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SPR imaging of potentials across metal thin films using electrochemical events

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**SPR IMAGING OF POTENTIALS ACROSS METAL THIN FILMS USING
ELECTROCHEMICAL EVENTS**

A thesis

Presented to

The Faculty of the Department of Chemistry

San Jose State University

In Partial Fulfillment

of the Requirements for the Degree

Master of Science

by

Wynn Allan Ray

August 2004

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A handwritten signature in black ink, appearing to be 'R. Terrill', written over a horizontal line.

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ABSTRACT

SPR IMAGING OF POTENTIALS ACROSS METAL THIN FILMS USING ELECTROCHEMICAL EVENTS

by Wynn Allan Ray

Utilizing Surface Plasmon Resonance (SPR), to map the potential boundaries across a metal thin film. Experiments have been performed that image the electrical potential distribution within thin metal films within which an electrical current is flowing. There have been three sets of experiments used to correspond image intensity of reflected light to potential lines. A silver film is electro-coated with lead, and gold films are coated with two different electro-chromic films. The electro-chromic films exhibit a potential dependent color change in electrochemical conditions. This color change can be detected by color videography or more sensitively by SPR imaging. These color changes therefore report the local surface potential. The film potential can be varied uniformly by the application of an in-plane electric current. This results in a varying potential difference between the metal film and the electrolyte solution that in turn result in varying electrochemical and optical responses.

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1.0 Introduction

This thesis presents results aimed at using a combination of surface plasmon resonance imaging and electrochemistry to visualize the electrical potential distributions in very thin metal films supporting substantial current flow. A voltage bias is applied across this very thin metal film electrode that results in a spatial gradient in potential between the two contacts, and the resulting 2D spatial distribution of voltage is imaged. We present experiments that employ both a static potential and a time varying one that illustrates spatio-temporal control of electrochemical events, (redox reactions) occurring at the electrode.

Electrochemistry of electroactive species coated onto the electrode surface provides a mechanism by which the local metal film potential produces an optical contrast. In other words, applying a bias potential across the metal film, (the working electrode: WE), creates a specific zone or zones where the location of the electrochemical changes in the redox reaction occur. This zone corresponds to the region in the plane of the WE film where the local potential changes from one that favors an oxidized to a reduced electroactive layer. For a perfectly ohmic and square WE film with perfect contacts on opposite edges for application of a potential bias, one would anticipate a linear potential gradient across the WE film face and hence a line somewhere in the plane parallel to the contacts that corresponds to the transition from oxidizing to reducing potentials. We also present results where a time-varying potential is applied to the electrolyte solution – experiments known to electrochemists as cyclic voltammetry (CV). In CV experiments, the electrochemical potential is varied with respect to time, and the

resultant currents produce electrochemical data. In this case, the optical changes are equally interesting, but in the experiments where images are acquired the electrochemical current is sacrificed because of the large in-plane currents being driven.

The working hypothesis is that the metal film is ohmic and therefore that uniform metal film thickness should give a uniform resistance and a corresponding linear distribution of potential across the film. Non-uniformity in the film resistance should therefore be evident by how experimental surface plasmon resonance images differ from the ideal images predicted by the above hypothesis. The presence of the electroactive layer on the metal film surface serves to create a potential threshold where the a large change in refractive index (η_R) will accompany the reduction or oxidation of the surface film. This η_R change will appear along the boundary between regions of the metal film where the electrochemical potential changes from favoring oxidation to reduction – essentially “decorating” an equipotential line within the metal film. So, to observe the equipotential line, the range of applied across the metal film must encompass the formal potential for the redox transformation, and secondly, the change of η_R must fall within a sensitive range for observation by surface plasmon resonance imaging.

The above conditions satisfied, then by altering the potential applied to the electrolyte solution, the electrochemical boundary can be moved across the metal film. Similarly, by increasing the bias potential across the metal film, the contrast across the boundary edges can be sharpened. The boundary separates regions of different η_R and therefore regions of greatly different reflectivity as seen by the surface plasmon resonance imager. Thus optical data encode the redox state of the coating and the coating

reports the local metal film potential. In the particular configuration used in these experiments, an Au or Ag metal film was applied to the 25mm square face of an equilateral glass prism. This film was then contacted along opposite edges with a conducting tape, and then with an electrolyte solution in a 19 mm circular region near the center of the film, this latter region serving as an electrochemical working electrode.

It is worthy of note that given the low bulk resistivities¹ (ρ) of gold and silver at room temperature, $2.255 \times 10^{-5} \Omega \text{ mm}$, and $1.617 \times 10^{-5} \Omega \text{ mm}$, respectively, the current densities (I) will be substantial for the modest electric field strengths (Φ) employed. A 0.5V total bias applied across the ca. 20 mm length of the film produces a field of $\Phi = 0.025 \text{ V mm}^{-1}$, so, assuming that the film and bulk resistances are equal and the contact resistance is negligible, $I = \Phi/\rho = 1.1 \times 10^3 \text{ amperes mm}^{-2}$ for Au and $I = 1.6 \times 10^3 \text{ amperes mm}^{-2}$ for Ag. The corresponding power dissipation $P = I^2\rho$ is similarly large, 27 and 39 W mm^{-3} respectively, but no evidence of metal film deterioration was observed. This level of power production is offset by the fact that the films are only 50 nm thick, so heat dissipation from the metal ‘bulk’ into the substrate and solution is very fast. The corresponding heat production per unit area is about 1.35 and 1.95 mW mm^{-2} , and the total heat dissipation about 675 and 975 mW. These values should be considered upper limits since the resistivity of the thin metal films are undoubtedly higher than the bulk values.

1.1 Electrochemistry

In the limit of perfect uniformity, a potential applied across a conductor or metal film leads to a linear distribution of potential. This relationship is expressed by Ohm's Law:

$$E = iR \quad \text{Eq 1}$$

Where E is the potential in Volts, I is the current in Amperes, and R is resistance in ohms (Ω). With a uniform current, the potential distribution becomes:

$$dE = idR \quad \text{Eq 2}$$

Or involving the bulk resistivity; ρ (Ωm)

$$dR = \frac{\rho dL}{A} \quad \text{Eq 3}$$

Where dR is the fraction of the linear distance (dL) across the range of the applied potential, times the resistivity constant of the material (ρ), divided by A, the cross-sectional area. Substituting equation 3 into equation 2 yields:

$$dE = \frac{i\rho dL}{A} \quad \text{Eq 4}$$

So dE is directly proportional to dL by the constant; $i\rho/A$. If the conductor is non-uniform in construction, variations will occur in the potential distribution. Note that this equation ignores the microampere currents that result from electrochemical (redox) processes, and current is assumed to be exclusively due to that supplied by the bias power supply.

