FEASIBILITY OF ELECTRODEPOSITION
OF YTTRIUM AND BARIUM

by

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Department of Materials Science and Engineering
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ABSTRACT

Investigation of the feasibility of separately electroplating yttrium and barium from solution each on a separate substrate has achieved successful deposition, reproducible electroplating parameters, and consistent material quality. The electrochemical deposition system common to the deposition of both elements utilizes a non-aqueous solvent, metallic salts, and an apparatus which isolates the solution from atmospheric moisture. Its assembly is explained in detail as is the deposition process used. Each electrodeposition system is governed by certain critical parameters. These parameters are determined and the supporting evidence showing their critical nature and impact on the system is explained. Plated samples are evaluated using visual analysis, SEM, EDAX, and XPS to determine macroscopic and microscopic morphology, adhesion, and composition. This barium and yttrium electrodeposition process achieved may offer a new approach to fabricating high temperature superconductor precursors.

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Mira Misra has also supported and helped in much of the detailed work. Because of her related work, the investigation of electrodeposition has allowed new possibilities in the area of process monitoring. As I choose a Ph.D. thesis, Mira's advice will likely be instrumental.

The generosity of the W. H. Brady Company and C. S. Draper Laboratory is gratefully acknowledged.

Above all, I cannot express the depth and breadth of love and encouragement my loving wife and best friend, Cathy, has provided through all of this. She has held a family together in the many hours of "Dad's" absence.

TO MY GOD WHO CREATED ALL
AND ALLOWS US TO
STUDY, TOUCH, AND USE
HIS CREATION

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Chapter 1 INTRODUCTION

1.1 General Background

1.1.1 Origins of Electrodeposition

Although electroplating and electrodeposition contribute to many of the products commonly available it is a relatively young science which extends from two much older independent disciplines: chemistry and electromagnetism.

In 1786, Luigi Galvani, an anatomy professor at the University of Bologna in Italy accidentally observed that a spark of electricity induced a contraction in a frog's leg. His attempt to reproduce this event by hanging a skinned rear leg of a frog from a copper hook was not successful; however, when he attempted to remove the leg using an iron bar, the desired contraction occurred.[1] Galvani published his theory in 1791 which was widely accepted but incorrectly identified the muscle as containing this "animal electricity" which was conducted by the blood and nerves. In 1800, Alessandro Volta stated his opposition to Galvani's theory posing instead that the electricity was due only to the contact of two dissimilar metals.[2] He proved his position by producing a spark of electricity from his voltaic pile, a stack of alternate silver and zinc plates. This was the first battery and truly the birth of electrochemistry.[3] Seemingly, the age-old dream of producing gold from less expensive materials was at last partially achieved.

Having electricity readily available through batteries greatly accelerated the study and application of electricity. In 1803, Brugnatelli, a pupil of Volta's, became the first to gild or plate a metal by means of galvanic current. De la Rive continued work on the process making it a practical technique.[4]

1.1.2 Common Plating Practices

The vast majority of electroplating is done in aqueous solutions by galvanostatic or potentiostatic techniques. In both techniques a metal salt is dissolved in water, at least two electrodes are introduced into the solution, and a current or voltage is applied. The metal then plates out from the ions in solution through reduction at the cathode. Table 1 shows an example of two plating baths used for decorative gold plating. Low and High refer to the concentration of gold cyanide in the bath. Each bath provides specific results.[5]

Each of the components or procedures of a plating system can be varied to obtain differing deposition morphologies, thicknesses, or process efficiencies. A final deposition product can be optimized by using a suitable combination of non-solvent parameters.

Aqueous plating systems[1] have allowed the common industrial plating of most transition metals, some non-transition metals, and even some alloys. Appendix A provides a listing in the form of a highlighted Periodic Table of those metals which are readily plated from aqueous solutions. Appendix B furnishes a listing of those alloys which can be commonly plated.

1.1.3 Plating of IIA And IIIA Metals

As can be seen from Appendix A, Group IIA and IIIA metals are not commonly plated from aqueous solution. These metals usually find purpose not in their pure metallic form, rather, they find it as a member of various compounds.

For the most part, these metals react violently with water.

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[1] Systems is used to refer to the entire sum of solvents, solutes, supporting electrolytes, electrodes, cell, procedures, and other controlling parameters which produce an electrodeposition.

Table 1

Gold - Cyanide Baths

(for decorative gold plate)

COMPOSITION	LOW METAL (oz/gal)	HIGH METAL (oz/gal)
Metallic Gold as cyanide	0.25	1.0
Potassium cyanide (Free cyanide, KCN)	2.0 (1.9)	1.4 (1.0)
Sodium Phosphate, $Na_2HPO_4*12H_20$	0.5	-
Temperature, (F)	145 - 160	140 - 160
Current Density, amp/square ft	1 - 5	1 - 10
Agitation, cathode preferred	no	no
Cathode efficiency, %	100%	100%
Ratio anode to cathode area	1:1	1:1
Anode:Gold, sometimes w/Fe or C as insol. anode	Yes	Yes
Volts	< 6	< 6
Characteristics of deposit	For appearance and color - 0.002 to 0.01 mil	Recommended for heavier coatings (up to 0.5 mil)

This precludes the use of water as the solvent. Presence of water could cause reaction of the metal ion in solution; or, as is found to be the general case, once the metal has been deposited, the water reacts to form a passivating, non-conductive product layer reducing the ability to deposit further. This difficulty will be discussed further in Chapter 5.

Deposition of Group IIA and IIIA metals, therefore, requires the use of non-aqueous solvents such as dimethyl sulfoxide (DMSO) and acetonitrile (AN). A survey of the literature indicates these solvents have been investigated for use in electrolyte systems only since the early 1960's and then primarily for electroanalytical chemistry. The youth of non-aqueous electrochemistry is exhibited in the current lack of establishment of a standard reference electrode from which all other chemical potentials can be measured.

Because aqueous plating fulfills the vast majority of plating needs and, to date, there has been a lack of need for Group IIA and IIIA metals in their plated pure form, little investigation of non-aqueous electrochemical deposition of these metals has taken place.

1.1.4 Application Of Plated IIA And IIIA Metals

Although barium(Group IIA) and yttrium(Group IIIA) elements have found only limited direct application, the recent discovery of high temperature superconductors composed of yttrium, barium, and copper offer new opportunities for use of these metals. Methods for producing the high temperature superconductor precursors have been limited to either conventional thin film or bulk techniques.

In the thin film techniques, a substrate to be coated with the superconductor is placed in vacuum, each component or a mixture of the components are evaporated from a source by such means as laser ablation or thermal evaporation. A thin film of the evaporant is formed on the substrate. It is possible to form the superconducting phase directly during deposition but normally the deposits are sintered in an oxygen environment to form the high temperature superconductor. Variations to this technique exist such as heating the substrate in vacuum and introducing oxygen at low pressure during evaporation or to use chemical spray pyrolyses as the source of the deposit. Because these are essentially line-of-sight techniques, their use has been limited to flat or nearly flat substrates precluding the use of this technique for important applications such as thick coatings or coating convoluted surfaces.

Bulk techniques allow the production of large pieces of superconductor. Normally a powder of correct stoichiometry is ground and mixed. It is then sintered and reground into a fine powder. This final powder, which is superconducting, is then pressed at high pressures to increase the density of the material. Finally, this material is sintered yielding a superconductor in much the same way as that described above. This final bulk piece can be machined to nearly any shape. However, machining the high temperature superconductor is difficult due to its hardness, and wasteful of expensive material. What's more, this technique does not provide for joining two pieces of superconductor nor the joining of superconducting material to conventional conductors.

Electrodeposition of Yttrium and Barium may provide greater flexibility in the application of HTSC precursor coatings. Conductive coatings can be deposited autocatalytically on non-conductors to furnishing a conducting surface for deposit or a conductor can be used. Sequential deposition of copper, yttrium, and barium (not necessarily in the order presented) in the correct stoichiometric ratios would provide a film which could be sintered and anodized to produce the superconducting phase. By controlling the amount of deposition and retaining correct stoichiometry, films of various thicknesses could be applied. Since HTSC materials are conductive, additional films could be applied to further thicken the films. The general processes used to perform these depositions are similar in many ways to those used to deposit decorative or engineering coatings. This may allow straight-forward transfer of the technology to industrial use.

1.2 Objective Of This Thesis

Because of the possible use of electrodeposition as a production technique for the making of HTSC precursor materials, it is important to determine the feasibility of electrodeposition of component metals. Given this as the motivation for this Master's Thesis, the thesis objective is as follows: to determine the feasibility of electrochemically depositing Yttrium and Barium individually from their metallic salts in non-aqueous solution on separate substrates. If successful, the author will build on this work in a Ph.D. dissertation aimed at determining an electrochemical approach to fabricating the full three-component precursor (which includes copper).

1.3 Direction Of Work

The fundamental requirements of a suitable common system to permit deposition of barium and yttrium are determined and a system selected. The deposition process is reported. Plating by galvanostatic (constant current) and potentiostatic (constant voltage) are examined with selection of a suitable reference electrode for the latter. Deposits were evaluated with respect to appearance, thickness, composition, adhesion, and uniformity. SEM, EDX, and XPS supplement visual evaluation, scratch tests, and optical microscopy. Reproducibility of the deposition technique is investigated.

The basic outline of this thesis and elucidatation of critical concepts are as follows:

Chapter 2 presents an overview of electrochemical deposition as a process. The origin of conductivity in solution, the critical nature of the interface reaction, the adsorption of ions, and their incorporation onto the surface are explained.

Controlling mechanisms for the reaction are described, including the manner in which they effect the deposition process. Each major component of the deposition process is discussed identifying the most critical of the controlling parameters.

Chapter 3 provides the specifics of these components as they apply to the actual experimental design used in this investigation. They are enumerated and the author's reasoning for selections explained.

Chapter 4 describes the actual apparatus, procedures, and tests which were based on these selections. The experimental setup is explained in detail. Preparation techniques for solutions a substrates are delineated. Techniques for controlling the environmental aspects important to the experiment are illustrated. The final procedure determined for depositions is presented. Testing and evaluation techniques used to analyze the results of the various experiments are discussed. This section also makes clear how each of the evaluation techniques used can or cannot support determination of critical information.

Chapter 5 presents the actual results of the experiments, general results, and conclusions. Specific results of the deposition process are also discussed for both yttrium and barium. Key controlling parameters and their effect on the plating process are illuminated. Experimental results are discussed in support of conclusions concerning these parameters and their importance on the process.

Chapter 6 summarizes, presents conclusions, and furnishes thoughts on future work. Proposals for experimental changes likely to effect the morphology and controllability of the deposition process are given.

Chapter 2 OVERVIEW OF ELECTROCHEMICAL DEPOSITION

2.1 Process Overview

Electrochemical deposition or plating is accomplished by dissolving the salt of a metal in a solvent which causes at least partial dissociation of the metal salt into anions and cations, the metal ion being the cation. At least two electrodes are placed in the solution and sufficient voltage is applied between the electrodes to cause a current to flow from the power supply used for plating. This current is the source of electrons at the electrode surface which reduces the metallic cations in solution allowing their adsorption. The metal deposited then becomes the new surface for deposition and the process continues until the current is discontinued or the cations are exhausted from the solution.

2.2 General Chemistry

Electrochemical deposition requires a solution which is conductive. Clearly the lack of long range order precludes conduction by means comparable to those of normal metals. Instead, the formation and role of ions in solution and ionic reactions at an interface must be understood. It is best to begin, then, with the formation of ions in solution.

2.2.1 Ions In Solution

Formation of ions requires the dissolution of the solid in such a way that the solid no longer retains its molecular form but is, instead, dissociated into charged atoms or groups of atoms known as radicals. The breaking of bonds between the components of the original molecule is central to the formation of ions. Consider a large metallic salt: sodium chloride. There is long range regular order with bonding between sodium atoms and their adjacent chlorine atoms.

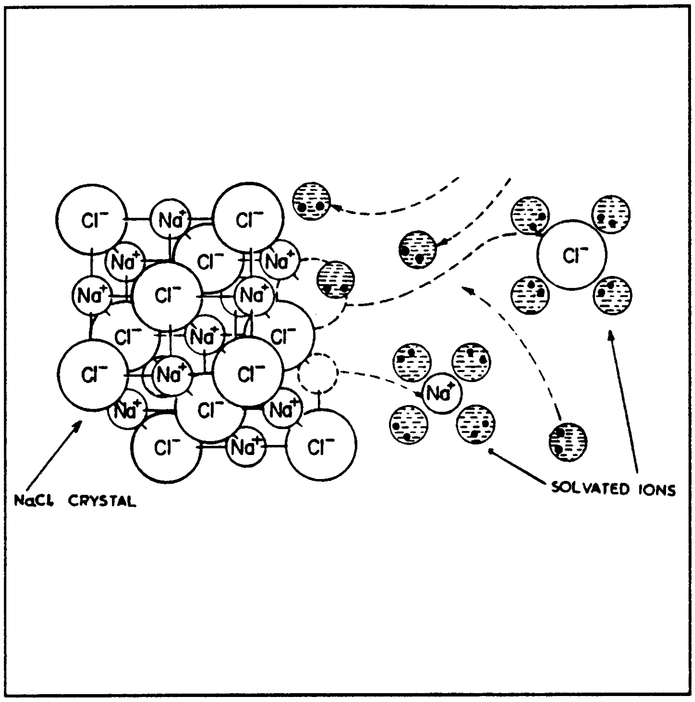

Figure 2.2.1-1 Dissolution Of Ions

The solvent molecules are polar and have a reasonably high dielectric constant. In the case of the example at hand, the solvent molecule is water. As solvent molecules arrive at the surface of the salt crystal, the solvent dipoles align themselves with respect to the positively and negatively charged atoms making-up the crystal. As this occurs, the bonds between the charged atoms of the crystal begin to weaken and eventually break.[6] In general, this process can be endothermic but is usually exothermic. The charged atom, now known as an ion, is surrounded by solvent molecules which have aligned their dipoles with respect to the charge of the atom they surround. This ion and its solvation sheath are free to wander from the original lattice site. It is because of this wandering that they earn their name ion from the Greek word for wanderer.

This process is the same for non-aqueous solvents as well. Water is an especially good solvent because of its high dielectric constant and resulting polarizability. However, a number of organic solvents also have relatively high dielectric constants and can also solvate an ion forming a solvent sheath.

It should be noted that it is also possible for an entire molecule to be separated from the solid without dissociation into ions. This occurs in all solvents but is most likely in those solvents with low dielectric constants. In these cases, a dissociation constant defines the percentage dissociated.

2.2.2 Formation Of Electrochemical Potential

When a metal surface comes in contact with a solvent, the same process as described for the metal salt occurs. Dissociation advances until a local equilibrium between the metal and metal ion occurs. When an atom has its valence state raised, the process is known as oxidation. Metal atoms in the surface become positively charged ions upon dissociation thereby being oxidized in the process. Should equilibrium not be reached and provided a passivating layer does not form on the metal surface, the metal continues to oxidize. This process is known as corrosion.

For the purposes of this work, it can be assumed that a passivating layer does not form and that local equilibrium is reached between the metal and metal ions in solution. When the metal of the surface is solvated, it leaves behind electrons which continue to build up until local equilibrium is reached. Should the solvent already contain ions, equilibrium may tend to favor adsorption of ions rather than dissolution of the metal surface. In this case, positive ions adsorbed on the surface would accept electrons from the metal until equilibrium is reached.

Since every metal placed in a solvent performs in the manner just described, there is no metal which can act as a neutral reference electrode. For this reason, a standard reference electrode has been established for aqueous solutions which tends to be unchanged for a wide range of solution concentrations or for a broad range of current densities for a given concentration. This reference is known as the Standard Hydrogen Electrode (SHE) and is defined as 0.0 volts. Because the SHE is inconvenient to construct, a suitable substitute known as the Standard Calomel Electrode (SCE) has be devised which remains at -.242 volts vs. SHE.[7]

If two dissimilar metal electrodes are placed in solution, they will each come to equilibrium with the solution. Their tendency to loose or adsorb ions from solution will result in an affinity for or excess of electrons with respect to each other or the SHE. This results in a potential being established between them in open circuit. This potential, $\mathscr{E}$, is known as the reversible emf of the cell. This reversible emf can be associated with the reversible work of the cell. Since this is normally reversible work at constant temperature and pressure, it is equal to the Gibbs Free Energy change.[8]

$$\Delta G = -n\,\mathscr{F}\mathscr{E} \tag{1}$$

where ΔG in the Gibbs Free Energy, n is the number of Faradays passed through the cell, $\mathscr{F}$ is the Faraday Constant (96,500 C equiv^{-1}), and $\mathscr{E}$ is the voltage. But, for a general cell reaction:

$$aA + bB + \ldots = mM + nN + \ldots \tag{2}$$

the Gibbs Free Energy equation can be written:

$$\Delta\ G = \Delta\ G_o + RT\ln Q \tag{3}$$

where

$$Q = \frac{M^m\ x\ N^n\ldots}{A^a\ B^b\ldots} \tag{4}$$

Equations (1) and (2) can be combined to form the Nernst Equation:

$$\mathscr{E} = \mathscr{E}^o - \frac{RT}{n\mathscr{F}}\ln Q \tag{5}$$

Note that $\mathscr{E}$ is characteristic of the composition of the electrodes, the type of solvent, and the solution concentration. By using a reference electrode, the value of $\mathscr{E}$ vs. SHE can be determined for each half of the cell. A corresponding $\mathscr{E}^o$ can then be determined for the given solvent and electrode material which is independent of concentration. These values are tabulated for water but are generally not available for non-aqueous systems due to the lack of established non-aqueous reference electrodes. By summing the two half cell emf, the emf of the entire cell can be determined. It is because the cell can be simply considered as a sum of two half-cells that further study can concentrate on what occurs at the half-cell electrode of interest. This electrode is normally referred to as the Working Electrode. Conclusions can be extended to the other or counter electrode.

2.2.3 Electrodics

Understanding the formation of ions in solution and the cause of electrochemical potential at conducting electrodes does not explain the manner in which conduction transpires in solution. This requires comprehension of the events at the electrode surface.

Consider a working electrode, M, in local equilibrium with a m1 molar solution of MSO_4. The presence of the electrode requires a higher concentration of M2+ ions locally than is in the general solution. Because of the solvation of some of the electrode metal to M2+ ions, the surface of the electrode to build up electrons. This, in turn, causes the polar solvent to form an oriented dipole layer called the Inner Helmholz Plane (IHP) along the electrode. Immediately outside the IHP, the solvated ions, which no longer have a dipole orientation, respond to the electric field caused by the excess negative

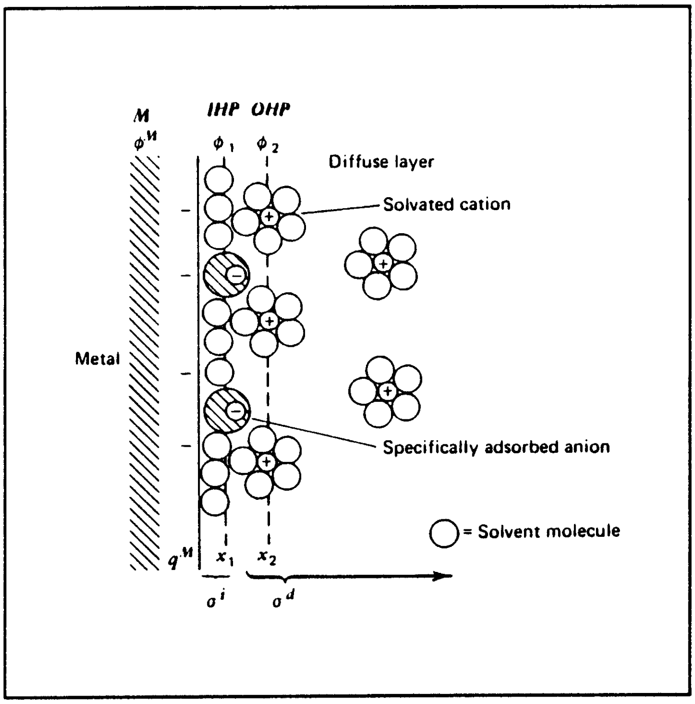

Figure 2.2.3-1 Double Layer

charge. A layer of solvated ions form and is called the Outer Helmholz Plane (OHP). This IHP-OHP formation is considered the Double Layer.[9] See Figure 2.2.3-1[10]. Subsequent layers may form but are normally not considered part of the dipole layer. The bulk of the solution which is not influenced by the direct presence of the electrode retains the concentration of solvated and dispersed ions with no net dipole orientation. The region from the electrode to where the solution concentration is that of the bulk constitutes the Interphase Region.[11]

If an outside power supply is connected to the electrode and a voltage applied, $\mathscr{E}$ can be raised from its equilibrium value. The Nerst Equation (5) requires that the equilibrium conditions change at the electrode surface. The increased surface charge density causes a response in the double layer by drawing solvated ions into the OHP. As the energy in the interface increases, more and more solvated ions have sufficient energy to cross the double layer and come in contact with the metal surface where the excess electrons reduce them to a metallic state. They then become the new surface of the electrode and the process continues provided there are ions in solution and electrons from the power supply. Thus, conduction in the electroplating process begins with the reduction of solvated metal ions at the electrode interface.

