Laser-induced metal-organic chemical vapor deposition (MOCVD) of Cu(hfac)(TMVS) on amorphous Teflon AF1600: an XPS study of the interface

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Abstract

Pulsed KrF excimer laser radiation (248 nm) was used to activate copper deposition from Cu(hfac)(TMVS) onto Teflon AF1600. The interface was examined using X-ray photoelectron spectroscopy (XPS) for thicknesses up to several monolayers. We found that Teflon carbons are the only substrate atoms involved in chemical bonding. Cu^0 and Cu^I-hfac were found to be uniformly distributed throughout the deposited film with additional Cu^I–C closer to the substrate surface. © 1998 Elsevier Science B.V.

1. Introduction

The need to fill increasingly high aspect ratio contact windows and vias in the multilevel on-chip and chip-to-chip interconnects of microelectronic devices has led to the current interest in Metal-Organic Chemical Vapor Deposition (MOCVD). Recently, laser-activated MOCVD was shown [1–4] to be a viable method for the fabrication of metal lines on various substrates. The laser process is noncontacting, maskless, low temperature and selective. Although the photolysis of organometallic compounds in the gas phase has been used to deposit numerous metals onto semiconductors [4–6], little work has been reported on laser-induced selective metal deposition onto polymeric materials [7], especially fluoropolymers [8]. This area is particularly important for high density, short signal delay time interconnect assemblies. The drive for higher circuit speeds has also prompted the consideration of high conductivity metals, such as copper, in order to replace the presently used but more resistive aluminum.

The Teflon AF series of fluoropolymers are, in fact, copolymers [9] of 2,2-bistrifluoromethyl-4,5-difluoro-1,3-dioxole (PDD) and tetrafluoroethylene (TFE). Our prior results [10,11] and those of others (see references in Ref. [11]) have clearly demonstrated that these copolymers are not random but exist as $[-(PDD)_2(TFE)-]_n$ in Teflon AF1600 and $[-(PDD)_7(TFE)-]_n$ in Teflon AF2400. Their distinct advantage in the present case arises from their solu-

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bilities in perfluorinated solvents, allowing spin-on deposition.

Teflon AF1600, the substrate used in our study, and Cu are an excellent combination of candidates for future high speed microelectronic devices requiring short signal transmission delay times, $\tau = RC$, due to both the lower resistivity of Cu and the lower permittivity of Teflon, compared to the presently used Al/polyimide technology. The well-known chemical inertness of Teflons has generated a special interest in metal/fluoropolymer interfacial reactions, which lead to the high levels of interfacial adhesion required in multilayer devices because good interfacial adhesion must be maintained both during manufacture and use-life.

In the present work, the Cu/Teflon AF1600 interface has been studied during laser MOCVD copper deposition. Progressively thicker copper coverages were grown by excimer laser-induced deposition from Cu^I (hexafluoroacetylacetonate) (trimethylvinylsilane), Cu(hfac)(TMVS), and chemical interaction at the interface was examined using X-ray photoelectron spectroscopy (XPS). The formation of new important species, such as metallic Cu^0, was also analyzed during the deposition.

2. Experimental procedure

Teflon AF1600, purchased from DuPont as a solution containing 12% solids, was diluted 1:3 with Sigma Fluorinert FC-77 and spun onto a freshly cleaned Si wafer at 4000 rpm. After air drying at room temperature, the samples were thermally treated at 110°, 165° and 330°C, as recommended by the manufacturer [9]. Teflon thicknesses of 1 to 3 μm were obtained.

The experimental set-up for laser MOCVD is seen in Fig. 1. The samples were positioned in the center of the reaction cell. In order to determine the modifications induced by the excimer radiation only, samples were also exposed to 12 000 laser pulses, in an Ar atmosphere at 4.5 Torr.

