The Pennsylvania State University
The Graduate School
Eberly College of Science

AU(111) SURFACE RESTRUCTURING FROM
SULFUR ADSORBATES

A Thesis in
Physics
by
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The development of gold-based catalysts, semi-conductor thin films, thiol-based self-assembled monolayers and sensors requires further atomic-level understanding of S adsorption on gold surfaces. To assist in this understanding, a Au(111) single crystal surface was exposed to SO$_2$ gas prior to adsorption of S under ultra high vacuum conditions (UHV). The adsorption of S was accompanied by formations of three phases observed by Low-Energy Electron Diffraction (LEED), namely the (1x1), (5x5) and ($\sqrt{3x}\sqrt{3}$)R30° Au(111)-S phases. The (1x1) and (5x5) phases were examined by LEED intensity versus energy (I(E)) analysis. The respective analysis showed best-fit models with top layer spacings of 2.33\(\pm\)0.19Å and 1.57\(\pm\)0.14Å. This confirms S can lift a Au(111) surface reconstruction ((1x1) Au(111)-S phase) and S atoms occupy 3-fold FCC hollow sites forming “rosette” structures suggested by a previous study ((5x5) Au(111)-S phase) [1].

A well-ordered “complex” phase was obtained by annealing an S coverage >.6ML from ~450K to ~525K. Within this temperature range, Auger Electron Spectroscopy (AES) measurements showed negligible sulfur loss. Further annealing led to S desorption with conflicting LEED observations presumably resulting from electron beam induced effects.
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Chapter 1
INTRODUCTION

The Unique Catalytic Properties of Au

Gold has been regarded for a long time as one of the least reactive metals, mainly due to the chemical inertness of bulk Au. This is certainly not true for gold nanoparticles, which have raised a lot of interest in the past decade. This is fueled by industrial interest pertaining to the high reactivity of small gold particles and potential application in heterogeneous catalysis [1, 16, 17]. For example, the discovery that a single Au atom could catalyze oxidation of CO as low as 10K [18, 19], led to further findings regarding the unique catalytic behavior of gold clusters and gold films. Gold clusters of Au₆(CO)₁₈ may have oxidation rates over 100 times greater than real gold surfaces [18]. And it has been shown gold films on Ir(111) can dissociate hydrogen and deuterium whereas gold single crystals cannot [18, 20]. However, a missing picture of the fundamental catalytic properties often leads researchers to examining the gold surface. The Au(111) surface, in particular, can be used to study partial reaction cycles to better understand gold-containing catalytic mechanisms [18].

The Au(111) Surface

The Au(111) crystal plane is of interest because it has properties similar to that found when depositing metal adlayers on metallic surfaces with larger atomic spaces [18, 21] and is the only (111) crystal face of all the chemical elements with a face centered cubic (FCC) structure, which reconstructs under UHV conditions. This reconstruction results from surface Shockley partial dislocations [18, 22] and relativistic effects of d-orbital participation in Au-Au bonds [18, 23, 24]. Interestingly, this reconstructed surface is lifted when the Au(111) surface is exposed to gases such as chlorine, oxygen, and NO₂ [18]. Exposure to SO₂ also lifts the reconstruction and S is adsorbed on the surface. The interaction between S and Au(111) is particularly unique since it can both enhance and inhibit gold-based catalytic systems, so hopefully the fundamental understanding gained by this study would be of benefit to industry.

Industrial Benefit

The behavior of a Au(111) substrate when exposed to sulfur is of particular interest in the development of gold-based catalysts [1, 8, 10, 11, 15, 25-27], semi-conductor thin films [11, 26], thiol-based self-assembled monolayers [1, 8, 10, 11, 25-27], and sensors [10, 25, 27]. Gold-based catalysts are known to undergo sulfur poisoning when sulfur blocks reactants from access to intermediate or active sites [8, 28-35]. This inhibits catalytic metals during the reformation and transformation of hydrocarbons [8, 28, 30-32]. Also, S-induced changes to the unique catalytic reactivity of gold with TiO₂, CrO₃, MnO₃, Fe₂O₃, Al₂O₃, and MgO oxide supports is of interest since theoretical models predict the disappearance of bulk Au(111) catalytic properties when subjected to sulfur [17, 28, 30-32, 36-43]. On the other
hand, a recent DFT study indicated pre-adsorbed S on Au(111) may be be an activator for water dissociation [26, 44].

Another benefit is to the semiconductor industry. For example, the first atomic layer of S is critical to control during the deposition of CdS and ZnS compound semiconducting thin films using EC-ALE (electrochemical atomic layer epitaxy) [11]. Furthermore, S-Au interaction, regarding the ability of gold surfaces to sustain the formation of self-assembled monolayers of various organics, has been of interest [26, 44]. Surface bonding of organic sulfur compounds and thiols occurs at the S-end of respective molecular chains [8, 10, 25, 45-50] and a sulfide can be considered the shortest alkanethiolate chain in alkanethiol monolayers (SAM) [11, 26, 44].

Other potential applications in molecular recognition, corrosion inhibition, and sensor development would also benefit industry. Sensor development relies on further knowledge of electrical resistivity properties, surface expansions/contractions, and charge density changes at the gold surface during adsorption of S (or S-containing species) [10, 27, 49-53]. Many previous studies have begun to shed light on these fundamental properties.

**Previous Work**

The stages of S adsorption for coverages <1ML have been studied extensively in both electrochemical environments and by gas adsorption under Ultra-High Vacuum (UHV) conditions. Under UHV conditions during gas adsorption experiments, the progression of Au(111)-S phases observed by LEED as S coverage increases to ~0.5ML are as follows: (1x1), (5x5), (√3x√3)R30°, and the Complex Au(111)-S phases. At coverage as low as 0.05ML the Au(111) herringbone reconstruction can be partially lifted [26, 27] and as coverage increases to ~0.1ML, LEED patterns show a (1x1) structure indicating the clean Au(111) reconstruction is no longer present [27]. Next, the formation of the (5x5) phase has been observed as low as .25ML [1] and the (√3x√3)R30° phase develops at a coverage ~0.3ML [10, 27]. Above coverages of 0.33ML a second reconstruction of the surface occurs leaving monoatomic etch pits alternating with regions of AuS clusters. Further coverage increases to ~0.6ML showed a diffuse LEED pattern, which when annealed to 450K produced an incommensurate AuS phase with long range order known as the “complex” phase. This coverage was experimentally estimated to be ~0.5ML [1, 10, 27, 54], however a more recent DFT study predicts a coverage of 0.41ML [25]. Additionally, Rodriguez et al. claim S_2 species was the more stable S formation above 0.4ML [8]. So, a clear picture of the “complex” phase is yet to be determined in both gas adsorption experiments (mentioned above) and via formation of sulfur layers formed by immersion of Au(111) in S-containing aqueous solutions.

Another recent DFT study suggested that the “complex” phase was not an extended 2D AuS phase, but rather a mixture of monomeric and polymeric chemisorbed sulfur in agreement with experimental STM images of high-coverage S phases formed by immersion of Au(111) in Na_2S aqueous solutions [26]. Also, similar experiments indicate the existence of polysulfides at higher formations to included S_8 rings [11, 14, 26, 55] and formations of a (4x4) Au(111)-S phase on select terraces [11]. It has been suggested that this (4x4)-S phase
was comprised of formations of $S_3$ [11, 14]; however, in addition, a (4x4) template was observed to remain on the Au(111) surface after desorption of a separate monatomic (4x4)-S adlayer [11]. Although a (4x4) Au(111)-S phase has not been observed during uptake in gas adsorption experiments, we discovered by subsequently annealing higher S coverage from a Au(111) crystal it was possible to obtain a clear (4x4) LEED pattern.

**Major Findings (details discussed in following chapters)**

First, the formation of the (4x4) Au(111)-S was observed via LEED observation by annealing a higher-coverage “complex” phase to 523K. Additionally, further annealing to 548K indicated both (4x4) and (5x5) Au(111)-S phases and can coexist. The (5x5) phase was observed by LEED not only by annealing higher coverage S-phases, but also by exposing the Au(111) crystal to SO$_2$ gas at a pressure of $10^{-5}$T for a period of 20 minutes.

![Au(111)-S Phases and Coverage vs. Exposure](image)

Figure 1: LEED patterns acquired with corresponding AES S/Au peak ratio measurements (left vertical axis) at 10 min SO$_2$ dosing intervals. Chamber pressures were at $10^{-5}$T during SO$_2$ dosing intervals and below $5x10^{-7}$T for subsequent measurements. The right vertical axis shows the estimated coverage using .28ML, the theoretical (5x5) Au(111)-S pure-phase surface coverage, as a fixed point corresponding to a 20 min. dosing period; a linear fit method (chapter 4) describes this S/Au → S coverage axis transformation.

After lowering the chamber pressure below $10^{-6}$T and annealing to 531K, (5x5) Au(111)-S LEED diffraction beam intensities were measured as a function of beam energy.
These experimental data were compared to I(E) theoretical curves from dynamical LEED calculations via the SATLEED program [64]. The theoretical I(E) curves were based on a seven atom rosette structure model proposed by Yu et al. [1].

The prediction by Yu et al. that S atoms occupy FCC hollow sites was confirmed by our findings, which additionally showed a top layer spacing of 1.57Å±0.14Å yielding an Au-S bond-length of 2.29±0.1Å; this was only ~0.01Å less than NIXSW structure analysis results by the same authors. Both M. Yu et al. and our results show a bond-length ~0.1Å shorter than predicted by DFT results [8].

Furthermore, we used a theoretical (5x5) coverage of ~0.28ML as a “fixed point” to scale AES S/Au peak ratio measurements to S coverage; this directly correspond to a dosing interval of 20 min., in which the best (5x5) LEED observation was observed.

By using this calibration, we confirm previous observations that (√3x√3)R30° structures likely cohabit with higher coverage phases such as the “complex” phase, which our measurements show at coverages ~0.01ML to ~0.04ML less than determined by previous experiments [10, 25, 27, 54]. Both a) (√3x√3)R30° phase observations and b) “complex” phase coverage measurements are consistent with previous studies as follows:

a) Our observations of a (√3x√3)R30° phase always occurred above 1/3ML, and often above coverage of the annealed “complex” phase in agreement with Yu et al. that the LEED pattern can be dominated by this well ordered phase even if it occurred as a minority phase in small domains [1].
b) By annealing high-coverage Au-S phases slightly above 450K, we found coverages corresponding to the “complex” phase to be between .47ML and .49ML close to the coverage predicted for the 2D AuS adlayer using Wannier-function-based techniques of .41ML [25], but even closer to the value of .51ML determined by a radioactive tracer technique [1, 54].

### Table 1: Coverage results calibrated to the best (5x5) LEED pattern corresponding to a theoretical coverage of .28ML. The best results are in **bold** and plotted in figure 1.

<table>
<thead>
<tr>
<th>Coverage (~ML)</th>
<th>Observed Phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1250</td>
<td>(1x1)</td>
</tr>
<tr>
<td>0.1467</td>
<td>~ (1x1)</td>
</tr>
<tr>
<td><strong>0.2105</strong></td>
<td>(1x1)</td>
</tr>
<tr>
<td>0.2953</td>
<td>(3x5)</td>
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<tr>
<td><strong>0.3254</strong></td>
<td>Best (5x5)</td>
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<td>0.3429</td>
<td>(5x5)</td>
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<tr>
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<tr>
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<td>(5x5) &gt; (3x√3)R30°</td>
</tr>
<tr>
<td>0.4444</td>
<td>(5x5)</td>
</tr>
<tr>
<td>0.4637</td>
<td>(√3x√3)R30° &gt; Diffuse</td>
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<tr>
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</tr>
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</tbody>
</table>

In addition to (4x4) observations, (5x5) quantitative findings, and (√3x√3)R30° “complex” phase coverage findings, we found a well-ordered (1x1) LEED pattern corresponding to coverages in the range 0.05 to 0.21ML. The (1x1) surface was examined following acquisition of I(E) data sets at ~83K. These data were compared to theoretical SALEED calculations confirming the lifting of the reconstructed Au(111) surface to that of values close to bulk interlayer spacing. Although affected by fairly large errors, the interlayer spacings tend to oscillate from less than the bulk interlayer spacing to the bulk value (of 2.355Å) for at least the top five spacings.
Profile of (1x1) Au(111)-S Structure

The (√3x√3)R30° surface was examined following acquisition of I(E) data sets at ~118K but because obtaining the correct theoretical model was difficult (to be discussed in remaining chapters), the pending results will not be covered in this thesis; only qualitative results of the (√3x√3)R30° phase will be examined.

