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EXCIMER LASER-INDUCED DEPOSITION OF COPPER FROM Cu(hfac)(TMVS)

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ABSTRACT

Copper films have been deposited on TiN and fluoropolymer substrates from the KrF excimer laser assisted decomposition of Cu(hfac)(TMVS). Using H_2 as the carrier gas, very uniform, shiny metal-like films were deposited with grain size of 50 to 100 nm. XPS measurements show that the precursor is reduced to metallic copper, and that a Cu/C atomic ratio of up to 17 is obtained.

INTRODUCTION

Copper has been proposed as a replacement for aluminum and aluminum-based alloys in the fabrication of ultra large scale integration (ULSI) interconnects. In the last few years, various techniques for the deposition of Cu have been investigated [1]. Among these, the chemical vapor deposition (CVD) using Cu(I) organometallic precursors has achieved good results, permitting the deposition of thin copper films having near bulk resistivities [2]. However, Cu is difficult to pattern with submicronic resolution. Therefore, in order to obtain the desired interconnects array, the deposition has to be done in a selective way. This is difficult to achieve since the control of the selectivity in thermal CVD depends greatly on the experimental conditions, as well as on the quality of the surface on which the copper is deposited [3,4].

A technique which deposits copper in a selective manner, without dependence on surface quality, would therefore be quite attractive. Laser-induced CVD is one such technique where the desired interconnects pattern can be projected on the surface with the appropriate mask and lenses (projection patterning) [5] or written by moving the sample under the focused laser beam (direct writing) [6]. The laser direct writing of Cu, using an Ar^{+} laser, has been recently demonstrated by Han et al. [7] but such a process, even if appropriate for circuit repair, is too slow for circuit production. Furthermore, submicronic resolution is difficult to achieve with this technique.

Excimer laser CVD of copper from various Cu(II) precursors has been studied by several groups [8,9]. Poor results have been obtained up to now showing the incorporation of very large quantities of carbon in the deposits. We have performed the excimer laser-induced CVD of copper using Copper^{I}(hexafluoroacetylacetonate)(trimethylvinylsilane) (Cu(hfac)(TMVS)), and we show here that these deposits are much purer than in the case of Cu(II) precursors. In this paper, we emphasize the deposition and characterization of unpatterned Cu films and the understanding of the process leading to deposition.

EXPERIMENTAL

The system for the laser-assisted deposition of copper has been described elsewhere [10]. The excimer laser (Lumonics TE-861S) was operated with a KrF gas mixture, emitting in the deep UV at 248 nm. The laser beam was incident perpendicularly to the substrate. Since Cu(hfac)(TMVS) is a liquid at room temperature, it was placed in a bubbler and heated to 45°C, giving a vapor pressure of about 0.5 torr. The rest of the tubing, as well as the reactor, were heated to 60°C to avoid condensation of the precursor. The substrate temperature can be varied from room temperature to 200°C, but was always kept bellow 120°C during the experiments to avoid thermal deposition. The precursor was carried to the deposition chamber by a flow of H_2 (20-100 sccm). To

avoid any deposition on the window, it was purged with an Ar flow (20 sccm) before and during laser exposure. The system was connected to a vacuum transfer apparatus with which the samples were transferred, without air exposure, to an X-ray photoelectron spectrometer.

Cu was deposited on TiN (80 nm) deposited on Si, and on Teflon® PFA fluoropolymer samples with thicknesses 125 and 250 µm. TiN was used because of its a good barrier properties, preventing copper diffusion into Si. Fluoropolymers were used as they are expected to be the low-κ dielectrics used in future microelectronic devices. Prior to the deposition, samples were degreased and dried at 115°C for 30 minutes. The reaction chamber was evacuated to a base pressure of 10^{-7} torr. The deposition was carried out at a laser repetition rate of 20 Hz. The laser beam was unfocused, giving energy densities at the substrate ranging from 9 to 31 mJ/cm^2 .