Cu(hfac)(TMVS) was obtained from Schumacher as a slightly yellow clear liquid, under the name of CupraSelect. The manufacturer indicates the CupraSelect to be stable at 50°C, and we have confirmed that this is so. It was carefully introduced into a
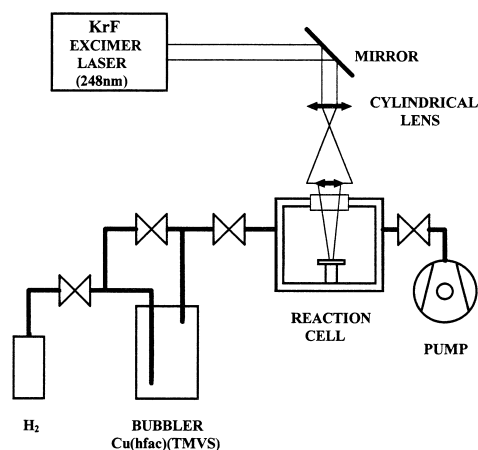

Fig. 1. Experimental set-up.

quartz bubbler using a nitrogen flow to prevent chemical degradation. A Sierra Side Trak III flowmeter was used to monitor the flux of the hydrogen carrier gas. A KrF excimer laser beam ($\lambda = 248$ nm) was first expanded by an anamorphic cylindrical lens and finally concentrated onto the substrate surface, minimizing copper deposition onto the window surface. The experimental conditions are summarized in Table 1. The number of laser pulses varied from 10 to 12 000, in order to obtain a range of coverages. The deposited samples were transferred to our XPS analyzer, using a nitrogen-filled transfer vessel, within 2 min.

The Cu/Teflon AF1600 interfacial reactions were analyzed using XPS, which is a highly surface-sensitive method, having a probe depth of < 100 Å. The spectral resolution of our VG Escalab 3 Mark II instrument was measured to be 0.7 eV, using Mg K_α radiation at 1253.6 eV. In order to avoid degradation of the Teflon interface during analysis [10], spectra

Table 1

	Parameters	Experimental values
Reaction cell	Sample temperature	50°C
	Initial vacuum	10^{-4} Torr
	Deposition pressure	4.5 Torr
Precursor	Precursor temperature	47°C
	H_2 flow	10 sccm
Laser beam	Fluence on sample	190–220 mJ/cm^2
	Pulse rate	20 Hz

were accumulated under low level X-ray source power (10 mA and 8 kV).

Spectral peaks were analyzed using a nonlinear least mean squares program developed in our laboratory. The background was subtracted before peak separation, while the FWHM values and Gaussian/Lorentzian ratios used were similar to those determined by us for other fluoropolymers. Charge shift compensation was carried out by peak alignment: the major C1s peak, for samples having low coverages, was placed at a binding energy of 289.9 eV, previously attributed by us to CF_3 in the original Teflon AF1600 [10,11]. This placed the F1s peak at 687.5 eV, which was the peak alignment used from then on; this procedure, which was necessitated because the substrate spectrum was progressively obscured by deposition while the F1s peak maximum remained at the same energy, gave an alignment error of less than ± 0.8 eV for C1s, O1s and Cu2p. Peak areas, used to determine experimental atomic ratios, were corrected with the appropriate sensitivity factors and electron mean free paths. The experimental error in the determination of the spectral peak was found to be less than $\pm 7.5\%$.

