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TITLE METAL FILM DEPOSITION BY LASER BREAKDOWN CHEMICAL VAPOR DEPOSITION

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ABSTRACT

Dielectric breakdown of gas mixtures can be used to deposit homogeneous thin films by chemical vapor deposition with appropriate control of flow and pressure conditions to suppress gas phase nucleation and particle formation. Using a pulsed CO₂ laser operating at 10.6 microns where there is no significant resonant absorption in any of the source gases, we have succeeded in depositing homogeneous films from several gas phase precursors by gas phase laser pyrolysis. Nickel and molybdenum from the respective carbonyls and tungsten from the hexafluoride have been examined to date. In each case the gas precursor is buffered to reduce the partial pressure of the reactants and to induce breakdown. The films are spectrally reflective and uniform over a large area. Films have been characterized by Auger electron spectroscopy, x-ray diffraction, pull tests, and resistivity measurements. The highest quality films have resulted from the nickel depositions. Detailed x-ray diffraction analysis of these films yields a very small domain size (~50 Å) consistent with rapid quenching from the gas phase reaction zone. This analysis also shows nickel carbide formation consistent with the temperature of the reaction zone and the Auger electron spectroscopy results which show some carbon and oxygen incorporation (8% and 1% respectively). Gas phase transport and condensation of the molybdenum carbonyl results in substantial carbon and oxygen contamination of the molybdenum films requiring heated substrates, a requirement not consistent with the goals of the program to maximize the quench rate of the deposition. Results from tungsten deposition experiments representing a reduction chemistry instead of the decomposition chemistry involved in the carbonyl experiments are also reported.

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INTRODUCTION

Chemical Vapor Deposition, in which vapor phase chemical reactants deposit a coating on a substrate, has a long history of applications in metal and other coatings. Inasmuch as these processes are thermally driven, the commercial availability of high power carbon dioxide lasers in the early 1970's made some fusion of these technologies inevitable.

In 1973, a method for local substrate heating for patterned chemical vapor deposition devised by Lydtin & Wilden was reported⁽¹⁾. A helical carbon resistor was fabricated on a ceramic substrate but details of the process were not fully reported. A diagram of their apparatus is shown in Fig. 1. Further development of this local heating technique was done by Christensen² and later by Allen and her collaborators³ at the University of Southern California starting in about 1978. This group investigated a number of metal systems using both pulsed and continuous wave (CW) carbon dioxide lasers operating in the infrared (IR) through a transparent reactant gas mixture. Writing of small scale patterns was one goal of this work although actual patterned circuits were not produced. This is a thermal surface process with no gas phase reaction intended.

At about the same time, a concerted effort at laser chemical vapor deposition for microelectronic applications was initiated at Lincoln Laboratories by Ehrlich, Deutsch, Osgood, Tsao, and their coworkers⁴. Using visible and ultraviolet (UV) wavelengths, they narrowed the spot size to submicrometer dimensions on the substrate, and directly photolysed reactants in the gas phase or on the substrate surface or both. This technique is illustrated in Fig. 2. This work has been quite highly developed for selective doping and metallization, resulting in complete circuits having been fabricated using the laser direct writing technique.

Bauerle and his collaborators⁵ at Linz has also used local illumination at visible and ultraviolet wavelengths to deposit patterns as well as single crystal needles of metals and semiconductors.

In another application to microelectronics, Collins, Solanki, and their coworkers⁶ at the Colorado State University have developed a technique for large area depositions of metals and insulators by gas phase photolysis of reactants by a UV excimer laser as illustrated in Fig. 3. The work is also well advanced with a number of metal and insulator coatings having been produced. A principal advantage of this technique over conventional vacuum deposition methods is excellent coverage of stepped features on the substrate. The use of an excimer laser also limits the number of dissociation channels available. Higher energy processes can thus be tuned out in some cases.

Haggerty and collaborators⁷ at the Massachusetts Institute of Technology and Bilenchi, Musci, and their collaborators⁸ at CISE S. p. A. have used a geometry similar to that of Collins but with a carbon dioxide laser as a heat source for gas phase pyrolysis of silane to deposit films of amorphous silicon for solar cells. In this case the 10.6 micrometer radiation is at resonance with the silane resulting in heating of the gas by multiphoton absorption.

