Excimer Laser-Induced Deposition of Copper Films

Suryadevara V. Babu, Raghunath Padiyath, and Moses David
Dept. of Chemical Engineering, Center for Advanced Materials Processing, Clarkson University, Potsdam, NY 13699
Lois Walsh
Rome Air Development Center, Griffiss AFB, NY 13441

Rapid advances in the speed and integration of electronic devices and associated reliability concerns have resulted in an increasing demand for new and improved manufacturing processes and materials. High-performance interconnect materials are especially needed at the submicron device level. Copper is an excellent interconnect material because of its very low resistivity, high resistance to electromigration, and low cost (Jensen et al., 1984). However, aluminum has remained the interconnect material of choice at the device level until recently because of process difficulties associated with deposition and subsequent patterning of copper films (Saxena and Pramanik, 1990).

Sputtering (Susa et al., 1985), thermal (resistance-heated) evaporation (Osaka et al., 1985), electron-beam evaporation (Bunshah and Deshpandey, 1988), chemical vapor deposition (CVD) (Sherman, 1987), laser-induced chemical vapor deposition (LCVD) (Bäuerle, 1984), and laser-induced evaporation (Cheung and Sankur, 1988) are widely used for the deposition of films of pure elements as well as compound materials and superlattices. Thin film deposition by sputtering or evaporation requires high vacuum (typically $< 1.3 \times 10^{-4}$ Pa) and selective deposition is not possible with these techniques. CVD with organometallic precursors having high vapor pressure is carried out at temperatures exceeding the decomposition temperature of the precursor (typically > 300°C). Since copper-containing precursors with high vapor pressures are few in number, progress in depositing thin copper films with this technique has been slow. Only recently, CVD studies on Cu have been carried out using copper (II) hexafluoroacetylacetonate [Cu(II) $(\text{hfac})_2$] (Temple and Riesman (1989); Kaloyeros et al., 1990).

A number of studies have been conducted on laser-induced deposition of copper using both pulsed and continuous-wave lasers. Thin copper lines as well as films have been deposited from a paste of copper formate and glycerol using an excimer laser (Ritz et al., 1987), from copper formate films on silica and glass using an Ar^+ laser (Gupta and Jagannathan, 1987), and from copper acetate using an Nd:YAG laser (Harish et al., 1988). Conducting films and lines have also been obtained by decomposing Cu(II) $(\text{hfac})_2$ photothermally in the gas phase (Houle et al., 1985; Markwalder et al., 1989). However, the films were heavily contaminated with carbon. Similarly, films produced by RF plasma reduction of copper formate were rich in copper only at the surface; the bulk of the film was contaminated with carbon (Padiyath et al., 1990).

In the present study, a new technique for deposition of thin copper films was investigated. Copper was deposited by reactive ablation of copper formate using a partially focused excimer (KrF, λ = 248 nm) laser beam in a flowing hydrogen gas or a hydrogen plasma ambient. Copper was deposited on a substrate located in close proximity to the target copper formate. A key feature of this laser deposition process is the laser-induced decomposition of target material, followed by evaporation/sputtering of the products and reaction in the gas phase. In contrast to the conventional laser evaporation technique (Cheung and Sankur, 1988), organometallic compound, instead of pure copper target, was used to obtain the copper deposit. Furthermore, a much smaller fluence was adequate (the laser focus spot on the target was about 20 mm^2) to deposit copper starting from copper formate. The laser deposition technique described here is somewhat similar to the activated reactive evaporation (ARE) method (Bunshah and Raghuram, 1972) and reactive sputterings (RS) method (Al-Jaroudi et al., 1989), with a key difference that a hydrogen ambient was necessary to reduce the oxygen content in the deposited copper film and to improve its purity.

Experimental System and Methods

An excimer laser (Lambda Physik model EMG 101) operating at 248 nm (krypton–fluorine gas mixture) was used in the deposition studies. The laser was operated at a repetition rate of 10 Hz with an average pulse energy of 300 mJ, measured with a Gentec joulemeter. The beam was focused to a 20 mm^2 area on the copper formate target using a fused silica biconvex lens (f = 150 mm). The laser beam entered a parallel plate plasma reactor (PlasmaTherm model 730) through a fused

---

Correspondence concerning this paper should be addressed to S. V. Babu.

