

EXCIMER LASER CHEMICAL VAPOR DEPOSITION OF COPPER FROM Cu(hfac)(TMVS)

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ABSTRACT

Copper films have been deposited on TiN and SiO₂ substrates from the KrF excimer laser assisted decomposition of Cu(hfac)(TMVS). XPS measurements show that the precursor is reduced to metallic copper, with the formation at the surface of some copper fluoride at high laser energy density (51 mJ/cm²). Using H₂ as the carrier gas and a low laser energy density, very uniform, shiny metal-like films were deposited with grain size of 50 to 100 nm and a Cu/C atomic ratio of 4.35.

1. INTRODUCTION

Since copper has been proposed as a replacement of aluminum and aluminum based alloys for the fabrication of ultra large scale integration (ULSI) interconnects, great interest in the field of copper deposition has spread. Many techniques including partially ionized beams [1], ionized cluster beam [2], electroless deposition [3], chemical vapor deposition (CVD) [4], plasma enhanced CVD (PECVD) [5] and laser induced CVD (LCVD) [6,7], have been further developed. Research has been particularly active in the CVD of copper, with a number of new precursors being introduced in the last few years [8-10]. Pure copper deposits, with resistivities approaching that of bulk copper, have been obtained with this technique [4], and selectivity has been demonstrated in some cases [8,11]. However, the control of this selectivity depends greatly on the experimental conditions, namely on the quality and the cleanliness of the surface on which copper is deposited [4,12].

A technique which could deposit copper in a selective manner, without dependence on surface quality, would be quite attractive. Excimer laser induced CVD is one such technique where the desired interconnects pattern can be projected on the surface with the appropriate mask and lenses [13]. Large area excimer laser CVD from various Cu(II) precursors has been studied for Cu deposition by various groups [6,14]. Poor results have been obtained up to now, since it appeared that undesired photochemical reactions were taking place, incorporating large quantities of carbon in the deposits. Although the use of alcohol as coreductant was shown to drastically decrease the impurity concentration [14], still the deposits were far from being pure enough for ULSI interconnect applications. However, these experiments were all performed before new Cu(I) precursors, easier to reduce, were introduced and successfully used in conventional CVD. We have performed the excimer laser-induced CVD of copper using one of those new precursors, Copper^I(hexafluoroacetylacetonate)trimethylvinylsilane (Cu(hfac)(TMVS)), and we show that the deposits are much purer than in the case of Cu(II) precursors. In this paper, the emphasis is on the deposition and characterization of large area Cu films and on the understanding of the process leading to deposition.

2. EXPERIMENTAL

The system for the laser assisted deposition of copper is shown in figure 1. The excimer laser (Lumonics TE-861S) is operated with a KrF gas mixture emitting in deep UV at 248 nm. The laser beam is incident perpendicularly on the substrate. Since Cu(hfac)(TMVS) is liquid at room temperature, it is placed in a bubbler and heated to 45 °C, giving a vapor pressure of about 1 torr. The rest of the piping, as well as the reactor, are heated to 60 °C to avoid condensation. The precursor is carried to the deposition chamber by Ar or H₂. To avoid any deposition on the window, it is purged with an Ar flow before and during laser exposure. The system is connected to a vacuum transfer rod by which the samples may be transferred without air exposure to an X-ray photoelectron spectrometer.

Cu was deposited on TiN (80 nm) on Si, and SiO₂ (600 nm) on Si. TiN was used as it is a good barrier layer, preventing copper diffusion into Si. SiO₂ was used for resistivity measurements, as well as to study the deposition selectivity on different substrates. Samples were degreased then dried at 115 °C for 30 minutes before experiments. The reaction chamber was pumped to a base pressure of 10⁻⁷ torr. The deposition was done at a laser repetition rate of 20 Hz. The laser beam was unfocused or slightly focused, giving energy densities ranging from 9 to 51 mJ/cm² at the substrate. The number of pulses was varied from 1000 to 20 000. In addition to 15 sccm of Ar purge gas at the window, 28 sccm of Ar or H₂ carrier gas was used, giving total pressures in the reaction chamber of 6.0 and 5.5 torr, respectively.

