Tuning Surface Chemoresistivity of Au Ultrathin Films Using Metal Deposition via Surface-Limited Redox Replacement of the Underpotentially Deposited Pb Monolayer

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ABSTRACT: The presented work investigates the chemoresistivity of Au ultrathin films, whose surface is modified by deposition of few monolayers of Au, Pd, or AuPd alloy. The model adsorbate in this study was the HS⁻ ion from 0.1 M NaCl solution having concentrations ranging from 0 to 40 ppm. The Au surface modification was carried out using deposition via surface-limited redox replacement of the underpotentially deposited Pb monolayer. Modified Au films have shown higher chemoresistivity than the pristine ones. Our results and analysis suggest that these improvements are due to increased concentration of surface defects and enhanced scattering cross-section per adsorbate induced by chemical modification of the surface by Pd. The significance of our findings is discussed for practical applications shining more light on the importance of surface preparation for chemoresistive sensor design and performance.

KEYWORDS: chemoresistivity, monolayer, adsorption, deposition, surface-limited redox replacement, underpotential deposition, defects, terraces, hydrogen sulfide

Studies of adsorbate-induced changes of surface resistivity have received considerable attention over the years.1 Surface resistivity provides a straightforward and powerful probe of adsorption kinetics,2-4 interadsorbate interactions,5 and adsorbate effects on the electrical resistance of metallic nanowires5-8 and carbon nanotubes.9,10 Our current understanding of surface resistivity is based on works by Fuchs11 and Sondheimer,12 and Persson and Volokitin.13-16 For chemisorbed molecules on the metal surface, the resistance change, that is, surface chemoresistivity is attributed to an increase in diffuse scattering of conduction electrons.1 The presence of an adsorbate perturbs locally the electronic structure of the metal surface and acts as an additional scattering center. As a consequence, the translational symmetry of the smooth and clean surface for electron transport is disrupted which decreases the electrical conductivity in the near surface region with depth of the order of the electron mean free path λ [nm]. The change in the thin-film resistivity due to the presence of an adsorbate can be written as1

\[ \frac{\Delta \rho}{\rho_B} = \frac{3}{16} \frac{\lambda}{t} \sum_i \Gamma_{ai} \xi_i \]  

(1)

Here, the term \( \Delta \rho/\rho_B \) represents the relative increase in resistivity of the sample due to the surface effects with respect to its bulk value, \( \rho_B \). The term \( t \) is the thickness of the metal film [nm], \( \Gamma_{ai} \) is the surface concentration of an adsorbate [cm⁻²], and \( \xi_i \) is the scattering cross-section per adsorbate, [cm²]. One can notice the sensitivity of the above expression in terms of the \( \lambda/t \) ratio. For ultrathin films, where \( \lambda \approx t \), the change in resistivity due to adsorbed species, that is, the term \( \Gamma_{ai} \xi_i \) controls the overall magnitude of \( \Delta \rho/\rho_B \). If there is a single adsorbate species and a single type of adsorption site with no interactions between the adsorbates, the scattering cross-section \( \xi_i \) is considered constant, and the surface resistivity varies linearly with the adsorbate coverage.3,5,19 If the surface contains energetically different adsorption sites induced by chemical inhomogeneity or morphological diversity (steps and terraces), it is possible that the scattering cross-section \( \xi_i \) is different for each of them. In that case, eq 1 has a more general form

\[ \frac{\Delta \rho}{\rho_B} = \frac{3}{16} \frac{\lambda}{t} \sum_i \Gamma_{ai} \xi_i \]  

(2)

Here, the summation term models diversity of the adsorption sites in terms of their particular scattering cross-section \( \xi_i \) and corresponding adsorbate coverage, \( \Gamma_{ai} \). It is certain that better

Received: June 6, 2019
Accepted: August 23, 2019
Published: August 23, 2019

DOI: 10.1021/acssensors.9b01045
ACS Sens. 2019, 4, 2442–2449
understanding of the surface modifications and surface engineering leading to the enhanced values of $\xi_i$ and $\Gamma_{ij}$ are of general interest for further developments in the area of chemical and biological sensor technologies based on the chemoresistivity phenomenon.

