MODIFICATION OF THE METALLIC SURFACE OF SILVER BY THE FORMATION OF ALKANETHIOL SELF-ASSEMBLED MONOLAYERS WITH SUBSEQUENT REACTION WITH CHLOROSILANES

Abdul Majid, Farid Bensebaa, Pascal L'Ecuyer, Gerry Pleizier and Yves Deslandes

ICPET, National Research Council of Canada, Ottawa, K1A 0R9

Abstract. This report describes effect of the preparation procedures on the quality of self-assembled monolayers (SAMs) on the silver surface for developing protective films against attack by atmospheric pollutants including oxidation. Various silver substrates covered with the 11-mercapto-1-undecanol (MUO) and chemically modified MUO with octyltrichlorosilane were analyzed by X-ray Photoelectron Spectroscopy (XPS). Difference in composition of monolayers from n-alkanethiols at Ag relative to the method used for cleaning the surface and other preparation details were observed. Contrarily to the assembly of high-quality alkanethiolate monolayers and its subsequent modification by chlorosilanes on gold surface preparation of SAMs on the surface of silver were more complex and the least reproducible.

1. INTRODUCTION

Self-assembled monolayers (SAM) are a versatile tool for the modification of surfaces, and allow the creation of well-ordered molecular assemblies [1]. It is a fast and fairly simple method for ultra-thin film formation. The introduction of functional groups by the functionalization of adsorbates allows the exact tuning of surface properties. The possibility of introducing the desired optical, electrical, and chemical properties in monolayers makes them attractive as photoresists or lubricants, and opto-electronic or sensing devices [2]. The formation of thiol monolayers on freshly evaporated silver films has been reported previously [3,4]. However compared to gold the formation of SAM of alkanethiolate on silver surface was reported to be complex [4,5].

The objective of this work was to investigate the reaction of 11-mercapto-1-undecanol on aged thin evaporated films of silver. The modification of the thiol layer by chlorosilanes was also attempted for the purpose of enhancing the protective power of

the organic monolayer allowing its use for sensor applications in harsh environments. Except for the substrate cleaning stage, we have used a similar approach used by Arakami group to modify copper substrate [6,7]. To the best of our knowledge the reaction of chlorosilanes with thiol monolayers adsorbed on silver surface has never been reported.

2. EXPERIMENTAL PROCEDURES

Materials. The silver coated glass substrates were purchased from EFM Corporation, Ithaca, NY. The substrates were individually wrapped and kept in a desiccator under vacuum. 11-mercapto-1-undecanol, and all other reagents were obtained from Aldrich. All solutions and solvents were deaerated with argon before use.

Cleaning of substrates. Before reaction with thiol the substrates were cleaned to remove surface contamination. Mild cleaning procedures were used for silver substrates because of its higher reactivity than gold. Various procedures used for the cleaning of

---

Corresponding author: Abdul Majid, e-mail: Abdul.Majid@nrc.ca

silver substrates included: (i) boiling ethanol; (ii) ethanol and chloroform followed by H_2O_2 ; (iii) a commercial detergent solution followed by deionized water and ethanol; (iv) 10% HNO_3 followed by deionized water and ethanol.

Preparation of self-assembled monolayer of 11-mercapto-1-undecanol HO(CH₂)₁₁SH (MUO). The cleaned substrate was placed in a 100 mL glass flask equipped with gas inlet and outlet tubes, a tube connected to a syringe for injecting solutions and a Teflon stopcock located at the bottom of the flask for draining solutions. An ethanol solution of $5 \cdot 10^{-3}$ M MUO was introduced under an Ar atmosphere. The Ag substrate was allowed to react with thiol solution for 15 minutes, and then the thiol solution was drained while keeping the substrate under an atmosphere of Ar. Excess thiol was removed from the surface by rinsing the surface with ethanol. The substrate was then dried under vacuum.

