

is mostly a function of the laser scan speed. The nucleated line is so thin and discontinuous that it could not be used for any practical purpose. When the substrate is uniformly heated to 150 °C and exposed to DMTEA (reactant partial pressure 0.8 torr, reactor pressure 40 torr), Al starts to deposit selectively on the nucleated area. After 30 minutes of selective deposition by thermal CVD, the thickness of the fully developed line has reached 1 µm as shown in Figure 4(c). The width of the line remains nearly the same as in nucleated state. Thus this technique may be used to write thick, narrow lines. The structure of the developed line is shown in the expanded picture, Figure 4(d).

#### SUMMARY

We have demonstrated pyrolytic laser CVD of high quality Al lines from dimethylsilane alone. The resulting Al deposits had no measurable O and C impurities, and the resistivity was about 1.5 times that of bulk Al. Deposition rates were strongly dependent on the nature of the substrate, suggesting that nucleation was a critical element in the deposition process. The growth rates on Pt and Au surfaces were higher than those on Si. This difference in growth rates was exploited in a two step fast writing process - laser nucleation followed by selective growth by thermal CVD.

#### ACKNOWLEDGEMENT

This work was supported at M.I.T. by the National Science Foundation (CTS - 8920651 and 9001872) and at the Univ. of Minn. by the Center for Interfacial Engineering, a NSF Engineering Research Center.

#### REFERENCES

1. J. Han, K.F. Jensen, and J.A.T. Norman in *Theories and Low Energy Particles in Surface Processing*, (Mater. Res. Soc. Proc. 236, Boston, MA, 1991) pp. 97-104
2. M.G. Simmonds and W.L. Gladfelter in *Chemical Aspects of Chemical Vapor Deposition for Metallization*, edited by T.T. Kodas and M.J. Hampden-Smith (VCH Publishers, New York, in press)
3. T.F. Deuel, D.J. Ehrlich, and R.M. Osgood, *Appl. Phys. Lett.*, **35**, 175 (1979)
4. I.P. Herman, *Chem. Rev.*, **89**, 1323 (1989)
5. J.Y. Tsao and D.J. Ehrlich, *Appl. Phys. Lett.*, **45**, 617 (1984)
6. G.S. Higashi, *Appl. Surf. Sci.*, **43**, 6 (1989)
7. W.L. Gladfelter, D.C. Hoyd, and K.F. Jensen, *Chem. Mater.*, **1**, 339 (1989)
8. D.B. Beach, S.E. Blum, and F.K. LeGosse, *J. of Vac. Sci. Technol.*, **A7**, 3117 (1989)
9. T.H. Baum and C.E. Larson, *High Temp. Sci.*, **27**, 237 (1990)
10. M.G. Simmonds, E.C. Phillips, J. Huang, and W.L. Gladfelter, *Chemtronics*, **5**, 155 (1991)
11. Y.S. Liu and H.S. Cole, *Mater. Res. Soc. Symp. Proc.*, **154**, 1989 pp. 11-20
12. C. Chang, *J. Mat. Res.*, **2**, 697 (1987)
13. L.H. Dubois, B.R. Zegarski, C.-T. Kao, and R.Z. Nuzzo, *Surf. Sci.*, **236**, 77 (1990)
14. L.H. Dubois, H.R. Zegarski, M.E. Gross, and R.Z. Nuzzo, *Surf. Sci.*, **244**, 89 (1991)
15. P.G. Blauner, J.S. Ro, Y. Bui, and J. Melngaitis, *J. Vac. Sci. Technol.*, **B7**, 609 (1989)
16. M. Yamada, K. Nambu, and K. Yamamoto, *J. Appl. Phys.*, **57**, 965 (1985)
17. M. Lax, *Appl. Phys. Lett.*, **33**, 786 (1978)

### THE REDUCTION OF Cu<sup>II</sup> COMPOUNDS BY EXCIMER LASER IRRADIATION FOR COPPER METAL DEPOSITION

M.SUYS, B.MOFFAT, M.-H.BERNIER, R.ZOUIERDO, S.POULIN, M.MENIER and E.SACHER

Département de génie physique and Groupe des Couches Minces, Ecole Polytechnique de Montréal, Montréal, Québec, Canada, H3C 3A7.