2.2.4 Solution Conduction

Ions in solution move under the influence of three factors: 1.) Diffusion due to concentration gradients, 2.) Migration due to electric field effects, and 3.) Convection due to bulk movement. Migration can, for the most part, be eliminated by not using excessively high voltages and by the addition of supporting electrolyte. Convection can occur by stirring or at an electrode surface when the solvent, depleted of ions, has a significantly different density than the bulk solution. By not stirring the solution and by arranging the geometry of the system so as to minimize density convection, these sources of ionic movement can be ignored.

This leaves diffusion as the primary source of movement of ions in solution. As the ions at the surface are consumed, diffusion transports more ions to the surface. Initially, the rate of consumption of ions is proportional to the voltage applied. (Figure 2.2.4-1) An increase in voltage results in a greater rate of consumption. This rate of consumption competes with arrival of ions due to concentration-dependent diffusion. At some potential, the rate of consumption will be as fast as the arrival of the ions. The surface concentration will go to zero and remain there for all higher potentials. This is known as the diffusion-limited regime.

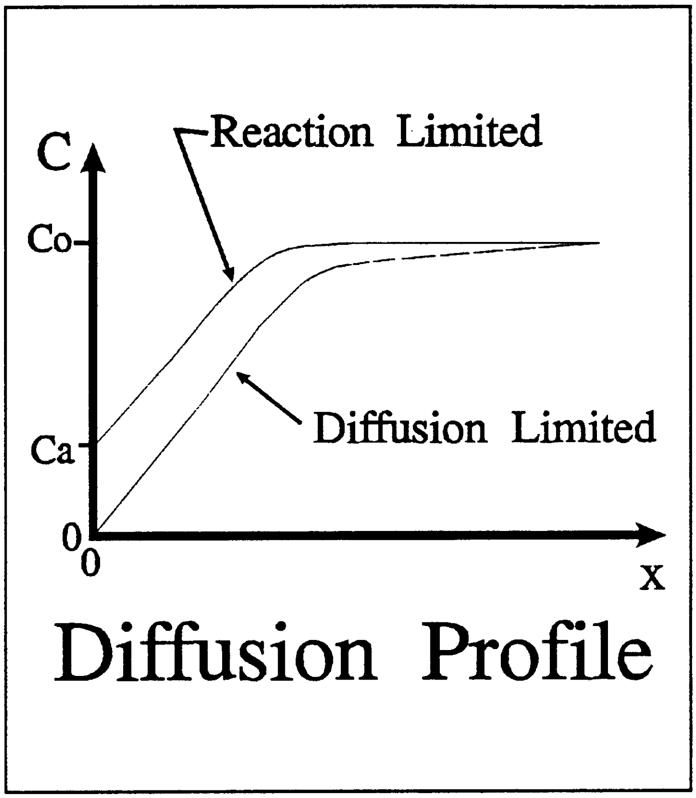

Figure 2.2.4-1 Diffusion Of Ions

Conduction occurs, then, because an applied voltage greater than the equilibrium voltage raises the free energy at the electrode surface. Ions gain sufficient energy to move across the double layer and electrons at the surface reduce the ion to a metal ion. The ion concentration at the surface then decreases causing diffusion from the bulk to the double layer feeding the process. This process occurs for the cations at the cathode and equally for the anions at the anode.

2.2.5 Surface Adsorption

The way in which ions are solvated and move through solution does not explain the manner in which they are adsorbed on the surface of the electrode, reduced to metal atoms, shed their solvation sheath, and become the new surface of the electrode. (Figure 2.2.5-1)[12] To account for this requires that solvated ions not be static rigid structures. The solvation atoms which comprise the sheath oscillate about their equilibrium positions. These oscillations are proportional to the temperature.

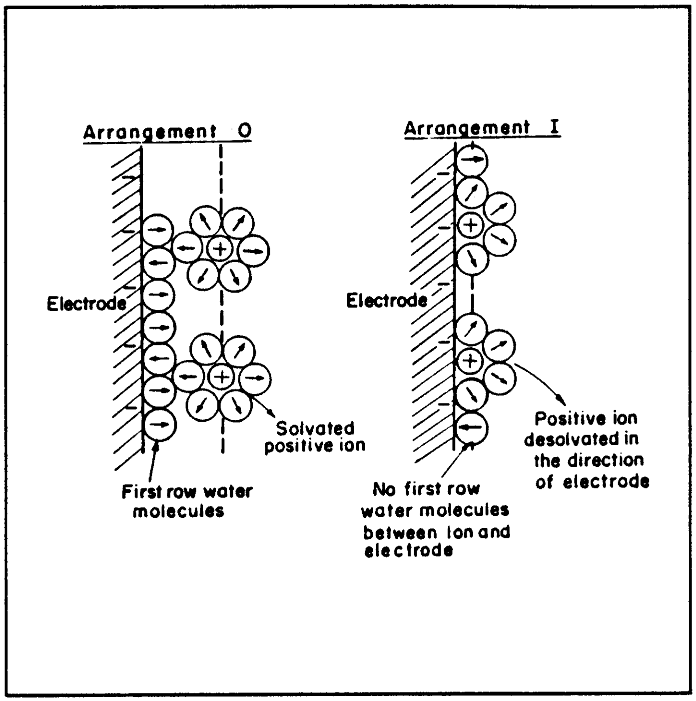

Figure 2.2.5-1 Ionic Adsorption

As a diffusing solvated ion approaches the OHP, it begins to feel the effect of the electric field caused by the excess of electrons on the cathode. Responding, the solvation sheath may move further from the protective equilibrium orientation, allowing the ion to get close enough to the surface of the metal electrode to gain an electron and become an adion.[13] It is possible for the ion to return the electron to solution or it can begin sharing its electron with the electron gas of the metal surface. Should the latter case occur, the adion still must rid itself of its remaining solvation sheath.

The adion, now on the surface, can diffuse freely along the surface with its solvent atoms still attached. (Figure 2.2.5-2)[14] As it does so, it may encounter a step, kink, or hole. In the case of a hole, the adion may simply fill the hole or vacant lattice site. Because of the great stability of this arrangement, the adion quickly becomes part of the lattice and sheds all solvent ions. Holes are, however, relatively infrequent. It is more likely a step would be encountered. Here the adion can rid itself of another solvent molecule as it adheres to the step surface. Still, there is no reason to expect it to be affixed in the position it first encounters. Again by random movement, it can travel up or down the step. It may encounter a kink or another adion. In either case, an opportunity is presented to rid itself of more solvent molecules. This process continues until the adion has fully rid itself of solvent molecules and is a metal atom integrated into the structure of the surface.[15]

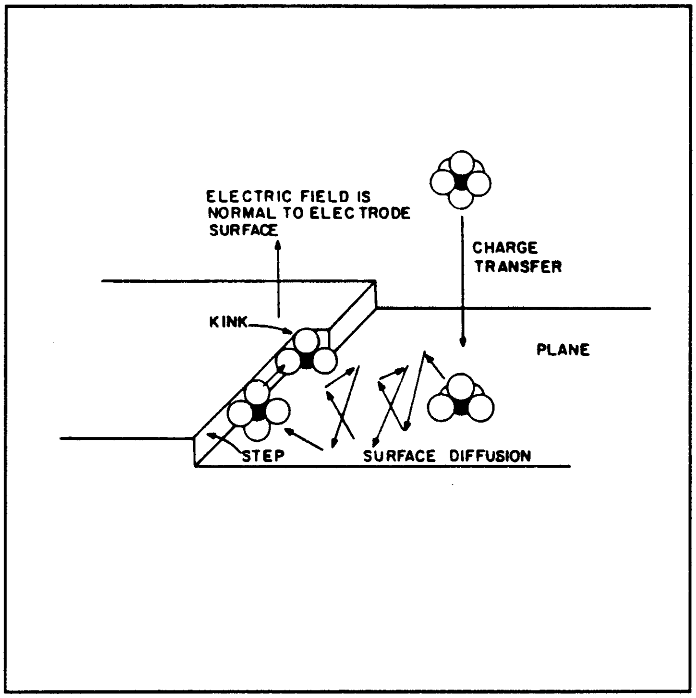

Figure 2.2.5-2 Lateral Surface Diffusion

2.2.6 Driving The System

Fundamental to the plating process is that it is a controlled, driven electrochemical reaction. An energy barrier must be overcome for the reaction to proceed in a forward direction by the application of a sufficiently large electric potential at the electrodes. Adsorption proceeds as discussed in section 2.2.5 above. Should the potential be increased above that necessary for the onset of adsorption, additional adions are adsorbed for a unit area of electrode surface in a given unit of time. The reaction rate appears to increase. Since increasing the potential only increases the number of ions adsorbed per unit of area per unit time rather than increasing the speed of the adsorption process, two significant effects may be observed. These effects are described below.

2.2.6.1 Crystal Formation And Growth

First, the mechanism described in 2.2.5 indicates adsorbed ions do not rest on the surface but move laterally by random motion until they attach to other surfaces and shed the remaining solvent sheath. This process has an average time, τ. As more are absorbed per unit of time, each is just as likely to find another adion in time τ as find the surface of a face or edge. When sufficient adions group together, a nucleus forms and growth of that nucleus begins. This new nucleus is stable and may form as an island separate from any other nucleus. As the potential is further increased, the effect is enhanced usually forming more nucleation and growth sites. Therefore, as the potential is increased above the onset of deposition, the morphology of the surface will likely become more and more polycrystalline. Other effects such as loss of adhesion, dendritic growth, and porosity may also be enhanced or inhibited as the potential is changed.

2.2.6.2 Diffusion-Limiting Effects

Second, the controlling kinetic process may change depending on the potential applied. Initially, the potential applied allows adsorption of a readily available grouping of ions. The overall rate of reaction is controlled by how facile the adsorption process is. Diffusion is capable of supplying as many ions as the reaction can consume. The ion profile concentration shown in Figure 2.2.4-1 (Reaction Limited) shows only a slight depletion in ion concentration at the surface of the electrode, which rapidly returns to the bulk concentration as one proceeds away from the electrode. As the potential increases, the increase in rate of reaction depletes the surface concentration further as shown in

Figure 2.2.4-1 (Diffusion Limited). At some point, the potential is high enough and the absorption kinetics fast enough to consume all of the ions at the surface of the electrode at a rate equal to or greater than the rate at which diffusion can transport the ions to the surface. This is known as the diffusion-limiting regime. Increasing the potential beyond this point does not result in an increase in rate of reaction. Should the potential be increased further, other reactions may be induced such as decomposition of the solvent. Usually plating potentials much greater than the diffusion-limiting potential are not desirable.

2.3 The Deposition System

Determining the source of conduction in solution and the factors which influence and control it gives insight into the critical parameters comprising an electrochemical deposition system. These parameters offer a wide variety of options in selecting the final components of the system. The selections made by the author for electrodeposition of yttrium and barium and the reasoning behind their selection is explained in Chapter 3.

CHAPTER 3 EXPERIMENTAL DESIGN

In Chapter 1 of this thesis it was explained that the motivation for selecting yttrium and barium as the two metals to be separately electrodeposited was not just their unique properties but the possible use of these deposits in making HTSC precursors. Chapter 2 presented the fundamental theories behind electrodeposition and described the basic components of an electroplating system. However, Chapter 2 did not specify the actual system necessary for achieving the goals set out in Chapter 1. It is the purpose of this chapter to present the options available for each component, the final selections made, and the reasoning used in making those selections.

3.1 Metallic Salts Selection

Both yttrium and barium are available in a wide variety of metallic salts. A review of the literature shows that few electrochemical studies of any type have been performed using these metals as salts. Barium perchlorate, nitrate, iodide, and chloride have been examined in various aprotic solvents, with the preponderance of studies done using perchlorates.[16] Yttrium shows only one study, done using yttrium perchlorate.

Having a common counter electrode reaction for both metallic salts would simplify system evaluation. If needed combined systems of both salts could be investigated knowing the only counter electrode reaction was common to both species. Based on the previous investigations cited, perchlorates were the author's first choice. However, perchlorates are generally unstable when dried and have been known to cause explosions. Additionally, the cost of perchlorates is significantly higher than nitrates. Therefore, the author chose to investigate both perchlorates and nitrates and select one for the final experimental sequences.

The actual form in which the salts are obtained from commercial sources are hydrated:

$$Y(ClO_4)_3 \cdot xH_2O$$
$$Ba(ClO_4)_2 \cdot 3H_2O$$
$$Y(NO_3)_3 \cdot xH_2O$$
$$Ba(NO_3)_2 \cdot 3H_2O$$

The addition of water to the chemical equation of a salt indicates some water is normally associated with the salt even in crystalline form. This is common to most salts, not just yttrium and barium. However, the commercial perchlorates usually arrived clearly wet. This made use of the perchlorates more difficult and weighing inaccurate. Once vacuumed dried, the hygroscopic nature of these salts made weighing inaccurate. Weights changed due to water adsorption from the atmosphere during weighing.

Solubility, conductivity, and the ability to deposit from solutions made with each of the possible solvents were investigated and the results of those investigations are reported in §3.2. Those results caused the author to conclude that there was no distinct advantage to using either the perchlorates or the nitrates in the deposition process. Therefore, cost became the final factor in selecting nitrates as the metallic salts to be used in the final electrodeposition process.

3.2 Solvent Selection

Water was initially considered as a possible solvent along with aprotic solvents. Appendix C shows the Pourbaix diagram for barium in water.[17] Note that barium metal is stable in water only at very negative potentials versus SCE. If the metal is not held at potentials more negative than -3.1 volts, alternate forms of barium occur. This may allow for the actual plating of barium metal from solution but the potential could not be maintained when the wet deposit is removed from solution. Since the metal would be simply exposed to water, it could be expected that barium hydroxide would immediately form.[18] Because one of the possible purposes of the barium film stated in Chapter 1 was as part of an HTSC precursor and that barium hydroxide does not form the HTSC material even in stoichiometrically correct proportions, the author decided to investigate only non-aqueous solvents. A fundamental requirement placed on the selection of a suitable solvent was that it provide acceptable deposits of both yttrium and barium. As with the selection of a common ligand, this would simplify developing solution preparation techniques and, if sequential deposition was pursued in the future, eliminate concerns of cross contamination between solvents. A review of the literature shows that of the aprotic solvents used for electrochemistry, the most common ones are [19] [20] [21]:

1.) Acetonitrile
2.) Dimethyl sulfoxide[22] [23]
3.) Dimethyl formamide

Both acetonitrile[24] and dimethyl sulfoxide[25] were recommended as suitable solvents.

To determine if either or both of these solvents would be acceptable, solubilities of the nitrate and perchlorate salts in each solvent were tested. Acetonitrile dissolved all salts quickly, with the barium salts dissolving most rapidly. On the other hand, dimethylsulfoxide (DMSO) was slow to dissolve both barium salts taking more than 12 hours with stirring at room temperature to completely dissolve sufficient salts to create a 1 M solution. DMSO dissolved both yttrium salts within one hour of stirring to form solutions of comparable strength.

Since both solvents dissolved all salts, conductivity of the solutions was confirmed indicating that the salts had not only dissolved but dissociated. This is a prerequisite to electrodeposition.

As a final step in the evaluation of these solvents, electrodeposition was attempted. Several cell configurations were used during this evaluation process and are described in §3.3. Although the results of the various depositions were generally inconsistent, some limited conclusions could be made.

- Deposition of yttrium from acetonitrile is far less predictable than from DMSO. Depositions are not just inconsistent from day to day using the same process, but inconsistent from deposition to deposition using the same process and solution.

- Deposits obtained in acetonitrile are not very adherent while those done in DMSO are. Once dried, deposits formed using acetonitrile often separate from the substrates.

Because deposits made using the metal salts in acetonitrile are less adherent, and the acetonitrile system produces less predictable results than those made in DMSO, the author selected dimethyl sulfoxide as the solvent to be used for the final investigation. The inconsistencies still occurring in the DMSO system were troublesome; but, experimentation presented in §5.2, Initial Experimental Results, showed that the cause of the inconsistency was water contamination in the solvent. The manner in which this problem was eliminated is discussed in §4.3.

3.3 Selection Of Supporting Electrolyte

Supporting electrolytes such as tetraethylammonium perchlorate (TEAP), tetra-n-butylammonium perchlorate (TBAP), tetra-n-butylammonium fluoborate (TBABF) are all highly polar molecules. They are also highly stable molecules which do not readily dissociate when dissolved. As a result, when in solution, they are not involved directly with any reaction at either the working or counter electrode but do interact with electric fields.

In solving the general mass transfer equation for an electrochemical system, one arrives at the Nernst-Plank equation:[26]

$$J_j = -D_j \nabla C_j - \frac{z_j F}{RT} D_j C_j \nabla \phi + C_j \mathbf{v} \qquad (6)$$

The first term on the right hand side reflects the contribution to the movement of the ions due to diffusion. The second term incorporates the effect due to electromigration. The right-most term reflects the effect of convection. If the latter two terms are discounted, the mass transfer of ions is controlled only by diffusion. This greatly simplifies analysis of an electrochemical system. The right-most term, convection, can normally be removed by not stirring the solution or electrode orientation. Polar supporting electrolyte molecules align with the electric field at the double layer. Farther away from the double layer, they are not so strongly influenced by the electric field move due to thermal energy. This reduces the apparent field seen by the ions in solution which are not very close to the double layer.[27] Supporting electrolyte performs this function in dilute solutions.

In concentrated solutions, electromigration contributes little to the movement of ions. The large electric fields generated by many anions and cations in close proximity to each other have significantly greater effect on the movement of ions in solution than the electric field caused by the electrodes. What's more, as the reaction at the electrodes increases, the concentration gradient becomes dominant in causing movement.

Interaction between supporting electrolyte and the salts in solution was not desired but observed. A solution of .5 M $Cu(ClO_4)_2$ was prepared in DMSO. The solution was transparent blue. When the supporting electrolyte, TBAP, was added, the TBAP crystals turned black and, after stirring, the solution turned translucent green indicating a reaction had occurred. In order to avoid any further undesired interaction, the author decided not to use supporting electrolyte in the plating solutions.

3.4 Working Electrode Selection

Browsing through the Electroplating Engineering Handbook[28] it is clear that copper is the base metal upon which most electroplating is done. If plating nickel silver, for example, a copper strike[2] is deposited prior to plating the nickel-silver.[29] Copper is easy to obtain and form as an electrode and inexpensive when compared with other metals. Procedures for cleaning and preparation for plating are well known and clearly defined.[30]

Chapter 1 suggested a possible use of the electroplated yttrium and barium as components of an HTSC precursor. One paper reported successful formation of a superconducting tape prepared by surface diffusion of yttrium and barium into a copper substrate.[31] In the experiment, a mixture of $BaCO_3$ and Y_2O_3 powders was emulsified using a small amount of ethyl alcohol. This emulsion was painted onto a copper ribbon then heat-treated at 900-980 °C for 10 minutes to 1 hour. It was found that the yttrium and barium diffused into the copper and formed a distinct layer of $YBa_2Cu_3O_{7-x}$ which was adherent to the copper.

By developing a process in which yttrium and barium could be electrodeposited on a copper substrate, it may be possible to perform a similar diffusion reaction to form the high temperature superconductor. Because of this possible future purpose and the general acceptability of copper as a plating substrate, it was

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[2] Strike is an electroplating term for a plating bath which is used to deposit a thin layer of a metal, usually different than the final metal to be deposited. This layer provides a surface more conducive to electrodepositing the final metal or alloys than does the metal upon which the strike was placed.

selected for the working electrode.

3.5 Counter Electrode Selection

In aqueous systems, the counter electrode reaction is often discounted. The counter electrode is often significant in non-aqueous systems. Because electrostatics dictates that no significant quantities of charge can be built up in solution, for all cations reduced at the working electrode an equal quantity of charge must be oxidized at the counter electrode. If the potential at which cationic reduction takes place is far below that at which anionic oxidation occurs, the reaction does not take place until the anodic reduction potential is reached. Two exceptions to this case are:

1.) A dissociation reaction of the solvent takes place at a potential below or near the cathodic reduction potential. Water may dissociate forming O_2 (g) and $2H^+$ ions which oxidize the anions.

2.) Cations can be returned to solution from the counter electrode. Should the silver be deposited at the working electrode, it is possible to replace the silver ions in solution by consuming a copper counter electrode. Then for every two Ag^+ ions reduced, one Cu^+ ion is oxidized into solution from the counter electrode surface.

Because non-aqueous solvents do not dissociate at the relatively low potential at which cations can be reduced, either reduction of the ligands must occur or a consumable counter electrode used. Both techniques were explored experimentally. For much of the initial investigation, non-consumable platinum gauze was used as the counter electrode. Passivating layers built up on the surface of the gauze slowing the reaction rate. Nitric acid was used to remove this material. Once removed, the reaction again returned to its original rate. The by-products of the production of this passivating film changed the solution usually to a transparent brown.