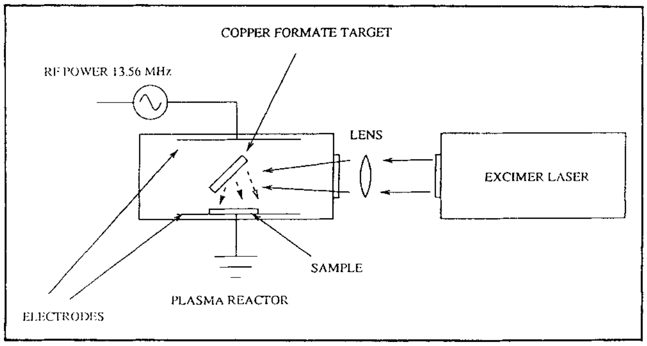

Figure 1. Experimental arrangement for laser-induced deposition process.

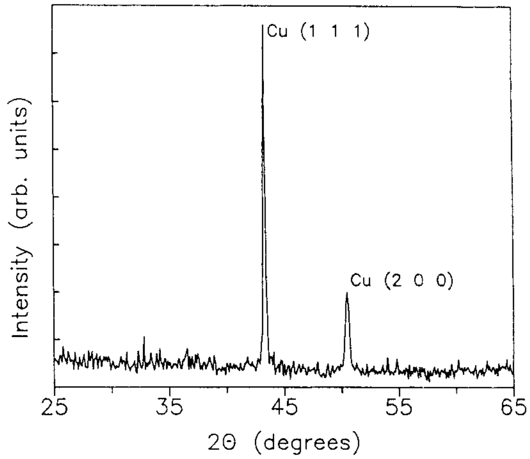

Figure 2. X-ray diffraction pattern of a copper film deposited by excimer laser reduction.

silica window. The arrangement is shown in Figure 1. RF power was supplied to the chamber through the upper electrode (0.28 m dia.), which was cooled by a water/ethylene glycol coolant mixture circulated from a heat exchanger. Heating of substrates placed on the lower, grounded electrode was achieved by a resistance heater and controller.

The copper formate target was placed at an angle of 45° to the incident beam. The substrate to be coated with copper film was placed making a small angle (20-40°) with the target, as shown in Figure 1. The reducing atmosphere of a hydrogen plasma or a hydrogen gas was maintained during the deposition. The discharge was sustained by 600 W RF power and a hydrogen flow rate in the range 35-500 sccm at 2 torr (266.6 Pa). The average pulse energy of the laser beam during the deposition process was held constant at 300 mJ, corresponding to a fluence of 1.5 J/cm^2 on the target. The deposition area on the substrate surface under these conditions was about 3 cm^2.

The deposited films were heat treated in the presence of a hydrogen plasma at 200°C for 30 min. The plasma was maintained with 200 sccm of hydrogen at a pressure of 3 torr (400 Pa) and 600 W RF power in a reactor that has been described earlier (David et al., 1990). All the samples were stored in a vacuum desiccator prior to any analysis. Film crystallinity was determined by an X-ray diffractometer (Siemens model D500). Elemental analysis and depth profiling of the deposited film was performed by Auger spectroscopy (Perkin Elmer model PHI 600 with a differentially pumped ion gun [04-303]). Atomic concentrations were determined from peak areas using sensitivity factors provided with the spectrometer by the manufacturer. A beam voltage of 3 kV and a beam current of 100 nA were used in Auger electron spectroscopy (AES) measurements while the ion gun was operated at 2 kV and 3 μA. Under these conditions, the sputter rate of the copper films was about 9 nm/min. Since AES is incapable of detecting hydrogen, the elemental composition of the films is reported on a "hydrogen-free" basis.