PROCESS AND FILM CHARACTERIZATION

Several laser CVD experiments were performed on TiN and fluoropolymers, 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). In this section, we present the results obtained on three different aspects: morphology, growth rate, and composition.

Films grown under various conditions on TiN or fluoropolymer samples appeared as shiny copper mirrors surrounded by a dark, narrow halo. Some of the deposits had regions with matte appearances; sometimes, the entire surface had a matte appearance. The differences between these various regions were observed with microscopy techniques. In the shiny copper region, the surface was very uniform and grain size, measured by SEM and AFM, was between 50-100 nm. In the matte regions, the surface was much rougher and the grains were larger (>200 nm). This difference in grain size was clearly evident, as seen in the SEM micrographs shown in Figure 1. Thin

deposits (less than 50 nm) were invariably shiny but become matte as thickness increased. Deposits on PFA, which is transparent, can be observed from both sides showing the aspect of the film at the Cu/PFA interface and at the Cu/air interface. All the deposits presented a shiny appearance at the Cu/PFA interface when viewed through the substrate, even the thicker films which are matte at the outer surface. This indicates that two different growth regimes take place, which may perhaps be related to the change in the optical absorption and the thermal diffusion that occurs as the film grows.

Film thicknesses were measured with a Dektak profilometer. Typical film thicknesses range from 0.1 to 0.5 μm for films deposited with a few thousand laser pulses. This corresponds to growth rates ranging from 0.1 to 0.5 Å/pulse.

Adhesive tape tests were performed on various samples, on both TiN and fluoropolymer. Cu films deposited on TiN were found to adhere well to the substrate. Only a very slight removal of some of the rougher regions was observed for a few samples. Cu films deposited on fluoropolymers also passed the tape test, again showing only the slight removal of the rough grain regions. Scratch test will be undertaken to quantify the adhesion strength.

XPS analysis were undertaken in order to evaluate the composition of the deposited films, as well as the chemical state of the Cu contained in the films. Figure 2 shows the Cu $2p_{3/2}$ spectra of various films, deposited on both TiN and fluoropolymers substrates, before and after sputter cleaning. The binding energy position of the main peak and its narrow full width at half maximum are indicative of metallic copper. We therefore conclude that complete reduction of Cu(hfac)(TMVS) was achieved.

Large quantities of carbon, oxygen and fluorine, in several chemical states (e.g. CF_x, CO and C), were detected at the surface. The concentration of these surface contaminants was reduced when the deposition temperature was increased from 60 to 120°C. The Cu:C ratio at the surface increased from 0.9 at 60°C to 2.4 at 110°C. The C-containing species probably originate from unreacted and/or partly-reacted reduction

products still adsorbed at the surface after laser exposure. No silicon was detected, indicating the absence of TMVS at the surface. This was expected, since a rapid dissociative desorption of the TMVS ligand was observed upon the adsorption of Cu(hfac)(TMVS), even at low temperatures [11].

After cleaning the samples with 2 keV Ar^+ ions, it was found that most of the impurities were removed. For the films deposited on TiN substrates, oxygen was no longer detected, while carbon was substantially reduced and only trace fluorine could be seen. A Cu concentration of 95 at. %, as measured by XPS, was achieved for substrate temperatures of 100 to 120°C, using hydrogen flow of 100 sccm and a laser energy density of 20 mJ/cm^2. For films deposited on the fluoropolymer samples, the F concentration was always greater, even after ion cleaning. AES profiles of a film deposited on a fluoropolymer sample showed that F is present throughout the film; this could be due to a laser-induced diffusion of F from the Teflon® substrate. The maximum Cu content obtained on films deposited on fluoropolymer samples was 80 at %, using the same deposition parameters used for the deposition on TiN. As hydrogen can not be detected by XPS, elastic recoil detection (ERD) measurements were performed on some samples. Hydrogen, possibly bonded to carbon, was detected at a relative concentration of 7 % in films deposited at 60°C on TiN.

