



**The Massachusetts Toxics Use Reduction Institute
University of Massachusetts Lowell**

**THE USE OF ENZYMATIC AND AQUEOUS
ELECTROCHEMICAL POLYMERIZATION OF
PHENOL AND AMPHYPHILIC ALKYL TYROSINE
BASED DERIVATIVES AS ENVIRONMENTALLY
BENIGN COATINGS**

**TOXICS USE REDUCTION INSTITUTE
UNIVERSITY RESEARCH IN SUSTAINABLE
TECHNOLOGIES PROGRAM**

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The Use of Enzymatic and Aqueous Electrochemical Polymerization of Phenol and Amphiphilic Alkyl Tyrosine Based Derivatives as Environmentally Benign Coatings

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The Toxics Use Reduction Institute
University Research in Sustainable Technologies Program

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University Research in Sustainable Technologies

The University Research in Sustainable Technologies program is a joint project of the Toxics Use Reduction Institute (TURI) and the Center for Environmentally Appropriate Materials (CEAM) at the University of Massachusetts Lowell, with support from the Commonwealth's Strategic Envirotechnology Partnership (STEP).

The program taps the research capabilities of the University of Massachusetts to advance the investigation, development and evaluation of sustainable technologies that are environmentally, occupationally and economically sound. The program provides research funding to UMass faculty from all campuses, annually, on a competitive basis and encourages faculty/industry partnerships and cross-campus collaboration. Industry partners provide guidance, propose applications for new technologies, and, in some cases, evaluate and/or adopt processes and technologies resulting from research.

Following is a list of the Fiscal Year 2000 projects.

- ❑ **Diffusion Dialysis and Acid Recovery in Metal Working and Finishing** - Prof. Francis J. Bonner and Prof. Alfred A. Donatelli, UMass Lowell, Department of Chemical and Nuclear Engineering
- ❑ **Solar Fuel Cell System** - Prof. John Duffy, UMass Lowell, Department of Mechanical Engineering, Solar Engineering Program
- ❑ **Developing and Analyzing Lead-Free Soldering Processes for Printed Wiring Boards** - Prof. Sammy G. Shina, UMass Lowell, Department of Mechanical Engineering
- ❑ **Natural "Green" Dyes for the Textile Industry** - Prof. Sukalyan Sengupta and Prof. Bal Ram Singh, UMass Dartmouth, Department of Civil and Environmental Engineering

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Abstract

The surface coating properties of enzymatically polymerized decyl esters of d-tyrosine from aqueous solutions onto gold surfaces have been investigated utilizing the complementary techniques of potentiometric titration, UV-VIC spectroscopy, and X-ray photoelectron spectroscopy (XPS). The aqueous-based coatings are of interest as environmentally friendly and cost-effective replacements for epoxy-based coatings currently employed in the microelectronics industry for both chemical protection and electrical insulation of gold-covered metallic conductors. In this final report on the project for FY2001, experimental results with respect to polymerization pH, immersion pH, and immersion time are presented and compared to the ionization behavior of the monomers in solution. Optimum processing conditions have been established which yield uniform aqueous-based polymeric coatings on gold conductor surfaces. Future research will be conducted to measure and optimize the coating thickness utilizing additional surface characterization techniques.

Introduction

The primary objective of this project during FY2001 was to identify process conditions which yield uniform aqueous-based polymeric coatings on the surface of model gold conductor substrates. This objective has been successfully accomplished. The principal investigators have taken the additional step of demonstrating that such conditions will also successfully coat the gold conductor surfaces of working devices. The polymeric coatings are based on decyl ester tyrosine derivatives (DELT or DEDT) enzymatically polymerized and deposited onto gold from aqueous solutions. These coatings are intended to replace bisphenol A (a suspected endocrine disruptor) based resins currently employed as insulating dielectrics between conductors.

