanatory.

Block 10. Sponsoring/Monitoring Agency Report Number. *(If known)*

Block 11. Supplementary Notes. Enter information not included elsewhere such as: Prepared in cooperation with...; Trans. of...; To be published in.... When a report is revised, include a statement whether the new report supersedes or supplements the older report.

Block 12a. Distribution/Availability Statement. Denotes public availability or limitations. Cite any availability to the public. Enter additional limitations or special markings in all capitals (e.g. NOFORN, REL, ITAR).

DOD - See DoDD5230.24, "Distribution Statements on Technical Documents."
DOE - See authorities.
NASA - See Handbook NHB 2200.2.
NTIS - Leave blank.

Block 12b. Distribution Code.

DOD - Leave blank.
DOE - Enter DOE distribution categories from the Standard Distribution for Unclassified Scientific and Technical Reports.
NASA - Leave blank.
NTIS - Leave blank.

Block 13. Abstract. Include a brief *(Maximum 200 words)* factual summary of the most significant information contained in the report.

Block 14. Subject Terms. Keywords or phrases identifying major subjects in the report.

Block 15. Number of Pages. Enter the total number of pages.

Block 16. Price Code. Enter appropriate price code *(NTIS only).*

Blocks 17 - 19. Security Classifications. Self-explanatory. Enter U.S. Security Classification in accordance with U.S. Security Regulations (i.e., UNCLASSIFIED). If form contains classified information, stamp classification on the top and bottom of the page.

Block 20. Limitation of Abstract. This block must be completed to assign a limitation to the abstract. Enter either UL (unlimited) or SAR (same as report). An entry in this block is necessary if the abstract is to be limited. If blank, the abstract is assumed to be unlimited.

CM Consulting
5202 Richmond Hills Campus
Stillwater, OK 74078

Phone 405.624.5751
Fax 405.624.5769

Contract Number: FO4606-97-C-0025

OSD96-021

Small Lot Repair/Manufacture of Microcircuit Boards by Laser Deposition

FINAL REPORT
1 AUGUST 1997

Table of Contents

1.0 Introduction

This is a final report and summary of the Phase I work performed on Contract # FO4606-97-C-0025. The intent of the project was to demonstrate the need and feasibility of using a technique called Laser Chemical Vapor Deposition (LCVD) to perform small lot repairs or manufacture microcircuit boards. Our results were conclusive in the six month period and demonstrated both the need and feasibility. The need for this technique is demonstrated by the interest shown from the government and commercial industry. The feasibility to use this as a repair/manufacture device can be shown by taking advantage of current laser, chemical and mechanical technology that is in existence today. CM Consulting has recognized the opportunity in this area and will continue to pursue the technology.

2.0 Microcircuit Needs

Microcircuits can vary in materials, size, design and name. It is known that line widths on the order of 0.18 microns are rapidly approaching as the standard. This is pushing the diffraction limit of using a coherent light as the radiation source for photolithography. Industry will continue to strive for smaller lines and continue to press the angstrom limit. These small features are known as thin film lines and packaged will make a monolithic microcircuit. Developing an LCVD system to reach 0.18 micron to compete in the monolithic business will be a challenge not to be overlooked. There are several problems that need to be overcome for this to become a realistic goal.

2.1 Repair/Manufacture of Hybrid Microcircuits

A larger scale, on the order of hundreds of microns in width, is a hybrid microcircuit. A hybrid microcircuit will typically use open or exposed monolithic circuits (chips) and place them on a common substrate using larger lines to make connections from one chip to another. This is for a special design that will only be done one to hundreds of times, therefore not justifying the expense of integration. The size of these hybrid boards can be on the order of inches up to feet in one dimension. If the hybrid circuit is damaged, it is not easily repaired. The LCVD technique would be an ideal tool to aid in the repair process. There are currently no effective methods to do this work which leaves an open invitation for a proven technique.

The process used to design and build a hybrid or monolithic circuit is the same. It requires a photolithographic technique. Photolithography is the optimal method when mass producing. Mass production involves tens to hundreds of thousands of pieces. The price of the equipment to complete the entire process is on the order of millions to billions of dollars. The photolithographic process is shown in Figure 2.1 below.

The mask must first be made, metal deposited and then the photoresist applied, exposed and developed. This process is time consuming and can cost in excess of $50,000 to produce one or one thousand devices. This makes it an inefficient prototyping technique, but it is the only technique available today. It is possible to replace this with the LCVD process for monolithic circuits, and probably for the hybrid circuits.

