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Copper metallization of Teflon AF1600, using evaporation and sputtering, for multilevel interconnect devices

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Abstract

X-ray photoelectron spectroscopy was used to assess the interaction of evaporated and sputter-deposited copper with Teflon AF1600. Both evaporation and sputtering caused defluorination, graphitization and crosslinking of the carbon chains, as well as the formation of Cu–C bonds and C–O· free radicals. Additionally, the higher energies of the sputter-deposited copper atoms led to a loss of oxygen and to the total reaction of the deposited copper as carbide and fluorides.

1. Introduction

The overall speed of large, high density semiconductor chips is presently not limited by the transistor speed but, rather, by the on-chip circuits that connect them [1]. Specifically, the resistance (R) of the conductor and the capacitance (C) of the insulator cause what is known as an "RC" time delay (i.e., $\tau = R \times C$), which limits the chip speed when τ is larger than the inherent delay time of the device. A goal of the microelectronics industry is to reduce the RC time delay by (1) decreasing R by using a higher conductivity metal, (2) decreasing C by using dielectrics having lower dielectric constants and (3) decreasing the lengths of the metal lines by using multilayer interconnect devices.

Copper is seen as the most promising metallic candidate because its resistivity is 65% of that of the presently used aluminium and it has relatively good electromigration resistance. Copper can be also deposited at relatively low temperature with excellent step coverage properties. Fluoropolymers such as the Teflons, which have dielectric constants near 2, are seen as potential replacements for the currently used dielectrics, such as polyimides and SiO_2. Teflon AF1600 has the distinct advantage of being soluble in perfluorinated solvents, permitting its deposition by spin-on techniques [1]. The notorious chemical inertness of fluoropolymers and the need for reliability during the fabrication process as well as during the lifetime of such multilevel devices have generated a strong interest in the structure of the metal–fluoropolymer interface [2]. Adhesion enhancement is deemed an important research topic for new multilayer technologies.

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In the present work, the copper/Teflon AF1600 interface is studied using X-ray photoelectron spectroscopy (XPS). Both evaporation and sputtering were used as metallization techniques in an attempt to elucidate the chemical interactions at the interface and how they are influenced by the energy of metallization.

2. Experimental

Teflon AF1600, the Teflon we have chosen to consider, is a copolymer of 35% tetrafluoroethylene (TFE) and 65% 2,2-bistrifluoromethyl-4,5-difluoro-1,3-dioxole (TDD) and is manufactured by DuPont; it has the repeat unit structure $-(TFE)-(TDD)_2-$. The solution purchased, containing 12% (w/w) solids, was further diluted 50% in Sigma Fluorinert FC-77 before being spun onto cleaned Si wafers. Teflon thicknesses of 1–3 μm were obtained at a spin speed of 3000 rpm. After drying at room temperature, the samples were thermally treated as recommended by the manufacturer [3].

Both vapor deposition and sputtering were performed in the preparation chamber of our VG ESCALAB 3 Mark II spectrometer. A Waldrop-Grand electron beam evaporator [4,5] and an Ar^+ sputtering unit were used to deposit copper. Both deposition systems were described in a previous paper [6]. Experimental conditions are given in Table 1. An evaporation rate of 2 Å/s was used to deposit Cu in the nominal thickness range (i.e. the sticking coefficient to Teflon AF1600 is unknown) 4–24 Å. In the case of sputtering, XPS showed that all the Cu had reacted and was uniformly distributed within the ~60 Å probed. Using a sputtering rate of 4 A/min, the nominal thickness range was 4–40 Å.

A nonlinear least-mean-squares program was used for spectral peak separation. To account for the charge shift during X-ray exposure, $Cu2p_{3/2}$ for the thickest vapor deposited copper layer was arbitrarily placed at 931 eV, which is the binding energy of bulk metallic copper [7], after a Shirley background subtraction.

