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Stable Perfluorosilane Self-Assembled Monolayers on Copper Oxide Surfaces: Evidence of Siloxy−Copper Bond Formation

E. Hoque,*,† J. A. DeRose,‡ R. Houriet,§ P. Hoffmann,|| and H. J. Mathieu†

LMCH, IMX; LTCM, ISE; LTP, IMX; LOA, IOA; Ecole Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland

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Formation of stable and hydrophobic self-assembled monolayers (SAMs) on an oxidized copper (Cu) surface has been accomplished via reaction with 1*H*,1*H*,2*H*,2*H*-perfluorodecyldimethylchlorosilane (PFMS). The perfluoroalkyl SAMs showed sessile drop static contact angles of more than 125° for pure water and stability against exposure to boiling water, boiling nitric acid solution, and warm sodium hydroxide solution for up to 30 min. X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared reflection/absorption spectroscopy (FT-IRRAS) data reveal a coordination of the PFMS silicon (Si) atom with a cuprate (CuO) molecule present on the oxidized copper substrate. The data give good evidence that the stability of the SAM film on the PFMS-modified oxidized Cu surface is largely due to the formation of a siloxy−copper (−Si−O−Cu−) bond via a condensation reaction between silanol (−Si−OH) and copper hydroxide (−CuOH). The extremely hydrophobic and stable SAMs on oxidized Cu could have useful applications in corrosion inhibition for micro/nanoelectronics and/or heat exchange surfaces exploiting dropwise condensation.

Introduction

This report presents the results of self-assembled monolayers (SAMs) formed on oxidized copper (Cu) substrates via reaction with 1*H*,1*H*,2*H*,2*H*-perfluorodecyldimethylchlorosilane (PFMS). These SAMs are able to protect the Cu substrate from very harsh, corrosive conditions. Although SAMs formed by reaction of alkylsilanes with silicon oxides and alkanethiols with Cu and gold (Au) substrates have been extensively investigated,[1−5] there is no report in the public domain on SAMs formed by perfluorosilanization of an oxidized copper (Cu) substrate (PFMS/Cu) to the best of the authors' knowledge. A significant obstacle to the implementation of SAMs in everyday applications is the poor durability of these thin films under ambient or more extreme conditions. Formation of SAMs on Cu substrates has become an important field of both fundamental and applied research, for example, corrosion inhibition[6−10] of Cu used in microelectronic device fabrication and heat exchange surfaces which exploit dropwise condensation.[11] Cu is destined to replace aluminum (Al) alloy as the principle VLSI/ULSI (very large- or ultra large-scale integration) interconnection material due to its lower electrical and thermal resistivity and higher resistance to electromigration. Despite these advantages, one of the major concerns when using it as an interconnection material is its susceptibility to corrosion and oxidation. SAMs and other thin films on Cu have been shown to inhibit corrosion,[6,7,12] however, the durability of alkanethiol SAM/Cu films is too low for most practical applications. Heat transfer is most efficient via condensation of a fluid medium onto a heat exchange surface. Dropwise condensation has been known to produce heat transfer coefficients up to 20 times that of filmwise condensation; it is for this reason that, over the past few decades, considerable attention has been paid toward the development of suitable dropwise condensation promoters, but the main problem has been durability of these promoters.[11,13]

The structure, chemical composition, wetting properties, and stability of the PFMS/Cu surface have been analyzed by using a multiple technique approach: X-ray photoelectron spectroscopy (XPS), Fourier transform infrared reflection/absorption spectroscopy (FT-IRRAS), atomic force microscopy (AFM), and contact angle measurement (CAM). The data show that the PFMS/Cu SAM is chemisorbed onto the

* Corresponding author. Fax: +41 21 693 3946. Tel: +41 693 2972. E-mail: enamul.hoque@epfl.ch.
† LMCH, IMX.
‡ LTCM, ISE.
§ LTP, IMX.
|| LOA, IOA.

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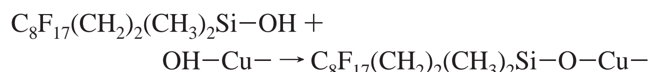
oxidized Cu surface via a siloxy−copper (−Si−O−Cu−) bond. As chlorosilanes are rapidly hydrolyzed by water and form silanols:[14]

$$-\text{Si}-\text{Cl} + H_2O \rightarrow -\text{Si}-\text{OH} + \text{HCl}$$

the data collected lead to the conclusion that perfluorodecyldimethylsilanol ($C_8F_{17}(CH_2)_2(CH_3)_2SiOH$) undergoes a condensation reaction with copper hydroxide (CuOH) present on the oxidized Cu surface to form a siloxy−copper bond:



$$C_8F_{17}(CH_2)_2(CH_3)_2\text{Si}-\text{OH} + \text{OH}-\text{Cu}- \rightarrow C_8F_{17}(CH_2)_2(CH_3)_2\text{Si}-\text{O}-\text{Cu}-$$

