

Investigation of Organic Molecules on Gold Surfaces

Research Topics in Physics: PHYS 4501

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Abstract

We grew several gold films on mica and flame annealed them to promote the growth of large Au(111) terraces. We studied both as-grown and the flame annealed gold surfaces with scanning tunneling microscopy (STM) and x-ray photoelectron spectroscopy (XPS). Analyzing the structure of the Au(111) surface showed large atomically flat terraces suitable for the deposition of threefold symmetric halogen terminated organic molecules. Comparison of the XPS results for the as-grown, and flame annealed gold surfaces revealed an increase in relative atomic concentrations of carbon and oxygen. XPS of the O1s spectra suggests a higher concentration of C-O bonds on the flame annealed surface. We continued our investigation by depositing molecules onto the flame annealed gold surface to produce a self-assembled monolayer (SAM). The SAM showed a structure defined by a single molecule unit cell with lattice vectors 1 nm by 0.8 nm.

Introduction

Since the isolation of graphene in 2004, two-dimensional (2-D) materials have become a major trending topic in materials science and nanotechnology. Organic layers on a metal surface have important applications, e.g. in catalysis, sensors, adhesion, corrosion inhibition, molecular recognition, optoelectronics and lithography [1,2]. The development of organic layers on metal surfaces depends on understanding the bonds and surface interactions that determine the orientation, and 2-D organisation of these molecules [1,2]. Following this trend, we are investigating an organic molecule on gold surfaces.

We evaporated a thin film of gold on mica for our experiments to use as a substrate. Mica is a complex silicate which provides a fresh atomic layer upon cleavage. This surface is suitable for the deposition of gold. Gold has a face centered cubic (FCC) crystal structure. An FCC crystal structure is a cubic lattice with an atom on each of the vertices of the cube and one at the center of each face. We can define planes of this crystal structure using Miller indices. For a three-dimensional crystal structure Miller indices are defined by coordinates (xyz) and (111) corresponds to the body diagonal.

During the evaporation of gold and its absorption on the mica surface, the surface structure is polycrystalline with small crystal domains. A thermal treatment process of flame annealing the as-grown promotes the growth of larger domains with (111) faces exposed [3]. Gold was chosen as a substrate because of its low reactivity and because the (111) face provides large flat terraces suitable for molecule deposition. The low reactivity allows the molecule to remain intact upon adsorption and enables noncovalent halogen bonding between monomers of the SAM [2].

The organic molecule we chose to study is a triangular molecule with bromine terminations, carbonyl bridging between benzene rings, and is referred to as TBTANGO. The molecule is similar to TBTANG which has been observed to form a high-quality SAM on Au(111) surfaces [2]. The primary difference between TBTANG and TBTANGO is that TBTANG has oxygen bridging the benzene rings.

The deposition of TBTANGO requires an Ultra-High Vacuum (UHV) system defined by pressures below 10^{-9} torr [4,5]. In this environment, contamination by gases is minimized and facilitates the clean absorption of molecules onto our surface. A SAM is formed by depositing molecules onto a surface which can then aggregate to form an ordered 2-D structure stabilized via noncovalent interactions. In the case of TBTANG, it has been demonstrated that halogen bonding between adjacent molecules stabilizes the layer leading to highly ordered domains [4].

Our investigation will focus on two techniques, scanning tunneling microscopy (STM), and x-ray photoelectron spectroscopy (XPS). STM is a technique used to image the surface of a sample with atomic scale resolution. This will be useful to analyze the atomic structure of our gold surfaces and the subsequent SAM. XPS is a surface analysis technique used to explore the chemical properties of a sample. The technique can identify the chemical bonding of elements at the surface of a sample. XPS will serve as baseline spectra for future XPS investigation of a TBTANGO SAM on Au(111).

Experimental Methods

Sample Preparation

A gold evaporator was used to make our gold film for molecular deposition (Fig. 1). We used green muscovite mica and deposited gold in a small high-vacuum evaporator. The evaporator includes two pumps, a mechanical roughing pump and a diffusion pump to achieve high-vacuum. The cleaved mica is placed within the vacuum chamber above the gold source. The oil heater and fan are then turned on to the diffusion pump. The mechanical pump roughs the diffusion pump down to approximately 10^{-3} torr [5]. A diffusion pump works by directing hot oil vapor upward, where it cools and is deflected back down toward the oil bath [5]. During the descent, it transfers momentum to gas particles towards the lower part of the pump where they are evacuated by the mechanical pump. The liquid nitrogen trap is then filled with liquid nitrogen. This acts as a cryogenic pump, condensing gas to its walls and prevents back streaming of pump oil into the vacuum chamber. Once the diffusion pump is warm, the mechanical pump is used briefly to rough the vacuum chamber. We then open the valve from the vacuum chamber to the diffusion pump. The diffusion pump and the liquid nitrogen trap remove more gas from the vacuum chamber until the pressure is between 10^{-6} - 10^{-7} torr. The mica can now be heated for several hours at 100°C to remove any water intercalated between the layers and prevent blistering of the surface during the subsequent flame annealing process. The gold source can now be opened to the mica. A tungsten conical basket holding the gold wire is supplied with a current of 12 A for approximately 3 minutes to evaporate the gold onto the mica slide. This produces an as-grown sample which can be removed from the vacuum chamber.

After preparing the as-grown sample, we need further treatment to promote the formation of large Au(111) terraces. The flame annealing process promotes the growth of large crystallites exposing the lowest energy face of the FCC crystal structure [3]. We cut a piece of gold film approximately 1 cm x 1 cm and using a butane blow torch in atmosphere we anneal the surface with several passes. Qualitatively, when the edge of the mica glows red, the gold is

at sufficient temperature to produce large Au(111) terraces. Allowing the sample to cool in air, we have completed the process of producing terraces of Au(111) on the polycrystalline sample.