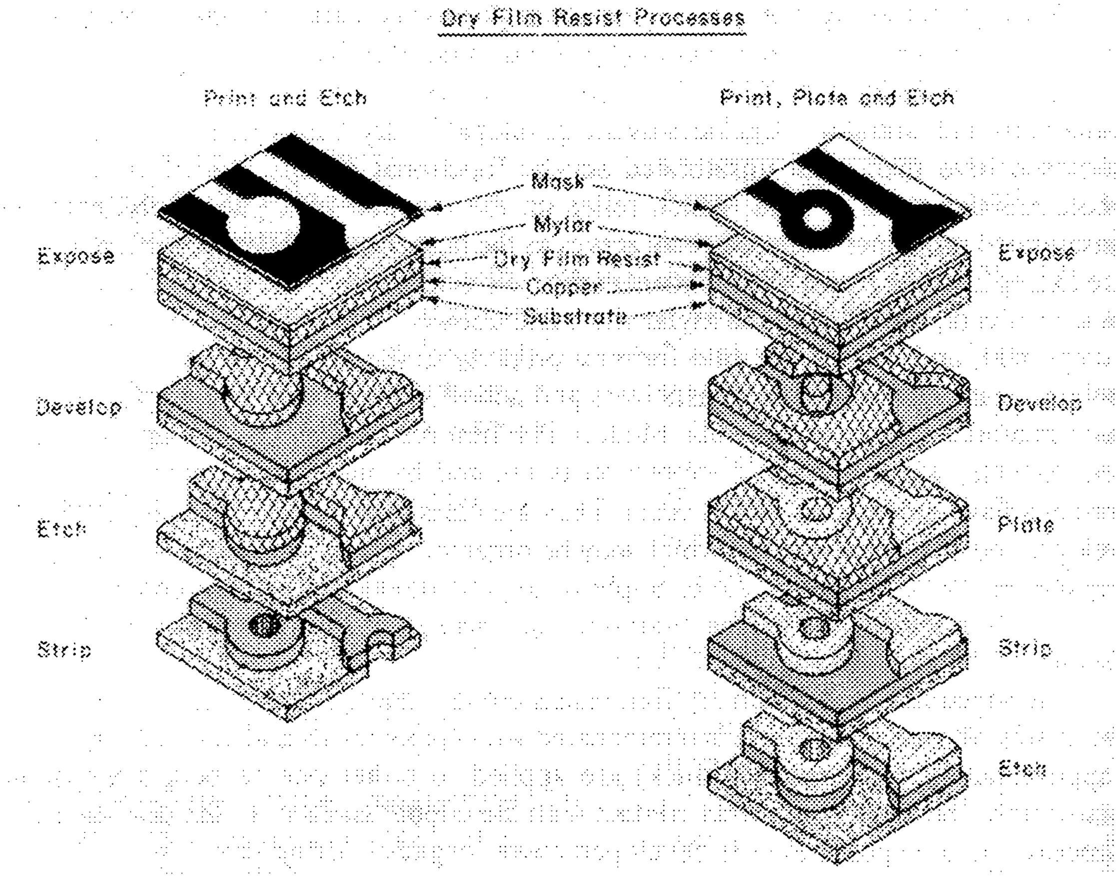


Figure 2.1 Photolithographic process.

2.2 Substrate Materials

There are several materials that are used in the semiconductor business for patterning circuits. We have worked with a few of those to determine the feasibility of writing metal lines on different substrates. Ceramic or Alumina material is used for hybrid substrates to mount and connect chips on a single, rigid surface. This is chosen due to the low electrical and high thermal conductivities. Polyimide is a polymer that is used as an insulator to separate or to layer the circuits. It can easily be applied and has high temperature and high electrical resistance. Silicon nitride is an insulator that is placed over an exposed circuit to prohibit oxidation of the metal lines and pads. The silicon nitride can easily be removed from the pads to wire bonding. There are many other materials of interest; these are a few of the most common in the industry. These materials were used in the demonstration stage which is described in section 5.0.

2.2 Metallic Lines

The metallic lines vary in dimension and composition. The smaller the integrated circuits, the higher the resistance which promotes a higher heat dissipation. Table 2.2 below is a list of metals and their resistivities.

Metal	**Symbol**	**Resistivity (ohm-cm x 10^{-6})**
Silver	Ag	1.62
Copper	Cu	1.69
Gold	Au	2.38
Aluminum	Al	2.62
Tungsten	W	5.52
Nickel	Ni	6.9
Indium	In	9.0
Platinum	Pt	10.52
Palladium	Pd	10.75
Tin	Sn	11.5
Tin-Lead	Sn-Pb (60-40)	14.99
Lead	Pb	20.65

Aluminum is readily available, inexpensive and a good conductor. Aluminum also has the added benefit of being stable and does not permeate with age. The disadvantage is the oxidation problem aluminum has when it is exposed to air. This promotes a thin insulating layer that prohibits a good contact when connecting to it. The semiconductor business has adapted to the oxidation problem and uses aluminum for a large portion of the integrated work. As the width of the lines decrease the heat in the device increases. Solutions to overcome this are currently being studied. One possibility is to change from aluminum to copper. The decrease in resistance will allow the next generation of semiconductors to be made.