Experimental Section

Circular Cu (99.98%) discs of 3-mm thickness and 12-mm diameter were used for all experiments. Copper discs were mechanically polished with silicon carbide (SiC) paper of grades 500−4000 and a micropolishing pad until the copper surface showed a highly reflective “mirror” finish. All the polished samples were ultrasonicated in ethyl acetate, isopropyl alcohol, and deionized water (DI H_2O) for 10 min each, blown dry, oxidized by exposure to a 5% aqueous hydrogen peroxide (H_2O_2) solution for 5−10 min at room temperature, and then reacted with 1*H*,1*H*,2*H*,2*H*-perfluorodecyldimethylchlorosilane ($F_3C(CF_2)_7(CH_2)_2(CH_3)_2SiCl$; CAS #74612-30-9) [PFMS] (ABCR, Germany) by immersion for 50 min into a 0.1% (wt) PFMS solution using hexane ($H_3C(CH_2)_4CH_3$; Merck, Darmstadt, Germany) as the solvent. Surface roughness of polished Cu and PFMS/Cu samples was measured from high-resolution topographic images obtained with a Park Scientific Instruments atomic force microscope (AFM) at room temperature and atmospheric pressure in contact mode. The polished, oxidized Cu and chemically modified Cu surface composition was analyzed by a Kratos Axis Ultra X-ray photoelectron spectrometer using Al $K\alpha_{1,2}$ monochromatic radiation at 15 kV and 150 W and operating in ultrahigh vacuum (UHV) with a base pressure below 10^{-9} mbar. Survey scans were performed in a range of 0−1100 eV binding energy with a pass energy of 80 eV and single peaks were measured with a pass energy of 20 eV. The core-level signals were obtained at a photoelectron takeoff angle of 90° (with respect to the sample surface). The binding energy (BE) values were referenced to the carbon C 1s photoelectron peak at 284.8 eV.[15,16] After linear-type background subtraction, the deconvolution of high-resolution XPS peaks has been done by mixed Gaussian−Lorentzian (G/L) fit. Quantitative analysis of the species at the sample surface was performed using the XPS area peak intensities. XPS analysis was performed using the standard software CASA XPS.[17] The estimated relative error for all XPS data used for elemental quantification is ±2%. Fourier transform infrared reflection/absorption spectroscopy (FT-IRRAS) was carried out with a Perkin-Elmer Spectrum optical bench using a Spectratech Grazing Angle FT-80 system equipped with a wire grid polarizer. The measurements were done with polarized light at grazing incidence (80° angle of incidence with respect to the surface normal). All spectra were recorded by collecting 256 scans over the 4000−400 cm^{-1} spectral region with a resolution of 4 cm^{-1}. Measurements were performed with a 90° polarization angle (electric field vector, **E**, direction with respect to the sample surface; p-polarized). Static water sessile drop contact angle measurements (S-CAMs) and dynamic water sessile drop contact angle measurements (D-CAMs) for determining the wetting properties of the unmodified Cu, PFMS-modified Cu, and stability-tested (treated) PFMS-modified Cu were performed with a GBX Digidrop contact angle system using ultrapure H_2O (Fluka) at 75−90% relative humidity (RH) and 23−25 °C. Liquid drops of volume $< 10\ \mu$L were used for S-CAMs and 5−10 μL for D-CAMs. All sessile drop contact angles have an absolute error or uncertainty of ±3°. Stability tests were done by immersing the PFMS/Cu samples in boiling H_2O, a boiling nitric (HNO_3) acid aqueous solution with a pH of 1.8, and/or a sodium hydroxide (NaOH) solution at 60 °C with a pH of 12 for 30 min.

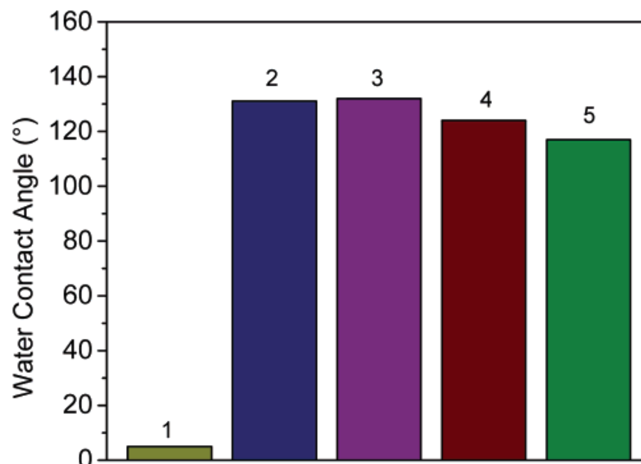


Figure 1. Water sessile drop static contact angle measurement (S-CAM) data taken on (1) unmodified, oxidized Cu; (2) untreated PFMS/Cu; (3) PFMS/Cu treated with boiling HNO_3 of pH 1.8 for 30 min); (4) PFMS/Cu treated with boiling H_2O for 30 min; and (5) PFMS/Cu treated with NaOH of pH 12 at 60 °C for 30 min.

