Vapour Deposition: Thermal Characterization and Application of
Metal Oxide Thin Films.

by

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Abstract

Three precursors of group 11 metals, gold(I) 1,3-diisopropyl-imidazolidin-2-ylidene hexamethyldisilazide, gold(I) tert-butyl-imino-2,2-dimethylpyrrolidinate, silver(I) tertbutyl-imino-2,2-dimethylpyrrolidinate were subjected to solution based NMR thermolysis studies. Rates of decomposition and order of reactivity were gathered by monitoring the disappearance of starting material.

Two novel antimony compounds, trimethyl phosphine antimony (III) chloride and bistrimethyl phosphine antimony (III) chloride were subjected to thermal characterization by TGA and CVD experiments in attempt to produce antimony or antimony oxide films. Few experiments gave varying depositions but reproducible coatings were not achieved.

Protective coatings of alumina and bilayers of alumina and titania were deposited on bronze and brass test tokens as well as on numismatic silver coins. Multiple tests examined the efficacy of such films against physical and chemical wear. Silver coins were compared to a traditional lacquer coating. The ALD coatings on test tokens provided improved wear and chemical protection *vs.* unprotected coins. Final numismatic coatings of alumina gave greatest adhesion, but did reveal small areas of chemical penetration.

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List of Acronyms

AFM- atomic force microscopy

Agttbip – silver (I) tert-butyl-imino-2,2-dimethylpyrrolidinate

ALD - atomic layer deposition

APCVD - atmospheric pressure chemical vapour deposition

Auttbip – gold (I) tert-butyl-imino-2,2-dimethylpyrrolidinate

CDI - carbodiimide de-insertion

CVD - chemical vapour deposition

E - Young's modulus

H – nanohardness

LPCVD - low pressure chemical vapour deposition

NHC - n-heterocyclic carbene

NMR – nuclear magnetic resonance

P2Au - 1,3-diisopropyl-imidazolidin-2-ylidene gold (I) hexamethyldisilazide

PVD - physical vapour deposition

TGA - thermogravimetric analysis

TMA - trimethyl alumina

TMS - tetramethyl silane

TTIP - titanium tetraisopropoxide

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1 Chapter: Introduction

1.1 Chemical Vapour Deposition

Chemical vapour deposition (CVD) is a method to deposit nano to micro thick layers through vapour phase chemistry. In its most basic form CVD utilizes thermally controlled volatility of a metal containing precursor. The volatility enables for transport to a substrate where the thermally driven reaction of the precursor, either through decomposition to a reactive intermediate or direct reaction with the surface forms the subsequent film.

Substrates are typically, but in no way limited to silicon or glass. Thermally driven reactions are common¹ but there also exist other methods to supply energy required for reaction. Incorporation of other forms of energy such as plasma or laser light can provide the energy needed to drive the reaction of precursor with the substrate.^{2,3} Other techniques utilize co-reactants. This could include a reductant gas, such as hydrogen in a stream of precursor vapour⁴ or another molecular species that will react with the initial metal-containing species.¹ There exist two conventional experimental constructions which employ thermally driven reactions (Figure 1.1.1): cold-walled and hot-walled reactors. Each of these designs must deliver reactant gases to the reaction chamber, supply adequate heat to effect the reaction and remove byproducts. Cold wall reactors have a heated stage where the substrate sits. As the name implies the walls of this type of reactor are not heated and therefore deposition occurs only on the heated stage. The other deposition method uses a hot wall reactor whereby the reactor walls are heated and the substrate sits in a tube furnace. Through this method all heated surfaces

are coated. Each reactor design brings about particular experimental considerations. Hot-wall reactors can achieve high throughput through batch processes while cold-wall reactors are typically of a single-wafer design. An advantage of a cold-wall reactor is a greater deposition rate since precursor is not taken up by the reactor walls. Because deposition occurs on all heated surfaces in a hot-wall reactor there is greater precursor depletion and the reactor vessel needs to be cleaned regularly. Also, byproducts of these reactions with the reactor walls could be a source of contamination.