Results and Discussion

The copper films obtained by this process displayed excellent deposit morphology. The deposit thickness was found to be in the range of 0.2 to 0.5 μm. The resistivity of the films, as measured by a four-point probe, improved from 18 $\mu\Omega$cm for the as-deposited films to 5 $\mu\Omega$cm after heat treatment. This value is comparable to that reported for copper films deposited by other techniques (Gupta and Jagannathan, 1987; Temple and Riesman, 1989; Harish et al., 1988) but higher than the 1.9 $\mu\Omega$cm reported by Kaloyeros et al. (1990) when the substrate temperature was in the range of 300-450°C.

The X-ray diffractogram of a heat-treated copper film deposited by the laser reduction technique, shown in Figure 2, contains only the peaks of copper. The peak intensities increased after heat treatment. AES depth profiles of as-deposited and heat-treated copper films are shown in Figures 3 and 4, respectively. The as-deposited films contained small amounts of carbon and oxygen as impurities. Heat treatment in a hydrogen plasma eliminated most of the oxygen from the bulk of the film. The reduction in the carbon content as a result of heat treatment was not as appreciable as the reduction in oxygen content. Post-heat-treatment oxidation was responsible for the observed surface oxygen content.

Copper formate absorbs the 248 nm UV radiation of the excimer laser strongly (Ritz et al., 1987), which leads to dissociation. In the absence of a hydrogen atmosphere, it is possible to envision several reaction pathways for the dissociation of the formate:

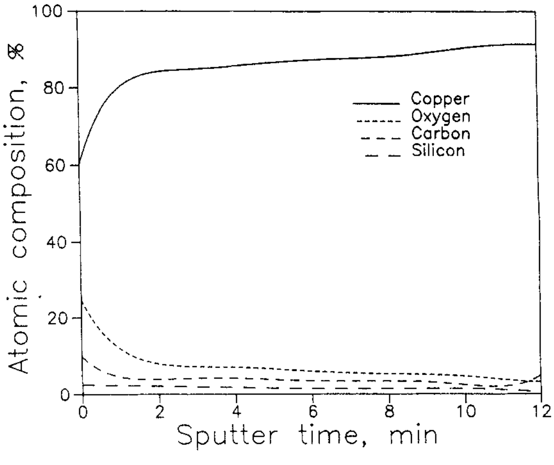

Figure 3. AES depth profile of an as-deposited copper film deposited by excimer laser reduction.

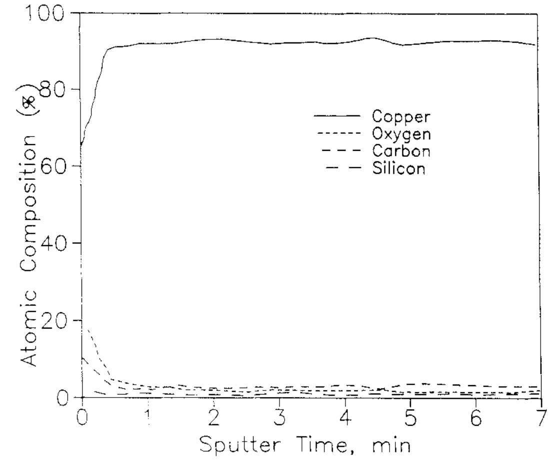

Figure 4. AES depth profile of a copper film deposited by excimer laser reduction and heat-treated for 30 min.

$$Cu(HCOO)_2 + h\nu \rightarrow Cu + 2\,CO_2 + H_2 \qquad (1)$$

$$Cu(HCOO)_2 + h\nu \rightarrow CuO + C + CO_2 + H_2O \qquad (2)$$

$$Cu(HCOO)_2 + h\nu \rightarrow Cu + CO + CO_2 + H_2O \qquad (3)$$

$$2\,Cu(HCOO)_2 + h\nu \rightarrow Cu_2O + 2\,CO_2 + 2CO + H_2O + H_2 \qquad (4)$$