The (√3x√3)R30° phase deteriorated during LEED electron beam exposure, so I(E) data were taken promptly. This deterioration was primarily due to electron beam induced effects, which is the final major finding to be further discussed.

The LEED e-beam seemed to influence S-adsorption during subsequent dosing intervals towards the mid sub-monolayer coverage range as shown below in figure 6. But this was only determined after first controlling AES e-beam effects as shown in figure 5 by ensuring AES e-beam exposure time was brief and the same for all measurements. We also found S-adsorption on Au(111) from SO₂ to be influenced by the ion gauge and conclude further experiments are necessary to determine the origins of S adsorption on Au(111) from SO₂ gas exposure.

Electron beam effects will be discussed more in later chapters along with coverage and LEED analysis results of Au(111)-S phases mentioned above. However, it is necessary to first describe experimental and theoretical details in the next two chapters.
Figure 5: S-uptake rate increased during constant exposure to an AES e-beam while backfilling the UHV chamber with SO$_2$ at 2.5x10$^{-7}$T.

Figure 6: AES peak ratio measurements before and after observing a subsequent LEED pattern. The mid-coverage range was most affected by LEED electron beam exposure.
Chapter 2

EXPERIMENTAL METHODS

Initial Sample Preparation

A Au(111) sample was prepared by polishing the surface with a 40µ diamond compound and then the (111) reflection from x-ray diffraction was aligned to the incident x-ray beam. This x-ray beam was located behind the film and in front of the Au(111) crystal, so the displayed images on the film showed a diffraction pattern relative to the incident x-ray beam and the mounted crystal. The mounted crystal was further polished until the (111) reflection and the incident x-ray beam overlapped on the exposed film. This ensured the [111] direction was normal to the mounted sample for LEED analysis under ultra-high vacuum (UHV) conditions. However, before sample mounting in the UHV chamber, the surface was polished using a .25µ diamond compound followed by further smoothing using a .05µ compound. The sample was then polished with a .025µ alumina compound, chemically etched with 3:1 HCL to HNO₃ (Aqua Regia) solution and mounted to a manipulator, which was placed in a UHV chamber.

Figure 7: AFM images of two separate Au(111) crystals identically polished, except the crystal in the bottom figure was chemically etched with a 3:1 HCL to HNO₃ (Aqua Regia) solution. Images courtesy of Tad Daniel, Materials Characterization Laboratory at The Pennsylvania State University.
The UHV Chamber: General Set-Up

The UHV chamber, as shown in figure 8, was custom designed by Vacuum Generators with multiple ports to attach typical instrumentation used in UHV experiments. In this experiment, the sample was mounted on a molybdenum plate attached to the end of a manipulator. The manipulator was inserted through the top portion of the chamber with the crystal located in the upper-center portion between the AES and LEED optics. The AES and LEED optics were located 180° apart and the manipulator, with 4-degrees of freedom, could be positioned accordingly while acquiring data. During data acquisition, the sample face was perpendicular to an incident electron beam from the LEED or AES systems. In addition to LEED and AES, an ion gun used for sputtering was located toward the front of the chamber along the same plane as the LEED and AES optics (not shown in figure 8).

Figure 8: UHV VG chamber by Hsin-I Li [2].
An 04-165 sputtering ion-gun from RBD Instruments was used in combination with argon from a nearly pure gas source which entered the chamber by opening a leak valve. The leak valve was connected to an aluminum vacuum line. This line was connected to a vent valve as shown in figure 8, but the vent valve was connected to another line leading to the Ar gas source and to an SO$_2$ gas source (not shown in figure 8). The vent valve was used to purge both gases from the line before (argon) and during experiments (SO$_2$). By opening the vent valve, gases were pumped from the line via a 2-stage Adixen SD 2010 rotary vane mechanical vacuum pump. This mechanical pump was also connected to another line leading to the main portion of the chamber and the exhaust-side of a Varian V 550 turbo vacuum pump.

**Pumping-Down the UHV Chamber:**

The line leading to the main portion of the chamber was maintained at pressures of \(~3.8\times10^{-2}\) T. The main portion of the chamber reached an ideal base pressure of approximately \(10^{-10}\) T during experiments and in-situ sample preparation. But first, the main chamber had to be pumped down from atmosphere (the chamber was at atmospheric pressure so that the top portion of the chamber could be opened and the manipulator containing the Au(111) crystal mounted). To pump down the main chamber from atmosphere, the valve connecting the line at \(3.8\times10^{-2}\) T to the main chamber at atmosphere was opened. By doing this, the pressure in the line and chamber reached equilibrium (~ 1 atm) until the SD 2010 mechanical pump brought the pressures of both the chamber and line to \(~3.8\times10^{-2}\) T. Then, the valve between the line and chamber was shut and the turbo vacuum pump was powered on. The turbo pump proceeded to lower chamber pressure to \(~10^{-8}\) T. Water vapor adsorbed on chamber walls and filaments of instruments prevented lowering the pressure any further. So the chamber was baked at 423K for 24 hours and filaments of instrumentation used before and during experiments were outgassed. The chamber was baked-out by surrounding it with thermally insulating shields. The air between the shields and the chamber was heated via resistive heating elements above the table. Heat from the surrounding air was transferred to the chamber and connecting instruments. After the bake-out, the filaments of these instruments were further heated in small increments until the power dissipated in each filament slightly exceeded that used during in-situ sample preparation and LEED/AES experiments (This was done to prevent the possibility of other contaminates desorbing at filament temperatures used during sample preparation and experiments). During the outgassing process, water vapor and partial pressures of other gases were monitored by an Extorr XT200(M) residual gas analyzer (RGA) until a base pressure of \(~10^{-10}\) T was obtained.

**Monitoring UHV Chamber Pressures and Gasses:**

The RGA was primarily used to observe partial pressure peaks of contaminates and gasses, however it also had an ion gauge to determine partial pressure. The Ion gauge had a lower pressure limit of \(2\times10^{-9}\) T, so a separate Bayard-Alpert ion gauge (Nude-type) was connected directly to the chamber. With a lower pressure limit of \(2\times10^{-11}\) T, this gauge was used exclusively <\(2\times10^{-9}\) T to determine a total base pressure of \(~2\times10^{-10}\) T suitable for most experiments. The general principles of operation of a) the RGA and b) the ion gauge will be discussed below:
a) The Extorr XT200(M) RGA: The RGA, a quadrupole mass spectrometer, functions on the principle of sorting ionized chamber gases into individual mass/charge components. Chamber gases are ionized by electron impact with a ~70eV electron beam. Ionization occurs based on the ionization cross section of a given molecule and the electron beam. Ionization cross sections are usually found using the Binary-Encounter-Bethe (BEB) model. Please refer to ref. [3] for a quantitative definition. The greatest ionization cross-section of a molecule as a function of electron beam energy is generally proportional to the highest probability the molecule will be ionized. The figure below shows the BEB ionization cross section for N₂:

![Figure 9: Total ionization cross section for N₂ from multiple experimental data sets courtesy of NIST [3].](image)

\[ \sigma_i = k \cdot \sigma \cdot e \]  

\( \sigma \) is the ionization cross section, \( k \) is the sensitivity factor, and \( e \) is the electron energy. The figure shows the ionization cross section for N₂ as a function of electron beam energy, with data points from multiple experimental sources.

\( N_2 \) is the RGA calibration point. Because of this, a partial pressure reading on the mass spectrometer for a peak of 28 (mass/charge ratio, mass=atomic mass number, charge=+1) are closest to the true partial pressure measurement with a sensitivity factor of 25.3T⁻¹. The sensitivity factor (\( k \)) is part of the pressure measurement:

\[ P = \frac{i}{k \cdot e} \]  

(2.1)
where $i$ is the ion current and $e$ is the electron current. The instrument is calibrated such that
$N_2$ has a relative sensitivity of 1.00, found by dividing $k$ for any given molecule by $k$ for $N_2$
[56]. Sensitivity factors of different gasses are found in tables, however there are two other
important factors to consider when observing mass spectrometer data.

First, separate cracking patterns of different gases are accounted for in calibration
parameters of the instrument. A 70eV electron beam corresponds to a singly-ionized cross
section for common gases so it is a set point of most RGAs, however many gases can be
doubly ionized and/or fragmented during 70eV e-beam collisions. These cracking patterns
should be considered if precise measurement of partial pressure peaks is necessary (For this
thesis, it was only essential to obtain consistent total pressure measurements to determine
coverage as described in chapter 4). Cracking patterns for many common molecules can be
found in tables. The mass fraction ($f$) of double ionized or fragmented molecules
corresponding to a given gas found in tables, multiplied by the electron current yields a more
accurate measurement of a given partial pressure as follows:

$$P = \frac{i}{k \cdot e} \Rightarrow P = \frac{i}{k \cdot e \cdot f}$$

(2.2)

The second consideration in determining partial pressure reading results from the quadrupole
transmission ion current being inversely proportional to the mass (Since the RGA is
calibrated to $N_2$, ion currents for all other partial pressures must be multiplied by
28(a.m.u)/m(a.m.u)).

Ions formed via collisions with the e-beam are directed parallel, at energies of ~5eV,
through a region of 4 cylindrical parallel rods (see figure 10). These rods, ideally with
hyperbolic cross sections near the origin, produce variable electric fields with negligible z-
direction components.

Figure 10: The bottom sections of two opposing quadrupole electrodes. The
two other electrodes, which are parallel in the z-direction but lie on the y-axis are not
shown [4].

This field is formed from biasing alternating radio frequency A.C. potentials in combination
with D.C. potentials. Qualitatively, the pair of rods in the z-x plane and the rods in the z-y
plane can be examined separately. First, considering an AC bias with a positive DC bias
applied simultaneously to both pair of rods in the z-x plane, trajectories of heavy ions entering the region between rods are directed towards the center of the rods. The heavier ions respond to the average RF-generated field, so net movement is primarily due to a constant force of the positive DC potential as the heavier ions transverse the longitudinal axis in the quadrupole region. The lighter ions however, are strongly influence by the RF bias and can collide with the rods, so this set of rods would act as a high-pass mass filter. On the other hand, the rods in the z-y plane are subjected to a negative DC bias and an RF bias 180° out of phase with z-x—plane rods, would act as a low pass filter [4]. With a DC bias slightly larger than the RF amplitude, low mass ions in the z-x plane experience a slight net force towards the x-axis rods when the RF signal is at –V. However, at that same moment the RF signal of the y-axes rods is +V and low-mass ions are directed towards the z-axis, passing through the quadrupole region. For this RGA, RF amplitude voltages and DC voltage bias could be varied to scan masses to 200 a.m.u.

To further discuss mass-scanning of the RGA, a more quantitative approach is necessary. The following canonical form of Mathieu’s differential equation describes the x and y motion of ions passing through the quadrupole region as discussed above:

$$\frac{d^2u}{d\xi^2} + [a_u + 2q_u \cos(2\xi)]u = 0$$  \hspace{1cm} (2.3)

In this equation, \(u\) represents either x or y and \(\xi = t/2\). The figure below defines \(a_u\) and \(q_u\), and shows stable solutions (shaded region) to the above differential equation:

![Figure 11: Diagram showing stable solutions to Mathieu’s equation in canonical form [4].](image)

Additionally, \(r\) is the distance from any rod to the center axis, \(U\) is the DC potential, and \(V\) is the magnitude of the applied RF potential with angular frequency \(\omega\). The slope of the number line (mass scan line) is 2U/V. Both the slope and proportional changes to U and V affect the bandpass region (resolution) and scan range respectively. For example, if U and V were suddenly halved, “B” in figure 11 would slide down and the mass scan line with a corresponding solution region of the same shape as “B,” but scaled down. However, an adjustment to the slope would be necessary to maintain the same resolution. Please see ref.
[4] for a detailed discussion of this and a more quantitative derivation of equation 2.3 from first principles.

The resolution of the XT200(M) was greater than 0.5 a.m.u. and adjustable so that constant peak width was maintained throughout the mass scan. Also, peak height resolution was enhanced by an electron multiplier so partial pressures could be increased by a factor of over 1000 [56]. Because of the electron multiplier, the lower partial pressures detection limit was below 10^{-14}T. This was much lower than the ion-gauge detection limit of 2x10^{-9}T, so as previously mentioned a Bayard-Alpert ion gauge was used to measure very low total chamber pressures.

b) Bayard-Alpert (nude-type) Ion Gauge: As the RGA, ionization in this ion gauge occurs via electron impact. However, instead of ionized gasses passing through a grid biased at +V, ions created near the grid move towards a collector pin. The collector pin, which measures the total ion current was grounded and located in the middle of the grid. The grid was biased at +180V and a tungsten filament at +24V. This filament, a hot cathode, released electrons that were accelerated towards a spiral shaped grid. Most electrons would swirl about the grid before impacting it, allowing for higher probabilities of electron impact with chamber gases in a small region near the ion gauge.

