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The copper/plasma-polymerized octofluorocyclobutane interface

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Abstract

To satisfy the demand for increased signal transmission speed and device density in the next generation of multilevel integrated circuits, a material with a permittivity less than 3 is needed, that has compatibility with copper and copper processing. The authors found that plasma-polymerized octofluorocyclobutane (PPOFCB) is a smooth, transparent, film that adheres strongly to the substrate and has a relatively high fluorine to carbon (F/C) ratio, indicative of a low permittivity. This paper considers the copper/PPOFCB interface by investigating the effects of an OFCB plasma both on copper and on the deposited PPOFCB. X-ray photoelectron spectroscopy (XPS) of copper surfaces exposed to an OFCB plasma, for times as short as 1 s and as long as 30 min, was used to characterize the copper, the PPOFCB and the interface between them.

During a 1 s OFCB plasma exposure, copper fluorination occurs, producing CuF (with a F ion peak appearing in the F_{1s} spectrum) as well as the deposition of fluorocarbon species (with a CF_n peak in the F_{1s} spectrum). During the next few seconds of OFCB plasma exposure, the amount of fluorocarbon deposited begins to dominate the surface, although oxidized copper and oxidized hydrocarbon contaminant are still observed. The copper substrate beneath a 15 nm PPOFCB film is not detectable via XPS. The F/C ratio for PPOFCB can be as high as 1.68 after brief deposition times (30 s), reaching a plateau value of 1.5 after several more minutes of plasma exposure; this reduction in F/C to a plateau is associated with ion bombardment and vacuum UV defluorination. PPOFCB is a smooth, planarizing film, with plasma polymerization occurring predominantly on the surface and reducing the RMS roughness from 0.97 to 0.46 nm for the copper substrate.

Keywords: Plasma polymerization; Fluoropolymer; Copper

1. Introduction

Two critical changes are needed for the development of ultra large scale integrated circuits (ULSI): reductions in both resistance (R) and capacitance (C) [1]. The reduction of resistance is presently taking place with the introduction of copper interconnects to replace aluminum. The current need for interlayer dielectrics (ILDs) is for a permittivity (κ) less than 3 and compatibility with copper and copper processing [2]. Fluoropolymers have such low permittivities but are difficult to process. The authors have investigated the plasma polymerizations of octofluorocyclobutane (OFCB), hexafluoropropylene and trifluoroethylene with the objective of synthesizing a smooth fluoropolymer film with a high F/C ratio [3]. Of the films investigated, plasma-polymerized OFCB (PPOFCB) exhibits the most interesting properties. PPOFCB is a smooth, transparent, yellow film that adheres strongly to the substrate and is capable of being deposited at approximately 0.03 μm/min. The relatively high fluorine to carbon (F/C) ratio of PPOFCB is indicative of a low permittivity. The refractive index (n) of PPOFCB, determined through variable wavelength ellipsometry, is 1.37 at 900 nm. This relatively low refractive index suggests that PPOFCB is a potentially attractive low permittivity material (a low κ dielectric) with a permittivity (i.e. n^2) below 2.0 at high frequencies [3].

This paper will describe the copper/PPOFCB interface by investigating the effects of an OFCB plasma both on a copper substrate and on deposited PPOFCB. X-ray photoelectron spectroscopy (XPS) of copper surfaces exposed to an OFCB plasma, for times as short as 1 s and as long as 30 min, was used to characterize the substrate, the PPOFCB and the interface between them.

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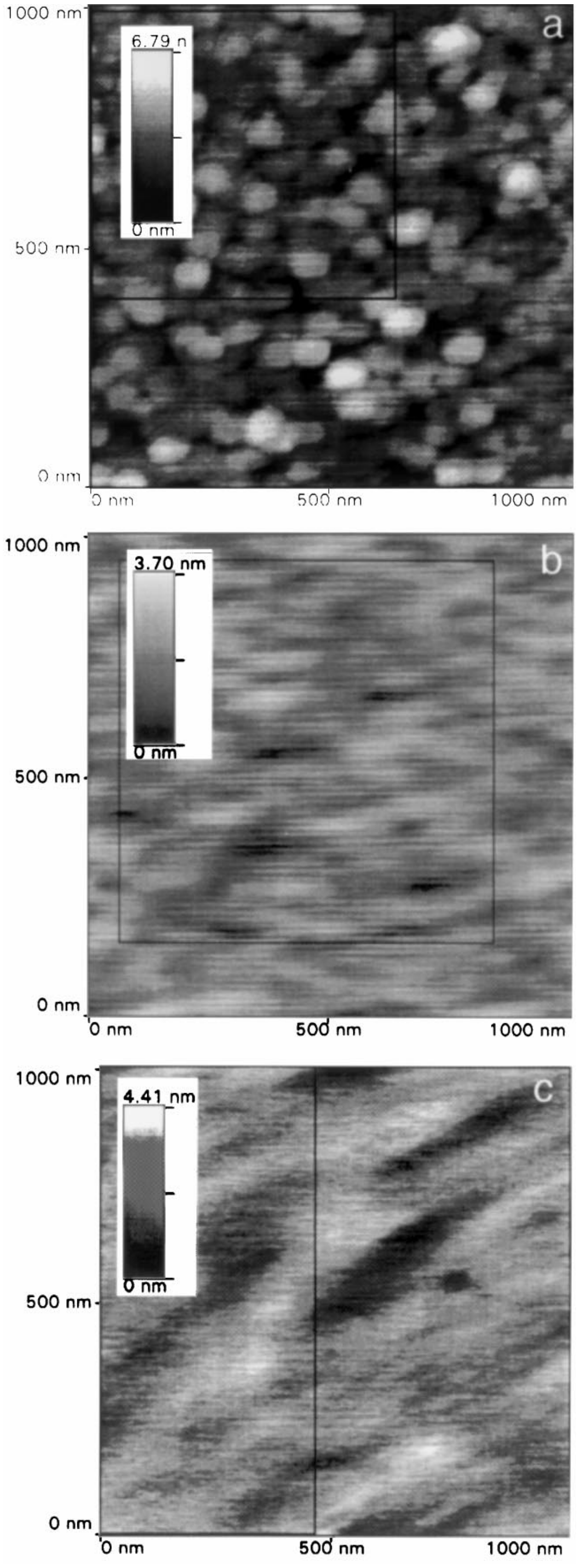