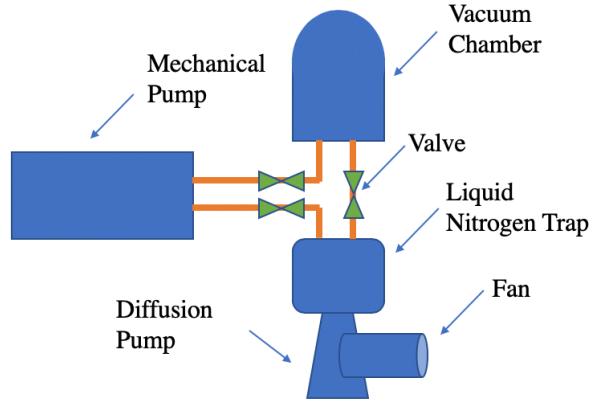


Figure 1: Gold Evaporator Component Diagram

Scanning Tunneling Microscopy

STM is an experimental surface imaging technique which exploits the principles of quantum mechanical tunneling. A scanning tunneling microscope brings a conducting tip extremely close to the surface of a sample. The vacuum region between the tip and sample is a potential energy barrier because the electrons inside the two materials have lower potential energy than they would in the free space between them due to the work functions of the materials [6]. In Fig. 2, we see how a wavefunction, describing the electron, exponentially decays within the barrier and leads to a non-zero tunneling probability. The tunneling current is described by:

$$I \propto e^{-2kd} \quad [5]$$

$$k = \sqrt{\frac{(2mV_0 - E)}{\hbar^2}} \quad [5]$$

I = Tunneling current

d = Distance between tip and sample

k = Decay constant

m = Mass of particle

V_0 = Energy of potential barrier

E = Energy of particle

\hbar = Planck's constant divided by 2π

Using a feedback loop, a constant tunnel current is maintained by STM to map the surface topography. This surface imaging technique is extremely sensitive to the separation distance due to the exponential dependence of the tunneling probability. A scanning tunneling microscope produces images with typical lateral resolution of 0.1 nm and depth resolution of 0.01 nm, sufficient to image individual atoms on a surface [6].

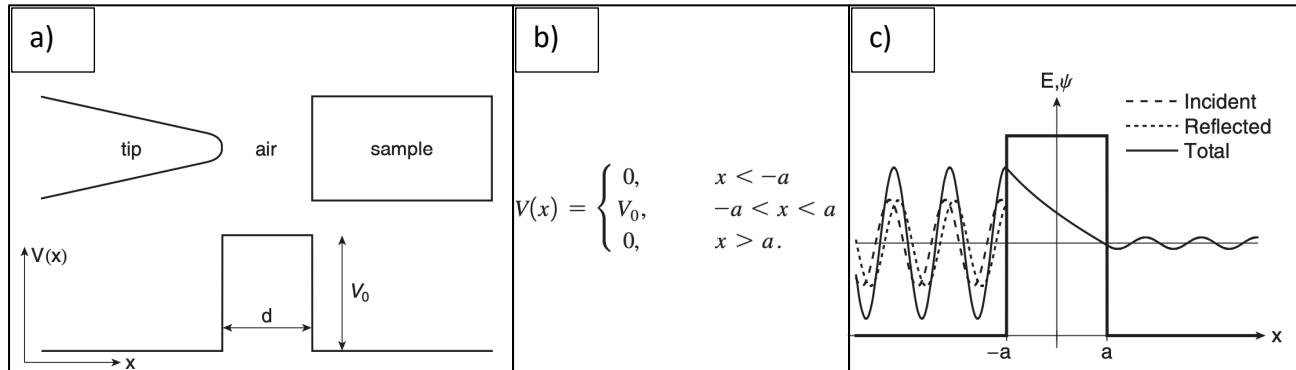


Figure 2: a) STM Operating Diagram with Potential Barrier b) Potential Expression] c) Quantum Mechanical Tunneling Through a Potential Barrier [6]

X-Ray Photoelectron Spectroscopy

XPS is a surface analysis technique used to explore the chemical properties of a sample. In XPS, a photon transfers its energy to a core electron which is photoemitted. XPS focuses on core electrons because their binding energy is higher and sharper compared with valence electrons. XPS interprets information based on the photoelectron's kinetic energy. The measured kinetic energy can be related to the binding energy of the electron in the material. Each element has well defined binding energy. That said, the chemical environment of the element does affect the core level binding energy. As such, XPS can detect changes in the chemical environment of the core electron.

For a conducting sample such as ours, the sample and spectrometer are held in electrical contact to bring the Fermi energies into alignment. The binding energy is measured by the spectrometer by the following equation:

$$E_B^F = \text{Binding Energy Referenced to Fermi Energy}$$

$$h\nu = \text{Photon energy}$$

$$E_B^F = h\nu - KE - \phi_{sp} \quad [7]$$

$$KE = \text{Kinetic Energy XPS Measures}$$

$$\phi_{sp} = \text{Work Function of Spectrometer}$$

This conservation of energy equation is shown schematically in Fig. 3. We can see that for conducting samples it is the work function of the spectrometer which determines the measured kinetic energy of the photoelectron. In our case, we want to state the binding energy of the electrons relative to the work function of the sample. To do this, we correct the spectra using the published Au 4f 7/2 binding energy. Once adjusted, and we have correctly accounted for

the work function of the sample (ϕ_s), the binding energy referenced to the fermi energy (E_B^{vac}) is easily determined by the spectrometer by:

$$E_B^{vac} = h\nu - KE_{True}$$

E_B^{vac} = Binding Energy Referenced to Vacuum Level

$h\nu$ = Photon energy

KE_{True} = Kinetic Energy of Sample's Photoelectron

These equations are shown graphically in Fig. 3

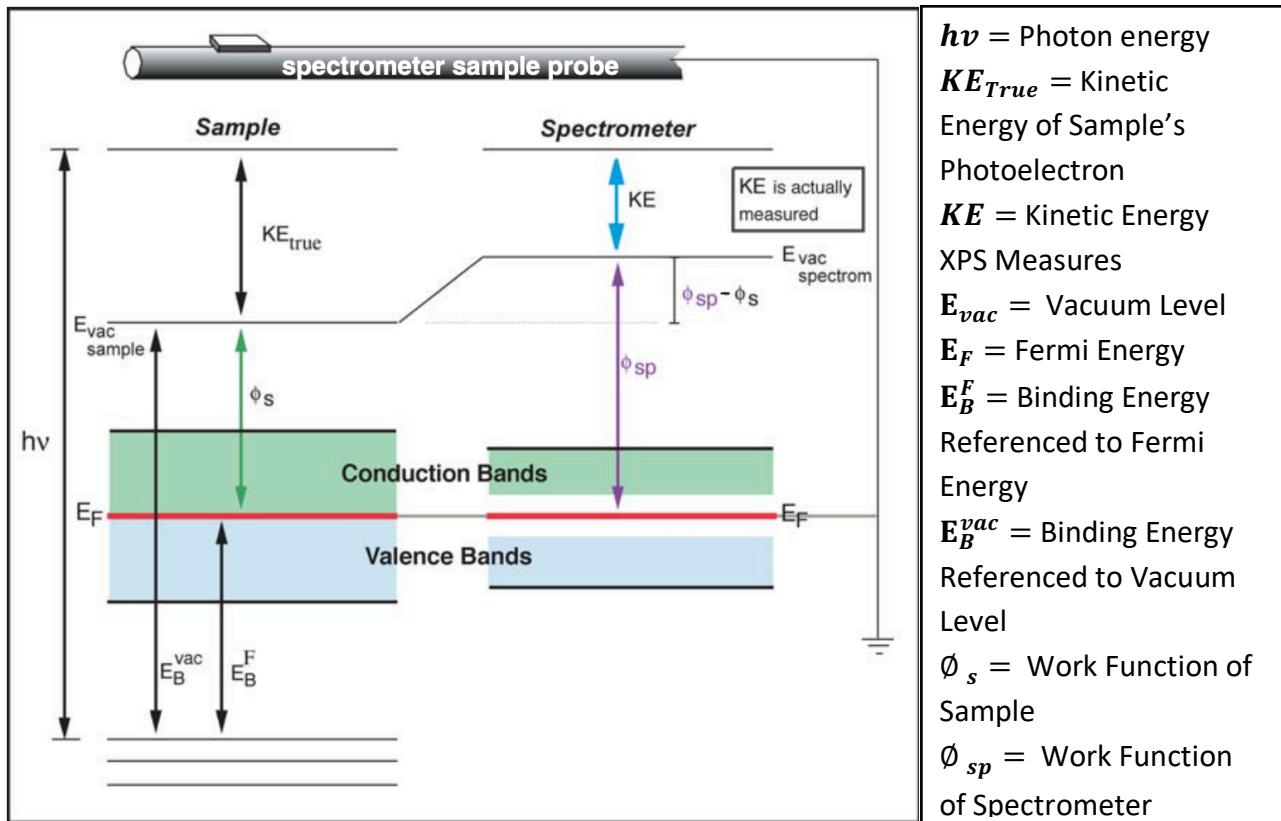


Figure 3: Energy Level Diagram [7]

XPS produces a preliminary survey scan over a range of energy (Fig. 4). The y-axis represents the counts of photoelectrons, and the x-axis is the binding energy with decreasing binding energy in the positive x direction. This XPS was done for a hard-segment polyurethane, an organic molecule [6]. We can see peaks due to carbon, oxygen, and nitrogen atoms which are present in the molecule. Hydrogen does not appear in XPS. The hydrogen atom does not have a core electronic orbital. Therefore, the H 1s electrons are valence electrons and their signal overlaps with the valence electrons of other atoms (Fig. 4).

Over a smaller energy range, XPS can reveal shifts in binding energy due to changes in chemical environment. Fig. 5 illustrates the powerful insights XPS can provide. The carbon bonds within the molecule can be identified, and we observe that the spectra shift depends on chemical environment (Fig. 5).

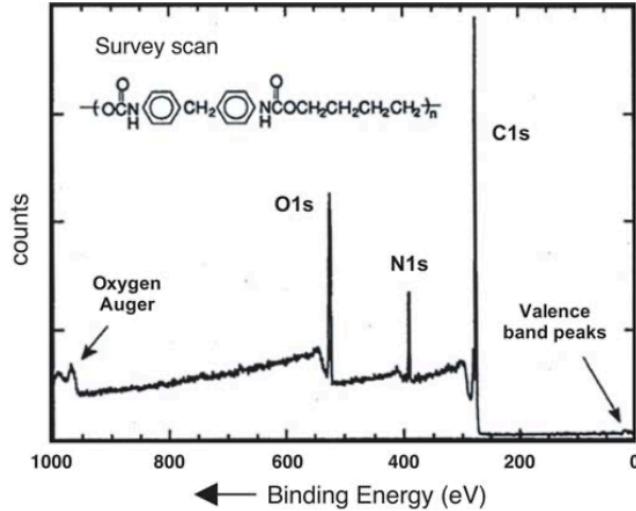


Figure 4: Sample Survey Scan [7]