The boundary conditions are that the potential is equal to zero at one contact and equal to E_{BIAS} at the other end where $L = 20\text{ mm}$. In the limit that the current density, i , and the film resistivity, ρ , are completely uniform, the integrated form of the above equation is simply:

$$E(L) = E_{BIAS} \left[1 - L / 20\text{mm} \right] \quad \text{Eq 5}$$

Variations in the thickness of the conductive plate, as well as the details of the contacts should be revealed in a non-uniform potential distribution – i.e. curvature in the equipotential lines.

Figure 1 describes a three terminal device. The first two terminals (1,2) are opposite edges of the square metal film and are connected to a variable power supply and ground respectively. The second (grounded) terminal (2) is also connected to the working electrode (WE) of the potentiostat – this creates no perturbation to the function of the potentiostat because the WE is normally held at virtual ground. Hard grounding the WE does negate the ability of the system to measure the current however. The third terminal (3) is the electrolyte solution, the potential of which is controlled in concert by the auxiliary electrode (a Pt coil) and a reference electrode (Ag/AgCl) in the electrolyte solution.² The potential difference between the solution and the metal film drives the electrochemistry. So, the edge of the metal film that is held at ground experiences essentially unperturbed electrochemical processes – i.e. the same ones that are expected when the potentiostat alone is connected to the metal film. The remainder of the metal film experiences electrochemistry characteristic of the *sum* of the potentials applied by the potentiostat and some fraction of that applied by the power supply.

Figure 1. Electrochemical Cell schematic (top view). Current flows across the face of the working electrode (WE) film from 1 to 2 as well as between the WE and the solution 3. The *average* potential between the WE film and the solution is controlled by the potentiostat using the auxiliary and reference electrodes. The potential of the left hand side of the WE is controlled relative to the right hand side by a variable power supply.

With the power supply, the electrochemical potential can be arranged to vary from oxidative to reducing towards a given species *on the same metal film*. Redox reactions are dependent on the *local* electrolyte-WE potential difference, and this varies as the bias voltage is divided across the metal film.

For the case of a uniformly conducting metal film the potential conditions at the WE can be described as:

$$E(L) = E_{BIAS}[1 - L/20mm] + E_{PSTAT} \quad \text{Eq 5}$$

Accordingly, at a given distance “L” from the bias-side contact, the threshold for a redox transformation, i.e., its E° value, will appear. Similarly, the “L” coordinate of this point is a linear function of E_{PSTAT} . Hence, the location of this point of transformation can be “translated” simply by adjusting E_{PSTAT} . All points with this potential are identifiable by their electrochemical state, so the electrochemical state or boundary reports an equipotential line on the surface.

1.2 Surface Plasmon Resonance (SPR)

In this thesis, the phenomenon of SPR is used to provide optical contrast for the electrochemical changes driven on the electrode surface. The SPR effect creates optical contrast via a change in the reflectance of the prism-metal interface as a function of the dielectric state of the opposite (outer) face of the metal film. So, the image formed by laser light reflected from that interface encodes the electrochemical state of the interface. A general description of the phenomenon of surface plasmon resonance follows.

Noble or precious metals have been prized for millennia for their high reflectivity – for example, the finest of the first mirrors were made of silver or gold. The surface

plasmon effect can be seen as a violation of this generally high reflectivity. Under certain precisely defined conditions (incident angle, substrate and superstrate η , wavelength and film thickness) a noble metal film (e.g. Ag or Au) will cease to reflect, but rather it will efficiently **absorb** the incident light and convert the energy into a resonant oscillation of electron density in the metal film.

When a surface plasmon is excited, the electron cloud in the metal film oscillates with the frequency of the incident light. The resultant oscillating EM field extends out of the metal film a fraction of the light wavelength (λ), and into whatever media (air, water, etc), is adjacent to the side of the metal film on the opposite side from the incident light. This EM field that penetrates through the metal film and into the opposite medium is termed the evanescent field and the penetration depth of this field corresponds exactly with the depth to which the SPR effect is sensitive to the superstrate η .

The phenomenon of SPR has been well documented³ and much of the groundwork for exploiting the SPR effect in a chemical sensor setting has been developed over the past 25 years. Commercial applications of SPR arose in the 1990s. Companies such as BIACORE®⁴ and GWC Instruments produce analytical instruments utilizing SPR for the study of biomolecular binding events. The surface enhancement properties of SPR are also utilized for Raman spectroscopy⁵. SPR has even been applied to such pedestrian applications as the monitoring of soda fountain mixing ratios. For this application an inexpensive optical unit made by Texas Instruments called the SPREETA™ was employed.

In the SPR imaging experiment, one subjects the outer (superstrate) face of the working electrode film to electrochemical stimulus, and the inner (substrate) face is contact with a prism and is probed with an expanded HeNe laser beam, though other monochromatic sources may suffice as well. If the metal film is of optimal thickness (40-60 nm), the electrochemical events acting on the outside of the film will dramatically influence the reflectivity of the inner side. The reflected light beam thus produces an image of the η variations, corresponding to the electrochemical (or other) events on the metal film.

In these SPR experiments, the Kretschmann⁶ geometry (Fig. 2) was employed. The thin metal film is deposited directly onto a face of a high refractive index (Schott glass type *SF10*) prism. With the previously described electrochemical changes in the medium that is chemisorbed on the surface of the working electrode, one can change the refractive index and therefore the SPR response. Potential distribution allows spatial control of electrochemical events by choosing the voltage range about the known threshold potential for the electrochemical event. Electrochemical control of the metal/solution interface results in images of the reflected light from the metal surface or lack of reflection due to SPR absorption.

The metal films employed are typically noble metals; only Ag and Au were used in this study. The simplest criterion for optical SPR-activity, satisfied in the optical frequency range by Au and Ag, is that ϵ' must be equal or less than -1. Where ϵ' is the real part of the complex dielectric function of the metal,

$$(\epsilon_m = \epsilon'_m + i\epsilon''_m) \quad \text{Eq 7}$$

Figure 2: SPR in the Kretschmann Geometry: a metal film is deposited directly onto one face of a prism, or onto a wafer, which is then optically matched to the prism. The incident p-polarized monochromatic light at the SPR angle is absorbed (attenuated total internal reflection) into the plasmon of the metal. This absorption results in a surface bound, non-radiative, evanescent wave along the opposite surface of the metal whose field extends well out of the metal film.

Ideally the metal will also have a small ϵ''_m , the imaginary (i.e. loss) component of the dielectric function. The higher oxidation potentials of Ag and Au make them more stable electrode materials – an important feature because oxidation of the electrode material due to the redox transformation would spoil or destroy the SPR response.

When photons of sufficient momentum couple into the thin metal film, the surface plasmon at the metal/prism interface absorbs the EM wave energy into the metal. Only the p-polarized component of the electric displacement vector (i.e. that component that is in the plane of incidence), can excite a surface plasmon wave – so the illumination source is generally polarized. As seen in Figure 2, the p-polarized light arriving at the prism/metal interface will excite charge density oscillations in the surface plasmons by inducing an oscillating image dipole. This image dipole is additive with the inducing field and the SPR field vectors results in local E-fields up to 200x larger than the incident light field very near to the metal surface. In this case, the weakly bound electron gas (plasmon), acts as a resonator pumped by the EM field of incident photons.