#### ABSTRACT

The short (UV) wavelength and the large beam cross-section of excimer lasers are expected to permit high resolution projection patterning and, for this reason, excimer laser deposition of Cu from organometallic precursors appears to be an interesting alternative for metallization in ULSI circuits. Unfortunately, the photochemical decomposition of those precursors leads to strong carbon contamination of the deposits. However, the valence state of the Cu in such deposits is unknown. In this paper, the reduction of two Cu (II) compounds, Cu(hmac)<sub>2</sub> and Cu(hlac)<sub>2</sub>, under excimer laser irradiation in a hydrogen ambient is discussed. It is shown, with X-ray Photoelectron Spectroscopy, that, under our experimental conditions, Cu(hmac)<sub>2</sub> is reduced to a Cu (I) compound while some of the Cu(hlac)<sub>2</sub> appears to be reduced to the metallic state. Furthermore, reaction of the SiO<sub>2</sub> substrate with the carbon from the Cu(hmac)<sub>2</sub> precursor is observed.

#### INTRODUCTION

Copper is known to have a high electromigration resistance, low resistivity and high melting point compared to the commonly used materials for interconnections, Al and Al-Cu. However, since it diffuses rapidly in silicon [1], Cu is a good candidate material only for upper level metallization. To achieve this metallization, several groups have discussed the Chemical Vapor Deposition (CVD) of Cu, using a variety of Cu (I) and Cu (II) organometallic precursors [2-12] chosen for their volatility at moderate temperatures, thermal stability, ease of reduction to metallic Cu and volatile organic products, and low toxicity [13]. Given the difficulty in etching copper with submicronic resolution, selective processes are an attractive alternative. Laser CVD of Cu, using some of those same precursors, is such a selective process and has been reported by a few authors [14-25]. From those reports, it appears that a pyrolytic reduction of the precursors, using a visible laser beam, leads to pure Cu while a photochemical reduction, using a UV beam, leads to deposits strongly contaminated with carbon. However, the short wavelength of an excimer laser is advantageous in that it would permit large surface projection patterning of high resolution interconnections.

To achieve the deposition of a pure metallic Cu film with an excimer laser, it is therefore essential to gain a better understanding of the reaction actually taking place and to determine the nature of the non-volatile carbon species contaminating the deposits. We present here results obtained from the study of the reduction of two Cu (II) precursors, Cu(hlac)<sub>2</sub> and Cu(hmac)<sub>2</sub>, under KrF excimer laser irradiation at 248 nm using hydrogen as both the carrier and the reductant gas.



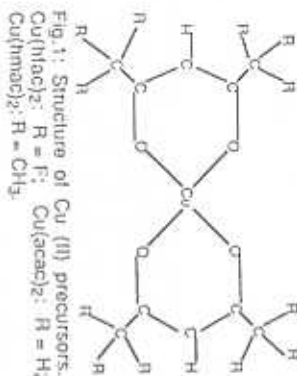


Fig. 1: Structure of Cu (II) precursors. Cu(hfac)<sub>2</sub>: R = F; Cu(acac)<sub>2</sub>: R = H; Cu(hmacc)<sub>2</sub>: R = CH<sub>3</sub>.

Table 1: Typical experimental conditions for the deposition with Cu(hmacc)<sub>2</sub>

Krf excimer laser:
λ = 248 nm
pulse rate: 10 Hz
number of pulses: up to 100000
energy density: ~100 mJ/cm <sup>2</sup>
Deposition conditions:
base pressure: 10 <sup>-3</sup> torr
precursor temperature: 50-80 °C
H <sub>2</sub> flow: 20-80 sccm
operating pressure: 2-10 torr

## EXPERIMENTAL

The oximer laser (Lumonics TE-8815) was operated with a Krf gas mixture emitting at 248 nm, and at a typical repetition rate of 10 Hz. The energy reflected off a quartz window was measured by a Gentec ED-200 Joulemeter to determine the energy density incident on the substrate. After a slight focusing, the beam reached the substrate by passing through a UV-grade fused silica window.