Clean copper was used as the counter electrode. As a consequence, copper ions were added to solution as the yttrium or barium was deposited. This was of little concern since the presence of copper ions would have no effect on the cation reduction. Any copper ions which did find their way into the film could be identified by EDX or XPS and their source known. No passivating layers built up on the copper counter electrodes during electrodeposition.

It should be mentioned that barium metal was tried as a consumable counter electrode in some experiments. Because of its high reactivity with water, a layer of $Ba(OH)_2$ was formed on the surface of the metal turnings after exposure to minute traces of water in the non-aqueous solvent, preventing further reaction. Since the purpose of the investigation was to determine feasibility of a deposition process and not to create a self-replenishing optimized system, the author selected copper as the metal for the counter electrode.

3.6 Reference Electrode Selection

Since there is no absolute zero electrochemical potential, a reference point is needed. The Standard Hydrogen Electrode (SHE) and the Standard Calomel Electrode (SCE) cannot be used in non-aqueous systems. Since such common reference electrode has been established for non-aqueous systems, one had to be developed.

Platinum, silver, and copper wires were used as reference electrodes in the first experiments.[32] [33] [34] They all performed well, with platinum furnishing the most reproducible results. All reference probes developed some passivating layer which altered their performance over time and required cleaning as did the platinum-gauze counter electrode described in §3.4. Because these references varied with time, the author decided to investigate other possible reference electrodes.

One technique for establishing a reference in a non-aqueous system is the Luggin Probe connected by a salt bridge to an aqueous cell containing an SCE. Figure 3.6-1 above shows this system. The Lugen probe is simply a glass tube pulled to a tip with a diameter smaller than 1 mm. The tip of the probe is placed no less than half the diameter of the opening from the working electrode. The top of the glass tube is attached by Teflon tubing to a cell and the probe, tube, and cell are filled with the working solution. Into this solution is placed the salt bridge comprised of a glass tube filled with an aqueous saturated potassium hydroxide solution which has been thickened by adding auger and heating. The other end of the tube is placed into a cell containing an aqueous saturated solution of potassium hydroxide which contains the SCE. Since only microamperes flow in this system, even highly resistive

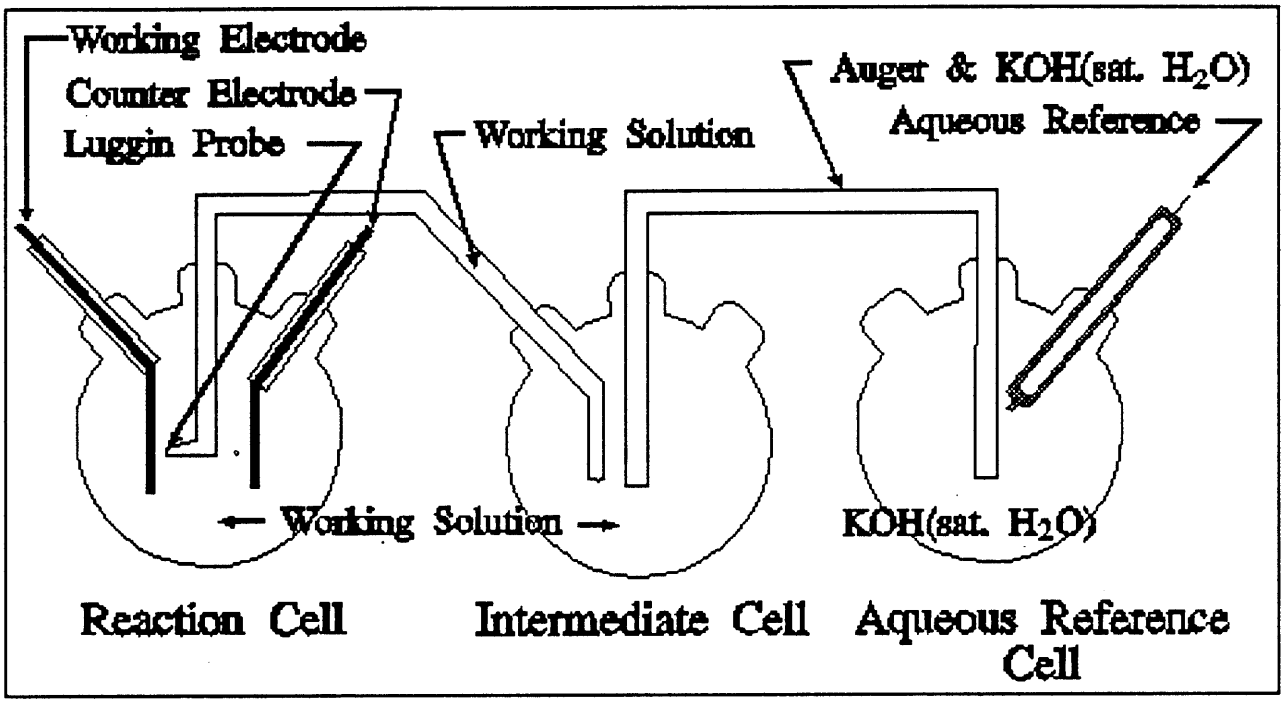

Figure 3.6-1 Luggin Probe and Salt Bridge

systems generate only negligible potential drops. The sampled voltage at the Lugen Probe is that read at the SCE. Water is prevented from contaminating the plating bath because of its low diffusivity in the auger.

The Luggin Probe-Salt Bridge-SCE described above was used to perform the first of the final depositions. The system was extremely awkward to use in the close confines of a glove box and the resistivity in the salt bridge for the nitrate-DMSO plating systems was sufficiently high to cause the potentiostat to not maintain a constant voltage. Another reference was pursued.

Review of the literature showed an alternative non-aqueous reference electrode system.[35] [36] A modified version of thallium amalgam electrode was recommended.[37] This reference electrode consists of a clean silver wire immersed in a solution of silver-ligand salt dissolved in the same solvent used in the electrochemical system. The ligand referred to is the same as that of the salt used in the electrochemical system. The solution and wire are inserted into a glass tube on which a glass frit had been attached by Teflon heat shrink tubing. Figure 3.6-2 shows the construction of the electrode. Solution concentration used are indicated.

Electrodeposition experiments using this reference electrode and Linear Sweep Voltammetry measurements were consistent and reproducible. The reference electrode showed no signs of deterioration or change even when switched between different solutions. The author selected this reference electrode system for the final deposition experiments.

3.7 Selection of Electronic Control

In Chapter 2, it was explained that electrodeposition can be controlled either potentiostatically or galvanostatically. Galvanostatic control is the primary technique used by industry. Potentiostatic control is most used for electrochemical analysis.

Both techniques were investigated. Special techniques such as pulse plating were not investigated in this thesis work because of their added complexity.[38]

3.7.1 Galvanostatic Deposition

Galvanostatic control offers simple monitoring which is desired by industry but does not assure control of the voltage being placed across the solution double layer. Whatever potential is required to maintain the set current is applied. Very high potentials could be applied and possibly cause undesired reactions including dissociation of the aprotic solvent.

A Hull Cell, described in §3.8.1 below, was used with copper plated steel as the working electrode. The counter electrode was a titanium basket filled with barium shavings. A current of 1 ampere was applied. This is the lowest current for which the Hull Cell was designed. The resulting deposits were very inconsistent. Potentials applied

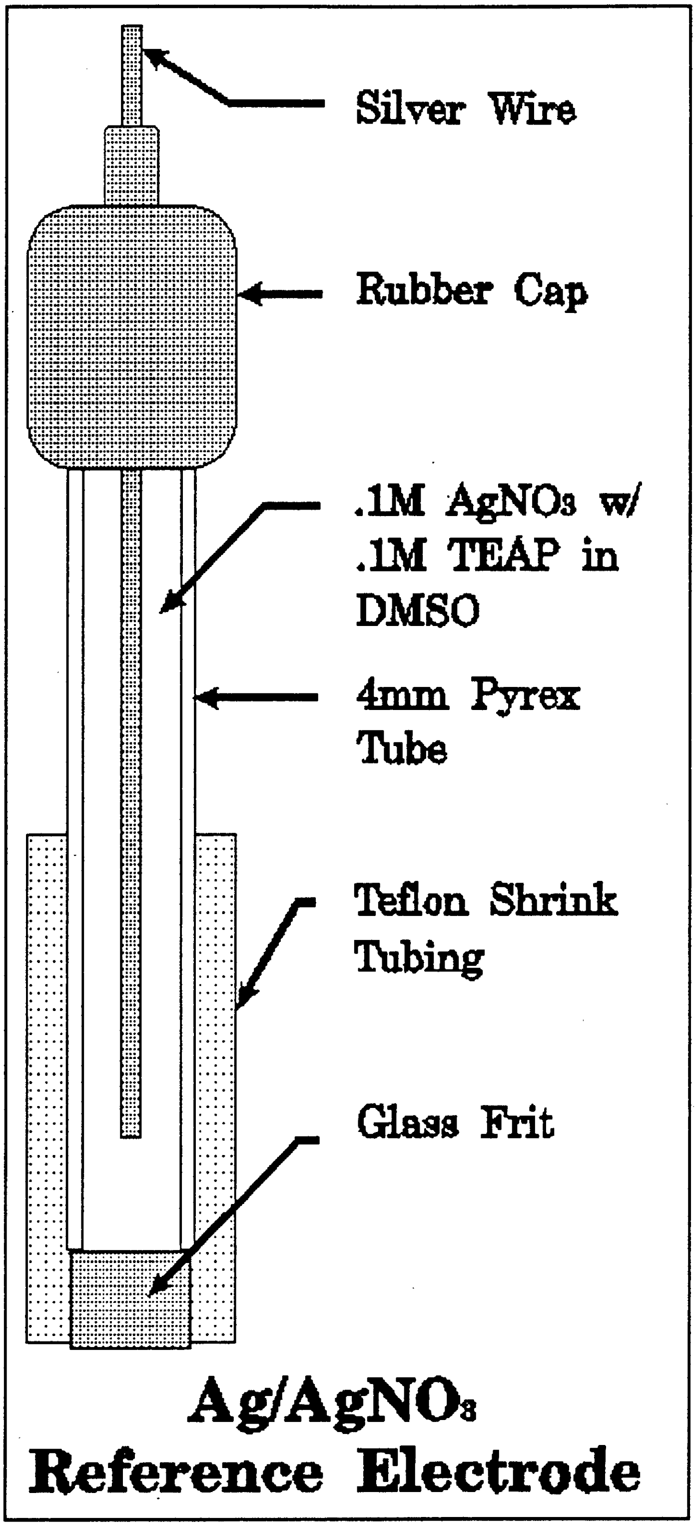

Figure 3.6-2 Ag/AgNO$_3$ In DMSO Reference Electrode

across the cell went as high as 60 volts causing immediate blackening of the solution and required making a new batch. A second attempt at .5 amperes, a current for which there is no cell data, caused gas evolution and a white crystalline deposit. Repeated attempts provided no significant improvement.

3.7.2 Potentiostatic Control

Potentiostatic control is most often used in the laboratory to extract data from the electrochemical system's response to applied voltage.[39] [40] Because applied potential is related to the free energy of the system as discussed in §2.2.2, excessively raising the free energy by raising the applied voltage can cause undesired reactions to become energetically favored. By controlling the potential of the system, these undesired reactions can be avoided.

A system of copper working and counter electrodes along with the $Ag/AgNO_3$ in DMSO reference electrode described in §3.6, was assembled and evaluated for its ability to provide reproducible Linear Sweep Voltammetry and electrodepositions without altering the solution. In all cases this system proved easy to control, achieved the desired objectives, and provided insight into the electrochemical system itself.

3.7.3 Final Selection Of System Control

Because galvanostatic control proved to be difficult and provided little insight into the electrochemical system and because the selected potentiostatic system produced consistent reproducible results and gave insight into the electrochemical system, the author selected potentiostatic control for use in the final plating experiments. The needs of industry suggest that a similar investigation be made at some time to develop a galvanostatically controlled system.

3.8 Cell Design Selection

Since both galvanostatic and electrostatic deposition techniques were investigated, a cell had to be selected for each technique. The selection of a suitable galvanostatic cell and the evolution of the final potentiostatic cell are explained below.

3.8.1 Galvanostatic Cell Selection

Galvanostatic deposition and solution testing is normally done in a commercially available cell known as the Hull Cell. This cell, pictured in Figure 3.8.1-1 below, arranges the electrodes so that the working electrode is longer than, and at an angle to, the counter electrode.

Since solution resistance is proportional to the distance

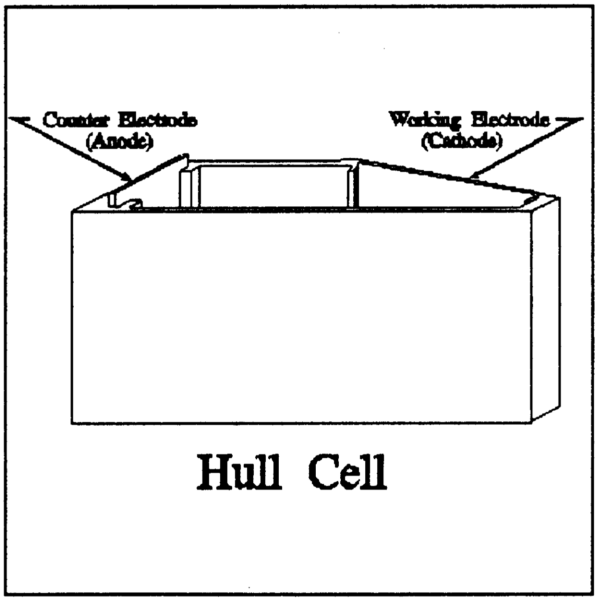

Figure 3.8.1-1 Hull Cell

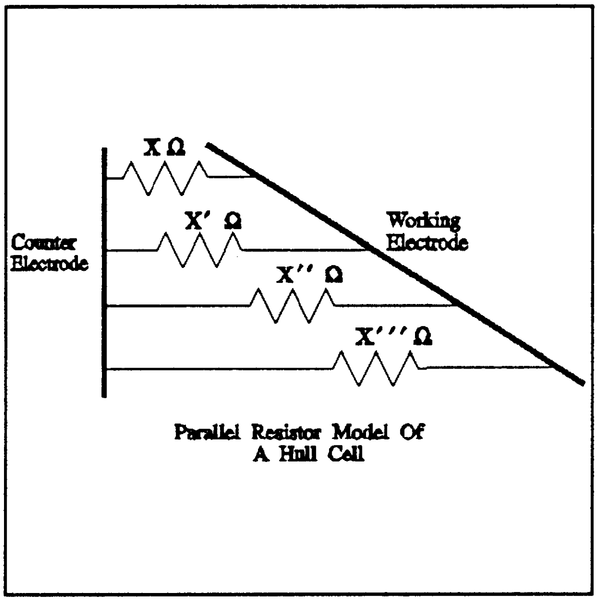

Figure 3.8.1-2 Hull Cell Resistor Model

between electrodes, the resistance seen by the working electrode close to the counter electrode will be much less than that of the end far away. This can be pictured as a set of parallel resistors which increase in resistance as does the solution resistance. The current which is fixed distributes itself based on the resistivity. If a given resistor were to correspond to an area of surface of the working electrode, the current density experienced by the working electrode would follow the dictates of Ohm's Law and the parallel resistor model of the solution. See Figure 3.8.1-2. The current density near the edge close to the counter electrode would have a much higher current density than the edge farther away. As a result, the Hull Cell affords an opportunity to evaluate electrodeposition along a spectrum of current densities. By arranging a specific geometry, R.O Hull was able to develop this cell to allow a predictable current density along the working electrode based on the net cell current.[41]

Because the distribution is based on the relative difference of the resistors in parallel, each of which is proportional to solution resistance and distance between electrodes, the predicted current densities are found to be fairly independent of the specific solution used. Differences in double layer resistance due to varied current densities is found to decrease the accuracy of predicted current densities.

A ceramic Hull Cell was purchased from Kocour Company along with a titanium basket for use with consumable counter electrodes and the standard test working electrodes, which consist of copper plated steel. This cell proved to be easy to assemble and work with; however, as was reported in §3.7.1, plating was consistently bad. In one case the solution formed a precipitate throughout. Also, the solution exposes a large surface area to its environment allowing water absorption which is very deleterious to barium deposition.

3.8.2 Potentiostatic Cell Selection

The basic potentiostatic cell must allow for the introduction of three electrodes, two in close proximity to each other. However, as an understanding of the need for control of water contamination of the solution became apparent, a more elaborate cell design emerged. Figure 3.8.2-1 shows the cell used in the final plating experiments. It allowed for introduction of the working, reference, and counter electrodes and well as a thermometer. Once these were inserted, the solution was isolated from the exterior environment decreasing the possibility of water contamination. A solution of 50 ml could be contained which supplied sufficient electrolyte for several platings, while minimizing waste. The cell body could be separated at the central joint to facilitate cleaning. All components in contact with the solution were either glass, Teflon, or cured epoxy.

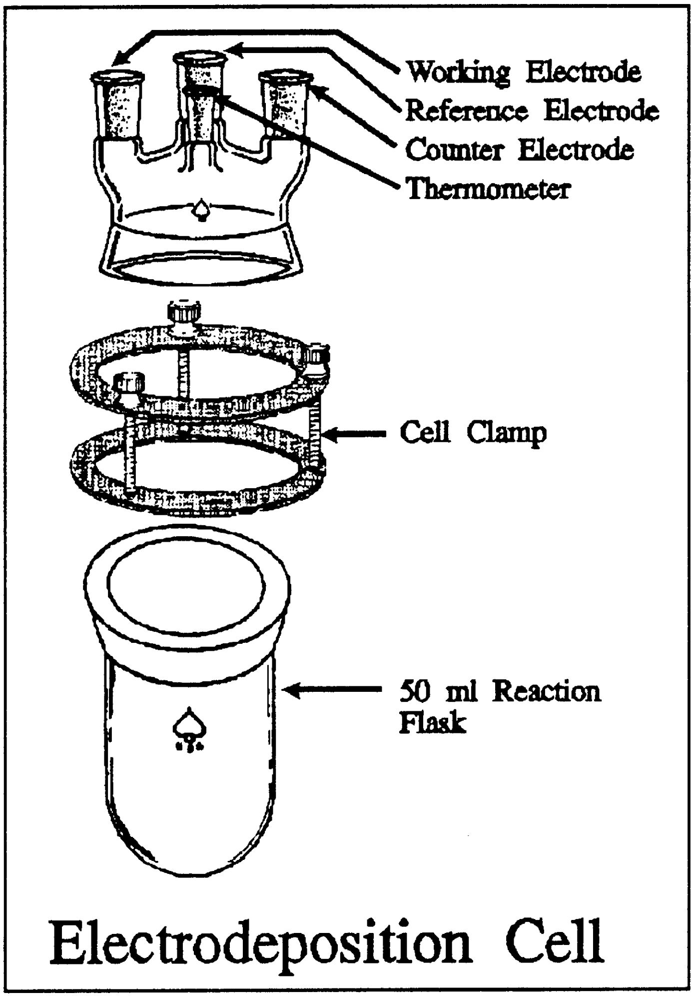

Figure 3.8.2-1 Final Plating Cell

3.8.3 Final Cell Selection

Of the potentiostatic or galvanostatic cells, the choice for potentiostatic was not determined by a particular value of one cell over another. The decision to investigate potentiostatic deposition explained in §3.7.3 dictated the use of the potentiostatic designs. The final design shown in Figure 3.8.2-1 occurred after some evolution. It could be cleaned, filled, emptied, electrodes inserted or removed and it decreased water contamination.

3.9 Selection Of Experimental Environment

The experimental environment consists of those factors which can influence the deposition process which are not electrochemically controlled. Water exposure, gas, and temperature were found to be significant to the deposition process and required control.

3.9.1 Water Exposure Control Selection

Section 5.1 discusses some of the initial experiments performed and concludes that water must be totally excluded from the system. Failure to recognize how sensitive the system is to water, and how hygroscopic DMSO is, allowed indeterminable amounts of water contamination and was likely the source of much early inconsistency of results. To combat water contamination many elaborate techniques can be found in the literature.[42] [43] [44] However, a simpler approach was taken by the use of a glove box. By conducting all weighing, mixing, and experimentation in the controlled dry environment of a glove box, water contamination was greatly reduced.

3.9.2 Gas And Gas Dryness Control Selection

The glove box was filled with argon at slight positive pressures. Argon was chosen because it is chemically inert and showed no impact on solution performance when bubbled through a plating solution. Bottled commercially available argon is not necessarily dry. Therefore a drying column consisting of a glass tube 3 feet long was filled with dryrite (calcium carbonate). Bands of indicator dryrite were separated by about 4 inches of white dryrite. Rubber stoppers with glass tubes through the centers were inserted in each end. The gas entered one end and flowed across the dryrite. Water contamination of the drying agent was detectable by a change in the color of the indicator dryrite. This was seen in the first two indicator bands.