Methodology

All samples were prepared by first cutting approximately 1 cm square sections from a gold-coated silicon wafer obtained from our industrial collaborator (IBM Corporation) utilizing a diamond scribe. Substantial carbon contamination was present on these substrates due to atmospheric CO₂. Hence, assessment of adsorbate coverage on gold using Au and C atomic percentages was conducted to take such contamination into account. Monomer solutions were prepared utilizing 99 ml of deionized water and the appropriate phosphate buffer to achieve the desired pH as well as sufficient DELT monomer dissolved in 1 ml methanol to yield a 0.10 mM concentration in 100 ml. DELT polymerization was achieved through the addition of 250 units of horseradish peroxidase (HRP) enzyme in 100 ml of the buffered monomer solution. Sufficient hydrogen peroxide was then added to achieve a final concentration of 10 mM DELT. The pH values were chosen on the basis of potentiometric titration results recently reported in a milestone report to UMass Lowell's Office of Collaborative Research (OCR). We have demonstrated that DELT is fully charged at a pH of 5, is of intermediate charge at pH 6, and that the amine is fully deprotonated at a pH of 7.

UV/VIS spectra were collected as a function of time once polymerization was initiated to confirm the presence of polymer. Polymerization was allowed to proceed to equilibration (a minimum of 24 hours) prior to immersion of the gold substrates. Adjustment of pH subsequent to polymerization was carried out by adding concentrated base or acid until the desired pH was attained. Microliter quantities of acid or base were found to be sufficient for this purpose such that the effect on the concentration of other constituents was negligible. Sufficient buffering capacity was present to ensure stability in the final pH desired. Substrates were immersed into these polymer solutions for various times. Since the presence of enzyme or buffer on the surface of gold could not be differentiated spectrophotometrically from that of the polymer, comparison studies were conducted by immersing substrates into solutions of comparable pH but containing no enzyme (only buffer and monomer) as well as solutions containing only buffer (no enzyme or polymer). A thick DELT monomer coating on gold was also prepared for comparison to the polymer adsorption studies by precipitating monomer from pure methanol.

As will be described in the following sections, the success of the simple immersion-dip process described above obviated the need to resort to back-up alternatives suggested in our original proposal for this project (*i.e.*, polyphenol electropolymerization and Langmuir-Blodgett film formation). Such alternatives are much more costly and their implementation into an industrial setting is much more complex than the immersion-dip process which proved capable of achieving the project objectives.

All samples were gently rinsed for three minutes in deionized water to remove un-adsorbed species subsequent to immersion into the desired solution. Excessive rinsing was avoided since it was discovered that the evaporated gold coating may become dislodged from the silicon wafer. All samples were subjected to XPS analysis and attenuation of the gold signal due to immersion was monitored. Complete attenuation of gold due to the presence of coating would yield the following expression for determining surface coverage:

$$\mathbf{f} = 1 - \mathbf{Au}/\mathbf{Au}_{\text{ref}} \quad (1)$$

where **f** is the surface fraction coated, **Au_{ref}** is the gold signal on the uncoated reference surface, and **Au** is the signal on the coated surface.

Surface coverage values obtained utilizing this equation will be too small if the gold signal is not completely attenuated by the presence of coating (*i.e.*, a coating thickness less than about 100 Angstroms). To confirm that gold attenuation in this study occurred primarily due to variation in surface coverage rather than variation in coating thickness, surface carbon content was employed as an independent measure of surface coverage in the following expression:

$$\mathbf{f} = \mathbf{C} / \mathbf{C}_{\text{ref}} \quad (2)$$

where **C_{ref}** is the carbon signal on a gold surface completely coated by polymer, and **C** is the signal obtained from a surface only partially coated.

The carbon content for a completely coated surface was obtained from the thick DELT monomer coating precipitated on gold. Comparable values for **f** were obtained using either equation 1 or equation 2, suggesting that variation in the gold signal occurs primarily due to changing surface coverage rather than changing thickness since the attenuation lengths of **Au** **4f**

and C 1s photoelectrons (employed in this study to quantify the gold and carbon content, respectively) are very different.