The ion gauge had a low pressure limit of 2x10^{-11}T, as previously mentioned. This limit (and the limit of the RGA) is due to x-ray interference resulting from collision of electrons with the grid, but it was negligible at pressures ~2x10^{-10}T needed for LEED experiments. An effect not negligible however, was the sensitivity settings of the ion gauge controlled by a Perkin-Elmer 605-0600 Digital Gauge Control (DCG) III. The DCG converted currents and voltages into pressure readings accurate for Nitrogen (the default setting) [57]. So the sensitivity factor was adjusted accordingly while back-filling the chamber with SO_2 and Ar^+ during dosing and in-situ prep respectively.

**In-situ Sample Preparation and SO_2 Dosing**

Once a base pressure of ~2x10^{-10}T was obtained, the chamber was filled with Ar gas to a pressure of ~5x10^{-5}T. The RBD 04-165 sputtering ion-gun ionized the Ar via electron bombardment and Ar^+ was sent through a potential difference of .5kV (adjustable) ejected from a small round opening in the grid. The Au(111) sample was grounded and positioned so the surface normal was parallel to the incoming beam of Ar^+.

In theory surface atoms having combined recoil and binding energies less than the kinetic energy of incoming Ar^+ ions can be expelled from the surface after collisions. In particular, surface atoms weakly bound will be more likely removed during sputtering. This includes unwanted adsorbed gases, so sputtering in small intervals assisted in flattening a rough surface and with removing surface contaminants. The polished and chemically etched surface was atomically very rough, so initial sputtering was performed at intervals up to an hour. This was following by long periods of annealing (also up to an hour) at temperatures above 800K. Cycles of sputtering and annealing were performed until a clear LEED pattern showed multiple satellite spots characteristic of the Au(111) surface reconstruction. Once a decent LEED pattern was obtained, further cycles of sputtering and anneal (in between
experiments) were performed at intervals less than 10 minutes. Smaller cycles were necessary because a nearly atomically smooth surface can be roughened by sputtering.

Once the sample was well sputtered and annealed, LEED observations immediately following AES relative surface coverage measurements, obtained on select days over the course of several weeks, led to consistent uptake results shown in figure 1. On a given day, the sample would be briefly sputtered and annealed followed by backfilling the chamber with SO$_2$ gas until S adsorbed on the surface and a Au(111)-S phase was observed. By recording multiple observations at different pressures and dosing intervals, a reproducible uptake curve at 10$^{-5}$T, as shown previously in figure 1, was obtained. However, electron beam effects led to many complexities, so factors usually considered negligible during gas adsorption experiments had to be considered. In addition to chamber pressure and dosing intervals, figure 1 is directly proportional to AES electron beam exposure, LEED e-beam exposure, and sample positioning relative to the ion gauge. This will be discussed further in following chapters, but first the operating principle of LEED and AES will be briefly discussed, followed by data acquisition techniques and tools used during experiments.

LEED Experiments:

Low-Energy Electron Diffraction (LEED): LEED can be considered the most comprehensive and versatile surface crystallography technique to date [58]. Since the 1960s, it has been widely used as a surface characterization tool [58, 59]. The basic principles of LEED come from conservation of energy and momentum.

A coherent beam of electrons with a wavelength of $(150/E)^{1/2}$Å (the energy of the incoming electrons is expressed in eV), ideally incident to a crystal surface, scatter off underlying crystal planes. The electron energy is a controllable parameter during experiments, and therefore the wavelength. This is due to the de Broglie wave relationship:

$$\lambda_e = \frac{h}{m_e v} = \sqrt{\frac{150 eV}{E_{k0}}} [\text{Å}]$$  \hspace{1cm} (2.4)

Waves of electrons are scattered off only a few surface planes because of a small inelastic mean free path typically around ~nm. In comparison to X-Ray diffraction, which has a photon path typically a few microns and periodicity lateral and perpendicular to the surface represented in the Laue equation,

$$\Delta k(m_1a_1+m_2a_2+m_3a_3)=2\pi n$$  \hspace{1cm} (2.5)

the shorter penetration depth of electrons (from LEED) only clearly shows periodicity parallel to the surface plane so the Laue equation for LEED becomes:

$$\Delta k(m_1a_1+m_2a_2+m_3a_3)=2\pi n \rightarrow \Delta k_||=g_{h,k}$$  \hspace{1cm} (2.6)

Where $\Delta k=k-k_0$, $k_0$ is the incoming wave vector and $k$ is the elastically scattered wave vector; $\Delta k_||$ is the component of $\Delta k$ parallel to the surface, $h$ and $k$ are integers and $g_{h,k}$ are reciprocal lattice vectors [58, 59]. A more quantitative treatment and further background of
the above equation can be found in ref. [60]. When including scattering from individual atoms, phase differences in path lengths and multiple scatterings, the lattice sum can be defined as follows:

$$A_{\Delta k} = \sum_n \sum_m \exp(i\Delta \mathbf{k} \cdot \mathbf{A}) F_{\Delta k}$$  \hspace{1cm} (2.7)

Where $\mathbf{A} = n\mathbf{a} + m\mathbf{b}$, a real surface vector and the geometrical structure factor, $F_{\Delta k}$ is defined as:

$$F_{\Delta k} = \sum_j f_j \exp(i\Delta \mathbf{k} \cdot \mathbf{r}_j)$$  \hspace{1cm} (2.8)

This is an important result because, because the amplitude of $A_{\Delta k}$ vanishes except when $\Delta \mathbf{k} = g_{h,k}$, so multiple scattering effects of $F_{\Delta k}$ can be separated out [60].

When the LEED beam is at normal incidence and $\Delta \mathbf{k}_{\parallel} \to \mathbf{k}_{\parallel}$, perpendicular $\mathbf{k}$-components ($k_z$) can be examined by considering conservation of energy and momentum of an elastically scattered incoming wave as follows:

$$k_z(h,k) = \sqrt{\frac{2m_eE_{k_{\parallel}}}{\hbar^2} - \left| k_z(h,k) \right|^2}$$  \hspace{1cm} (2.9)

Because $|k_0|^2 = 2mE/h^2$, for fixed values of $|k_{\parallel}|$, only $k_z$ values change as a function of beam energy [58]. By considering both this and the scattering amplitude of $A_{\Delta k}$, $z$-component information buried in intensity patterns of LEED $(h,k)$ beams can be found by varying incident beam energies (I(E) or I(V) data). These intensities usually have peak values similar to Bragg peaks at specific energies in X-Ray diffraction. But, instead of sharp peaks corresponding to periodic $z$ components, LEED I(E) intensity peaks are broadened due to multiple scatterings. Also, the beam only probes top surface layers so Bragg peaks are much less pronounced. On the contrary though, surface features are more pronounced in LEED I(E) data. For a full discussion on I(E) peak data pertaining to specific surface features, please see discussion in ref. [58] and [60].

A further discussion of I(E) data requires a brief explanation of the experimental apparatus. First, an electron beam was generated by sending current through a tungsten-rhenium filament biased at $-V$ as shown in the BLD800 LEED schematic below:
The beam then passed through a suppressor (EG1) biased at 0 to -17V (Wehnelt Voltage) with respect to filament. The suppressor adjusted the beam width of electrons moving towards the grounded sample from 1mm to 250µm. But the beam width was limited to 50µm as it passed into the next focus region [5].

This focus consisted of three cylindrical regions of different length. The top and bottom could be positively biased with a factor of 0.7 to 1.8 of the beam voltage and the center region was common to the shield that passed through the grids. The electron beam was widened when entering and exiting the first region before entering a second zero-field region. After exiting the grounded region the beam was again widened by the third region at the same bias as the first. Then, the beam entered a field-free region from the grounded shield, sample and first grid before scattering off the sample.

Only a very small percent of electrons scattered off the sample were elastically scattered, so a negative retarding voltage between 70% and 80% of the beam energy was applied to grids 2 and 3 of figure 12 shown above. This voltage prevented most inelastically scattered electrons from striking the phosphor screen. The phosphor screen was positively biased to further accelerate the elastically scattered electrons. Typical settings applied to the LPS300 power supply are shown below:
Figure 13: Example of standard settings used at -100eV incident beam energy by OCI [5].

The illumination resulting from electrons striking the phosphor screen was viewed from behind the electron gun through a glass port cover on the UHV chamber. Beam intensities displayed on the phosphor screen represent a projection of reciprocal lattice points that modulated with changing energy. The Ewald Sphere construction shows a sphere in reciprocal space swept by \( k \) (or \( k_0 \) since this pertains to elastic scattering).

![Ewald Sphere Construction](image)

Figure 14: Ewald Sphere construction by Hsin-I Li [2].

Increasing the LEED beam energy increases \( k \) and the Ewald sphere. So higher beam energies include more reciprocal lattice rod projections appearing on the phosphor screen. This can similarly be thought of as a fixed sphere with modulating rods moving inwards with increasing beam energy [59]. LEED diffraction beam intensities are explained by
intersection points of these rods with any given Ewald Sphere. The reciprocal lattice rods for LEED become points in 3-dimensional reciprocal space in X-Ray diffraction due to an added \( k_z \) component. However for LEED, intensity variations along reciprocal lattice rods can be further described by dynamical LEED theory. Dynamical Theory is the basis for LEED quantitative calculations of this thesis and described in refs. [2, 58-60]. This theory is an extension from what was just discussed, but accounts for large electron cross sections of ion cores so that multiple scatterings become important [61, 62].

**AES Experiments**

Similar to LEED, AES generates a primary beam current ideally with normal incidence to the sample. Instead of e-beam energies <1keV as in LEED though, the AES e-beam energy was fixed at ~2.5kV to probe a maximum range of Auger transition energies. AES transition energies, are proportional to kinetic energies of ejected electrons released following the removal core electrons of higher binding energies. This is an ABC transition process and shown in the figure below:

![AES and X-ray emission processes](image)

To analyze the intensity of AES electrons, a bias between the inner and outer cylinder of a Perkin-Elmer 10-155 cylindrical mirror analyzer (shown below) was modulated. Ejected electrons with fixed kinetic energies pass via the openings at particular corresponding sweep energies.

Figure 15: A comparison between the Auger electron and X-ray emission processes. In both cases an inner shell electron is removed, but vacancy filling in the ABC transition ejects an unstable electron instead of photon [6].

To analyze the intensity of AES electrons, a bias between the inner and outer cylinder of a Perkin-Elmer 10-155 cylindrical mirror analyzer (shown below) was modulated. Ejected electrons with fixed kinetic energies pass via the openings at particular corresponding sweep energies.
Spectra were recorded either as intensity (N) plotted against kinetic energy of ejected Auger electrons (E), or dN/dE versus E. The latter is most commonly found in AES tables and reference spectra for most elements. This is because narrow peaks of Auger electrons are more pronounced in dN/dE spectra. Also, dN/dE plots eliminate much of the slowly increasing N(E) background resulting from inelastically scattered electrons due to the primary electron beam.
Chapter 3

LEED DATA ACQUISITION AND ANALYSIS

The acquisition of the required LEED images during experiments lasted approximately 10 minutes, in which time the probing electron beam swept an energy range from nearly 50eV to 450eV (depending on phase). The temperature of the sample during I(E) experiments of the (1x1) Au(111)-S phase was ~83K; temperatures of (5x5) and (√3x√3)R30° Au(111)-S phases were ~118K. These temperatures were obtained by cooling the cryostat in the manipulator with liquid nitrogen to ~118K. Using HotLEED, two separate sets of data were obtained for each phase. The first set was obtained starting below 70eV to above 200eV and the second set below 200eV to over 400eV. This was to maximize the observable range of (h,k) beams at a set focus. Adjusting LEED e-beam focus voltages and CCD camera saturation levels while running the frame-acquire mode in HotLEED was not practical. Thus ideal e-beam, camera focus and saturation levels were set at midrange of each subset of I(E) data. Symmetric LEED e-beams of each set were averaged when data showed obvious symmetry. The figure below shows an example of this for the (1/5,2/5) equivalent beams from the (5x5) structure:

![Example of beam averaging](image)

Figure 17: Example of beam averaging: The (1/5,2/5)n (5x5) beams were compared (left). If data were reliable (all curves compared well), symmetric LEED beams were averaged and a linear background was subtracted (right) before theoretical comparisons.