Preliminary four-point and two-point probe resistivity measurements were performed on the samples and a minimum resistivity of 41 $\mu\Omega$-cm was obtained. Good conductive contacts were hard to establish 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. However the possibility of increased resistivity due to poor morphology or contaminant accumulation at the grain boundary can not be ruled out. Further experiments are under way to clarify this.

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 in the precursor molecule adsorbed at 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, photothermal mechanisms cannot be ruled out because the estimated temperature rise induced in TiN by the laser (50-400°C) is sufficient for thermal CVD to occur. However this temperature increase is expected to be lower for fluoropolymers samples, which are partially transparent to the UV radiation. The fact that deposits were grown on the UV transparent quartz windows, when performing experiments without any purge gas, strongly suggests that a photolytical process must be occurring. The relative importance of the two mechanisms, as well as their influence on the spatial resolution in the projection patterning deposition mode, are presently under investigation.

CONCLUSIONS

Metallic copper was deposited on TiN and fluoropolymer 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 is still incorporated in the deposits. Although this is still not usable for ULSI interconnect applications, the optimization of the deposition parameters is far from complete.

ACKNOWLEDGMENTS

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Figure captions

Figure 1. SEM micrographs of the surface of a Cu film deposited on TiN: a) Shiny region; b) Matte region.

Figure 2. Cu $2p_{3/2}$ XPS peaks of air exposed, vacuum transferred, and sputtering cleaned Cu films deposited on: a) TiN and b) Teflon® PFA.

Figure 1 a)

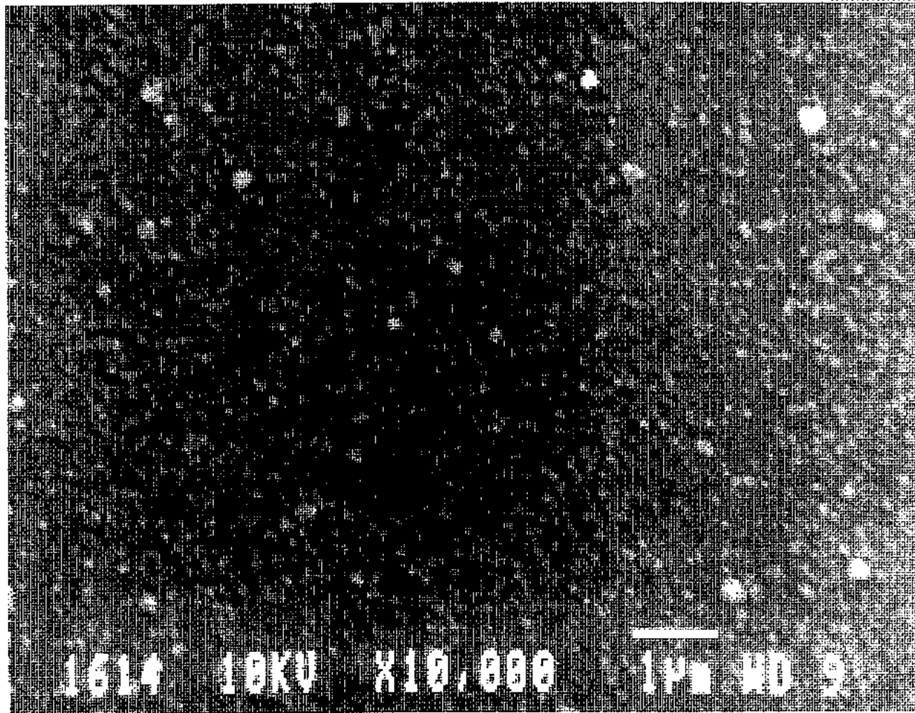
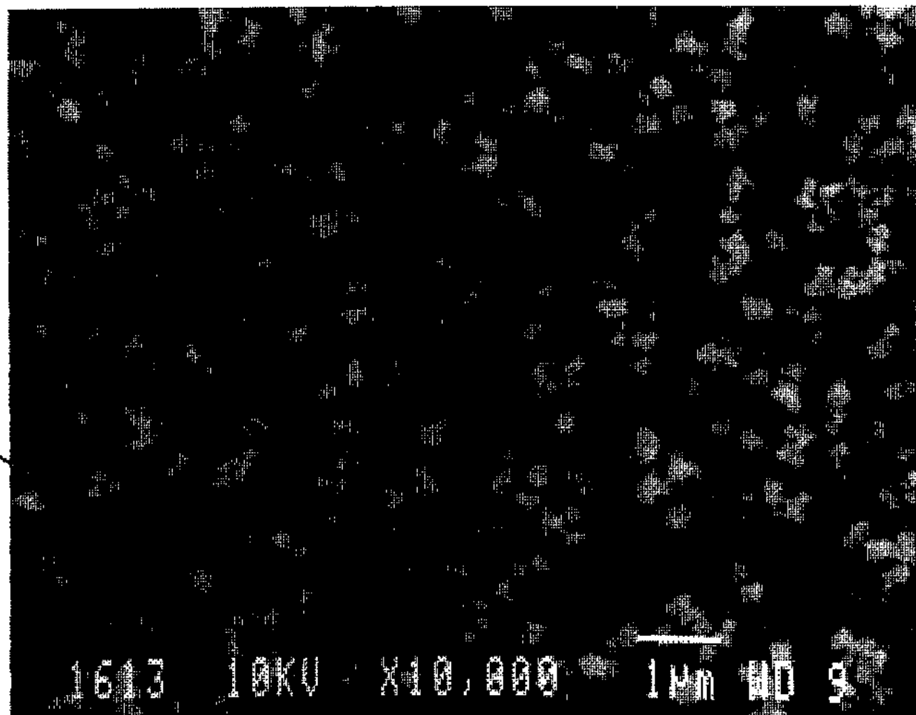


