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AUGER ELECTRON AND X-RAY PHOTOELECTRON SPECTROSCOPIC STUDY OF THE BIOCORROSION OF COPPER BY ALGINIC ACID POLYSACCHARIDE

John G. JOLLEY *
Idaho National Engineering Laboratory/EG&G Idaho, Inc., Idaho Falls, ID 83415, USA

Gill G. GEESEY
Department of Microbiology, California State University, Long Beach, CA 90840, USA

Michael R. HANKINS, Randy B. WRIGHT and Paul L. WICHLACZ
Idaho National Engineering Laboratory/EG&G Idaho, Inc., Idaho Falls, ID 83415, USA

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Thin films (3.4 nm) of copper on germanium substrates were exposed to 2% alginic acid polysaccharide aqueous solution. Pre- and post-exposure characterization were done by Auger electron spectroscopy and X-ray photoelectron spectroscopy. Ancillary graphite furnace atomic absorption spectroscopy was used to monitor the removal process of the copper thin film from the germanium substrate. Results indicate that some of the copper was oxidized by the alginic acid solution. Some of the copper was removed from the Cu/Ge interface and incorporated into the polymer matrix. Thus, biocorrosion of copper was exhibited by the alginic acid polysaccharide.

1. Introduction

When a surface becomes exposed to a non-sterile environment, a series of chemical and biological events can occur, resulting in the surface microbial colonization and the propagation of microbial activities. The activity of micro-organisms on surfaces can be beneficial (such as biomining) or deleterious (such as biofouling and biocorrosion). Biologically induced corrosion has been shown to be responsible for a significant portion of materials failure [1–4].

In an attempt to gain a better understanding of the biological reactions that occur on surfaces under biofilms and, perhaps, exploit microbial activity,

* To whom correspondence should be addressed.

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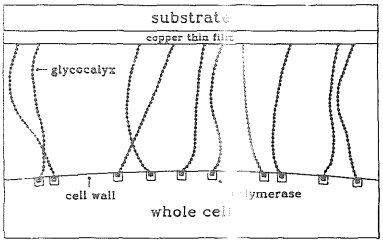

Fig. 1. Schematic of whole cell attached to surface. (Note: not to scale). The glycocalyx is comprised of long chains of polysaccharides that are formed by bacterial enzymes called polymerases (C-shaped structures). The polymerases are affixed at or near the cell surface. The whole cell uses this structure network to adhere to a nearby surface (e.g. copper thin film).

investigators have directed their attention to the near-surface region (μm range of interaction) using Fourier transform infrared/attenuated total reflection spectroscopy (FT-IR/ATR) [5–15]. This approach had led to the finding that bacterial exopolysaccharides which anchor the cells to surfaces (see fig. 1) also promote the destruction of the surface [16,17]. X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES) make it possible to examine such surface (nm range of interaction) phenomenon [18–20].

In this work alginic acid (a polymer polysaccharide produced by Kelp) interactions with copper were investigated with XPS and AES to further elucidate the nature of the destruction of a copper surface exposed to acidic polysaccharides.

2. Experimental

2.1. Sample preparation

The surface of the Ge discs (6 mm diameter by 1 mm thick) was polished using a sequence of 400 grit SiC paper, 600 grit SiC paper, 6 μm diamond paste, 1 μm diamond paste, 0.3 μm alumina and 0.05 μm alumina. Polishing cloth was used with the diamond paste and alumina. All polishing materials were manufactured by Buehler. Thin films (3.4 nm) of copper were deposited on the germanium substrates and Pyrex microscope slides in an Enerjet Model UCV-18/6 magnetron sputtering system. Substrates were mounted on Teflon fixtures in the vacuum chamber. Target materials consisted of 99.999% pure

copper supplied by Kurt J. Lesker, Co. A pumpdown pressure of 2×10^{-7} Torr was achieved before sputtering. Neon working gas (99.99% pure from Matheson Gas Products) was introduced into the sputtering chamber at a pressure of 30 mTorr. The deposition rate was 0.12 nm s^{-1}. A quartz crystal oscillator, manufactured by R.D. Mathis Co. was used to monitor the Cu thin film thickness while graphite furnace atomic absorption spectroscopy (GFAAS) was used for analysis of the Cu thickness on the substrates for system calibration. A shutter assembly was used to allow the target surface to be sputter cleaned before deposition. After two minutes of sputtering, the shutter was opened to allow deposition of the copper onto the substrates. Substrates were at ambient temperature during sputtering. Auger maps with 200 nm lateral resolution (Cu LMM at 920 eV and Ge LMM at 1147 eV) were used to evaluate the uniformity of the copper thin film on the substrate. The films appeared to be continuous, void of island effects or porosity.