3. Results

XPS C1s spectra for non-irradiated and irradiated (in the presence of Ar) Teflon AF1600 are shown in Fig. 2. Their superposition shows the irradiated sam-
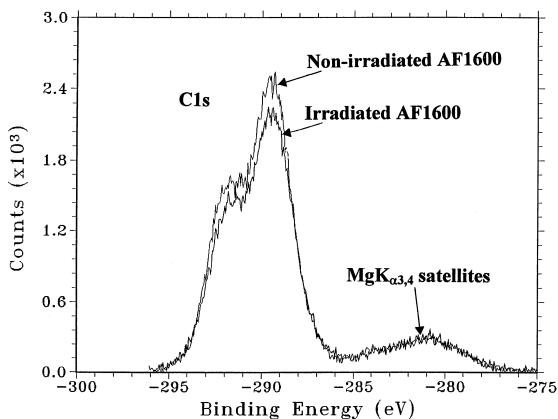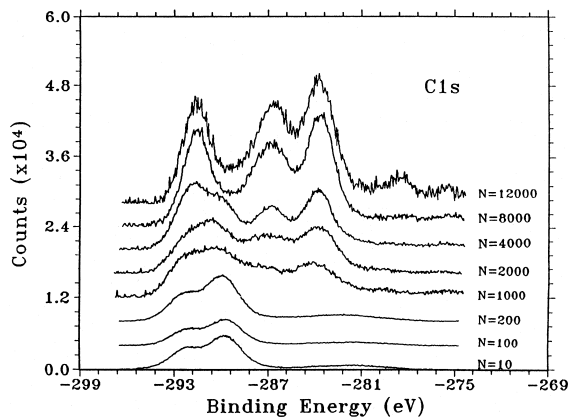

Fig. 3. C1s spectra for various numbers of laser pulses.

ples to be identical to the non-irradiated samples, even under the most severe conditions used in these experiments. The peak structure below a binding energy of 285 eV is due to the Mg $K_{\alpha 3}$ satellite, and no other peak is formed during laser irradiation.

3.1. C1s spectra

XPS C1s spectra for various numbers of laser pulses are shown in Fig. 3. The pure Teflon AF1600 [10,11] is easily recognizable at lower coverages. It changes into a three-peaked structure, which characterizes the Cu-hfac molecular fragment chemically bound to the Teflon surface. The *chemical* bonding of the deposition is indicated by the continued pres-

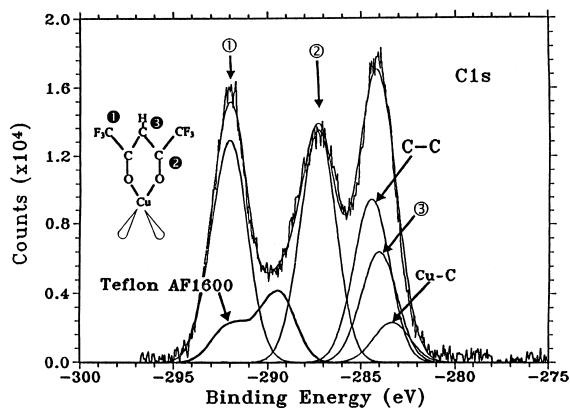Fig. 2. C1s spectra for non-irradiated and irradiated Teflon AF1600.

Fig. 4. C1s peak separation for 8000 laser pulses, as well as C-hfac chemical structure.

ence of these fragments on the substrate surface in the extremely high vacuum of 10^{-9} Torr in the analysis chamber. Fig. 4 shows the peak separation for the case of the highest coverage used in our experiments, as well as the chemical structure of Cu-hfac. The three peaks situated at 292.9, 288.2 and 284.8 eV, in the ratio $2:2:1$, are attributed to $\underline{C}F_3$, $\underline{C}$–O and $\underline{C}H$, respectively and correspond to the hfac carbon atoms in positions 1, 2 and 3, as seen in Fig. 4. We have found that two supplementary peaks, each at the same FWHM as the others, are necessary to fit the envelope of the structure near 285 eV in Fig. 4. The supplementary peak at 285.0 eV, attributed to the C–C bond, is due to CupraSelect degradation products; while this peak may also be attributed to adventitious carbon from the back-streaming of our pumping system, we discount this explanation because this peak is found uniquely when CupraSelect is used.

The peak at 283.6 eV is clearly a metal carbide, since only carbides have the negatively charged C necessary for a binding energy below 285 eV. We have reported the appearance of this peak previously [12]. In addition, a small residual component of the original spectrum has been found; it represents the Teflon AF1600 substrate, attenuated by the CupraSelect deposit.