It is also common to use a platinum line to attach to the pads for an outside connection. Platinum is corrosion resistant and will not oxidize. Platinum is more expensive and has a higher resistance; therefore it is not used to pattern. Gold has many of the same properties as platinum with a lower resistivity. Gold has been used on hybrid circuits for its good conductivity and low corrosion attributes. Alloys, such as Platinum-Tin, have been used as pads for better solder connections and good adhesions. There are several metal options and many of the optimal techniques and materials have been discovered using trial and error techniques.

3.0 Laser Chemical Vapor Deposition

The technique of laser-assisted chemical vapor deposition (LCVD) consists of the introduction of a vapor-phase carrier of the compound to be deposited (frequently a metal or semiconductor component) into the system containing the substrate, then irradiating the system with laser light to initiate a photolytic or pyrolytic chemical reaction which leads to the deposition of the desired compound onto the substrate in a controlled manner. In the present case of writing lines of gold onto various substrates, the vapor-phase carrier is dimethyl(1,1,1-trifluoro-2,4-pentanedionato)gold(III), or dimethyl gold trifluoroacetylacetonate (DMGT). The system of substrate and DMGT contained within a vacuum chamber is then irradiated by an argon-ion laser. As DMGT does not strongly absorb in this region, the vapor transmits essentially all of the laser light to the substrate, which then is heated to temperatures high enough to initiate thermal decomposition of the DMGT, leaving deposits of gold metal controlled by such factors as laser spot size, scan rate, and fluence.

4.0 Metallic Gases

After review of the literature on the LCVD of gold, there appears to be basically two families of organometallic gold compounds useful for gold LCVD. These are (1) the dimethyl gold diketonates (acetylacetonate and its fluorinated analogues), Me_2AuL, where L is an acetylacetonate (acac), trifluoroacetylacetonate (tfac), or hexafluoroacetylacetonate (hfac) ligand; and (2) the alkyl gold(I) or gold(III) trialkylphosphines, $RAuPR'_3$ or $R_3AuPR'_3$, where R and R' are methyl or ethyl groups.

Both families of compounds have similar LCVD performance, and both are highly expensive and have limited commercial availability. Because the phosphine ligands are highly odoriferous and toxic, leading to serious handling and environmental problems, it was decided to focus upon the less hazardous diketonate ligands. Unfortunately, the commercial availability of dimethyl gold diketonates is simply not viable for our purposes. After consulting such chemicals producers as Aldrich, Alfa-Aesar, Atomergic, ESPI, Fluka, Gelest, GFS, ICN, Pfaltz & Bauer, Sigma, Strem, and a few others, a single price quotation was obtained for Me2Au(tfac)—on the order of $600 per gram, five grams minimum. It was therefore resolved to attempt the synthesis of the Me_2AuL precursors in-house.

To that end, a method patterned after the original developed by Brian and Gibson in 1939, which is still the standard procedure referenced by much more recent publications, was chosen:

A. Synthesis of Dimethyl Gold Iodide

1. Tetrachloroauric acid ($HAuCl_4$) is dissolved in excess pyridine (py) at elevated temperatures (<100°C), forming dichlorodipyridinogold(III), $AuCl_2(py)_2$ (which precipitates upon cooling to room temperature).

2. After the reaction mixture is cooled to at least 0°C, the Grignard reagent methylmagnesium iodide (MeMhI) in ether is carefully added to form dimethyliodogold(III), Me_2AuI. This is the most air-sensitive step.

3. Water, heptane, and concentrated hydrochloric acid are each added to the reaction mixture in sequence, then the aqueous and organic phases are separated.

4. The Me_2AuI is separated from the organic layer by the addition of ethlenediamine (en) to form a precipitate of dimethyl(ethylenediamino) gold(III) iodide, $Me_2Au(en)I$. The addition of acid allows the recovery of Me_2AuI.

B. Synthesis of Dimethyl Gold Diketonates

1. The diketone (acetylacetone, trifluoroacetylacetone, or hexafluoroacetylacetone, all of which at room temperature) is diluted with absolute ethanol.

2. Potassium hydroxide id dissolved in a mixture of absolute ethanol and the minimum amount of water possible.

3. The two solutions are combined to form the potassium diketonate salt, which may be collected by evaporation of the solvent.

4. The potassium diketonate, dissolved in ethanol, is added to Me2AuL, which may then be collected and purified.

After careful review of the literature on the dimethyl gold β–diketonates, especially dimethyl (1,1,1-trifluoro-2,4-pentanedionato) gold(III) or dimethyl gold trifluoroacetylacetonate (DMGT), it becomes readily apparent that no detailed toxicological studies of these materials have been reported. Therefore, the hazards of the reagents used to synthesize DMGT will be discussed first, followed by the observations made during the course of these experiments.