3. Results

The C1s, F1s, O1s and $Cu2p_{3/2}$ spectra were taken at different evaporation and sputtering times. Table 2 summarises our XPS analysis. New peaks (ref. [8] contains the original, undegraded spectra), indicating chemical changes, arise due to some specific reactions between the evaporated and sputtered Cu or Teflon AF1600. For evaporation, the relative concentration of carbide present at the interface was determined from the ratio between the total amount of copper and the concentration of

Table 1
Metallization conditions for evaporation and sputtering

Experimental conditions	Evaporation	Sputtering
Predeposition vacuum (Torr)	10^{-9}	10^{-9}
Deposition vacuum (Torr)	10^{-9}	5×10^{-6}
Power (W)	6 (6 kV × 1 mA)	0.06 (6 kV × 10 μA) current density at target = 10 μA/cm^2

Table 2
Summary of the new peaks and reaction processes from the XPS analysis

	Evaporation			Sputtering		
	new peaks (eV)	attribution	reaction process	new peaks (eV)	attribution	reaction process
C1s	283.7	C–Cu	carbide formation	283.7	C–Cu	carbide formation
	285.4	C–C	graphitization and crosslinking	285.4	C–C	graphitization and crosslinking
	287.3	C–CF [9]	partial loss of F	287.3	C–CF	partial loss of F
F1s	none		uniform defluorination			uniform defluorination
				682.5	F	fluoride formation
O1s	529.6	two slightly different O sites	free radical formation	529.6	two slightly different O sites	free radicals formation
	530.4			530.4		~30% loss of oxygen
Cu $2p_{1/2}$	931	C–Cu and Cu^0	copper carbide and metallic copper ($Cu^+/Cu^0 \approx 1$)	932	C–Cu	copper carbide
				934.3	Cu^+	CuF
				936	Cu^{2+}	CuF_2
						no Cu^0

C–Cu measured from the C1s spectra. This ratio remained essentially unchanged with deposition thickness, showing that about 50% of the deposited copper remained in the metallic state. The evolution of the carbide peak area from the C1s spectra is shown in Fig. 1.

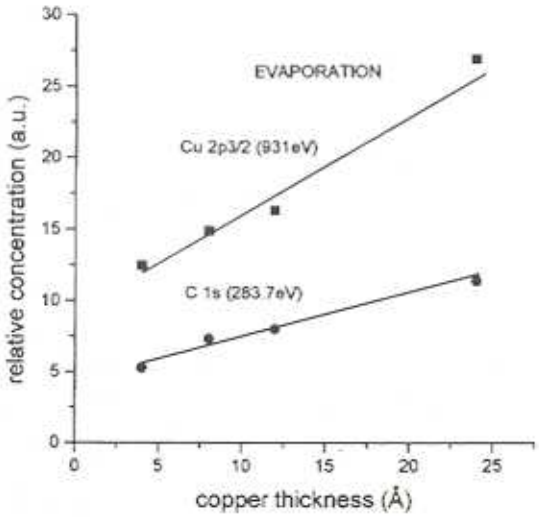

Fig. 1. Evolution of Cu^0 and Cu^+ for vapor deposition (Cu^+ was estimated from 283.7 eV peak of the C1s spectrum, assuming CuC formation).

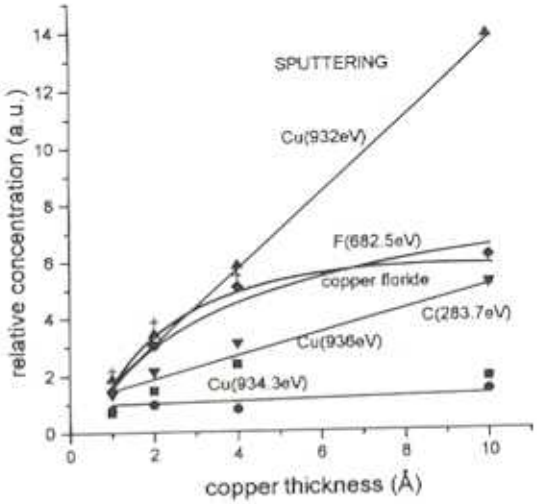

Fig. 2. Correlation between concentrations of elements (C, Cu, F) for different species formed during sputter deposition (CuC, $Cu^{+}F^{-}$ and $Cu^{2+}F_2^{-}$).

