COMMUNICATIONS

Reductive deposition of Au^{3+}(aq) on oxidized silicon surfaces

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Abstract: X-ray photoelectron spectroscopy (XPS) is used to determine the oxidation state of gold deposited from an aqueous solution of AuCl$_4^-$ on to various oxidized surfaces of silicon. Although the observed Au4f signal decreased with the thickness of the oxide layer, the oxidation state of Au was determined as 0 for all the samples analyzed. From the angular dependence of the Si2p and Au4f signals it was determined that Au is deposited on top of the oxidized surfaces of metallic silicon. It is postulated that from an aqueous solution of AuCl$_4^-$, gold would deposit in its zerovalent form on to any surface due to its large and positive electrochemical reduction potential ($\varepsilon^{\circ}_{red}$(Au^{3+}/Au) = +1.50 V) and the substrate plays a role only in providing active deposition sites. To further support the proposal, it is shown that the same process takes place even in inert and hydrophobic polypropylene substrates. Similarly, it is also shown that more gold deposits if the surface of the polypropylene is made less hydrophobic (but probably more active) via the industrially used corona discharge treatment.

Key words: XPS, gold, electroless deposition, oxidized silicon surface.

Résumé : On a utilisé la spectroscopie photoélectronique aux rayons X pour déterminer l'état d'oxydation de l'or déposé à partir d'une solution aqueuse de AuCl$_4^-$ sur diverses surfaces oxydées de silicium. Même si le signal observé pour Au4f diminue avec l'épaisseur de la couche d'oxyde, on a déterminé que l'état d'oxydation de l'or est égal à zéro pour tous les échantillons analysés. En se basant sur la dépendance angulaire des signaux Si2p et Au4f, on a déterminé que l'or se déposé au sommet des surfaces oxydées du silicium métallisé. On a fait l'hypothèse que, à partir d'une solution aqueuse de AuCl$_4^-$, l'or se déposerait dans sa forme zérovalente sur toutes les surfaces en raison de son potentiel de réduction électrochimique élevé et positif [$\varepsilon^{\circ}_{red}$(Au^{3+}/Au) = +1,50 V]. Pour appuyer cette hypothèse, on montre que le même processus se produit même dans des substrats inertes et polypropyléniques hydrophobes. De la même manière, on a démontré qu'il y a plus d'or qui se dépose si la surface de polypropylène est rendue moins hydrophobe (mais probablement plus réactive) par le biais d'un traitement industriel par effluve.

Mots clés: spectroscopie photoélectronique à rayons X, dépôt sans électrode, surface de silicium oxydée.

Introduction

Interest in the chemistry of gold has renewed especially to the ability of molecular self-assembly of aliphatic thiols on gold colloids (1) and also to form clusters in nm scales with potentially useful optical, optoelectronic, and material properties (2–4). Successful methods of preparation usually involve vapour-deposition or deposition from solution via chemical and (or) electrochemical routes. An electroless deposition of zerovalent gold nano-clusters was reported using electroactive poly(3-alkylthiophenes) from a solution of the polymer and AuCl$_4^-$ in nitromethane (5). Similar studies were reported using other electroactive poly-

mers, such as, polyaniline and polypyrrole (6). The same group later reported on the uptake of gold and palladium from acidic solution of AuCl$_3$ and PdCl$_2$ using electroactive polymer-SiO$_2$ nano-composites (7). In a recent study it was claimed that porous silicon could be utilized for reductive deposition of gold nano-clusters again from an aqueous solution AuCl$_4^-$ (8). In our XPS investigation of metal ions deposited on the surface of silica tubes for atom-trapping atomic absorption spectrometric determinations, we had also reported that Au was deposited in its zerovalent state both from the vapour phase of the flame and also from the aqueous solution of AuCl$_4^-$ (9). In a later study in which we had also examined Mn and Bi, we claimed that reductive deposi-

Table 1. XPS data of the $AuCl_4^-$ deposited from a 10^{-5} M aqueous solution on to silicon with different oxide thickness and polypropylene substrates.