Hazards of the Reagents According to the Supplier

- A number of gold(III) halides may be used for the gold source; while somewhat unusual for a heavy metal, gold compounds are not particularly toxic unless they contain a toxic anion. The main one used in this synthesis, gold(III) bromide, carries "corrosive" and "hygroscopic" warning labels. Its corrosivity primarily applies to its tendency to oxidize metals, plating out metallic gold on the surface, and requires the use of plastic or glass implements in handling. Its hygroscopic properties are minimized by keeping the container sealed until use.

- The primary solvent in the synthesis, diethyl ether, is dangerous because it is extremely flammable (NFPA class 4) and is mildly toxic (class 1). It must be stored in a proper flameproof refrigerator, preferably handled in a fume hood, and kept away from ignition sources. In spite of all this it is still the most convenient solvent for this type of organometallic synthesis.

- The methylating agent, methyllithium solution in diethyl ether, is extremely reactive to oxygen and moisture and in fact carries a "pyrophoric" warning label. It may be safely handled using standard air-sensitive-reagent glassware and syringe transfer techniques.

- The β-diketone, 1,1,1-trifluoro-2,4-pentanedione or triofluoroacetylacetone, like most other organic liquids carries "flammable" and "irritant" warnings, but it does not warrant a "toxic" label. Handling requires only the precautions already in use for the gold(III) bromide and methyllithium.

Observed Hazards of the Product and Byproducts

The main product of the synthesis, DGMT, and its breakdown products are the only chemicals with which CM Volux's customers would possibly come into contact. Moreover, according to the design plans for the Phase II project, the CVD precursor and breakdown product traps will both be sealed into the system; therefore, the customer will not encounter **any** chemical in normal use. The following observations were made during the course of these experiments:

☐ DGMT and its breakdown products are **not** corrosive to metals in the manner of gold(III) halides. No damage to the stainless steel of the vacuum chamber or of the lab spatula used to load the DMGT into the sublimation chamber was observed.

☐ Because it is somewhat unstable with regard to dissociation and has an inherently high vapor pressure (indeed, the sources of its utility as a CVD precursor), it must be stored carefully. It has been stored safely prior to CVD experiments in a freezer with minimal degradation. It must be considered somewhat flammable (NFPA 1).

☐DGMT does have a very noticeable odor which is detectable in very low concentrations, enough to possible merit a "stench" warning label form a commercial producer. The odor detection threshold does not appear to become desensitized with exposure, so exposure to the compound is readily noted and avoided. The known properties of gold compounds and the synthetic reagents lead to the conclusion, without full toxicological evidence, that DMGT is at least mildly toxic. One manufacturer has assigned it an NFPA health rating of 3, but this rating is probably deliberately overstated pending a full evaluation, which would likely lower it to 2. DGMT can nevertheless be safely handled through proper laboratory techniques including the use of gloves, a fume hood, and eye protection.

☐ The synthesis byproducts and breakdown products of DGMT are primarily metallic gold (in powder or thin-layer form) and simple organics, some of them fluorinated. While a definitive study of the decomposition process has not been done, it is believed to result in the cleavage of the central bond of the trifluoroacetylacetonate ligand, leading to such products as acetic acid and trifluoroacetic acid, while the methyl groups detach to form lightweight hydrocarbons, principally methane and ethane. None of these are particularly dangerous when handled properly and can be vented into a fume hood or captured with liquid-nitrogen cold trap. The possible presence of corrosive products, in particular hydrofluoric acid, was not observed.

Considering all of the hazards associated with the synthesis of DMGT, it can be safely controlled, as can those of its decomposition products, through air-sensitive-reagent procedures during the first parts of the synthesis and normal laboratory procedures afterwards.

5.0 Prototype for Demonstration

A prototype to demonstrate the feasibility of this project was built and tested. It has been our goal to develop a process, using prior art techniques, which will write gold lines. There have been three major goals set to prove the LCVD process.

⇒ Demonstration of Laser Chemical Vapor Deposition.
⇒ Implement the necessary translation stages along with the focusing optics and chamber to write gold lines.
⇒ Characterize these results using SEM and X-Ray

At the end of the six month project CM Consulting demonstrated the LCVD process by not only writing spots and lines, but also a demonstration of patterning.