The objective of this study is to investigate the chemoresistivity of Au ultrathin films whose surface is modified by deposition of a few monolayers of Au, Pd, or AuPd alloy. The model adsorbate was the HSO$_3^-$ ion from 0.1 M NaCl solution with concentrations ranging from 0 to 40 ppm at pH = 9. This value of pH ensured that the HSO$_3^-$ ion is the main solvated species and the HSO$_3^-$ adsorption is the dominant phenomenon. The Au surface modification was carried out using deposition via surface-limited redox replacement (SLRR) of the under-potentially deposited (UPD) Pb monolayer (ML).\textsuperscript{20,21} The Au films modified by few MLs of Au, Pd, and AuPd deposit have shown higher chemoresistivity than the pristine ones. Our results and analysis suggest that this improvement is due to increased concentration of surface defects and enhanced scattering cross-section per adsorbate molecule induced by chemical modification of the surface by Pd. Our findings are discussed for practical applications shining a new light to the importance of surface preparation for chemoresistive sensor performance.

\section*{Experimental Section}

The 5 nm ultrathin Au films with the 1 nm Ti adhesion layer were supplied by Platypus Co. They were deposited on 7.5 cm × 2.5 cm glass slides using molecular beam epitaxy. The Au thin-film thickness was well below the electron mean free path of the bulk Au or Pd\textsuperscript{22,23} which ensured that the surface scattering phenomenon has the main contribution to the overall thin-film resistance. The working samples were cut out from these slides with an approximate dimension of 1.8 cm × 2.5 cm, and they were subjected to selective etch and patterning to define current path over the sample area exposed to the test solutions. The schematics of our sample geometry is shown in Figure 1, indicating the area of the sample exposed to the test solution and of the test solution as well as solutions used for modification of the Au ultrathin film surface by Au, Pd, and AuPd layers are described in Table 1. Before each experiment, all solutions were deaerated for 1 h with ultrapure nitrogen in order to minimize concentration of dissolved oxygen. The volume of the cell for in situ chemoresistivity measurements was 0.5 dm$^3$, while the starting solution volume was 0.15 dm$^3$. Concentration of HSO$_3^-$ in the test solution was increased by addition of 1–50 cm$^3$ aliquots containing a higher concentrated of HSO$_3^-$ ions in 0.1 M NaCl (pH = 9) under a constant mixing condition. All HSO$_3^-$ containing solutions were prepared by dissolution of Na$_2$S into a 0.1 M NaCl at pH = 9. The decrease of HSO$_3^-$ concentration in the test solution was achieved by simple dilution, that is, addition of aliquots containing 0.1 M NaCl (pH = 9) only. All potentials in the text related to the protocol for Au surface modification are presented as the value of Pb-underpotential, $\Delta E$. The deposition experiments and ac measurements of the thin-film resistance were performed using the Autolab PGSTAT 12 unit with the frequency response analyzer module.

Deposition via SLRR of the Pb UPD ML\textsuperscript{20,21} has been used to modify the surface of Au ultrathin films. In this approach, the Pb UPD ML acts as a sacrificial material to reduce/deposit a more noble metal such as Au and Pd (SLRR reaction i.e., galvanic displacement). The generalized stoichiometry of the SLRR reaction is presented below:\textsuperscript{24}

$$
\left(\theta_{Pb}^{UPD}\right) \cdot Pb_{\text{sol}}^{2+} / Au(h, k, l) + \left(\theta_{Pb}^{UPD}\right) \cdot Pb_{\text{sol}}^{2+} + \left(\theta_{Pb}^{UPD}\right) \cdot Pb_{\text{sol}}^{2+} + \left(\theta_{Pb}^{UPD}\right) \cdot Pb_{\text{sol}}^{2+} = \left(\theta_{Pb}^{UPD}\right) \cdot Pb_{\text{sol}}^{2+} / Au(h, k, l)
$$