CVD does not require line-of-sight for deposition to occur, which is an advantage over other physical deposition methods (PVD) such as sputtering and evaporation. However film growth does depend upon substrate position which can affect uniformity. The rate of deposition for CVD is also relatively higher compared to PVD, so thicker layers are attained much quicker and CVD does not require ultra-high vacuum. The higher temperatures required for thermal CVD do make it unsuitable for certain applications with thermally sensitive substrates such as plastics or aluminum. Precursors are required to have sufficient volatility which can be controlled by increasing steric bulk while lowering molecular weight.⁵ These conditions can lead to hazardous precursors with byproducts that are also hazardous. Ideally in such thermally driven systems a precursor must not decompose while being heated or while in the gas phase. This thermal stability must be conversely balanced with sufficient reactivity with the substrate and consequent deposited film. Precursors must avoid elements that are detrimental to target films, for instance halides are detrimental for film conductivity and oxygen in nitride films may decrease hardness.⁶

Thermal CVD is governed by thermodynamics of volatilization and energy of reaction with the substrate/resultant film. With adequate heat, a limit to the rate film formation may be dictated by mass transport of gas phase precursor to the substrate. Control of pressure in the reactor can permit regulation of this limit. This can be achieved by either the use of an inert carrier gas or by performing the reaction *in vacuo*. Control of both temperature and pressure can lead to greater uniformity in deposited films. These conditions are what lead to the further classification of CVD processes.

Deposition can be achieved at atmospheric pressure (APCVD), which does not require a vacuum pump.⁷ The particular drawback to APCVD is that deposition rates are low unless a high partial pressure of reactant gas is used. Low pressure CVD (LPCVD) does not require carrier gas, gives greater diffusivity and therefore more conformal deposition. Also because of greater diffusivity the rate limiting effects of mass transport are reduced. This makes the system more dependent on temperature to control reaction, and therefore deposition rate. Substrate geometry in both AP and LP CVD reactors can influence film uniformity.

Interest in films grown by CVD has led to the utilization of this technique in a variety of applications. Common targets for films grown by CVD are metallic elements such as gold for use in plasmonic applications⁸. The low resistivity of Ni⁹, Cu¹⁰ and Ag¹⁰ make them viable for low resistivity circuits and electrical contacts in microelectronics. Also transparent conductive films of InSnO¹¹, InGaAs¹² are possible candidates for use in liquid crystal displays. Other multi-component films are used as diffusion barriers^{13,14} and high-k dielectrics¹⁵ (WN, TiN, TiO₂, HfO₂, ZrO₂). Films grown by CVD have found use in the semiconductor industry, particularly Si¹⁶ but also solar cells, LEDs, thin film transistors, and other optical sensors.^{17,18,19} Some films (TiO₂, Al₂O₃, SiC, TiN) are known for their hardness as protection from mechanical wear as well as films that protect against corrosion.^{20,21,22} CVD of graphene grown on copper^{23,24} has been reviewed in depth as graphene has very promising electronic properties.

1.2 Atomic Layer Deposition

ALD was developed in the 1970's under the name atomic layer epitaxy, whereby the growing film was intended to display the same crystalline face as the underlying substrate.²⁵ It can be considered a modification of the CVD process. Where, in CVD the precursor flux is generally continuous, in ALD the precursors are pulsed in sequentially with intermediate purge steps to inhibit gas-phase reactions (Figure 1.2.1). The sequential pulsing is designed such that a precursor will chemisorb and form a self-limiting monolayer on the substrate. Ideally it is self-limiting in that the chemical species saturates reactive surface sites and further film growth is arrested. After a monolayer forms there is no further reaction and excess precursor is removed from the reaction chamber by a purge with inert gas. It is explained well by A+B chemistry where chemical 'A' is pulsed into the reactor, forms a monolayer on a substrate and excess is removed. After an adequate amount of purge time to ensure there is no gas-phase reaction, precursor 'B' is pulsed, reacts with surface 'A' which again forms a monolayer and excess precursor and byproducts are removed. This pulsing procedure is repeated and proceeds layer-by-layer until a desired film thickness is achieved. Further layering with multiple components is possible. This technique affords a high degree of thickness control and excellent conformity over CVD. ALD films have found use in similar applications as CVD, but where high conformity at great thickness control is required. Initially developed for electroluminescent displays²⁵ other applications include conductive films in microelectronics,²⁶ protective films,²⁷ and further development of semiconductors.²⁸

Figure 1.2.1: ALD cycle. A) Precursor is brought into reactor. B) The precursor reacts with surface sites and forms a monolayer. There is no further reaction, excess precursor and reaction by-products are purged from the reaction chamber. C) Secondary precursor is brought into reaction chamber and D) reacts with surface sites to regenerate the surface. Again excess precursor and by-products are removed. E) & F) Repetition of cycles affords atomic control of thickness.