5.1 Setup

A piece of Alumina was used as the substrate. The organometallic gas was synthesized by our group with the following equipment list:

- Two ring stands, two crossbars, and associated clamps
- One combination magnetic stirrer and hot plate
- One three-necked flask
- One addition funnel with side branch and rubber septum attachment
- One condenser
- One bubbler and one trap
- One funnel for gravity filtration
- One separatory funnel
- Disposable specimen vials
- Disposable pipettes
- Solvents and reagents

The equipment list for initial LCVD experiment is as follows:

- Argon-Ion Laser, with water circulation
- Optical Mirror Mounts and Mirrors
- Vacuum Chamber
- Turbo Pump
- Vent Hood
- Hot Plates
- Nikon Microscope w/ CCD attachment

5.2 Procedure

The output of the laser used has a range from miliwatts CW to 4 watts CW. The chamber has a window on top made from ½" glass. Steering optics were used to focus the beam through the window of the vacuum chamber. The laser was focused at specified locations on the Alumina substrate for varying times and powers. Figure 5.2.1 below is a picture of the experimental setup in the Noble Research Center at Oklahoma State University.

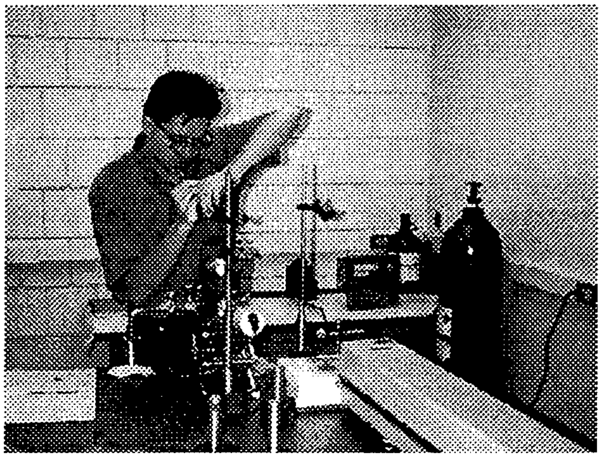


Figure 5.2.1 Experimental setup for LCVD procedure

The experimentation process began by writing varying spots. The size of the spot deposited depends upon the focus, time on the substrate and the power output. An optimal spot was chosen and the necessary settings recorded. A line was then drawn by steering the laser beam via optics. These deposition processes were characterized using an SEM/Xray. The system was then converted to write patterns (wrote the software to control the laser and stages via a computer). A demonstration of those results are shown in Figure 5.2.2 below.

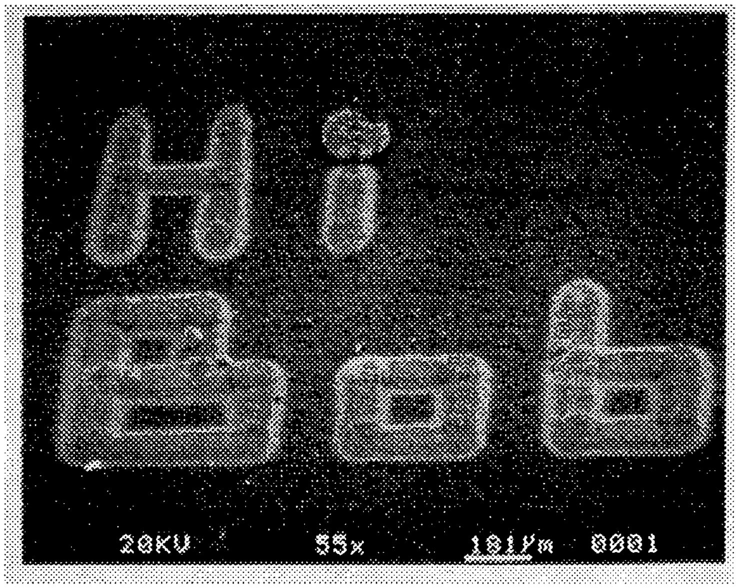


Figure 5.2.2 Gold pattern written on an Alumina substrate using LCVD.