Fig. 1. AFM micrographs of PPOFCB for various deposition times: (a) Cu substrate; (b) 30 s; and (c) 10 min.

2. Experimental

2.1. Materials

The fluorocarbon monomer used for plasma polymerization was OFCB (C_4F_8) (Matheson). The base materials used were crystalline silicon wafers.

2.2. Copper sputtering and plasma polymerization

Copper sputtering and OFCB plasma polymerization were carried out using the innovative reactor previously described [3]. A unique feature of this reactor is the specimen stage for copper sputtering which, when rotated, becomes the upper parallel plate electrode for plasma polymerization. In this manner, a plasma polymer could be deposited on sputter-coated copper without breaking vacuum. The copper sputtering/plasma polymerization procedure was described in detail elsewhere [3]. The conditions for OFCB plasma polymerization were 7 W, 33 Pa, and 24 sccm.

2.3. Film thickness

The thicknesses of the PPOFCB films were measured using both a profilometer (model 3030ST, Dektak) and a variable angle spectroscopic ellipsometer (model 200, J.A. Woollam) in reflection.

2.4. Molecular structure and topography

The molecular structure was characterized using XPS with a non-monochromated Mg K_α source (ESCALAB Mk II, Vacuum Generators). Both low resolution survey spectra and high resolution C_{1s}, F_{1s}, Cu_{2p} and O_{1s} spectra were taken. Elementary concentrations, in atomic percent, were evaluated from the high resolution peak areas following Shirley background subtraction [4]. The concentration of group i on the surface was calculated from the area, $A(i)$, of the peak associated with group i in the curve fits for the high resolution spectra. The topographies were characterized using atomic force microscopy (AFM) in contact mode (model 2010, Topometrix). Scans of 1×1 and $0.2 \times 0.2\ \mu m^2$ were taken at 5 and 1 μm/s, respectively. Roughnesses were obtained from the scans, using the associated software.

3. Results

3.1. AFM

The changes in topography with deposition time are seen in the $1 \times 1\ \mu m^2$ AFM micrographs in Fig. 1. The RMS roughness obtained from the AFM micrographs is plotted as a function of polymerization time in Fig. 2 for both 1×1 and $0.2 \times 0.2\ \mu m^2$ scans.

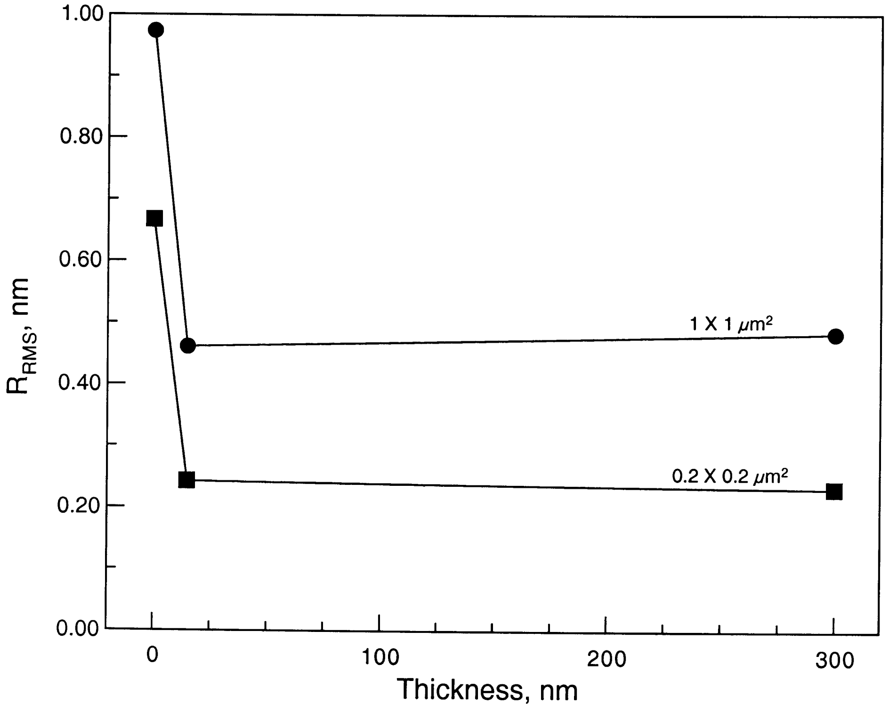

Fig. 2. Roughness of PPOFCB as a function of deposition time.