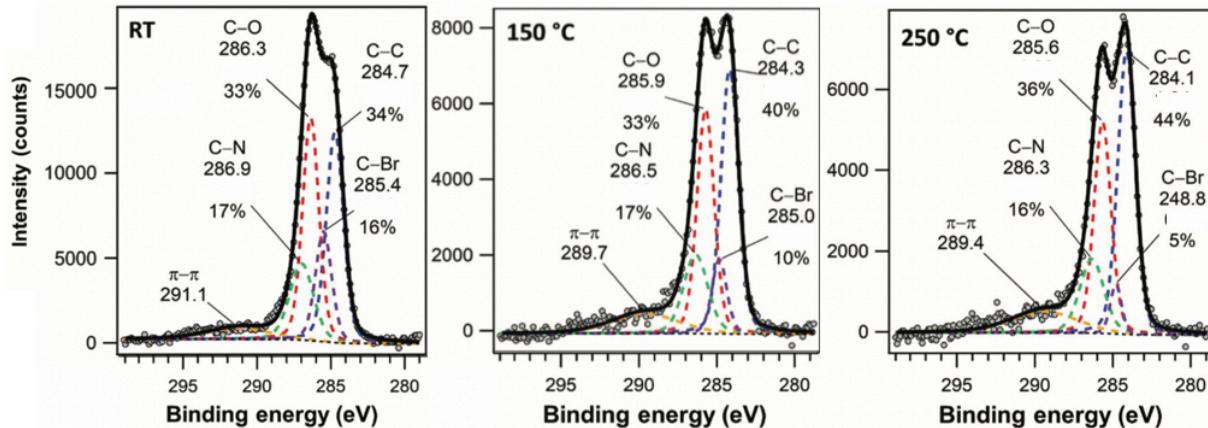


Figure 5: XPS C1s Spectra for TBTANG SAM on Au(111) at different temperatures with bond, binding energy, and intensity percentage labelled [2]

To conduct XPS, our samples need to be mounted so they are electrically conducting. This is accomplished with copper straps (Fig. 6). Once the samples have been mounted, they can be placed in a load lock which is pumped to achieve reach UHV pressures and then remotely introduced into the main analysis chamber. This process takes a couple of minutes and allows the main vacuum chamber to maintain UHV pressures without the need to depressurize when introducing, or removing samples. Thus, protecting the spectrometer from atmospheric gases and contaminants. Once inside the main vacuum chamber, XPS spectra can

be obtained and curves appear in real time on the control computer. Scans can vary in length, for better resolution a longer sweep time is required.

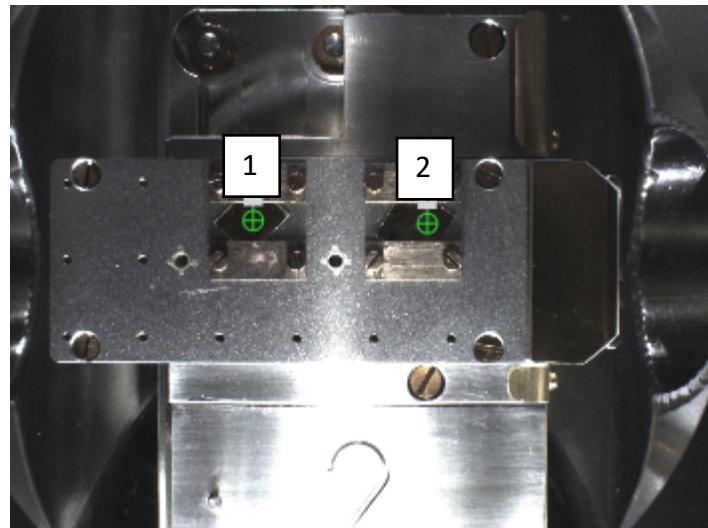


Figure 6: XPS Sample Holder with Gold Samples; 1) As-Grown and, 2) Flame Annealed

Results

Au(111) Terraces

We confirmed the success of the annealing process by analyzing the surface structure of the sample with STM (Fig. 6). The STM image shows the topography of the sample, with light colours showing higher elevations and darker colours showing lower elevations. Visible in Fig. 6 are multiple Au(111) terraces. The largest 100 nm wide terrace as shown in Fig. 6, is enclosed by the blue loop which is considered suitable for molecule absorption.

XPS of As-Grown and Au(111)

We performed XPS measurements on an as-grown gold film and a flame annealed sample. The spectra were corrected for the work function of the sample by comparing the Au 4f 7/2 spectral line with literature values [8]. A correction of 0.275 eV was required to account for the work function of the sample. The XPS survey scan, which includes Au 4f, O 1s, and C 1s transitions are compared for both the as-grown and flame annealed samples. The spectra were collected to detect any differences between the samples and to provide a baseline for future XPS measurements of deposited molecules on gold surfaces.

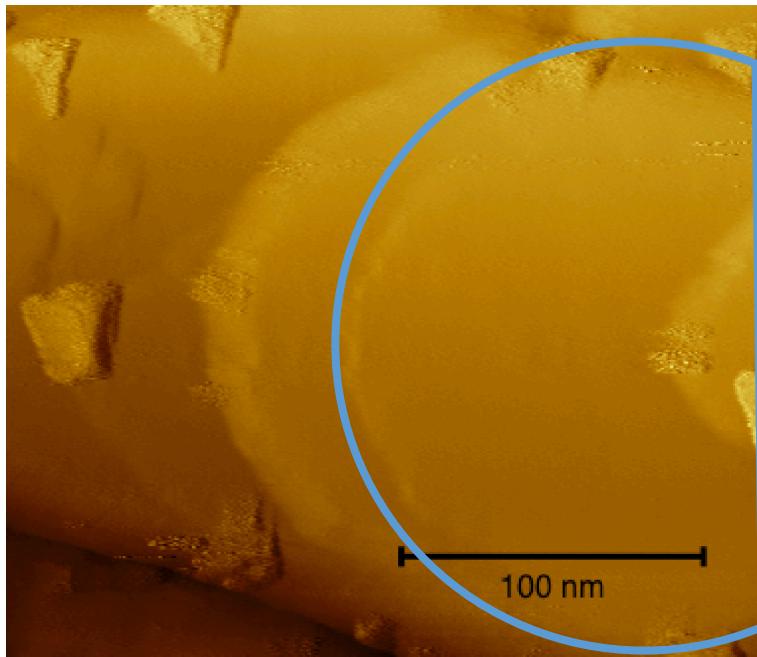


Figure 7: STM of Au(111) Terraces With Largest Terrace Enclosed by Loop

From the survey scans in Fig. 8 and Fig. 9 I used the XPS acquisition software to determine the relative atomic concentration of gold, carbon and oxygen by measuring the area under the curves attributed to their respective core electron orbitals [9]. The software normalizes the components I've identified and calculates the area under the peaks accounting for the sensitivity of the identified spectra [9]. Comparing the ratios of these areas, the software calculates the relative atomic concentration. The results are as follows:

Table 1: Relative Atomic Concentrations by Percentage

Component	As-Grown		Flame Annealed	
	Atomic Concentration (%)	Error (%)	Atomic Concentration (%)	Error (%)
Au4f	78.90	2.64	72.15	1.38
C1s	16.96	2.52	22.91	1.26
O1s	4.14	1.37	4.94	0.99

Observing Table 1, a small increase in the relative concentration of C1s is evident after the annealing process. Whether or not this increase can be attributed to the annealing process would require data on more samples to confirm these results.

Upon closer inspection, the Au 4f spectra exhibits two peaks due to the spin coupling of the 4f orbital (Fig.10). Furthermore, after our correction for the work function of the sample the peaks align with literature values of 87.7 eV for 5/2 and 84.0 eV for 7/2 [8].

The two C 1s spectra in Fig.11 appear similar. We know that the concentration has increased from the relative atomic concentrations determined from the survey scan, however no chemical shifts are apparent. Deconvolution of the data to investigate chemical shifts is not possible with these curves. If our signal to noise ratio were higher, the XPS software could identify peaks attributed to different bonds.

Each scan of the O 1s spectra in Fig. 12 represents 10 sweeps of 52s in an effort to reduce noise. It is clear that, like the C 1s spectra, more sweeps would be required to identify possible chemical shifts. That said, comparing the O 1s spectra in Fig. 10 we see higher relative counts at higher binding energies for the annealed gold at around 532.5 eV. This is suggestive of an organic C-O bond with a binding energy of approximately 533 eV [8]. However, due to the low signal to noise ratio, it is hard to analyze. This shows the importance of taking XPS of the gold samples before deposition of molecules as a baseline.

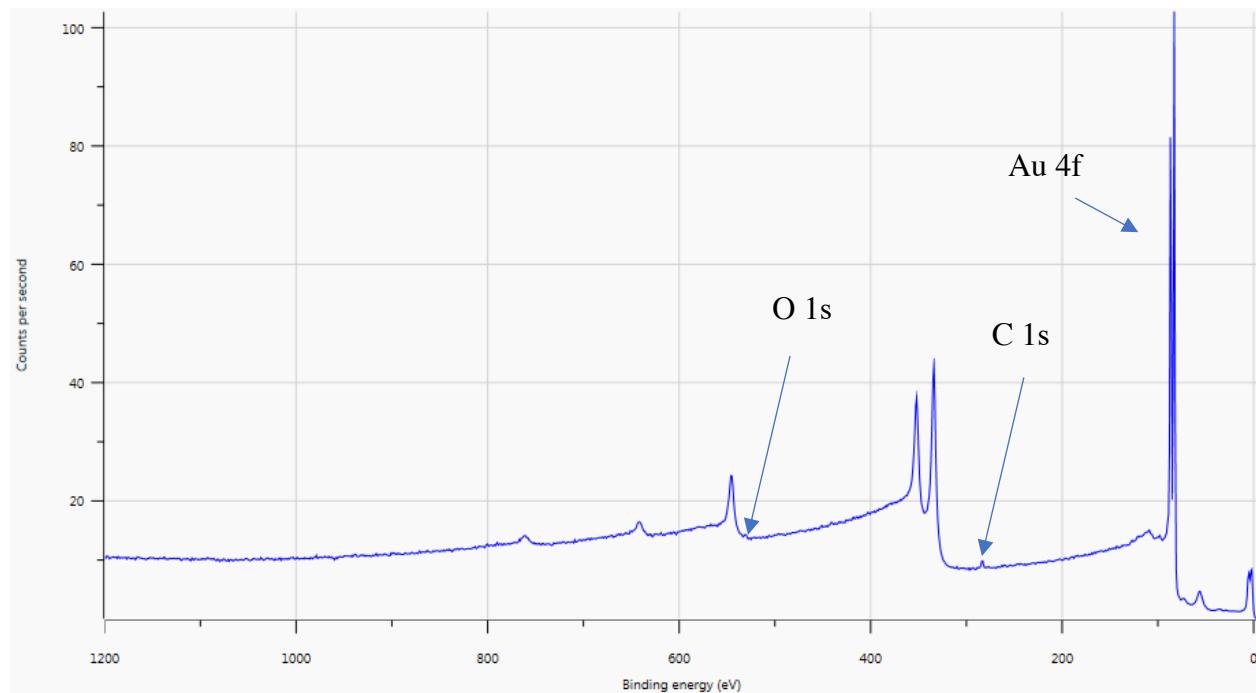


Figure 8: XPS Survey Scan of As-Grown Gold Sample with Identified Core Electron Orbitals