Figure 1 b)



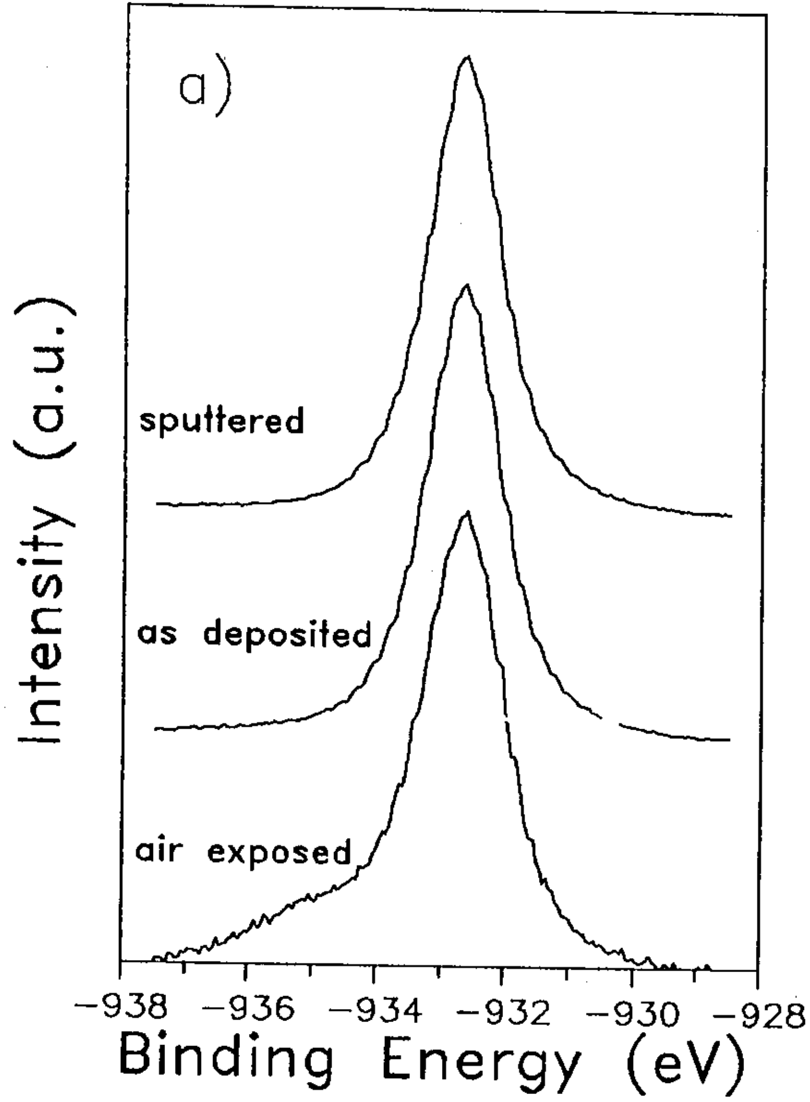


Figure 2 a)

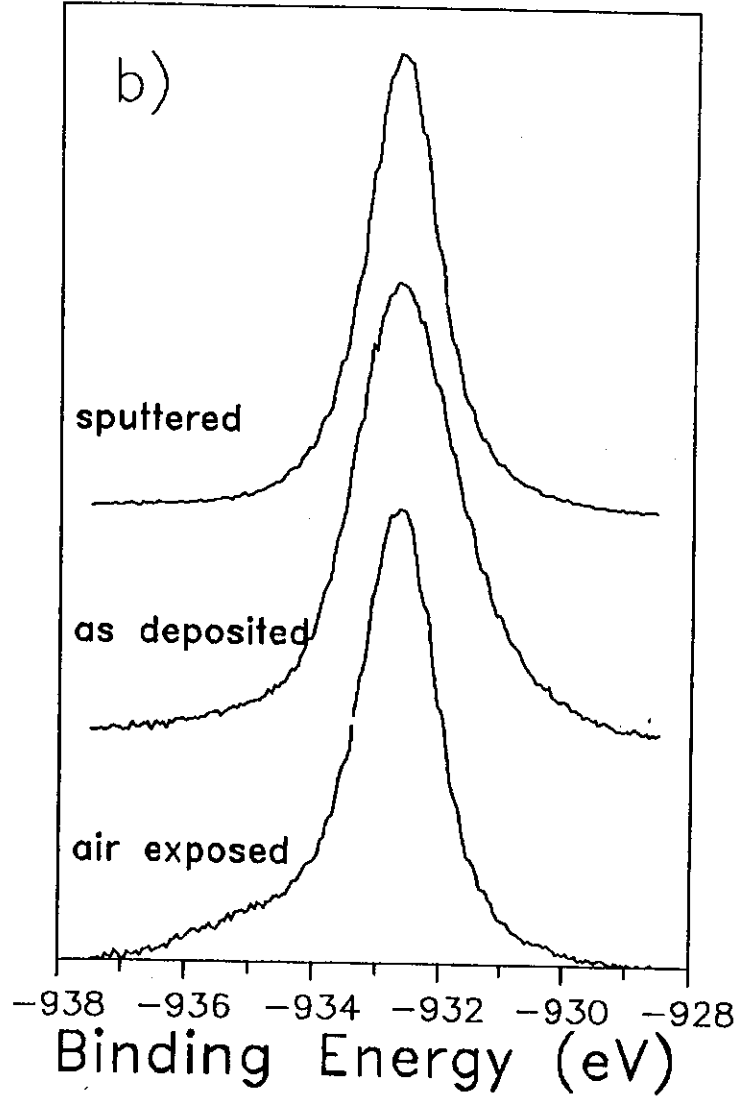


Figure 2 b)