The (h,k)n beam labeling above corresponds to the unit cell below for each phase (n=1,2,3,...are all symmetric beams of (h,k)). This labeling is shown below; the curves (1/5,2/5)n shown above correspond to the labeling diagram below:
Integer order beams show the rotational and reflection symmetries of Au(111) A-B-C-A stacked substrate. Non-integers beams (in these data) give information about the S overlayers <1ML, which could be correlated with a Au(111)-S phase.

For beams outside a unit reciprocal cell, symmetries between individual beams were more difficult to see, mainly because of normal incidence precision. Misalignment in normal e-beam incidence caused a larger error in reciprocal rod projections displayed towards the outer portion of the screen. This was mostly due to basic geometry, i.e. if a plane initially perpendicular to a rod was tilted about the rod, points near the rod would be displaced less than those further away. This meant error in experimental I(E) data of reciprocal lattice rod projections would increase with increasing h and k, or features giving information about the surface were averaged out. Precision of normal incidence beyond a visual inspection could be obtained via live imaging of profiles between symmetric beams far from center screen. By using the profile tool in HotLEED, a line or circle could be drawn over a live LEED image, and a direct intensity profile would appear in a window. This window was also used to display I(E) data while extracting intensities from a series of previously saved images.

The intensity profiles were acquired through circular integration windows. The arbitrary intensity axis (y-axis in figure 17) would change as a set of images with increasing beam energy unfolded and integration windows “tracked” LEED beams moving inward. The integration windows summed all pixels during the I(E) extraction process, which when the background was subtraction, yielded the arbitrary intensities shown in figure 17. The background was subtracted, due primarily to non-uniform inelastic suppression, by subtracting the average window parameter pixel intensity times the total number of pixels in that window [59].

Figure 18: Example of beam labeling: This (5x5) phase beam labeling shows reciprocal lattice vectors of the substrate.
After an I(E) data set of symmetric beams was obtained, they were averaged via HotLEED and saved in separate files. A separate HotLEED utility, “Normalize” was used to correct x-axis (E) values (stored in image files during data acquisition) to calibrated values of true e-beam energy and to adjust y-positioning of data if negative values of intensity resulted during I(E) extraction. Next, average intensities of symmetric \((h,k)\) beams extracted in subsets of data were merged by using the program “Plot” [63]. In order to do this, it was important that both data subsets overlapped so they shared one or two obvious features. Then, data of one subset was normalized to the other by equating overlapping peak and valley differences and saved as new data files with full x-axis energy ranges.

All average \((h,k)\) experimental curves were compared with theoretical I(E) curves calculated using the Barbieri/Van Hove Symmetrized Automated Tensor LEED package (SATLEED) [64]. The following graph shows the \((1x1)\) un-annealed results and curve comparisons extracted via experiments versus theoretical beams optimized using SATLEED:

![Au(111)-(1x1) LEED Analysis Results](image)

Figure 19: \((1x1)\) Au(111)-S un-annealed data demonstrating experimental versus theoretical I(V) comparisons.
The Pendry r-factor reflects similarity between theoretical and experimental curves. It accounts for the derivative of intensity \((I)\) by introducing a logarithmic derivative function, \(L(E)\), expressed as follows:

\[
L(E) = \frac{dI / dE}{I}
\]  

By including the imaginary part of an interaction potential \((V_0i)\), which is related to attenuation of scattered electrons that affect \(I(E)\) peak widths, the following term can be defined:

\[
Y(E) = \frac{L^{-1}}{L^{-2} + V_0^2}
\]  

And the Pendry r-factor is defined as follows:

\[
R = \frac{\int (Y_t - Y_e)^2 dE}{\int (Y_t + Y_e)^2 dE}
\]  

\(Y_e\) and \(Y_t\) are from experimental and theoretical data respectively. This expression, being normalized to 1 for two completely uncorrelated curves, vanishes when \(Y_t \rightarrow Y_e\) [2].

\(Y_t\) can be fine-tuned by adjusting several SATLEED parameters until the smallest r-factor for a given model is obtained. Generally, the smallest r-factor is considered to show best agreement, but the range of data should also be considered. For example, the (0,2) beam in figure 19 has a Pendry r-factor of .09, but only compares the relative positioning of two peaks over a range of roughly 125eV. On the contrary, the (1,0) beam with a Pendry r-factor of .18 compares 7 beams over an energy range of about 350eV; although the Pendry r-factor is higher, this beam really shows better evidence of agreement. To account for this, a weighted average of individual beams gives an overall r-factor. But the total energy range for all individual beams of a given overall r-factor should also be considered when assessing the comparison.
Chapter 4

SURFACE COVERAGE ANALYSIS

Surface coverage calculations were performed based on previous works in combination with reasonable assumptions regarding AES S-uptake results. Initially, the random results obtained while attempting to devise a repeatable AES surface coverage experiment led to determining the magnitude of multiple e-beams effects. The random error of these effects was reduced by carefully controlling and limiting electron beam exposure time, while positioning the sample at the same distance from the ion gauge during exposure to SO$_2$ (the behavior of SO$_2$ under influence of electron beams will be further discussed in chapter 7). Once repeatable results were obtained with precise time measurements between dosing intervals, random uncertainty in the dosing time could be considered negligible. Because of this, in combination with a predominately linear appearance in S and Au dominant AES peaks during S-uptake of the most reliable experimental data set, two Least-Squares fits for a line were calculated using Microsoft Excel.

![Figure 20: Intensity of Au and S peaks during S-uptake (Temp.=300K and Pressure=10^{-2}T)](image)

The S (152eV) to Au (69eV) peak ratios shown in figure 1 corresponded to data shown above. However, the coverage shown in figure 1 was not determined for the last two data points.
The last two data points above corresponded to observations of diffuse LEED patterns (A plateau in S/Au primary peak measurements occurred beyond 70 minutes). This plateau or often a “kink” in substrate and adsorbate peak and peak ratio measurements is typical at n-adsorbate layer formations. Peak ratios can also be used to determine monolayer coverage and saturation points if gas adsorption is more linear between monolayers. Monolayer coverage was determined this way from AES peak ratio measurements of a i-Al–Pd–Mn quasicrystal [65]. But with S adsorption on Au(111) using SO₂, it was not reasonable to make the assumption that either monolayer or saturation coverage occurred at 70 minutes as falsely suggested in the figure below.

Figure 21: Before and after LEED adsorbate/substrate peak ratios with average values used to determine coverage. Average values up to 60 min. are those shown in figure 1.

There were a couple of reasons saturation or monolayer coverage could not be determined this way. First, the mechanisms of SO₂ dissociation at Au(111) during e-beam exposure was unknown. Second, it was not clear if attenuation of S/Au (152eV/69eV) peak ratios resulted from e-beam induced desorption/dissociation of Sₙ species occupying most of the surface above coverages of .4ML (as determined from XPS measurements [8]). Although more obvious AES and LEED e-beam effects occurred in what appeared to be predominately a sub-monolayer coverage regime, it is not known if such effects are on fractional domains of Sₙ species coexisting with monatomic phases, monatomic phases
weakly bounded to substrate atoms, or the more recently proposed formations of AuS clusters by S. Kurokawa et al. [15].

In an attempt to better understand the magnitude of LEED e-beam effects during I(E) experiments and to minimize the effects for coverage calculations, AES measurements before and after LEED exposure were averaged. The average Au and S primary peak-peak measurements, corresponding to peak ratios and clear LEED observations as indicated in figure 1 of ordered Au(111)-S phases suggests, at least fractional surface coverage less than a monolayer increases approximately linear during exposure time. Therefore a linear fit of the first five data points of figure 20, were re-fitted (figure 22) to exclude most data above ~.4ML where contributions from adsorbate-adsorbate (S_2) sticking coefficients would add a significant error to a fit based on the assumption of a constant sub-monolayer adsorbate-substrate (S_1) sticking coefficient defined by:

\[ S_1 = N_m \left( \frac{\partial \theta}{\partial t} \right) \]  

(4.1)

where \( \theta \) is the fractional coverage and \( N_m \) is the number of molecules in one monolayer. The fit shown in the figure 22 assumes a constant \( S_1 \) and no contributions from \( S_2 \). In previous models the same assumptions (regarding sticking coefficients) were made, but \( S_2 \) is proportional to the fractional coverage beyond formation of a single monolayer and \( S_1 \) can be written as:

\[ S_1 = \frac{I_A}{RI_t t} \]  

(4.2)

where \( R \) is the arrival rate of the adsorbate at the substrate in monolayers sec\(^{-1} \) and \( t \) is the dosing time; \( I_1 \) and \( I_A \) are monolayer and measured 152eV-peak Auger currents respectively [66]. By assuming a model with a constant submonolayer \( S_1 \), then \( I_1 \) and \( I_A \) are proportional to peak-peak measurements and coverage up to a monolayer can be determined by

\[ \theta = \frac{I_A}{I_{A_1}} = \frac{I_{S_0} - I_{S_1}}{I_{S_1} - I_{S_0}} \]  

(4.3)

Now \( I_A \) is a given adsorbate peak-peak intensity at a coverage \( \theta \) up to a monolayer; \( I_s \) is the corresponding substrate peak-peak intensity; \( I_{AI} \) and \( I_{SI} \) are respective peak-peak intensities at 1ML and \( I_{S0} \) is the initial substrate intensity [67]. The authors who proposed this model however, base assumptions that coverage between monolayers can be determined if \( I_{AI} \) and \( I_{SI} \) are experimentally measured quantities. The calculations we used to determine S coverage described below, use a) the same linear relationship shown above, but b) assume theoretical fractional coverage of \( \theta = .28 \)ML corresponding to the best (5x5) Au(111)-S LEED observation.
Figure 22: First five Au and S Peak-Peak AES intensities showing error and linear fit equations used to determine total S coverage.

a) First, values of $I_A$, $I_S$, and $I_{S0}$ were determined by linear fits to the experimental data as shown in figure 22. Since uncertainty in x-axis dosing intervals was negligible, true values of $I_A$, $I_S$, and $I_{S0}$ would lie on the line directly above or below the actual peak-peak measurements of $I_S$ and $I_A$ with uncertainty in y-axis measurements. This uncertainty was statistically determined by standard deviation of the mean from before and after LEED measurements ($\sigma_{A,S}$) and from the average signal to noise ratio of AES spectra ($\delta_{A,S}$) as follows:

$$\Delta I_{A,S} = \sqrt{\sigma_{A,S}^2 + \delta_{A,S}^2}$$  \hspace{1cm} (4.4)$$

Other error, not include above, would be systematic error. For example, between measurements the AES filament current was adjusted to 1mA; however gauge readings often increased by 1/10 mA during a short data acquisition time. This could lead to a small fluctuation in primary beam current with resulting error in $I_A$ and $I_S$ measurements. Another small influence of error was the precision of the sample at normal incidence with respect to the primary electron beam. To measure incidence initially, the tilt and rotational angle of the sample were adjusted to maximize intensity of the elastically scattered beam at $\sim$2.5kV. However moving the crystal between LEED, AES, and dosing positions was only accurate to rotation angle of $\sim$0.5° (the tilt angle was constant). Since measured Auger intensities, $I_A$ and $I_S$ are proportional to both the primary beam current and the angle of Auger electrons [6], these
small sources of error could have been notable. Furthermore, unknown e-beam influences coupled with unknown SO₂ dissociation origins would most likely account for possible additional substantial error.

Second, returning to coverage determination, by solving for \( y(x) \) at \( y(x=20) \) in the fits of figure 22, values of \( I_A \) and \( I_S \) were determined. Also, \( I_{S0} \) was found at \( y(0) \) from the Au peak-peak fit. Now, basic algebra of equation 4.3 yielded a value of \( I_{AI} \) and \( I_{SI} \) based on calibrating the fit at \( x=20 \) to a fractional coverage, \( \theta=.28\text{ML} \).

b) The determination of this calibration is based on both our results and previous studies. The model proposed by M. Yu et al. and confirmed by our LEED results suggests a “pure” (5x5) Au(111)-S phase theoretical coverage of .28ML. The authors also claim this phase can coexist with the “complex” phase, which occupies up to 30% of the surface [1]. The work of this thesis shows desorption of “complex” phase species at ~530K, via LEED observations and AES measurements shown in the figure below:

![S 152eV and Au(111) 69eV Primary Peak Ratios Before and After LEED (Annealing)](image)

Figure 23: Annealing back a high-coverage phase >.6ML shows less obvious e-beam effects on total coverage (AES) with an apparent mixed phase/disordered surface in the mid-coverage range (LEED).