3.2. O1s spectra

Fig. 5 shows typical O1s spectra for various coverages. For low coverages, the broad structure of
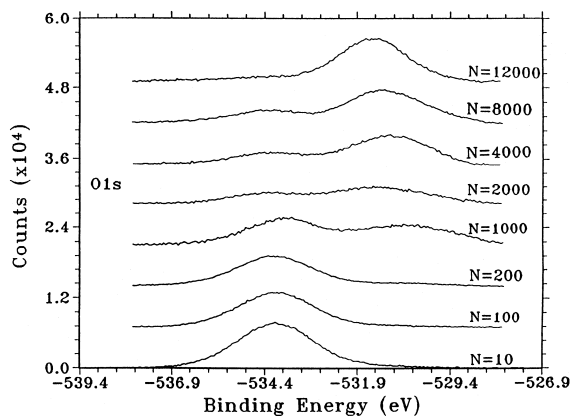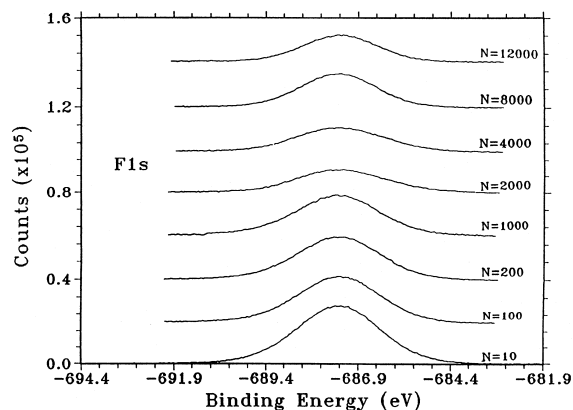

Fig. 6. F1s spectra for various numbers of laser pulses.

pure Teflon AF1600, attributed to a doublet, at 534.5 and 533.7 eV [10,11], is found; the doublet is due to different environmental positions of oxygen atoms in the Teflon AF1600 chemical structure [11]. With increasing coverage, a new peak develops at 530.6 eV; it has a FWHM of 2.15 eV, indicating a single component; it is attributed to the $\underline{O}$–C in the hfac ring. The initial O1s twin peaked structure is attenuated by the presence of the layer growing on the Teflon surface; less than 10% of the original substrate oxygen is observed for the maximum coverage we used.

3.3. F1s spectra

Typical F1s spectra are found for increasing coverages in Fig. 6. The initial peak keeps its symmetrical shape throughout the deposition, but its FWHM narrows slightly from 2.60 to 2.30 eV; it is attributed to the $\underline{C}F_3$ in the hfac. This indicates that the initial three-peaked structure of Teflon AF1600 [11] is continuously attenuated and masked by the CF_3 peak of hfac, at the same energy maximum.

3.4. $Cu2p_{3/2}$ spectra

$Cu2p_{3/2}$ spectra for various numbers of laser pulses are shown in Fig. 7, and a typical deconvolution is presented in Fig. 8. The absence of any shake-up peak indicates the absence of Cu^{II}, so that the peaks formed must be due to Cu^0 and Cu^I. The presence of Cu^0 is demonstrated by the metallic
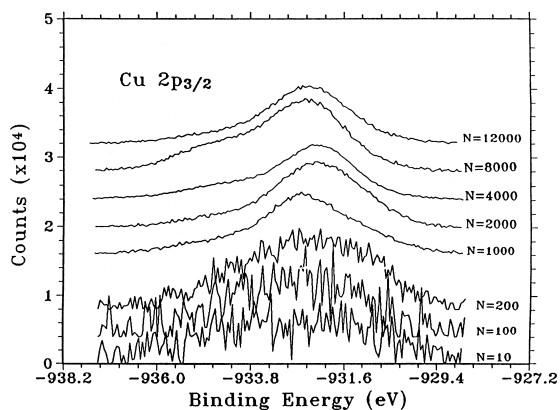

Fig. 5. O1s spectra for various numbers of laser pulses.

Fig. 7. Cu2p$_{3/2}$ spectra for various numbers of laser pulses.

Fig. 9. Relative copper concentration vs. the number of laser pulses.

sheen of the deposit while Cu(hfac) and carbide were both shown to be present in the C1s spectrum.