3.9.3 Temperature Control Selection

Both hot plate and heating mantle methods of temperature control were examined. The heating mantle method was chosen because of the shape of the final cell and because it was simpler to use in the glove box environment.

CHAPTER 4 ELECTRODEPOSITION PROCEDURES AND EVALUATION

The purpose of this chapter is to provide an overview of the electrodeposition apparatus used, to explain in detail the experimental procedures, and to present the test and evaluation procedures used to evaluate the samples.

4.1 Experimental Apparatus Configuration

Electrode preparation and cleaning could take place in the laboratory environment; however, solution preparation and electrodeposition had to be conducted in a glove box. The laboratory work space was divided into two areas as shown in Figure 4.1-1. The workbench area was open to the laboratory. It was easy to work in and allowed ready access to the solutions used to clean the electrodes prior to plating. Immediately adjacent to this area was the glove box. Electrodes, once prepared, could be quickly moved into the vacuum chamber at the end of the glove box. Between the two was the argon cylinder and dryer and a vacuum roughing pump. Both vacuum and dry argon gas could be supplied either to the vacuum chamber at the end of the glove box or to the glove box itself. Their uses are explained in the sections below.

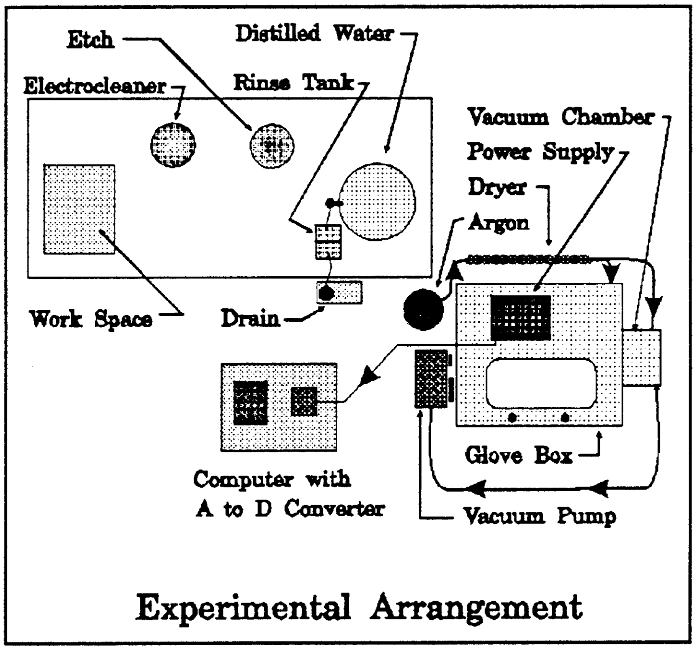

Figure 4.1-1 Laboratory Work Area

Within the glove box, equipment was arranged as per Figure 4.1-2. This provided a working space for weighing, measuring, mixing, and any other physical manipulation needed. Scales, solvents and chemicals were stored in the areas indicated. Barium nitrate and yttrium nitrate chemicals along with any electrodes coated by deposits were normally stored under vacuum in the glove box vacuum chamber. The plating cell pictured in Figure 3.8.2-1 was centrally mounted on a ring stand with temperature control rheostat to the rear.

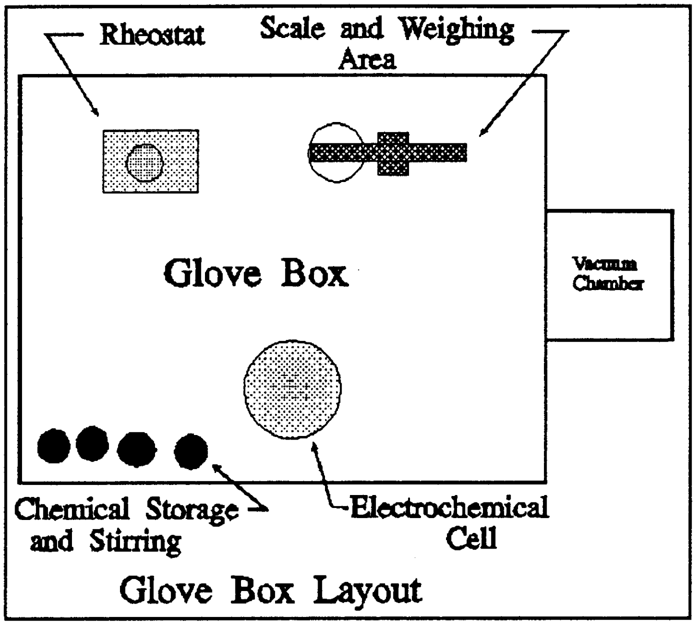

Figure 4.1-2 Glovebox Layout

A Wenking potentiostat was mounted on top of the glove box and feed-throughs were made in the glove box wall using BNC male-male connectors. Adjacent to the glove box on a movable cart was a Microsmart 386 IBM compatible computer with a National Instruments AT-MIO-16 data acquisition board arranged to provide 8 differential inputs in +10 to -10 volts. The potentiostat, cell, and data acquisition system were connected as shown in Figure 4.1-1.

4.2 Electrode Preparation

Electrode preparation consisted of construction of the electrode itself using copper discs as substrates and subsequent cleaning of the working surface prior to use. The procedures described below were used equally for both the working and counter electrodes.

4.2.1 Electrode Construction

Commercially available copper sheet, 0.5 mm thick, was punched using a hole punch on which the guide dimples have been ground off. This provides a flat circular copper disk about 1cm in diameter. These disks were dipped in the acid etch described in §4.1.2 for 10 seconds, removed, and rinsed in flowing distilled water. If any surface tarnish remained, this process would be repeated. Once clean, the disks would be allowed to air dry.

The holder pictured in Figure 4.2.1-1 consists of a similarly prepared disk to which a copper wire had been soldered. This wire was then passed through a 4mm pyrex glass tube bent as to facilitate electrode placement in the cell. The solder side of the disk was sealed with epoxy to prevent exposure of the solution to any contaminants which could be in the solder. The epoxy also sealed the glass tube preventing filling by the solution and positioned the soldered disk for reproducible placement in the cell.

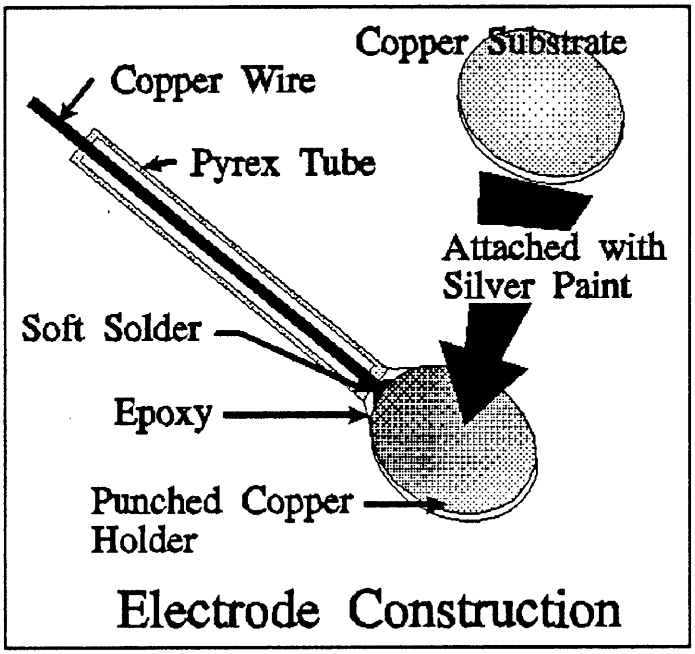

Figure 4.2.1-1 Working Electrode

A punched copper disc was adhered to the surface of the soldered disc on the end of the holder using silver paint. Once dry the edges of the substrate were sealed using a rubber epoxy and allowed to dry.

4.2.2 Electrode Cleaning

ASTM B281 provides recommended cleaning procedures for copper when used in aqueous electroplating.[45] This was used as the framework for the final procedure which was slightly modified to allow for the presence of epoxies. The procedure is as follows.

1.) A dry copper electrode prepared in accordance with §4.1.1 is placed in the alkaline electrocleaning bath described in Appendix D.[46] A stainless steel cathode is used for this bath. The copper electrode is connected as the anode. This prevents oxidation of the cleaned surface by O_2 (g) generated during the cleaning process. Sufficient cleaning occurred when a 6 volt lantern battery was connected to the system for 1 minute.[47]

2.) The electrode was rinsed in running distilled water for 30 seconds.

3.) An acid dip followed to neutralize any retained alkaline electrocleaning solution and to remove any oxide layer which may have built up. Appendix E reports the components of the acid dip.[48] Although the recommended time for the electrode in this bath was from 5 seconds to 5 minutes, the author found that dipping the electrode into the acid, allowing a uniform layer of bubbles to form on the surface, removing the electrode, and rinsing produced the best results. This process, when repeated two or three times, produced a smooth shiny clean surface.

4.) The electrode was rinsed in running distilled water for 30 seconds.

5.) Methanol was squirt on the electrode to rinse any trace of water from the electrode and facilitate drying. While still wet with methanol, the electrodes were placed in the vacuum chamber attached to the glove box. The author found that, if left to air dry, the clean copper surface would develop an oxide layer.

6.) The electrodes were vacuum dried.

4.3 Solution Preparation

Solution preparation required first drying the solvent and metallic salts then weighing and mixing the solutions to the desired molarity.

4.3.1 Solvent Drying

A review of the literature shows several methods for drying dimethyl sulfoxide.[49] [50] [51] A method which involved the addition of fresh activated alumina as a drying agent and storing the solvent over 4A molecular sieve was found to be commonly used, simple to perform, and reportedly successful.[52] [53] This technique was used to prepare the solvent.

The specific steps followed:

1.) All solutions began with new bottles of .5 L Fisher Spectral Grade Methyl Sulfoxide analyzed at <0.04% water.

2.) The bottles were placed in the glove box unopened through the vacuum chamber. To ensure no moisture entered the glove box, a vacuum of approximately 300 torr was applied to the chamber and a small amount of flowing dry argon flushed across the bottle for 5 minutes. The vacuum chamber was then filled with dry argon to atmospheric pressure and the bottle moved into the glove box.

3.) 250 ml of DMSO was poured into a clean dry flask fitted with a Teflon plug, a Teflon stirring bar inserted, and dry activated alumina added. The flask was then placed on a magnetic stirrer and allowed to stir over night.

4.) The DMSO was poured into a glass filter funnel having a 20 micron glass frit filter in the bottom and a vacuum applied to separate the dry DMSO from the alumina. The dry DMSO was collected in a 250 ml flask.

5.) 100 ml of dry DMSO was measured in the glove box using a clean dry glass graduated cylinder and placed in a clean dry flask fitted with a Teflon stopper.

6.) In the few cases when this dry solution was stored over long periods of time, 4A molecular sieve was placed in the bottom of the flask. The sieve must be allowed to settle and the liquid poured off careful to avoid fine particles being transferred.

4.3.2 Drying The Metallic Salts

All metallic salts contain some water and often are received wet. This water content can be greatly reduced but not totally eliminated through the use of the following drying method. Section 5.1.3 explains the final drying step to remove water introduced in the system by the metallic salts.

1.) A sheet of aluminum foil is placed in the bottom of a large vacuum desiccator and the wet salt poured onto the sheet. Large clumps of salt are broken apart with a stainless steel spatula.

2.) The desiccator is closed and connected to a vacuum roughing pump. Vacuum is applied for 24 hours. A warming lamp may be used to enhance the drying but care must be taken not to heat the salt in vacuum above its decomposition temperature.

3.) Dry argon is used to back fill the desiccator and the salt quickly checked for dryness. If the salt is dried, it will be made up of powdery crystals which may be stuck together. These clumps should break apart readily. Dry salt is then poured into a jar which can be sealed and placed in the vacuum chamber of the glove box.

4.) The salt is removed from the vacuum chamber only for weighing and should remain a crystalline powder. If adhesion occurred, it was re-dried.

4.3.3 Mixing Solutions

Mixing solutions was done only in the dry argon atmosphere of the glove box. DMSO prepared as per §4.3.1 and dry metallic salt prepared as per §4.3.2 were used to mix each 100 ml. solution. Sufficient salt was added to make the molarity desired, a Teflon stirring bar added, and the flask stoppered and placed on a magnetic stirrer. Vigorous stirring was applied until all crystals dissolved. This was found to be a slow process for the $Ba(NO_3)_2$, (several hours), but rather fast, (less than one hour), for $Y(NO_3)_3$.

4.4 Electrodeposition Procedure

Once the preparations described in §4.2 and §4.3 was completed, the following final electrodeposition process was employed:

1.) 50 ml of solution is poured from the flask into the reaction cell through one of the cell electrode ports. Use of a side port, those used for the working or counter electrodes, prevents excessive mixing when poured reducing the possibility of moisture absorption from the argon.

2.) A calibrated rheostat connected to a hemispherical heating mantle stabilizes temperature at 25°C ±0.5°C. Temperature was determined by a thermometer inserted into the solution through an opening in the reaction cell.

3.) The reference electrode is removed from storage in a .1M $AgNO_3$ in DMSO solution, rinsed in dry DMSO and inserted into the center opening of the reaction cell. Note a Teflon retainer used to position the electrodes in the cell can slide on the reference electrode to facilitate insertion. A hook of bent glass also helps insert or remove the Teflon retainer without damage.

4.) Two electrodes prepared in accordance with §4.2 are placed into the cell each through one of the two side openings. Some manipulation is required to do this because of the bends in the shafts which are necessary to properly position the electrodes. The electrodes fit in the Teflon retainer at the bottom of the reference electrode and may be moved vertically to ensure the working and counter electrodes are directly opposed.

5.) Alligator clips connect to the wires leading to the potentiostat are attached to the electrode leads. The working electrode is cathodic during plating and close to the reference electrode.

6.) Electrodeposition as described in §5.2 and §5.3 is conducted. Appendix E shows the run record used.

7.) The working electrode is removed from the cell and rinsed for 30 minutes in dry DMSO which has been stored over 4A molecular sieve.

8.) A razor blade or another sharp instrument is used to separate the copper substrate from the electrode assembly. Any rubber epoxy remaining on the substrate is removed by pulling with a tweezers. The substrate is then placed in a small cubical plastic storage box with lintless Kimwipe in the bottom. The lid was marked to keep track of the sample.

9. The sample was stored under vacuum.

4.6 Test And Evaluation

4.6.1 Data Acquisition

Data acquisition was obtained during deposition using the system described in §4.1.1. The program used to take the data was written in "C" using the interactive programming environment of LabWindows. Appendix G is a listing of the program used. Data was stored in ASCII format using " and , delimiters. This allowed importing the data into spread sheet programs. Borland's Quatro Pro was used to make the graphs of the data obtained during cyclic voltammetry and deposition.

4.6.2 Visual Inspection And Physical Testing

Observations were recorded on the run sheets as to the condition of the electrodes, solution, and plated samples before, during and after the deposition. Changes which occurred in the sample during drying were also recorded. Each sample was scratched with a sharp metal object when wet to determine if the deposit had adhered to the sample or could be easily removed. Specific items observed were:

1.) Electrode discoloration prior to deposition.

2.) A build up of a white coating on either electrode during deposition, indicating the presence of water and passivation occurring.

3.) Uniformity, color, density, and morphology of the deposit during plating, in the rinse, and after drying. Changes were noted.

4.) Any changes in the solution color or transparency.

4.6.3 Microscopy

Scanning Electron Microscopy (SEM) was performed on all samples to gain an understanding of the surface morphology of the depositions and any changes caused to the underlying copper substrates. Magnifications from 400x to 4000x were used. Greater magnifications did not provide additional detail or information on the deposits. Some charging of the samples was experienced, making clear images difficult to obtain. If significant degradation of the image occurred, the sample was removed and a thin gold layer evaporated on it in vacuum.

EDAX analysis was used to analyze the first samples. This technique was found to sample too deeply for good analysis of a thin film such as those deposited. The copper signal became the prominent feature for all analyses. It was possible to detect some yttrium and barium but the accuracy of quantitative analysis was unacceptable.

4.6.4 XPS Analysis

X-Ray Photoelectron Spectroscopy (XPS), also known as Electron Spectroscopy for Chemical Analysis (ESCA) is a surface analysis technique widely used for the investigation of chemical composition. Quantitative data can often be obtained from peak heights or areas and identification of chemical states can be made from the exact position of the peaks.[54] By irradiating the sample with monoenergetic soft x-rays and energy analyzing the electrons emitted, these photons which penetrate only 1-10 microns cause surface electrons to be emitted. An analyzer determines the energy of these electrons. The emitted electrons have a kinetic energy of:

$$KE = h\nu - BE - \phi_s \qquad (7)$$

where $h\nu$ is the photon energy, BE is the binding energy, and ϕ_s is the spectrometer work function. The binding energy is related to the energy level of the shell in which the emitted electron had been while the work function provides information about the closeness of the electron to the Fermi level. Because each element has a distinct arrangement of electrons, they will correspondingly give a unique spectrum of emitted electrons. The work function relates the bonding energy of those electrons involved in ionic or covalent bonds to a shift in the discrete energy peaks.

Application of this technique to surface analysis of the electrodeposits was very effective. The samples' elemental composition was readily determined. However, because charging was a significant problem, exact peak energy values could not be obtained. This prevented determining bond energies and exact chemical form.

The system used offered the opportunity to argon sputter the surface. This was used to remove surface contaminants which built up during the rinse and when the samples were transferred into the SEM or XPS systems. (Sufficient surface contamination occurred to warrant the special handling techniques explained in § 4.6.5.)

4.6.5 Special Handling Techniques

During some of the initial XPS and SEM analysis, it was noted that the black smooth barium films began to turn white during the time the were exposed to air. This has been suggested in the literature to be due to decomposition of barium metal to barium hydroxide. Since a chemical change occurred in the films so quickly due to exposure to atmospheric moisture, a technique to insolate the samples from the atmosphere was devised.

Samples stored in vacuum as described in §4.3.2 were removed from vacuum back into the dry argon environment of the glovebox where they were placed in sealable plastic bags. This exposed them only to dry argon. The bags were placed back in the vacuum chamber, the glove box sealed, and the bags removed to the outside. They were transported immediately to the analysis equipment where they were placed in a glove bag flushed with dry argon. Any stages or tools needed to mount the samples in the test apparatus were also put in the glove bag. The sealed plastic bags opened in the dry argon atmosphere in the glove bag and the samples mounted. To insert the samples in the instrument, the opening of the glove bag was placed around the opening of the test instrument while the samples were still in the bag. At all times a flow of dry argon kept moisture from entering the bag. The samples were then mounted as called for by the instrument using the appropriate stages and tools placed in the bag. The bag was removed from the opening only when the sample was in the instrument and under vacuum. The process was reversed to remove the sample.

By following this technique, decomposition of the barium samples stopped. The same procedure was used for the yttrium samples as well. Following this procedure proved effective in eliminating surface damage on both yttrium and barium samples. This technique should be employed when any sample of yttrium or especially barium may be exposed to any moisture.

Chapter 5 RESULTS AND DISCUSSION

In the early period of this investigation, many of the results lacked consistency. Solutions and procedures which on one day provided good deposition, performed very differently on another. As a result, experimentation became a search for the key factors to control the final outcome of the deposition process. To better understand the identification of these key factors is the purpose of this chapter.

Section 5.1, Initial Experimentation, describes key experiments and results which lead to the determination of the controlling parameters. Lack of success in gaining control of reproducibility provided as much information as successes itself.

Once the possible controlling parameters were identified, experiments were designed to regulate them to achieve successful deposition. Section 5.2, Barium Deposition, describes the resulting experimental investigation.

Section 5.3, Yttrium Deposition, will follow much the tack taken with Section 5.2.

The author's intent is to provide the reader insight into the parameters controlling reproducibility. What's more, the final results of this thesis investigation are the starting point for further development of processes for industrial use, and will be pursued as a doctoral dissertation.

5.1 Initial Experimentation

Non-aqueous electrochemical deposition systems in many ways are similar to better known aqueous systems. For a system to be non-aqueous is not simply a matter of replacing water with an organic solvent. In §3.2, the requisite attributes of a solvent useful for electrochemical systems are discussed. Many organic solvents fulfill these requirements. Fully appreciating the factors which control electrochemical processes in these non-aqueous solvent requires some initial investigation into solvent performances in general. This section provides these key initial investigations and the results of the experiments.