3.2. XPS

XPS reveals significant changes on the surface with increasing exposure to an OFCB plasma. The variations in elemental composition, as determined from the XPS spectra, are seen in Fig. 3 and Table 1 (where $A_1(i)$ is the atomic concentration of element i). The high resolution XPS spectra for each element reveal the variations in molecular structure with increasing OFCB plasma exposure time. The C_{1s}, Cu_{2p}, F_{1s} and O_{1s} spectra for various OFCB plasma exposure times are presented in Figs. 4–7, respectively.

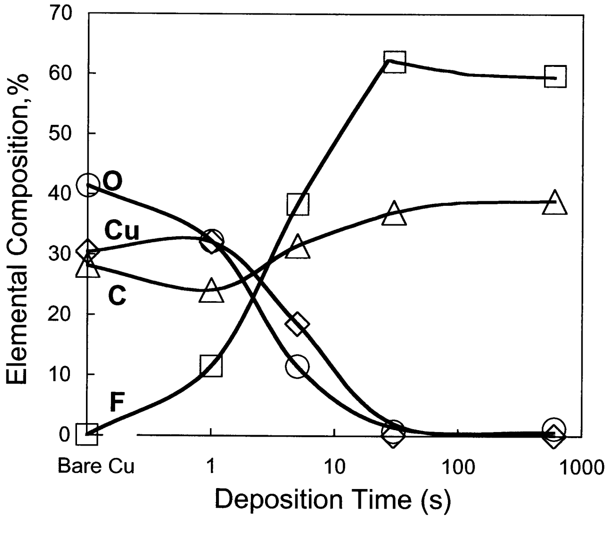

Fig. 3. Atomic composition as a function of thickness.

3.2.1. PPOFCB

The variation of PPOFCB molecular structure with film thickness can be described through the variation in the fluorine to carbon ratio (F/C). The F/C in Fig. 8 are calculated from the high resolution XPS spectra for films that were sufficiently thick for the copper substrate not to be detected. The 15 nm PPOFCB thick film from a 30 s OFCB plasma exposure has the highest F/C, 1.68. The F/C decreases rapidly in the first few minutes of OFCB plasma exposure, reaching 1.5 for an 84 nm thick PPOFCB film. It then remains relatively constant, at a value of 1.5, with further exposure to the OFCB plasma (measured up to a PPOFCB thickness of 840 nm).

The evolving molecular structure of PPOFCB was characterized through the curve fits for the C_{1s} spectra, as described elsewhere [3]. The C_{1s} spectrum spans a large binding energy range, and the most distinct peaks are the two with the highest binding energies. These peaks were associated with CF_3 (highest binding energy) and

Table 1
XPS elemental analysis of copper following various OFCB plasma exposure times

Exposure Time, s	0	1	5	30	600
PPOFCB Thickness, nm	–	–	–	15	300
Element	$A_1(i)$, %				
C	28.2	24.1	31.6	37.1	39.0
F	–	11.5	38.4	62.1	59.8
O	41.4	32.3	11.5	0.8	1.2
Cu	30.4	32.1	18.5	–	–

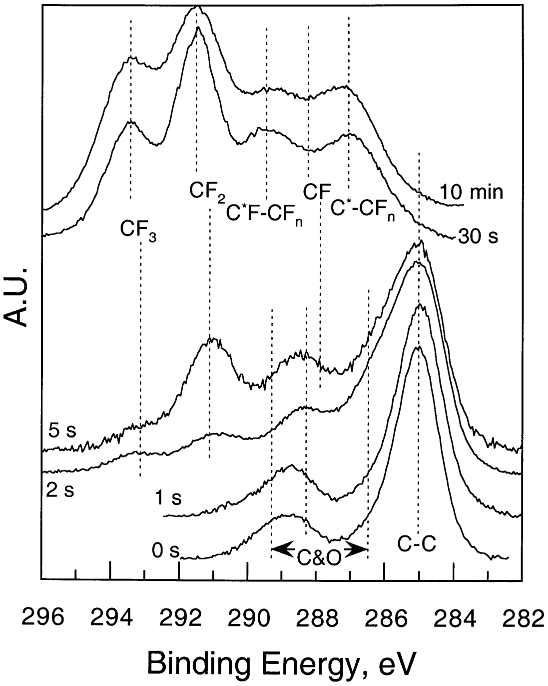

Fig. 4. C_{1s} spectra for various deposition times.

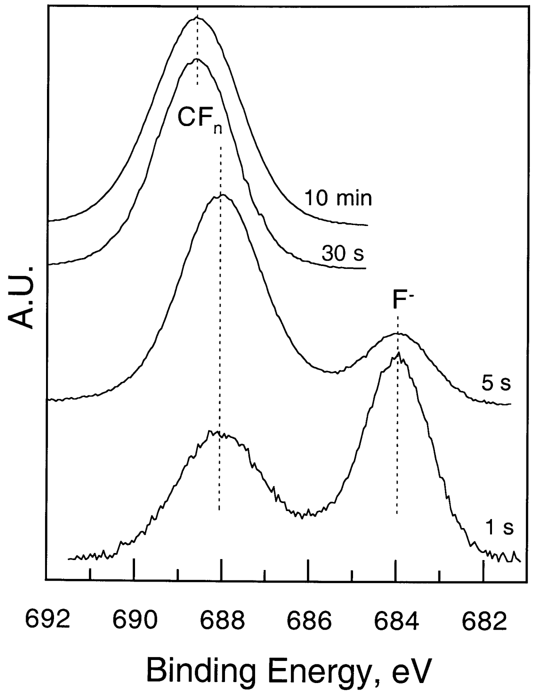

Fig. 6. F_{1s} spectra for various deposition times.