We observed the “complex” phase existing between annealing temperatures of 448K to 526K
among various observations with subsequent AES measurements showing no evidence of S removal, being consistent with figure 24 from an XPS-DFT study by Rodriguez et al.[8].

Figure 24: Rodriguez et al. show changes in S-species coverage during annealing ~1ML by assigning XPS-determined binding energies to adsorption site occupancies [8].

Figure 24 suggests sulfur atoms bound to FCC hollow sites are maximized when annealing to ~500K with very little contribution from states of higher binding energies. By comparing the figure above to our “complex” phase AES measurements acquired at different annealing temperatures (data shown in figure 24 compared to figure 37 and table 1) it appears our results showing “complex” phase S desorption occurs within the same proximity as the decrease in total S coverage witnessed by Rodriguez et al.; by considering the likelihood of a calibration discrepancy (~30K), it seems some S atoms occupying states with higher binding energy become mobile during annealing and move towards lower FCC hollow energy states (This can be associated with the decomposition of a 2D AuS corrosion layer, or “complex” phase to be further discussed later). Therefore, since our LEED analysis shows that (5x5) phase S atoms occupy FCC hollow sites and our LEED observations show that ordered “complex” phase domains vanish when annealing past ~530K, we conclude annealing a (5x5) phase to ~530K would result in a coverage closest to a theoretical value of .28ML as predicted by the model of M. Yu et al. [1]. This was based on the assumption additional S atoms exist as part of small domains of “complex” phase arrangements (30%) on the surface during LEED observations of (5x5) phases after a dosing. Also, our results indicate annealing a predominately “complex” phase coverage past ~525K results in desorption of additional S atoms required for its stability. Furthermore we see from the results by Rodriguez et al., that annealing to ~525K should remove, if any, only a small portion of S atoms in FCC hollow sites.
During a separate experiment to obtain I(V) data, dosing for 20 minutes yielded an AES Au/S (152eV/69eV) primary peak measurement of .2764 and after slowly annealing to 531K (and confirming the phase via LEED observation), the second AES Au/S (152eV/69eV) primary peak ratio measurement was .2733. And since all controllable conditions were the same between both experiments, the linear fits as shown in figure 22, as previously mentioned, were calibrated such that \( I_A \) and \( I_s \) \( \Rightarrow y(x=20) \) for each respective linear fit at \( \theta=.28\text{ML} \). However, to obtain a concise representation of coverage, the ratio of \( I_A \) to \( I_s \) was examined.

By first plotting a set of fitted points at all respective dosing intervals to corresponding coverages determined by equation 4.3, an \( I_A/I_s \) calibration curve was established as follows:

Fitted S 152eV and Au(111) 69eV Primary Peak Ratios Used to Determine Coverage

Figure 25: A polynomial fitted coverage calibration for S/Au 69eV/152eV peak ratios. \( I_A/I_s \) fitted ratios were plotted against corresponding coverage.

This fit was necessary to establish a second y-axis (coverage) shown in figure 1. Not displayed in this figure however, was the error or an explanation why the second y-axis (coverage) vanished at \( \sim .55\text{ML} \). The missing error and second y-axis cut-off was because linear fits of \( I_A \) and \( I_s \) were calculated using the first five data points, so beyond this coverage data were not reliable. The figure below showed the reliability of the fitted data:
Figure 26: Data was only fitted up to observation of ($\sqrt{3}x\sqrt{3})R30^\circ$ LEED phase (40 min) where uptake could be considered roughly linear. Fitted data was not reliable beyond ~50 min. dosing interval because of non-linearity without confirmation of ML coverage.

The fitted calibration line shows that around the observation of the diffuse LEED pattern, coverage determination is not accurate within error calculations. The error for coverage was determined using propagation of error for $\Delta I_{A,S} \rightarrow \Delta(I_{A}/I_{S}) \rightarrow \Delta(\text{Coverage})$; the final coverage results during S uptake with error are displayed below:

<table>
<thead>
<tr>
<th>Coverage Approximation of Best AES Data For Au(111)-S Phases</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coverage (~ML)</td>
</tr>
<tr>
<td>----------------</td>
</tr>
<tr>
<td>0.2105±.1182</td>
</tr>
<tr>
<td>0.3262±.1156</td>
</tr>
<tr>
<td>0.4099±.1243</td>
</tr>
<tr>
<td>0.5115±.1373</td>
</tr>
</tbody>
</table>

Table 2: Total S coverage and error during first 40 minutes of S exposure at $10^{-5}$T.

These coverage results, in relation to LEED analysis and surface morphology of many phase changes will be discussed in the following chapters.
Chapter 5
AU(111) SURFACE MORPHOLOGY DURING S EXPOSURE

*Clean Au(111) Surface Reconstruction*

A Au(111) sample placed in UHV conditions, upon adequate cleaning, exhibits the characteristic Au(111)-(22x√3) “herringbone” reconstruction pattern (figures 27 & 28) that is caused by the presence of tensile surface stress. This results in the compression of the surface layer, along the <110> direction, such that 23 Au atoms occupy the same distance as 22 atoms of the same relaxed, unreconstructed surface, leading to a ~4% increase in the number of surface gold atoms [9]. These atoms are also pushed along the <110> direction away from FCC sites towards higher energy HCP sites. The accompanying elevation increase of HCP-like atoms is evident by grain boundary ridges occurring between HCP-like and FCC-like valleys as shown in figures 27 & 28 [9, 68-71]. The suggested unit cell is a rectangular entity in which 46 surface atoms occupy 44 bulk-like positions (figure 29); the structure is also observed in LEED investigations of the surface, a respective LEED pattern being shown in figure 30.

Figure 27: Clean Au(111) surface showing the herringbone structure characteristic to the Au(111)-(22x√3) reconstruction. B.K. Min et al. [9].

Figure 28: Atomic resolution STM image of the reconstructed Au(111) stretching over two pairs of corrugation lines (white); the unit cell is marked in the figure. J. V. Barth et al [70].
Figure 29: Schematic representation of the Au(111)-(22x√3) reconstructed unit cell, containing 2 rows of 23 Au atoms each, occupying the same distance as 22 atoms of an unreconstructed Au(111) surface. The dimension of the unit cell is roughly 63.5Å x 5Å.

Figure 30: LEED patterns corresponding to the (22x√3) reconstructed Au(111) surface.

The reconstruction of gold is regarded as the tendency of the system to minimize the surface free energy, which increases due to the loss of coordination upon cutting the crystal along the (111) direction. This in itself is a proof of a strong Au-Au bond, which can be explained by the increased participation of the 5d Au orbitals to the metal-metal bond [18]. In the case of gold, with its large nuclear charge, relativistic effects predict an expansion of the 5d (and f) orbitals, and a contraction of the 6s orbitals, making the 5d band a focal point of gold chemistry [18, 72-75].

“Lifting” of the Reconstructed Au(111) Surface

Although the reconstruction is stable in air at room temperature [18, 76] it can be lifted upon adsorption of certain gases, such as sulfur and oxygen as mentioned earlier. The addition of sulfur, for instance, even in small amounts, is capable of lifting the herringbone reconstruction, and a sulfur coverage of only 0.1 ML has been shown to completely lift the reconstruction, at room temperature, as seen by real time STM [27]. This can be explained by a S-Au interaction which increases in strength, to the detriment of the Au-Au surface bond, therefore bringing changes to the charge density of the surface layer and thus driving the lateral expansion of the Au surface layer back to bulk-like values. The adsorbate induced reversal of the Au(111) herringbone reconstruction determines the release of the additional
4% Au atoms which eventually agglomerate at step edges or form small Au islands [10, 27].

Above a 0.1ML sulfur coverage, an unreconstructed (1x1) Au surface structure is observed in LEED and STM experiments [9, 10, 27]. Distinctive STM images (figure 31) as well as LEED patterns (figure 32) indicate the presence of such a structure.

Figure 31: Atomically resolved STM image of the (1x1) unreconstructed Au(111) surface structure; the unit cell is marked in the figure. B. K. Min et al [9].

Figure 32: LEED patterns corresponding to the (1x1) unreconstructed Au(111) surface, taken at an electron energy over ~325eV.

Au(111)-S Formations Above ~.25ML

As the sulfur coverage increases and approaches 0.3ML, sulfur atoms form an ordered (√3x√3)R30° adlayer, with one S atom per unit cell chemisorbed in 3-fold coordinated surface sites [12, 14, 38, 77-79]. Although seen in LEED experiments (figure 33), an atomically resolved STM image of this ordered sulfur layer was not attained, possibly due to the high mobility of the S atoms [10, 27]; nevertheless, the Au(111) (√3x√3)R30°-S has been imaged by STM at an electrochemical interface with the S deposited from a solution containing Na₂S [1, 14].
The Au(111) $\sqrt{3} \times \sqrt{3} R30^\circ$-S commonly seen in LEED patterns starting at a sulfur coverage of about 0.3ML, seems to be preceded by a less-known phase, also observed in LEED experiments only. It has been identified as a (5x5) structure, with sulfur atoms forming a local $\sqrt{3} \times \sqrt{3} R30^\circ$ ordering within a (5x5) ordered domain structure [1, 10]. The experimental results are best interpreted by fitting 7 sulfur atoms in the (5x5) unit cell, each occupying FCC hollow sites [1] and the present work. The (5x5) phase forms at a sulfur coverage as low as 0.25ML [1], and gradually gets replaced by the true $\sqrt{3} \times \sqrt{3} R30^\circ$ phase as the coverage increases toward 0.33ML, at which point only the $\sqrt{3} \times \sqrt{3} R30^\circ$ ordering exists. For this reason, this particular S coverage is chosen to be used as an AES calibration point by certain authors [10].

As previously mentioned, more recent XPS results suggest both $\sqrt{3} \times \sqrt{3} R30^\circ$ and (5x5) phases coexist with the higher coverage “complex” phase. Similar to the results of this thesis, but using XPS instead of AES, these authors observed the $\sqrt{3} \times \sqrt{3} R30^\circ$ slightly below and above the “complex” phase coverage. Also, within agreement of these results, we found the ordering of the $\sqrt{3} \times \sqrt{3} R30^\circ$ phase irreversibly destroyed by annealing to ~330K [1]. These most recent conclusions, in combination with findings of significant electron beam effects near coverages coinciding with $\sqrt{3} \times \sqrt{3} R30^\circ$ phase LEED observation, led us to an AES calibration of .28ML based on the theoretical maximum coverage of the more stable (5x5) structure.

Figure 33: LEED pattern of the $\sqrt{3} \times \sqrt{3} R30^\circ$-S structure on Au(111); the image was taken at an electron beam energy of 208 eV.

Figure 34: Succession of LEED patterns corresponding to: the (5x5) phase for a S-coverage of ~0.30ML (left), the $\sqrt{3} \times \sqrt{3} R30^\circ$ phase at a ~0.50ML coverage (right), and a coexistence of both (5x5) and $\sqrt{3} \times \sqrt{3} R30^\circ$ phases corresponding to a ~0.40 ML coverage (middle).
The “Complex” Phase

Even though the LEED pattern continues to show an ordered (√3x√3)R30° structure formed by sulfur on the gold substrate for a S-coverage up to ~0.57ML, it is more plausible that this phase coexists in fact with the “complex” phase originally reported by Kosterlitz et al. [54]. Although no consensus has been reached, it appears that the “complex” phase is overall incommensurate, but local distortions in the surface layer facilitate the formation of local commensurate patches, which, in STM images, have the appearance of a structural motif repeating itself [1]. Due to the fact that any crystal diffraction technique is sensitive to the regions of a surface which exhibit the best long-range order, regardless of how much of the actual surface exhibits that particular order, the LEED pattern will give the impression of a neatly organized sulfur overlayer, with a suggested unit cell [1, 54] expressed in matrix notation:

\[
\begin{pmatrix}
1 & -8 \\
3 & 3 \\
10 & 7 \\
3 & 3
\end{pmatrix}
\]  

(5.1)

Figure 35: Suggested unit cell for the “complex” phase (left) and the related reciprocal space lattice points (right). Yu et al. [1].