There have thus been four basic techniques demonstrated for the use of lasers in chemical vapor deposition: gas phase pyrolysis by resonant absorption of IR radiation, gas phase photolysis by UV radiation, substrate heating with subsequent surface pyrolysis by IR and visible radiation, and a combination of surface and gas phase photolysis by UV radiation. In general, the gas phase techniques are useful for large area depositions and the surface focused techniques for selective area deposition.

A number of other laboratories⁹⁻²³ have also reported results on various laser chemical vapor deposition activities using one or more of these methods as well as various photoelectrochemical methods for etching or depositing films. A more complete discussion is beyond the scope of this brief introduction but the most significant efforts in the field of laser chemical vapor deposition have been described above.

RESULTS

We have used dielectric breakdown of gas mixtures to drive chemical vapor deposition reactions²⁴ in a geometry similar to that of Collins as shown in Fig. 4. The focussed beam of a pulsed carbon dioxide laser operating on the 10.6 micrometer line creates a region of high electric field sufficient to break down the gas. This in turn creates a high temperature reaction zone at a distance of 2 to 3 mm from the substrate which is at room temperature. The deposition on the cold substrate results in rapid quenching of the deposit from the gas phase and very fine grain structures. In fact, the principal goal of this work is the deposition of amorphous alloy films and the reason for choosing this method of deposition is the promise it holds for creation of very fine grain or amorphous materials. We have chosen gas phase processing for the advantages of relatively large area depositions, low substrate temperatures for rapid quenching of the deposited material, and spatially defined reaction volume to eliminate wall effects.

Consideration of available source gases and the existence of known amorphous phases of Ni-Mo alloys^{25, 26} led to the choice of this system for initial investigation. Because $\text{Ni}(\text{CO})_4$ is a well understood if highly toxic chemical vapor deposition source, we began our investigations in this material.

We first attempted to heat the gas by resonant absorption in $\text{Ni}(\text{CO})_4$ at 10.93 micrometers using tuned CW and pulsed CO_2 lasers in the hope that the Ni-CO bond could be broken by multiphoton absorption without dissociating the C-O bond. These experiments were not successful. We were, however, able to create dielectric breakdown conditions using the pulsed laser and these conditions could be created without the need for tuning to a difficult line.

We have therefore pursued the use of laser breakdown for the chemical vapor deposition of metal films and have had some success in this new technique for laser deposition. Using the dielectric breakdown technique, we have been able to produce films of Ni and Mo from the respective carbonyls, and W from WF_6 and H_2 by adding argon to the gas mixture. Concentrations in the case of the carbonyls were 2-3% carbonyl in argon at a total pressure of about 13 Torr. In the WF_6 experiments, breakdown could only be achieved at higher pressures at concentration of about 1% WF_6 with varying mixtures of H_2 and Ar. In all cases, total flow rates through the chamber were from about 100 to several thousand standard cm^3 per minute. Although total flow rates did not seem to alter the deposition, any turbulence in the chamber increased the residence time of the gas over the substrate and increased the chance of powder deposition on the substrate. The addition of argon to the gas mixture promotes the breakdown of the gas and serves to buffer the reactant species so that homogeneous nucleation does not occur in the gas phase. At high (greater than about 1 Torr) partial pressures of reactant gas, powder formation occurs and this must be suppressed if homogeneous metal films are to be obtained.

The table below shows the results of Auger electron spectroscopy profiles on representative samples of the films produced. The high rate of incorporation of carbon and oxygen in the Mo films is due to the condensation of $Mo(CO)_6$ on the substrate between laser pulses. Because of our interest in low substrate temperatures, we do not wish to heat the substrate to prevent this condensation. We have therefore abandoned $Mo(CO)_6$ as a source and will concentrate on the MoF_6 reduction process in the future. Thus although we have been able to produce spectrally reflective Mo films indicative of good metallurgical quality depositions, we will not report detailed results on these Mo depositions.