The two precursors, copper (II) bis-hexafluoroacetylacetonate (Cu(hfac)<sub>2</sub>) and copper (II) bis-hexamethylacetylacetonate (Cu(hmacc)<sub>2</sub>) were purchased from Strem Chemicals. The structure of such compounds is illustrated in Fig. 1, where we can see that only the group in the meta position varies from one precursor to the other. A small quantity of the desired precursor was transferred to a chamber which could then be heated to a stable temperature. Short exposure to air was unavoidable during the loading of the precursor, and the formation of hydrates at the surface of the exposed Cu(hfac)<sub>2</sub> is possible. Nevertheless, previous reports suggest that this does not affect the purity of the deposit but, rather, the deposition rate [5,12], which is not a concern of this study. Hydration of the Cu(hmacc)<sub>2</sub> is not expected, based on the data given by the manufacturer indicating that this material is air and moisture-stable.

Films were deposited on a 0.6 μm thick plasma-grown SiO<sub>2</sub> layer over silicon. Substrates were first degassed in successive baths of hot trichloroethane, acetone and 2-propanol, rinsed in deionized water and dried in flowing N<sub>2</sub>. After insertion of the substrate into the stainless steel reaction cell, the system was purged with a continuous flow of argon and heated to the desired operating temperature to permit the removal of contaminants that entered the system during the transfer. It was then pumped to a base pressure of 10<sup>-3</sup> torr with a rotary mechanical pump. During the experiments, care was taken to heat all gas distribution pipes and the reaction cell to a slightly higher temperature than that of the solid precursor, to avoid condensation. Typical conditions for deposition with Cu(hmacc)<sub>2</sub> are given in table 1.

The shape of the deposits was examined with a Dektak profilometer and SEM. The composition of both the deposits and the solid precursors were studied by X-ray Photoelectron Spectroscopy (XPS) on a VG Escalab MKII, using the Mg Kα line (1253.6 eV). The samples were transferred in air to the preparation chamber of the spectrometer. The precursor powders were finely crushed and pressed into an indium sheet to permit their mounting on the sample holder; they were exposed very

briefly to air before entering the preparation chamber. All samples were degassed to a pressure of 10<sup>-6</sup> mbar before measurements.

## RESULTS AND DISCUSSION

Since both precursors absorb at 248 nm [16,25], there is no doubt that the photochemical reaction and its products have not yet been clearly identified, and it was our purpose, through the use of XPS analysis, to gain a better understanding of this UV laser-induced decomposition. To our knowledge, no reports have been made concerning the chemical state of the Cu in excimer laser-deposited films: is it metallic or in a higher valence state?

In order to identify the free and bonded chemical species in the deposits, it was first necessary to obtain XPS spectra of the pure solid precursors. Fig. 2 illustrates the Cu 2p binding energy region for the two precursors studied and for copper bis-acetylacetonate (Cu(acac)<sub>2</sub>), also purchased from Strem Chemicals. Although all three compounds are Cu (II), we note the absence of the typical Cu (II) shake-ups, originating from the d<sup>9</sup> electronic configuration of Cu<sup>2+</sup>, on the spectra of both Cu(hmacc)<sub>2</sub> and Cu(hfac)<sub>2</sub>. This can tentatively be explained by the inductive effect of the ligands shown in Fig. 1. It is known that the CH<sub>3</sub> group has a strong electron-donating effect that pushes electrons toward the Cu atom, giving it more of a d<sup>10</sup> configuration. Hydrogen has a similar inductive effect, although not as strong, so we can still detect shake-ups on the Cu(acac)<sub>2</sub> spectrum. Fluorine, on the other hand, has a strong electron-withdrawing effect, imparting a d<sup>9</sup> configuration (Cu (III)) to the Cu atom in Cu(hfac)<sub>2</sub>, thus explaining the absence of shake-ups in its spectrum.