Results and Discussion

Characterization of PFMS/Cu SAM Film. The rms surface roughness of unmodified Cu and PFMS/Cu was measured over an area of 5 × 5 μm^2 by AFM and found to be less than 15 nm. The AFM images for both the samples showed similar morphology.

Figure 1 is a histogram showing the S-CAM data for pure H_2O on the following: (1) unmodified Cu (<5°); (2) untreated PFMS/Cu (132°); (3) PFMS/Cu exposed to boiling HNO_3 of pH 1.8 for 30 min (133°); (4) PFMS/Cu exposed to boiling H_2O for 30 min (124°); and (5) PFMS/Cu exposed to NaOH of pH 12 at 60 °C for 30 min (118°). The results above were reproducible with multiple Cu samples modified

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Table 1. Dynamic Water Sessile Drop Contact Angle Measurement (D-CAM) Data for Untreated and Boiling-HNO_3-Treated PFMS/Cu[a]

substrate	advancing (°)	receding (°)	hysteresis (°)
PFMS/Cu	132	98	34
PFMS/Cu (HNO_3)	133	95	38

[a] The advancing and receding angles and the corresponding hysteresis remain virtually the same before and after treatment.

with PFMS at different times. Table 1 lists D-CAM data (advancing and receding contact angles, as well as the corresponding hysteresis) for pure H_2O on untreated PFMS/Cu and PFMS/Cu exposed to boiling HNO_3 of pH 1.8 for 30 min. CAM data were obtained to determine the wetting properties of the sample surfaces (hydrophilic oxidized Cu versus hydrophobic PFMS/Cu) before and after different types of harsh treatment to determine SAM film stability. Contact angles are dependent on the surface energy which is related to the orientation of the molecules in the SAM film.[18] In well-ordered monolayers, the terminal trifluoromethyl ($-CF_3$) group of the perfluoroalkyl chain is oriented outward, reducing the surface energy for PFMS/Cu. S-CAM data clearly show that PFMS/Cu is very hydrophobic compared to unmodified oxidized Cu; H_2O gave static contact angles of 132° for PFMS/Cu compared to <5° for unmodified oxidized Cu. Although, on the basis of S-CAM data, PFMS/Cu treated with boiling H_2O and warm NaOH for up to 30 min shows some degradation, no significant change in S-CAM nor D-CAM data is observed for PFMS/Cu after exposure to boiling nitric acid for 30 min, thus demonstrating that the PFMS/Cu SAM film is quite stable and has a significant resistance to harsh treatments, although stability results reported for films formed on oxidized Cu by reaction with perfluorodecyltrichlorosilane ($(F_3C(CF_2)_7(CH_2)_2SiCl_3)$) are still better.[12]

Figure 2a shows a C 1s core-level high-resolution XPS spectrum taken on PFMS/Cu. The peak component at the binding energy of 283.8 eV can be attributed to $SiCH_x$ which arises from the 1 methylene ($-CH_2-$) and 2 methyl ($-CH_3$) groups coordinated with Si in the alkyl chain of the PFMS molecule. The binding energy at 284.8 eV is assigned to CH_x which arises from the 1 non-Si coordinated methylene ($-CH_2-$) present in PFMS molecule and a small amount from adventitious carbon contamination. The characteristic oxidized carbon species of alcohol or ether type (C−O−) and ester, ketone, or carboxyl type (CO−O−C/C−CO−C/CO−O−H) adsorbed from the air are observed due to atmospheric exposure between oxidation and XPS analysis.[7,12,16] Similar oxygenated carbon species are observed in the deconvoluted C 1s spectra taken on polished only and polished, oxidized Cu (data not shown here). The high-binding-energy peaks[19] of 291.1 and 293.3 eV can be unambiguously attributed to the difluoromethylene ($-CF_2-$) and $-CF_3$ functional groups, respectively, present in the perfluoroalkyl chain of PFMS. The ratio of the peak areas for $-CF_2-$ and $-CF_3$ is 6.6 ± 0.3, which is close to the expected value of 7. The binding energies of all the resolved functional groups are listed in Table 2. Table 3 summarizes the surface composition (atom %) and elemental ratios (F/