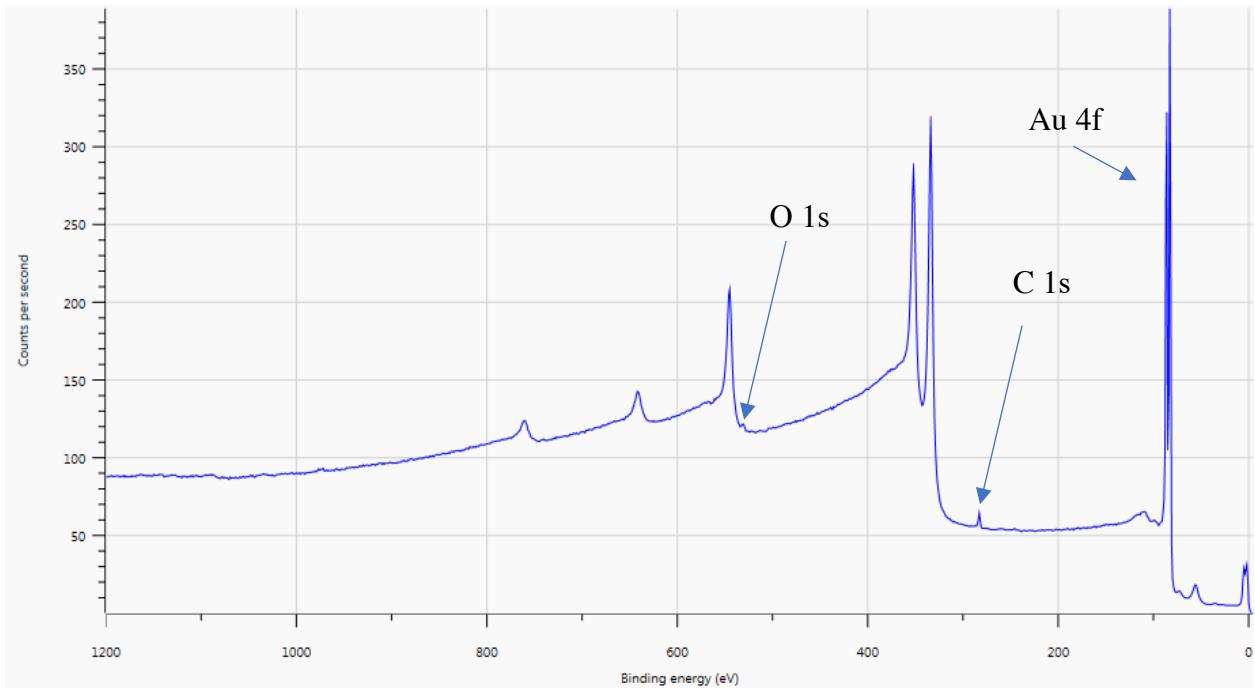


Figure 9: XPS Survey Scan of Flame Annealed Gold Sample with Identified Core Electron Orbitals

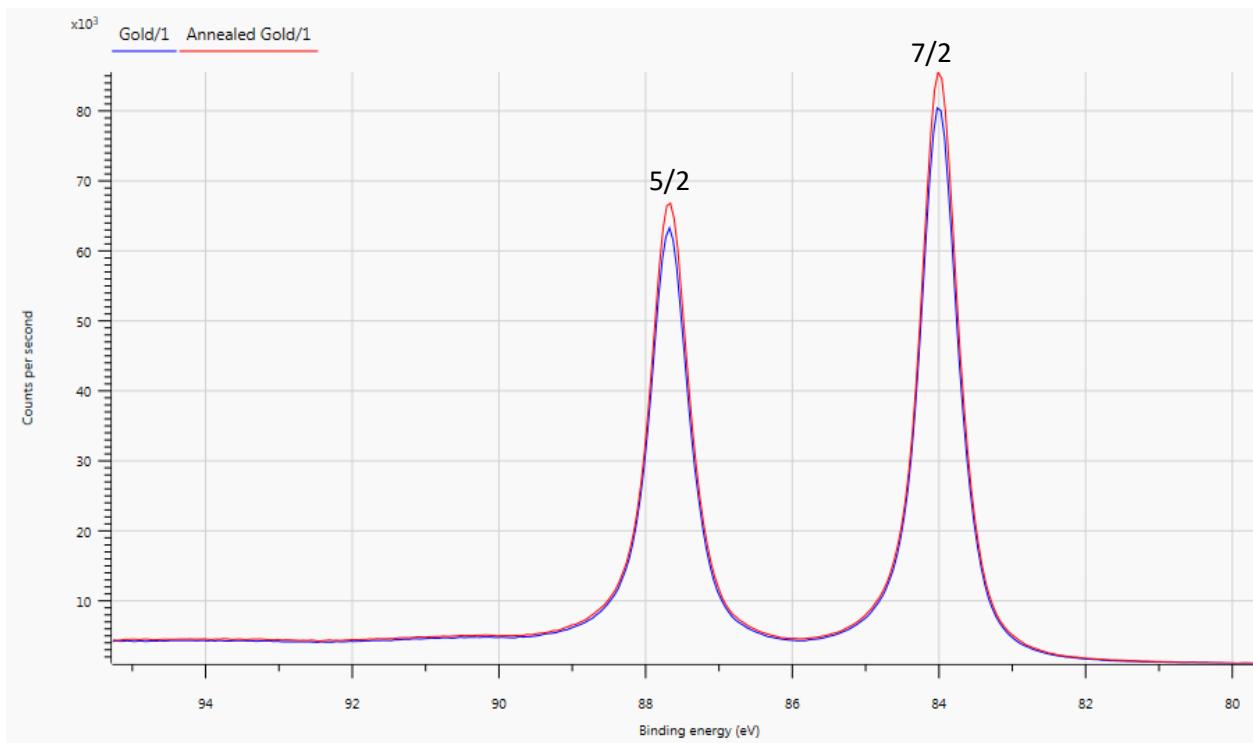


Figure 10: XPS Au4f spectra for As-Grown and Flame Annealed Gold with Labelled Orbitals