Results

Representative Kinetic Polymerization Data Obtained from UV/VIS

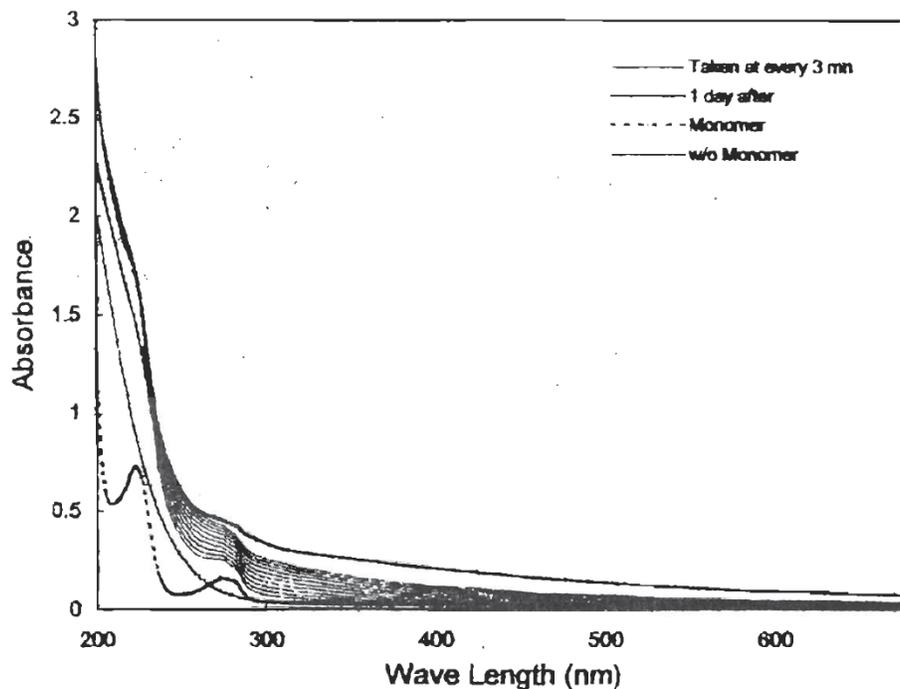


Figure 1. UV/VIS of DELT polymerization at pH 6

All XPS data obtained during the course of this study is appended to the back of this report. In the remainder of this section, only representative figures obtained from the data are shown.

Kinetic Adsorption Data via XPS

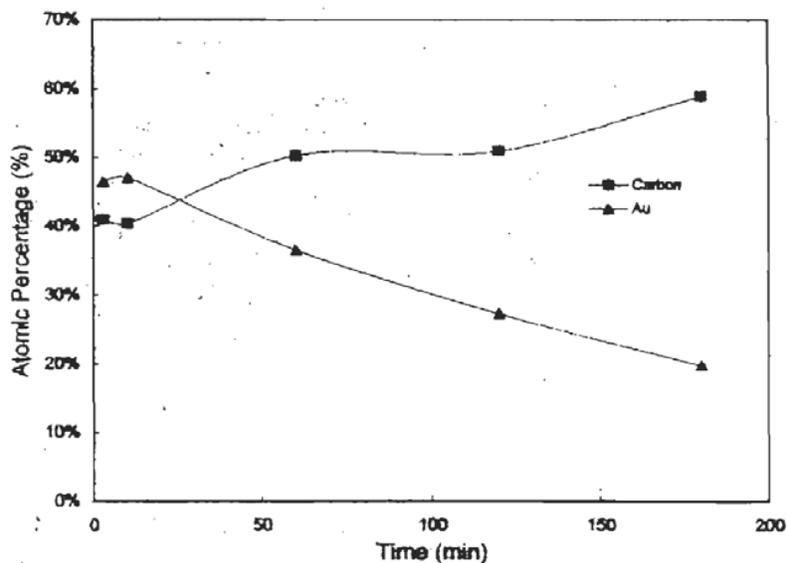


Figure 2. XPS for DELT polymerized at pH 6 adsorbed onto gold in pH 6 solution as a function of immersion time.