Chemical modification of the MUO monolayer. The vacuum dried substrate with the self-assembled monolayer of MUO was placed in the glass flask as described above. The substrate was immersed in a $5 \cdot 10^{-2}$ M octyltrichlorosilane solution in hexadecane-carbon tetrachloride-chloroform (80:12:8, v/v). [6] at room temperature under Ar for one minute. At the end of the incubation, the solution was drained and the surface was rinsed thoroughly with chloroform to remove excess of cholorosilane. The surface was subsequently treated with chloroform saturated with water under Ar for 5 minutes to convert the remaining Si-Cl bonds to Si-OH bonds. Finally the surface coated with the layer was washed with acetonitrile and dried in air. During the final treatment, a silanol group, SiOH, in the modified monolayer reacted spontaneously with another silanol group of a neighboring modified thiol molecule adsorbed on the metal. A laterally combined polymer of the monolayer with siloxane bonds on the surface [7,8] is then formed.

X-ray photoelectron spectroscopy (XPS). The surface of Ag substrates, before and after treatment, were analyzed by XPS. Survey and high resolution spectra of Ag (3d), S (2p), Si (2p), O (1s) and C (1s) were recorded on a Kratos Axis XPS using monochromate Al $K\alpha$, X-ray-radiation and charge neutralization. Binding energies (BEs) of peaks in the spectra were referred to the BE of C (1s) peak at 285.0 eV.

3. RESULTS AND DISCUSSION

XPS data of three types of Ag surfaces are presented below. First part discusses the XPS data of Ag substrates before modification. In the remaining two parts, XPS data of Ag substrates modified with alkanethiolate monolayer, and with alkanethiolate-chlorosilane bilayer are discussed.

Cleaning of silver coated substrates. Compared with gold, silver has a higher chemical reactivity and lower resistance to deleterious environments [8]. The cleaning of silver to eliminate the oxide film is therefore difficult. An attempt was made to clean the silver surface by washing with boiling ethanol, a detergent, 10% nitric acid solution and hydrogen peroxide. The XPS data for un-cleaned as well as cleaned samples are listed in Table 1.

The XPS lines of the carbon and oxygen photoelectron show envelopes that can be curve fitted into a series of peaks corresponding to different functional groups (Table 1). The carbon peak at the lowest binding energy is assigned to carbon atoms that are linked only to carbon ($\underline{C}$-C) and/or hydrogen atoms ($\underline{C}$-H). The peak shifted by approximately 1.5 eV corresponds to carbon atoms linked to carbon/hydrogen atoms and one oxygen atom via a single bond ($\underline{C}$-OH or $\underline{C}$-O-C). Carbon peaks corresponding to ($\underline{C}$=O) and O-$\underline{C}$=O functions appear shifted by about 3 to 4 eV respectively from the $\underline{C}$-C peak.

Peak fitting is more challenging for oxygen because of the broad range of BE for the various functional groups. For some samples, instead of reduction in the amount of oxygen on the surface of Ag as a result of cleaning, it increased. The maximum increase was observed on treatment with hydrogen peroxide, which is attributed to its strong oxidizing power. The relative concentration of oxygen for blank-4 and blank-5, did not change significantly.

The ratio of Relative Surface Concentrations (RSC) value of Ag/O (and Ag/C) is probably a better parameter to compare the different cleaning methods. Values for Ag/O (Ag/C) are estimated to be 3.6 (0.80), 3.6 (2.2), 1.95 (2.15), 3.7 (1.2) and 4.4 (1.6) for Blank-1, Blank-2, Blank-3, Blank-4 and Blank-5 respectively. Because of the highest value for Ag/O ratio for blank-5, it is probably the best substrate for thiol modification. However, blank-2 cleaned with just boiling ethanol is also a relatively clean sample. The relatively large amount of carbon remaining on the surface (mostly in the physisorbed state) is easily removed during the thiol adsorption process.

Two different types of oxygen are observed. One with a BE around 531 eV assigned to silver oxide, and another with BE energy of 532-534 eV assigned to hydroxide and groups containing CO bonds [9] An interesting feature of the XPS spectra of these samples is the disappearance of the O(1s) lowest

Table 1. Relative surface concentrations (%)* and BE (eV) by XPS for blank cleaned and un-cleaned Ag samples.