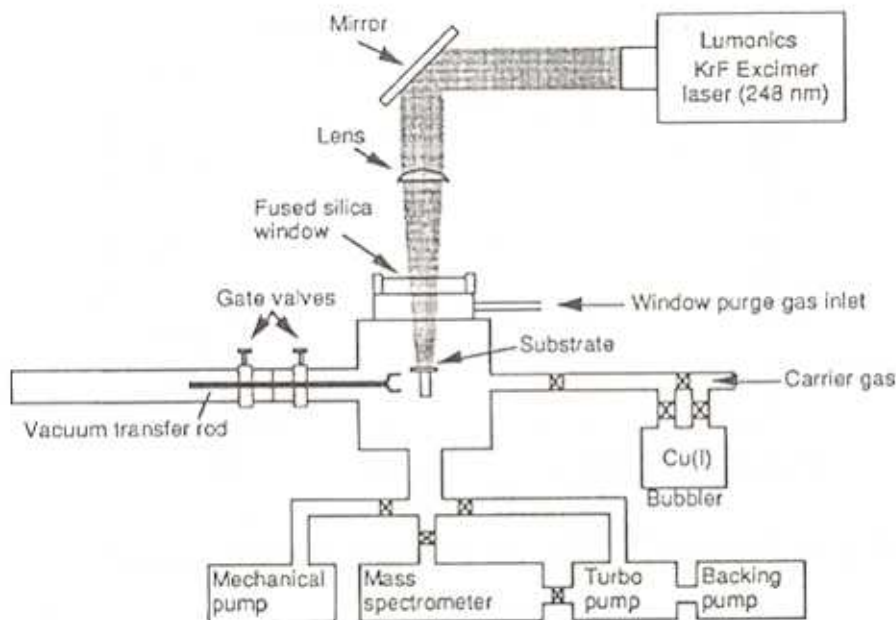


Figure 1. Deposition system.

3. PROCESS AND FILM CHARACTERISTICS

A number of laser CVD experiments were performed on TiN, and the resulting deposits were studied with various techniques: optical, electronic (SEM) and atomic force (AFM) microscopy, profilometry, x-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES). Adhesive tape tests were also performed on all samples. In this section, we present the results obtained on three different aspects: growth rate, composition and morphology. These characteristics were found to vary significantly with the studied experimental conditions.

3.1 Growth rate

The thickness of the copper films was measured with a Dektak profilometer, and was studied as a function of both the number of laser pulses and the energy density incident on the substrate. Figure 2 shows the variation of the film thickness with the number of pulses, using Ar as the carrier gas, and at an average energy density of 51 mJ/cm². These thicknesses were measured at the center of the deposits, where the energy density is the largest. It can clearly be seen that two growth regimes are obtained: until about 4000 pulses, the film grows at an average rate of 0.15 Å/pulse, while for a higher number of pulses, this rate goes up to 0.70 Å/pulse. For a laser repetition rate of 20 Hz, these values correspond respectively to 3 Å/s and 14 Å/s. This transition between two deposition rates was seen to occur at the various energy densities studied, but could not be related to a particular thickness or number

of pulses. For instance, at an energy density of 18 mJ/cm^2 , the transition was observed after about 10 000 laser pulses. Furthermore, the films grown at low energy densities, without focusing the laser beam, have a very uniform thickness compared to the ones grown with a high fluence, focused laser beam, for which thickness varies significantly along the diameter of the deposits. It should also be noted that the use of hydrogen appeared to enhance the growth rate, but a more deliberate study should be performed to quantify this phenomenon.

These two growth regimes not only influence the deposition rate, but seem to affect both the composition and morphology of the films. Further reference to them will appear in the following sections under the "low growth rate" and "high growth rate" appellations.

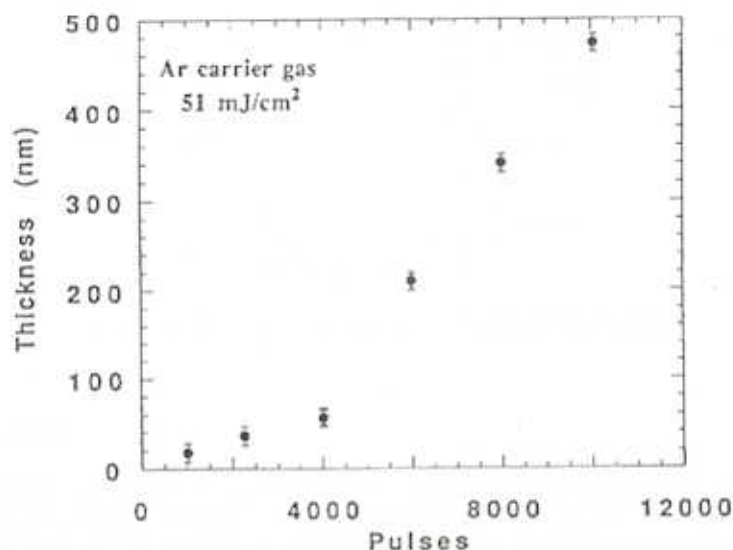


Figure 2. Thickness as a function of the number of laser pulses.