Here $h\nu$ represents the 248 nm excimer laser photons. The photons may initiate a photochemical dissociation and/or the dissociation follows the heating of the film by the laser. In the presence of hydrogen, the reduction of the oxides of copper formed during reactions 2, 4, or both can occur in the laser plume or on the target surface according to the following reaction:

$$CuO, Cu_2O + H_2, H \rightarrow Cu + H_2O \qquad (5)$$

The dissociation of the hydrogen molecules themselves is perhaps catalyzed by the metallic copper or its oxides in the laser heated zone. The hydrogen atoms for this reduction are also available from the ambient when a hydrogen discharge is maintained. Thus, complete reduction of copper formate might be a two-step process. Alternatively, hydrogen may take part in the dissociation of the copper formate on the surface of the target under the influence of excimer laser pulses according to the following reactions:

$$Cu(HCOO)_2 + H_2, 2H + h\nu \rightarrow Cu + C + CO_2 + 2H_2O \qquad (6)$$

$$2\,Cu(HCOO)_2 + H_2, 2H + h\nu \rightarrow 2\,Cu + C + 2\,CO_2 + CO + 3H_2O \qquad (7)$$

It is not known what intermediate reaction steps, if any, may be involved in each of the reactions 1-7. Also it has not been determined if one or more of these reactions dominate. Analysis of gas phase products by mass spectrometry should be helpful in this connection.

In any case, it is quite likely that during the reduction of the copper formate, the composition of the target film changes to mostly Cu, CuO, Cu_2O, and C. The large power densities of the pulsed excimer laser beam lead to elevated surface temperatures (of the order of 1,000°C) (Kotecki and Herman, 1988), resulting in the evaporation of a large part of the products formed by reactions 1-7. While most of the decomposition products evaporate to deposit on the substrate, an extremely thin film of copper is left behind on the target due to product depletion to the vapor phase. The copper film remaining on the target does not conduct electrically. Interestingly enough, Houle et al. (1986) were able to deposit only very thin (< 50 nm) copper films from Cu $(hfac)_2$ using an excimer laser beam (λ = 248 nm) incident perpendicularly on a quartz or silicon substrate. However, they obtained much thicker (0.05 to 1.0 μm) films when an argon ion laser was used.

The deposition rates of the various vapor phase species generated by the laser pulse depend on their rates of nucleation, which in turn depend on supersaturation, among other things. Since the vapor pressure of carbon is much lower than that of copper and oxides of copper, evaporation of carbon is the least probable. However, volatilization of carbon can occur by the formation of high vapor pressure oxides of carbon. Hydrocarbon species having high vapor pressures may also form if sufficient reactive hydrogen is available. The plume generated by a laser beam targeted on copper formate will, therefore, comprise mostly Cu, CuO, Cu_2O, H_2O, CO_2, CO, C_mH_n, and H species. Of these, oxides of carbon, hydrocarbons, and water have relatively high vapor pressure and less supersaturation. Consequently, a cold substrate placed in the laser plume will be coated preferentially with copper and oxides of copper due to their higher supersaturation. Hence, films deposited by laser decomposition in the presence of hydrogen should consist of mostly Cu and O. The very small amount of carbon in the films confirms that a significant amount of carbon is being transformed into high vapor pressure oxides or hydrocarbons.

In order to study the role of the ambient during the deposition, films were deposited in the absence of the glow discharge. Since the plasma environment is richer in highly reactive species, the films deposited in plasma ambient were expected to display better quality. However, the films deposited with and without the plasma ambient displayed almost identical compositions, indicating very little influence of the plasma environment on the deposition process. Several plausible conclusions may be drawn based on this observation:

- The residence time of the evaporated species in the laser plume [estimated as 10^{-5} s based on the measured velocities of species ejected from polymer surfaces by excimer laser ablation and the spacing between the target and the substrate (Srinivasan, 1984)] is not sufficient for gas phase reactions to occur prior to the condensation on the substrate.
- The nature of the processes occurring during the laser pulse and afterward must be such that atomic hydrogen or excited hydrogen molecules are not essential for them.
- The reactivity of the carbon-containing species and the oxides of copper, generated during the laser pulse, with