S. ID	Description	C(1s) BE	RSC	S(2p) BE	RSC	Si(2p) BE	RSC	O(1s) BE	RSC	Ag(3d) BE	RSC
Blank-1	No treatment	285	44.2	–	–	–	–	530.9	7.2	368.8	23.2
		286	2.6					532.1	2.3	374.8	16.0
		288	3.4					534.2	1.1		
Blank-2	Cleaned with boiling ethanol	285	19.4	–	–	–	–	531.5	13.3	369.2	32.1
		286.5	3.2					533.3	1.8	375.2	22.2
		287.3	2.6								
Blank-3	Cleaned with C_2H_5OH + $CHCl_3$, followed by H_2O_2	285	16.3	–	–	–	–	531.2	22.2	368.8	28.9
		286.8	3.1					533.6	3.7	374.4	20.1
		288.8	4.2								
Blank-4	Cleaned with detergent followed by distilled H_2O	285	24	161.5	1.5	–	–	532	11.8	368.5	26.4
		286.6	7.7	162.6	2.3	–	–			374.5	17.3
		288.5	4.6								
Blank-5	Cleaned with 10% HNO_3	285	24.0	–	–	–	–	532.5,533.3	9.1	368.4	54.3
		286.7	–						3.3	374.0	
		287.6	6.2								
		288.8	3.0								

* Calculated directly based on atomic composition, BE: Binding Energy (eV); RSC: Relative surface concentration (%).

Table 2. Relative surface concentrations (%)* and BE (eV) by XPS for Thiol Monolayer on Ag surface.

S. ID	Description	C(1s)		S(2p)		Si(2p)		O(1s)		Ag(3d)	
		BE	RSC	BE	RSC	BE	RSC	BE	RSC	BE	RSC
Test-1	Thiol adsorption on un-cleaned Ag (Ar)	285	35.3	161.8	2.3	–	–	531.6	10.7	368.7	26.3
		286.6	2.5	163	2.0					374.7	17.4
		288.4	2.4	164.5	0.7						
				168.2	0.6						
Test-2	Thiol adsorption on un-cleaned Ag (GB)	285	48.9	161.6	0.43	–	–	532.3	7.1	368.5	21.6
		286.5	3.3	162.7	0.44					374.6	14.2
		289	1.6	164	0.23						
Test-3	Thiol adsorption on Ag cleaned with 10% HNO$_3$(Ar)	285	31.9	161.8	1.3	–	–	531.3	2.3	368.6	22.4
		286.4	7.8	163	0.8			532.8	10.2	374.8	15.5
		289.3	3.6								
Test-4	Thiol adsorption on Ag cleaned with Ethanol (Ar)	285	23	162.5	0.6	–	–	532.5	7.2	368.6	32
		286.5	4.1	163.6	0.4					374.8	21.7
		288.3	1.4								
Test-5	Thiol adsorption on Ag cleaned with detergent (Ar)	285	24	161.5	1.5	–	–	532	11.8	368.5	26.4
		286.6	7.7	162.6	2.3					374.5	17.3
		288.5	4.6								

* Calculated directly based on atomic composition, BE: Binding Energy (eV); RSC: Relative surface concentration (%), Ar: Under Argon in a bag; GB: Under Argon in a glove box.

Abdul Majid, Farid Bensebaa, Pascal L'Ecuyer, Gerry Pleizier and Yves Deslandes

Table 3. Relative surface concentrations (%)* and BE (eV) by XPS for Modified Thiol Monolayer on Ag surface.

S. ID	Description	C(1s) BE	RSC	S(2p) BE	RSC	Si(2p) BE	RSC	O(1s) BE	RSC	Ag(3d) BE	RSC	Cl(2p) BE	RSC
Test-1	Un-cleaned Ag set-1	285	46.5±4.7	162.4	2.0±0.2	102.2	1.4±0.4	530.7	2.4±0.4	368.5	17.7±3.2	–	–
		286.6	5.4±0.3	163.7	1.2±0.2			532.7	9.4±0.6	374.4	12.2±2.3		
		288.4	1.6±1.2	168.1	0.5								
				169.6	0.4								
Test-2	Ethanol cleaned Ag set-1	285	40.5±3.1	162.4	1.6 ± 0.3	102.3	3.5±0.8	530.5	3.4±1.3	368.4	20.4±2.5	–	–
		286.7	9.2±4.2	163.4	0.95±0.04			532.7	9.5±1.3	374.5	14.1±1.9		
								534.1	1.6				
Test-5	Above in glove box under Argon	285	24.8±1.6	162.5	0.4±0.2	102	1.2±0.1	532.6	6.7±0.6	368.7	31.4±0.2	198.6	5.4±0.4
		286.6	3.7±1	163.8	0.3±0.1					374.7	21.2±0.1	200.2	2.8±0.2
		288.4	2.1±0.2	164.9	0.23								