Under the assumption that the unit cell indeed resembles the suggested one, 4 or 5 sulfur atoms are assigned per cell, and the approximate surface of the cell, in real space, would be around 70Å² [54]. The LEED pattern corresponding to the “complex” phase can be made sharp by annealing the sample to ~450K [1], and it afterward exhibits a remarkable stability (of days) at room temperature. Auger measurements attribute a S-coverage of 0.51ML for a well-defined “complex” phase [54], a value which has been occasionally suggested as an AES calibration when sulfur coverage is concerned.
Figure 36: Actual LEED images of a “complex” phase, which is interpreted as 3 domains, similar to the ones suggested in figure 35, rotated by 60° with respect to one another, around a direction perpendicular to the Au surface. LEED images acquired at ~120K with beam energies of 161eV (Left) and 253eV (Right).

It is worth mentioning that NIXSW [1] and high-resolution XPS data [8], as well as DFT calculations meant to interpret STM images [25], point toward the coexistence of $(\sqrt{3}\times\sqrt{3})R30^\circ$-S and the “complex” phase over a fairly large S-coverage range, all the way up to maybe 0.6ML. LEED observations from multiple authors are displayed below to emphasize the strong evidence of phase coexistence and an overarching need of a better understanding of S adsorption processes on Au(111).
Figure 37: LEED observation of the changes in the Au(111) structure: in the absence of sulfur (reconstructed phase) and upon sulfur adsorption (all the other phases). Depending on the actual experimental conditions, various groups observed similar phases occurring at slightly different S-coverage. The sulfur coverage used for calibration by each group, if known, is specified in the figure.

The comparison above only includes gas adsorption experiments, in which no substantial structure information above .6ML can be determined. In chapter 8, Au(111)-S formations above .6ML pertaining to experiments where sulfur originates from solutions will be discussed. But first a discussion below of STM studies pertaining to S-induced surface morphology of gas adsorption experiments is necessary.

Previous STM Observations and Analysis (gas adsorption experiments)

A fair amount of information can be extracted by comparing LEED results (how the LEED patterns relate to various phases of S on the Au substrate) with STM images of the same S-Au(111) systems. The clean Au(111) (22x3) herringbone reconstructed phase, and the (1x1) unreconstructed phase have both been observed in STM experiments, but the (√3x√3)R30°-S as well as the (5x5)-7S structures have eluded the STM imaging technique, one reason provided being the high mobility of the S atoms [1, 10, 27].

A better understanding of the succession of STM images following sulfur adsorption on Au(111) can be achieved by taking into consideration the changes which take place in the chemistry of the adsorbate-substrate system, as the S-coverage increases. The behavior of S on Au(111) finds its explanation in the relative strength of the three types of bonds involved: the Au-Au bond, the S-Au bond, and the S-S bond. Sulfur is an electronegative element [18, 80] and it is expected to withdraw charge from the metal surface [8, 33, 35], but on the other hand, Au has the highest electronegativity of any metal, being only slightly more electropositive than sulfur [8, 81]. Under these conditions, sulfur behaves as a weak electron acceptor, but the amount of Au→S charge transfer decreases as the sulfur coverage increases [8, 10, 82]. At the same time, at all coverages, S substantially decreases the density of states that Au exhibits near the Fermi edge [8]. This explains why sulfur adsorbates lift the clean Au reconstruction (the changes to the charge density of the surface layer drive the lateral expansion of the Au surface layer back to unreconstructed values), and why, upon increasing coverage, the Au-S bond weakens (which facilitates possible changes in the sulfur adsorption sites), and the S-S bond gradually increases (which will determine, at coverages above 0.4ML, the higher stability of S2 rather than atomic S on the Au surface [8]). In anticipation of the results which will be presented below, one might notice that sulfur coverage greater than 1ML will bring the presence of SN (i.e. S2, S4, S6, and S8) species on the gold surface [8], in agreement with the idea that the S-S bond strength increases with increasing coverage.

Comparing the strength of the S atoms bonding to the Au(111) surface, to the bonding of the same sulfur atoms to Pt(111), Mo(110) and W(100) [8, 83-85], one finds that the S-Au bond is the weakest. In contrast, the S-S bond formed within the sulfur overlayer on a Au(111) surface is stronger than similar S-S bonds when the substrate happens to be Mo, W and Pt. This points toward a unique mobility/reactivity of sulfur on Au(111), not seen on surfaces of early or late transition metals [8].

As specified above, STM imaging (of gas adsorption experiments) shows the unreconstructed (1x1) phase of Au(111), noticeable up to a S-coverage of about 0.3 ML, but fails to register both the (√3x√3)R30°-S phase and the (5x5) phase as well. Instead, as the coverage increases, pits and islands start forming on the surface. Real-time STM imaging monitoring the changes in Au(111) surface with increasing S coverage at room temperature [10], shows monoatomic etch pits that start developing through the removal of Au atoms while islands start to nucleate by incorporating the removed atoms into regions of AuS conglomerates. Progressively, the density of pits and islands increases, until the surface becomes completely covered with a 2D gold sulfide (AuS) layer, which happens at a sulfur saturation coverage of approximately 0.6ML. The corresponding STM image (figure 38) provides a picture of a sponge-like morphology [9, 10].
Annealing the “Complex” Phase

The AuS phase formation implies a massive Au transport which becomes possible through the weakening of the Au-Au bonds and the strengthening of the S-Au ones, such that the energy required to remove gold atoms from regular lattice sites is compensated by the energy released at the formation of the mobile Au-S species [9, 10, 27]. Although the gold sulfide layer forms at S-coverages up to 0.6ML, once the saturation coverage is reached, upon annealing the sample to 420-450K, the sulfur coverage drops by approximately 20%, stabilizing at an approximate value of 0.5ML (measured by AES). High-resolution STM images taken at this particular 0.5ML S-coverage, show a well-ordered AuS overlayer, with a quasi-rectangular unit cell (figure 39), with lattice parameters of (8.8±0.4) x (8.2±0.4) Å² and an angle of 82º ±4º between the lattice vectors [10, 25, 27]. An approximate calculation results in a value for the surface area of the quasi-rectangular unit cell of about 72Å².

Figure 38: STM image of the sponge-like AuS phase formed after a deposition of ~0.6ML of sulfur. B. K. Min et al. [9].

Figure 39: STM image of the long-range order developed on the Au(111) surface upon saturation with sulfur and subsequent annealing the sample at 450K. The AuS phase uniformly covers the surface and a quasi-rectangular feature appears to repeat itself throughout the image. M. M. Biener et al. [10].
It is believed that excess sulfur (that cannot be accommodated by this ordered 2D AuS phase) desorbs via S$_2$ at around 450K [10]. Additional annealing to ~525K most likely decomposes the AuS film as opposed to desorbing AuS units since Au$_2$S has been shown to decompose at temperatures above 490K [10, 86]. In agreement with these authors, we observed “complex” phase ordering to disappear at ~530K accompanied by a decrease in S coverage when annealing past this temperature (see figure 23 in previous chapter). Additionally, coverages corresponding to “complex” phase LEED patterns also confirm S desorption is unlikely when annealing the 2D AuS phase between ~450K and ~525K.

Corroborating the STM images like the one shown in figure 39 together with their interpretation, with the LEED patterns (and their interpretation) obtained for the same system under similar conditions (figures 35,36), one can identify the ordered AuS phase with the “complex” phase previously described. Indeed, there are strong reasons for matching the two structures: the quasi-rectangular unit cell observed in STM of ~72Å$^2$ compares well to the unit cell suggested for the “complex” phase of about 70Å$^2$; both STM and LEED patterns show a long-range ordering of the surface upon annealing the Au sample at ~450K; in both cases the sulfur coverage for the ordered phase is around 0.5ML, close to our findings of .47ML, .48ML, and .49ML obtained by annealing to 478K, 526K, and 450K respectively.

During gas adsorption UHV experiments, both STM and LEED observation of sulfur adsorbed on the Au(111) substrate does not reveal any ordered structure when the sulfur coverage exceeds 0.6ML. But this is not true in studies using Electrochemical STM (EC-STM), and ultrahigh electrochemical techniques (UHV-EC) [11] which will be further discussed in chapter 8. Also discussed in chapter 8 are comparisons between these EC studies, gas-adsorption studies, and much of the work within this thesis; so first it is best to discusses quantitative findings of two Au(111)-S phases found during initial adsorption processes ((1x1)-S phase) and at low coverage ((5x5)-S phase).
Chapter 6

LEED INVESTIGATION OF TWO PARTICULAR AU(111) SULFUR INDUCED PHASES: THE UNRECONSTRUCTED (1X1) AND (5X5)-7S STRUCTURE

The (1x1) Au(111) Unreconstructed Phase

Although one expects an ordinary (1x1) structure of the gold surface once the reconstructed (22x√3) overlayer gives way to the unreconstructed Au(111) bulk-like surface upon sulfur adsorption, the Au(111) (1x1) phase surprises with interesting structural parameters which seem to depend on the way the sample is prepared. In particular, a somewhat different annealing procedure applied to the Au(111) sample, together - of course - with the exposure of the sample to sulfur from an SO$_2$ source, appeared to cause a variation of the first several gold interlayer spacings, as further described.

The two samples, prepared slightly differently, are going to be referred to as: (a) the unannealed sample and (b) the annealed sample.

a) The Unreconstructed (1x1) Au(111) Surface Following S Dosing:

After 10 minutes of dosing at 10$^{-5}$T (procedures discussed in chapter 2) and cooling the sample to ~83K, the LEED pattern confirmed that the presence of sulfur lifted the reconstruction, leaving a (1x1) configuration of the gold surface. Upon analyzing the experimental I(E) curves, a best fit structure was found which corresponds to an overall Pendry r-factor of 0.23, and individual r-factors as shown in figure 40. These results are also displayed in figure 19.

![Figure 40: Comparison between the experimental (solid line) and theoretical (dotted line) I(E) curves, corresponding to the best fit Au(111) (1x1) structure obtained for the unannealed sample.](image)

The scattering effect of the gold atoms was described by phase shifts of the incoming electron waves, and a number of 10 phase shifts, calculated with the Barbieri/Van Hove Phase-Shift package, have been used in the analysis. Within a LEED computation, the match
between experimental and theoretical beams was altered by allowing several structural as well as non-structural parameters to change. In the current calculation, the depth of the top six Au atomic layers, the imaginary and real part of the inner potential, and the perpendicular and parallel vibrations of the atoms in the top layers were treated as variable parameters.

The relaxation of the six topmost layers resulted in interlayer spacings as illustrated in figure 41; their values are to be compared to the bulk interlayer spacing of 2.355Å.

An inner potential of the form \((6.32\pm0.14 - 7i)\) eV was found to best describe the interaction of the probing (scattered) electrons with the Au atomic layers.

**b) The Unreconstructed (1x1) Au(111) Surface After Annealing to 528K**

An alternative approach to the sample preparation involves an in-between annealing step, which takes place after subjecting the sample to sulfur deposition. Following the idea that any small amount of coexisting \(S_n\) species (i.e. \(S_2, S_4, \ldots\)) desorb at temperatures above 400K [8], the sample has been annealed for a short time to 528K, and only afterward cooled down to 83K in order to acquire the LEED images. The additional annealing was intended to ensure that only atomic sulfur would determine the relaxation of the Au(111) surface into the unreconstructed (1x1) phase.

The LEED analysis proceeded along the same lines as described for sample (a). Figure 42 shows the I(E) curves for the best fit structure; the overall Pendry r-factor was 0.24.
Upon optimizing the structural and non-structural parameters, the outcome was a succession of the first five interlayer spacings, which vary as shown in figure 43.

An inspection of figures 41 and 43 suggests opposite tendencies for the first interlayer spacing corresponding to the two samples (contraction versus expansion when compared to the bulk interlayer spacing of 2.355 Å). It is also obvious that both values are affected by large errors, therefore a clear conclusion regarding a relaxation of the surface cannot be drawn. The errors themselves might be due to the ample thermal vibrations of the Au atoms in the first two layers, but might also reflect an actual depth variation of the atoms involved. One cannot rule out the possibility that S atoms intercalate between the first Au layers.
The (5x5)-7S Phase

Similar to the (1x1) phase, the (5x5)-7S phase was examined before and after annealing. The gold surface was exposed for 20 minutes to SO$_2$, at 10$^{-5}$T, prior to obtaining the un-annealed data, and the annealed data was acquired after heating the surface to 531K. The temperature during I(E) data acquisition for the un-annealed and annealed sample was 79K and 118K respectively.