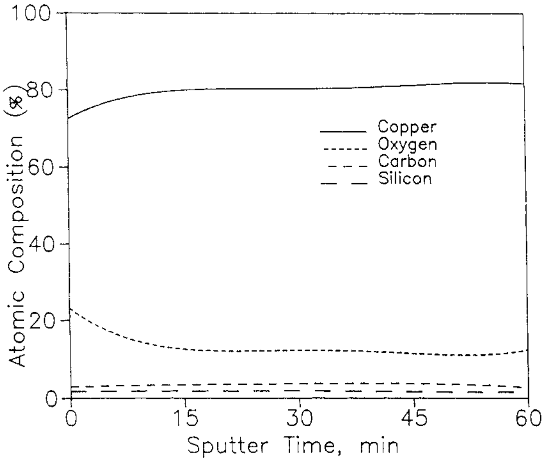

Figure 5. AES depth profile of a copper film deposited by excimer laser reduction in an argon ambient.

molecular hydrogen is high enough to facilitate their conversion into high vapor pressure species.

- Freshly formed oxides of copper (from reactions 2 and 4) are sufficiently energetic to be reduced by molecular hydrogen to atomic copper according to reaction 5, accounting for the low oxygen content in the films deposited in the absence of plasma.
- The minimal impact of the plasma discharge on the carbon concentration in the deposited films suggests that the formation of oxides of carbon, and not hydrocarbon formation, is the primary process for the consumption of carbon.

In-situ probing by optical emission spectroscopy or laser-induced fluorescence should facilitate the identification of exact reaction pathways and produce more evidence to support these conclusions.

To further understand the role of hydrogen during the deposition process, copper films were deposited in a pure argon atmosphere under conditions that were otherwise identical to those with hydrogen. The AES depth profile of such a film is shown in Figure 5. The resulting films contain similar amounts of carbon but a higher concentration of oxygen, and have much lower electrical conductivity. The similar amounts of carbon in the films deposited with and without hydrogen ambient supports the argument that volatilization of carbon occurs primarily due to the formation of oxides of carbon. Hydrocarbon formation, if any, should be minimal. The crystallographic orientation of the formate molecules in the target film must be such that the hydrogen and oxygen necessary for the volatilization of carbon are supplied by the dissociating formate molecules themselves. The films deposited in the absence of hydrogen have a higher concentration of oxygen, since, in the presence of argon the decomposition of formate resulting in CuO or Cu_2O is not succeeded or accompanied by reduction to metallic copper. Finally, the sputter time for the film deposited in the presence of argon is much higher, perhaps because the film is somewhat thicker and the sputter yield of CuO and Cu_2O is lower than that of Cu.

The laser deposition technique described here, when combined with laser patterning (Brannon, 1989) or other forms of patterning (Jensen et al., 1984), should be an efficient way to create submicron copper patterns over large areas. The ability to process uneven topography as well as temperature-sensitive substrates is one of the advantages of this technique. Furthermore, this deposition method should be more efficient than direct laser-writing of the pattern, especially for complex submicron patterns. The minimum feature size for copper metallization obtained so far by direct laser-writing is only about 5 microns. Preliminary experiments indicate that the laser/plasma reduction technique can be utilized to deposit other metals, such as silver and titanium, as well.

Acknowledgment

This research was supported in part by the Center for Advanced Materials Processing (CAMP) at Clarkson University through a grant from the New York State Science Foundation.

Literature Cited

Al-Jaroudi, M. Y., H. T. G. Hartzell, and S. E. Hornstrom, "Deposition of Titanium Nitride on Surface-Hardened Structural Steel by Reactive Magnetron Sputtering," *Thin Solid FIlms*, **182**, 153 (1989).

Bäuerle, D., "Laser-Induced Chemical Vapor Deposition," *Laser Processing and Diagnostics*, D. Bäuerle, ed., Springer-Verlag (1984).

Brannon, J. H., "Micropatterning of Surfaces by Excimer Laser Projection," *J. Vac. Sci. Technol.*, **B7**(5), 1064 (1989).

Bunshah, R. F., and C. Deshpandey, "Evaporation Processes," *MRS Bulletin*, **12**, 33 (1988).

Bunshah, R. F., and A. C. Raghuram, "Activated Reactive Evaporation for High Rate Deposition of Compounds," *J. Vac. Sci. Technol.*, **9**(6), 1385 (1972).