The SPR is a surface EM wave, essentially bound to the outer surface of the metal film. This result is a non-radiative, evanescent wave whose electric field strength is a maximum at the metal-dielectric interface, and decays exponentially into both the metal film and the dielectric. The metal film and the dielectric layers act as a coupled waveguide that supports an evanescent wave. Importantly, changes in the composition of the dielectric (η) near the metal surface will cause changes in the response characteristics i.e. reflectivity (r) as a function of both wavelength (λ) and SPR angle (θ_{SPR}).

1.2.2 Analysis of $\Delta\eta$ with SPR

The distance the decaying EM field extends out from the Au film and into the sample dielectric to a depth of about 200 nm for optical frequency experiments. This depth also defines the maximum acceptable thickness range for the metal film: if the film is too thin (< 45 nm), the resonant interaction is poor and if it is too thick (> 100 nm), and little or no resonance is seen. By keeping the thickness of the metal film at 50 nm, nearly optimal, changes effected in the η_R of the dielectric are reflected in real time as changes in the intensity of the reflected laser beam with lateral resolution as small as $\approx 5 \mu\text{m}^7$. In this work the effective spatial resolution is about 1 mm. This is the basis of many analytical techniques utilizing SPR in organic and biochemistry.^{8,9,10,11,12}

The refractive index and surface quality of the coupling prism onto which the metal film is deposited, the quality of the metal film and the dielectric on the outer side of the film are all important determinants of the position, width and intensity of the surface plasmon absorption. For example, surface roughness in the prism material or metal layer were observed to decrease the SP absorption.

In Figure 3, experimental results obtained by workers in the Terrill laboratory illustrate the presence of a surface plasmon resonance – a band of low reflectivity in the angle-(visible) wavelength plane.¹³ This response can also be accurately calculated with a multiphase Fresnel calculation that describes light reflection at the interface of two or more layers of different materials. For example: a 4-phase Fresnel calculation can yield the reflectivity of the prism-metal interface by using the refractive indices and thicknesses of the prism, metal film, electro-chromic film and solution.

Figure 3: Reflectivity vs. λ (x axis (nm)), and θ (y axis ($^{\circ}$)) red indicates high reflectivity, and blue is low (absorbance).

Figure 4: SPR Response curves in λ space (top) and angle space (bottom) for a clean gold surface (Blue), and the same surface with 20 nm of absorbed dielectric material with an index of refraction of 1.4 (red).

Fresnel equations were not used in this work. Rather, the angle corresponding to SPR was determined by manually rotating the prism and observing the reflected light image. Nonetheless, changes in reflectivity are expected to be a quasilinear function of changes in refractive index when the reflectivity is set to an angle on the side of the SPR reflectivity dip (see below) where $dR/d\theta$ is large.

Figure 4 illustrates Fresnel-computed vertical and horizontal “slices” of the above reflectivity surface. Examining Figure 4, one may observe that the reflected signal shows a total internal reflection of the light while scanning through angle space (bottom graph), with a sudden loss of reflected signal (darkness) at the SPR angle (θ_{SPR}). The total internal reflection resumes once past θ_{SPR} (bottom graph). Figure 4 also demonstrates the effect of the addition of a theoretical material layer 20 nm thick with an n of 1.4 applied to a clean gold surface. This small physical perturbation leads to a substantial shift in the SP resonance in either angle or wavelength space.

For the purposes of imaging with SPR, one typically uses a collimated and expanded monochromatic light source and observes the interface in the reflected light image. In this way, differences in sample-side refractive index induce changes in the resonance condition and hence the light intensity. Note that for angles above and below θ_{SPR} , the $dR/d\theta$ function is actually of opposite sign, and that $dR/d\theta$ is greater on the low angle side of θ_{SPR} (see bottom graph of Figure 4). For the purposes of SPR imaging, where reflectivity is monitored at a fixed angle and wavelength, setting the observation to the sharper shoulder gives greater contrast because a smaller change in refractive index effects a greater change in the reflectivity.

The correct angle (θ_{SPR}) for coupling into the metal film must be met for any specific wavelength. For Au/air, at $\lambda=632.8$ nm (the HeNe laser wavelength used), it can occur over a range of 2-3 degrees at a θ_{SPR} of $\approx 53.7^\circ$. For Ag/air the range is tighter ($\pm 0.5^\circ$) for the same λ . The angle of incidence is measured from normal to the phase boundary (0°) to grazing parallel to the metal surface (90°). The θ_{SPR} increases with the substitution of other dielectrics for air (water, alcohol, and aqueous solutions), with higher index materials resulting in higher θ_{SPR} . The nominal value for the angle θ_{SPR} is dependent upon both the nature of the dielectric on the outside of the metal film, as well as the wavelength of the incident light.

The SPR angle ranges described above, as well as the intensity enhancement, is affected by the quality of the metal film (grain size, and homogeneity¹⁴), that give rise to scattering and dispersive loss effects. The high frequency limit of light that will evoke an SPR response is known as the “plasma frequency” of the metal. The plasma frequency is that frequency at which the evanescent wave is damped out by both the mass of the electron and the electrostatic binding forces acting upon it. Frequencies below the plasma frequencies are reflected, while light frequencies above the plasma frequency are either transmitted or strongly absorbed. Photon energies greater than the metal work function are also inappropriate since their energy is efficiently converted in the photoelectric effect. The plasma frequencies for metals are typically in the area of 10^{16} s^{-1} (Hz). For silver, the plasma frequency is $9.18 \times 10^{14} \text{ s}^{-1}$; this corresponds to a wavelength of 326.3 nm or, $(30646 \text{ cm}^{-1})^{15}$, (UV). For Gold, the plasma frequency is $7.5 \times 10^{14} \text{ s}^{-1}$

corresponding to a wavelength of 399.0 nm (25062 cm^{-1})¹⁴. The visible range of light is $4\text{--}8 \times 10^{14}\text{ s}^{-1}$.

Both Ag and Au have a two-electron system: a nearly free “s” electron ($5s^1$ for Ag, $6s^1$ for Au) and a bound “d” electron that fills the d orbital shell ($2d^{10}$, $3d^{10}$ respectively). It is these loosely bound “s” electrons that populate the surface plasmon. Both Ag and Au were used in the experiments described in this thesis. Silver was used for the under-potential deposition of lead. Gold was used for electro-chromic film experiments. Several factors made silver the more attractive metal film. Silver has a narrower range of angles over which it exhibits SPR so the response is crisper. The adhesion of gold onto the prism could not be achieved without a chromium interlayer, affecting signal strength, and further broadening the SPR peak. While Ag is cheaper than Au, it does suffer from electrochemical oxidation at relatively low (+) potentials. Since both metals are popular for SPR, this also meant plenty of reference sources were available.