For thermally driven ALD systems there can exist an optimal ALD temperature range, or ALD window. Below this range there is no growth, above growth increases and resembles CVD deposition. This technique also brings about another caveat to the production of its precursors in that they must not react with each other in a way that would disrupt monolayer formation. In terms of thin layer processing a drawback is found in the increase in time processing films. This is due to the pulse and purge steps required to prevent gas phase reaction where the growth of layers can be much slower than CVD.

2 Chapter: Thermolysis

2.1 Introduction

Recently there has been an increased interest in gold and silver films. These metal nanoparticles are known to possess surface plasmon resonances in the visible region of the electromagnetic spectrum²⁹ which has led to use in optical devices.³⁰ Also these films can be further modified since they exhibit tunability of the plasmon resonance similarly to metallic-core dielectric-shell nanostructures.³¹ Films of gold or silver produced by various methods are also used extensively in catalytic applications.³² Herein is described a novel ligand system to produce these films by vapour deposition.

New precursors for use by CVD are produced to improve on the deposition characteristics of existing precursors, such as the morphology and function of the deposited film. When designing precursors it is imperative that they are volatile and do not decompose considerably before deposition. A primary method by which to characterize volatility vs. decomposition of potential precursors is thermogravimetric analysis (TGA). This apparatus measures a mass loss over a programmed temperature sequence. It affords important data on thermally induced volatilization and possible decomposition. Unfortunately this method does not directly allow identification of the volatile species or decomposition products.

The determination of products and rates of decomposition in precursor design is important in current vapour deposition chemistry, particularly in the fields of (CVD) and (ALD).³³ Products of decomposition can give important information about the

mechanism through which a precursor could react with a surface. This information can help deduce reaction byproduct(s) that are most likely to form at particular temperatures and is very useful when coupled with surface exposure experiments.³⁴ The acquisition of rates can help further characterize precursor stability at particular temperatures, and help find proper handling temperatures if a precursor is deemed viable. Herein thermolysis methods are described that help determine decomposition products and kinetics of decomposition via solution based NMR techniques.

Products of the decomposition of ALD/CVD precursors can typically be observed via ^1H NMR. Flame-sealed NMR tubes with a known concentration of precursor in deuterated benzene are placed in an oven. Rates can be obtained by following these decomposition products of thermal reactions for weeks or even months by ^1H NMR. The intensity of the corresponding peaks can be integrated to determine concentration with respect to time. Although solution based methods are not always truly indicative of gas phase reactions because they are fundamentally different thermodynamic systems, results from these experiments aid in the determination of rates and products. This method has the potential to yield very useful results in the field of precursor design for vapour deposition.

2.1.1 Ligand Design

Much work has previously gone into fabrication of the iminopyrrolidinate ligands used herein.³³ This work examined decomposition pathways of copper precursors and led to precursors of greater thermal stability. Both copper guanidinate and amidinate

precursors have shown to decompose through two similar pathways: either through carbodiimide deinsertion or by abstraction of the ligand's β -hydrogen by the metal center³⁵ (Figure 2.1.1). Solution based NMR studies of gold amidinate precursors show carbodiimide deinsertion (CDI) but parent compounds (amidinate ligand) do not.³⁵ This indicates that gold amidinates thermally decompose to the carbodiimide and not through some intermediate. Calculations show this is not intuitive as more energy is required to break a C-C bond rather than a N-C bond.³⁶ The guanidinate family of ligands in these solution NMR studies show products of de-insertion as well as non-oxidised parent ligand.³⁶ It should be noted that CDI products may be due to further decomposition of the product of β -hydrogen abstraction which adds a level of complexity to interpretation of thermolysis results. When the bridgehead moiety of the ligand is dimethyl amine, no CDI products are seen by this method in either gold or silver analogues.³⁶ Gas-phase experiments with time-of-flight mass spectroscopy coupled with matrix isolation FTIR show the dominant thermolysis species of gold dimethyl amine guanidinate as oxidised ligand³⁵. This would follow the β -hydrogen abstraction pathway. This particular guanidinate affords improved thermal stability through the elimination of the carbodiimide deinsertion thermolysis pathway and lead to the formation of a new set of precursors whereby the β -hydrogens were eliminated.