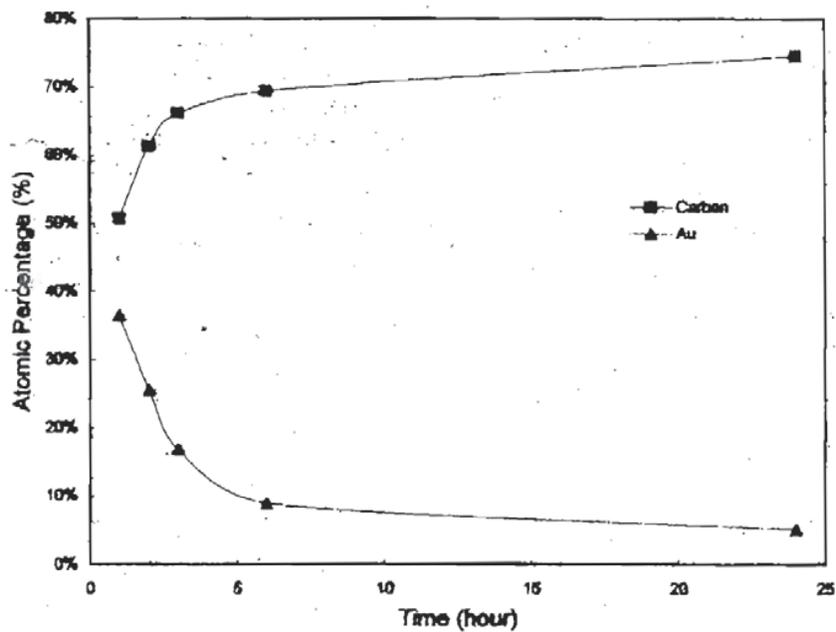


Figure 3. XPS for DELT polymerized at pH 6 adsorbed onto gold in pH 7 solution as a function of immersion time.

Adsorption Data via XPS

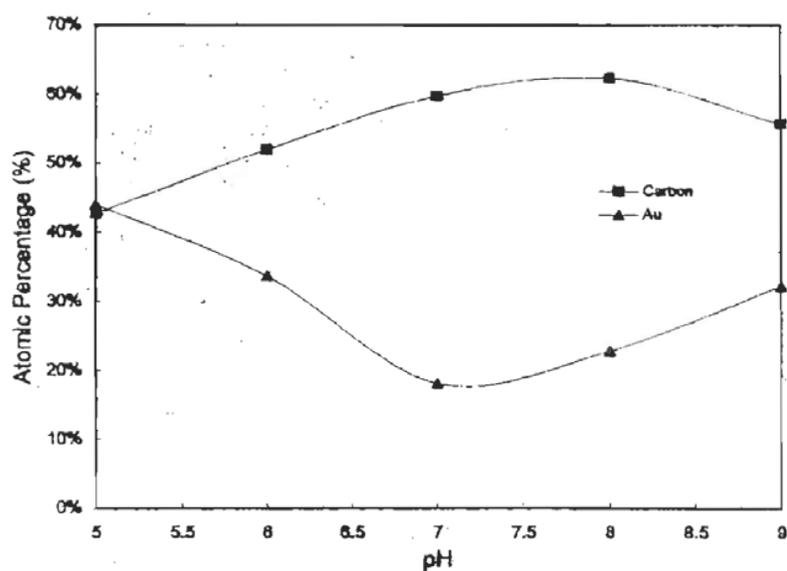


Figure 4. XPS for DELT adsorbed onto gold after one hour immersion in polymerization solution at the indicated pH

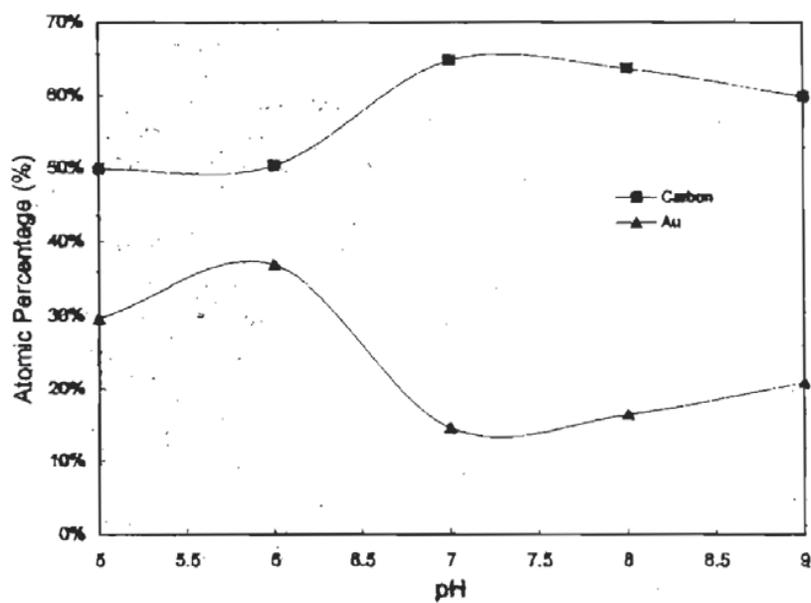


Figure 5. XPS for DELT polymerized at pH 6 adsorbed onto gold after one hour immersion in adsorbate solution at the indicated pH

Working devices as shown in Figure 6 have been obtained from the IBM Corporation. These devices have been subjected to the optimum coating process and have been submitted to Dr. Luis Matienzo of the IBM Corporation for analysis and evaluation.