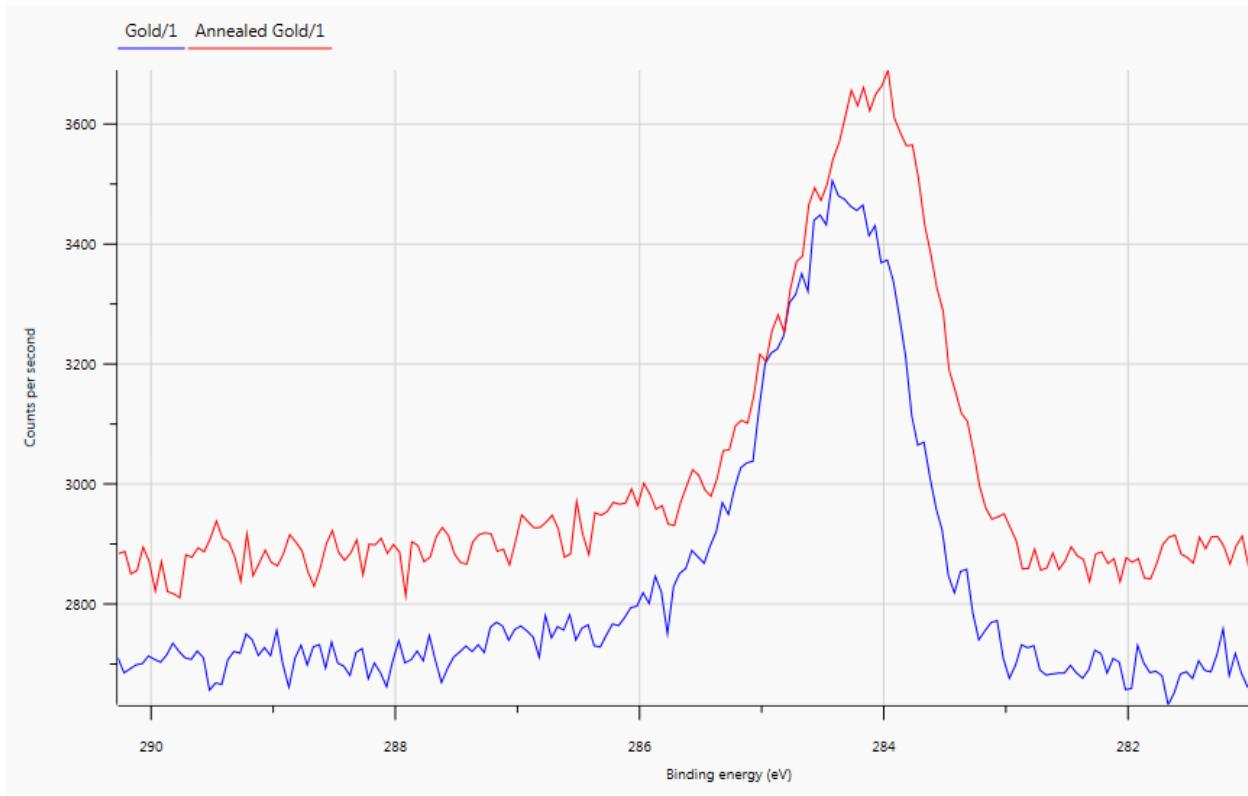


Figure 11: XPS C1s spectra for As-Grown and Flame Annealed Gold

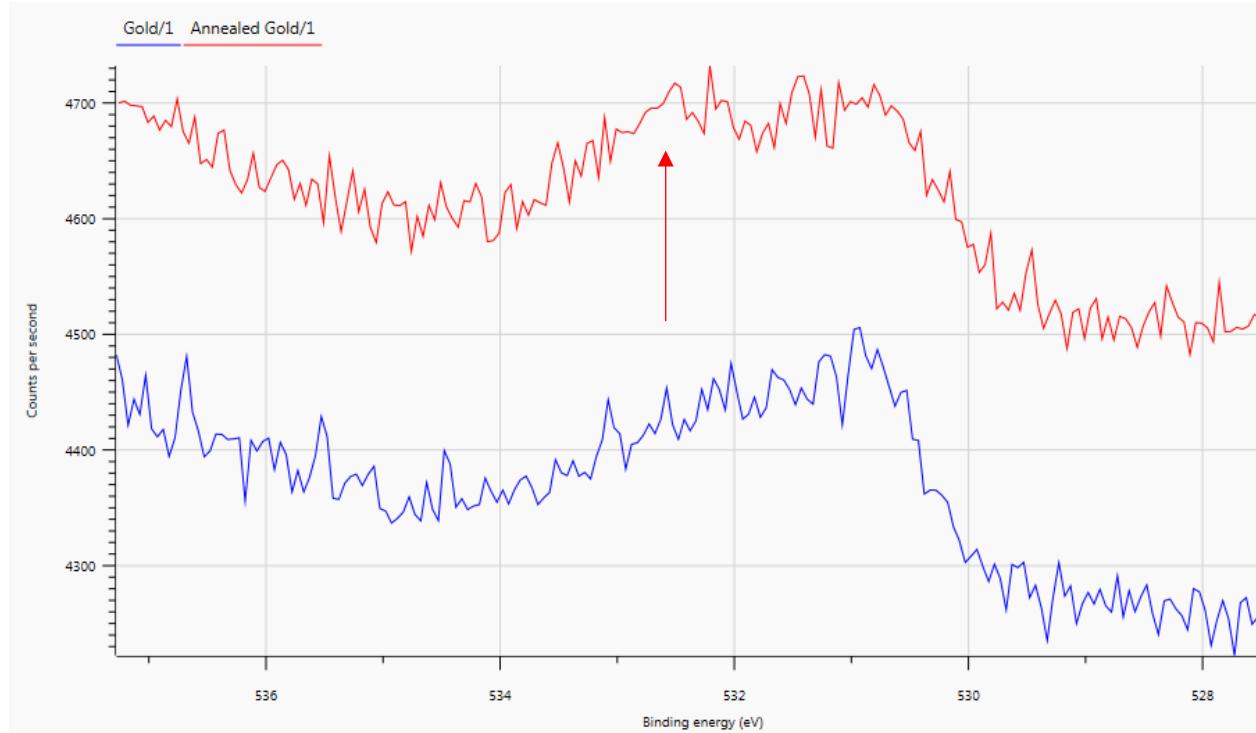


Figure 12: XPS O1s spectra for As-Grown and Flame Annealed Gold with Identified Higher Counts in Annealed Sample at 532.5 eV