New precursors of iminopyrrolidines, lacking β -hydrogens gave excellent thermal stability.³⁷ By TGA the residual mass of copper tert-butyl-imino-2,2-dimethylpyrrolidinate in each trace of greater mass was below 2% while solution ^1H NMR studies showed no appreciable deterioration at 165°C after 21 days.³⁸ This particular iminopyrrolidinate did not exhibit thermolysis by β -hydrogen abstraction, but underwent another mechanism of alkene elimination from the chelating nitrogen during chemisorption after 275°C. This particular precursor was found to be thermally stable to 350°C.³⁴

Iminopyrrolidinate analogues of gold and silver were produced and characterized by TGA. They did not afford the same thermal stability and decomposed at temperatures above 170°C. These analogues were found to deposit nanoparticulate films of Ag and Au by CVD on both silicon and silica slides.³⁸ Characterization to further understand the thermal characteristics was undertaken by solution NMR, similarly to the amidinates and guanidines and described herein.

Along with the characterization of the gold and silver iminopyrrolidines, another gold precursor was tested. Work in the field of catalysis has shown copper(I) *N*-heterocyclic carbenes (NHC) as thermally stable and led to the production of novel NHC compounds for vapour deposition of Group 11 metal films.³⁹ A promising copper carbene precursor, 1,3-diisopropyl-imidazolidin-2-ylidene copper(I) hexamethyldisilazide demonstrated excellent thermal stability by TGA. It was employed as a precursor whereby nanoparticulate films were produced by plasma-assisted ALD.⁴⁰ Because of the success of this precursor in the deposition of copper films a gold analogue was synthesized. This work also describes the solution based NMR of 1,3-diisopropyl-imidazolidin-2-ylidene gold(I) hexamethyldisilazide.

2.2 Experimental Design

2.2.1 Precursors

Three different precursors (Figure 2.2.1) were examined by thermal decomposition: 1,3-diisopropyl-imidazolidin-2-ylidene gold(I) hexamethyldisilazide

(**P2Au**), gold(I) tert-butyl-imino-2,2-dimethylpyrrolidinate (**Auttbip**) and silver(I) tert-butyl-imino-2,2-dimethylpyrrolidinate (**Agttbip**).

<p>1,3-diisopropyl-imidazolidin-2-ylidene gold(I) hexamethyldisilazide</p>	<p>gold(I) tert-butyl-imino-2,2-dimethylpyrrolidinate</p>	<p>silver(I) tert-butyl-imino-2,2-dimethylpyrrolidinate</p>
<p>Figure 2.2.1: Precursors used in the thermolysis study, a) P2Au, b)Auttbip, c) Agttbip</p>		

2.2.2 Boil-up Method

These experiments were performed in an inert atmosphere either in a drybox or with a Schlenk line. Measured amounts of precursor, deuterated benzene and tetramethyl silane (TMS) were placed in a thick-walled NMR tube. The solution was frozen in liquid nitrogen and placed under vacuum to below 100 mTorr. The tube was then flame-sealed, cooled and an initial NMR spectrum taken. For each precursor two tubes were prepared whereby one was covered in aluminum foil for protection from light. Each tube was placed in a preheated oven fitted with a 100 W light-bulb. The samples of **P2Au** and **Auttbip** were kept at an oven temp of 100°C, but **Agttbip** proved to be more robust and

was kept at a temperature of 120°C. An NMR spectrum of each sample was taken every 24 hours. The tubes were removed from the oven, left to cool for half-an-hour and inverted four times to ensure the solution was well mixed before taking each spectrum. Precursor decomposition was recorded as a decrease in the integrated area of precursor peaks and the appearance of the shifted ligand peaks. Peaks to be recorded were chosen such that there was no interference from other changing peaks. With the decrease in integrated peak area over time, rates and half-lives were interpreted. This involved fitting the data to either zero, first or second order rate equations and assessing the validity of the fit (R^2) to determine an order. During the experiment, the time when concentration reached half of the starting concentration, as measured by a decrease in normalized integration is defined as the experimental concentration midpoint. This is different from the half-life which will be used in the stricter kinetic theory sense.

2.2.3 NMR Spectra and Rate Determination Plots

Each NMR plot was referenced to trimethyl silane (TMS) and manually phase corrected. Peaks were chosen such that there was no overlap with other peaks that would appear due to decomposition and hence not interfere with integration. Integration was conducted by recording the shift range in which a peak of interest appeared. The ppm range was then integrated over the course of the study (Appendix A). Integration values were normalized and plotted vs. time. In the case of first and second order plots, the natural logarithm and the inverse of the normalized integration were plotted vs. time, respectively. The experimental concentration midpoint is taken at the final time the

concentration is decreases below half of the initial concentration and no longer increases above half of the initial concentration.