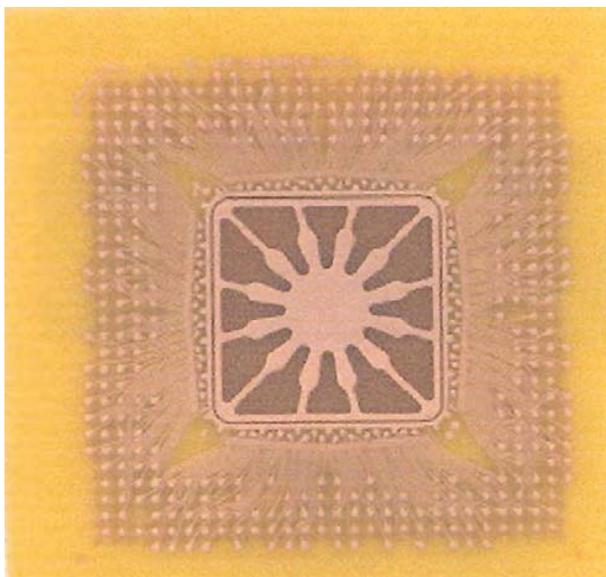


Figure 6. Microelectronic device from IBM Corporation with gold-coated conductors

Discussion

The kinetics of the polymerization reactions were followed by measuring the increase in light absorption by the solutions at 290 nm. After 24 hours, the pH 6 solution exhibited the most prominent peak (Figure 1), indicating that this is the optimum pH at which to carry out polymerization. In all cases except when polymerization was carried out at pH 5, substrates immersed in the polymer solution exhibited substantially higher carbon content and correspondingly lower gold content as measured via XPS than substrates immersed in either the monomer solutions, enzyme solutions, or pure buffer solutions. This result indicates that polymer adsorption is primarily responsible for increased carbon content. Thus, the carbon and gold signals from XPS may be employed to infer polymer surface coverage utilizing equations 12 and 2. Comparable polymer surface coverage values were obtained for all conditions investigated regardless of whether equation 1 or 2 was used. As previously indicated, this result suggests that changes in the XPS signal intensity results primarily from changes in polymer surface coverage rather than coating thickness.

Figures 2 and 3 demonstrate the time dependence of the adsorption process. We note from Figure 3 that the gold surface is nearly completely saturated with polymer after 6 hours (90% surface coverage). The precise level of coverage depends on the pH of both the polymerization solution as well as that of the adsorption solution. This is demonstrated by Figures 4 and 5. We note that, whereas optimum polymerization was found to occur at pH 6 (on

the basis of UV/VIS), optimum surface coverage occurs at pH 7. However, the pH referenced in Figure 4 is that of both the polymerization and adsorption processes. In Figure 5, the pH is that of the adsorption process, and the polymerization pH had a value of 6 in every case. We note that the carbon content reaches a maximum while the gold content reaches a minimum at pH 7 in both cases. However, the gold content is much lower at pH 7 in Figure 5 than it is in Figure 4, suggesting greater adsorbate coverage in the former case. The data shown in both Figures 4 and 5 were obtained for one hour.

A very unusual finding in this study is that none of the coatings prepared thus far exhibit surface nitrogen when analyzed with XPS, despite the fact that nitrogen constitutes a substantial part of the bulk molecular structure of the coatings. This result suggests that the hydrophobic alkyl chains on the polymer coat the hydrophilic amine groups when adsorbed onto gold, thus screening and preventing detection of photoelectrons from nitrogen. Angle resolved XPS by the IBM Corporation as well as additional adsorption studies with analogous tyrosine-based coatings at UMass Lowell are currently planned as part of a FY2002 GTURI proposal to verify this adsorbate structure. In addition, we were unable to obtain precise coating thicknesses during FY2001 to permit coating thickness optimization. Such measurements can be obtained utilizing atomic force microscopy (AFM) and quartz-crystal microbalance (QCM) and will also be part of the study proposed for FY2002.