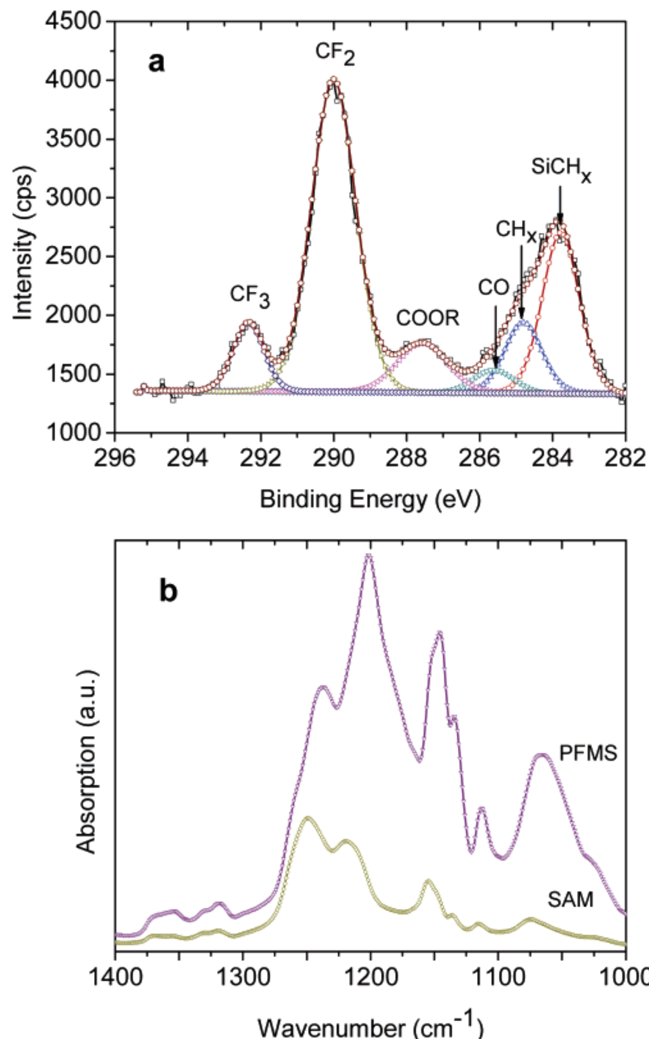

Figure 2. (a) C 1s core-level high-resolution deconvoluted XPS spectra obtained on PFMS/Cu, and (b) FT-IRRAS nonpolarized spectra taken for bulk PFMS liquid as a reference (upper) and PFMS/Cu SAM (lower).

Table 2. Corresponding Binding Energy Values for Functional Groups Typically Found on PFMS/Cu[a]

substrate	CF_3 (eV)	CF_2 (eV)	COOR (eV)	CO (eV)	CH_x (eV)	$SiCH_x$ (eV)
PFMS/Cu	292.4	290.1	287.6	285.6	284.8	283.8

[a] Each peak representing the group is deconvoluted from C 1s high-resolution XPS spectra taken on modified Cu.

Table 3. Atom Percent Concentration (atom %) for the Elements Cu, F, O, C, and Si and the Elemental Ratio of F/Si Measured on Untreated PFMS/Cu, Boiling-HNO_3-Treated PFMS/Cu, Boiling-H_2O-Treated PFMS/Cu, and Warm-NaOH-Treated PFMS/Cu[a]

substrate	Cu (atom %)	F (atom %)	O (atom %)	C (atom %)	Si (atom %)	F/Si
PFMS/Cu	5.8	48.0	11.5	32.0	2.7	17.7
PFMS/Cu (HNO_3)	7.7	47.0	13.9	28.7	2.7	17.5
PFMS/Cu (H_2O)	3.7	44.4	17.3	32.1	2.5	17.7
PFMS/Cu (NaOH)	10.0	44.9	17.5	25.1	2.5	17.9

[a] Quantified from the XPS Multiplex of Cu 2p, F 1s, C 1s, and Si 2p.

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Si) quantified from a high-resolution XPS multiplex taken on untreated PFMS/Cu, boiling-HNO_3-treated PFMS/Cu, boiling-H_2O-treated PFMS/Cu, and warm-NaOH-treated PFMS/Cu. Both F and Si are detected for the untreated PFMS/Cu. Moreover, the elemental ratio for F/Si is 17.5 to 17.9, which is close to the expected value of 17. These values remain essentially the same for all the treated PFMS/Cu samples analyzed. XPS data collected at different places on the PFMS/Cu surface indicate the formation of a chemically uniform perfluoroalkyl film on the oxidized Cu substrate. These results clearly lead to the conclusion that a perfluorinated alkyl chain film is present for both untreated and treated PFMS/Cu. As shown in Table 3, for boiling-HNO_3-treated PFMS/Cu, no significant change in XPS data for the atom % of F is detected, while for both boiling-H_2O- and warm-NaOH-treated PFMS/Cu a significant change in the atom % of F is detected. The XPS data indicate that the boiling-HNO_3 treatment does not degrade the SAM film, while the boiling-H_2O and warm-NaOH treatments degrade it somewhat, thus showing agreement with the CAM data.

Figure 2b shows FT-IRRAS nonpolarized spectra for a thick liquid film of PFMS deposited onto an unrelated substrate (as a reference) and a PFMS/Cu SAM. For the thick PFMS liquid film, absorption peaks for C−F stretching modes are observed at about 1236, 1201, and 1145 cm^{-1} with relative intensities (absorptions) of 65, 100, and 80, respectively. For PFMS/Cu, the absorption peaks for C−F stretching modes are found at about 1248, 1219, and 1154 cm^{-1} with relative intensities of 100, 82, and 52, respectively. Thus, FT-IRRAS data agree with the XPS data concerning the presence of a perfluorinated alkyl chain film for PFMS/Cu.