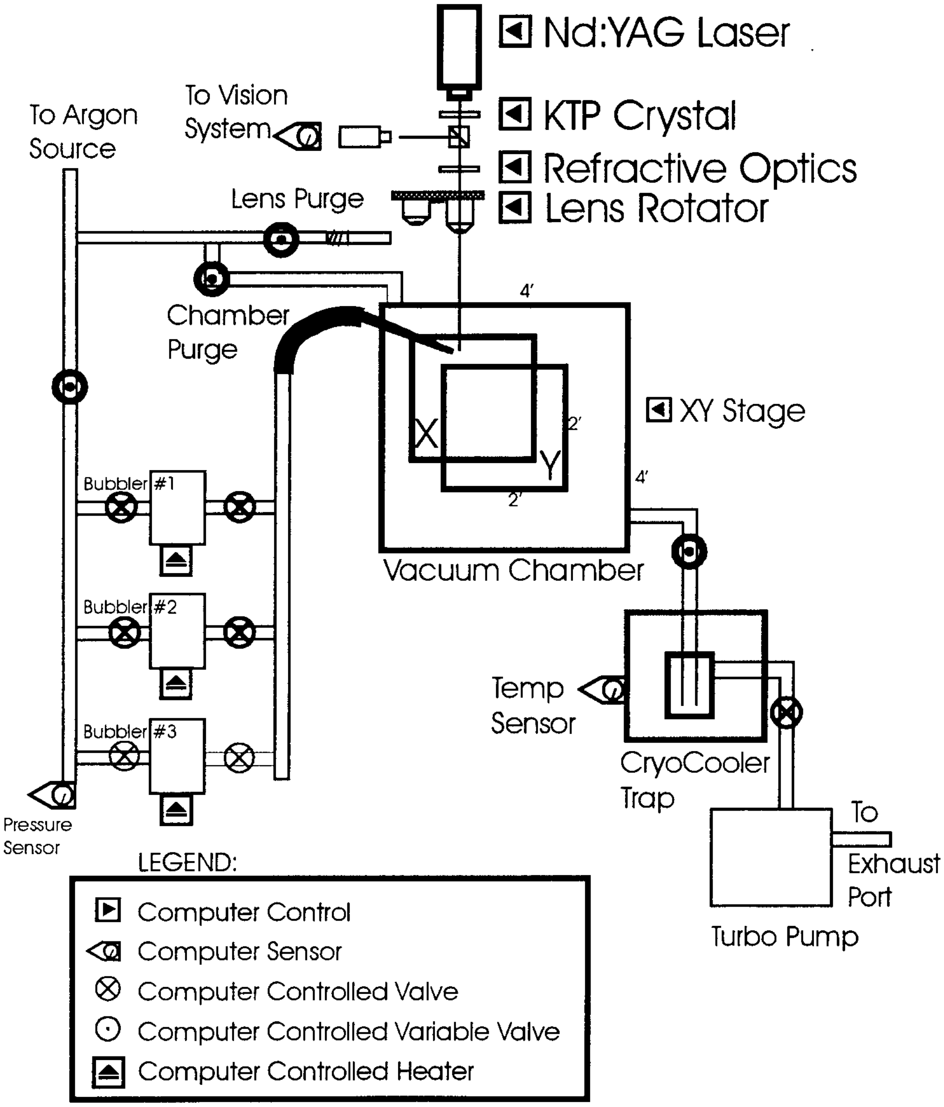
The experimentation process continued through the sixth month and lines were written on other substrates of interest to the semiconductor business. Polyimide and silicon nitride were written on in addition to the alumina substrates.

6.0 Proposed Design for Phase II

A detailed explanation of the Phase II prototype is given in the Phase II proposal. A schematic drawing or block diagram of the system is given in Figure 6.0. This provides a list and integration diagram of the major items required.

Two aspects of the apparatus now in the design stages for the laser-assisted chemical vapor deposition (LCVD) of gold microcircuitry, in SBIR Phases II and III, and how they are expected to offer enhancements over the working apparatus constructed in Phase I. The first is a nozzle system designed to increase the local concentration of the organogold vapor at the deposition site, while the second is a recycling system designed to recover and recycle any unreacted organogold precursor and to remove from the waste stream and possibly recycle the organic byproducts. Both systems are part of the wide-scale improvements being considered in

Schematic Diagram of LCVD System



the design of the next-generation LCVD apparatus.

6.1 Nozzle System

The LCVD of gold by thermal decomposition of an organogold precursor[1] is a chemical reaction which generally obeys first-order reaction kinetics,[2] meaning that the reaction rate is directly proportional to the concentration or partial pressure of the organogold compound: $R = kc$ or $R = k'p$. For this reason it is desirable to make the local concentration of organogold as high as possible, while still keeping the environment relatively free of possible contaminants. It is also desirable to avoid even the presence of inert gases, which has been shown to decrease deposition growth rates and adversely affect deposit morphology.[3]

In the search for practical solutions to these considerations, it has been concluded that producing a reasonably high vacuum, on the order of 10^{-4} or 10^{-5} torr, should be sufficient to purge the environment of contaminants. If necessary multiple purge and inert-gas (preferably helium) fill cycles could be performed. But a residual inert-gas atmosphere is not desirable, and maintaining this level of vacuum creates additional problems when attempting to write gold microcircuitry upon commercial circuit boards, which are approximately two feet (61 cm) square. One such problem is mechanical stress on the apparatus, which can be anticipated and compensated in its design. Another is the creation of a relatively large volume which would have to be charged with the organogold vapor, which would be then used in unnecessarily large quantities.

For these reasons the design of a nozzle system to produce locally high concentrations of organogold vapor while avoiding high use has been contemplated. In one proposed design, the nozzle would be placed upon the same translator stage as the laser optics, and its entrance would be so positioned as to place a jet of organogold vapor at the heated substrate surface in the optimum location for thermal decomposition. In a second proposed design, now more highly favored, the laser optics and nozzle are still fixed with respect to one another and the substrate is translated instead.