5.1.1 Formation of $Ba(OH)_2$

Barium is known to react violently with water. To confirm just how violent this reaction is, a 40 mesh grain of barium metal was dropped into a 50 ml beaker containing 10 ml of distilled water. Upon contacting the water, the barium began to generate gas bubbles and move around the surface of the water resting on these bubbles. As it did so, a milky white precipitate became partially suspended in the water. The reaction ended when the grain of barium was completely consumed. The chemical reaction which occurred is:

$$Ba + 2H_2O \rightarrow Ba(OH)_2 + H_2 \qquad (8)$$

To obtain a sample of barium hydroxide for use later in analysis, several grains of barium were placed in a clean petri dish partly filled with distilled water. A reaction similar to that described above took place. Because the volume of water was low the precipitate settled to the bottom of the dish where it could be collected. The collected material was placed on a substrate cleaned as described in §4.2.1. The substrate was then placed on a hot plate warm to the touch. After five minutes, all the water evaporated leaving a white, somewhat adherent, rough film on the substrate. XPS

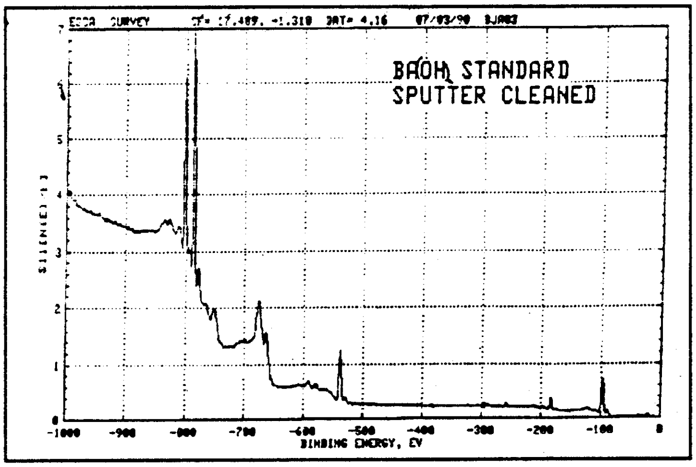

Figure 5.1.1-1 XPS of $Ba(OH)_2$ Calibration Sample

analysis of this sample is presented in Figure 5.1.1-1 and is compared to the reference standard shown in Figure 5.1.1-2. As can be seen from the results of the XPS, the barium peaks of the sample match well with those presented as the standard. Uniform charging of the sample due to low conductivity occurred indicated by a uniform shift in peaks from the sample versus the standard. This effect makes it difficult to use energy peak values to determine the chemical form of barium.

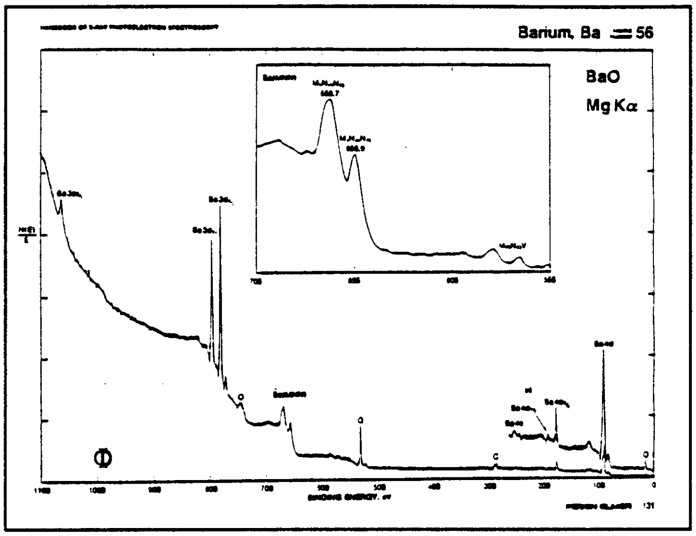

Figure 5.1.1-2 XPS Standard For Barium

5.1.2 Effects of Water In The System

Non-aqueous electrochemical systems use organic solvents rather than water as the medium for dissolution of the salts. It would seem that the name also implies the complete absence of water from the system. The author found this to be easily implied and difficult to achieve.

Since barium is highly reactive with water, the presence of water in DMSO would be indicated if barium grains formed the milky white precipitate. In an argon-filled glove box, about 5 grams of 40 mesh barium metal grains were placed in a titanium basket which was put into 100 ml of Fisher spectral grade DMSO (0.04% water) and allowed to stand. No violent reaction occurred; however, after one hour a thick white foam had formed on the top of the basket. When removed and dried, this foam had the same appearance as the milky white precipitate formed using water. XPS of this material was compared to and matched the prepared standard presented in Figure

5.1.1-1. This confirmed that the water content of the DMSO as obtained from commercial sources was too high to preclude significant decomposition of metallic barium. Any metallic barium present as deposit would then be attacked during deposition if water was not completely eliminated from the solution.

In a second experiment, the hygroscopic nature of DMSO was examined. A beaker of 100 ml of DMSO was exposed to dehumidified laboratory air for approximately 12 hours. The beaker was then transferred to the argon filled glove box and one gram of 40 mesh barium grains in a titanium basket were placed in the DMSO. A vigorous reaction similar to slow boiling occurred immediately creating a thick milky white foam atop the entire beaker indicating significant water had been absorbed from the dehumidified air.

These experiments establish:

- Barium is highly reactive with water and forms a milky white precipitate shown by XPS to be $Ba(OH)_2$.

- Reagent grade 0.04% water content DMSO available from suppliers contains enough water to form barium hydroxide on pure barium, albeit slowly.

- DMSO is greatly hygroscopic. It exposure to dehumidified air for even relatively short periods of time is likely to further degrade its stability in the presence of barium.

5.1.3 Elimination Of Water From Metal Salts

When shipped, the metal salts are hydrated. Their packaged configuration are labeled as:

$$Ba(NO_3)_2 \cdot 3H_2O$$
$$Y(NO_3)_3 \cdot 6H_2O$$

This implies some water is contained in the salt crystals; however, the salts often were visibly wet. To dry them, the procedure outlined in §4.3.2 was developed. This procedure removes all the water not trapped in the crystal matrix and some which is trapped in the matrix. The procedure does not completely remove all trace of water from the metal salt. What's more, some water is then added to the solution when the salts are dissolved in the dry DMSO. The method for determining the presence of this water and the technique for removing it is discussed in §5.1.4.

Both salts are extremely hygroscopic. When weighed in a Metlar balance in open atmosphere, the crystals absorbed sufficient water to become wet and dissolved into liquid droplets. The weight changed rapidly and an accurate measurement was impossible to obtain in open atmosphere. Weighing became accurate once conducted in the dry glove box environment.

These observations establish:

- Barium Nitrate and Yttrium Nitrate require drying by vacuum desiccation, prior to use.

- The salts are hygroscopic. Accurate weights can only be obtained when measured in a dry environment.

- The final contribution of water to a solution by the salts is not determined by these experiments.

5.1.4 Determination Of Water In Solution

Because barium is highly reactive with water and yttrium is somewhat reactive in water, determination of water in solution after dissolving the dried salts in dry DMSO is necessary. LSV has been used to determine the presence of water in solution. Figure 5.1.4-1 shows a LSV of pure dry DMSO. Since pure DMSO is stable at the potentials applied, very little conduction occurs. addition of metal salt to dry DMSO, $Y(NO_3)_3$ in the case of Figure 5.1.4-2, produces a LSV with a significant wave around -0.85 volts. Figure 5.1.4-3 shows the effect of adding water to the solution. Much less conduction occurs and the wave disappears. A similar trend can be seen in barium solutions.

This experiment established:

- Dry DMSO is stable within the range of voltages to be used for this deposition process.

- Dry DMSO is essentially a non-conductor within the range of voltage to be used for this deposition process.

- The presence of water in DMSO can be detected by use of Linear Sweep Voltammetry.

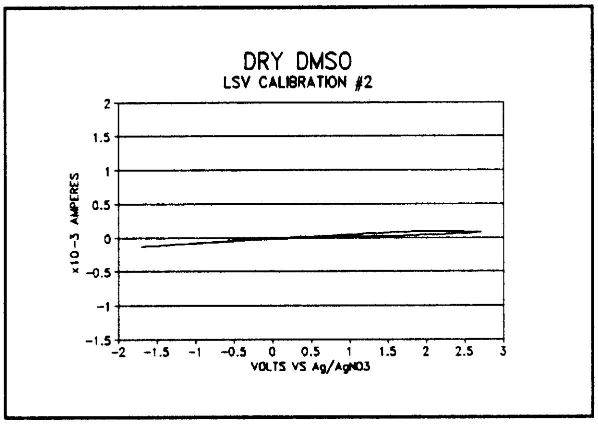

Figure 5.1.4-1 LSV Dry DMSO

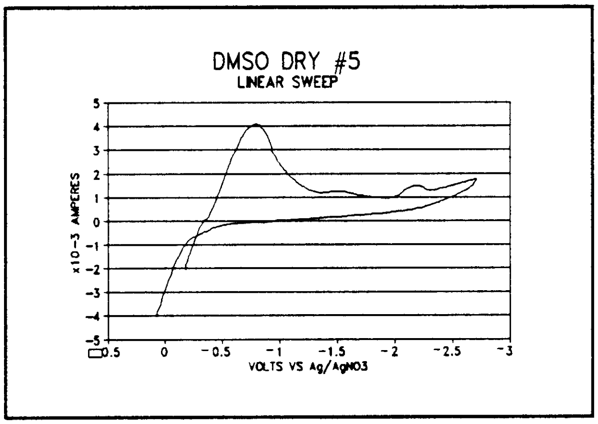

Figure 5.1.4-2 Dry 0.2M $Y(NO_3)_2$

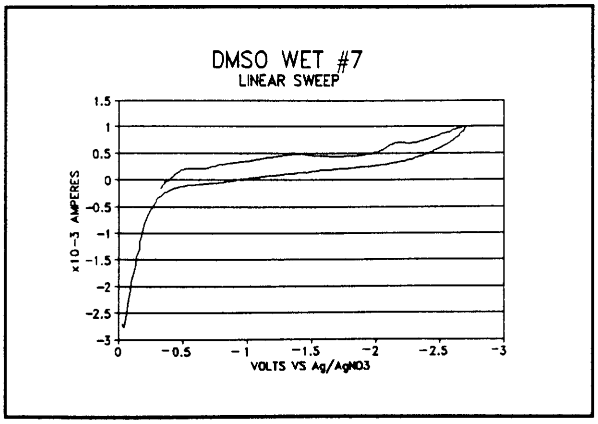

Figure 5.1.4-3 Wet 0.2M $Y(NO_3)_2$

5.2 Barium Deposition

One hundred milliliters of 0.1M $Ba(NO_3)_2$ solution in dry DMSO was prepared in accordance with the procedure outlined in §4.3. Two copper electrodes were prepared as specified in §4.4, as was the reference electrode in accordance with §3.5. Fifty milliliters

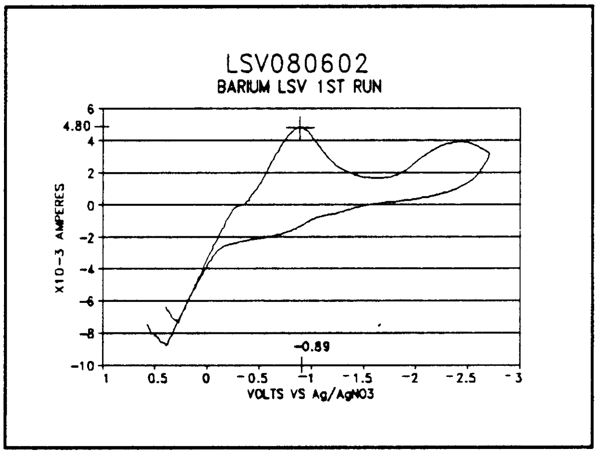

Figure 5.2.1-1 Barium LSV-Dry

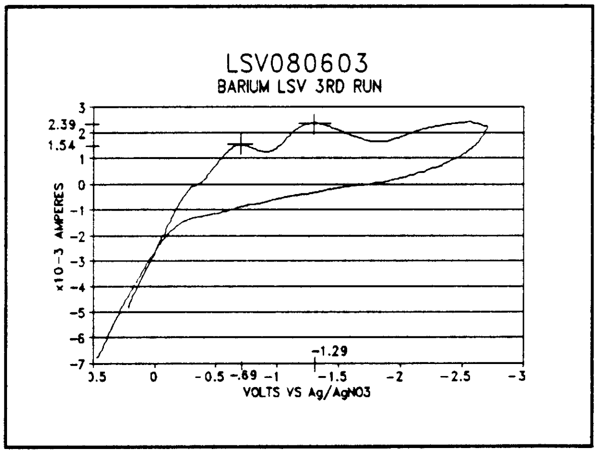

Figure 5.2.1-2 Barium LSV-Wet

of the solution were added to the electrochemical cell shown in Figure 3.8.2-1, the electrodes inserted, and connected as in Figure 4.1-1.

5.2.1 Linear Sweep Voltammetry - Barium

Before attempting to electroplate barium, a linear sweep voltammogram was conducted on the solution from +2.3 volts to -2.3 volts and back at a rate of 1.15 volts per minute to determine water content and the potential at which the onset of deposition of barium begins.

A full cycle LSV was conducted from +2.3 volts to -2.3 volts and back at a rate of 1.15 volts per minute. Upon beginning, the counter electrode began generating gas slowly in the form of two or three pin head size bubbles per second. No deposition was visible on either electrode. As the voltage sweep moved into the negative range the gas generation stopped. A black film began to appear on the working electrode at approximately -2.0 volts. This film continued to darken through -2.3 volts and continued to darken as the LSV began to return to +2.3 volts. As the potential exceeded (positive) -1.5 volts, the black film on the working electrode began to lighten. As the potential neared +2.3 volts, the counter electrode began to develop a dull grey film. Figure 5.2.1-1 shows the results of the LSV. Note that some water was found to be present by the peak appearing at -0.8 volts. The onset of the deposition believed to be barium cannot be determined conclusively by this experiment since it is obscured by the decomposition curve for water.

A second and third LSV were conducted immediately following the first the results of which the third is presented in Figure 5.2.1-2. The potential for the onset of barium deposition can be projected to be -0.90 volts. Notice the significant reduction in current around -0.5 volts due to water decomposition. Since solution was essentially unchanged from the original configuration, this is likely due to the decrease in water content in the solution caused by its dissociation during the first LSV. Implied is that a technique occasionally used in industrial process may assist in reducing final water contamination. Since the water begins decomposition at a potential below that used to deposit the desired material, in this case barium, a sacrificial cathode may be set to a potential below which the barium will begin deposition but above which the unwanted material decomposes or is deposited. The system is allowed to remain at this potential until no current flows. All the water will have been decomposed.

During the LSV, the black film which had developed on the working electrode darkened. The light grey film which had developed on the counter electrode disappeared. The appearance of the solution did not change. Since the solution did not darken, change color or transparency, and no precipitates formed, it is likely that the black deposit believed to be barium resolvated as ions. LSVs conducted on new solutions showed a potential wave identified with water dissociation on the first cycle and a greatly reduced or absent wave in subsequent sweeps on the same solutions. All LSVs, upon completion, yielded fairly uniform dark grey to black films which were adherent.

These experiments determined:

- Dissolution of vacuum dried barium salts in dry DMSO contributes measurable quantities of water to the solution.

- This water can be eliminated from the solution by setting the potential of the system described to -0.50 volts and allowing current to flow. When the current flow becomes approximately equal to that of pure dry DMSO at the set potential, the water contamination has been eliminated.

- Potentials with respect to the Ag/$AgNO_3$ reference electrode described in §3.6 for barium deposition are:

Onset of Deposition: $E' = -0.90$ volts

Half-Wave Potential: $E_{1/2} = -1.15$ volts

Diffusion Limited: $E_d = -1.29$ volts

- The deposit is a smooth, adherent, black thin film on the exposed surface of the working electrode believed to be barium.

- The solution appears unchanged by the LSV, suggesting dissolution of the deposit.

5.2.2 Electrodeposition of Barium

The initial deposition would be attempted using the same solution and cell as the LSV described in §5.2.1 but with freshly prepared working and counter electrodes. In order to obtain the highest deposition rate possible, the potential applied would be more negative than the diffusion limiting potential. Concerns about adhesion problems and possible loss of film at this high potential were allayed. Because no adhesion problems were noted during the LSV none were expected at this potential. In performing the deposition, the computer's data acquisition system was started, the

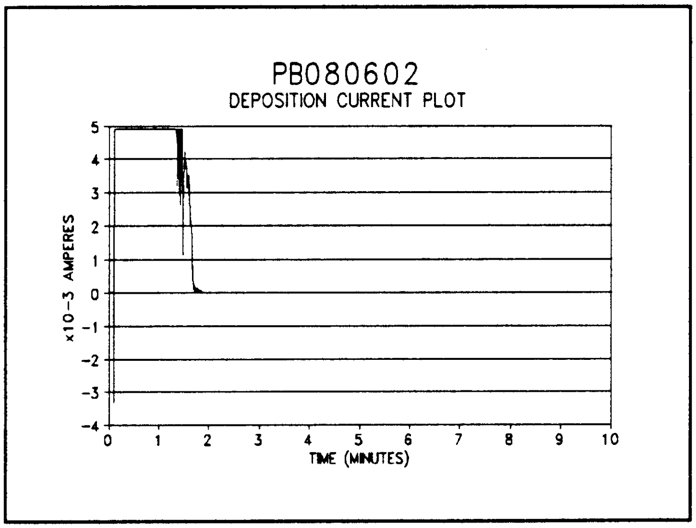

Figure 5.2.2-1 Ba - No Deposition

manually controlled potentiostat was set and turned on, and a 9.25 minute deposition was executed.

At the conclusion of this deposition, no film was found on either the working or counter electrode. No changes in solution were visible. Figure 5.2.2-1 shows the current dropped rapidly to zero. These results were inconsistent with the results of the Linear Sweep Voltammetry presented in §5.1.1. Another LSV was conducted resulting in deposition. The author concluded that despite use of rather elaborate cleaning techniques as described in §4.1.2, the surfaces of the electrodes were insufficiently prepared for the deposition process. A final stripping of the surface layer in solution immediately prior to deposition is required.

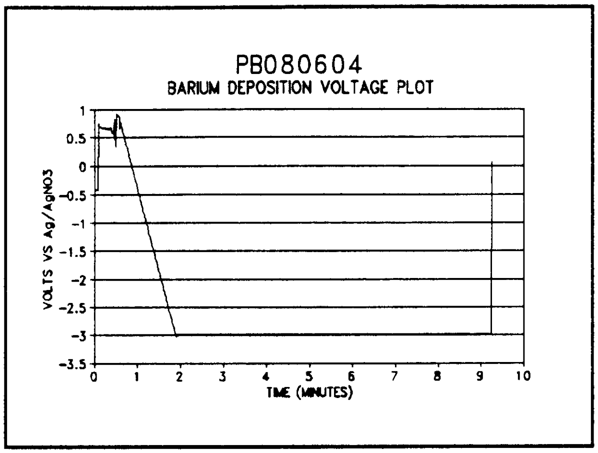

Figure 5.2.2-2 Barium Deposition Voltage Plot

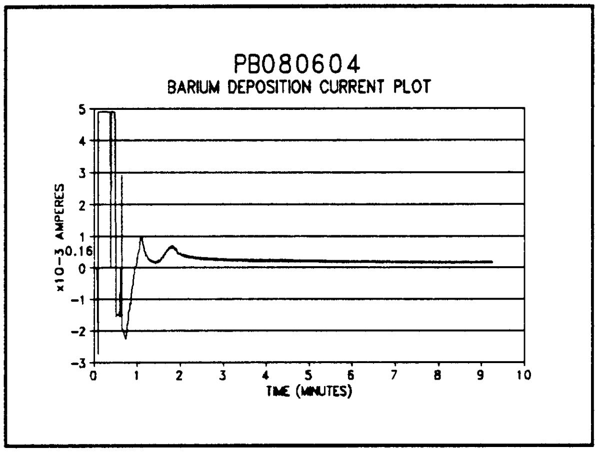

Figure 5.2.2-3 Ba Deposition Current Plot

Another pair of electrodes was prepared in accordance with §4.2 and placed in the same cell as the above two experiments. A stripping potential of +2.3 volts was applied, then, ramped to a potential of -2.989 volts was applied to the same electrodes. An adherent, uniform, thin, black film began to develop immediately. Figure 5.2.2-2 shows the potential applied to the working electrode while Figure 5.2.2-3 shows the current response of the system. Note the current did not decrease to zero but decayed to a value of 0.16 mA.

Additional solutions were made and the process described above repeated yielding the identical results. When no stripping was performed in solution immediately prior to deposition, no deposition occurred.