As reported by others, the carbon contamination was high in all deposited films (C/Cu=13 for Cu(hmacc)<sub>2</sub> and C/Cu=8 for Cu(hfac)<sub>2</sub>), but it should be noted that the deposits obtained were always too thin and discontinuous to allow sputtering of the surface contaminants before XPS measurement. These contaminants originate from unreacted and partly-reacted species adsorbed on the film after laser exposure, and from air exposure during the transfer of the samples to the spectrometer. For these reasons, C, O and F (in the case of Cu(hfac)<sub>2</sub>) signals detected with XPS are believed to be greater than their actual concentrations in the bulk of the deposits. It was also noted, as reported by others [14], that all spots were surrounded by a thin halo. It is of interest to point out that some of the deposits show thick (3000 Å) island structures, consequent with previous reports that Cu deposition is enhanced on metallic surfaces [12]. Once Cu starts forming on the SiO<sub>2</sub> surface, it acts as a seed layer where further growth is promoted. The "films" are therefore constituted of areas (islands) with thick deposits and others where no germination has taken place.

The XPS Cu 2p<sub>3/2</sub> peak for typical laser-deposited films from the two precursors are shown on Fig. 3. We see that no shake-ups are detected (the small peak at higher binding energy being the Kα satellite of the 2p<sub>1/2</sub> peak), which is indicative that the laser and He exposure have reduced the initial nominal Cu (II) molecules to Cu(I) or metallic Cu. Calculated Auger parameters (α') reinforce this observation. It can also be seen that the Cu 2p<sub>3/2</sub> peak is much narrower in the case of the deposits made with Cu(hfac)<sub>2</sub>, as found for metallic Cu, suggesting that this molecule is more effectively reduced to metallic Cu under our experimental conditions.

One of the most interesting results revealed when one compares the C 1s and Si 2p spectra of the laser-deposited Cu(hmacc)<sub>2</sub> with that of the adsorbed Cu(hmacc)<sub>2</sub> (Fig. 4). In this latter case, only part of the sample was irradiated with the beam, but XPS measurements were made both on that region and the unirradiated region. It can be clearly seen that the laser exposure provoked a reaction between the SiO<sub>2</sub> substrate and the carbon from the precursor, resulting in a Si-C compound which appears as a peak at lower binding energy on the carbon XPS spectrum, and

as a corresponding peak, at lower energy than that of the  $\text{SiO}_2$ , on the silicon spectrum. Calculation of the area of the silicon carbide peaks gave a C/Si ratio very close to 1. Others have previously reported the formation of W-C from thermal MOCVD of Cu on tungsten with  $\text{Cu}(\text{hac})_2$  as the precursor [2], and the thin halo surrounding the laser induced deposits observed by Houle et al. [14] were said to be mostly composed of carbon. These results and ours indicate a reaction of the substrate with the precursor which contaminates the interface between the Cu metallization layer and the substrate, resulting, among other things, in poor contact resistivity with vias connected to the lower level interconnections.

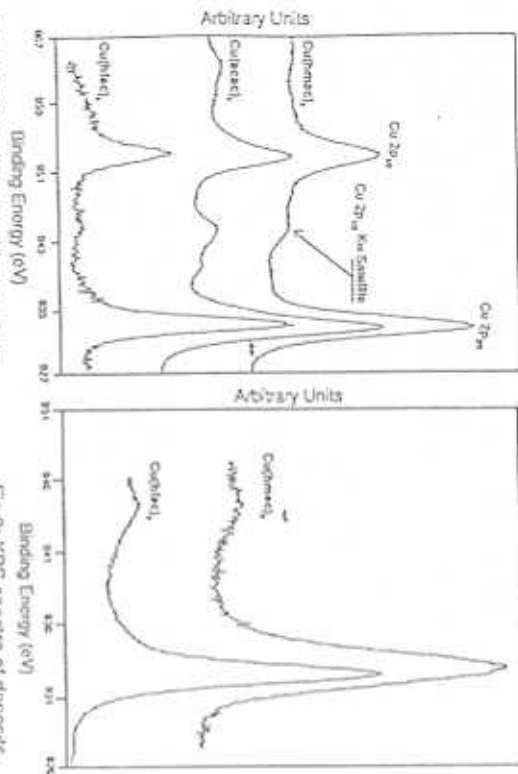


Fig. 2: XPS spectra of solid precursors.