Saturated polysaccharide suspensions were prepared from dehydrated preparations. Alginic acid (Sigma, A-7003) was prepared as a 2% w : v solution in 18 MΩ nanopure (np) water (obtained from a Barnstead NANOpure II water system), the pH adjusted to 7.0 with dilute HCl and NaOH, sterilized by filtering through a 0.45 μm pore size membrane, dialyzed (to reduce cation concentration by diffusion through a semipermeable membrane) [21] against np water and frozen at $-70\,^{\circ}C$ for storage.

Cu deposited Ge discs were placed into analytically clean (leached for 24 h in 10% HNO_3, rinsed with np water) vials. One mℓ (pipetted by Eppendorf pipet) of the polymer solution (np water was used as the control) were placed into the corresponding vial for copper/polymer exposure (24 h duration) at ambient temperature. At the end of the exposure time period, the Ge discs were removed from the vials with analytically clean plastic hemostats, rinsed with np water to remove residual polymer solution (rinse was not placed into vials), excess water wicked off Ge discs via side using Kimwipes and dried with N_2 gas stream from LN_2 boiloff. The np water used to rinse the Ge discs was not added to the vials in order to minimize any Cu erosion contribution from the rinsing process. Within 30 min after disc removal, the Ge discs were placed in the sample introduction system of the AES/XPS analysis system. Exposed polymer and water solutions were kept for subsequent GFAAS analysis.s

2.2. X-ray photoelectron spectroscopy

Qualitative and quantitative analyses of the Cu coated Ge substrates were done on a Perkin-Elmer Physical Electronics Model 548 XPS system which was equipped with a Model 04-151 Mg Kα X-ray source. The source was equipped with an Al window, set at 40 mA of emission current and operated at 400 W of X-ray power. A double-pass cylindrical mirror analyzer was used

with a constant pass energy of 25 eV (2% resolution). High resolution spectra were taken using multiple scan, multiplexed pulse height counting methods. Energy resolution was 5 points eV^{-1}. Chamber pressure during analyses was $< 5 \times 10^{-9}$ Torr. The energy scale was calibrated by analyzing sputter-cleaned Cu ($2p_{3/2}$ at 931.6 eV) and Au ($4f_{7/2}$ at 84.0 eV) standards. Samples were monitored (in electrical contact) on a 60° Al mount (axis of analyzer was oriented at 30° with respect to sample surface normal). The mount was installed on a 12 sample carousel. Sample exposure to X-ray radiation was < 2 h. The peak positions for the non-polymer exposed samples were referenced to the C 1s line (284.6 eV). The peak positions for the polymer-exposed samples were referenced to the Ge 3d line (29.8 eV) since the C 1s line was complex due to the polymer [22]. No peak position corrections were needed. The XPS spectra were smoothed once using a three-point weighted average.

To evaluate the possibility of X-ray or thermal (from X-ray source) induced oxidation changes of the Cu, anhydrous $CuSO_4$ was exposed to X-ray radiation from the XPS analyzer for 11 h [23,24]. No noticeable changes in the Cu 2p and Auger lines were noted.

After the XPS analyses the samples were moved, using a carousel manipulator to the opposite side of the vacuum chamber for Auger depth profile analysis.