5.2.3 Electrodeposited Film Analysis - Barium

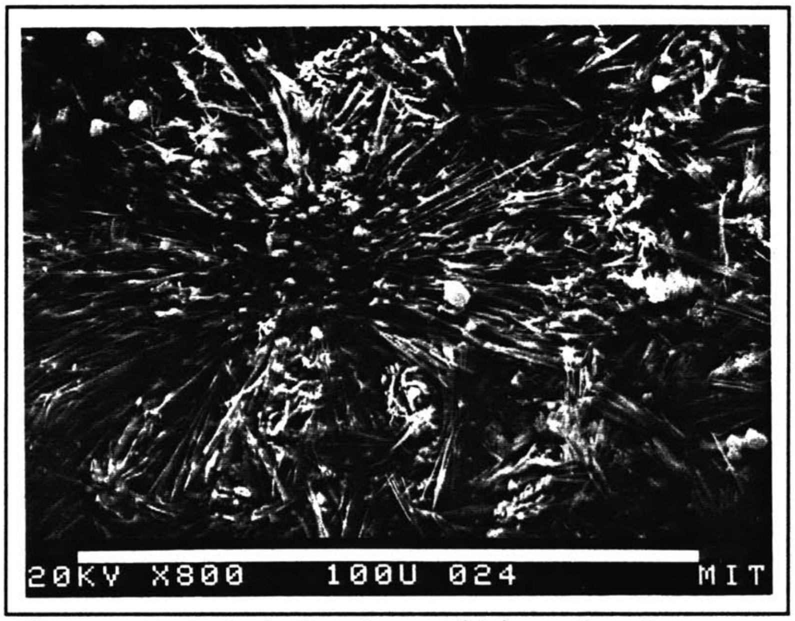

Figure 5.2.3-1 Ba Deposition Surface

Electron microscopy of the film was performed using the AMR SEM. Figure 5.2.3-1 shows the surface of the final deposit described in §5.2.2. It is comprised of a uniformly coarse surface with small nodular protrusions. Greater magnification showed no additional features smaller than 1μm. The nodules were not separate from but an intricate part of the films. XPS presented in Figure 5.2.3-2 shows the deposit was indeed a form of barium. The carbon peak indicates some carbon contamination found on the surface. However, after sputtering for one minute with argon, the carbon contamination was removed and the film showed a deposit free of carbon contamination. Comparing Figure 5.2.3-2 to Figure 5.2.3-3 shows the lack of a carbon peak. The most likely source of this surface carbon is believed to be DMSO not fully removed from the surface of the film by vacuum drying.

Because the film is a poor conductor, charging occurred during XPS testing. This prevented accurate determination of peak energies; therefore, it was not possible to determine the actual form of barium comprising the black film. Possible forms include pure metal barium, barium oxide, barium peroxide, or barium hydroxide. Each of these except metallic barium were eliminated by

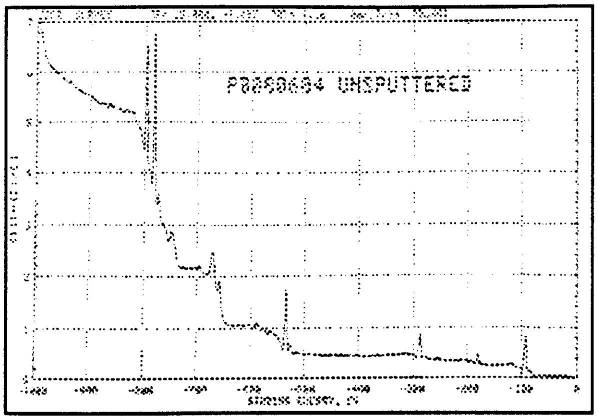

Figure 5.2.3-2 XPS Ba Before Sputtering

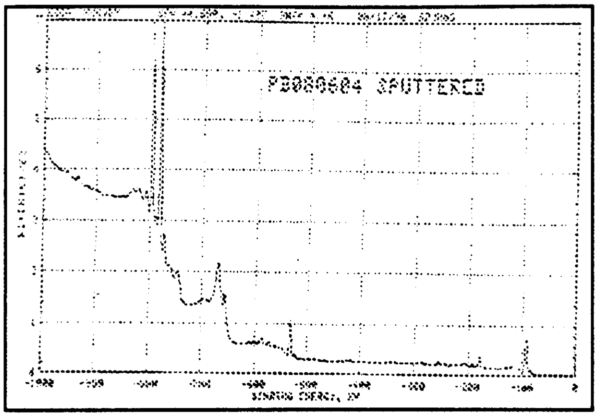

Figure 5.2.3-3 Ba After Sputtering

their appearance. That is, of these compounds, only barium metal appears in a dark grey or black form.[55]

This experiment determined:

- A black, adherent, smooth, uniform deposit could be obtained at a potential of -2.989 volts vs Ag/$AgNO_3$ reference.

- This deposit could not be obtained even on a clean copper surface unless the working electrode underwent stripping in situ prior to deposition.

- This deposit was metallic barium.

- Some surface carbon contamination remained from the DMSO after rinsing and vacuum drying but could be removed by sputtering.

- Because the sputtering was able to remove the carbon, the deposition was sufficiently dense to exclude solvent incorporation in the film itself.

5.2.4 Water Damage of Electrodeposited Barium

The electrodeposited barium films proved susceptible to water damage. A vacuum of below 200 millitorr was maintained for storage of the films. They were exposed only to what was believed to be a dry argon environment for brief (less than 10 minutes at a time) periods to remove selected samples from storage for examination and testing. Uniform, dense, black, films were found to become light grey, white, or thinly transparent after this short exposure to atmospheric moisture. Figure 5.2.4-1 shows the surface of electrodeposited barium after 4 days of storage. Note the center of the surface retained the same morphology as the that seen for freshly deposited barium seen in Figure 5.2.3-1. However, crystal whiskers are found to emanate from central nodes. These whiskers begin to impinge on each other as the node sites increase in number as this is shown in Figure 5.2.4-2. When these nodes become sufficiently dense, they appear as in Figure 5.2.4-3. Note how when compared with Figure 5.2.4-4,

Figure 5.2.4-1 Ba - 4 Day Storage

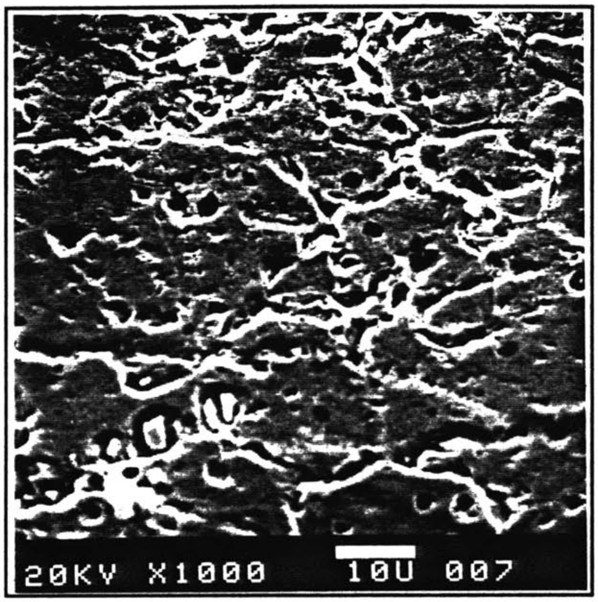

Figure 5.2.4-2 Ba No Damage

a micrograph of barium hydroxide, the dense nodes appear similar to the small particle sites of the latter figure. This suggests the formation of barium hydroxide.

5.3 Yttrium Deposition

Similar preparations were conducted for the deposition of yttrium as for barium. One hundred milliliters of .1M $Y(NO_3)_3$ solution in dry DMSO was prepared in accordance with the procedure outlined in §4.3, two copper electrodes prepared as described in §4.2, and 50 ml of solution added to the cell shown in Chapter 3. The working and counter electrodes were added to the cell and the $Ag/AgNO_3$ reference electrode was introduced.

5.3.1 Linear Sweep Voltammetry - Yttrium

To determine solution response to applied potential and at what potential successful deposition might occur, a full cycle LSV was conducted from +2.3 volts to -2.3 volts and back at a rate of 1.15 volts per minute. The system's response was also similar to that of barium. The counter electrode began generating gas slowly in the form of two or three pin-head-sized bubbles per second. Initially, no deposit occurred on either electrode. As the potential became negative with respect to the reference electrode gas generation stopped. A black film began to appear on the working electrode at

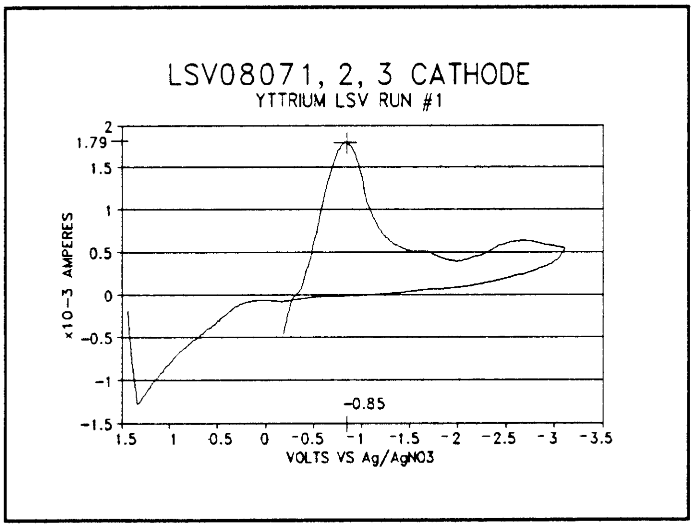

Figure 5.3.1-1 Yttrium - LSV with Trace Water

approximately -1.8 volts. This film continued to darken through -2.3 volts. As the potential reversed, the black film on the working electrode remained dark and uniform even as the potential neared +2.3 volts. Figure 5.3.1-1 shows the results of the LSV. Note that some water was also found to be present by the peak appearing at -0.85 volts. The onset of the deposition believed to be yttrium also cannot be determined conclusively by this experiment since it is obscured by the decomposition curve for water.

The second LSV conducted immediately following the first using the same system as above and presented in Figure 5.3.1-2 shows a reduction in current around the potential of -0.85 volts. The decrease in water content in solution allows this onset of yttrium deposition to be seen. During this LSV, the working electrode retained a dark black film uniformly across the surface. Some slight lightening of the film on the working electrode was noted when the electrode was left at +2.3 volts for several minutes. Since the appearance of the solution did not change and no precipitates formed, it is likely that the black deposit, believed to be yttrium, resolvated as ions. As with the barium LSVs, subsequent LSV of the yttrium solution yielded no significant change to the voltage/current curve. All LSVs, upon completion yielded fairly uniform dark grey to black films which were adherent to the copper substrate.

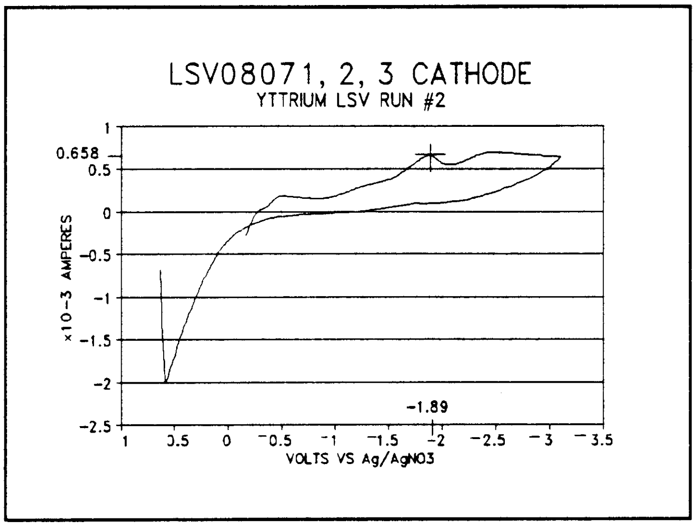

Figure 5.2.1-2 Yttrium - LSV Dry

These experiments determined:

- Dissolution of vacuum dried yttrium salts in dry DMSO contributes measurable quantities of water to the solution.

- This water can be eliminated from the solution by setting the potential of the system described to -0.5 volts and allowing current to flow. When the current flow becomes approximately equal to that of DMSO at the set potential, the water has been eliminated. Because the onset of deposition of the desired yttrium or yttrium compounds occurs at about -1.4 volts, a lower potential must be used to eliminate water contamination or unwanted loss of the desired plating components may occur.

- Potentials with respect to the Ag/$AgNO_3$ reference electrode for barium deposition are:

Onset of Deposition: $E' = -1.4$ volts

Half-Wave Potential: $E_{1/2} = -1.6$ volts

Diffusion Limited: $E_d = -1.89$ volts

- The deposit is a smooth, adherent, black, very dense, thin film on the exposed surface of the working electrode believed to be yttrium or a compound of yttrium.

- The solution appears unchanged by the LSV to include dissolution of the deposit.

5.3.2 Electrodeposition of Yttrium

Since a deposition range was determined, a deposition potential of -2.3 volts was selected. This would ensure the maximum deposition rate possible being above the diffusion limiting potential. As with barium, the LSV had not shown loss of adhesion at this potential. In order to determine if electrode preparation was sufficient without stripping, the first deposition was attempted without applying a stripping potential. Because potentialcontrol and data acquisition were manually controlled as described in §5.2, deposition would again be for approximately 9 minutes.

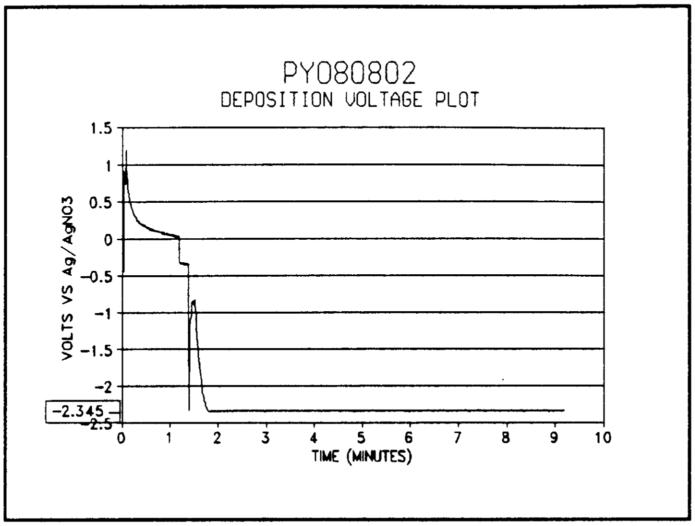

Figure 5.3.2-1 Yttrium Deposition Voltage Plot

No film developed on the surface of either electrode during this deposition. To determine if stripping was also required for yttrium deposition, a stripping potential was applied to the same electrodes; then, -2.3 volts were again applied for 9 minutes. Figures 5.3.2-1 and 5.3.2-2 show the applied potential and current response. At the completion of the deposition cycle, a thin, dense, opaque, black film had developed on the copper working electrode as would be expected by the current response of the system. No change in the appearance of the solution was occurred.

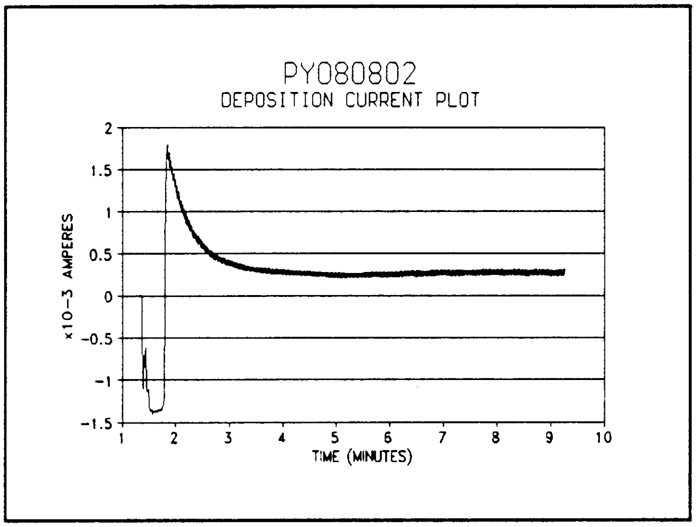

Figure 5.3.2-2 Yttrium Deposition Current Plot

A second deposit was attempted with the same solution but new working and counter electrodes prepared in accordance with §4.1. A stripping potential was applied; then, the plating potential of -2.3 volts was applied. An adherent, uniform, dense, opaque, black film began to develop on the working electrode immediately. The film continued to darken as the process continued. Figure 5.3.2-3 shows the voltage applied to the system while the current response

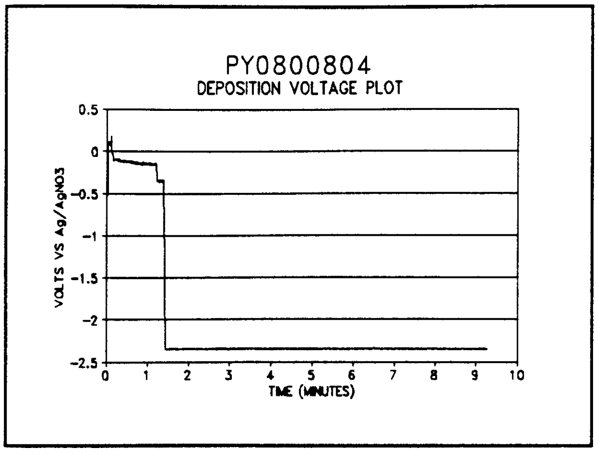

Figure 5.3.2-3 Yttrium Deposition - Voltage Plot - 2nd Run

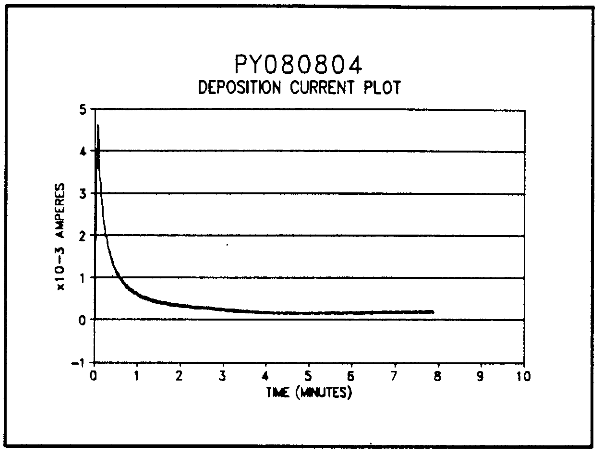

Figure 5.3.2-4 Yttrium Deposition - Current Plot - 2nd Run

is shown in Figure 5.3.2-4. Note that the current decayed quickly settling to a current of 0.3 mA. This experiment confirmed stripping to be a required step in this deposition of yttrium.

5.3.3 Electrodeposited Film Analysis - Yttrium

Electron microscopy of the films were performed using an AMR SEM. Figure 5.3.3-1 shows the surface of the deposit which appeared smooth and uniform to the eye was comprised of a microscopically uniformly smooth surface. The greater magnification of Figure 5.3.3-2 did show that, although quite smooth, steps were visible. Further magnification did not yield any additional features. The small particles sitting on the surface of the deposit are believed to be contaminants of alumina used to dry the solution. XPS presented in Figure 5.3.3-3 shows the deposit was indeed a form of yttrium. Carbon was also a surface contaminant as seen by the carbon peak indicated. However, as with barium, after sputtering for one minute with argon, the carbon contamination was removed and the film showed a deposit free of carbon contamination as seen in the XPS conducted after sputtering and presented in Figure 5.3.3-4. The most likely source of this surface carbon is also believed to be DMSO not remaining on the surface of the film following vacuum drying.

Figure 5.3.3-1 Yttrium Deposit - Low Magnification

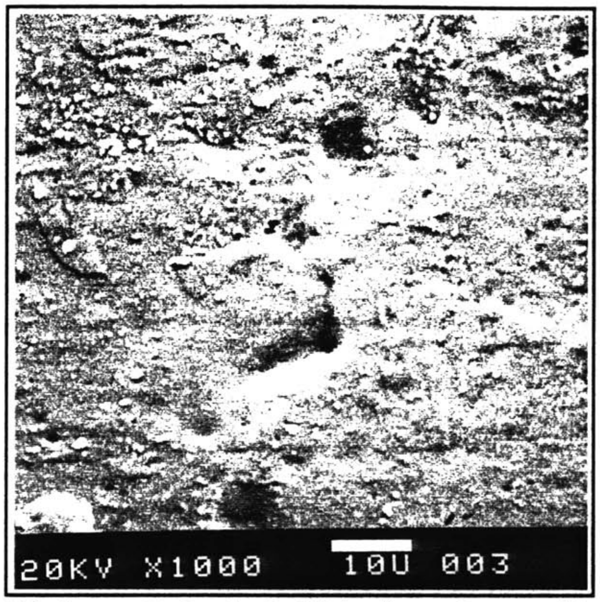

Figure 5.3.3-2 Yttrium Deposit - High Magnification

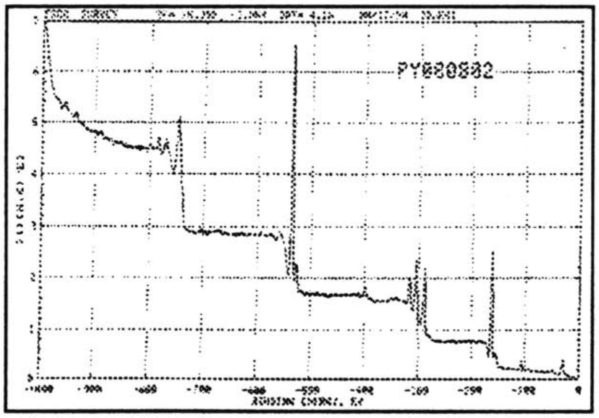

Figure 5.3.3-3 XPS of Yttrium Deposit

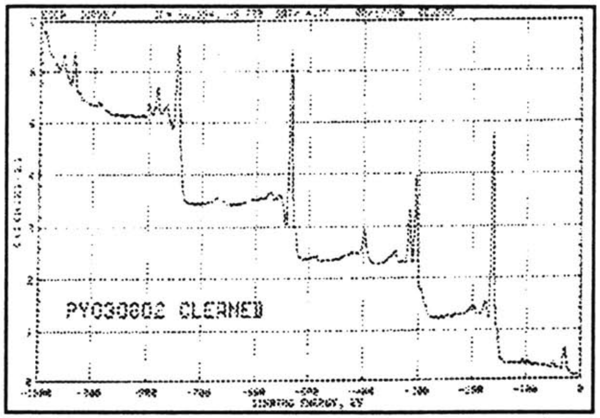

Figure 5.3.3-4 XPS of Yttrium Deposit - After Sputtering

Because charging was less of a problem in this films than in the barium films the XPS peaks of Figure 5.3.3-4 when compared with Figure 5.3.3-5, the standard for yttrium indicated the deposit likely to be in the form a metallic yttrium. As with barium, consideration of possible compounds which could have been formed such as yttrium oxide and yttrium hydroxide were eliminated not just by the XPS results but because these compounds do not exhibit physical characteristics similar to the deposit.[56]

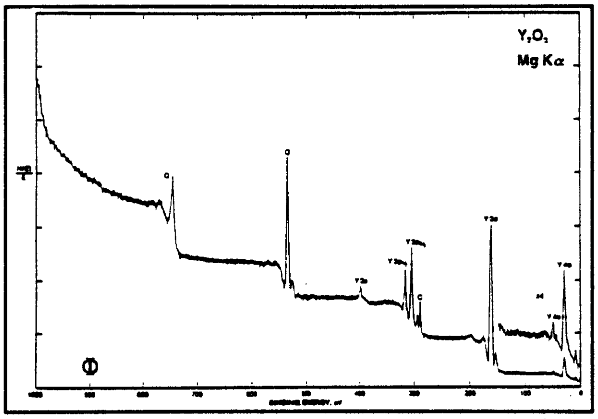

Figure 5.3.3-5 XPS of Yttrium Standard

This experiment determined:

- A black, adherent, smooth, opaque, dense, uniform deposit could be obtained at a potential of -2.3 volts vs $Ag/AgNO_3$ reference.