---

[1] The organogold precursors under consideration are (1) dimethyl(1,1,1-trifluoro-2,4-pentanedionato)gold(III), commonly called dimethylgold trifluoroacetylacetonate, Me_2Au-(tfac); and (2) dimethyl(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)gold(III), commonly called dimethylgold hexafluoroacetylacetonate, Me_2Au(hfac). The nonfluorinated analogue, dimethyl(2,4-pentanedionato)gold(III) or dimethylgold acetylacetonate, Me_2Au-(acac), has been eliminated from consideration because its room-temperature vapor pressure is too low.

[2] R. B. Klassen and T. H. Baum, *Organometallics* **1989**, *8*, 2477.

[3] T. T. Kodas, T. H. Baum, and P. B. Comita, *J. Appl. Phys.* **1987**, *62*, 281.

In either case, the result is that the bulk of the evacuated volume can be kept in a reasonably high vacuum, while the active area can be kept under a relatively high local pressure of organogold vapor. In addition, the molecules of the vapor will be directed towards the heated substrate, increasing the probability of appropriate reactive collisions and hence the reaction or deposition rate. Continued evacuation would also provide the benefit of aiding the removal of the organic byproducts and unreacted organogold vapor. Therefore, using the nozzle system approach the rate of deposition can be enhanced, additional control is gained over deposit quality and morphology, and the amount of organogold precursor required is reduced.

6.2 Recycling System

In its current conception, the recycling system of the next-generation apparatus is not radically different from that of the current apparatus. It still consists of a cold trap on the line leading to the vacuum pump, but in the proposed case the trap contains a container which can be sealed and removed from the apparatus without the risk of exposing the technician to its contents. It is therefore necessary to review the properties of the organogold compounds, members of the dimethylgold β-diketonate family.

Decomposition Chemistry

In the gas phase, $Me_2Au(acac)$ has been shown to be monomeric, and the metal center has the usual square-planar configuration of gold(III) complexes.[4] This property reduces the complexity of the system, and it is expected that $Me_2Au(tfac)$ and $Me_2Au(hfac)$ have similar properties.

The authors of a study on the decomposition of $Me_2Au(hfac)$ on a germanium substrate by pulsed LCVD make a number of observations relevant to the current study, even though there are differences in experimental technique between the two studies, chiefly in the types of substrate and laser used.[5] First, a sample of Ge exposed to $Me_2Au(hfac)$ vapor but not to laser light showed presence of an oxidized gold species strongly chemisorbed to the surface. The authors note that such chemisorption of organogold is weaker on oxides and halides but present nevertheless. They also report that even after a single pulse both metallic and oxidized gold are present. Furthermore, they observed luminescence from the excited gas near the point of deposition, but spectral analysis showed that the luminescence did not arise from intact $Me_2Au(hfac)$, the parent compound, but instead matched the spectrum reported for Au_2; the luminescent fragment did not contain the β-diketonate ligand. They postulate that these reactive gold dimers then attach themselves to the substrate and form the building blocks of the gold deposit.

The same authors discuss two methods of thermal decomposition, both of which occur simultaneously in proportions which are functions of the reaction environment. The first is the reductive elimination of ethane (the two methyl groups separate from $Me_2Au(hfac)$ and link)

---

[4] S. Shibata, K. Iijima, and T. H. Baum, *J. Chem. Soc. Dalton Trans.* **1990**, 1519.

[5] D. Wexler, J. I. Zink, L. W. Tutt, and S. R. Lunt, *J. Phys. Chem.* **1993**, *97*, 13563.

followed by decomposition of the unstable Au^I(hfac) molecule; and the second involves homolytic cleavage of all of the metal–ligand bonds in the Me_2Au(hfac) to produce Au^0 and $Me^\bullet$ and $(hfac)^\bullet$ radicals. They also note that in photochemical as opposed to thermal decompositions in solution the radical-pathway is favored, but in the vapor phase solvation effects are necessarily much less important and reductive elimination of ethane is more significant.

The authors of an earlier study of the thermal decomposition of Me_2Au(acac) in solution claim that its decomposition occur via reductive elimination of the two *cis* methyl groups.[6] Besides Au^0, the other major product of the decomposition was 2,4-pentanedione or acetylacetone, the hydrogenated form of the ligand obtained by extraction of hydrogen from the solvent by the 2,4-pentanedione radical. In solution the rate-limiting step was protonation of the 2,4-pentanedionate ligand, and less than 20% of the reaction proceeded via the radical pathway. The major decomposition products they observed were ethane (50%) and 2,4-pentanedione (43%), with lesser amounts of methane (1%) and 3-methyl-2,4-pentanedione (4%), $CH_3COCH(CH_3)COCH_3$, formed by the union of methyl and pentanedione radicals. They also reported similar observations for photolytic decomposition via UV irradiation, which resulted in the reductive elimination of ethane and liberation of the (hfac) group.