Formation of Siloxy−Copper (−Si−O−Cu−) Bond. Figure 3 shows a proposed schematic representation of the 1*H*,1*H*,2*H*,2*H*-perfluorodecyldimethylsiloxy−copper bond for the PFMS/Cu SAM surface. The XPS, FT-IRRAS, and CAM data give evidence that the PFMS/Cu SAM film is able to withstand harsh conditions of warm water, acid, and base with little or no degradation due to the formation of a siloxy−copper bond. The same type of bond has been proposed to explain the strong adhesion of Cu monolayers on silica (SiO_2) films.[20] In addition, it has been seen as a byproduct of copper silicon oxide ($Cu-SiO_x$) synthesis.[21] The data which support this conclusion to explain film stability are discussed below.

XPS is capable of resolving neutral copper (Cu(0)), copper with a valence of +1 (Cu(I)), and copper with a valence of +2 (Cu(II)) through the analysis of the core-level Cu 2p peaks and their corresponding "shakeup satellite" peaks, as well as the X-ray-excited Cu Auger electron $L_{2,3}M_{4,5}M_{4,5}$ line. For PFMS/Cu, the Cu $2p_{3/2}$, Si 2p, O 1s, and X-ray-excited Cu Auger lines have been inspected carefully. Figure 4a (upper) shows the deconvoluted Cu $2p_{3/2}$ spectrum of nonmodified polished, oxidized Cu. The Cu $2p_{3/2}$ component observed at 932.9 eV is not readily assigned, because Cu_2O is shifted from Cu(0) by only 0.1 eV and these two species are, thus, not distinguishable.[6,10] The most distinguished feature in the spectrum is the pronounced satellite peak in the 2p region for Cu(II); this peak is separated from the $2p_{3/2}$ peaks of Cu(0) and Cu(I) by around 10 eV.[10,22] These so-called "shakeup satellite" peaks arise on the high-binding-energy side due to the simultaneous excitation of outer-shell 3d electrons during the ejection of core-level 2p electrons.[23−26] The peak due to CuO assigned at 934 eV is shifted to higher energy by 1.1 eV from the Cu(0) and Cu_2O peaks. The deconvoluted third peak at energy 935.1 eV can readily be attributed to $Cu(OH)_2$ which is again shifted 1.1 eV from the CuO peak on the high-energy side.[12,15,27] $Cu(OH)_2$ is formed on the surface at some point between oxidization and silanization of Cu. Although CuO and $Cu(OH)_2$ are readily identifiable, they overlap with the Cu(0) and Cu_2O peaks, resulting in an overall wider peak. Figure 4a (lower) is a representative deconvoluted Cu $2p_{3/2}$ spectrum for PFMS/Cu. In this spectrum, only one main peak at 932.9 eV is identified which is unambiguously at the energy position of Cu(I)/Cu(0). The loss of the satellite peak denotes a change from Cu(II) to Cu(I). The chemical state identification can also be done by using the most intense component of the X-ray excited Auger $L_{2,3}M_{4,5}M_{4,5}$ transition. Figure 4b (upper) shows X-ray-excited Auger spectra for unmodified oxidized Cu. The broad peak at 569.4 eV corresponds to Cu(II). Figure

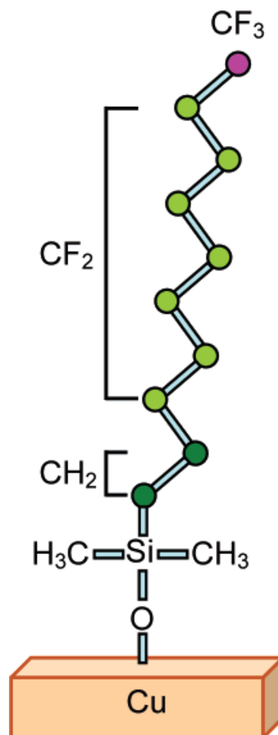

Figure 3. Proposed scheme for the 1*H*,1*H*,2*H*,2*H*-perfluorodecyldimethylsiloxy−copper bond leading to SAM formation after PFMS modification of oxidized Cu.