CF_2 (second highest binding energy, having the highest magnitude). The deposition of a thin PPOFCB film (about 15 nm) on a polyethylene substrate was used to assign binding energies to the peaks [3], with the peak assignments and the curve fit results listed in Table 2 (where $A_2(i)$ is the concentration of group i) [3,5–7]. PPOFCB contains about 35% CF_2, about 20–25% CF_3, about 20–25% CF, and about 15% C^*–CF_n

3.2.2. Copper substrate

The XPS spectrum of the copper substrate (0 s deposition), following approximately one day of exposure to the atmosphere, exhibits approximately 30% copper, 41% oxygen and 28% carbon (Table 1). The low resolution XPS spectrum (not shown) exhibits a Cu_{2p} peak at 932.7 eV and a shake-up satellite at about 942 eV, the 9 eV binding energy difference expected for Cu(II) [8–10]. The high resolution

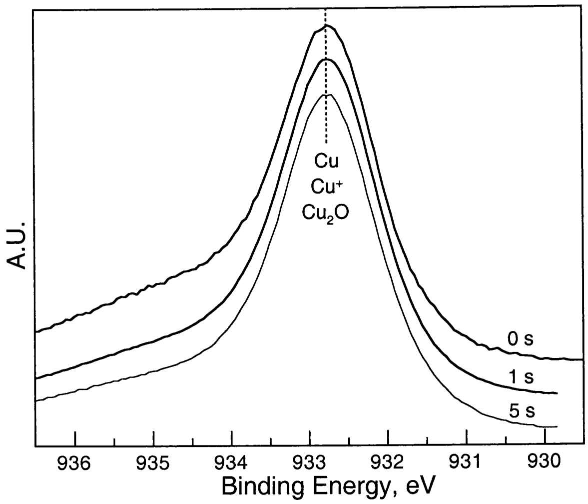

Fig. 5. Cu_{2p} spectra for various deposition times.

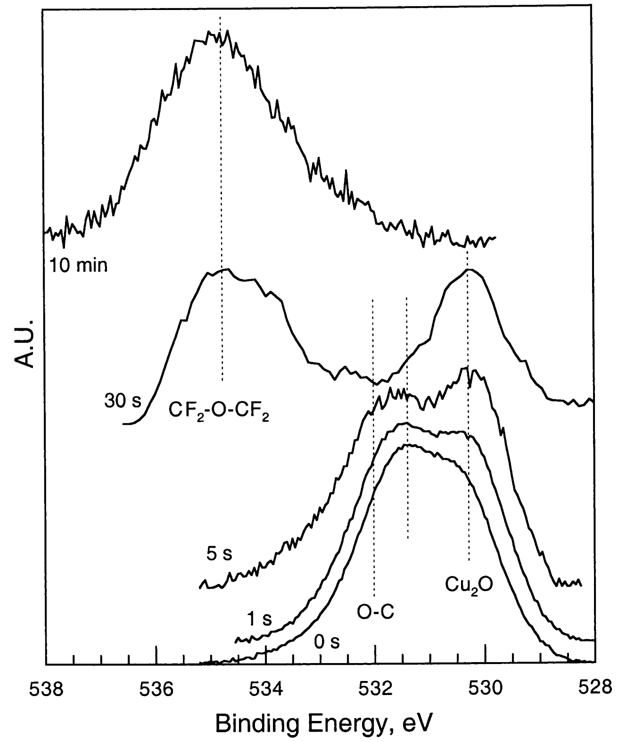

Fig. 7. O_{1s} spectra for various deposition times.

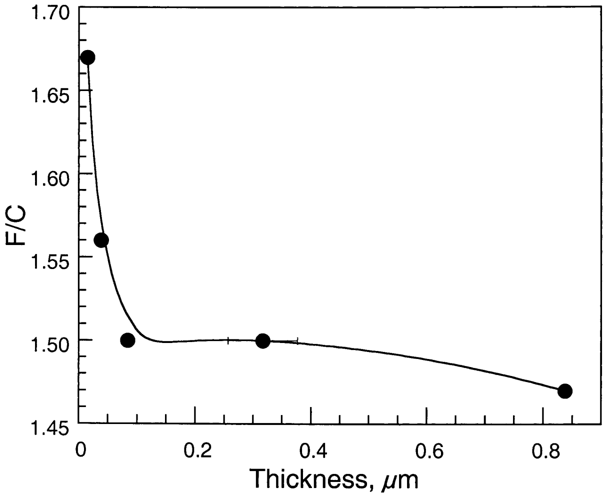

Fig. 8. F/C ratio as a function of film thickness.

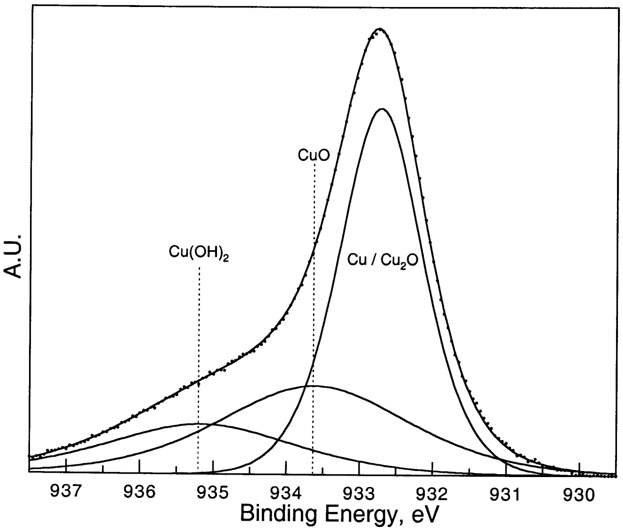

Fig. 9. Curve fit for the Cu_{2p} spectrum for bare copper substrate.