Based on this information, what decomposition products can be expected in the gas-phase reaction of an LCVD apparatus? In this case the radical pathway gains preeminence and the first species produced by the decomposition of Me_2Au(tfac) are Au^0, 2 $Me^\bullet$, and $(tfac)^\bullet$, or $(hfac)^\bullet$ in the case of Me_2Au(hfac). The Au^0, possibly in the form of Au^0_2, is of course the desired product and adheres to the substrate, while the organic radicals are free to react and eventually reach the trap, which will be held at the normal boiling temperature of nitrogen, 77.4 K or −195.8 °C. This temperature is low enough to solidify even the lightest expected byproducts, methane and ethane, which solidify at 91 and 90 K respectively. From the literature review the list of expected byproducts should include methane, ethane, the intact β-diketone, and the β-diketone methylated at the central carbon. But in the present gas-phase reaction of, for example, Me_2Au(tfac), where there is little or no free hydrogen for a $(tfac)^\bullet$ radical to extract, it should be expected that the primary byproducts will be those formed by the union of two radicals, including ethane, Me(tfac) (actually 1,1,1-trifluoro-3-methyl-2,4-pentanedione), and several possible $(tfac)_2$ dimers, one of which could be 3-(1-ethanone)-1,1,1-trifluoro-4-(2,2,2-trifluoro-1-ethanone)-2,5-hexanedione, $CF_3COCH(COCH_3)CH(COCF_3)COCH_3$. Other products which might be found in lesser amounts could arise from the breaking of the (tfac) backbone at C_3, leading to two- and three-carbon fragments. All of these byproducts, plus unreacted Me_2Au(tfac), would be caught within the cold trap. Final determination of the exact product distribution would require a gas chromatography/mass spectroscopy (GC/MS) study.

Recycling

Once the material caught within the cold trap has been extracted, a number of products could be recovered and recycled. Of these, the most important would be the unreacted organogold

---

[6] R. B. Klassen and T. H. Baum, *Organometallics* **1989**, *8*, 2477.

compound, in this example $Me_2Au(tfac)$. This species could be recovered in much the same way that it was separated from the reaction mixture, *i.e.* through liquid chromatography or comparable separation technique, and reloaded into a sublimation capsule.

For commercial considerations, $Me_2Au(tfac)$ is quite expensive, currently on the order of $600 per gram if purchased directly. Prices from the Aldrich catalog for three projected byproducts are as follows:[7] methane, 99.0+%: $109.40 for 57 L (lecture bottle); ethane, 99+%: $170.75 for 110 g (lecture bottle); and 1,1,1-trifluoro-2,4-pentanedione, 98%: $23.40 for 10 g or $45.80 for 25 g. The expected byproduct 1,1,1-trifluoro-3-methyl-2,4-pentanedione is not listed in the Aldrich Catalog or several others, and it is extremely doubtful that the various $(tfac)_2$ dimers would be commercially available. Of these trapped species, then, the ones potentially worth recovering, depending upon the costs of purification, would be $Me_2Au(tfac)$ itself, possibly ethane, probably (tfac), and possibly 3-Me(tfac). Methane is so widely available from natural gas that its recovery would probably not be commercially viable for a small company, and the same may well be true of ethane, although ethane is much less common in natural gas than methane. Viable recovery of (tfac) seems likely, and this is also true of 3-Me(tfac) if a market or distributor for it could be found. The more complex $(tfac)_2$ dimers might not be stable or easy to separate, or in any case might not be produced in large quantities, so this issue would require further study.

Disposal and Environmental Concerns

If a byproduct cannot be recycled in a commercially viable manner, it must be disposed of in a prescribed manner consistent with the relevant environmental regulations, most notably those of California, which are stricter than elsewhere in the U.S.A. To that end, the lightweight gases, methane and ethane, could be burned with little concern, and they are essentially nontoxic. Disposal of fluorocarbons not containing chlorine is also relatively straightforward. The pentanediones are somewhat toxic but not greatly so, generally scoring a 1 or 2 on the 0–4 NFPA scale; the properties of other byproducts would have to be researched once identified. But nowhere does the current study require the use of highly toxic reagents, and the only dangerous ones are used in the synthesis of the organogold compound, not in its use.

7.0 Conclusion

The Phase I work has been successfully completed. All areas that were addressed in the Phase I proposal have been demonstrated or designed in the six month time period. The necessary information needed to move forward with this project is adequate and the results are positive. The industrial interest is high with many of the major semiconductor corporations continuing to research in this area. The success of a Phase II program will depend on the desire and effort put into the project and not on science. The science or chemistry has been proven, the engineering design or layout has been given and therefore this project will provide the end result the government is looking for.

---

[7] *Aldrich Catalog Handbook of Fine Chemicals 1996–1997*, Aldrich Chemical Co., Inc., Milwaukee, WI, 1996.