In both cases, the LEED calculation used 12 phase shifts to describe the scattering effect of the gold atoms upon the probing electrons. Since the overlayer unit cell contains 7 sulfur atoms and 25 gold ones (as shown in figure 44), it was concluded that allowing the sulfur atoms to relax in a direction perpendicular to the surface, and allowing the first gold layer to do the same, resulted in enough variable parameters which could influence the Pendry r-factor, to the extent that allowing deeper gold layers to relax would result in changes of the r-factor not necessarily relevant to the real structure of the surface. The vertical coordinates of the sulfur atoms, and the vertical coordinates of the top-layer gold atoms were consequently averaged, thus leading to average values of the interlayer spacings.

![Figure 44: A model of the optimized (5x5) surface structure with the S atoms in FCC hollow sites. The red parallelogram represents the overlayer unit cell.](image)

The two sets of data – un-annealed and annealed - generated the I(E) curves illustrated in figure 45; the curves are shown for the best fit structures (which correspond to the lowest values of the r-factor).
Figure 45: Best fit I(E) curves for the Au(111)-(5x5)-7S: panel (a) - the un-annealed data resulted in an overall r-factor of 0.28; panel (b) - the annealed data gave an overall r-factor of 0.33.

We attribute the difference in the overall r-factors (with the lowest corresponding to the un-annealed data set), to the fact that the energy range of the annealed data almost doubles the energy range of the un-annealed set; also, the annealed data contains two additional beams: the (2,0) and the (0,2), out of which one at least drove the r-factor value up.
The average interlayer spacings are marked in figure 46. The first value corresponds to the un-annealed data set (i.e. \(d(\text{S-Au}_1)=1.65\pm0.11\text{Å}\)), and the second value corresponds to the annealed experimental data (for example, \(d(\text{S-Au}_1)=1.57\pm0.14\text{Å}\)).

![Figure 46: Average interlayer spacings for the Au(111)-(5x5)-7S structure. The two separate distances in top layer spacings are written as un-annealed/annealed.](image1)

The results obtained compare well with studies of the same structure by two other groups - Yu et al. (reference [1]) and Rodriguez et al. (reference [8]). To summarize:

1) the S-Au\(_1\) interlayer spacing of \(1.57\pm0.14\text{Å}\) (annealed data set) or \(1.65\pm0.11\text{Å}\) (un-annealed data set) compares well with the \(1.56\pm0.07\text{Å}\) value found by Yu et al. and the \(1.71\text{Å}\) value resulting from DFT calculations by Rodriguez et al. (figure 47).

![Figure 47: Top-layer spacing comparison of single FCC hollow-bound layers formed at coverages where (5x5) Au(111)-S phases are observed [1,8].](image2)
2) The S-Au bond length varies between 2.29±0.1Å (annealed data set) and 2.34±0.08Å (un-annealed data set) both slightly larger than the 2.28±0.04Å found by Yu et al., but still smaller than the calculated value of 2.39Å by Rodriguez et al.

3) As expected from FCC (111) metal surfaces, the Au₁-Au₂ relaxation is very small: the 2.36±0.02Å and 2.34±0.03Å topmost interlayer spacing is to be compared to the 2.355Å value of bulk interlayer spacing.
Chapter 7

S ADSORPTION PROCESSES AND ELECTRON BEAM EFFECTS

Initial S Adsorption Processes

The lifting of the “herringbone” reconstruction is followed by adsorption on step edges. This adsorption on step edges is noted as chemisorption in both EC-STM and UHV gas adsorption experiments [10, 13, 26, 27]. On the contrary, it is believed physisorption occurs on terraces [14, 89]. In gas adsorption experiments, S adsorption occurs after a dissociative energy barrier is overcome, such as exposing the crystal to S₂ and SO₂ gas.

SO₂ Adsorption and Dissociation

On Au(111) it is known SO₂ physisors at low temperature. TDS data by G. Liu et al. [90] showed nearly all SO₂ desorbs by annealing to ~145K, which similarly our results below show adsorption starting at ~135K (as noted by the decrease in one set of symmetric LEED beam intensities):

Figure 48: SO₂ Physisorption: Two sets of three-fold symmetric first order (1x1) Au(111) LEED beam intensities during SO₂ exposure at 1x10⁻⁶ T.
In the above figure, three-fold symmetric LEED e-beams were probed with a constant beam current at a fixed gas pressure. I(T) plots, similar to I(V) but instead of varying energy, images were acquired at decreasing temperatures following liquid N\textsubscript{2} cooling of the cryostat.

**Further Electron Beam Effects**

The figure below displays three different experiments with consistent AES e-beam exposure, but with ion-gauge in both on and off positions. We also compared the results to a “roughened” surface to see if this had an effect of lowering the SO\textsubscript{2} dissociation or S adsorption energy barrier, which it did not. A BOC-MP study some time ago suggested SO\textsubscript{2} did not chemisorb on a Au(111) crystal at room temperature, but did on other transition metals [91]. Theoretical predictions were considered for two dissociation paths of SO\textsubscript{2} on (111) metals, but only Ni had a dissociation barrier lower than the adsorption barrier of its constituents [91] which contradicts more recent results suggesting dissociation of oxygen can occur in low-coordinated Au active sites [8, 9, 85, 92-94]. This may not be so if the gas was ionized prior to desorption.

![Graph showing S uptake during initial adsorption with ion gauge off except at small fixed intervals to briefly observe pressure after an AES measurement](image)

**Figure 49:** The two similar curves show S-uptake during initial adsorption with ion gauge off except at small fixed intervals to briefly observe pressure after an AES measurement. AES beam exposure was brief and fixed for all measurements of and between each three data sets. The top curve shows adsorption-induced ion-gauge effects likely occur when the ion gauge is left on during entire exposure time.

Other researchers have ruled out ion gauge effects [10, 27], but based on evidence of AES stimulated adsorption (shown in figure 5), the magnitude of AES e-beam effects were likely unknown in previous work. Much earlier work has suggested that caution be used...
during LEED and AES experiments because they are known to stimulate the decomposition of \( \text{SO}_2 \) [91, 95], but it seems like more questions than answers exist regarding this topic.

In particularly AES assisted adsorption can occur on irradiated areas after pumping out adsorbate-containing gas, in which following exposure results in greater uptake on irradiated areas; but it can also occur during the whole exposure time and can be the result of beam-induced dissociation [96]. Since some earlier studies do not agree with recent findings regarding \( \text{SO}_2 \) dissociation at the Au(111) surface, the nature of S adsorption from \( \text{SO}_2 \) requires further clarification.
Chapter 8

NOVEL LEED OBSERVATIONS COMPARED TO PREVIOUS ELECTROCHEMICAL AND S-GAS ADSORPTION STUDIES

LEED Observations and Electrochemical Studies

In UHV-EC experiments, Lay et al. observed (2x2) structures by LEED with corresponding coverages between .59ML and 1.6 ML as determined by AES. These coverages of 1.6ML, 1.21ML and .59ML were at K₂S immersion potentials of .40V, .20V, and 0V respectively. Fixed potentials were applied to a .20 mM K₂S solution preceding the immersion of a clean and ordered Au(111) crystal for 2 minutes. The sample was then transferred to a UHV chamber before LEED observations and AES measurements. Experiments were performed at immersion potentials between -1.20V and .40V. AES measurement of lower coverages showed partial potassium coverage, but LEED showed a (√3x√3)R30° S structure at immersion potentials of -.80, -.60, and -.40V [11].

Lay et al. also observed a (√3x√3)R30°-S structures in a separate set of EC-STM experiments. For these experiments, the solution composed of .2mM K₂S + 1mM Na₂SO₄ and 1.0 mM Na₂S₂O₃ + 1.0 mM KOH. The EC-STM results revealed the (√3x√3)R30°-S between potentials of -0.85V and -.40V. Between potentials of -.40V and -.50V, two (3√3x3√3)R30°-S structures were observed, which when compared to TLEC voltammetry results, corresponds with beginning bulk sulfide oxidation processes. Bulk S or polysulfide were deposited into this oxidation process and (√3x√3)R30°-S and (3√3x3√3)R30°-S structures appear to be composed with the same density of S atoms, so the nature of bulk S deposit was a major question by Lay et al. [11].

Figure 50: (√3x√3)R30°-S (left) and (3√3x3√3)R30°-S (right) structures observed by Lay et al [11] with EC-STM.
The \((3\sqrt{3}\times3\sqrt{3})R30^\circ\)-S structure was also believed to be a precursor for a layer of \(S_8\) rings or chains consistent to bulk S structures [11, 87]. One model suggests the first step to higher density S layers, such as an \(S_8\) structure, forms at a coverage of .9ML [11, 55, 78, 88].

Another EC-STM study showed Au(111) thin film electrodes deposited on glass formed \((\sqrt{3}\times\sqrt{3})R30^\circ\) and \(S_8\) structures in a \(Na_2S\) aqueous solution. Vericat et al. show by changing potentials from -0.60V to -0.80V \(S_8\) structures transformed into \((\sqrt{3}\times\sqrt{3})R30^\circ\) structures, which was reversible when changing back to -0.60V. The authors suggest that when \(S_8 \rightarrow (\sqrt{3}\times\sqrt{3})R30^\circ\), 4 S atoms desorbed while remaining 4 S atoms moved to nearby hollow sites through low-energy paths. It was also noted S atoms vacancies were observed in the \(S_8\) structure, but are rarely detected during the adsorption process [13].

![Figure 51: Model (left) and EC-STM images (right) of \(S_8 \rightarrow (\sqrt{3}\times\sqrt{3})R30^\circ\) transformation processes by Vericat et al. [12, 13].](image)

In publication the following year, Vericat et al. concluded \(S_8\) spontaneously forms and coexists with \((\sqrt{3}\times\sqrt{3})R30^\circ\) and bulk S structures [12], while also finding the chemical state of S in octomers (\(S_8\)) to be the same as S for the \((\sqrt{3}\times\sqrt{3})R30^\circ\) phase. Furthermore, our LEED \((\sqrt{3}\times\sqrt{3})R30^\circ\) phase observations and corresponding AES coverage determination as shown in figure 1 and table 1 is consistent with this study, namely that the annealed “complex” phase AES measurements yielded coverages similar to those as with domains of \((\sqrt{3}\times\sqrt{3})R30^\circ\) phases. On several occasions, we even observed that annealing a surface with a clear \((\sqrt{3}\times\sqrt{3})R30^\circ\) LEED pattern resulted in a well-ordered “complex” phase. It is interesting we observed a \((\sqrt{3}\times\sqrt{3})R30^\circ \rightarrow “complex”\) phase transition upon annealing and suggests perhaps more consistency between EC and gas adsorption studies exist than previously noted.

**A Comparison of Electrochemical STM and S-Gas Adsorption Studies**

Our \((\sqrt{3}\times\sqrt{3})R30^\circ\) observations also support the proposal of phase coexistence witnessed by Yu et al. during S-gas adsorption experiments where a solid state
The electrochemical cell was heated under UHV conditions to produce S₂ gas. The researchers’ XPS coverage measurements, with corresponding observations of (√3x√3)R30° LEED patterns, occurred at or slightly above coverages of the annealed “complex” phase. Additionally, M. Yu et al. report surface preparations consisting of mostly poorly ordered “complex” phase arrangements with small (√3x√3)R30° domains, the LEED pattern was dominated by the well ordered (√3x√3)R30° structures [1]. This more recent claim, together with our findings, add further consistency of phase coexistence proposed by Vericat et al. via electrochemical methods some 6 years earlier [12]. In another paper, Vericat et al. indicated it was possible to obtain surface qualities by electrochemical methods similar to those attained in UHV environments [14], which seems likely true given the above consistencies observed. But on the other hand, vapor-deposited Au(111) on glass (used as electrodes in EC-STM studies) seems to have a higher number of step edges and kinks than single-crystal samples prepared under UHV conditions [12]. So, caution should be used when comparing studies since step-edge morphology is an essential component in S/Au(111) adsorption processes [10, 12, 27].

Biener et al. observe retraction at step edges preceding “complex” phase formations of a 2D AuS phase under UHV conditions as previously mentioned [10, 27], but Lustemberg, Vericat et al. conclude the high coverage phase is best described as a mixture of monomeric and polymeric chemisorbed sulfur rather than a 2D AuS phase in an electrochemical study [26]. The experimental work from both authors was justified in separate DFT calculations [25, 26]. Both calculations describe the high-coverage rectangular structures observed via STM experiments. The first set of experiments, as previously mentioned, was observed under UHV conditions using a well-annealed Au(111) crystal [10, 27]. The second set of experiments from Lustemberg, Vericat, et al. were performed by immersion of evaporated Au(111) films on glass in aqueous solutions of Na₂S at room temperature [26]. Perhaps large atomically smooth terraces as shown in figure 52b above for single Au(111) crystals were
grounds for justification of better experimental accuracy in findings by Quek and Biener et al. [10, 25, 27], but we found experimental discrepancies in observations between two different LEED systems using the same single Au(111) crystal, surface preparation, and gas adsorption method.