- This deposit could not be obtained even on a clean copper surface unless the working electrode underwent stripping in situ prior to deposition.

- This deposit was metallic yttrium.

- Some surface carbon contamination remained from the DMSO after rinsing and vacuum drying but could be removed by sputtering.

- Because the sputtering was able to remove the carbon, the deposition was sufficiently dense to exclude solvent incorporation in the film itself.

5.3.4 Water Damage of Electrodeposited Yttrium

Unlike barium, the yttrium appears significantly more stable in the presence of water. Despite being stored in the same environment as the barium samples showed no deterioration after 4 days.

Chapter 6 CONCLUSIONS

This thesis has two stated objectives:

1.) to determine the feasibility of electrodeposition of barium on a copper electrode.

2.) to determine the feasibility of electrodeposition of yttrium on a separate copper electrode.

Implied within each of these objectives is that to be potentially practical, the process must be reproducible and that the result must be predictable. This, in turn, requires a knowledge of the controlling parameters of the process. The purpose of this chapter is to state unequivocally the conclusions of the investigation with respect to the two stated objectives and reproducibility. Possible future steps will also be discussed.

6.1 Feasibility Of Electrodeposition Of Barium

Initially, it appeared electrodeposition of barium metal on a copper electrode from a solution of barium nitrate in dimethyl sulfoxide would be a straight-forward process. In fact, the first experiments provided deposits which were confirmed to be contain barium. However, the deposition process often produced inconsistent results from seemingly identical steps. Depositions performed one day would provided results very different when identically executed on subsequent days. It became essential to determine the controlling parameters of barium deposition.

When grains of barium metal were put into a beaker of water, a violent exothermic reaction occurred producing gas and a milky white precipitate. The reaction is known to be:

$$Ba + 2H_2O \rightarrow Ba(OH)_2 + H_2$$

The gas produced was hydrogen and the milky white precipitate was barium hydroxide. A second experiment in which a comparable amount of barium metal was placed in dimethyl sulfoxide contaminated with small amounts of water caused the same reaction. Further, this reaction did not occur in DMSO void of water. Therefore, <u>water present in DMSO will cause any barium metal present to undergo the reaction above.</u>

No milky white precipitate formed when barium nitrate was dissolved in DMSO which was slightly contaminated with water. The solution appeared identical to that formed from dry DMSO. What was noted was that deposition from the 'wet' DMSO was extremely difficult, requiring application of a much higher potential between the reference and working electrode than for the 'dry' DMSO. The 'wet' deposition yielded a white crystalline deposit rather than the black smooth deposit for the 'dry' DMSO. XPS analysis of this white crystalline deposit, proved the presence of barium and oxygen; however, charging prevented confirmation of it being barium hydroxide. Of the substances the deposit could be, the only one fitting the physical characteristics was barium hydroxide. To ensure the substance was not barium oxide, the deposit was placed in water producing no change to the deposit.

It is the author's conclusion then:

- Barium metal to include electrodeposited barium metal is not able to coexist with water. Barium hydroxide will be formed.

- Barium ions in solution are protected from reaction with water contamination in DMSO by the solvation sheath. This is evidenced by water contaminated DMSO not causing precipitation of $Ba(OH)_2$ from solution.

- Barium metal can be deposited from 'wet' solutions but the deposit will be attacked by water in solution changing the metallic deposit to barium hydroxide. This hydroxide acts as a passivating layer requiring higher potentials be applied to continue the deposition process.

In the face of these conclusions, the experimental procedures and apparatus described in Chapter 4 proved sufficient to remove all the water from the solvent DMSO. When dried, barium nitrate salt was added to this dry DMSO. A measurable increase in the presence of water was found in Linear Sweep Voltammograms. This trace amounts of water was then removed by a sacrificial electrode having a negative potential versus reference great enough to cause dissociation of water. Using the counter electrode as the sacrificial electrode and a reversed potential was found to be sufficient to eliminate trace water without a deleterious effect on the deposition process at the working electrode.

The author concluded then:

- The apparatus and techniques described in Chapter 4 were sufficient to dry the DMSO solvent for use.

- Vacuum drying of barium nitrate metallic salts eliminated most but not all water from the salts. When dissolved in dry DMSO, this water was detectable.

- This trace water could be eliminated from solution by use of a sacrificial electrode to cause dissociation of the remaining water.

- The counter electrode could be used as the sacrificial electrode with no adverse effects on later plating processes.

A dry electrolyte and clean copper electrode do not ensure deposition. The cleaning process described in §4.1.2 proved insufficient to allow deposition of barium from a water-free solution. A final stripping of the copper electrode in the plating bath was required to ensure deposition occurred. Failure to perform this stripping consistently resulted in no deposit forming. Once stripped, a black, uniform, smooth dense deposit always formed.

The author concludes then:

- Standard cleaning techniques are insufficient to allow for electrodeposition of barium.

- A stripping potential must be applied to remove the final vestiges of surface contaminates and oxides immediately prior to deposition.

- Failure to strip the electrode consistently prevents deposition.

XPS analysis of the smooth, black, uniform deposits proved to be barium. The form of barium could not be definitively identified by XPS because charging shifted the energy peaks from known values. However, the possible forms of barium which could have been made from the constituents present in solution are listed below. A comparison to the actual deposit is made.

Name	Chemical Formulae	Physical Appearance	Melting Point, °C	Solubility in Water
Barium	Ba	grey	725	Decomposes to $Ba(OH)_2$
Barium Hydroxide	$Ba(OH)_2$	colorless crystal	78	slightly soluble
Barium Hydride	BaH_2	grey crystal	675	decomposes to $Ba(OH)_2$
Barium Peroxide	BaO_2	whitish-grey powder	450	slightly soluble
Barium Oxide	BaO	whitish-yellow	1923	slightly soluble
Barium Deposit		smooth grey-black film	>>600	decomposes to $Ba(OH)_2$

It is clear from this chart that all possible forms are excluded except for metallic barium and barium hydride. The sample deposit was exposed to the flame of a propane burner with no visible change occurred in this deposit. This would exclude barium hydroxide because of its low melting point. SEM showed the deposit to be smooth and not crystalline in form.

The author then concludes:

- The deposit produced from electrodeposition at -2.3 volts versus $Ag/AgNO_3$ reference electrode in .1 M $Ba(NO3)_2$ in dry DMSO is barium metal.

In summary, the experimental results described in detail in Chapter 5 and the conclusions derived from those experiments and delineated above support the following general conclusion concerning electrodeposition of barium:

> Electrodeposition of barium metal on a copper substrate from a non-aqueous solution of barium nitrate in dimethyl sulfoxide is achieved. When the procedures outlined in Chapter 4 and amended to include copper stripping and final elimination of water through use of sacrificial dissociation of water as described in Chapter 5 are used the process is fully reproducible.

6.2 Feasibility Of Electrodeposition Of Yttrium

Consistent deposition of yttrium was far easier to achieve than for barium. The presence of small amounts of water in DMSO had no noticeable effect on the overall deposition process. However, the techniques and apparatus used for deposition of barium were also applied to the deposition of yttrium in order to maintain the same high standard of reproducibility and to ensure compatibility in deposition systems between the two metals. The similarity would allow for further investigation of sequential or concurrent deposition processes without concern for the effects of water contamination resulting from yttrium deposition in a system not totally devoid of water.

Yttrium does not form yttrium hydroxide as readily as barium hydroxide is formed. Yttrium metal placed in water shows no significant signs of deterioration for 24 hours.

The author concludes then:

- Water only slowly forms yttrium hydroxide.

- Slight amounts of water present in solution do not adversely effect the plating process.

Yttrium deposition is as sensitive as barium deposition to the cleanliness of the electrode surface. Despite cleaning the copper electrode in accordance with the procedures described in §4.1.2, deposition did not occur. If the copper surface of the working electrode was stripped in solution smooth, black, uniform, adherent films could be consistently obtained.

The author concludes then:

- Standard cleaning techniques are insufficient to allow for electrodeposition of yttrium.

- A stripping potential must be applied to remove the final vestiges of surface contaminates and oxides immediately prior to deposition.

- Failure to strip the electrode consistently causes no deposit to form.

The deposited smooth, black, uniform films were examined using XPS and the deposits were found to contain yttrium. Section 5.3.3 shows the films to be a form of yttrium. Below is listed a table of the possible forms of yttrium which could have resulted from the compounds in solution. Comparison to the properties of the actual deposit is made.

Name	Chemical Formula	Physical Appearance	Solubility in Water
Yttrium	Y	grey-black metal	slightly soluble, decomposes
Yttrium Hydroxide	$Y(OH)_3$	whitish-yellow gelatin or powder	insoluble
Yttrium Oxide	Y_2O_3	colorless to yellowish powder or cube	very very slightly soluble
Deposit		smooth grey-black uniform film	no solubility noted [3]

This chart supported by XPS the conclusion that the deposits formed on the copper substrate are metallic yttrium.

The author then concludes:

- The electrodeposited films produced at -2.3 volts versus $Ag/AgNO_3$ reference electrode in .1 M $Y(NO_3)_3$ in dry DMSO is yttrium metal.

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[3] Solubility in water of the deposit was tested only as a secondary observation to rinsing in water contaminated DMSO. At no time was sufficient material dissolved to produce a noticeable change in the deposit. No yellow hue was detected which would have indicated dissolution and reaction to form yttrium hydroxide.

In summary, the experimental results described in detail in Chapter 5 and the conclusions derived from those experiments and delineated above support the following general conclusion concerning electrodeposition of yttrium:

> Electrodeposition of yttrium metal on a copper substrate from a non-aqueous solution of yttrium nitrate in dimethyl sulfoxide has been achieved. Although slight amounts of water do not have a significant effect on the deposition process, avoiding water contamination improves the ion concentration available for plating. When the procedures outlined in Chapter 4 are amended to include copper stripping Chapter 5 the process is fully reproducible.

6.3 Initial Results Of Sequential Deposition

In examining the purpose for embarking on this investigation, the possible uses for either electrodeposited yttrium or barium were considered. Each metal could find some use in the form of separate films; however, the most intriguing prospect is the use of the two films in a sequential deposition to be interdiffused and reacted forming one of the High Temperature Super Conductor films known as 123 or YBC and having the chemical equation:

$$YBa_2Cu_3O_{7-x}$$

Electrodepositing each film allows separate control of the deposition process for each metal. Since morphology of deposit is often effected by temperature, concentration, and applied potential, each of these could be individually adjusted to fit the specific needs of the deposition process. For example, should yttrium be deposited in a specular form at -1.5 volts at 26°C from a 0.4M solution while barium produces a specular film at -2.1 volts at 35°C from a .2M solution, the overall process could be developed to produce exactly the desired film.

Because the current used during the process is directly proportional to the amount deposited, the ratios of yttrium to barium to copper can be controlled by monitoring the net current passed during each deposition. This affords a valuable measure of control.

The experiments conducted in support of this thesis only demonstrated the feasibility of separately electrodepositing yttrium and barium each on a clean copper substrate. Therefore, the next step is to determine if one could be deposited by similar technique on the other. One metal would be deposited on a copper substrate and the second metals would then be deposited on the first. Evaluation of these films to show presence of both metals would then be required.

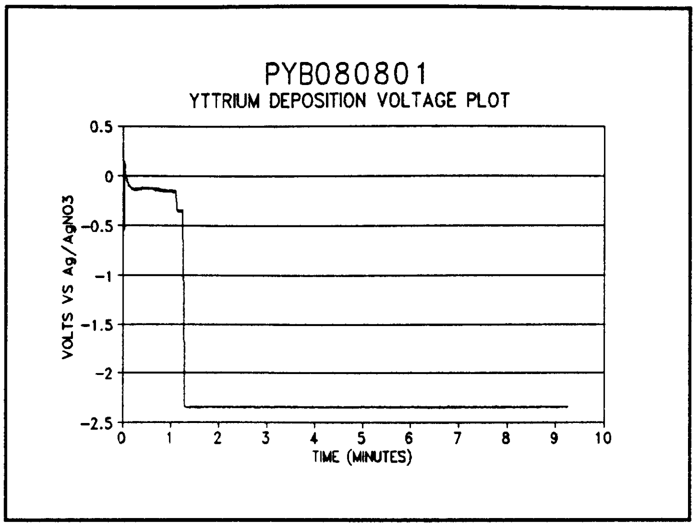


Figure 6.3-1 Yttrium Deposition Voltage Plot - Sequential Deposit

Yttrium has been selected to be the first metal to be deposited because it is, in general, easier to deposit and provided a smoother more uniform surface upon which to deposit the barium.

A 0.2M $Y(NO_3)_3$ in dry DMSO was mixed in accordance with §4.3.substrates were cleaned as described in §4.1 and, along with the $Ag/AgNO_3$ reference electrode, assembled into a cell. Figure 6.3-1 shows the potentials applied for the yttrium deposition. Note that the stripping potential was set to +2.3 volts but the conductivity of the solution was so great that the instrument went to compliance. After approximately 1 minute, the potential was reversed to -2.3 volts and maintained for approximately 9 minutes. Figure 6.3-2 shows the current passed. A smooth, uniform, black film developed on the working electrode as with previous experiments. At the conclusion of the deposition, the electrodes removed and rinsed in dry DMSO for 20 minutes as the cell was rinsed and prepared for barium deposition.

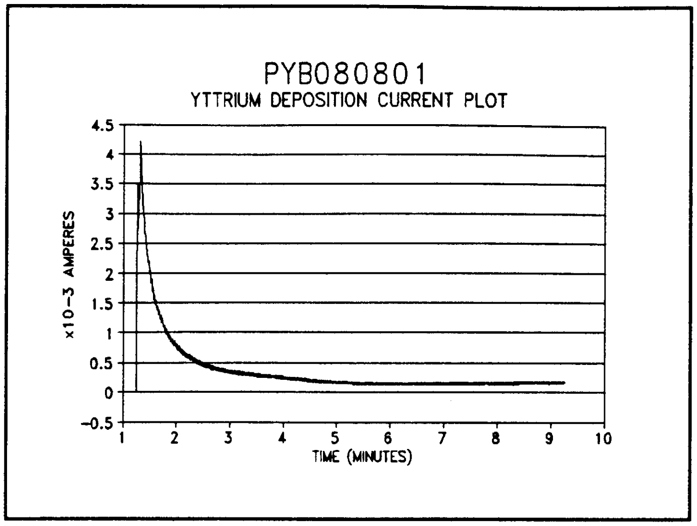


Figure 6.3-2 Yttrium Deposition - Current Plot - Sequential Deposit

A .2M $Ba(NO_3)_2$ in dry DMSO was mixed in accordance with §4.3. Copper substrates were cleaned as described in 4.1 and, along with the Ag/AgNO3 reference electrode,assembled into a cell. the cell reassembles with separate working and counter electrodes, and a linear sweep voltammogram performed in solution to decrease water content. The same electrodes used in the deposition of yttrium were again inserted into the cell and connected to the potentiostat. A stripping potential of +2.3 volts was applied for approximately 1 minute. Potential applied can be seen in Figure 6.3-3. Note again, some initial difficulty on the part of the potentiostat to respond to the system caused some irregularities in the stripping potential. Before reversing the potential to begin barium plating, it was observed that the yttrium film had become less dense but that a dark grey film remained. The potential was then set to -2.3 volts and allowed to deposit for approximately 9 minutes. The plating current is presented in Figure 6.3-4. The electrode was removed from the cell and rinsed for 20 minutes in dry DMSO. It was then dried in vacuum for 24 hours.

Figure 6.3-5 is an SEM micrograph of the Cu-Y-Ba specimen. Most prominent are the large nodules on fairly smooth planes. AES surveys of the two sites marked are presented in Figure 6.3-6. Both sites showed significant barium deposits with the large nodule providing a very strong signal. Oxygen and copper to a far lesser degree could also be found. No significant yttrium signature was found in either location. The minor copper signal could have been due to holes in the overall film allowing sampling of the electrode surface.

Auger depth profiling was then conducted on a smooth site on the surface. Figure 6.3-7 shows the profile developed from 21 sputtering events of 0.15 minutes each for a total of 3.0 minutes of sputtering. Specific elements sampled for were barium, oxygen, copper, and yttrium. Sputter time reflects sampling from deeper

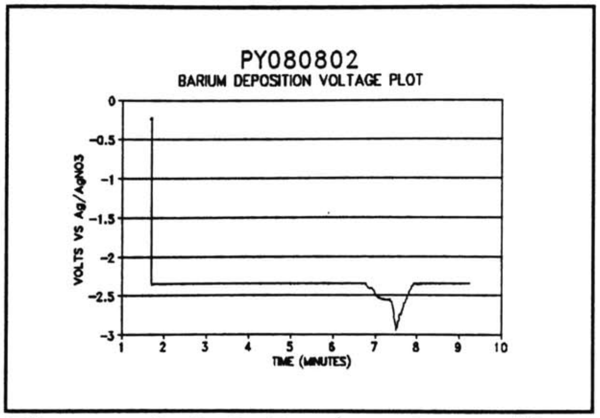


Figure 6.3-3 Barium Deposit - Voltage Plot - Sequential Deposition

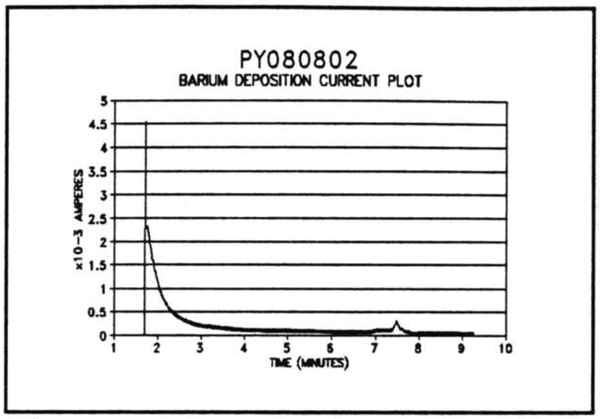


Figure 6.3-4 Barium Deposit - Current Plot - Sequential Deposition

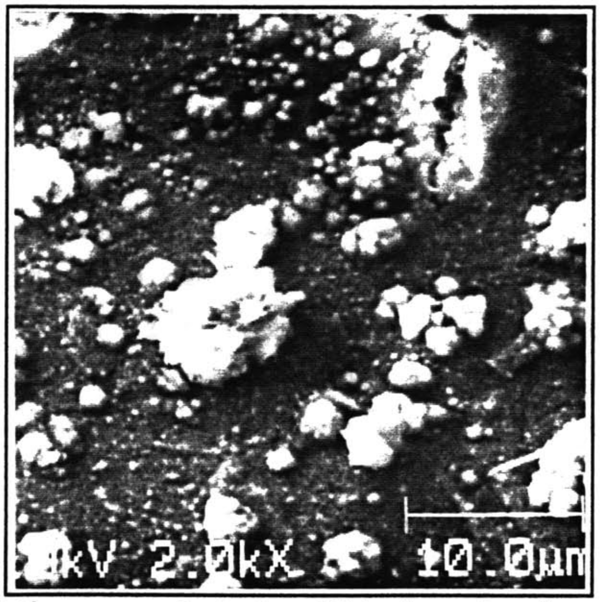


Figure 6.3-5 Yttrium-Barium Sequential Deposition Micrograph

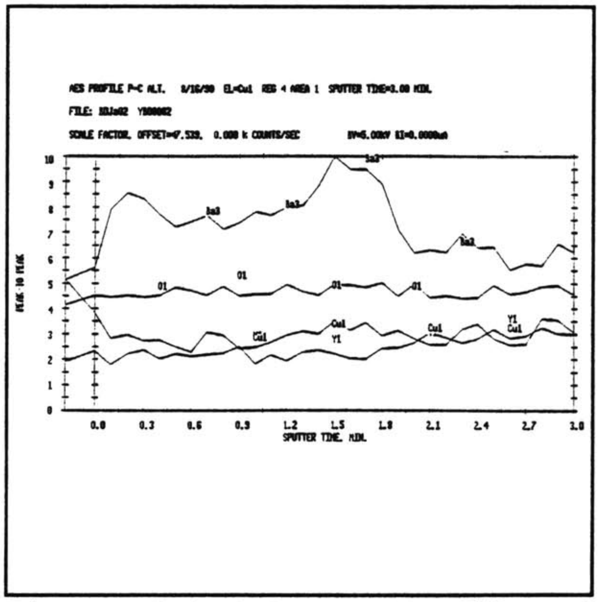


Figure 6.3-6 Auger Profile of Yttrium-Barium Sequential Deposition

level within the sample. Clearly the barium decreased significantly between 1.8 and 1.95 sputtering minutes. Yttrium was detected from the initial stages and increased from a level of about 1.9 to 3.0 in arbitrary intensity units with the most significant increase coming about the point at which the barium decreased. The source of initial yttrium is likely to have been the yttrium returned to solution during stripping in the barium plating bath. An attempt to sputter to a deeper level in search of a specific increase in yttrium caused damage to the sample. Some of the surrounding surface appeared to have been sputtered onto the site being sampled, causing a large increase in barium signal.