The concentrations of the metal precursors are; **P2Au**: 8.3mM, **Auttbip**: 1.8mM, **Agttbip**: 1.6mM. Each sample was diluted in deuterated benzene NMR solvent. For the kinetics calculations, each concentration was normalized to 1 through integration of peaks with the first NMR spectra.

2.3 Results and Discussion

2.3.1 P2Au

The concentration of both ‘light’ and ‘dark’ samples was 8.3 mM. The septet peak of the methine proton for the precursor, **P2Au**, was used to trace decomposition over time (Figure 2.2.2). No other peaks were viable since decomposition led to many product peaks that interfered with integration. Decomposition data was taken over 31 days for the sample exposed to light and 38 days for the covered sample. This is because the sample covered in aluminum foil took longer to decompose. The sample covered in aluminum foil had a longer observed experimental concentration midpoint of 22 days compared to the uncovered sample which was 12.5 days. Both samples plated-out a gold film which grew over time on the inside of the NMR tube. Characteristic to this experiment only, protection from light produced data sets that fluctuated less than those exposed to light.

From Table 2.3.1 it appears that the first-order approximation for thermolysis of **P2Au** when exposed to light is most valid. There was a great degree of fluctuation in the data, particularly in the first few data points for the illuminated sample (Figure 2.3.1). This is represented by the greatest fit parameter and corroborated by the experimental midpoint matching closely with the half-life associated with first-order decomposition kinetics. When protected from light the kinetic data is slightly ambiguous as the linear fit parameter for first and second order kinetics are similar (Table 2.3.2). The calculated half-life for the zero-order assumption matches more closely to the experimental concentration midpoint.

Assigning first-order to the exposed sample and zero-order to the protected sample is not necessarily contradictory or problematic. Gold atoms have a large atomic radius, possess a low electronegativity and are thus easily polarizable. Therefore light may provide enough energy to weaken these bonds through oscillation, depending on the bond strength of ligands. It would appear that this compound is particularly sensitive to light as the experimental concentration midpoint of the exposed sample (300 h) occurs much sooner than the protected sample (525 h). It is expected that the light-induced acceleration would taper off as metal plates out on the walls and eventually prevent further interaction with light. This would make the reaction appear to take on first order kinetics.

Along with the precursor, the carbene ligand appears to undergo thermolysis as well. This is seen in the NMR spectra of the decomposing precursor (Appendix A, Figure 4.9.1). There are a number of small peaks that appear over time that suggest that the carbene is not free in solution, but decomposing. The number of peaks makes identification of the carbene products difficult. The protonated HMDS ligand however remains intact and appears slightly downfield to the TMS signal. Also, attempting to monitor ratios of the growing products to the starting material is not entirely viable due to overlap.

2.3.2 P2Au - Summary Conclusions

The sample of **P2Au** exhibited first-order decomposition when exposed to light and zero-order decomposition when protected from light. This is indicated by highest fit parameter and their consequent half-life values matching more closely to the experiment. The order change is suspected to be due to the interaction with light on the Au-ligand system. This is shown as the experimental concentration midpoints of the samples differ greatly and the protected sample takes 200 h longer than the exposed sample. The first-order decomposition of the exposed sample is likely due to accelerated decomposition by light. This is eventually prevented as gold coats the walls.

Peak(ppm)	septet		
Order(R^2)	zero (0.8863)	first (0.9564)	second (0.9059)
rate, k	0.0011 mM/s	0.0030/s	0.0106/mMs
$t_{1/2}$, theoretical	455 h	231 h	94 h
Experimental midpoint	300 h	300 h	300 h

Table 2.3.1: Order determination by fit parameters of P2Au when exposed to light.

Peak(ppm)	septet		
Order(R^2)	zero (0.9654)	first (0.9437)	second (0.8855)
rate, k	0.0009 mM/s	0.0016/s	0.0033/mMs
$t_{1/2}$, theoretical	555 h	433 h	303 h
Experimental midpoint	525 h	525 h	525 h

Table 2.3.2: Order determination by fit parameters of P2Au when protected from light.