Here, $p$ is the oxidation state of the noble metal P (3 for Au and 2 for Pd) which defines the overall stoichiometry coefficients in the above equation. Factors $\theta_{Pb}^{UPD}$ and $\theta_{Pb}^{UPD}$ are the Pb UPD ML coverage and the deposition/stripping of the Pb UPD ML characteristic feature of the deposition/stripping of the Pb UPD ML is shown in Figure 2A. The ultrathin film sample geometry with indicated current path and sensing area.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{ultrathin.png}
\caption{Schematics of ultrathin film sample geometry with indicated current path and sensing area.}
\end{figure}

current path during testing. All solutions in our study were prepared with high purity grade chemicals (99.999%, Alfa Aesar, Merck) and >18.2 MΩ ultrapure water (Millipore Direct Q-UV with Barnstead A1007 predistillation unit). Experiments are performed using ultraclean glassware under oxygen-free environment. The composition

\begin{table}[h]
\centering
\caption{Details of Test Solution and Solution Design for Metal Deposition via SLRR of the Pb UPD ML}
\begin{tabular}{|c|c|}
\hline
experiment & solution design \\
\hline
Au/Au(hkl) via SLRR of the Pb UPD ML & $10^{-5}$ M Pb$^{2+} + 10^{-4}$ M Au$^{3+} + 0.1$ M HClO$_4$ \\
Pd/Au(hkl) via SLRR of the Pb UPD ML & $10^{-5}$ M Pb$^{2+} + 10^{-4}$ M Pd$^{2+} + 0.1$ M HClO$_4$ \\
PdAu/Au(hkl) via SLRR of the Pb UPD ML & $10^{-5}$ M Pb$^{2+} + 10^{-4}$ M Au$^{3+} + 10^{-4}$ M Pd$^{2+} + 0.1$ M HClO$_4$ \\
test solution/(0 ≤ X ≤ 40) & X ppm HSO$_3^-$ + 0.1 M NaCl, pH = 9 \\
\hline
\end{tabular}
\end{table}
vs Ag/AgCl), allowing natural HS\textsuperscript{−} adsorption to take place on Au and modified Au surfaces. The AC method, that is, impedance measurements, with 0.1 V amplitude and 100 kHz frequency was used to evaluate the resistance change of ultrathin films. This approach alleviated issues with contact resistance and other capacitive contributions to the measurements. It also provided the maximum reproducibility, quick response, and stability of the measurements.

The example of in situ AC resistance measurements of the AuPd-modified ultrathin Au film exposed to different concentrations of HS\textsuperscript{−} ions in the test solution is presented in Figure 3. Within one set of measurements on a particular sample, the area of the sample exposed to the test solution remained the same (≈1 cm\textsuperscript{2}). This means that the length of the current path and the sample thickness also remained constant. Therefore, the results presented as \( \frac{Z_{(HS^{-})}}{Z_{(0)}} \) indeed represent the surface chemoresistivity dependence of Au and modified Au ultrathin films as a function of HS\textsuperscript{−} ion concentration in solution described by eqs 1 and 2.

**RESULTS AND DISCUSSION**

**Au/Au(hkl) Modification.** The starting, pristine Au ultrathin film [Au(hkl)] displays a high-quality surface which is almost atomically smooth having a saturation surface roughness of only 0.4 nm, Figure 4A. The observed change in resistivity with an increasing HS\textsuperscript{−} concentration ([HS\textsuperscript{−}]) shows a modest and linear increase, Figure 4B. Further Au surface modification by the Au layer is carried out using 30 SLRR cycles. The stoichiometry of the SLRR reaction involved in a single cycle is shown below and indicates a nominal deposition of approximately a half Au ML per cycle.

\[
\text{Pb}^{0}_{\text{UPD/Au(hkl)}} \rightarrow \left( \frac{2}{3} \right) \text{Au}^{3+}_{\text{solv}} + \left( \frac{2}{3} \right) \text{Pb}^{2+}_{\text{solv}} + \left( \frac{2}{3} \right) \text{Au}^{0}_{\text{solv}} + \text{Au(hkl)}
\]

Therefore, in 30 SLRR cycles, an approximate amount of 15 MLs of Au is deposited on the pristine Au surface. This represents a 100% increase in nominal thickness of the Au ultrathin film from 5 to 10 nm. The chemoresistivity of the modified Au ultrathin film surface is shown in Figure 4B. The resistivity change is significantly larger as compared with the pristine Au surface although the nominal thickness of the Au film is increased. The trend is not monotone as observed previously but rather displays two distinct linear regions. The
Table 2. Fitting Results of the Model Described by eqs 7 and 8 to the Experimental Data in Figures 4 and 5 and 6B