* Calculated directly based on atomic composition, BE: Binding Energy (eV); RSC: Relative surface concentration (%), Ar: Under Argon in a bag; GB: Under Argon in a glove box.

BE peak (~531 eV) for samples blank-4 and blank-5, suggesting that the procedures used to clean these samples are probably the most successful in removing oxides. However, treatment with a detergent results in the appearance of additional peaks in the S(2p) region because of the presence of a sulfur impurity in the detergent, indicating that sulfur may have replaced oxygen as an adsorbate.

Adsorption of Thiol on the surface of silver. 11-mercapto-1-undecanol (MUO) is adsorbed on five silver substrates cleaned using different procedures as summarized in Table 2. Samples were analyzed by XPS to determine the oxidation state and the relative concentration of C, S, Si, O and Ag. The details of these results are shown in Table 2. As is evident from the data in Table 2, three different types of sulfur were observed [10-12]. One assigned to thiolate group with a BE around 161.6 eV, a second type of sulfur was assigned to un-reacted thiol with a BE around 164.5 eV and a third type of sulfur was observed around 168.2 eV and was assigned to sulfate. Following are some general conclusions that could be reached from the data in Table 2:

· Cleaning of silver surface with a strong oxidizing acid (HNO_3) results in an increase in the amount of surface oxygen. The highest levels of oxygen were detected for the samples cleaned with 10% nitric acid. Lowest levels of oxygen were detected for samples cleaned with ethanol. Also, the largest alkanethiolate coverage was obtained for substrates cleaned with HNO_3.

· The sulfur detected in samples from Test-5 is probably not due to SAM MUO. We assigned the origin of sulfur to trace sulfur in detergent (compare Table 1 and Table 2).

· The XPS data for the reaction of thiol with un-cleaned silver surface suggest that some of the sulfur atoms in this monolayer are oxidized as suggested by the additional sulfur peak at high BE.

· The ratio C/S and C/O of relative concentration (only lowest BE of C and S are considered) are expected to be exactly 11:1. Based on Table 2, C/S (and C/O) ratio are estimated to be: 8.2 (3.3), 55.6 (6.9), 15.1 (2.6), 23(3.2) and 6.3(2.0) for Test-1, Test-2, Test-3, Test-4 and Test-5 respectively. The large discrepancy between these values reveals the presence of large and un-controllable amount of contamination on the surface of the MUO film and/or Ag substrate. Based on these ratios, Test-1 and Test-3 are probably the best procedures to produce a good MUO film.

However, Test-1, shows the presence of sulfate not seen in Test-3 (see below).

Modification of Thiol monolayer on the surface of silver. The modification of the thiol layer on silver was also attempted using alkylchlorosilane followed by hydrolysis and condensation steps. The XPS data shown in Table 3 for these tests suggests the presence of C, S, Si, O and Ag in all tests and chlorine in a few tests. Following are the conclusions that could be drawn from the data in Table 3:

· Modified thiol monolayer of un-cleaned silver samples contains two types of sulfur. One assigned to S-Ag bond (XPS peaks at 162.4 and 163.7 eV). The second type is assigned to oxidized sulfur (XPS peaks at 168.1 and 169.6 eV). This suggests the presence of oxidized sulfur impurities presumably adsorbed on the modified monolayer [12]. While any soluble contaminants can be easily removed from surfaces by rinsing off the solid support, monolayers cannot be purified from by-products or un-reacted materials that are attached to the surface [13].

· There is no significant difference in the alkanethiolate coverage for cleaned and un-cleaned modified silver substrates as suggested from the RSC ratio of S/Ag (0.08 and 0.11 respectively).

