Influence of Surface Adsorption on Work Function Measurements on Gold-Platinum Interface Using Scanning Kelvin Probe Microscopy

To cite this article: Simon Mugo and Jun Yuan 2012 J. Phys.: Conf. Ser. 371 012030

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Influence of Surface Adsorption on Work Function Measurements on Gold-Platinum Interface Using Scanning Kelvin Probe Microscopy

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Abstract. Surface potential difference (SPD) on freshly coated gold and platinum electrodes have been found to be much smaller than bulk work functions consideration and to be dependent on time. We show these discrepancies arise due to formation of surface dipoles caused by adsorbed contaminants in ambient environments. The process is reversible by gentle annealing consistent with contaminant hypothesis. Examination of potential changes on individual electrodes suggest that the Pt surface is more sensitive to ambient conditions than the Au surface in accordance with their relative chemical activities. The result has great implication for interpretation of Kelvin probe measurements obtained on practical devices exposed to ambient environments.

1. Introduction
The nanoscale resolution [1,2] and quantitative measurements achievable with scanning Kelvin probe microscopy (SKPM) makes it attractive in measuring materials’ electrical properties and surface reactions [3,4]. The physical principle of the technique is based on contact potentials [5]. A metallic tip is vibrated above the sample and its electrostatic interaction with the sample minimized by application of a bias voltage [3,6]. This voltage corresponds to the contact potential difference (CPD) for clean metals [2]. For metal surfaces with a double layer, the net electric potential is the surface potential difference (SPD) and it gives information about surface charging [2,7]. Gold and platinum have often been used as reference electrodes in the CPD measurements, since they are chemically inert at room temperature [8]. However, various works have reported inconsistency in measured values [9,10], with variations only discussed qualitatively [10,11,12]. These variations present a great challenge for actual Kelvin probe measurements on devices exposed to ambient conditions.

In this work, we not only report discrepancies in measured surface potential values on Au and Pt electrodes, but we also show systematic trends as a function of time and sample treatment. The variations are explained by surface dipoles caused by adsorption of contaminants in ambient environments. The process is reversible by gentle annealing in H₂/Ar environment and is attributed to elimination of volatile adsorbed species. Our result offer simple interpretation of Kelvin probe measurements which is useful in deducing stable electrodes and for examining practical devices exposed to ambient conditions.
Figure 1. SKPM measurement in vacuum across Au-Pt interface obtained with a Pt-coated tip: (a) Topography showing a Pt step, 43 nm high, deposited on Au surface (b) SPD scan showing contrast along the Au-Pt boundary (c) line profiles across the interface (notice the non-zero potential on Pt electrode)

2. Experimental procedure
A 2 nm chromium film was first deposited on clean 2 x 2 cm² n-type silicon. This was followed by deposition of 100 nm gold film. The samples were then half masked and a 50 nm Pt film was subsequently deposited to produce Au-Pt interface. Kelvin probe measurements were immediately obtained in high vacuum and in air with a JSPM 5200 AFM made by JEOL. Scanning was done with Au-coated and Pt-coated AFM tips (resonant frequency = 300 KHz and spring constant = 40 N/M), which had been supplied by Mikromasch. Figure 1 displays results obtained in vacuum with a Pt-coated tip. Topography, figure 1a, shows sharp peaks from contaminating particles from the mask. A clear potential contrast is visible along the Au-Pt boundary, figure 1b. A gradual variation across the interface is observed in line profiles, figure 1c, which is due to a slanting deposition coupled with tip convolution. Measurements are however homogeneous away from the interface. To obtain a representative potential value, we measured several line profiles extending the full scan range. We then repeated the process for two other areas of the same sample and on one other sample prepared in similar conditions. Measurements for samples prepared in similar conditions were reproducible within ± 8 mV error margin. The final measurement was extracted by averaging SPD profiles across each scan.

3. Results
3.1. Effects of exposing samples to ambient environments on the surface potential
Table 1 displays results for electrodes SPD in air and in vacuum environments. On using both Au-coated and Pt-coated tips to scan across the interface, the residual potential was non-zero and with the Pt electrode recording a higher value. Measurements in high vacuum were slightly higher by about 20 mV compared to measurements in air for all results obtained with both AFM tip materials. However, the measured values are much smaller than theory predicts [13, 14].