3.2 Composition

The vacuum transfer rod mentioned previously permitted the XPS study of a number of deposits without any air exposure, thus avoiding any oxidation or external contamination of the films. The surface of both as-deposited and Ar^+ sputtered samples was examined, providing information about surface and bulk composition of the deposits.

3.2.1 Surface composition

Figure 3 shows the $\text{Cu } 2p^{3/2}$ spectra of various deposits. The binding energy position of the main peak and its small full width at half maximum are indicative of metallic copper. We therefore conclude that complete reduction of $\text{Cu}(\text{hfac})(\text{TMVS})$ was achieved. However, large quantities of carbon, oxygen and fluorine were also detected at the surface. These elements originate from unreacted and/or partly-reacted reduction products still adsorbed on the surface after laser exposure. No silicon was detected, indicating the absence of TMVS on the surface. This was expected, since a rapid dissociative desorption of the TMVS ligand is observed upon the adsorption of $\text{Cu}(\text{hfac})(\text{TMVS})$, even at low temperatures [15].

We can also see on figure 3 that, when using high energy densities, some copper at the surface is bonded to fluorine. This is indicated by the presence of a secondary peak at higher binding energy, which is what we expect since fluorine is more electronegative than copper. Although not appearing on the figure, shake-up peaks, characteristic of copper in its $\text{Cu}(\text{II})$ oxidation state, were also observed at still higher binding energies. Since the relative intensity of XPS peaks is proportional to the relative concentration of the corresponding molecule or element, we note that the use of hydrogen as the carrier gas, and more importantly the lowering of the energy density, inhibit the formation of this copper fluoride. The rest of the fluorine present at the surface was found to be bonded to carbon, forming various CF_x . Carbon was detected under various forms, consisting of CF_x , CO and C.

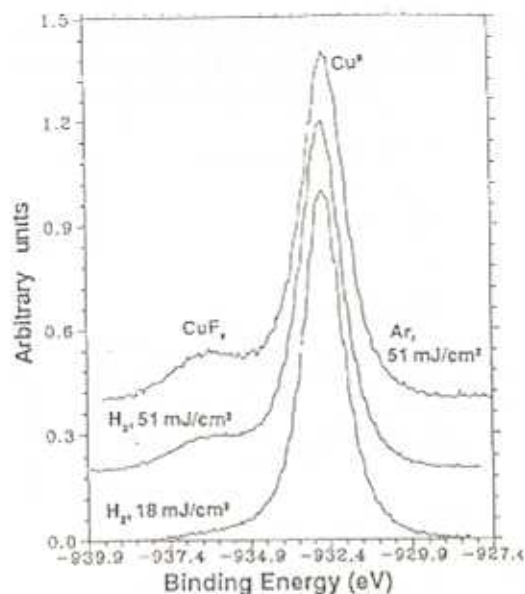


Figure 3. Cu $2p^{3/2}$ spectra for various deposits.

3.2.2 Bulk composition

After sputtering the samples with Ar⁺ (2 keV, slightly focused ion beam), it was found that most of the impurities are only present at the surface. In the bulk, oxygen is not detected, while fluorine and carbon concentrations are reduced by a factor of ten compared with their surface values. Table I lists the various atomic ratios evaluated from analysis of the XPS spectra. Those results were also supported by AES profiling.

sputtered samples	Cu/C	Cu/F
Ar, 51 mJ/cm ² , 10 000 pulses	1.69	3.57
H ₂ , 51 mJ/cm ² , 10 000 pulses	2.17	3.57
H ₂ , 9 mJ/cm ² , 15 000 pulses	4.35	15.0

Table I. Atomic ratios for various deposits.

Using hydrogen and operating in the low growth rate regime result in films with less carbon and fluorine incorporation. Although the impurity levels are still non-negligible, the obtained ratios represent an extremely significant improvement when compared to previous results of excimer laser-induced CVD of copper, using Cu (II) precursors[6,14]. In all those cases, films could not be grown thick and uniform enough to allow sputtering, and deposits consisted mostly of carbon and, to a lesser extent, of non-reduced copper. The results reported here, however, clearly show that although some carbon and fluorine are still present in the film, copper is completely reduced and found only in its metallic state.