<table>
<thead>
<tr>
<th>sample</th>
<th>P</th>
<th>λ/nm</th>
<th>#SLRR</th>
<th>[HS⁻]/ppm</th>
<th>t/µm</th>
<th>f_D</th>
<th>f_T</th>
<th>(B_P[θ_D] + B_P[θ_T])/cm²·ppm⁻¹</th>
<th>figures</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au(hkl)</td>
<td>Au</td>
<td>37.7</td>
<td>0</td>
<td>&gt;0</td>
<td>5</td>
<td>0</td>
<td>1</td>
<td>1.5 ± 0.03 × 10⁻¹⁷</td>
<td>3B</td>
</tr>
<tr>
<td>Au/Au(hkl)</td>
<td></td>
<td>30</td>
<td>&lt;10</td>
<td>&gt;0</td>
<td>10</td>
<td>1</td>
<td>0</td>
<td>37.1 ± 0.06 × 10⁻¹⁷</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.04</td>
<td>0.96</td>
<td></td>
<td></td>
<td>3.0 ± 0.01 × 10⁻¹⁷</td>
<td></td>
</tr>
<tr>
<td>Pd/Au(hkl)</td>
<td>Pd</td>
<td>25.5</td>
<td>30</td>
<td>&lt;5</td>
<td>11</td>
<td>1</td>
<td>0</td>
<td>85.5 ± 0.04 × 10⁻¹⁷</td>
<td>4B</td>
</tr>
<tr>
<td>PdAu/Au(hkl)</td>
<td>PdAu</td>
<td>31</td>
<td>30</td>
<td>&gt;5</td>
<td>13</td>
<td>0</td>
<td>&gt;0</td>
<td>5.6 ± 0.04 × 10⁻¹⁷</td>
<td>4B</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>&gt;0</td>
<td>&gt;0</td>
<td></td>
<td></td>
<td>6.9 ± 0.01 × 10⁻¹⁷</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>&gt;0</td>
<td>&gt;0</td>
<td></td>
<td></td>
<td>4.5 ± 0.02 × 10⁻¹⁷</td>
<td>5B</td>
</tr>
</tbody>
</table>

*The value of Γ_ML for all fits is taken as 0.5 × 10¹⁵ cm⁻²･ppm⁻¹. b_P[Au] = \sqrt{b_P[Au]/b_P[Pd]}.*

First one is for very low concentrations, [HS⁻] < 10 ppm, and the second one is for subsequently higher range of [HS⁻] above 10 ppm.

To further proceed with analysis of these data, we assume Langmuir adsorption formalism to describe the relation between the surface coverage of adsorbed HS⁻ ions (θ) and its concentration in solution [HS⁻].

θ = \frac{B_P[\text{HS}^-]}{1 + B_P[\text{HS}^-]} \approx B_P[\text{HS}^-] \tag{5}

Here, the term B_P is the equilibrium adsorption constant with subscript P, indicating the type of the metal surface on which adsorption occurs (P = Au, Pd, or AuPd). For [HS⁻] in our study being very low, we can assume a linear form of the Langmuir isotherm presented above. Further assumption is that we model the surface concentration of the HS⁻ adsorbate Γ_HS⁻ [cm⁻²] as a product between the HS⁻ surface concentration in the full monolayer, Γ_ML, and corresponding HS⁻ adsorbate coverage θ.

Γ_HS⁻ = Γ_ML [θ] \approx Γ_ML B_P[\text{HS}^-] \tag{6}

Combining eqs 1, 5, and 6 we arrive to the analytical model which is used to analyze the chemoresistivity trend observed for the pristine Au surface [Au(hkl)].

\frac{\Delta \rho}{\rho_B} = \frac{3}{16} \cdot \frac{1}{t} \cdot \Gamma_M \cdot B_P[\text{HS}^-] \cdot \zeta \tag{7}

Here, the only adjustable parameter is the product B_Pζ which adopts the subscript notation to B_P[Au] for the particular experiment. The values of other constants are taken from the literature. They are summarized in Table 2 together with the fitting results.