2.3.3 Agttbip

Two samples of **Agttbip** were prepared as above with a concentration of 7.8 mM. For each sample two unadulterated NMR peaks (triplets at 2.55 ppm and 1.66 ppm) were integrated over time to find the order of decomposition. They correspond to protons on the backbone of the pyrrolidine ring. For the exposed sample, data was taken over a period of 22 days. After this period the normalized peak integrations for the triplet peak reached zero and the singlet peak stabilized around 0.1. Data for the protected sample was recorded over 25 days. The normalized peak integration values never reached zero, but began to fluctuate around 0.3 for each sample. Both triplets from the sample exposed to light had an experimental concentration midpoint of about 12 days. This thermolysis study was carried out at 120°C.

With the exposed sample, the graphs of both NMR peaks of both samples follow the same trend. They both tend towards a zero-order rate of decomposition (Tables 2.3.3, 2.3.4). This is shown as the graphs of concentration vs. time have the fit parameters which are considerably higher than the others. Unfortunately the fluctuation in the data given by both triplet peaks does not yield great precision with the fit parameters significantly below unity. Further indication of zero-order decomposition is attained from the calculated half-lives. The half-life value calculated from the zero-order rate approximation closely matches that of the experimental midpoint concentration. This is true for both triplet NMR peaks in the sample.

For the sample that was protected from light, the data from the monitored triplet peaks does not yield confident linear fit parameters. However, the trend that both monitored peaks exhibit is similar to the exposed sample. The triplet at 2.55 ppm indicates first-order decomposition kinetics with the greatest fit parameter value ($R^2 = 0.8087$). This also produces a half-life value (19 d) that was closer to the experimental concentration midpoint. Unfortunately the calculated value is still about 50% longer than observed in the experiment. Although the confidence is poor in the first-order assumption, the other plots yield data that is considerably worse.

The triplet at 1.66 ppm similarly indicates zero-order decomposition with comparable confidence. The linear fit parameter value ($R^2 = 0.7912$) is slightly lower than for the triplet at 2.55 ppm ($R^2 = 0.8087$), but the calculated half-life is identical (19 d). Again the poor confidence in the zero-order assumption is boosted by the much poorer data for the other kinetic assumptions.

The products of decomposition for both samples of **Agttbip** is protonated ligand. There were no significant peaks in the NMR spectra that indicated other decomposition products. The mechanism through which the precursor deposits silver on the tube wall is not known. It is believed that there is a reaction with the silanol moieties on the glass tube where the ligand exchanges the metal center with silanol hydrogens. The zero-order rate likely arises from a high stability and an indifference to react with either the glass NMR tube walls or the subsequent silver film. This also indicates a single thermolysis

pathway when either protected from light or when exposed, both requiring a temperature of 120°C and available protons in solution.

Similar protons in similar chemical environments should lead to similar conclusions regarding this experimental thermolysis. This is supported as monitored peaks in within a sample are in close proximity and display the same trend in decomposition order and calculated half-life. What is also evident is that light plays a negligible role in the decomposition of this precursor. The experimental concentration midpoints of either sample are close to each other, with the exposed sample decomposing about one day faster. Even though the covered sample does not reach a zero concentration decomposition appears to taper-off.

2.3.4 Agttbip - Summary Conclusions

All monitored peaks in both samples lead to the assumption of zero-order decomposition kinetics (Figures 2.3.3, 2.3.4). The exposed sample had best confidence with greater linear fit and half-life values closely matching the experimental concentration midpoints. The covered sample does not share the same high confidence in linear fit and calculated half-life values, but the trend in the data set indicates the same zero-order decomposition kinetics. In this experiment the exposed sample decomposes slightly faster than the protected, but does not greatly influence its decomposition. The main products of decomposition are identifiable as protonated ligand. It is hypothesized

reduction is occurring with protons that originate from silanol moieties on the NMR tube wall. This is evident as metallic films are seen growing over time.

Exposed to light

Protected from light

Figure 2.3.2: Linear fit graphs for the determination of order of decomposition for Agttbip by triplet at 2.55 ppm.