SAM of TBTANGO

The flame annealed sample was preheated in the UHV system for 1 hour at 3 A and the TBTANGO molecules were preheated to 0.7 mV in a crucible which sublimed onto the Au(111) surface for 15 minutes. This process produced a SAM of TBTANGO on Au(111) with a one molecule unit cell defined by lattice vectors of 1 nm and 0.8 nm respectively (Fig. 13). This structure is somewhat unexpected since it differs from the structure of a previously reported TBTANG network on Au(111) (Fig.14) [2]. Given the similarity between the two molecules, this difference requires further investigation. For example, density-functional calculations may be used to understand the stability of this ordered phase, in comparison to the ordered phases observed in the TBTANG SAM [10].

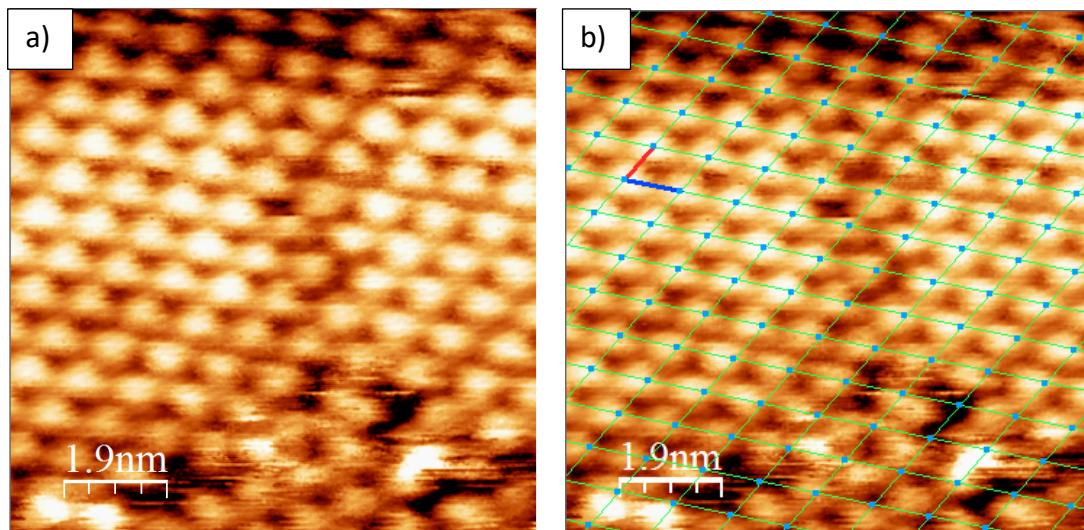


Figure 13: a) STM of SAM of TBTANGO b) STM of SAM of TBTANGO With Overlaid Lattice

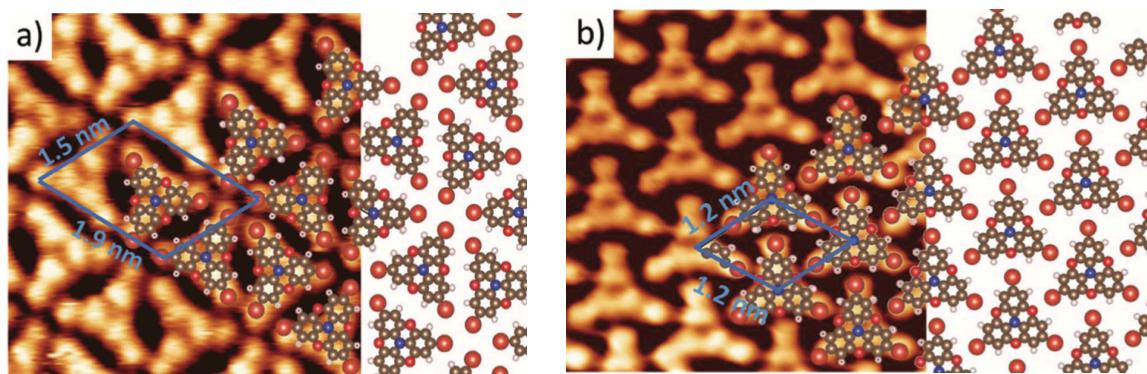


Figure 14: a) TBTANG SAM at Room Temperature b) TBTANG SAM Annealed at 150C [2]

Conclusion

We successfully prepared multiple Au films for use in our experiments, and conducted STM measurements to confirm large Au(111) terraces suitable for the deposition of organic molecules. We were able to flame anneal several samples and analyze the resulting layers using STM. We conducted XPS of as-grown and flame annealed samples as a preliminary trial for future investigation of molecular SAMs. I was able to correct this preliminary data for the work function of the sample by adjusting the Au 4f spectral lines with literature values. The annealing process showed the possible introduction of more carbon onto the surface of our gold sample because of an increase in the relative atomic concentration of carbon. This requires more samples to investigate to confirm these results. We also saw the need to reduce noise in the C1s and O1s spectra which would require more passes and longer sweep times to obtain higher signal to noise ratio. We successfully prepared a SAM of TBTANGO molecules on gold and identified an unexpected arrangement of TBTANGO molecules. Future research should be conducted to provide more insight into the layer.

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