Despite the fact that both Cu(hfac) and carbide have Cu in the monovalent state, their Cu peaks must be different because of their different environments: the Cu in Cu(hfac) is bonded to a far more electronegative group than the Cu in carbide. Thus, one expects two Cu^I peaks. Since only two peaks exist, both must contain Cu^I components. Because the binding energy of 932.4 eV is that expected for Cu^0 and for Cu^I compounds having low electronegativity ligands [13], that peak is tentatively attributed to Cu^0 and carbide, while the peak of 934.7 eV is attributed to Cu(hfac). The justification for these attributions is

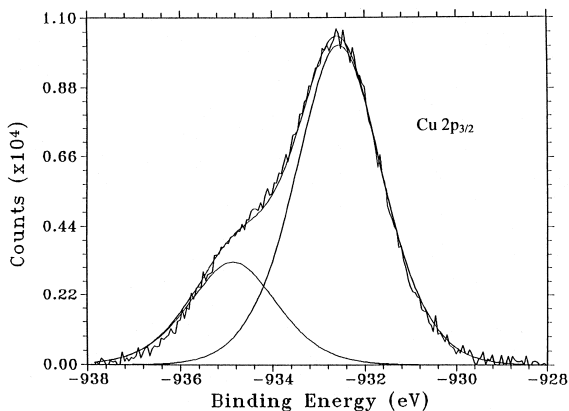that there is excellent agreement between the results obtained from the C1s peak separation and those obtained from the Cu2p$_{3/2}$ peak separation.

The Cu2p$_{3/2}$ envelope may be used to determine the relative concentrations of C–$\underline{\text{Cu}}$(hfac) and C–$\underline{\text{Cu}}$ species at the Teflon surface. To separate the concentrations of Cu^I–C and Cu^0, which have indistinguishable peak positions, the following manipulation was carried out: the Cu2p$_{3/2}$ equivalents of the Cu–$\underline{\text{C}}$ peaks in the C1s spectra (283.6 eV) were calculated and subtracted from the $\underline{\text{Cu}}$–C + Cu^0 2p$_{3/2}$ peak areas (932.4 eV). The results, in arbitrary units, are shown in Fig. 9, plotted vs. the number of laser pulses.

3.5. F:C:O:Cu ratios of deposited Cu^I(hfac)

The three-peaked structure of the C1s spectra, in Fig. 3, indicates that the deposited layer is mainly composed of Cu(hfac), which has a theoretical F:C:O:Cu ratio of 6:5:2:1. Experimental peak areas were divided by the appropriate sensitivity factors, verified in our laboratory, to obtain relative concentrations; these were then normalized to unit depth by further division by the appropriate electron mean free path [14]. These ratios were found to be constant as a function of coverage, remaining, to within ±7.5%, at 6:4.6:2:1.05.

Fig. 8. Deconvolution of typical Cu2p$_{3/2}$ high resolution spectrum.

4. Discussion

Fig. 2 indicates that excimer laser irradiation does not produce detectable degradation of the Teflon AF1600 surface. This demonstrates that the C1s structure in the presence of CupraSelect is due to the deposition of CupraSelect and not to UV-induced modifications.

Fig. 9 shows the yield of different copper species vs. coverage resulting from our XPS analysis. The experimental points can be fit to a function proportional to $1 - \exp(-CN)$, where C is an experimental constant (0.00025 for Cu^0 and 0.00026 for $\underline{Cu^I}$-hfac) and N is the number of laser pulses.