1.3 Imaging SPR

Variations in the SPR reflectivity are brought about by controlling the electrochemistry. Graphs of reflected light intensity reveal boundaries in the plane of the electrode where electrochemical states change from reduced to oxidized – these boundaries typically appear where the local electrode potential crosses the E° value for the operative redox reaction.

SPR has been used in conjunction with electrochemistry to provide an alternative metric of the extent of a given interfacial transformation.

A handful of reports have appeared in which in-plane electrical currents have been used in electrochemical settings to exert spatiotemporal control over local redox processes – one of these used SPR to visualize the events.¹⁶ As in this latter report we are controlling, at least in the dimension of the current flow, the *location* of electrochemical events by applying a potential gradient across the face of the metal film. The two electrical handles by which this boundary is controlled are illustrated in Figure 1 and are: **a.** the potential applied between opposing edges of the Au film, termed E_{BIAS} , and **b.** the potential applied to the solution layer with the potentiostat. This boundary was moved across the film in some experiments, or held it in one location under varying voltage gradient conditions in other experiments. These two modalities, termed translation and expansion respectively, are explained graphically in Figure 5. Simply stated, changing E_{PSTAT} alone *translates* the $E^{\circ'}$ transition point across the film, where maintaining the average of $E_{\text{PSTAT}} + E_{\text{BIAS}}$ and E_{PSTAT} while decreasing their difference *expands* the gradient – the limit of which is simply $E_{\text{BIAS}} = 0$, where the entire film is uniformly oxidized or reduced. The peak shape on the vertical axis represents the electrochemical peak. The small dashed lines denote the local film potential at a given point within the Au film plane assuming uniform conductivity and perfect contacts. The bold, dashed line denotes the potential where electrochemical oxidation occurs ($E^{\circ'}$). Intersections between $E^{\circ'}$ and the local potential correspond to regions where the film property (i.e., color) changes. Part A is a consequence of changing the potentiostat setting E_{PSTAT} at constant E_{BIAS} . This moves the intersection between the local potential (sloping lines) and the formal potential

Figure 5: An idealized illustration of the consequences of in-plane electrical gradients on the distribution of redox states (encoded in grayscale) across the electrode surface.

of the electrochemical transition (E° , bold, horizontal dashed line) in the x-dimension – a process termed “translation”).

Part B illustrates a process wherein the average potential ($E_{\text{BIAS}} + E_{\text{PSTAT}}$ and E_{PSTAT}) are maintained, but their difference, i.e., the in-plane gradient, is decreased. Such a process expands the transition region between oxidized (dark) to reduced (light) areas. When E_{BIAS} is zero, the entire film is identical electrochemically, but as E_{BIAS} is increased, from a,a' to c,c' an increasingly sharp gradient is produced. This process is termed “expansion.”

Electrochemical events are thus controlled through the combination of E_{BIAS} and E_{PSTAT} . The resulting SPR image yields a surface contour in the image that reveals the potential threshold boundary for the electrochemical event. Because E° is well known from CV experiments, the boundary line in the image is an equipotential contour line. Various image analysis software packages were used to illustrate this boundary line and comparison with expectation are illustrated below.

2.0 Experiments

The experimental apparatus is similar to that used by the Gerhard Ertl group (Fritz Haber institute of the Max Plank Society in Berlin).^{17, 18} The Ertl group used SPR imaging to explore electrochemical catalysis mechanisms, and kinetics, growth and pattern formation in non-equilibrium electrochemical systems,^{19, 20} oscillating electrochemical systems,^{21, 22} and electron-phonon interactions at surfaces.^{23, 24} This and other electrochemical SPR work is characterized by the use of SPR imaging to reveal

subtle interfacial phenomena. In contrast, this thesis describes the use of SPR imaging to reveal the gross level redox changes that we control using in-plane potential gradients.

The electrochemical systems used for this study were diverse. To test the feasibility we first used the Under-Potential Deposition (UPD) of Lead onto a silver film. The second electrochemical event studied was the reaction of an electroplated Prussian Blue film on a gold film surface being reduced to Prussian White (transparent). The third electrochemical event was the electro-polymerization of aniline. These events are all electrochemical and therefore dependent upon certain potential conditions.

2.1 Under-Potential Deposition (UPD) of Lead

Lead deposits on silver at a potential more positive than that at which lead would normally bulk deposit: first, a monolayer is deposited ($\approx 5 \text{ \AA}$), followed by bulk deposition. These two events happen at different applied potentials due to the difference in the work functions of Ag and Pb. This difference in the electro-chemical potential of the Ag/Pb monolayer and the Pb/Pb bulk deposition phase creates an opportunity to have multiple events occurring simultaneously across the working electrode, that effect the SPR response to differing degrees. Boundaries for both the first monolayer of lead (UPD), and the bulk layer that follows with a more negative potential, have been resolved in the same image differentiated by their respective changes in reflectivity (Θ_{SPR}). The observation angle was set just off resonance in such a way that monolayer deposition shifted the affected area of the WE towards a resonance condition (low reflectance). The much larger impact of bulk Pb deposition was observed to further shift the Θ_{SPR} back out of resonance yielding increased reflectivity. The UPD monolayer of Pb changes the

dielectric of the silver film surface because water molecules are replaced with lead atoms. The formation of a monolayer of lead has a lesser effect on SPR than the deposition of the bulk layer because of the difference in thickness of the material on the silver surface.

The kinetics as well as the electrochemistry of Pb UPD are well documented.²⁵ The deposition conditions were set according to Stevenson, et al.²⁶ See below for details.

2.2 Prussian Blue Reduction to Prussian White

Prussian Blue, aka Turnbull's blue is an inorganic compound ($\text{Fe}_4^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_6]_3 \cdot 4\text{H}_2\text{O}$) that was commonly used in making blueprints, but obtained its name from its use in dyeing the uniforms of the Prussian military. By reduction, it can be converted into a colorless form called Prussian White, ($\text{KFe}_4[\text{Fe}(\text{CN})_6]_3$). PB can be electrochemically deposited as a thin film on an electrode surface. In depositing the PB onto the gold surface, we used both the potentiostatic and galvanostatic methods described by Brennan et al.²⁷ The loss of the blue color indicates a shift in the refractive index. This shift is manifested in the SPR response during the electrochemical cycling. This shift was more visible to the eye than was the UPD of lead. It was found that a thinner PB film worked better for our system (≈ 5 nm).

The oxidation of Prussian Blue (PB) to Prussian White (PW) on Au yielded a much more subtle change in comparison to the UPD of lead on Ag. The PB preparation conditions described Brennan, Sun, and Weber were used in this work.

2.3 Electro-polymerization of Aniline

There has been plenty of work using SPR to measure thin organic films.^{28,29,30}

Preparation conditions for the electro-polymerization of polyaniline followed Baba et al.

³¹ Aniline forms a conductive polymer that is used in a broad spectrum of applications.