Gas-Adsorption Experimental Inconsistencies

By annealing a high-coverage phase obtained after dosing SO$_2$ for 100 minutes at $10^{-5}$T (such as shown in figure 21), LEED images corresponding to figure 23 are shown below:

![LEED images](image)

Figure 53: LEED images (acquired at room temperature) corresponding to AES data in figure 23. LEED beam energy: 119eV; annealing temperatures: a) 373K, b) 428K, c) 478K, d) 526K, e) 575K, f) 629K, g) 674K, h) 726K, i) 781K, j) 831K
In addition to the figure above, multiple attempts were made to observe a clear (5x5) or a (\(\sqrt{3}\times\sqrt{3}\))R30° Au(111)-S LEED upon annealing a crystal with diffuse coverage >.6ML but only “complex” phases and (1x1) phases were reproducible as shown in the figure above. This was not the case however, when the sample was probed by a different LEED system (next paragraph).

In another set of experiments, the same Au(111) sample was place in a separate UHV chamber having no AES optics, but a LEED system with a micro-channel plate. A micro-channel plate basically accelerated diffracted electrons prior to impingement on the phosphor screen. This meant the sample could be probed by much smaller beam currents of ~nA versus ~\(\mu\)A currents used by the other LEED system described in chapter 2 (and used in all other work described in this thesis). After preparing the sample in-situ similarly as previously described, SO\(_2\) was exposed to the Au(111) crystal overnight and upon annealing the following day, a (4x4) formation was observed:

![Figure 54: (4x4) Au(111)-S LEED image.](image)
Figure 55: LEED images a-j taken at 122eV. Image a captured prior to annealing; Images b-j acquired immediately after annealing to the following respective temperatures: b) 373K, c) 473K, d) 498K, e) 523K, f) 548K, g) 573K, h) 598K, i) 623K, j) 648K
At ~523K the “complex” phase disappeared and the LEED pattern was dominated by a (4x4) pattern. It is likely this phase shows further evidence of a mixed-phase surface and may support a conclusion by Vericat et al. that mixed phases of (\(\sqrt{3}\times\sqrt{3}\))R30°, S₈, and S₃ coexist at higher coverages [14]. S₃ has been observed in electrochemical studies described above and shown in the figure below:

![Figure 56: Vericat et al. observe (4x4) formations of S₃ structures [14].](image)

Domains of S₃ may be responsible for formation on select terraces identified as (4x4) structures [11]. The possibility of S₃ domains with periodic (4x4) vacancies was just one of three (4x4) configurations observed by these authors. This particular structure, occurred during a second positive scan following electrochemical desorption of two other (4x4) structures.

The initial structures were observed to be quite stable, consistent with our (4x4) phase observations after annealing, which was stable through a range of ~50K. We cannot be certain if (4x4) formations observed result from S₃ structures (previously mentioned), S structures, or an ordered (4x4) Au template as observed by Lay et al. [11]. These researchers claim a (4x4) template remained on terraces after electrochemical desorption of (4x4)-S phases. This (4x4) –S phase was best characterized by a (1x1) array of S atoms with periodic (4x4) pits, but the authors noted the structure was still not well defined [11]; this (4x4) structure was clearly different than a potential S₃ (4x4) phase shown in figures 56, and on the upper terrace of 57c.

![Figure 57: Lay et al. observed the following three (4x4) structures [11]: a) (4x4)-S adlayer; b) (4x4) templated Au surface after removal of (4x4)-S adlayer; c) (4x4) arrangement of clusters presumed to be S₃ (figure 56) by Vericat et al [14] on upper terrace and a (\(\sqrt{3}\times\sqrt{3}\))R30°-S phase on lower terrace.](image)
New Findings and New Possibilities: AuS Clusters

There is a strong possibility some of these (4x4) formations coexist with AuS clusters or may themselves be ordered arrangements of AuS clusters. If, for example, the rectangular structures comprising the “complex” phase are best described as an incommensurate AuS 2D adlayer rather than a mixed state of polynomeric and monomeric chemisorbed sulfur [26], it is plausible S$_3$-type (4x4) formations are arrangements of clusters or cluster types. This suggestion is based on recent observations of AuS cluster formation during initial adsorption processes [15] coupled with a missing picture of processes occurring below top-layer formations.

Adsorption of initial monatomic S occurs at FCC stacking regions of the herringbone reconstruction, but the number density of gold atoms agglomerating towards step edges was questioned. Kurokawa et al. claim the removal of Au atoms into clusters would preclude many additional Au atoms of the reconstructed surface from migration towards step edges, suggesting these arguments presented by Beiner et al. [10, 27] are based on rough calculations and more detailed investigations are needed [15].

It is intriguing that EC studies indicate a mixed surface of (√3x√3)R30º, S$_8$ and S$_3$ [44], M. Yu et al. suggest (5x5) and “complex” phases coexist, and Biener et al. suggest monatomic etch pits and AuS cluster form at higher coverages; yet current work shows monatomic S occupying FCC sites while three separate types of clusters form at low coverage. When combining these past conclusions, it seems plausible that higher coverage phases can support (5x5), (√3x√3)R30º, S$_8$, and S$_3$ formations and that answers would be found in dynamical rearrangements of type I, II, and III clusters into S$_8$ and S$_3$ structures, since it is likely monatomic S continues to adsorb in FCC sites until domains of (5x5) and (√3x√3)R30º structures form. But as previously mentioned, (√3x√3)R30º phases are not stable upon annealing and deteriorate during LEED observations. Annealing back coverages of ~.6ML usually resulted with LEED images showing mixed phases.

Figure 58: Exotic mixing of Au(111)-S phases obtained when annealing back coverages of ~.6ML to temperatures between ~530K and ~600K.
**New Findings and New Possibilities: Experimental Techniques**

As previously mentioned we could not obtain a well ordered \((\sqrt{3}\times\sqrt{3})R30^\circ\) phase when annealing and it substantially deteriorated during LEED observations, which made acquisition of I(E) data very difficult. On the contrary, we were able to observe (5x5) and (4x4) phases probing the sample with a low beam current in a separate set of experiments after a very long SO\(_2\) dosing period. These results were not repeatable when using the LEED system requiring higher beam currents, suggesting the LEED electron beam had an effect on coverage obtained after annealing past ~525K, in addition to LEED e-beam effects during S-uptake as previously discussed.

Another consideration is STM tip effects on Type I clusters. Type I clusters contain S atoms spaced at \(\sqrt{3}\) distances with respect to the underlying substrate. They are considered stable and should not spontaneously disintegrate at liquid nitrogen temperature, but the authors elucidate disintegration may occur during interaction with the STM tip as shown below:

![Figure 59: Kurokawa et al. consider STM tip effects of type I AuS clusters. The triangle (a) \(\Rightarrow\) three dots (b), possibly due to STM tip interaction [15].](image)

Many points addressed above are just speculation and inconsistencies mentioned between EC and gas adsorption experiments require further clarification. On the other hand, a strong argument has been made which emphasizes the need for a concise quantitative atomic-level understanding that clearly describes dynamical Au-S surface interactions.


Chapter 9

CONCLUSIONS

LEED Analysis of (1x1) and (5x5) Au(111)-S Phases

Dynamical LEED calculations, using the Barbieri/Van Hove Symmetrized Automated Tensor LEED package (SATLEED) \[64\], confirmed sulfur atoms occupy FCC hollow sites in (5x5) Au(111)-S phases. The (5x5) Au(111)-S phase model predicted by M. Yu et al. showing a split-order (\(\sqrt{3}\times\sqrt{3})R30^\circ\) phase identified by a 7-atom “rosette” structure was the overarching best fit model. The coordinates of the sulfur atoms obtained via LEED calculations show a rumpling of the sulfur overlayer and of the top-most gold layer. By averaging the analogous vertical coordinates, we were able to get mean values for interlayer spacings (S-Au\(_1\) and Au\(_1\)-Au\(_2\)) which compare well with previously published results \[1,8\]. The structural parameters obtained for the (1x1) analysis show slight deviations of the Au-Au interlayer spacings from the interlayer spacing of bulk gold. These variations are somewhat different for a Au(111) sample exposed to sulfur and afterward immediately cooled off for LEED image acquisition, as compared to a similar experiment in which upon sulfur exposure, the sample was annealed and then the process of extracting LEED images followed. Structure determination of both (1x1) and (5x5) phases indicate sulfur adsorbates can restructure the top few substrate layers and that dynamical interactions likely go below the top layer.

Sulfur Coverage

The overwhelming experimental evidence for the coexistence of several sulfur induced phases on the Au(111) surface, indicates that “pure” (1x1), (5x5) or (\(\sqrt{3}\times\sqrt{3})R30^\circ\) configurations are hard to pinpoint during sulfur adsorption. The existence, on the surface, at the same time, of atomic sulfur and possibly of AuS adsorbed molecules and S\(_N\) molecules, indicates that although the LEED pattern points toward a certain repetitive arrangement of atoms, it is possible that additional sulfur atoms are present maybe intercalated between top gold layers, or agglomerate along steps, or form islands on the terraces. In any case, the large errors in the value of the interlayer spacings obtained through the LEED analysis of the (1x1) and (5x5) structures, could be explained by the existence of such intercalated atoms. Another explanation could be the high mobility of sulfur atoms on the surface which gets translated into large vibrations of those atoms - the vibrations being one of the fitting parameters in a LEED calculation. Nevertheless, the problem of matching the Au(111)-S phase to a certain sulfur coverage persists.

A previous gas-adsorption study showed by annealing past 400K, S\(_N\) desorbed from the surface and further annealing to ~500K maximized S-hollow occupancy \[8\]. By combining these results with our findings S did not desorb during complex phase formations while annealing from ~450K to ~525K, we determined annealing a (5x5) phase obtained after S exposure to slightly above 525K would lead to the most uniform (5x5) Au(111)-S surface coverage occupying FCC hollow sites. This experimental condition yielded the best (5x5)
structure determination and was used as a theoretical calibration point of .28ML to determine coverage. The most reasonable approximation of S coverage was determined by assuming linearity during initial S-uptake. Although not clearly linear, deviations from the linear fit can be explained by signal to noise error, partial attenuation of a sub-monolayer sticking coefficient from small contributions of S_N domains, unknown SO_2 reaction rates, and e-beam effects.

$\sqrt{3}X\sqrt{3}R30^\circ$ and (4x4) Phases

We found annealing coverages showing a $\sqrt{3}X\sqrt{3}R30^\circ$ LEED pattern, S desorption preceded formation of a “complex” phase. Because theoretical coverage of the “complex” phase exceeds that of a monatomic ($\sqrt{3}X\sqrt{3}$)R30° phase and ($\sqrt{3}X\sqrt{3}$)R30° structures cannot be reproduced by annealing, the stability of this phase must depend on intercalated S atoms, S_N species, or AuS cluster types. These formations vanishes upon annealing, LEED electron beam exposure, and possibly with STM tip interaction [15].

Furthermore, our only observation of a (4x4) LEED pattern was by a LEED system capable of probing the surface with a very low beam current; this adds more evidence that e-beam effects are impeding progress in Au(111)-S UHV gas-adsorption experiments.

Future Research

A closer look at S-gas adsorption experiments show the magnitude of electron beam effects may also add insight to fundamental Au-S interactions. One possibility is that an AES beam may cause dissociation of an adsorbed molecule prior to diffusion of a species into bulk layers, thus enhancing adsorption [96]. Also, since additional LEED e-beam effects have been observed from different S-gas sources (SO_2 and S_2 gas ~around coverages with corresponding ($\sqrt{3}X\sqrt{3}$)R30° LEED patterns), a series of experiments would be necessary to separate possibilities of ionized molecules forming away from the Au(111) surface, or from molecular adsorption preceding e-beam induced bulk diffusion processes. For example, ionized gas adsorption could be ruled out by biasing the sample [96], and work function measurements could be acquired using a Kelvin probe. But most importantly, finding the right model for LEED I(E) analysis of higher coverage phases would bring further insight to atomic-level understanding of Au(111)-S surface interactions.
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