Cu_{2p} spectrum in Fig. 5 is asymmetrical, exhibiting a shoulder at higher binding energies. The curve fit for the Cu_{2p} spectrum, in Fig. 9, and the resulting $A_2(i)$, suggest the presence of 54.5% copper metal and/or Cu_2O at 932.7 eV, 29.7% CuO at 933.6 eV and 15.8% $Cu(OH)_2$ at 935.2 eV.

The C_{1s} spectrum of the copper substrate, in Fig. 4, exhibits its strongest peak at the lowest binding energy. The curve fit for the C_{1s} spectrum from the copper substrate, in Fig. 10, yields 6.5% hydroxyl/ether (286.5 eV), 9.3% carbonyl (288.3 eV) and 10.8% carboxyl (289.3 eV) (Table 2) [11].

The elemental composition of the copper substrate is affected by its exposure to the atmosphere. Values of C/Cu and O/Cu calculated from the XPS spectra of the copper substrate are seen in Fig. 11. Samples A and B, in Fig. 11, result from exposure of the freshly deposited copper substrate to the atmosphere for periods of one day and one month, respectively; sample A is the copper substrate discussed above. The XPS survey of sample B, following one month's atmospheric exposure, reveals an increase in the carbon content, from 28% for sample A to 36%, and a decrease in copper content, from 30 to 18%. Sample C, in Fig. 11, is the result of exposing Sample B to an argon plasma for 2 min. The argon plasma exposure took place in the sample preparation chamber attached to the XPS chamber, which permitted transfer from the sample preparation chamber to the XPS chamber without breaking vacuum; the XPS spectrum reveals a significant drop in carbon and oxygen contents, and a copper content of 61%.

The variations in the C–C, CF_2 and CF_3 contents with OFCB plasma exposure time, in Table 2 and Fig. 12, are derived from C_{1s} spectral curve fits such as that in Fig. 11.

4. Discussion

The change in the copper substrate on exposure to an OFCB plasma can only be evaluated following characterizations of the copper substrate surface and the PPOFCB formed on relatively long OFCB plasma exposure times.

4.1. PPOFCB

The copper-sputtered silicon wafer substrate surface (Fig. 1(a)) consists of spherical islands 50 to 100 nm in diameter with an RMS roughness of 0.97 nm. The surface becomes smoother following a 30 s OFCB plasma exposure (Fig. 1(b)) which yields a PPOFCB film approximately 15 nm thick [3]; the 0.46 nm RMS roughness for the 15 nm thick PPOFCB film in Fig. 1(b) is about half that

Table 2
Peak contributions to C_{1s} spectra for various OFCB plasma exposure times

Exposure Time, s		0	1	5	30	600
PPOFCB Thickness, nm		–	–	–	15	300
Group	BE, eV	$A_2(i)$, %				
C–C	285.0	73.4	72.0	37.7	–	–
C–O, C^*–CF_n	286.4–287.0	6.5	6.3	14.5	15.6	17.7
C=O, CF	288.0–288.4	9.3	8.6	14.3	8.1	9.9
O–C=O, C^*F–CF_n	289.1–289.6	10.8	11.0	8.5	17.5	15.3
CF_2	290.9–291.3	–	2.1	20.5	38.2	32.9
CF_3	293.1–293.4	–	–	4.5	20.6	24.2

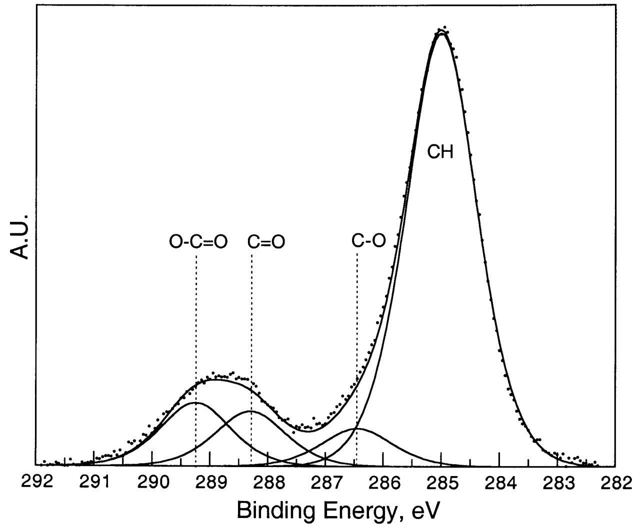

Fig. 10. Curve fit for the C_{1s} spectrum for bare copper substrate.

of the Cu substrate. The deposition of a 15 nm PPOFCB film thus planarizes the rougher substrate; the roughness is unchanged with further PPOFCB deposition, as seen for a 300 nm thick film after a 10 min deposition in Figs. 1(c) and 2. The variations in surface roughness with deposition time are similar for the 1×1 and 0.2×0.2 μm^2 scans, although the RMS roughness values are different. The smoothness of the films suggests that plasma polymerization occurs predominantly on the surface rather than in the gas phase: spherical particles would have been deposited from a predominantly gas phase polymerization, yielding a significantly rougher surface [3,12].