Conclusions

We have discovered that the surface of gold conductors is nearly completely coated by tyrosine-based polymers in aqueous solution if enzymatic polymerization is carried out at pH 6, whereas adsorption is carried out at pH 7. Thus, whereas optimum enzyme activity occurred at pH 6, where protonated amines give the polymer partial positive charge, optimum surface coverage on gold occurred at pH 7 adsorbate solution, where the amines are fully deprotonated and the polymer is neutral. Nearly complete coverage is achieved after 6 hours immersion into the polymer solution. Investigations are currently planned to measure and optimize the thickness of the coating which is produced under these conditions on both model and industrial surfaces. In addition, we are currently awaiting the results of evaluations at the IBM Corporation of working devices coated with the optimum process described in this report.

Appendix – Data XPS Results

Gold plate (Reference)

	Atomic Percentage (%)			
	Gold Plate (Ref)	Monomer (Thick)	Chloroform	Gold Plate (XPS made)
O 1s	5.050	14.411	9.467	10.239
C 1s	26.268	80.210	43.302	12.718
Au 4f	67.682		47.231	77.043
N 1s		5.379		

(1)

(2)

Gold plate immersed in pH 5 reacted DELT solution

(1) ↘

Immersing time	Atomic Percentage (%)					
	3 min	10 min	60 min	60 min (monomer)	60 min (w/o mon)	Buffer solution
O 1s	8.811	12.206	13.23	8.599	16.016	12.599
C 1s	38.211	45.483	42.729	30.535	43.693	34.303
Au 4f	52.979	42.311	44.04	60.866	40.291	53.097

Gold plate immersed in pH 6 reacted DELT solution

(1) ↘

Immersing time	Atomic Percentage (%)					
	3 min	10 min	60 min	60 min (monomer)	60 min (w/o mon.)	Buffer solution
O 1s	12.515	12.476	14.383	7.331	19.454	10.008
C 1s	41.030	40.434	51.943	33.721	44.672	31.915
Au 4f	46.454	47.090	33.674	58.948	35.874	58.077

Immersing time	Atomic Percentage (%)	
	2 hours	3 hours
O 1s	21.842	21.406
C 1s	50.914	58.887
Au 4f	27.244	19.707

(2)

Gold plate immersed in pH 7 reacted DELT solution (1)

Immersing time	Atomic Percentage (%)					
	3 min	10 min	60 min	60 min (monomer)	60 min (w/o mon.)	Buffer solution
O 1s	8.881	10.223	22.225	10.485	19.689	14.487
C 1s	45.405	42.923	59.696	51.405	38.678	32.167
Au 4f	45.713	46.854	18.079	38.110	41.632	53.345

Gold plate immersed in pH 8 reacted DELT solution (2)

Immersing time	Atomic Percentage (%)					
	3 min	10 min	60 min	60 min (monomer)	60 min (w/o mon.)	Buffer solution
O 1s	11.439	26.668	14.962	15.125	12.109	7.384
C 1s	42.959	40.9	62.277	44.958	39.191	30.682
Au 4f	45.602	32.431	22.761	39.918	48.700	61.934

Gold plate immersed in pH 9 reacted DELT solution (2)

Immersing time	Atomic Percentage (%)					
	3 min	10 min	60 min	60 min (monomer)	60 min (w/o mon.)	Buffer solution
O 1s	9.451	7.631	12.04	9.822	14.395	2.120
C 1s	36.371	45.598	55.756	46.951	37.602	30.094
Au 4f	54.178	46.771	32.205	43.227	48.003	67.786

Gold plate immersed in pH 6 reacted DELT solution in various pH condition for 60 min (2)

Immersing pH	Atomic Percentage (%)				
	pH 5	pH 6	pH 7	pH 8	pH 9
O 1s	20.506	13.193	20.735	20.095	20.408
C 1s	49.922	50.321	64.754	63.579	58.798
Au 4f	29.572	36.486	14.511	16.326	20.794

Gold plate immersed in pH7 DELT solution, reacted at pH6, for various time period (Z)

Immersing Time	Atomic Percentage (%)				
	1 hour	2 hours	3 hours	6 hours	24 hours
O 1s	12.773	13.162	17.074	21.739	20.390
C 1s	50.704	61.283	66.118	69.380	74.522
Au 4f	36.523	25.555	16.807	8.880	5.088