Our interest in it stems from the process of electro-polymerization that occurs between 0.5 – 1.0 V_{DC}. As the aniline is polymerized onto the gold surface, it changes the index of refraction by replacing the solution as the dielectric. The change in the refractive index is proportional to the length of the polyaniline chain, this can be resolved by SPR imaging of the surface to which the polyaniline is attached. This is similar to the UPD of Lead, in that the more deposition, the greater the change in resonance conditions. In addition, PANI can be made to undergo electro-chromic cycling, a process easily reversible, unlike the initial polymerization.

Aniline

Polyaniline base unit

2.4 Apparatus

The optical data are the variations in signal intensity of the reflected probe beam.

The optical path consists of the probe laser beam (5 mW HeNe (632.8 nm)), a beam expander, a variable polarizing filter, the SF10 coupling prism (onto which is deposited the metal film WE), a mirror, a paper screen, and a CCD camera (SBIG ST-8T, CCD

Soft) to record the image (Fig. 6). The image is difficult to see visually as the speckle from the laser tends to obscure the contrast of the SPR response image. The CCD camera yields digital data that can be manipulated. Analysis of the images is a digital map of the intensity levels across the image. The electrochemistry takes place in a Teflon cell. The metal-coated side of the SF10 coupling prism is held against an o-ring seal on the side of the Teflon cell. Access to the cell is through the top; a cap holds a reference cell, counter, or auxiliary electrode approximately an inch cube of machined Teflon, (Fig 7). Connection to the film surface is made either using a copper tape with a conductive adhesive, run in a strip along a side of the coated plane of the prism and outside of the o-ring seal, or a thin silver ribbon is attached to the same location with silver paint. This is the working electrode. A similar connection is made on the opposite side of the metal film, where the bias potential provided by a HP 6205B Dual DC Power Supply and monitored with an HP 34401A Multimeter. The reference electrode (Ag/AgCl in 3M NaCl) is inserted through the lid. The counter (auxiliary) electrode is a platinum wire coil, one end of which extends through the lid of the cell. Another small hole is in the lid for either a N₂ sparging line or another wire electrode.

The volume of this cell is approximately 7 ml. Since the prism face is 25 mm on each side, the cell cube was built to the same size for alignment in the holder. For the stability of the connections, a wiring halo surrounds the prism/cell assembly holder providing, a solid through connect between instrumentation and the connections to the electrochemical cell (Fig. 8). The silver or gold film is the working electrode for the potentiostat (EG&G Princeton Applied Research model 263A).

Figure 6: Beam line with experimental set up and instrumentation.

Figure 7: The Electrochemical cell L to R; SF-10 prism coated with Cr/Au, The e-chem container with o-ring, and the lid with the Pt coil Auxiliary electrode and the (Ag/AgCl) reference electrode.

A PC is used to control the potentiostat and the CCD camera. For the UPD of lead we used the same PC for both controls. For the other two experiments, we used separate PCs to control the camera (CCDsoft from Santa Barbara Instruments Group “SBIG”) and the potentiostat (EG&G PAR M273 software). Future improvements: machine Teflon cube for better access to metal face for contacts, use of translucent screen to replace paper screen.

2.5 Design of Experiments

Experimental design sought to establish threshold lines of potentials at which multiple electrochemical events would occur. Demonstration of control of the location of the boundary line was established in two ways: First, a bias voltage was held constant, while the potentiostat swept through a programmed range of voltages and currents. After the sweep, the bias voltage would be adjusted, and the potentiostat would repeat the sweep to show movement of the electro-chemical boundary, these are referred to in section 1.3 as a “translation”. This is termed “translation” because the boundary for the electrochemical events is moved across the face of the metal film. Second, was to change both bias voltage and applied voltage to maintain the boundary in a stationary position while the gradient of the potential is increased across the film; this we referred to as an “expansion”. “Expansion” is so called because the bias potential gradient across the metal film is increased, while the electrochemical boundary is kept at the center of the film by reducing the applied voltage. Both these techniques were applied to the first two electrochemical events: UPD of Lead, and PB reduction to PW. The electro-polymerization of aniline was only “translated” to confirm control for the electro-

Figure 8: Assembled electrochemical cell with wiring halo and attached copper tape leads. Note the resonance condition across the Au electrode surface 1/2 reflective, 1/2 dark.

chemical event since the electro-polymerization process is non-reversible. However, aniline does undergo multiple electro-chromic changes during CV, which have been recorded to show extent of coverage of the WE.

2.5.1 UPD of Lead

The underpotential deposition of lead onto silver occurs as a single monolayer and is formed at potentials positive to the E^0 (Pb^{+2}/Pb) by .100-.200 V. Once this monolayer is formed, bulk deposition begins at E^0 (typically $\approx$ -.300 V (vs. Ag/AgCl)) and below (negative). A thin film of silver (nominal 45 nm of .9999 Ag) is laid down by metal vapor deposition upon one face of the SF-10 prism. This is then placed in the holder along with the Teflon electrochemical cell. A solution was prepared: 0.1M NaClO_4 , 0.01M HClO_4 , 0.005M $\text{Pb}(\text{ClO}_4)_2$ (all reagent grade), and poured into the e-chem cell to provide for electrochemical deposition of the lead ions.

Voltages are applied across the silver film using the power supply: these are referred to as the Bias Voltage. The voltage applied between the silver film and the solution by the potentiostat is referred to as the applied voltage. These naming conventions will hold throughout this thesis. Tables 1 and 2 correspond to the conditions for “expansion” and “translation” respectively. Prior to setting these conditions, a Cyclic Voltammogram (CV) of the UPD of lead is run to confirm the electrochemical events. This has been video taped (see movie 1 on CDRom). The extent of the electro-deposition of lead in the monolayer is approximated by the following form of the Nernst equation:

$$E = E^0 + \frac{RT}{nF} \ln \left(\frac{\gamma_o A}{\gamma_R V_s N_A A_a} \right) + \frac{RT}{nF} \ln \left[\frac{(1-x)}{x} \right] \quad \text{Eq 8}$$

The first term is E^0 the standard potential. The second term deals with the UPD monolayer where γ_o is the activity coefficient of the oxidized species, γ_R is the activity coefficient of the reduced species. R is the Gas constant (8.314510 J/mol-K), F is Faraday's constant (9.6485309 x 10⁴ C/mol) n is the number of electrons exchanged (mol), T the temperature (K), N_A avagadro's number (6.0221367 x 10²³ /mol, A_a is the cross-sectional area of the molecule being reduced, V_s is the volume of the solution. The last term is for the bulk deposition and x is fraction of the oxidized species that is reduced. The distribution of bias potential is assumed to be Ohmic ($E=IR$) in that R varies linearly with the distance between the two sides of the metal film. We found our peak θ_{SPR} for the bare silver film at 57° between the normal to the silver film, and the laser beam line.