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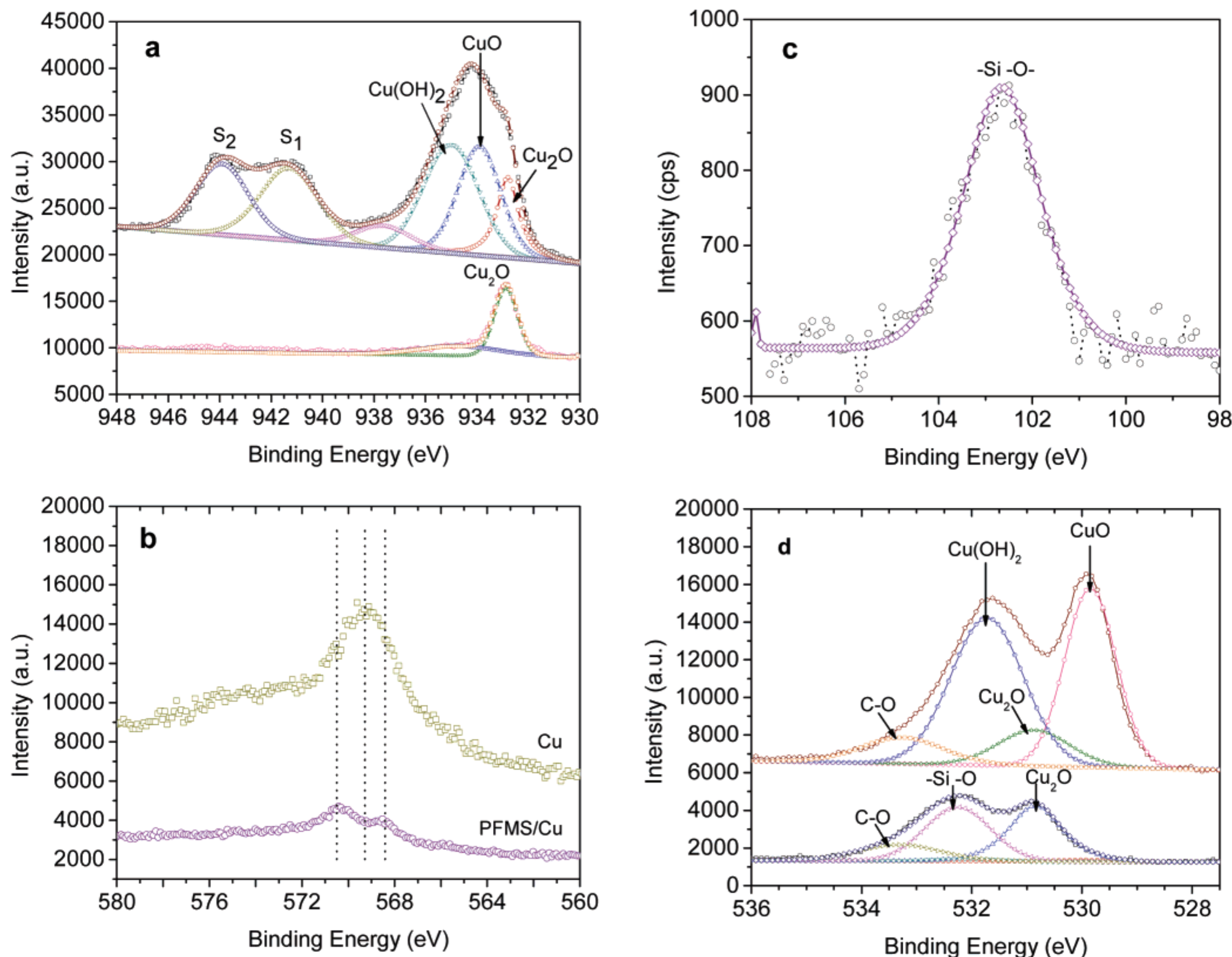

Figure 4. (a) The high-resolution Cu $2p_{3/2}$ spectra (deconvoluted) for unmodified Cu (upper) and PFMS/Cu (lower), (b) photoelectron Auger spectra on unmodified Cu (upper) and PFMS/Cu (lower) where the dashed lines mark the peaks at 568.2, 569.4, and 570.4 eV, (c) Si 2p peak for PFMS/Cu, and (d) O 1s spectra for unmodified Cu (upper) and PFMS/Cu (lower).

4b (lower) shows the X-ray-excited Auger spectrum for PFMS/Cu. After reaction with PFMS, two distinct peaks appear at 568.2 and 570.4 eV corresponding to metallic Cu-(0) and Cu(I), respectively,[10,28] which confirms again the presence of Cu(I) for PFMS/Cu.

Figure 4c shows the high-resolution XPS Si 2p spectrum. The only observed peak is at a binding energy of 102.6 eV. For Si, binding energies of around 102−102.5 eV have been found for siloxane molecules, such as polydimethylsiloxane (PDMS),[29−31] a polymer which has a repeating chemical structure with subunits of $[-O-Si(CH_3)_2-O-Si(CH_3)_2]_n$ where *n* equals the number of subunits. Once the PFMS molecule has been hydrolyzed, a silanol (−Si−OH) forms and HCl is produced as a byproduct. At this point in the reaction, it is quite possible that PFMS can dimerize to form bis(perfluorodecyldimethyl)disiloxane $[F_3C(CF_2)_7(CH_2)_2-(CH_3)_2Si-O-Si(CH_3)_2(CH_2)_2(CF_2)_7CF_3]$, which can physisorb onto the oxidized Cu surface. However, in general, a film composed of molecules physisorbed onto an oxide surface would not withstand the harsh treatments (boiling nitric acid, boiling water, warm sodium hydroxide) that PFMS/Cu has been subjected to for this study. A previous study by the authors has shown that the stability of alkylsiloxy films on oxidized Cu correlates with perfluorination of the alkylsilane molecule (thus, non-perfluorinated alkylsiloxy SAM films formed on oxidized Cu tend to be less stable against harsh treatment than perfluorinated ones, such as PFMS/Cu).[12] Also, reaction of PFMS with Au substrates leads to a film composed of physisorbed bis-(perfluorodecyldimethyl)siloxane molecules on the Au surface (PFMS/Au). PFMS/Au degrades rapidly after exposure to warm nitric acid (60 °C, pH 1.8, 10 min) on the basis of CAMs (unreported data). The PFMS/Cu film stability against harsh treatments can be explained by the hypothesis that silanol is capable of reacting with copper hydroxide (−CuOH) on the substrate surface (as is the case for free silanol molecules which react with surface-bound silanols on silicon oxide[32]), then the similarity between the siloxane bond (−Si−O−Si−) and the siloxy−copper bond (−Cu−O−Si−)