In order to identify the nature of the carbon and fluorine species incorporated in the film, XPS spectra of the C 1s peak were taken on various samples, and are shown on figure 4. When comparing the spectrum obtained from the adsorbed precursor on a TiN substrate and the one from a deposit, we conclude that the laser exposure has broken some of the CF₃ present in the precursor molecule to form various CF_x, indicated by XPS peaks located at binding energies intermediate to those of CF₃ and C. However, after sputtering, we find that almost no carbon bonded to fluorine remains. Also, after comparing this sputtered sample's carbon spectrum with the one of the same sample after air exposure, we note that, in the bulk, carbon is not bonded with oxygen. Indeed, the CO XPS peak, quite important on the spectra of the air exposed sample, cannot be seen on the spectra of the sputtered sample. It is of interest to note that, although the concentration of carbon in the bulk of the film is influenced by the experimental conditions (see Table I), no variation is observed in the nature of the carbon containing species from one sample to another.

The bulk of the film is therefore composed mostly of metallic copper with some carbon and, to a lesser degree, carbon fluoride. Hydrogen, possibly bonded to carbon, could also be present in the deposits, but cannot be detected by XPS.

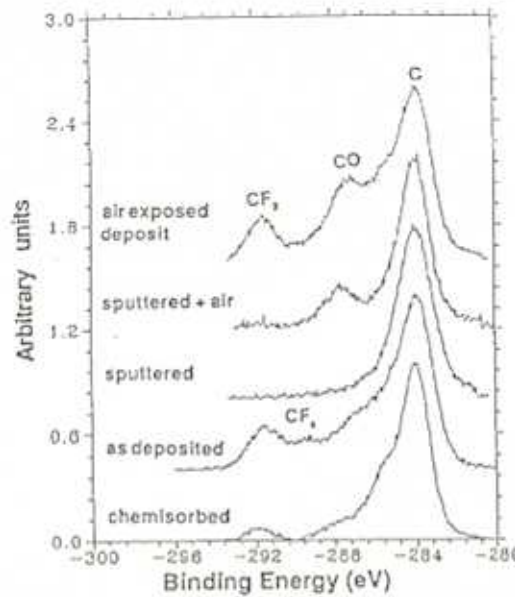
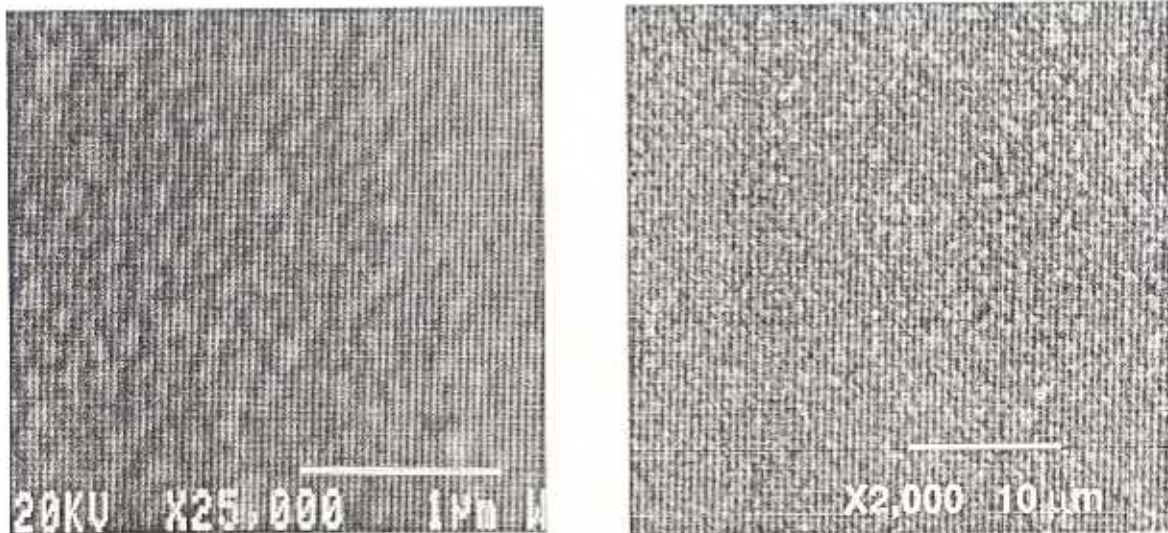


Figure 4. C 1s spectra for various deposits.

3.3 Morphology, adhesion and resistivity

Although both composition and growth rate were shown to vary significantly with experimental conditions, variations in morphology were perhaps the most noticeable. While films grown at low energy densities appeared as shiny copper mirrors surrounded by a dark, narrow halo, the ones grown at high energy densities consisted of many different concentric areas. These deposits have central regions, where thickness is greatest, with matte appearances. The differences between these various regions were also observed with microscopy techniques. In the shiny copper region, the surface is very uniform, and grain size measured by SEM and AFM is between 50-100 nm (figure 5a). In the matte regions, the surface is much rougher and the grains are larger. This difference in grain size is clearly apparent in figure 5.