Sample	Au4f$_{7/2}$	Si2p Si°	Si2p Si^{4+}	C1s	O1s
		Binding energy (eV) and atomic abundances (in parenthesis)			
Si/SiO$_x$ (reference)	—	99.7 (0.78)	102.4^a (0.22)		
Si/SiO$_2$ (~3 nm)	84.0 (0.03)	99.7 (0.57)	103.3^a (0.43)		
Si/SiO$_2$ (~5 nm)	84.0 (0.02)	99.7 (0.25)	103.7^a (0.75)		
Si/SiO$_2$ (~10 nm)	84.0 (0.01)	99.7 (0.12)	104.3^a (0.88)		
PP (as is)	84.0 (0.001)	—	—	285.0 (1.00)	532.0 (0.06)
PP (corona treated)	84.0 (0.0005)	—	—	285.0 (1.00)	532.0 (0.15)

^{a}The energy difference between the Si^0 and Si^{4+} levels (the chemical shift) increases as the oxide layer becomes thicker due to the differential charging of the layers (12).

tion of gold was mainly dictated by its electrochemical reduction potential rather than the properties of the substrate (10). In this contribution we demonstrate this property of gold by depositing zerovalent gold from aqueous $AuCl_4^-$ solution on to different substrates.

Experimental

Si wafers with their polished surfaces are used to deposit gold from a dilute ca. 10^{-5} M aqueous solution of $AuCl_4^-$. Si samples were cut into 5×15 mm slices and cleaned by 10% HF before thermal treatment and analysis. Different oxide thicknesses were obtained by heating the substrate in air at different temperatures or for different periods. The substrates were then immersed into the solution for 10 h without stirring after which they were washed with acetone, dried in air, and inserted into the spectrometer. A Kratos ES300 spectrometer with MgK X-rays was used for XPS analysis. The X-ray anode power is kept below 40 W to reduce the possibility of reduction under severe X-ray bombardment (11). SEM images were obtained using a Jeol 6400 electron microscope.