2.5.2 PB reduced to PW

The deposition of PB onto the gold surface and the subsequent reduction to PW was performed following Brennan et al¹⁷. A solution was prepared for the deposition of PB onto the gold film consisting of: 0.010M FeCl₃, 0.010M K₃Fe(CN)₆, in 0.010M HCl using all reagent grade source chemicals. While both potentiostatic and galvanostatic methods were investigated, the galvanostatic method proved to work best. Initial investigations into this electrochemical system were performed on a microscope slide coated with Cr/Au. These were immersed in the above solution and coated with PB. A

TABLE 1: UPD “Expansion”

Bias Voltage	Applied Voltage	Photo (Fig 13)
0.0	-.35	12A
-0.5	-.30	12B
-0.1	-.30	12C
-.20	-.25	12D
-.30	-.20	12E
-.40	-.15	12F
-.50	-.10	12G
-.60	-.05	12H
-.70	0.0	12I

TABLE 2: UPD “ Translation”

Bias Voltage	Applied Voltage	Photo (Fig 9)
-.50	-.35	9F
-.50	-.30	9E
-.50	-.25	9D
-.50	-.20	9C
-.50	-.15	
-.50	-.10	9B
-.50	-.05	
-.50	-.00	
-.50	+.05	9A

Tables of experimental parameters used in the UPD of Lead.

0.1M solution of KCl (reagent grade) was used for the electrolyte. Preliminary tests were done to characterize the formation of the PB film, as well as testing control of the redox between PB and PW using a bias potential (see movie 6 on CDROM). After confirming these processes, we proceeded to apply a PB film to a gold-coated prism. Initial attempts at film deposition resulted in many destroyed Au films until we switched from potentiostatic deposition to galvanostatic deposition – likely a problem with the reference connection to the potentiostat – this was refreshed the 3M NaCl solution inside the body of the reference electrode and fitted with a new frit. After arriving at a suitable recipe for film deposition, it took a three more trials to determine a nominal thickness for the film. Using this formula¹⁷ to calculate the thickness:

$$d = \frac{QtN_A}{4nF} \quad \text{Eq 9}$$

(where d is thickness, t is time Q is charge, N_A is Avogadro's number, n is the number of electrons transferred, and F is the Faraday constant), a target of 5 nm thickness of PB film was determined to be optimal. To achieve this a current of 10 μ A was applied for 118 s. Optimal SPR response was seen at 52° between the laser beam line and the normal to the gold surface. An initial CV was performed to test the film. To expedite data acquisition we utilized the auto feature of the camera that allowed us to photograph at preset intervals and by adjusting the CV sweep rate, we were able to resolve every 20 mV increment. Setting the bias voltage to 300 mV and the CV sweep from –200 mV to +200 mV at a sweep rate of 5 mV/s an image was captured every 4 seconds for the “translation” data. For the “expansion” data, we had to manually adjust the bias power

supply for each setting. The bias voltage was varied in 50 mV increments between 0 and 700 mV, while the applied voltage from the p-stat varied from +179 mV to – 171 mV in 25 mV increments. For each pair of voltage settings, an image was captured. The settings for the “expansion” data are in table 3.

2.5.3 Electro-polymerization of Aniline

The formation of polyaniline through electro-polymerization is a straightforward process. Deposition occurs between 0.5 and $-1.0 V_{DC}$ and each successive sweep adds length to the polymer chain. By controlling the bias voltage to exclude portions of the gold surface from electro-polymerization, and including multiple sweeps, control of the process can be shown and allows us to thereby map the potential across the gold surface. Aniline was inhomogeneously polymerized onto a gold surface in two steps. The first step was to coat PANI across 50% of the gold surface, then 75%. After each electro-polymerization, the film underwent electro-chromic cycling. A solution of 0.1M aniline was prepared in 0.5M H_2SO_4 – all source chemicals were reagent grade. Sparging was done with clean dry N_2 . Deposition was done by CV sweeps between -0.200 to $1.00 V_{DC}$. The bias voltage settings were; 0.872 and $0.840 V_{DC}$, for these CV sweep parameters. For the electrochromic cycling of PANI we used a bias voltage of $0.402 V_{DC}$ and swept the potentiostat between -0.400 to $+0.400 V_{DC}$. The auto-imaging feature described above was used again to obtain the images for this portion of the experiment.

Table 3: “Expansion” experimental parameters for PB-PW

Bias Voltage (mV)	Applied Voltage (mV)	Image
0	179	18A
50	154	18B
100	129	18C
150	104	18D
200	79	18E
250	54	18F
300	29	18G
350	4	18H
400	-21	18I
450	-46	18J
500	-71	18K
550	-96	18L
600	-121	18M
650	-146	18N
700	-171	18O

3.0 Results

The data results from these experiments come in three forms: recorded images, cyclic voltammogram (CVs) and digital movies. The digital movies are for documentation and visualization of the processes recorded. The CVs are for coordination of electro-chemical events with potential conditions as well as presentation of the data. The main source of hard data lies in the digital images recorded during the course of the experiments as they relate to electro-chemical conditions.

3.1 UPD of Lead

The CV in Figure 9 exhibits behavior that matches literature references for the CV of UPD of lead; the monolayer beginning to form at $\approx -0.30 V_{DC}$ and bulk deposition at $\approx -0.42 V_{DC}$ the cathodic sweep sees the removal of the bulk layer immediately and removal of the monolayer at $\approx -0.30 V_{DC}$. By adjusting where these potential boundaries lie on the silver plane the location where the UPD monolayer occurs as well as bulk deposition can be moved and therefore the SPR response can be positioned on the metal plane. This is the basis for the “translation” strategy. Figure 10 is a series of images depicting the formation of the monolayer followed by the bulk layer. Figure 10A has no deposition, 10B shows the beginning of the monolayer forming at the bottom of the circle. 10C shows more of the monolayer forming at bottom, 10D shows the monolayer at the midpoint as well as the start of the bulk deposition at the bottom. Figure 10E has the monolayer 3/4 of the way across the image, 10F has the monolayer almost at the top of the image. It is important to note that in Figures 10D, 10E, and 10F that the width of the monolayer is consistent as determined by the electrochemistry.

Figure 9 Cyclic Voltammogram of the deposition of lead onto a silver film.

10A

10B

10C

10D

10E

10F

Figure 10: UPD and bulk deposition of lead on a silver film

The intensity plot in Figure 11 demonstrates the ability to map the potential boundary across the silver film. Looking at the intensity map, we see that the line corresponding approximately to C19 generally defines the boundary for the monolayer/bulk layer interface. The imaging angle was set just off peak resonance and such that the monolayer deposition further reduces resonance and yields a brighter region. The boundary between monolayer and bulk is approximated by the resumption of the dark resonance conditions and subsequent transition off resonance. This sequence of light-dark-light for the monolayer-bulk transition implies that the first and subsequent Pb layers have an opposite impact on the effective interfacial dielectric. The prism angle was set initially off resonance just enough that both for monolayer and bulk deposition were visible in the same image. The series of images in Figure 10 are recorded as movies 2 and 3 on the CDROM. Figure 12 is comprised of six images depicting the removal of lead from the metal film. This removal occurs in the reversal of deposition in that the bulk layer is removed first then the monolayer. The boundary is not as crisp or clear as in the deposition perhaps implying that the kinetics of removal are not as uniform as those of deposition. Interestingly, the removal of bulk Pb from the surface tended to leave an island of bulk Pb as seen in 12D.