Fig. 3: XPS spectra of deposits.

## CONCLUSION

We have studied the reduction of  $\text{Cu}(\text{hac})_2$  and  $\text{Cu}(\text{Imac})_2$  compounds under excimer laser irradiation in the presence of  $\text{H}_2$ . It appears from those results that the reaction taking place is enough to reduce these Cu (II) precursors to Cu (I), but full reduction to metallic Cu is only partially achieved under our experimental conditions. We have also shown the formation of SiC in the case of the  $\text{Cu}(\text{hac})_2$  precursor reacting with the substrate. Such a contamination of the interface between substrate and deposit would increase contact resistance in circuits and should therefore be eliminated, possibly by using an oxidant during the deposition.

Further redox studies are necessary if one hopes to deposit pure, contaminant-free, Cu films with an excimer laser. The problem of the thickness and uniformity of the deposits also needs to be addressed more thoroughly. The advent of new Cu (I) precursors might prove to be an interesting alternative for the photochemical generation of Cu thin films, since their decomposition to metallic Cu proceeds through a disproportionation reaction rather than a reduction.

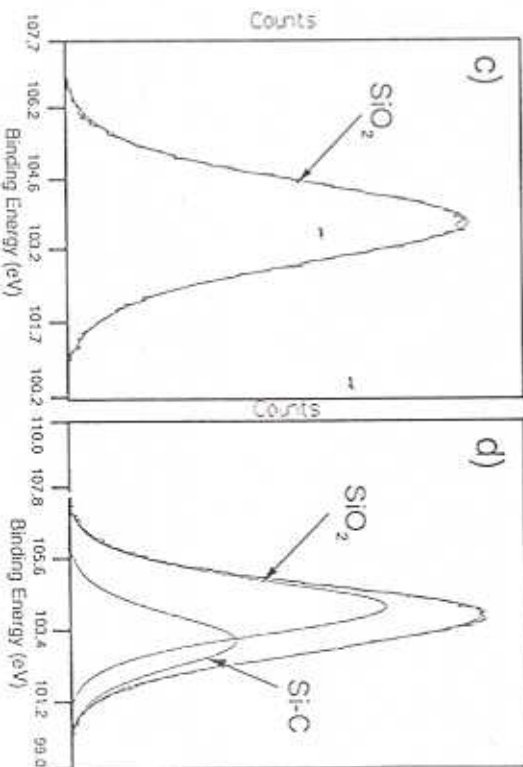
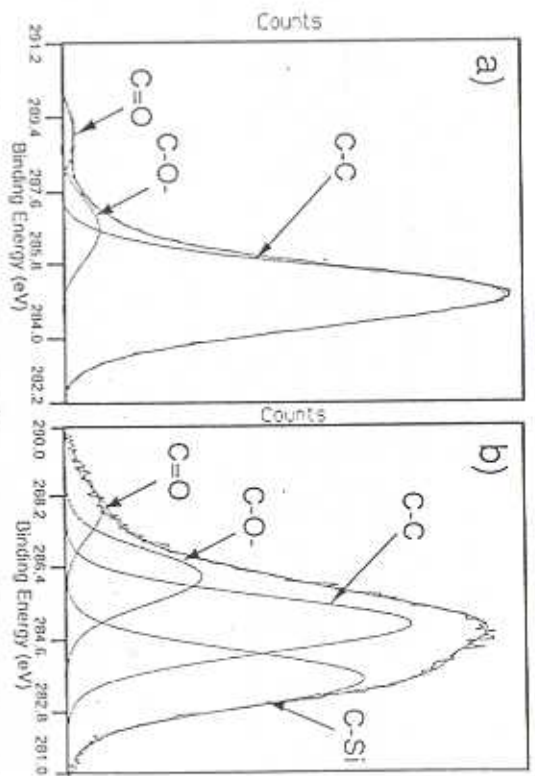


Fig. 4: XPS spectra of: a) C 1s, adsorbed  $\text{Cu}(\text{hac})_2$ ; b) C 1s, deposit  
c) Si 2p, adsorbed  $\text{Cu}(\text{hac})_2$ ; d) Si 2p, deposit.