Table 1. Surface potential measurements at Au-Pt interface in ambient conditions

<table>
<thead>
<tr>
<th>Reference</th>
<th>In air (mV)</th>
<th>In vacuum (mV)</th>
<th>Theoretical (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au tip on Au sample</td>
<td>50 ±5</td>
<td>40 ±5</td>
<td>0</td>
</tr>
<tr>
<td>Au tip on Pt sample</td>
<td>87 ±5</td>
<td>96 ±5</td>
<td>350-700</td>
</tr>
<tr>
<td>SPD</td>
<td>37</td>
<td>56</td>
<td>350-700</td>
</tr>
<tr>
<td>Pt tip on Pt sample</td>
<td>75 ±5</td>
<td>56 ±4</td>
<td>0</td>
</tr>
<tr>
<td>Pt tip on Au sample</td>
<td>120 ±5</td>
<td>120 ±5</td>
<td>350-700</td>
</tr>
<tr>
<td>SPD</td>
<td>45</td>
<td>64</td>
<td>350-700</td>
</tr>
</tbody>
</table>
3.2. Time-dependence SPD on individual electrodes
The time-dependence SPD shows an initial decrease on Au and an increase on Pt, figure 2. The rate of change on Pt is higher compared to Au over the same time and in similar ambient conditions. After 14 days, measurements converged to a constant value which was almost similar for both electrodes. However, potential fluctuations on Pt electrode increased as the sample aged whereas they remained constant on Au electrode, as shown by error bars.

3.3. Effect of temperature on individual electrode SPD
Samples which had been exposed to ambient were then annealed systematically for 30 minutes in H\textsubscript{2}/Ar and surface potential measurements repeated. The potential trend was observed to be reversible, figure 3, with an increasing trend on Au electrode and a decrease on Pt electrode. After annealing at 300 °C, changes of 15 mV and 45 mV were recorded on Au and Pt respectively. Since this result is obtained with a Pt-coated tip, it is clear that the changing trend on Au is towards the Au/Pt metal bulk and on Pt is towards the residual potential. These improvements are however far from bulk work function consideration of 350-700 mV for Au/Pt and zero for the residual potentials [14].

4. Discussion
Work functions of metals are known to be affected by intrinsic surface dipole [14]. However, this change does not depend on time as metal surface remain the same at low temperatures. We believe the observed time dependence is due to adsorbed species on metal electrodes. The AFM cantilevers had been stored in ambient condition for long time and tip adsorption is likely to be saturated. This contamination on tips only affects absolute values and does not contribute to these variations. Proof for adsorption is confirmed by exposing the annealed sample to ambient conditions, where the potential trend became similar to the 'as deposited' sample. Related studies have shown oxygen, water and hydrocarbons to be the most probable contaminants on Au and Pt [15,16]. Such adsorption results in dipole layer [17], given by eqn. (1) [14]: where $N_{mol}$ is density of adsorbed species, P is dipole moment, $\epsilon$ is dielectric constant and $n$ is vector normal to surface. Table 2 summarizes molecular adsorption approximated using this relation.

$$V_{dipole} = \frac{N_{mol}(P \cdot n)}{\epsilon}$$

(1)
Table 2. Calculated molecular density

<table>
<thead>
<tr>
<th>Condition</th>
<th>Electrode</th>
<th>$\Delta V$ (mV)</th>
<th>$N_{mol}$(m$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aging</td>
<td>Au</td>
<td>9</td>
<td>2.5x10$^{16}$</td>
</tr>
<tr>
<td></td>
<td>Pt</td>
<td>32</td>
<td>1 x 10$^{17}$</td>
</tr>
<tr>
<td>After annealing</td>
<td>Au</td>
<td>15</td>
<td>4.3x10$^{16}$</td>
</tr>
<tr>
<td></td>
<td>Pt</td>
<td>45</td>
<td>1.3x10$^{17}$</td>
</tr>
</tbody>
</table>

Adsorbed molecular densities on Pt are higher compared to Au, which is consistent with their chemical activities. Initial changes in potential sign (figure 2) is attributed to the fact that Pt oxidizes easily in air, with initial oxygen reorienting adsorbed dipole direction $^{16}$. These values are close to reported hydrocarbons adsorption $^{18,19}$, with the slight deviation accounted for by different molecular chains and closest packing imposed by surface $^{20}$. Equalization of SPD with time is not clear from our experiments, but we think it is caused by induced dipoles. This is possible if polarization for physisorbed or charge transfer for chemically absorbed species occur $^{21}$. The net dipole becomes the sum of individual electric fields due to each of the other dipoles.

5. Conclusion
We have measured large SPD on Au and Pt surfaces far from bulk work function consideration. The time-dependence SPD and which we have shown to be reversible by annealing is explained by surface adsorption forming a dipole layer. Such reproducible experiments in ambient conditions are important in interpreting Kelvin probe measurements on real time devices.

5.1. Acknowledgments
This research has been done using facilities at the York JEOL Nanocentre at the University of York. Funding from Commonwealth scholarships commission is highly appreciated.

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