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Table 4. Infrared Vibrational Modes for PFMS/Cu SAMs on Cu

mode[a]	wavenumber (cm^{-1})
$\nu_a(CH_2)$, d^-	2924
$\nu_s(CH_2)$, d^+	2853
$\nu_a(CF_2)$; $\delta(CH_2)$ bending	1444
$\nu(CF_2)$ progression, axial CF_2 stretch	1375
$\nu(CF_2)$ progression, axial CF_2 stretch	1332
$\nu_a(CF_2)$, and $r(CF_2)$	1245
$\nu_a(CF_2) + \nu_a(CF_3)$; δ(CCC), ν(CC)	1217
$\nu_a(CF_2) + \nu_a(CF_3)$	1205
$\nu_s(CF_2)$; $\delta(CF_2)$	1151
ν(CC) stretch	1136
ν(CC) stretch	1117
ν_a(Si−O)	1040
ν_s(Si−O)	1002
$\nu_3(CF_2)$ progression	873
δ(Si−O)	822
$r(CF_2)$ wag(CF_2)	710
wag(CF_2)	665
wag(CF_2), $r(CF_2)$	623

[a] d^- = asymmetric mode, d^+ = symmetric mode, r = rocking mode, δ = bending mode, and wag = wagging mode.

proposed above becomes obvious. Thus, this peak in the Si spectrum at 102.6 eV can be a direct indication that such a bond has formed for PFMS/Cu.

Figure 4d (upper) shows a high-resolution XPS O 1s spectrum taken on unmodified oxidized Cu. The careful inspection of the O 1s XPS spectra is very important to verify the chemical changes on Cu after PFMS modification observed by deconvolution of Cu $2p_{3/2}$, Auger, and Si 2p spectra. The O 1s lines (upper) at 529.8, 530.8, and 531.7 eV are attributed to CuO, Cu_2O, and $Cu(OH)_2$, respectively. The line at 533.2 eV is due to an oxidized carbon species.[19,33] Figure 4d (lower) shows the XPS O 1s spectrum for PFMS/Cu. The lack of the CuO peak indicates that Cu(II) has disappeared after modification with PFMS. The new line at 532.2 eV is assigned as SiO as this binding energy value is in very good agreement with that reported for SiO in the literature.[34,35] The disappearance of the CuO and $Cu(OH)_2$ peaks for PFMS/Cu supports further the conclusion that a siloxy−copper bond has formed as already stated above.

Polarized FT-IRRAS is able to probe molecular conformation changes in SAM films.[36] In the case of metal surfaces, IR radiation with the electric field direction polarized perpendicular to the plane of incidence (0° polarization or s-polarized) does not result in observable dipole transitions, so only p-polarized (electric field direction polarized parallel to the plane of incidence) IR radiation can be used.[37] The vibrational modes of the perfluoroalkyl chain molecules composing the SAM film are listed in the Table 4. These vibrational modes listed are mainly based upon data published in the literature.[36,38−43] Figure 5a shows a FT-IRRAS spectrum taken over 3000−2800 cm^{-1} at a polarization angle of 90° (p-polarized) for a PFMS/Cu sample after exposure to ambient conditions for more than 240 days. The symmetric (d^+) and asymmetric (d^-) C−H stretching modes for the $-CH_2-$ groups present in the spacer perfluoroalkyl chain are assigned at 2853 and 2924 cm^{-1}, respectively, which are in agreement with data reported in the literature, 2854 (d^+) and 2925 (d^-), for perfluorinated phosphonate SAMs on Al.[36] Although the head group (reacts with the substrate) of the phosphonate SAM discussed in ref 36 differs from that of the PFMS/Cu SAM discussed here, the spacer chains and tail groups (perfluorinated *n*-alkyl chains) are homologues. The IR absorption spectra of homologous molecules can be directly compared.[44]