Figure 13 is a series of nine images depicting the range of conditions for the “expansion “ portion of the UPD experiment (Refer to Table 1 for the conditions for each image). The significance of these images is that they show that as the potential gradient increases across the film, so does the contrast and sharpness of the transition boundary increase. This can be seen in movies 4 and 5 on the CDROM. This is expected from the

Figure 11: 3-D Intensity plot of image 9E shown above.

12A

12B

12C

12D

12E

12F

Figure 12: Removal of lead from silver film

13A

13B

13C

13D

13E

13F

13G

13H

13I

Figure 13: Expansion of bias and applied voltages for the UPD of lead. From A-I an increasing gradient is introduced into the Ag film surface. See table 1 for details.

electrochemistry; a larger gradient assures that at the more positive side of the silver film, no lead is deposited, and on the negative side, more lead is plated. The conditions were chosen to keep the center of the silver film at a $-0.35 V_{DC}$ potential difference between the film and the solution.

By varying the incrementally increasing E_{PSTAT} and decreasing E_{BIAS} the center of the Ag film was maintained near: $(V_{Bias}/2) + V_{Applied} = -0.35 V_{DC}$, ensuring that the electrochemical boundary between monolayer and clean Ag would remain at the center of the film, while the electrical gradient within the film was systematically increased. Figure 13 is an intensity plot for image 12I, the sharpest of the boundary conditions. Intensity plots for the other images in figure 12 show a trend towards increasing contrast between the two sides of the center potential boundary as the series progresses (see movie 5 on CDROM). Deviation from an ideally linear potential boundary may be due to any combination of three possible sources (see Figure 14): **1.** Inhomogeneity in and/or scattered multiple electrical contacts between the gold film and the copper adhesive tape (see Figure 7) may cause the irregularities in the boundary lines. **2.** Defects or inhomogeneity in the metal film will change both the conductivity and the SPR response. **3.** Optical aberrations, possibly related to the Gaussian beam profile.

3.2 Reduction of PB to PW

Figure 15 is a cyclic voltammagram (see movie 6 on CDROM) illustrating the reduction of Prussian Blue to the transparent Prussian White (lower curve) and the reverse oxidation of PW to PB (upper curve). These correspond closely with the work published by Brennan et al. Their peaks were better defined as might be expected since

Figure 14: Intensity plot of figure 12I showing the boundary at R26

15A

15B

15C

15D

15E

15F

15G

15H

Figure 15: Cathodic sweep of lead on silver

Figure 16: Cyclic Voltammogram of the electro-chromic cycling of Prussian Blue to Prussian White (clear).

they were using a thick Au film (> 500 nm). The reduction of PB to PW occurs when the potential is swept between $+0.40$ to -0.11 V_{DC}.

The contrast in the SPR images for the PB/PW transformation is less than that observed for Pb on Ag. This may be due to a small effective change in refractive index for the PB/PW couple, or the sharper resonance observed for Ag. A quantitative analysis of such differences is beyond the scope of the present thesis. This is evident in the small changes in the images in Figures 17 and 19, as well as the lower gradient slope across the intensity plot in Figure 18. Contrasted with the similar analysis of the deposition of lead seen in figure 13, the boundary is less well defined, yet definitely present (see movies 7 and 8 on CDROM). The visual data in Figures 17 and 19 is not as well defined as the UPD of lead. Intensity plot analysis shows a definite boundary at the PB-PW interface (see movies 9 and 10 on CDROM). This gradual slope is reflected in the smooth gradual lines of the CV in Figure 16. Contrast the peaks in the CV in figure 9 with the CV in figure 16. The sharpness of the SPR response mirrors the difference in peak sharpness. The data gathered for this portion of the experiment employed a software feature that automatically takes pictures at preset time intervals. The time intervals were determined by the CV sweep rate and the process time for each image. By adjusting the sweep, we were able to take an image for every 25 mV step of the potentiostat.

3.3 Electro-polymerization of aniline to polyaniline

Figure 20 is the CV for the electro-chromic cycling of a PANI film (see movie 11 on CDROM). There are three color states in this CV. This electro-chemical behavior is evidence of the presence of the PANI film. By using an electrostatic barrier (bias

17A

17B

17C

17D

17E

17F

Figure 17: Translation sweep of PB to PW

Figure 18: 3-D intensity plot of figure 16C.

19A

19B

19C

19D

19E

19F

19G

19H

19I

19J

19K

19L

19M

19N

19O

Figure 19: "Expansion" of PB reduction to PW

voltage), one half of the Au electrode was coated with PANI as the electro-chromic cycling appears on only half of the electrode face (see movie 12 on CDROM). Reducing the electrostatic barrier we allowed the PANI formation over seventy five percent of the electrode face, and again it underwent electro-chromic cycling (see movie 13 on CDROM). Figure 21 shows part of a voltage sweep across the Au surface, note the image only changes on the right side. In Figure 22 the steep change in intensity that occurs in zone across the image between C16 and C19 denotes where the PANI begins. Figure 23 is a photo of the partially covered Au surface on the PANI trials it appears dark green.

4.0 Analysis

To map the potential boundary layers, images were simply inspected for regions of pronounced change in the intensity of the reflected light. To do this the intensity plotting function of CCDSoft was used again, but with an altered the perspective angle such that a to give us a 2-D map of the surface intensity change was encoded clearly in color. If the electrochemical system is Nernstian, the $E^{\circ'}$ boundary should correspond to a maximum in dI/dx and hence dR/dx i.e., the peak spatial variation in reflectivity appear at $E^{\circ'}$. So, maxima in ΔI define the electrochemical boundary line(s) and thereby map an equi-potential boundary line across the surface. This was *not* done analytically because the noise level in the data is prohibitive of a derivative analysis. But visual inspection of images, for example the translation experiments of Figures 10 and 17 qualitatively reveal this to be the case. Revisiting Figures 13 and 19 it is clear that the slope of ΔI increases with the slope of the bias potential at the boundary. In Figure 24,

Figure 20: Cyclic Voltammogram of polyaniline film on a gold surface.

21A

21B

21C

21D

21E

21F

Figure 21: Electrochromic voltage sweep across polyaniline.

Figure 22: 3-D plot of figure 20E.

Figure 23: Polyaniline inhomogeniously coated onto Au metal film (dark green material in the lower half of the circle). Note remnants of silver strip/silver adhesive electrical attachments on either side (the prism is laying on one side)

the intensity surfaces for Figure 10 have been labeled with hypothetical equi-potential lines (assuming a linear potential distribution between electrical contacts to the metal film according to Equation 5) for 0.34 and 0.42 V_{DC} , these being the potential boundaries for the UPD and the bulk deposition of lead. By increasing the bias voltage, we “translated” these barriers across the film. Figure 25 comprises intensity surface plots for Figure 17. The single equi-potential line corresponds to the barrier potential for the reduction of PB to PW ($\approx 0.3 V_{DC}$).