The linear increase of surface resistivity for increasing HS⁻ concentration in the solution points out that only one type of adsorption sites influences electron scattering and determines the chemoresistive behavior of pristine Au surfaces. Considering that Au(hkl) is almost atomically smooth, Figure 4A, we assume that adsorption sites are mainly associated with terraces, while the defect contributions to the overall adsorption process can be neglected. Therefore, the B_Pζ term extracted from the fit is associated with the HS⁻ scattering cross-section at the terraces (ξ_T), that is, B_Pζ = B_P[ξ_T]. However, the situation changes significantly after the additional 15 ML of Au is deposited. The surface morphology changes to the one populated with numerous Au nanoclusters. Figure 4A. This results in saturation roughness increase for approximately five times, Figure 4A. The repetitive nucleation of 2D Au nanoclusters in each SLRR cycle yields the surface morphology with large number of defects such as cluster edges and/or steps. Because of this, the relative ratio between terrace sites and defect sites for the adsorption process changes significantly as compared to a pristine Au surface. As a consequence, the modified Au surface displays chemoresistive behavior which is characterized by more than one type of adsorption site. Nevertheless, at very low HS⁻ concentration, <10 ppm, one expects that the coverage of the surface is very low and that preferential adsorption of HS⁻ occurs exclusively at the defects. Therefore, we can still assume that the initial region of chemoresistive behavior for the modified Au surface is dominated by a single type of adsorption site, in this case, by defects as energetically more favorable having a larger subordination. Because of this, we can use eq 7 to analyze the initial chemoresistivity trend while keeping in mind that the ξ_T term now stands for scattering cross-section of HS⁻ adsorbed on the Au surface at defect sites. The obtained B_P[Au]ζ value is presented in Table 2. The mutual comparison between B_P[Au]ζ and B_P[Au]ζ values indicates that the scattering cross-section for the adsorbate at the defect sites is an order of magnitude larger (ξ_T/ξ_T ≈ 25). Obviously, the Au surfaces with higher contribution of defects to the overall adsorption sites population represent a more effective morphology for HS⁻ sensor design. After [HS⁻] is further increased, >10 ppm, the coverage of the modified Au surface increases, and the adsorption on terrace sites proceeds as well. Therefore, we must take into account that now we have two qualitatively different adsorption sites determining the overall chemoresistive behavior of the modified Au film. For this purpose, we can express the HS⁻ coverage as the sum of the coverages coming from the adsorption on defects, θ_D, and from the terrace sites, θ_T. Thus, θ = θ_D + θ_T applies. The relative contribution of each type of the adsorption site to an overall adsorption process is quantified by partitioning coefficients f_D = θ_D/θ and f_T = θ_T/θ. They are combined with eqs 2, 5, and 6, yielding the analytical model describing modified Au surface chemoresistivity (P = Au) in the range of HS⁻ concentration beyond 10 ppm.

\frac{\Delta \rho}{\rho_B} = \frac{3}{16} \cdot \frac{1}{t} \cdot \Gamma_M \cdot [\text{HS}^-] \cdot (B_P f_D Σ_D + B_P f_T Σ_T) \tag{8}

One should notice that the above expression is more general, but it is easily reduced to shape of eq 7 if one of the partitioning coefficients equals to 0. This fact is used to consolidate the content in Table 2 showing all results (slopes) in one column with {B_P f_D Σ_D + B_P f_T Σ_T} connotation. The reader is advised to observe the value of f_D and f_T first in order to assess the type of the model (eqs 7 or 8) applied in particular data analysis. The fit of eq 8 to the experimental results in Figure 4B for [HS⁻] ≥ 10 ppm is shown with the solid blue line. In the above mentioned equation, we used values of B_P[Au]ζ and B_P[Au]ζ determined in previous analysis.
we expect a nominal deposition of approximately 0.67 Pd ML
on the Pd surface is practically the same as on Au. Therefore,
we assume that the first regime is controlled by predominant contribution of adsorbate scattering at the defect sites. This statement is supported with higher saturation roughness of the Pd-modified Au(hkl) films as compared with the pristine Au(hkl) surface. The chemoresistivity for the >5 ppm [HS⁻] regime is likely a combination of adsorbate scattering from both types of adsorption sites, defects, and terraces. The latter is expected to dominate this regime. We can get more quantitative information about the adsorbate scattering cross-section at defect sites on the Pd-modified Au(hkl) surface using the same approach as in the case of Au/Au(hkl) analysis. The fit of eq 7 (B_pξ = B_pξ_T) to the initial part of the chemoresistivity data in Figure 5B for the sample with 30 SLRR cycles is shown by the red line. The extracted value of B_pξ_T is larger than the B_pξ_T value, Table 2. The reason for this is much stronger overall interaction of the Pd surface with the HS⁻ adsorbate. Therefore, B_pξ_D ≫ B_pξ_T is likely a relation which reflects both B_p(D) ≫ B_p(Au) and ξ_T(Pd) ≫ ξ_T(Au) individual relations too.