· Modification of the thiol layer on silver surface, resulted in considerable amounts of chlorine on the surface. Two peaks in the Cl(2p) region of XPS appeared at BE of 198.3 ± 0.2 eV and 199.9 ± 0.2 eV, suggesting the presence of uncharged chlorine such as of chlorosilane or a solvent [14]. Un-reacted chlorosilanes are very difficult to remove from the monolayers adsorbed on metal surfaces. Chlorosilane molecules are said to form very resistant structures in the adsorbed state, presumably through covalent bonding with the substrate [6].

· The formation of siloxane linkages within the layer was further confirmed from the peaks at 532.3 eV in the spectra of O ($1S_{1/2}$). Our work on gold surface also suggest that some of the sulfur atoms in this monolayer are oxidized as judged by the additional S($2p_{3/2}$) core level at a binding energy of > 164 eV [4]. In one test there was no peak detected in the S(2p) region after modification, suggesting that the thiol may have been desorbed during modification [6].

· The amount of oxygen and sulfur on the silver surface was the minimum and the amount of chlorine was the highest for the tests carried out in an inert atmosphere in a glove box under Ar. This suggests that the inert atmosphere favors

the de-sorption of thiolate from silver surface and the adsorption of chlorosilane on the oxidized silver surface.

4. CONCLUSIONS

Because of the relatively chemically inert nature of gold the assembly of high-quality alkanethiolate monolayers and its subsequent modification by chlorosilanes is straightforward on its surface. However, similar reactions on the surface of silver were more complex and the least reproducible. This is because of the greater reactivity of silver that leads to the ready formation of oxides on its surface. The oxide layer on silver surface adsorbs polar contaminants. This suggests that the formation of modified MUO monolayer on the surface of silver coating obtained using vapor deposition process would be a complex process. The formed monolayer may not provide protection from atmospheric oxidation for bare silver. Encapsulation of silver in another matrix such as silica using sol-gel process may have greater potential. Work in this direction is in progress and shall be reported in future.

REFERENCES

[1] A. Ulman, *An introduction to Ultrathin Organic Films: Langmuir- Blodgett to Self- Assembly (*Academic Press: New York, 1991*); Chem.Rev.* **96**, (1996) 1533

[2] S. Flink, C. J. M. Veggel and D.N. Reinhoudt // *Adv. Mater.* **12** (2000) 1315.

[3] A. Abdelghani, J. M., Chovelon, J. M. Krafft, N. Jaffrezie-Renault, A. Trouillet, C. Veillas, Ronot-Trioli and H. Gagnaire // *Thin Solid Films* **284-285** (1996) 157.

[4] P. E. Laibinis, G. M. Whitesides, D. L. Allara, Y. T. Tao, A. N. Parikh and R. G. Nizzo // *J. Am. Chem. Soc.* **113** (1993) 7152.

[5] F. Bensebaa, T. H. Ellis, A. Badia and B. Lennox // *J. Vac. Sci. Technol. A* **13** (1995) 1331.

[6] K. Nozawa, H. Nishihara and K. Aramaki // *Corrosion Science* **39** (1997) 625.

[7] R. Haneda, H. Nishihara and K. Aramaki // *J. Electrochem. Soc.* **145 (**1997) 1215.

[8] E. Fontana, R. H. Pantel and S. Strober // *Applied Optics* **29** (1990) 4694.

[9] *Handbook of X-ray Photoelectron Spectroscopy*, ed. by J. F. Moulder, W. F. Stickle, P. E. Sobol and K. D. Bomben (Perkin-Elmer, 1992) p.45.

[10] D. G. Castner, K. Hinds and D. W. Grainger // *Langmuir* **12** (1996) 5083.

[11] F. Bensebaa, Y. Zhou, Y. Deslandes, E. Kruus and T. H. Ellis // Surface Science **45** (1998) L472.

[12] NIST XPS data base (http://srdata.nist.gov/xps/).

[13] V. Chechik, R. M. Crooks and J. M. Stirling // *Adv.Matter*. **12** (2000) 1161.

[14] R. Haneda and K. Aramaki // *J. Electrochem. Soc.* **145** (1998) 1856.