Cheung, J. T., and H. Sankur, "Growth of Thin Films by Laser-Induced Evaporation," *CRC Crit. Rev. Solid State Mat. Sci.*, **15**(1), 63 (1988).

David, M., S. V. Babu, and D. H. Rasmussen, "RF Plasma Synthesis of Amorphous AlN Powder and Films," *AIChE J.*, **36**, 871 (1990).

Gupta, A., and R. Jagannathan, "Direct Writing of Copper Lines from Copper Formate Film," *Appl. Phys. Lett.*, **51**, 2254 (1987).

Harish, C. M., V. Kumar, and A. Prabhakar, "Direct Writing of Copper Film Patterns by Laser-Induced Decomposition of Copper Acetate," *J. Electrochem. Soc.*, **135**, 2903 (1988).

Houle, F. A., C. R. Jones, T. Baum, C. Pico, and C. A. Kovak, "Laser Chemical Vapor Deposition of Copper," *Appl. Phys. Lett.*, **46**, 204, (1985).

Houle, F. A., R. J. Wilson, and T. H. Baum, "Surface Processes Leading to Carbon Contamination of Photochemically Deposited Copper Films," *J. Vac. Sci. Technol.*, **A4**(6), 2452 (1986).

Jensen, R. J., J. P. Cummings, and H. Vora, "Copper/Polyimide Materials System for High Performance Packaging," *IEEE Trans. Components, Hybrids, Manufac. Technol.*, **CHMT-7**, 384 (1984).

Kaloyeros, A. E., A. Feng, J. Garhart, K. C. Brooks, S. K. Ghosh, A. N. Saxena, and F. Luehrs, "Low-Temperature Metal-Organic Chemical Vapor Deposition (LTMOCVD) of Device-Quality Copper Films for Microelectronic Applications," *J. Electron. Mater.*, **19**, 271 (1990).

Kotecki, D. E., and I. P. Herman, "A Real-Time Monte Carlo Simulation of Thin Film Nucleation in Localized-Laser Chemical Vapor Deposition," *J. Appl. Phys.*, **64**(10), 4920 (1988).

Markwalder, B., M. Wichner, D. Braichotte, and H. van den Bergh, "High-Speed Laser Chemical Vapor Deposition of Copper: A Search for Optimum Conditions," *J. Appl. Phys.*, **65**, 2470 (1989).

Osaka, T., I. Koiwa, and L. G. Svendsen, "Behavior of Evaporated Palladium Catalyst for Electroless Nickel Phosphorus Film Formation," *J. Electrochem. Soc.*, **132**, 2081 (1985).

Padiyath, R., M. David, and S. V. Babu, "RF Plasma Induced Deposition of Copper Films on Polymer Surfaces," Paper 50, *Proc. 177th Meet. Electrochem. Soc.*, Montreal (1990).

Ritz, M., S. V. Babu, V. Srinivasan, and R. C. Patel, in *Photon, Beam and Plasma Stimulated Processes at Surfaces*, V. M. Donnelly et al., eds., Mat. Res. Soc., Pittsburg, **75**, 433 (1987).

Saxena, A. N., and D. Pramanik, "Aluminum Metallization for ULSI," *Solid State Technol.*, **33**(3), 73 (1990).

Sherman, A., *Chemical Vapor Deposition for Microelectronics*, Noyes, Park Ridge, NJ (1987).

Srinivasan, R., "Ultraviolet Laser Ablation of Organic Polymer Films," *Laser Processing and Diagnostics*, D. Bäuerle, ed., Springer-Verlag (1984).

Susa, N., S. Ando, and S. Adachi, "Properties of Tungsten Film Deposited on GaAs by RF Magnetron Sputtering," *J. Electrochem. Soc.*, **132**, 2245 (1985).

Temple, D., and A. Reisman, "Chemical Vapor Deposition of Copper from Copper(II) Hexafluoroacetylacetonate," *J. Electrochem. Soc.*, **136**, 3525 (1989).

Manuscript received July 2, 1990, and revision received Aug. 27, 1990.