The PPOFCB composition is relatively constant for films thicker than 15 nm, approximately 60% F, 39% C and 1% O (Table 1). The low oxygen content, approximately 1%, is typical of plasma fluoropolymers [3,12], the incorporated oxygen originating in the reaction of long-lived plasma polymer radicals with atmospheric oxygen [3,12].

The initial rapid decrease in F/C (Fig. 8) may reflect the unsteady state of the plasma polymerization and plasma etching reactions in the first few minutes of plasma exposure: fluorine-rich groups are removed from PPOFCB under the influence of ion bombardment and vacuum UV [13]. The F/C would reach a plateau once these reactions have reached their steady states. The F/C calculated from the C_{1s} curve fit corresponds to that calculated from the spectra of the individual elements [3]. The CF_2 peak for the 30 s OFCB plasma exposure in Fig. 4 seems more prominent than that for the 600 s exposure and this is reflected in the curve fit (Table 2). There is also a slight decrease in fluorine content between the films from the 30 and 600 s deposits (Fig. 3, Table 1), although this may be within experimental error. These changes in the nature of the PPOFCB film probably reflect ion bombardment and vacuum UV defluorination.

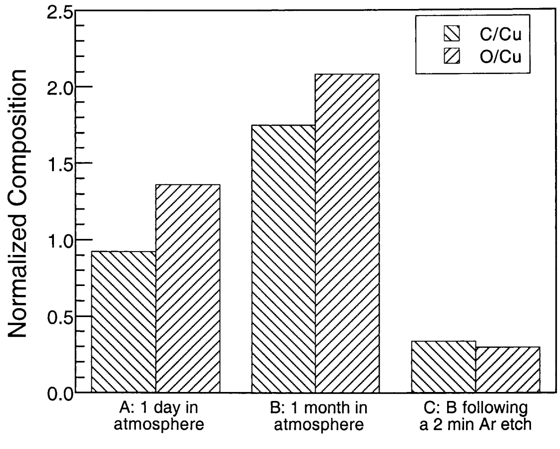

Fig. 11. Contaminated and cleaned copper.

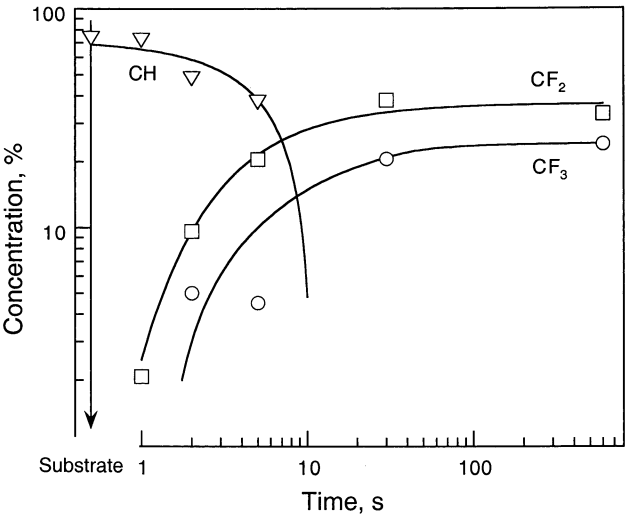

Fig. 12. Concentration of various groups as a function of deposition time.

The CF_3 and CF_2 peaks exhibit K_α satellites at binding energies 8.4 and 10.2 eV beneath those of the main peak, accounting for the tail at approximately 285 eV and below. The full width at half maximum (FWHM) of about 2 eV is typical of the random-fragment molecular structure of plasma polymers [3,14], and certainly reflects the composite natures of the peaks. The F_{1s} spectra of the thicker PPOFCB films (30 and 600 s OFCB plasma exposure) in Fig. 6 exhibit a peak at 688.6 eV, typical of CF_n [11].

4.2. Copper substrate

Copper, when exposed to the atmosphere, initially oxidizes to Cu_2O; however, depending on the atmospheric conditions, some CuO and $Cu(OH)_2$ may also be formed [15,16]. The bare copper surface was exposed to the atmosphere prior to XPS analysis. The significant amounts of carbon and oxygen on the surface (Table 1) indicate that the copper metal is covered by both oxidized copper and a hydrocarbon contaminant, as expected [15,16]. This was confirmed by the curve fit for the Cu_{2p} spectrum (Fig. 9), which revealed a peak associated with Cu_2O (and Cu metal) that dominated the spectrum, as well as peaks representing CuO and $Cu(OH)_2$. Given that copper oxidizes at several nanometers per day [16], the peak at 932.7 eV is most likely Cu_2O, rather than copper metal or a combination of the two. The FWHM of the Cu/Cu_2O peak was 1.4, while the FWHM of the CuO and $Cu(OH)_2$ peaks were 3.1. These FWHM are similar to those reported in the literature [10,17]. A smaller FWHM for metals and a larger FWHM for oxides has been attributed to a greater vibrational broadening for the oxide [18]. In addition, the broader peaks at higher binding energies may be composite peaks and include contributions from various $Cu(OR)_2$ species whose peaks cannot be resolved. The R represents the hydrocarbon contaminant that deposits when the fresh copper surface is exposed to the atmosphere. Typical binding energies of such $Cu(OR)_2$ species lie between 934 and 935 eV [8].