In Figure 5A, the OCP transients during 1st, 15th, and 30th SLRR cycles are shown. One sees that after the 15th SLRR cycle, the OCP transients achieve a steady shape and that OCP of Pd modulation produced by 30 and 40 SLRR cycles is 20% higher P_p(D) ≫ ξ_T(Au) is true as well. An interesting information about the relative importance of defect sites to the overall chemoresistive behavior of Pd-modified Au(hkl) is obtained by mutual comparison of data sets in Figure 5B. One can see that Pd modification using 40 SLRR cycles produces a more comparable value of B_pξ_D [P(M) + B_pξ_T] are shown in Table 2. As one can see, the modification by the Pd layer with comparable thickness as the Au layer on the Au(hkl) surface yields ≈90% larger value, that is, 90% larger chemoresistivity. Therefore, we conclude that ξ_T(Pd) > ξ_T(Au) is true as well. An interesting information about the relative importance of defect sites to the overall chemoresistive behavior of Pd-modified Au(hkl) is obtained by mutual comparison of data sets in Figure 5B. One can see that Pd modification using 40 SLRR cycles produces a more comparable value of B_pξ_D [P(M) + B_pξ_T] are shown in Table 2. As one can see, the modification by the Pd layer with comparable thickness as the Au layer on the Au(hkl) surface yields ≈90% larger value, that is, 90% larger chemoresistivity. Therefore, we conclude that ξ_T(Pd) > ξ_T(Au) is true as well. An interesting information about the relative importance of defect sites to the overall chemoresistive behavior of Pd-modified Au(hkl) is obtained by mutual comparison of data sets in Figure 5B.
SB (triangles) indicate that higher chemoresistivity of Pd/Au(hkl) is also associated with larger irreversible retention of the resistivity upon reduction of the $\mathrm{HS}^-$ concentration in solution. It is likely that $\mathrm{HS}^-$ desorption from some defect sites at the Pd surface is not 100% reversible and that population of this type of defects increases with the number of SLRR cycles. This data also point out that there is an optimum Pd overlayer morphology in terms of roughness and defect density if one considers $\mathrm{HS}^-$ sensor design.