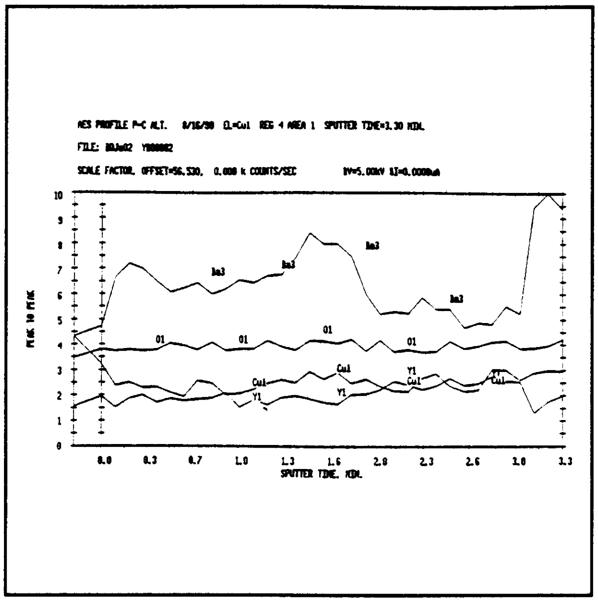


Figure 6.3-7 Auger Profile of Yttrium-Barium Sequential Deposition - 2nd Series

In summary, deposition of yttrium was performed in a manner commensurate with reproducible results as described in this thesis. Yttrium deposition was observed and even after stripping, a grey-black film remained. Barium was then deposited on the yttrium and formed a smooth, black, adherent film. Uneven deposits were found on the to exist on the film with large barium nodules on a uniform barium layer. Depth profiling showed the presence of yttrium even in the initial stages and becoming more pronounced as the depth profile continued. As barium decreased, yttrium increased.

The author then concludes:

- Deposition of barium from a barium nitrate in dry DMSO solution on electrodeposited yttrium is feasible.

Investigation of sequential deposition shows the processes which support individual deposition are fundamentally sound for sequential deposition. Refinements in the individual deposition processes, the sequential process, and the order of deposition will likely improve the character and reproducibility of the deposit. The possible promise of electrodepositing HTSC 123 precursor material warrants further investigation.

Appendix A - Commonly Electroplated Elements

PERIODIC TABLE OF THE ELEMENTS

KEY TO CHART

Atomic Number → 50 +2 ← Oxidation States
Symbol → Sn +4
Atomic Weight → 118.69
18 18 4 ← Electron Configuration

Transition Elements

Transition Elements

Group 8

1a	2a	3b	4b	5b	6b	7b	8			1b	2b	3a	4a	5a	6a	7a	0	Orbit
1 +1 −1 H 1.0079 1																	2 0 He 4.00260 2	K
3 +1 Li 6.94 2-1	4 +2 Be 9.01218 2-2											5 +3 B 10.81 2-3	6 +2 +4 −4 C 12.011 2-4	7 +1 +2 +3 +4 +5 −1 −2 −3 N 14.0067 2-5	8 −2 O 15.9994 2-6	9 −1 F 18.998403 2-7	10 0 Ne 20.17$_9$ 2-8	K-L
11 +1 Na 22.98977 2-8-1	12 +2 Mg 24.305 2-8-2											13 +3 Al 26.98154 2-8-3	14 +2 +4 −4 Si 28.0855 2-8-4	15 +3 +5 −3 P 30.97376 2-8-5	16 +4 +6 −2 S 32.06 2-8-6	17 +1 +5 +7 −1 Cl 35.453 2-8-7	18 0 Ar 39.948 2-8-8	K-L-M
19 +1 K 39.0983 -8-8-1	20 +2 Ca 40.08 -8-8-2	21 +3 Sc 44.9559 -8-9-2	22 +2 +3 +4 Ti 47.90 -8-10-2	23 +2 +3 +4 +5 V 50.9415 -8-11-2	24 +2 +3 +6 Cr 51.996 -8-13-1	25 +2 +3 +4 +7 Mn 54.9380 -8-13-2	26 +2 +3 Fe 55.847 -8-14-2	27 +2 +3 Co 58.9332 -8-15-2	28 +2 +3 Ni 58.71 -8-16-2	29 +1 +2 Cu 63.546 -8-18-1	30 +2 Zn 65.38 -8-18-2	31 +3 Ga 69.735 -8-18-3	32 +2 +4 Ge 72.59 -8-18-4	33 +3 +5 −3 As 74.9216 -8-18-5	34 +4 +6 −2 Se 78.96 -8-18-6	35 +1 +5 −1 Br 79.904 -8-18-7	36 0 Kr 83.80 -8-18-8	-L-M-N
37 +1 Rb 85.467$_8$ -18-8-1	38 +2 Sr 87.62 -18-8-2	39 +3 Y 88.9059 -18-9-2	40 +4 Zr 91.22 -18-10-2	41 +3 +5 Nb 92.9064 -18-12-1	42 +6 Mo 95.94 -18-13-1	43 +4 +6 +7 Tc 98.9062 -18-13-2	44 +3 Ru 101.07 -18-15-1	45 +3 Rh 102.9055 -18-16-1	46 +2 +4 Pd 106.4 -18-18-0	47 +1 Ag 107.868 -18-18-1	48 +2 Cd 112.41 -18-18-2	49 +3 In 114.82 -18-18-3	50 +2 +4 Sn 118.69 -18-18-4	51 +3 +5 −3 Sb 121.75 -18-18-5	52 +4 +6 −2 Te 127.60 -18-18-6	53 +1 +5 +7 −1 I 126.9045 -18-18-7	54 0 Xe 131.30 -18-18-8	-M-N-O
55 +1 Cs 132.9054 -18-8-1	56 +2 Ba 137.33 -18-8-2	57* +3 La 138.9055 -18-9-2	72 +4 Hf 178.49 -32-10-2	73 +5 Ta 180.947$_9$ -32-11-2	74 +6 W 183.85 -32-12-2	75 +4 +6 +7 Re 186.207 -32-13-2	76 +3 +4 Os 190.2 -32-14-2	77 +3 +4 Ir 192.22 -32-15-2	78 +2 +4 Pt 195.09 -32-16-2	79 +1 +3 Au 196.9665 -32-18-1	80 +1 +2 Hg 200.59 -32-18-2	81 +1 +3 Tl 204.37 -32-18-3	82 +2 +4 Pb 207.2 -32-18-4	83 +3 +5 Bi 208.9804 -32-18-5	84 +2 +4 Po (209) -32-18-6	85 At (210) -32-18-7	86 0 Rn (222) -32-18-8	-N-O-P
87 +1 Fr (223) -18-8-1	88 +2 Ra 226.0254 -18-8-2	89** +3 Ac (227) -18-9-2	104 +4 Rf (260) -32-10-2	105 Ha (260) -32-11-2	106 (263) -32-12-2													O P Q

*Lanthanides	58 +3 +4 Ce 140.12 -20-8-2	59 +3 Pr 140.9077 -21-8-2	60 +3 Nd 144.24 -22-8-2	61 +3 Pm (145) -23-8-2	62 +2 +3 Sm 150.4 -24-8-2	63 +2 +3 Eu 151.96 -25-8-2	64 +3 Gd 157.25 -25-9-2	65 +3 Tb 158.9254 -27-8-2	66 +3 Dy 162.50 -28-8-2	67 +3 Ho 164.9304 -29-8-2	68 +3 Er 167.26 -30-8-2	69 +3 Tm 168.9342 -31-8-2	70 +2 +3 Yb 173.04 -32-8-2	71 +3 Lu 174.967 ± 0.003 -32-9-2	N O P
**Actinides	90 +4 Th 232.0381 -18-10-2	91 +5 +4 Pa 231.0359 -20-9-2	92 +3 +4 +5 +6 U 238.029 -21-9-2	93 +3 +4 +5 +6 Np 237.0482 -22-9-2	94 +3 +4 +5 +6 Pu (244) -24-8-2	95 +3 +4 +5 +6 Am (243) -25-8-2	96 +3 Cm (247) -25-9-2	97 +3 +4 Bk (247) -27-8-2	98 +3 Cf (251) -28-8-2	99 +3 Es (254) -29-8-2	100 +3 Fm (257) -30-8-2	101 +2 +3 Md (258) -31-8-2	102 +2 +3 No (259) -32-8-2	103 +3 Lr (260) -32-9-2	O P Q

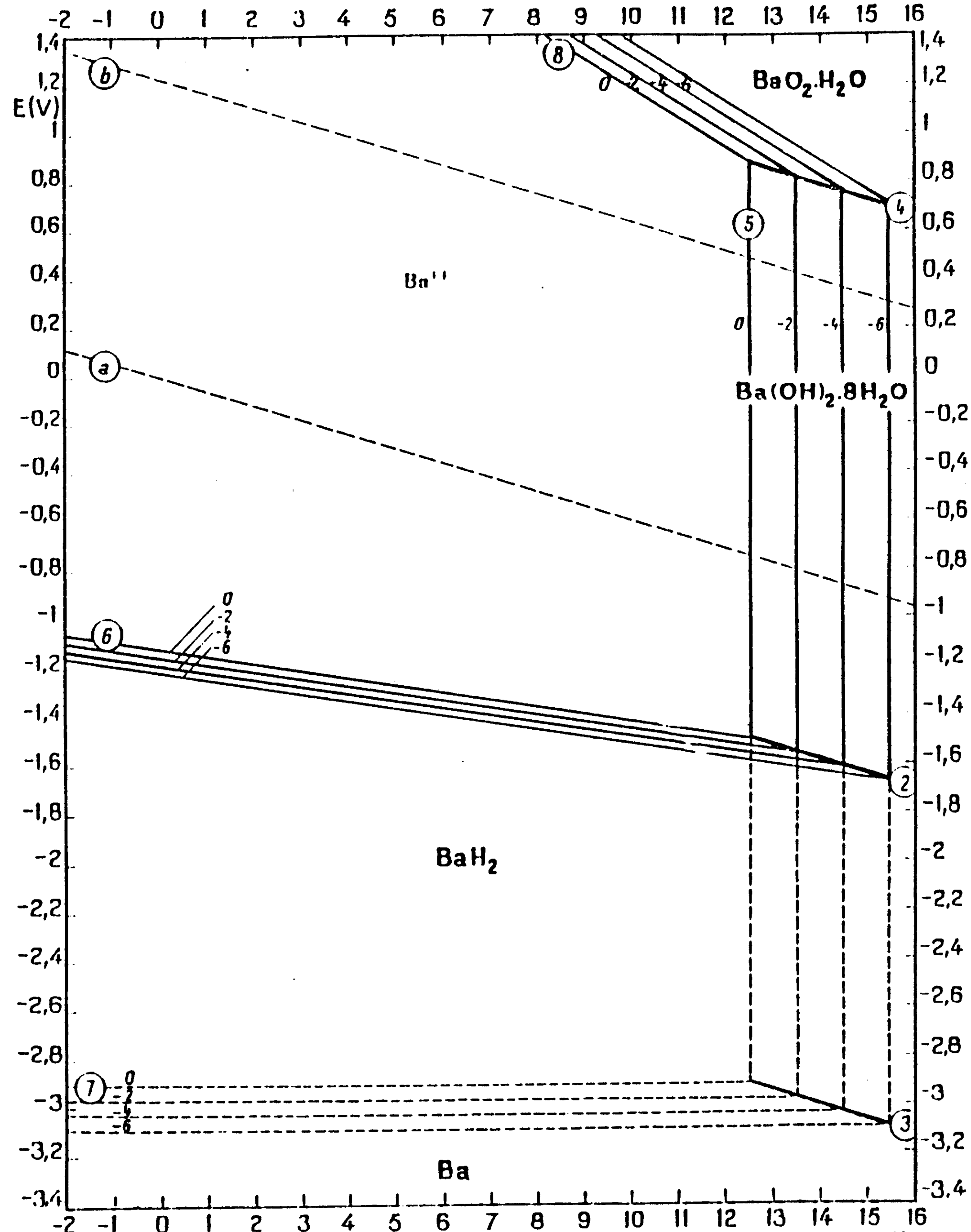
Numbers in parentheses are mass numbers of most stable isotope of that element

Appendix B - Alloys Commonly Electroplated

The following alloys are commonly electroplated from aqueous solutions. This list is not exhaustive.[57]

Tin-Zinc
Tin-Nickel
Tin-Copper
Tin-Lead
Copper-Nickel
Copper-Zinc
Copper-Chromium
Zinc-Nickel
Zinc-Chromium

Appendix C - Pourbaix Diagram For Barium[58]



Appendix D - Alkaline Electrocleaning Bath[59]

The following alkaline electrocleaning bath was used in substrate preparation.

Sodium Hydroxide	NaOH	25%
Sodium Metasilicate	Na_2SiO_3	40%
Sodium Triphosphate	$Na_5P_3O_{10}$	10%
Sodium Carbonate	Na_2CO_3	23%
Surfactant		2%
Cleaner Concentration	gms/ltr	30-60
Current Density	A/m2	200-500
Temperature	Centigrade	70-80

Appendix E - Acid Dip Or Etch Bath[60]

The following acid dip or etch bath was used in substrate preparation as a final cleaning step.

Nitric Acid	20.0%
Acetic Acid	25.0%
Phosphoric Acid	54.5%
Hydrochloric Acid	0.5%

Operating Temperature 190F[4]

---

[4] It was found that acceptable performance could be obtained with solutions at room temperature.

Appendix F - Run Record

Run Number: ___________

Date: __ / __ / __

Type:

Galvanostatic - __
Potentiostatic - __

Solution:

__ M _______ Batch No: __ Mixed __ / __ / __

Cell:

Working Electrode - ___________ Prep. Method - __
Prep. Date - __ / __ / __

Reference Electrode - ___________ Prep. Method - __
Prep. Date - __ / __ / __

Counter Electrode - ___________ Prep. Method - __
Prep. Date - __ / __ / __

Substrate Preparation:

1. Punch __
1a. Peal __
2. Mount __
3. Polish __
4. Tap Water Rinse __
5. Ultra Sonic
   Soln. _____
   Temp. _____
   Time. _____
6. Water Rinse __
7. Air Dry __
8. Lacquer __
9. Air Dry __
10. Ultra Sonic
    Soln. _____
    Temp. _____
    Time. _____
11. Water Rinse __
12. Alk. E. Clean
    Soln. _____
    Temp. _____
    Time. _____
    mA/cm^2 _____
13. Water Rinse __
14. Acid Etch __
15. Water/Ar Rinse __
16. Glove Box __
17. Drag Out 1 __

Appendix F - Run Record - Continued

Run Number:____________

18. Drag In __

19. Plate
    Potential _____ Current _________
    Time __________
    Temp __________
    Agitate _______
    Comment:

20. Drag Out __
    Time _____
    Temp _____

21. Rinse __
    Soln _____
    Temp _____
    Time _____

22. Dry __

Observations:

Preparation:

Plating:
Computer: __________ File: ____________
(Current or voltage swings, gas evolved, counter e. effects convection, events, color change)

Visual Characterization: (See evaluation sheet topics)

SEM Characterization: (See evaluation sheet topics)

Adhesion Test:

Thickness Test:

Appendix G - Data Acquisition Program

"C" language data acquisition program developed in LabWindows for use with National Instrument AT-MIO-16 D-A/A-D board in 8 channel differential mode.

```
#include        "d:\lw\include\lwsystem.h"
#include        "d:\lw\include\gpib.h"
#include        "d:\lw\include\formatio.h"
#include        "d:\lw\include\graphics.h"
#include        "d:\lw\include\analysis.h"
#include        "d:\lw\include\dataacq.h"
#include        "d:\lw\include\rs232.h"

static int filerr;
static int initial_error;
static int items_fmtd;

static int board_code;
static double sample_rate;
static double scan_rate;
static int total_points_scanned;

static int channel_lst[2];
static int gain_lst[2];
static int scan_error;

static int i, j, count;

static int buffer_int[2000];                /*total number of
                                              possible points*/
static double buffer_real[2000];            /*total number of
                                              possible converted
                                              points*/
static double graph_buffer_1[1000];         /*total number of
                                              points from 1st
                                              channel */
static double graph_buffer_2[1000];         /*total number of
                                              points from 2nd
                                              channel */

/* static double graph_buf_1_integ[1000];*/

main()
{
gain_lst[0] = 1;               /*gain for first channel */
gain_lst[1] = 1;               /*gain for second channel */
channel_lst[0]= 0;             /*first channel sampled */
channel_lst[1]= 1;             /*second channel sampled */
```

```
scan_rate = 1000.0;               /*total conv. per second*/
sample_rate = 4.0;                /*rate at which samples are taked
                                    -total */
total_points_scanned = 2000;      /*total number of conversions*/
                                  /* to get the total number of
                                    seconds */
                                  /* use the following equation:  */

                                /*total_sec =total_points_scanned */
                                /*           -------------------- */
                                /*sample_rate * no. of chan. */

initial_error = Init_DA_Brds (4, &board_code); /* initializes
                                                  board */

breakpoint();  /*This breakpoint allows you to start the scan */

scan_error = SCAN_Op (4, 2, channel_lst, gain_lst,   /* scan */
  buffer_int, total_points_scanned, scan_rate, sample_rate);


breakpoint(); /*this breakpoint tells you that the scan is over*/


        for(i=0; i<2000; i++){               /* converts buffer
                                                to real */
        buffer_real[i]=buffer_int[i]*.005; /* for both channels*/
        }

        for(i=0; i<1000; i++){               /* picks out first
                                                 channel data */
        graph_buffer_1[i] = -1 * buffer_real[i*2];
        }

        for(i=0; i<999; i++){                /* picks out second
                                                channel data */
        count = (i*2)+1;
        graph_buffer_2[i] = buffer_real[count];
        }


/* This routine plots the first variable data */
GrfReset (4);
SetPlotMode (2);
SetCurv2D (0);
SetYDataType (4);
GrfYCurv2D (graph_buffer_1,999);
```

```
/* This routine plots the second variable data */
GrfReset (4);
SetPlotMode (2);
SetCurv2D (0);
SetYDataType (4);
GrfYCurv2D (graph_buffer_2, 999);

/* The following lines will integrate the data of a specified
variable */
/* and plot it.  I have pulled it out for now. */

/*Integrate (graph_buffer_1, 1000, 1.0, graph_buffer_1[1], 0.0,
graph_buf_1_integ);

GrfReset (4);
SetPlotMode (2);
SetCurv2D (0);
SetYDataType (4);
GrfYCurv2D (graph_buf_1_integ, 999);
*/

/* The following puts the data in qpro format into a file*/

filerr = OpenFile ("d:\\users\\bdj\\lw\\data\\mark3.dta", 2, 0, 1);
for (j = 0; j<1000; j++)
items_fmtd  =  FmtFile  (filerr,  "%f,%f\n",  graph_buffer_1[j],
graph_buffer_2[j]);
CloseFile (filerr);


 }
```

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