2.3. Depth profile analysis

Depth profile analyses were done using a Perkin-Elmer PHI Model 590 Scanning Auger Microprobe and Model 04-177 sputter ion gun with argon gas. Instrumental parameters consisted of a 3.0 keV electron beam voltage, 200 nA electron beam current, 1.4×10^{-7} cm^2 rastered exposure area, 0.03 s time constant, 0.6% energy resolution, 4 eV peak-to-peak modulation and 3 eV s^{-1} scanning rate. Beam voltage was read direct. Derivative spectra were taken in the analog mode using a lock-in amplifier. A 1.0 keV, 25 μA cm^{-2} current density Ar^+ beam was used to sputter the samples with a 5 mm × 5 mm raster incident at 60° with respect to the sample surface normal. Chamber pressure (back-filled with Ar) was 5×10^{-5} Torr. A 3.4 nm thick copper thin film on germanium standard was used with each sample set. Sputtering rate was 0.65 nm Cu min^{-1}. The spectral ranges (monitored while simultaneously sputtering) were 240 to 290 eV (for C KLL at 272 eV), 900 to 930 eV (for Cu LMM at 920 eV) and 1130 to 1160 eV (for Ge LMM at 1147 eV) [25]. Peak-to-peak heights were measured. Concentrations (at%) were determined and plotted versus thickness. The C_p (crossover point) results were calculated by determining the thickness were the half distance (0.5y where y equals the total distance between the maximum and minimum concentration) crosses the trace of the data (see fig. 2).

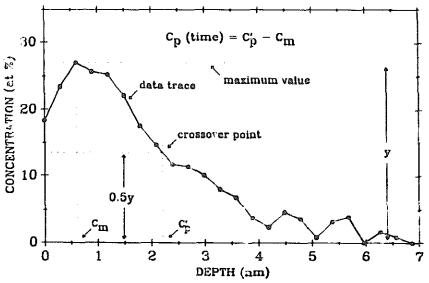

Fig. 2. C_p determination example for Auger depth profile analysis. The alginic acid Auger depth profile analysis data were used in this example.

2.4. Graphite furnace atomic absorption spectroscopy

The Cu thin films that were deposited on the microscope slides were dissolved with concentrated HNO_3. np water was used for rinsing. The resulting solutions were quantitatively transferred to 10 mℓ volumetric flasks. Aliquots (0.020 mℓ) of solutions (diluted as required for the linear absorbance range) were pipetted (using an Eppendorf pipet) into the L'vov platform equipped Perkin-Elmer HGA-400 graphite furnace which was installed in a Perkin-Elmer 703 atomic absorption spectrometer. The resulting concentration determinations were then used to calculate the Cu thin film thickness for the Ge substrates and quartz crystal oscillator response. The density of the Cu was assumed to be 8.93 g cm^{-3}.

Due to matrix effects (light scatter from polymer smoke) exhibited by the polymer, an electrochemical separation technique was used to isolate the copper from the bulk of the polymer solution [26]. The polymer solutions were transferred to an analytically clean beaker, diluted to 80 mℓ with np water and acidified with 0.50 mℓ of concentrated H_2SO_4. Two analytically clean platinum electrodes were placed into the resulting solutions and a 2.6 V potential was applied across the electrodes using a JQE 0–6 V, 0–10 A Kepco power supply. The Cu which was plated onto the Pt cathode electrode was dissolved off using 10% HNO_3. The resulting solutions were analyzed by GFAAS as above. Copper spiked controls (polymer solutions) were used to evaluate the separation yields. The control data indicated 93% separation yield. The resulting concentration determinations were then used to calculate the yield of Cu which was incorporated into the polymer solution from the Cu deposited upon the Ge substrates.

3. Results and discussion

3.1. X-ray photoelectron spectroscopy

The XPS binding and kinetic energies of the uncoated Ge disc, a metallic copper reference, copper reference compounds and samples are summarized in table 1. The resulting spectra are shown in figs. 3–5.

The Cu° was a standard left inside of the AES/XPS vacuum chamber for instrumental calibration. Prior to analysis, Ar^+ sputtering was used to remove any oxide layers. The $Cu\,2p_{1/2,3/2}$ binding and LVV kinetic energy (LVV refers to $L_3M_{4,5}M_{4,5}$) positions were 951.2, 931.4 and 919.4 eV, respectively.

Cu_2O (Alfa Products) and CuO (Johnson Matthey) powders were mounted on indium foil and used as reference standards. The $Cu\,2p_{1/2}$ positions were 951.2 and 952.4 eV; the $Cu\,2p_{3/2}$ were 931.4 and 932.0 eV; and the Cu LVV were 917.4 and 918.6 eV, respectively. The Cu_2O had the characteristic Auger shift to lower energy while the CuO 2p showed the characteristic shake-up structure. The CuO LVV displayed a shoulder at 917.4 eV. These were in agreement with previous literature findings [27–31].