The XPS signal attenuation as a function of depth is known to follow an equation of similar form, assuming uniform concentration: $I(d) \propto 1 - \exp(-d/\lambda_0)$ [14], where λ_0 is the mean free path of the electrons (~ 13 Å for copper). Introducing k, so that $N = kd$ and equating the two, one obtains values of $k(= 1/C\lambda_0)$ of 307.7 Å^{-1} for Cu^0 and 295.9 Å^{-1} for Cu^I. These k values were used to calculate the thickness at any laser exposure. For $N = 12\,000$, thicknesses of 39 Å and 40.5 Å are obtained, for Cu^0 and Cu^I-hfac, respectively, based solely on signal attenuation. They appear to be in agreement with the fact that, at $N = 12\,000$, the substrate spectrum is almost obscured, as expected for 95% attenuation at a value of 3λ (~ 39 Å). For Cu^I–C, the experimental data cannot be fit by a uniform distribution. The initial high values indicate a built-up of carbide for low coverages, before decreasing and following the production of Cu^I-hfac.

This XPS spectral analysis permits us to have an overall picture of the reaction at the deposited copper layer/Teflon AF1600 interface. The initial chemical reaction is activated by the energy of the excimer laser radiation. Like most β-diketonates, Cu(hfac)(TMVS) has an absorption band near 250 nm, due to an electronic charge transfer from a σ bond to copper [15]. After absorbing the 248 nm radiation, the excited molecules break in two, with the release of volatile TMVS and the chemisorption of Cu(hfac). The nature of the Teflon–Cu(hfac) chemical bond is not clear; however, the appearance of a peak, at about 210 nm, in the UV spectra of Teflon AF after excimer irradiation in vacuum, indicates the presence of C=C, which may be implicated
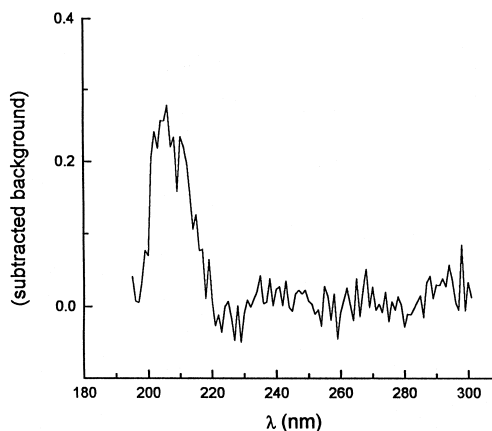

Fig. 10. UV spectrum of Teflon AF1600 after irradiation; non-irradiated spectrum has been subtracted.

in the bonding of Cu(hfac); This is shown, as a difference spectrum (after laser irradiation − before irradiation), in Fig. 10. A small fraction of these adsorbed Cu(hfac) molecular fragments undergoes a disproportionation reaction, producing Cu^0 and releasing volatile Cu(hfac)$_2$ [16]. Further, a fraction of the Cu^0 reacts with carbon sites, forming carbides. The C–$\underline{Cu}/\underline{Cu}$-hfac ratio, initially large, decreases with increasing coverage, indicating an initial accumulation of carbides at the interface. As the layer thickness increases, the Cu–C is limited to the chemical bond between Cu-hfac groups.

The deposited layer is rich in carbon from both hfac groups and organic molecules (impurities incorporated during the deposition). For the greatest coverage used in our experiments, 94% of the initial Teflon AF1600 C1s peak is attenuated by the deposited layer, in agreement with the estimated layer thickness of 39–40 Å.

5. Conclusions

XPS analysis was used to assess the chemical reactions of copper deposited by laser MOCVD of Cu(hfac)(TMVS) onto Teflon AF1600. Low coverages were intentionally chosen in order to be able to examine the interface by XPS. Because of the very small thicknesses of the deposited films, conductivity measurements are not relevant and therefore, they have not been performed in the present study. For

the initial stages of the deposition, Teflon carbons are the only sites to react with copper forming Cu-hfac and carbide. The Cu–C/Cu-hfac ratio, initially large but decreasing with coverage, indicates carbide accumulation at the interface. The constant Cu^0/Cu^I-hfac ratio of 3.8 indicates that these two copper species are produced uniformly during the film deposition. Because the laser-induced MOCVD of Cu(hfac)(TMVS) onto Teflon AF1600 under our experimental conditions produces relatively little copper and only 55% in the metallic state, optimization will be necessary before commercialization of the process.

Acknowledgements

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