PRECURSOR GASES	FILM COMPOSITION
$Ni(CO)_4$, Ar	Ni 90%, C 9%, O 1%
$Mo(CO)_6$, Ar	Mo 40%, C 30%, O 30%
WF_6 , H_2 , Ar	W 53%, O 41%, N 6%

Our work in the WF_6 system is in preparation for work in the MoF_6 system as the two materials are similar in their thermal chemical vapor deposition behavior. Our work to date has not yielded definitive results with respect to the nature of the tungsten deposits. The higher pressures which have been required to break down the gas mixture have resulted in powder formation in all samples analysed to date. The high oxygen content revealed in the Auger results is due to the rapid oxidation of the high surface area tungsten powder. The nitrogen present is presumed to be due surface adsorption on the powder particles. Scanning electron microscopy shows particle sizes of the order of a few 10's of Angstroms. Work is continuing on this system.

Although carbon incorporation is a remaining problem in the Ni depositions, we will present complete characterizations of these films, as they demonstrate the small grain size which is a principal feature of the technique and goal of the work.

Nickel deposition rates of from 5 to 15 angstroms per shot even at a repetition rate of 0.5 Hz result in measurable films in a short time. Films as thick as 1.0 micrometer were produced although typical thicknesses were more of the order of a few thousand Angstroms. Although a point focus is used in contrast with the line focus used by Collins, rather large area films (1 x 2 cm) were obtained. The films were fairly uniform in thickness over the deposited area with variations of about 15% over a centimeter. Because high vacuum is not required, the chamber can be recycled with a clean substrate in a few minutes, resulting in a high throughput of films.

Rapid determination of overall film quality and integrity was done by adhesion tests. Powder films, a common occurrence, can usually be identified by the lack of spectral reflection from the surface, but poor quality films may show spectral reflections. Yield strengths of from 1.0 to 2.5×10^8 dynes/cm² (1.5 - 3.5×10^3 psi) were obtained regularly from the Ni films. These figures, while not outstanding, are adequate and demonstrate the homogeneous character of the films.

Composition results have already been mentioned. Fig. 6 shows an Auger depth profile of a typical Ni film demonstrating uniform deposition. Incorporation of oxygen at the 1% level may be significant or may be the result of contamination of the Auger system.

Structural analysis of the Ni films was done by digital diffractometer analysis of several films. Films of the order of a few thousand angstroms thick yielded widths for the (111) Ni peak indicating a diffracting domain size of about 25 angstroms. More detailed analysis of data on a 1.0 micrometer film is shown in Fig. 7. The raw data for this 42 hour scan at 0.1 degree steps is shown at the top of the figure. The strong amorphous signal is from the substrate, a glass microscope slide. A fit to the (111) and (200) Ni peaks with the amorphous background subtracted out was obtained but showed distinct fitting errors as can be seen in the figure. Fig. 8 shows a three peak fit to the same data with the addition of the Ni₃C (101) peak to the two Ni peaks. As can be seen, the fit is quite good. The peak height of the Ni₃C (101) is consistent with the Auger results of about 9% carbon incorporation, leading us to believe that the impurity in the film is entirely in the carbide. Analysis of the width of the Ni peaks indicates some preferential orientation to the (111) direction and a maximum diffracting domain size of 47 angstroms. The Ni₃C peak is very broad indicating a grain size of less than 20 angstroms. Stretching of the Ni lattice spacing due to the carbon incorporation is of the order of 1%. The diffracting domain size, which is about an order of magnitude smaller than that of comparable vacuum deposited films, indicates that rapid quenching from the gas phase is occurring as anticipated.

Resistivity measurements were made on Ni lines formed by lift off on glass substrates. Line widths of from 0.6 mm to 3.5 mm and thicknesses from 400 Angstroms to 900 Angstroms were measured. Contact was made to the lines with silver loaded epoxy and resistance measurements were made at line lengths from 1.2 cm to 0.4 cm. Contact resistance was measured at about 10^{-3} of line resistance. The data were reduced by linear regression of the resistance against the ratio of line length to cross sectional area with a final figure of 5×10^{-3} ohm-cm.

Variance was about 40% reflecting what seems to be large scale nonuniformity in the deposits. The high value of the resistivity (pure Ni has a resistivity of 6.8×10^{-6} ohm-cm) may be indicative of the presence of Ni₃C or of less than full density in the deposits.

CONCLUSIONS

We have demonstrated that laser dielectric breakdown can be used to drive chemical vapor deposition reactions in both decomposition and reduction chemistries. We have also shown that the properties of the Ni films which have been most fully characterized are consistent with rapid quenching from the gas phase to the deposited film. The flexibility of the method leads us to believe that amorphous alloy films can be produced using this technique.