The C_{1s} curve fit in Fig. 10 reveals the nature of the hydrocarbon contaminant; the contaminant is dominated by C–C groups (73.4%) and also includes oxidized carbon groups (Table 2, 0 s). The oxidized groups include C–OR (hydroxyl, ether), C=O (carbonyl) and COOR (acid, ester). Based on Table 2, C/O for the oxidized hydrocarbon contaminant is 2.7. The FWHM is about 1.5 eV, much narrower than that for PPOFCB. The FWHM reflects the molecular structure, with narrower peaks for the oxidized hydrocarbon contaminant absorbed from the atmosphere and significantly wider composite peaks for the random fragment plasma polymer.

The C_{1s} and Cu_{2p} curve fits, in Figs. 10 and 11, respectively, may be used to attribute the oxygens bound to copper and carbon, respectively; the oxygen contents in the oxidized copper and in the oxidized hydrocarbon contaminant can be derived based on the $A_2(i)$ values from the spectral curve fits. The contributions of these oxygens to the total composition can be calculated using the elemental compositions, $A_1(i)$, in Table 1. Eq. (1) was used to calculate O(Cu), the oxygen content associated with the oxidized copper (assuming that the peak at 932.7 eV is Cu_2O only), and Eq. (2) was used to calculate O(HC), the oxygen content associated with the oxidized hydrocarbon contaminant.

$$\mathrm{O(Cu)} = (0.5A_2(\mathrm{Cu_2O}) + A_2(\mathrm{CuO}) + 2A_2(\mathrm{Cu(OH)_2}))^* A_1(\mathrm{Cu})/100 \quad (1)$$

$$\mathrm{O(HC)} = (A_2(\mathrm{C{-}OR}) + A_2(\mathrm{C{=}O}) + 2A_2(\mathrm{COOR}))^* A_1(\mathrm{C})/100 \quad (2)$$

An oxygen content of 27% is associated with the oxidized copper but only 11% is associated with the oxidized hydrocarbon contaminant. The total oxygen content calculated from these curve fits is, therefore, 38%, within experimental error of the 41% calculated from the spectra of the individual elements. The O_{1s} spectrum of the contaminated copper substrate, Fig. 7 (0 s), is quite broad. This spectrum contains peaks typical of bonds to carbon (531.8 eV) and to copper (Cu_2O, 530.5 eV; CuO, 533 eV; and $Cu(OH)_2$, 535 eV) [8,11].

The amount of oxidized hydrocarbon contaminant continues to increase with increasing atmospheric exposure. C/Cu and O/Cu increase significantly as the atmospheric exposure increases from 1 day to 1 month (Fig. 11), indicating the presence of a thicker layer of oxidized hydrocarbon contaminant on the copper surface. The brief argon plasma exposure removes a significant portion of the oxidized hydrocarbon contaminant, leading to a significant reduction in C/Cu and O/Cu.

All the specimens in this work were exposed to about 1 day of atmospheric conditions between the copper sputtering/OFCB plasma exposure and the XPS analysis. No oxidized hydrocarbon contaminant was detected on the PPOFCB films. The lack of an oxidized hydrocarbon contaminant reflects the low surface energy of the plasma fluoropolymer [12]. Any exposed copper on the surface of a specimen is expected to oxidize and to be covered with an oxidized hydrocarbon contaminant. Thus, if PPOFCB coverage of the surface is incomplete during the initial stages of deposition, the surface that is not covered with PPOFCB will be covered in a fashion similar to that of the exposed copper substrate.

4.3. Copper-fluoropolymer interface

4.3.1. First second of OFCB plasma exposure

The most significant change on the surface following exposure to an OFCB plasma for 1 s is the appearance of a significant amount of fluorine; the XPS survey scan detects 11% fluorine, 32.1% copper, 24.1% carbon and 32.3% oxygen (Table 1). The C_{1s}, Cu_{2p} and O_{1s} spectra for a 1 s OFCB plasma exposure in Figs. 4, 5 and 7, respectively, are quite similar to those of the copper substrate (0 s). These similarities suggest that the surface, following a 1 s OFCB plasma exposure, consists mainly of copper oxide and oxidized hydrocarbon contaminant. Such a brief OFCB plasma exposure does not yield an identifiable fluoropolymer coating on the copper that would prevent copper oxidation and the deposition of an oxidized hydrocarbon contaminant. The Cu_{2p} spectrum for the 1 s OFCB plasma exposure in Fig. 5, however, is somewhat less asymmetrical than that of the substrate (0 s), suggesting that there is somewhat less CuO and $Cu(OH)_2$ (and, probably, less Cu_2O).

The nature of the 11.5% fluorine on the surface, following a 1 s OFCB plasma exposure, was characterized through the C_{1s} and F_{1s} spectra in Figs. 4 and 6, respectively. The curve fit (not shown) of the C_{1s} spectrum in Fig. 4 for the 1 s OFCB plasma exposure reveals the presence of a small additional peak at 290.9 eV, representing CF_2. The F_{1s} spectrum following 1 s OFCB plasma exposure exhibits two distinct peaks; the smaller peak at 688.0 eV, representing CF_n from a fluorocarbon deposition, and the larger peak at 684.0 eV, found neither for the copper substrate nor in the plasma polymer, representing the F ion [8]. This suggests that some copper fluorination occurs during the first second of OFCB plasma exposure, yielding CuF. The binding energy of the copper associated with the F ion would be approximately the same as that for copper metal and Cu_2O, accounting for the similarity in the Cu_{2p} spectra for 0 and 1 s OFCB plasma exposures in Fig. 5. In the Cu_{2p} spectrum for 1 s OFCB plasma exposure (Fig. 5), there is no peak at 935 eV (nor its associated shake-up satellite) that would correspond to the formation of CuF_2 [9].