Figures 5. a) SEM micrograph of the central zone of a copper film deposited at low energy density. b) Optical micrograph of the central zone of a copper film deposited at high energy density.

The deposits on SiO₂ had the same appearance as the ones on TiN. However, no dark halo was seen to form around the films. Preliminary four-point and two-point probe resistivity measurements were performed on the samples and a resistivity of 41 $\mu\Omega\text{-cm}$ was obtained. The most conductive deposits, made at low energy densities, were also relatively thin because of the low growth rate. Therefore, good conductive contact was hard to establish during measurements and our results probably include high contact resistance effects. Therefore, the actual resistivity of the film is expected to be smaller than the measured value. To our knowledge, this is the first reported resistivity value for an excimer laser-induced CVD grown copper film. Further measurements, with thicker deposits are currently under way.

Deposits on TiN were found to adhere well to the substrate. Only a very thin removal of some of the rougher regions was observed for a few samples after the adhesion test. The rougher regions of the films grown on SiO₂, however, did not adhere well and were easily stripped off, leaving behind a smoother surface.

4. DISCUSSION

In UV laser-induced CVD, the identification of the mechanism responsible for the deposition is always problematic when the beam is incident on the substrate (perpendicular geometry). Deposition can be induced either (i) photolytically, with the photons directly breaking bonds of the precursor molecule adsorbed on the substrate surface or in the gas phase, or (ii) pyrolytically, with the substrate heating up under laser exposure. Both processes can be (and often are) present at the same time. In this case, photochemical mechanisms cannot be ruled out because the estimated temperature rise induced in TiN by the laser could be sufficient for thermal CVD to occur. However, two strong indications that photolytical processes are taking place are found. Firstly, the fact that deposits were grown on the quartz window, when performing experiments without any purge gas, strongly indicates photolytical decomposition, since the window is UV transparent and therefore cannot heat up under excimer laser exposure. Secondly, a rough evaluation of the temperature rise of TiN and that of copper under our laser exposure conditions shows that TiN reaches a higher temperature, due to its lower thermal conductivity. Therefore, if the reaction was entirely pyrolytic, it would be expected that the growth rate when depositing directly on TiN (i.e.: for the first few thousand laser pulses) would be higher than the growth rate when depositing on an already formed copper film (i.e.: for the next few thousand laser pulses). However, we could clearly see on figure 2 that this is not the case, the high growth rate regime taking place after a certain thickness of copper is already deposited. A photolytical process must then be occurring. The relative importance of the two mechanisms cannot yet be determined, but further experimentation, using very low energy densities are under way. Under these conditions, the temperature rise of the substrate will not be sufficient to induce the thermal CVD of Cu(hfac)(TMVS), which occurs at temperatures as low as 120°C [8].

5. CONCLUSIONS

Metallic copper has been deposited on TiN and SiO₂ by excimer laser-induced CVD using Cu(hfac)(TMVS) as the precursor. The purity level obtained is much higher than those reported for the excimer laser-induced CVD of copper using Cu(II) precursors. However some carbon and fluorine are still incorporated in the deposits. Two growth regimes have been identified: at high energy densities, the growth rate and impurity incorporation are high, and the grains are large, while at low energy densities the growth rate and impurity incorporation are lower and the grains smaller. The use of hydrogen as carrier gas instead of argon is shown to further increase the purity of the deposits. Preliminary resistivity measurements made on deposits on SiO₂ yield a value of 41 $\mu\Omega\text{-cm}$.

Although this is still not usable for ULSI interconnect applications, the optimization of the deposition parameters is far from complete. Furthermore, the use of ethanol as a coreductant during the deposition might improve the purity of the films, as it is shown to do in other cases of UV-induced CVD of copper [14].

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ACKNOWLEDGMENTS

We thank Dr. J.A.T. Norman of the Schumacher Company for providing the Cu(hfac)(TMVS), Mrs. Marie-Hélène Bernier for SEM, Mrs. Isabelle Bacon for AES, Mr. Jean-Paul Lévesque for technical assistance and Mrs. Suzie Poulin for valuable discussions on XPS analysis. We would like to thank the Fondation J.A. Bombardier for financial assistance. We would also like to acknowledge the financial support of the Natural Sciences and Engineering Research Council of Canada (NSERC).

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