The Cu/air sample had 3.4 nm of Cu sputtered upon a Ge disc which was exposed to ambient air for 5 min. The $Cu\,2p_{1/2,3/2}$ and LVV positions were 951.2, 931.2 and 919.2 eV, respectively. Due to the similarity of the Cu/air and Cu°, it was determined that the thin film of Cu had undergone undetectable oxidation and was metallic in nature. Kinetic investigations performed by Pinnel et al. indicate that the rate of copper oxide film growth at ambient conditions was $< 10^{-4}$ nm/h [32]. Thus, one would expect negligible oxidation.

Table 1
XPS photoelectron binding and Auger electron kinetic energies (eV)

Sample	Exposure time (h)	$Cu\,2p_{1/2}$ [a]	$Cu\,2p_{3/2}$ [a]	Cu LVV [b] Auger	Ge 3d [a]
Cu/AA [c]	24.0	951.4	931.4	918.8	30.2
Cu/water	1.0	951.6	931.8	917.8	N.D.
Cu/air	0.08	951.2	931.2	919.2	29.4
CuO	N.A.	952.4	932.0	918.6	N.A.
Cu_2O	N.A.	951.2	931.4	917.4	N.A.
Ge	N.A.	N.A.	N.A.	N.A.	29.8
Cu°	N.A.	951.2	931.4	919.4	N.A.

[a] Binding energy.
[b] Kinetic energy (LVV refers to $L_3M_{4,5}M_{4,5}$).
[c] Alginic acid.
N.D. = Not detectable.
N.A. = Not applicable.

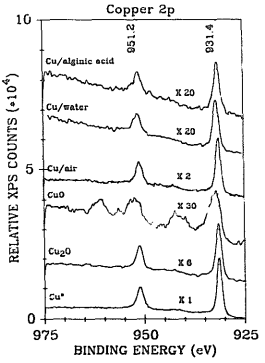

Fig. 3. Cu 2p photoelectron lines. Scaling factors are included (e.g. $\times 10$).

The Cu/water sample was prepared in the same manner as the Cu/air sample and exposed to np water for 1 h. The $Cu\,2p_{1/2,3/2}$ and LVV positions were 951.6, 931.8 and 917.8 eV, respectively. Due to the similarity of the

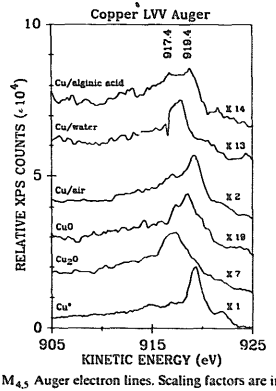

Fig. 4. $Cu\,L_3M_{4,5}M_{4,5}$ Auger electron lines. Scaling factors are included (e.g. $\times 5$).

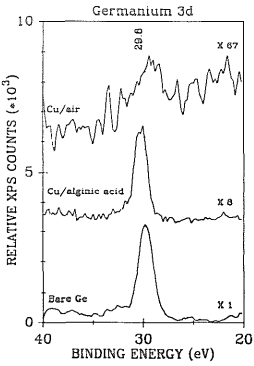

Fig. 5. Ge 3d photoelectron lines. Scaling factors are included (e.g. ×40).

Cu/water and Cu_2O spectra, it appears that the Cu had oxidized to a +1 oxidation state. One would expect some oxidation since the total oxygen concentration in ambient water is approximately 3000 times larger than in ambient air (ratio based on 56 M oxygen in water and 17 mM oxygen in air), thus resulting in a greater interaction probability.

The Cu thin films on the Ge substrates were prepared in the same manner as the Cu/air sample and then exposed to alginic acid polysaccharide solution for 24 h. The Cu 2p showed no shake-up structure while the Cu LVV peak was broadened and shifted down in kinetic energy with respect to Cu°. The Cu appears to have +1 and zero oxidation state character over the escape depth.