4.3.2. Increasing OFCB plasma exposure

The XPS characterization (Table 1, Fig. 3) shows that the copper and oxygen contents decrease, and the fluorine content increases, with increasing OFCB plasma exposure. These changes in atomic composition correspond to the formation of a PPOFCB film on the copper substrate. Following a 5 s OFCB plasma exposure, the fluorine content is 38.4%. The relative height of the F_{1s} spectrum peak at 684.0 eV, representing the F ion, decreases with OFCB plasma exposure while the relative height of the peak at 688.6 eV, representing CF_n, increases (Fig. 6).

The PPOFCB deposition also affects copper oxidation and contaminant deposition. Following a 5 s OFCB plasma exposure, XPS detects 18.5% copper and 11.5% oxygen (Table 1). The oxygen content and O/C are relatively low. This suggests that there is significantly less oxidized hydrocarbon contaminant deposited as PPOFCB begins to cover the surface. The Cu_{2p} spectrum in Fig. 5 for a 5 s OFCB plasma exposure is quite similar to that for the 1 s exposure. The main peak, at 932.7 eV, is attributed to Cu_2O and/or copper metal. The O_{1s} spectrum for a 5 s exposure to an OFCB plasma in Fig. 7 is similar to that of the copper substrate (0 s) in many respects, having the same peaks representing oxidized copper and oxidized hydrocarbon contaminant.

The deposition of PPOFCB, and the subsequent decreases in copper oxidation and in oxidized hydrocarbon contaminant, continue with increased OFCB plasma exposure. Following a 30 s OFCB plasma exposure which deposited a 15 nm thick PPOFCB film, the copper substrate could not be detected by XPS (Fig. 3). The substrate is thus uniformly coated with a PPOFCB film (Fig. 1b) whose thickness is significantly greater than the Cu_{2p} photoelectron's mean free path through the polymer film. The F ion peak is not seen in the F_{1s} spectrum, only the CF_n peak representing PPOFCB (Fig. 6). A trace of the substrate was discerned in the O_{1s} spectrum (Fig. 7), with two peaks exhibited for the 0.8% oxygen detected by XPS. The peak at 539.4 eV is typical of the thick PPOFCB films and represents CF_n–*O*–CF_n [11]. The peak at 530.5 eV is typical of the oxidized copper. The ability to discern the oxidized copper peak for the O_{1s} spectrum, but not the Cu_{2p} peak, most likely reflects the higher mean free path of the electron emitted by the oxygen [19]. No peak at 530.5 eV is found for PPOFCB films that are thicker than 15 nm.

The natures of the changes on the surface are also reflected by the changes in the C_{1s} spectra in Fig. 4 and the variation in the C–C, CF_2 and CF_3 contents in Fig. 12. There are distinct CF_2 and CF_3 peaks at 291.0 and 293.1 eV, respectively, after a 2 s OFCB plasma exposure. With increasing OFCB plasma exposure time, the CF_2 and CF_3 peaks become more prominent, and occur at slightly higher binding energies, while the C–C peak at 285 eV becomes less prominent; there is no discernable C–C peak following a 30 s OFCB plasma exposure. The C–C peak associated with the hydrocarbon contaminant thus disappears within 30 s of OFCB plasma exposure. The relative heights of the C_{1s} peaks associated with CF_n increase rapidly in the first 10 s and reach a plateau after 30 s.

The variations in elemental composition and group concentration thus provide a detailed description of the effects of OFCB plasma exposure on the copper substrate, beginning with the incorporation of the F ion in CuF during the first second of OFCB plasma exposure and ending in the deposition of a smooth, planarizing PPOFCB film, with no exposed copper, following a 30 s OFCB plasma exposure.

5. Conclusions

The effects of an OFCB plasma on a copper substrate and on the nature of the deposited PPOFCB were investigated. The surfaces of copper exposed to an OFCB plasma for times as short as 1 s to as long as 30 min were characterized using XPS. The copper on the surface is oxidized, on exposure to atmosphere, and covered by an oxidized hydrocarbon contaminant. During the first second of OFCB plasma exposure, CuF is produced (with an F ion peak at 684 eV); as well, fluorocarbon species deposit (with a CF_n peak at 688 eV). Following several more seconds of OFCB plasma exposure, the deposited fluorocarbon begins to dominate the surface, although oxidized copper and oxidized hydrocarbon contaminant are still observed. However, the copper substrate beneath a 15 nm PPOFCB film (30 s OFCB plasma exposure) could no longer be detected via XPS nor was oxidized hydrocarbon contaminant found on the low energy PPOFCB surface. The F/C for PPOFCB can be as high as 1.68 after brief deposition times (30 s), reaching a plateau value of 1.5 following several minutes of plasma exposure. This reduction in F/C is associated with ion bombardment and vacuum UV defluorination. PPOFCB is a smooth, planarizing film with plasma polymerization occurring predominantly on the surface and reducing the RMS roughness from 0.97 nm to 0.46 nm.

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