Results and discussion

Figure 1 displays the Si2p and Au4f region of the XPS spectra of gold deposited on to silicon wafers containing approximately 3, 5, and 10 nm oxide layers and the relevant data are given in Table 1. One of the relevant observations in this investigation is that the oxidation state of gold is zero in all samples. Secondly, it is observed that the Au4f signal decreases as thickness of the oxide layer is increased. At normal electron take-off angle, the sampling depth of XPS using the MgKα X-rays is around 10 nm which can be further reduced by decreasing this electron take-off angle (11, 12). Figure 2 displays Si2p and Au4f signals recorded at normal (90°) and 30° electron take-off angles from two gold deposited samples containing ca. 3 and 5 nm oxide layers,
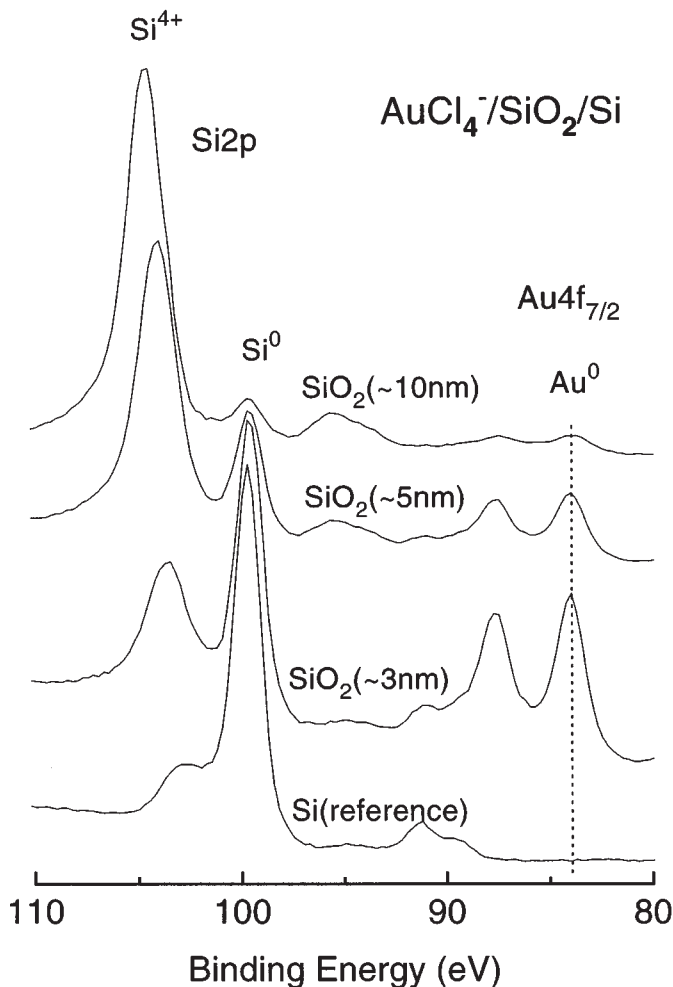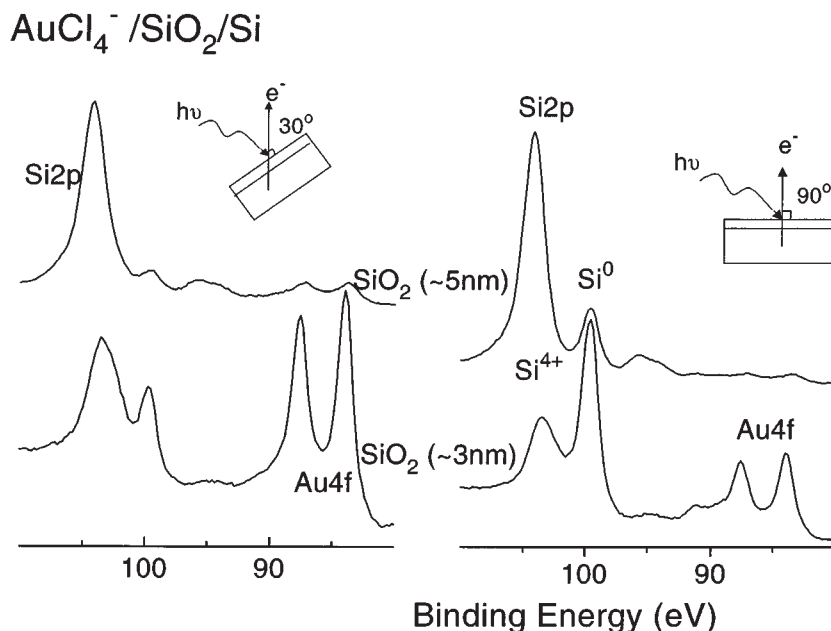
Fig. 1. Si2p–Au4f region of the XPS spectra of oxidized silicon surfaces containing gold deposited from a 10^{-5} M aqueous solution of HAuCl$_4$. A spectrum of a reference Si is also given for comparison.

Fig. 2. Si2p–Au4f region of XPS spectra of two samples recorded at two different take-off angles.

$AuCl_4^-$ /SiO$_2$/Si

respectively. As can be seen from the figure the intensity of the $Si^0 2p$ signal goes down and the intensity of the $Si^{4+}2p$ and the $Au^0 4f$ signals go up indicating that Au is on top of the Si^{4+} layer and is not in direct contact with the underlying Si^0 substrate. The SEM image of the samples indicate that gold is deposited on the surface of the substrate as colloidal particles of varying sizes of less than 100 nm as shown in Fig. 3.

Two important questions arise: (*i*) why does gold deposit in its zerovalent state as opposed to deposition in ionic form, and (*ii*) why do we get seemingly more deposition when we have a thinner oxide layer? The first can be related to the large and positive reduction potential of Au^{3+}, $\varepsilon^\circ_{red}(Au^{3+}$ /Au) = +1.50 V in aqueous solutions which is inherent to gold. The second, however, must be related to the activity of the substrate surfaces (voids, defects, pores, reduction centres, or domains etc.). Since the thicker oxide layers are obtained by the corresponding longer heating/annealing times the number of active sites must also be diminished during this process. Hence we propose that gold would deposit as zerovalent form its aqueous solution on to any substrate as long as there are active reducing sites. This of course brings the more difficult question related to the nature of the surface reducing agents at this point which we can only speculate about. The role of the substrate surface is only important, if active sites are present or created which may facilitate this deposition. As a result the claim of Coulthard et.al. (8) that porous silicon is utilized as a reducing agent for reductive deposition of gold must be interpreted as the porous silicon providing ample active sites. This point is further supported by our observation that this deposition even takes place on relatively inert and hydrophobic substrates like polyethylene and (or) polypropylene as shown in Fig. 4. It is also interesting that relatively more gold is deposited if the surface of the polypropylene is made less hydrophobic