**PdAu/Au(hkl) Modification.** Modification of the pristine Au surface with PdAu alloy was carried out using 30 SLRR cycles from solution containing both Pd and Au ions, Table 1. Their concentrations were equal, however, a slightly different kinetics of their reduction by Pb UPD adatoms resulted that composition of the alloy surface after each SLRR cycle slightly changes toward more Pd-rich surface. This is illustrated by representative 1st, 5th, 10th, 20th, and 30th OCP transient presented in Figure 6A. One can see that OCP transients do not reach a steady shape. Instead, they keep changing toward the transient shape that resembles the Pd-like surface (Figures 5A vs 6A). According to elementary stoichiometry for each metal SLRR reaction (eqs 4 and 9), the nominal thickness of the PdAu alloy layer on top of Au(hkl) is estimated to be between 5 and 6 nm. The X-ray photoelectron spectroscopy analysis did not show sufficient sensitivity to discern the composition of the top most surface layer but rather gave an integral signal from the top most region of $\sim 3$ nm thickness which indicated a slightly Pd-rich alloy ($\sim 55$ at. %). Nevertheless, this type of alloy layer has shown a qualitatively different chemoresistive behavior with respect to Au/Au(hkl) and Pd/Au(hkl) samples. The data are shown in Figure 6B. There are two obvious peculiarities for this data set. First, there is no defect-controlled region at low concentration of $\mathrm{HS}^-$ but a single linearly increasing trend for the entire range of $[\mathrm{HS}^-]$. Second, the reversibility of chemoresistive behavior is preserved in three consecutive $[\mathrm{HS}^-]$ sweeps. This is different than Pd/Au(hkl), however, the linearity and reversibility of the surface chemoresistive behavior are very much desirable when practical sensor design is considered. The interpretation of this data is somewhat more complex as we do have surface, which possesses chemical and structural diversity, that is, defect and terrace sites, and Pd and Au atoms at the surface. The saturation roughness of the PdAu layer is comparable (2.5 nm) with other samples produced by 30 SLRR cycles and an apparent lack of the defect-controlled region at low $[\mathrm{HS}^-]$ is surprising. Considering that Au and Pd form a binary alloy in the broad range of compositions, it is likely that the chemical property of each atom on the surface is influenced by its neighbors and for slightly reaching the Pd surface, a Pd-like behavior is expected. However, considering the difference in surface energy between Pd and Au, where $\gamma_{\text{Pd}} > \gamma_{\text{Au}}$ a surface enrichment in Au can be expected in particular at the defect sites, where mobility of the adatoms is higher and the surface segregation effects are more pronounced. Therefore, we can expect that this alloy surface consists of defects sites predominantly decorated by Au atoms, while the terrace sites are populated by majority of Pd atoms. In this scenario, preferential adsorption at Au defects might not be dominant as they would be competing for $\mathrm{HS}^-$ adsorbates at low coverage with the active Pd adsorption sites at the terraces. Therefore, one can expect a trend, which is influenced by adsorbates at both types of adsorption sites from the very beginning. This would result in the linearly increasing trend such as the one observed in Figure 6B. Their slopes are shown in Table 2 having notation as $B_{\text{PdAu}}=B_{\text{PdAu}}^* + B_{\text{PdAu}}^{\text{Pd}}$. The asterisk at subscripts indicates a dominant element in particular adsorption site configuration. Interestingly, their values fall inbetween the values extracted for Au- and Pd-modified Au(hkl) (30 SLRR cycles). To some extent, this result validates our discussion; however, more experiments are necessary to elucidate the true origin of the chemoresistive behavior for PdAu alloy-modified Au ultrathin films.

**CONCLUSIONS**

The interaction of $\mathrm{HS}^-$ with the Au surface has been the phenomenon of considerable interest due to its relevance as the surface linker group for many complex molecules, proteins, antibodies, and 3D molecular structures. The adsorption of $\mathrm{HS}^-$ to the Au changes the energetics of the surface states and does affect the surface resistivity of Au ultrathin films. This is clearly demonstrated in this study, and the qualitative and quantitative importance of surface defects for an optimum chemoresistive response of Au ultrathin films is highlighted. Modification of the Au surface with Pd as the more active metal/layer for the $\mathrm{HS}^-$ adsorbate does improve the overall chemoresistivity but also results in partial irreversibility of the $\mathrm{HS}^-$ adsorption process. This deems this approach somewhat impractical for surface chemoresistive sensor design although its true qualification is pending more detailed studies. Modification of Au ultrathin films with the PdAu alloy layer was shown as a promising concept for surface chemoresistive sensor design. The PdAu alloy-modified Au ultrathin films show improved chemoresistivity as well as linear response and reversibility. These attributes are still to be studied in more detail in relation to the surface morphology and surface.

Figure 6. (A) OCP transients during PdAu alloy layer deposition via SLRR of the Pb UPD ML. (B) Chemoresistivity of PdAu/Au(hkl) films obtained via 30 SLRR cycles of the Pb UPD ML. Circles and triangles represent data for increasing and decreasing $[\mathrm{HS}^-]$. DOI: 10.1021/acsensors.9b04945 ACS Sens. 2019, 4, 2442–2449
composition, but the presented data are certainly very encouraging and promising.

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**Notes**

The authors declare no competing financial interest.

- ACKNOWLEDGMENTS

The experimental material is based upon work supported in part by the National Science Foundation under the contracts CHE-0955922 and CBET 1605331 and Baker Hughes a GE Company gift grant.

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