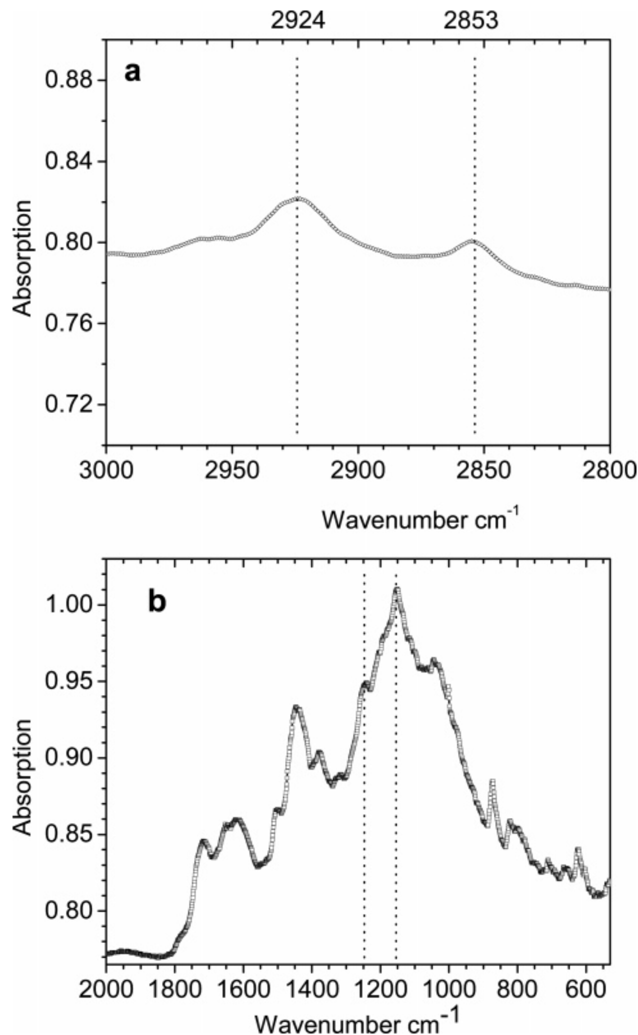

Figure 5. (a) FT-IRRAS spectrum taken on a PFMS/Cu sample after exposure to ambient conditions for more than 240 days at a polarization angle of 90° (direction of **E** with respect to the surface) over 3000−2800 cm^{-1} showing C−H stretching mode peaks (dashed lines at 2853 and 2924 cm^{-1}), and (b) FT-IRRAS spectrum taken on the same PFMS/Cu sample at a polarization angle of 90° over 2000−600 cm^{-1} (dashed lines at 1245 and 1151 cm^{-1}).

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Figure 5b shows a FT-IRRAS spectrum taken over 2000−600 cm^{-1} at a 90° polarization angle for the same PFMS/Cu sample as in Figure 5a. The asymmetric and symmetric C−F stretching mode vibrations for $-CF_2-$ groups are indicated with dashed lines at 1245 and 1151 cm^{-1} having relative intensities of 68 and 100, respectively, while the d^- stretching mode vibrations of C−F for the $-CF_3$ tail and $-CF_2-$ groups are assigned at 1205 cm^{-1} with a relative intensity of 75. An interesting feature is observed in the high-frequency region of the spectra taken on PFMS/Cu. The absorption intensity of the O−H stretch assigned at 3350 cm^{-1} is reduced dramatically for PFMS/Cu when compared to unmodified oxidized Cu (data not shown), which is in good agreement with the XPS data reported above, and it can be argued that this decline in the O−H mode occurs because $-Cu(OH)_2$ is reduced after reaction with PFMS resulting in a siloxy−copper bond. In addition, there is a Si−O stretching mode seen at 1040 cm^{-1} which is in good agreement with the literature.[34]

Conclusions

This paper presents the first study on the formation of a self-assembled-monolayer (SAM) film by reaction of 1*H*,1*H*,2*H*,2*H*-perfluorodecyldimethylchlorosilane (PFMS) with oxidized Cu (PFMS/Cu). The PFMS/Cu samples have been investigated using complementary techniques, such as X-ray photoelectron spectroscopy (XPS), Fourier transform infrared reflection/absorption spectroscopy (FT-IRRAS), and contact angle measurements (CAMs). The stability of PFMS/Cu has been determined by subjecting it to harsh conditions, and it was found that the PFMS/Cu SAM film can survive boiling water, boiling nitric acid solution, and warm sodium hydroxide solution for up to 30 min with little or no degradation. The robustness of the PFMS/Cu SAM film can be attributed, at least in part, to the formation of a siloxy−copper bond (−Si−O−Cu−) after reaction of PFMS with the oxidized Cu substrate. This conclusion is based upon XPS and FT-IRRAS data indicating the presence of copper hydroxide ($Cu(OH)_2$) and absence of siloxy (−SiO−) groups on oxidized Cu before reaction with PFMS, the presence of siloxy groups and absence of copper hydroxide on PFMS/Cu, and the resistance of PFMS/Cu to harsh treatments.

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