Fig. 3. SEM image of gold deposited on silicon containing an approximately 5 nm oxide layer.
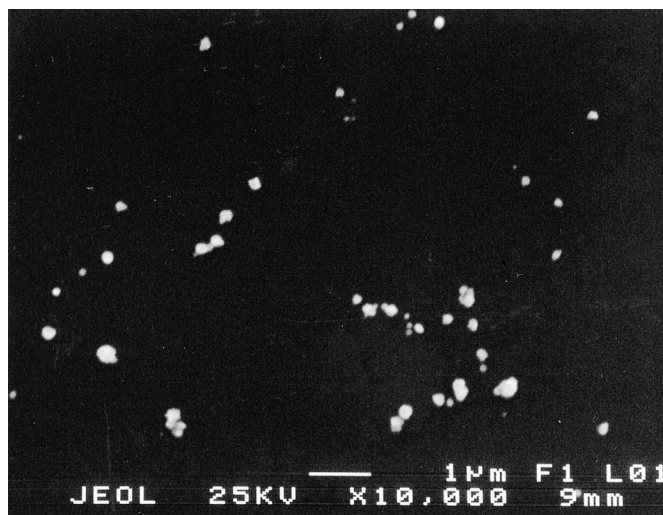
Fig. 4. O1s, C1s, and Au4f regions of XPS spectra of gold deposited from a 10^{-5} M aqueous solution of HAuCl$_4$ on polypropylene and corona-treated polypropylene.
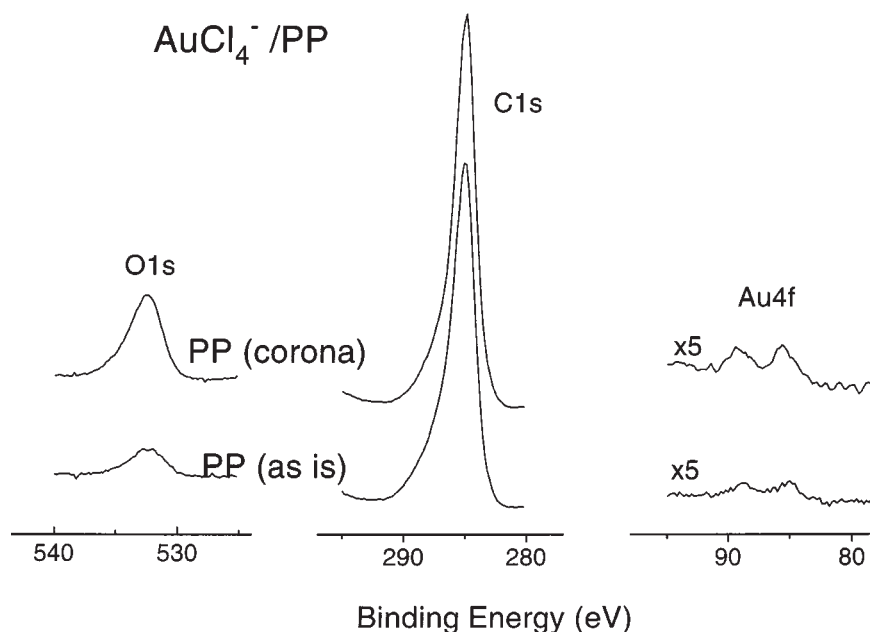
via the corona treatment which increases the number of -COH (hydroxyl groups) as well as other active sites like defects on the surface (13) as also shown in Fig. 4. Further investigations are definitely needed to identify/clarify the mechanism of the process.

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