In general, the XPS spectra on sputtering presented characteristics similar to those found for vapor deposition. The positions of the separated peaks remained identical to those in the case of vapor depositions to within ±0.1 eV. Nevertheless, there are several differences in the evolution of the peaks. Further, several new peaks indicated the formation of new species, attributed to Cu–C, Cu^{+} and Cu^{2+}. Fig. 2 shows the evolution of these new peaks as a function of sputtering time.

4. Discussion

An overall picture of those chemical reactions provoked by evaporation and sputtering may be gained from an analysis of the XPS spectra. The driving force for such reactions on the deposition of evaporated copper is the energy of condensation of the metal [9]. The increased energy at the interface induces degradation reactions in the surface structure. Degradation is due to the uniform loss of fluorine. The copper bonds uniquely to carbon, forming carbide throughout the deposition, with approximately half of the deposited copper atoms remaining in the metallic state. There is no important oxygen loss, although modifications of the original Teflon AF1600 O1s spectrum indicate single bond breaking of the oxygens of the dioxole rings, to produce free radicals.

In the case of sputtering, the kinetic energy of the copper atoms, which is at least an order of magnitude greater than the condensation energy released by the condensation of evaporated copper [10], leads to new reactions. The depositing copper reacts entirely, with the formation of carbide and fluoride species, while the carbon spectrum indicates degradation processes similar to those found in the case of evaporation. The intense energy causes not only single bond breaking to produce –C–O·, but the breaking of the second C–O bond, as well, resulting in the loss of oxygen atoms. While C–F bonds are broken, not all the F is lost: some is retained as copper fluorides. As shown in Fig. 2, correlation between Cu and F concentrations reveals a consistent overall picture of chemical reactions at the interface.

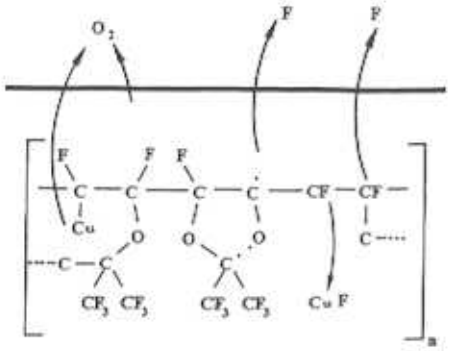

Fig. 3. Overview of the possible reactions for evaporation and sputter deposition.

5. Conclusions

XPS analysis was used to study the interfacial interactions of vapor-deposited and sputtered copper with Teflon AF1600. In the case of evaporation, only half of the deposited copper remained in the metallic form, while the higher energies of the sputtered atoms led to total copper reaction, with carbide and fluoride formation. Fig. 3 shows an overview of the possible reactions that we have been discussing.

Acknowledgments

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References

[1] P. Singer, *Semiconductor International* November (1994) 52.
[2] E. Sacher, *Prog. Surf. Sci.* **47** (1994) 273.
[3] DuPont Specialty Polymers, Technical Information Bulletins H-16577-1 and H-52454.
[4] J.R. Waldrop and R.W. Grand, *J. Vac. Sci. Technol.* **A1** (1983) 1553.
[5] J.R. Waldrop, P. Kowalczyk and R.W. Grand, *J. Vac. Sci. Technol.* **21** (1982) 607.
[6] D. Popovici, J.E. Klemberg-Sapieha, G. Czeremuszkin, A. Alptekin, L. Martinu, M. Meunier and E. Sacher, in: K. Mittal, ed., *Metallized Plastics*, submitted.
[7] C.D. Wagner, W. M. Riggs, L.E. Davis, J.F. Moulder and G.E. Mulinberg, *Handbook of X-ray Photoelectron Spectroscopy* Perkin-Elmer Corporation, Eden Prarie, MN, 1979.
[8] E. Sacher and J.E. Klemberg-Sapieha, *J. Vac. Sci. Technol.*, submitted.
[9] R.E. Honig, *RCA Rev.* **18** (1957) 195.
[10] *The Handbook of Thin Film Technology*, C.I. Maissel, R. Glang, eds., McGraw-Hill, N.Y., 1970.