## ACKNOWLEDGMENTS

One of us (M.S.) would like to thank the Fondation J.A. Bombardier for financial assistance. The authors would like to acknowledge the financial support of the Fonds pour la Formation de Chercheurs et l'Aide à la Recherche du Québec and of the Natural Science and Engineering Research Council of Canada. We also thank Mr. Mallock Tabbal and Mrs. Geneviève Bérque for their help with the XPS measurements, and Mr. Jean-Paul Lévesque for his technical assistance.

## REFERENCES

1. M.E. Gross and V.M. Donnelly, *Advanced Metallization for ULSI Applications*, edited by V.V.S. Rana, R.V. Joshi and LOhndomari (MRS Symp. Proc. ULSI-VII), 355 (1992)
2. T. Welton, J. Prasad, J.A. Kasper, R.D. Lujan, J. Fleming, and R.S. Blewett, *Advanced Metallization for ULSI Applications*, edited by V.V.S. Rana, R.V. Joshi and LOhndomari (MRS Symp. Proc. ULSI-VII), 303 (1992)
3. R.L. Van Hemert, L.D. Spondrove, and R.E. Stevens, *J. Electrochem. Soc.*, **112**, 1123 (1965)
4. L.H. Dubois, P.M. Jeffries, and G.S. Girolami, *Advanced Metallization for ULSI Applications*, edited by V.V.S. Rana, R.V. Joshi and LOhndomari (MRS Symp. Proc. ULSI-VII), 375 (1992)
5. N. Awaya and Y. Arita, *Advanced Metallization for ULSI Applications*, edited by V.V.S. Rana, R.V. Joshi and LOhndomari (MRS Symp. Proc. ULSI-VII), 345 (1992)
6. S.L. Cohen, M. Liehr, and S. Kasl, *Appl. Phys. Lett.*, **60**, 50 (1992)
7. H.K. Shin, K.M. Chi, A. Jain, M.J. Hampden-Smith, T.T. Kodas, M.F. Parfitt and J.D. Farr, *Advanced Metallization for ULSI Applications*, edited by V.V.S. Rana, R.V. Joshi and LOhndomari (MRS Symp. Proc. ULSI-VII), 403 (1992)
8. D.B. Beach, F.K. LeGoues, and C.-K. Hu, *Chem. Mater.*, **2**, 216 (1990)
9. D. Templo and A. Reisman, *J. Electrochem. Soc.*, **136**, 3525 (1989)
10. W.S. Hoar, Jr. and C.R. Caballero, *Adv. Mater. Opt. Electron.*, **1**, 59 (1992)
11. A. Jain, K.-M. Chi, T.T. Kodas, M.J. Hampden-Smith, J.D. Farr, and M.F. Parfitt, *Chem. Mater.*, **3**, 995 (1991)
12. B. Lecailler, B. Calpini, J.-M. Philippoz, and H. van den Bergh, *J. Appl. Phys.*, **72**, 2622 (1992)
13. M.E. Gross, *J. Electrochem. Soc.*, **138**, 2422 (1991)
14. F.A. Houle, R.J. Wilson, and T.H. Baum, *J. Vac. Sci. Technol. A*, **4**, 2452 (1986)
15. C.R. Jones, F.A. Houle, C.A. Kovac, and T.H. Baum, *Appl. Phys. Lett.*, **46**, 97 (1985)
16. D. Braichotte and H. van den Bergh, *Springer Series in Optical Science* **448**, 39 (1989)
17. R.J. Wilson and F.A. Houle, *Phys. Rev. Lett.*, **55**, 2184 (1985)
18. F.A. Houle, C.R. Jones, T. Baum, C. Pico and C.A. Kovac, *Appl. Phys. Lett.*, **46**, 204 (1985)
19. C.R. Moylan, T.H. Baum, and C.R. Jones, *Appl. Phys.*, **A40**, 1 (1986)
20. B. Markwalder, M. Widmer, D. Braichotte, and H. van den Bergh, *J. Appl. Phys.*, **65**, 2470 (1989)
21. D.-M. Mau, Z.-K. Jin, and Q.-Z. Qin, *J. Appl. Phys.*, **71**, 6111 (1992)
22. C.G. Dupuy, D.B. Beach, J.E. Hurel, Jr., and J.M. Jasinski, *Chem. Mater.*, **1**, 16 (1989)
23. J. Han, K.F. Jensen and J.A.T. Norman, *MRS Symp. Proc. Vol. 236*, 97 (1992)
24. J.-Y. Zhang and H. Esrom, *Appl. Surf. Sci.*, **54**, 465 (1992)
25. T. Ushida, K. Higashiyama, I. Hirabayashi, and S. Tanaka, *Jap. J. Appl. Phys.*, **30**, L35 (1991)