Since the intensity of the Ge 3d substrate signal would be expressed as follows:

$$I_B = I_B^0 \exp(-d_A C), \tag{1}$$

where I_B is the intensity of the Ge substrate with a thin overlayer, I_B^0 is the intensity of pure Ge, d_A is the thickness of the Cu thin film and constant C is equal to $(\cos\theta)/\lambda_A(E_B)$ (θ is the angle between the surface normal and detector and $\lambda_A(E_B)$ is the inelastic mean free path of the Ge 3d photoelectrons through the Cu thin film), quantitative evaluation of the Cu removal by the polymers could be done by determining the relative Ge 3d peak heights from fig. 5. d_A (air exposed) was calculated to be 2.7 nm by using the following expression:

$$\lambda_A(E_B) = 0.41 a_A^{1.5} E_B^{0.5} \tag{2}$$

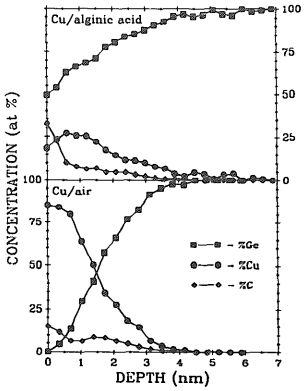

Fig. 6. Auger sputter depth profiles. Atomic percent concentrations were plotted as a function of depth.

(where a_A is the atomic size of Cu (0.361 nm) and E_B is the binding energy of the Ge photoelectron (29.8 eV for the Ge 3d)) to determine the approximate inelastic mean free path, setting I_B^0 and I_B to equal 1.51×10^3 and 13.2 relative XPS counts for the peak heights, respectively and setting θ to equal 30° [33,34]. d_A (alginic acid exposed) was calculated to be 1.1 nm by setting I_B to equal 2.07×10^2 relative XPS counts for the peak height. The data indicate that 58% of the copper had been removed by the alginic acid solution.

3.2. Auger depth profile

The sputter depth profiles are shown in fig. 6. The Cu/air sample was used for the Cu/Ge depth profile. The Cu, C and Ge maximum concentration (at%) values were 85%, 15% and 100%, respectively. The Ge started at a minimum of 0%. The C_p values were 1.6, 1.9 and 1.6 nm, respectively.

The Cu/alginic acid sample (24 h exposure) was used for the alginic acid/Cu/Ge depth profile. The Cu, C and Ge maximum concentration (at%) values were 27%, 33% and 100%, respectively. The Ge started at a minimum of 49%. The C_p values were 2.2, 0.4 and 1.6 nm, respectively. The data indicated that 68% of the Cu thin film had been removed by the polymer solution prior to analysis. FT-IR/CIR/ATR investigations performed by Jolley et al. indi-

Table 2
Graphite furnace atomic absorption spectroscopy yield

Sample	Exposure time (h)	Percent Cu removed
Cu/AA [a]	24	41
Cu/water	262	< 0.1

[a] Alginic acid.

cated that 64% of the Cu thin film had been removed by the polymer solution [35].

3.3. *Graphite furnace atomic absorption spectroscopy*

The quantitative evaluations by GFAAS of the removal of Cu for the water and polymer solutions are summarized in table 2. Less than 0.1% of the total available Cu was removed from the substrate and solubilized into the water during 262 h of exposure to np water. This result indicated that the Cu thin film was relatively stable while being exposed to np water.

Of the total Cu available, 41% was removed by the alginic acid solution from the substrate and incorporated into the solution. One would expect to find that the above value is low (as compared to the true bulk concentration) since the disc rinse was not analyzed. The concentration of removed Cu would be expected to be higher at the near-surface disc/Cu thin film region than in the bulk. Thus a significant Cu contribution may have been not accounted for. Nevertheless, the GFAAS data indicate the same general trends as the XPS and AES depth profile determinations which was the purpose of the GFAAS analysis. The polymer solution was thus able to remove a fairly large amount of the deposited Cu.

4. Summary

The XPS, AES depth profile and GFAAS data indicate that the 2% w:v alginic acid polysaccharide solution was able to oxidize some of the Cu thin film to a +1 oxidation state and also remove some of the Cu from the substrate and incorporate it into the solution. Thus, biocorrosion of copper was exhibited by alginic acid.

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