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FIGURE CAPTIONS

Figure 1. Diagram of apparatus used by Lydtin and Wilden for CVD of carbon film resistors.

Figure 2. Schematic diagram of process for direct writing of very fine lines using surface activation as described by Ehrlich.

Figure 3. Schematic diagram of process for excimer laser CVD of large area films as described by Collins.

Figure 4. Schematic diagram of process for laser breakdown CVD.

Figure 5. Auger depth profile of 1500 Angstrom Ni film.

Figure 6. X-ray diffraction results for 1.0 micrometer Ni film with fit to Ni (111) and (200) peaks.

Figure 7. X-ray diffraction results for 1.0 micrometer Ni film with fit to Ni (111) and (200) and Ni_3C (101) peaks.

fig. 2.

fig. 3

Fig 4.

fig 6.

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**Metal Film
Deposition by
Laser Breakdown
Chemical vapor Deposition**

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NATO

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LASER CHEMICAL VAPOR DEPOSITION OF AMORPHOUS METAL FILMS

**Explore the use of laser CVD to produce
metastable amorphous alloy films**

**Explore the metallurgical properties of
photodeposited films in comparison with
those prepared by other methods**

Laser CVD System

CO₂ Laser, 10.6 microns

Pulse energy : 0.5-1.0 j/pulse

Rep rate 0.5 Hz.

Deposition Chamber

Horizontal laminar flow

KCl windows

External lens

Gas System

Mixture of metal carbonyls & argon

Flow rate: 100-2000 scc/m

Pressure: 10-20 Torr.

Pressure and flow controlled

Exhaust hot scrubbed & cold trapped

**Entire gas handling and deposition
system in hood for safety**

DEPOSITION OF Ni FILMS

**Pyrolysis of mixture of Ni(CO)_4
and Argon by dielectric breakdown**

**Ar used as a buffer gas (98%) to
suppress powder formation**

**Metallic, spectrally reflecting films
over 1 x 2 cm area**

**Turbulence causes long residence time
of reacting gas and consequent
powder deposition**

ADHERENCE TESTS ON Ni FILMS

Glass substrates

Adherence is uniformly good

**Yield strengths: $1.0-2.5 \times 10^8$ dynes/cm²
 $1.5-3.5 \times 10^3$ psi**

COMPOSITIONAL ANALYSIS OF Ni FILMS

Auger depth profiles

Some carbon and oxygen incorporation

STRUCTURAL ANALYSIS OF Ni FILMS

X-ray diffraction on 0.2-1.0 micron films

Diffraction domain size < 50 Angstroms

Best fit is Ni & Ni₃C

Peak shift due to C incorporation

PK #	2-THETA	FWHM
1	44.1119	2.458
2	50.8826	3.690

PK #	2-THETA	FWHM
1 -	44.0551	1.840
2 -	44.4115	4.654
3 -	50.9183	3.819

Resistivity of Ni Films

$$\rho \approx 5 \times 10^{-3} \text{ ohm-cm}$$

Variance 50%

DEPOSITION OF Mo FILMS

**Pyrolysis of mixture of Mo(CO)_6
and Ar by dielectric breakdown**

**Ar used as buffer gas to
suppress powder formation**

**Metallic, spectrally reflecting films
over small areas**

Condensation of source gas on substrate

COMPOSITIONAL ANALYSIS OF Mo FILMS

Auger depth profiles

Substantial C & O incorporation

**Carbon to oxygen ratio suggests
condensation of metal carbonyl**

Deposition of W Films

**Pyrolysis of mixture of WF_6 ,
hydrogen, & argon by
dielectric breakdown**

1% WF_6 , 20% H_2 , 79% Ar

**Metallic films over
0.5 x 1.0 cm. area**

Copious powder formation

CONCLUSIONS

**Laser Breakdown Chemical Vapor Deposition
is a flexible process potentially adaptable
to many CVD systems**

**Demonstrated rapid solidification is
of interest in amorphous alloy formation**

**Compatibility of cold substrate with some
source gases may be a problem**

WORK IN PROGRESS

Expand range of demonstrated source materials and chemistries

Improve fluid dynamics to suppress powder formation

Improve laser-gas interaction to obtain larger area films

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