As can be seen in the CV in Figure 16 the redox reaction does not have a well defined boundary for the reaction, hence the lessened resolution for the barrier. The reason that the lines are at about 45° with respect to the image is that, in an effort to make better contacts, copper tape was applied at opposing corners to maximize surface area for adhesion/contact. Both Figures 24 and 25 demonstrate an ability to translate the electro-chemical boundary/barrier across the surface, and even into regions of the surface dependent upon contact locations. A simple test of this would be to make a four corner contact with potential control over each corner to push the electro-chemically active region around the surface.

Figure 26 is the intensity surface plots for Figure 13. The single equi-potential line across the plot corresponds to the barrier potential of $-0.35 V_{DC}$. This potential is maintained in place while the potential gradient is expanded to both sides of the barrier. The effect is to sharpen the electro-chemical boundary as can be seen in the progression of the plots, each succeeding plot has more intensity and detail on the upper right half and less intensity/detail on the lower left side. This demonstrates the effect of the

Figure 24: Intensity surfaces for Figure 10

Figure 25: Intensity surfaces for Figure 17. Equi-potential line $\approx 0.3 V_{DC}$.

Figure 26: Intensity surface plots for Figure 13. The equi-potential line represents a potential barrier of $-0.35 V_{DC}$ held constant while the gradient of the potential is increased. Note the recession of the image to the upper right corner as the gradient is increased.

“expansion” criteria stated above. The fifteen images that comprise Figure 19 were also converted to intensity surfaces in Figure 27. These series of images exhibit the same behavior as in Figure 26, but as in the translation contrast, the sharpness of the Prussian Blue/Prussian White system is not as crisp as in the lead UPD system. By increasing the potential gradient while maintaining the barrier potential fixed at the midpoint of the electrode surface the contrast in the SPR response is increased. This boundary in the optical image corresponds to an equi-potential line across the charged metal surface. Another contrast between the UPD and PB-PW systems is the quality of the electrical contacts. With the UPD system the boundary lines have odd shapes corresponding to spotty contact points along the length of the Cu tape connections applied along the very narrow edges of the metal coated prism. In the PB-PW system the Cu tape was applied to opposite corners and the results were more uniform. With the PANI depositions we used thin silver ribbon applied with paint-on silver conductive adhesive and figure 27 shows a better uniformity of the boundary line across the film. PANI was done a bit differently; a bias voltage was used to *deposit* the PANI across half the gold surface, as opposed to simply observe electro-chromic boundaries in a uniform coating. The PANI was then electro-chromically cycled such that only the coated half could be observed to oscillate the SPR reflectivity (see movie 12 on CDROM). The lines across the intensity plots are not equi-potential lines, but the limits of coverage of PANI across the film. The same surface was then re-coated at 3/4 coverage of PANI and again electro-chromic cycling was done (see movie 13 on CDROM). Figure 28 is four intensity surfaces of images from the electro-chromic cycling of the 3/4 covered film. The electro-chromic changes detailed in

Figure 27: Intensity plots of Figure19

Figure 28: PANI electro-chromic cycling on 50% covered film.

Figure 29: PANI electro-chromic cycling on 3/4 coverage. Red line is limit of PANI coverage on the electrode surface.

the CV of Figure 20 are occurring only on the coated portion of the film. These last two figure demonstrate control over PANI electro-polymerization by use of a potentiostatic barrier (bias voltage).

Thus far we have shown the basic premise behind this work, and some image analysis with equipotential lines drawn across some figures to show control. While the data corresponds to what we see in the images a simple and crude numeric analysis can confirm these correlations. Using Figures 10C, 10D, 10E, and 10F we can perform a numerical analysis based on Equation 5, and compare these to the data in Figure 9. From Figure 9 it was ascertained that the monolayer forms beginning at $-.30 V_{DC}$ and that the bulk layer forms at about $-.42 V_{DC}$. With this data a line profile of the intensity distribution along the axis of the bias voltage was generated by means of image analysis software. By measuring the width of the image, and the position of the features observed in the UPD of lead, the portion of the bias voltage at positions along the plot was determined. Using Equation 5 a potential value was assigned to these features and compared with the E° data from the CV. Figure 30 shows the results of hand measurements and calculations. The results show a correlation with a calculated difference of only 5 % from the literature for the monolayer/bulk deposition image boundary. This is clearly within the error expected for a hand measurement. Within this variance, the monolayer image boundary corresponds to the peak of the monolayer deposition rather than the onset. The graphically determined values for the bulk/monolayer boundaries are very consistent; varying $\pm 0.005V$ for the monolayer boundary. No significant variation was observed for the bulk boundary at $-0.40V_{DC}$.

Figure 30: Line plots of figures 9C through 9F

Image Ag 09 (9E)

Intensity profile of arrow ROI

3-D profile of intensity.

Area plot of image Ag 09

Figure 31: Image, Intensity line plot, 3-D Intensity plot, Area plot, all of the same image with the CV for lead on silver.

5.0 Conclusions

Figure 30 is a summation of the data for the Figure 10E. A correlation between the electrochemical data in the CV, and the analysis of the SPR image by correspondence to the electrochemical conditions at the surface of the electrode was shown. By linking SPR response to electro-chemical events that can be controlled by a bias potential across the surface of a metal surface SPR resonator (the working electrode in the electro-chemical systems), lines of equi-potential value can be mapped from images of the surface image SPR response as variations in the intensity of reflected light. The distribution of potentials within the metal films was observed in many cases to be nearly Ohmic.

6.0 Future Work

We would like to establish a mathematical link between the Nernst equation, and the term for the index of refraction of the dielectric in the Fresnel equation. This would involve a mathematical link between the extent or percent reduced/oxidized species ratio and the change in refractive index of the superstrate species. The PB/PW system may work best for this since there are only two species with distinct indices of refraction. This would possibly give a linear mathematical relationship. Each electrochemical system would have its own set of conditions dependent to varying extent on the chemical kinetics involved, and their relation to changes of the refractive index. Can this be used as an analysis technique for chemical kinetics?

J.B. Pendry of the Blackett Laboratory of Imperial College in London has done some interesting work on optical responses of thin metal films with AC signals fed through them.^{32,33,34,35,36,37,38,39,40}

It is of interest to us to extend and utilize Pendry et al. work to further investigate the SPR response to metal films under oscillating voltage conditions. Some changes in the experimental set up may be called for. In the electrochemical cell: replace the Pt coil with a Pt grid to eliminate possible inductive effects, reconfigure e-chem. cell/prism/mount to improve electrical contact geometries towards greater linearity in the potential field lines. Possibly investigate paint-on seal materials. In the beam line: a possible neutral density filter to reduce the number of photons at the metal surface, use a translucent plastic film for imaging rather than a paper surface, thus enabling imaging from the reverse side of the film. This may eliminate the specular reflection from the laser. Perhaps investigate alternate substrate/superstrate materials such as lithium niobate.

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