## LASER-INDUCED SELECTIVE COPPER DEPOSITION ON POLYIMIDES AND SEMICONDUCTORS

Seong-Don Hwang<sup>1</sup>, S. S. Kher<sup>2</sup>, J. T. Spencer<sup>2</sup> and P. A. Dowben<sup>1</sup>  
<sup>1</sup> Department of Physics, Syracuse University, Syracuse, New York, 13244-1130  
<sup>2</sup> Department of Chemistry, Syracuse University, Syracuse, New York, 13244-4100

## I. ABSTRACT

It has been demonstrated that copper can be selectively deposited on a variety of substrates including Teflon (polytetrafluoroethylene or PTFE), Kapton (polyimide resin), silicon and gallium arsenide from solution by photo-assisted initiated deposition. A copper containing solution was prepared from a mixture of copper(I) chloride (Cu<sub>2</sub>Cl<sub>2</sub>) and decaborane (B<sub>10</sub>H<sub>12</sub>) in diethyl ether and/or THF (tetrahydrofuran). The copper films were fabricated by ultraviolet photoolytic decomposition of copper chloride and polyphedral borane clusters. This liquid phase deposition has a gas-phase cluster analog that also results in copper deposition via pyrolysis. The approach of depositing metal thin films selectively by photolysis from solution is a novel and an underutilized approach to selective area deposition.

## II. INTRODUCTION

Laser-induced metal depositions on semiconductor surfaces have received much attention for possible use in electronic device fabrication. Also, metal/polyimide interfaces are important in microelectronic applications. Copper is one of the essential conducting metals in the microelectronic industry. Laser-induced copper deposition has recently been reported [1-14]. These investigations involve both UV laser photolysis [1-4] as well as laser pyrolysis [1,5-7] from the gas phase. A few laser assisted deposition studies of copper from solution have also been reported [8-14]. It has been demonstrated that copper (from solution of Cu<sub>2</sub>Cl<sub>2</sub> + B<sub>10</sub>H<sub>12</sub>) can be deposited on Teflon (polytetrafluoroethylene or PTFE), Kapton (polyimide resin), silicon and gallium arsenide substrates using a pulsed nitrogen laser.

In our work, copper was deposited on substrates via pulsed nitrogen laser irradiation of a copper solution in contact with the substrate surface. Copper deposition was found to occur via a UV photochemically induced reaction in solution between the substrate and the copper(I) chloride mediated by the borane cluster. The scheme is unique. Due primarily to its physical properties [15] decaborane (B<sub>10</sub>H<sub>12</sub>) was found to be the borane of choice. The postulated chemical reaction for deposition from this solution is:



The roll of the U.V. photolysis is that the extremely intense pulses can supply a sufficiently high density of incoming photons to initiate and sustain reaction (1). Since U.V. photolysis is not known as a thermal process, the localized light provides enough energy to deposit copper on plastic substrates such as Teflon and Kapton which have low thermal conductivities without heating the substrate. This may also be advantageous for certain applications where either high temperatures can result in for conventional alloying or otherwise.