Exposed to light

Protected from light

Figure 2.3.3: Linear fit graphs for the determination of order of decomposition for Agttbip by triplet at 1.66 ppm.

a)

	Agttbip Exposed to Light		
Peak(ppm)	Triplet 2.55 ppm		
Order(R^2)	zero (0.9590)	first (0.7656)	second (0.3553)
rate, k	0.0021 mM/s	0.0069/s	0.0796/mMs
$t_{1/2}$, theoretical	238 h	100 h	13 h
Experimental midpoint	290 h	290 h	290 h

b)

	Agttbip Protected from Light		
Peak(ppm)	Triplet at 2.55 ppm		
Order(R^2)	zero (0.8087)	first (0.0123)	second (0.0217)
rate, k	0.0011 mM/s	0.0004/s	0.0009/mMs
$t_{1/2}$, theoretical	455 h	1733 h	1111 h
Experimental midpoint	260 h	260 h	260 h

Table 2.3.3: Summary of order determination by linear fit of Agttbip from triplet at 2.55 ppm when a) exposed to light and b) protected to light.

a)		Agttbip Exposed to Light		
	Peak(ppm)	Triplet 1.66 ppm		
	Order(R^2)	zero (0.9505)	first (0.8699)	second (0.6889)
	rate, k	0.0020 mM/s	0.0046/s	0.0162/mMs
	$t_{1/2}$, theoretical	250 h	151 h	62 h
	Experimental midpoint	290 h	290 h	286 h
b)		Agttbip Protected from Light		
	Peak(ppm)	Triplet 1.66 ppm		
	Order(R^2)	Zero (0.7912)	first (0.0452)	second (0.0037)
	rate, k	0.0011 mM/s	0.0007/s	0.0003/mMs
	$t_{1/2}$, theoretical	455 h	990 h	3333 h
	Experimental midpoint	290 h	290 h	290 h

Table 2.3.4: Summary of order determination by linear fit of Agttbip from triplet at 1.66 ppm when a) exposed to light and b) protected to light.

2.3.5 Auttbip

Monitoring decomposition was achieved by following the most deshielded triplet peak from the pyrrol back bone and the singlet from the t-butyl group. Both triplets were not used as the signal from products of decomposition, i.e. protonated ligand, interfered with signal from the most shielded triplet. Similar to **Agttbip**, the products of decomposition for both samples of **Auttbip** is protonated ligand. The mechanism is also believed to require reaction with silanol moieties on the glass tube wall. For 15 days the exposed sample was monitored before normalized integration values were calculated as being negative. This is due to integration close to the baseline. These negative values were not used in the rate-determining plots. The covered sample was monitored for 26 days, after which the normalized integration value did not yet reach zero. Unfortunately the covered sample displayed large fluctuations which made kinetic decomposition order assumptions difficult. The initial concentration was calculated to be 1.8mmol/L and decomposition proceeded at a temperature of 100°C. Both NMR peaks indicate an observed experimental concentration midpoint of 24 hours and gold metal was observed plating out on the walls of the NMR tube.

The exposed sample shows strong first-order decomposition with respect to the triplet peak. It has the largest fit parameter and is considerable greater than the other rate assumptions (Table 2.3.5). The calculated half-life is more than twice the experimental concentration midpoint, but again matches better than the others. Oddly this is not corroborated with the monitored singlet peak. Considering the fit parameters for the

singlet when exposed to light, the second-order assumption has a slightly better fit (Table 2.3.6). The corresponding calculated half-lives again show a better fit for the second order assumption as it very closely matches the experimental value. The mismatch between the decomposition rates determined from these peaks does not necessarily mean that one is incorrect. This data may indicate a decomposition mechanism that is complex.

With the samples that were protected from light the data set does not give much confidence. The entire set of points in each rate assumption yields very poor linear fit values and half-lives that are an order of magnitude larger than experimental observations (Appendix B, Figure 4.9.4). The graphs strongly indicate an initial uniform decomposition which begins to taper-off after an inflection at 120 h to decompose at a much slower rate. This diminishing rate is not observed as significantly in other samples. It could be assumed that as gold plates-out on the NMR tube, reactive surface hydroxyl sites are being removed. This is effectively removing a reactive species from solution. In this case the second order rate would be that of **Auttbip** reacting with the walls of the NMR tube and not of the precursor's decomposition. The following decay may be more indicative of decomposition of only precursor, but the great fluctuation in these data points makes that rate determination difficult.

Considering only the data before the inflection point (120 h), the graphs strongly indicate second order decomposition in in both monitored peaks of the sample protected from light (Tables 2.3.5, 2.3.6). The triplet peak has highest fit parameter ($R^2=0.9872$) in second-order. The calculated half-life of 50 h is closest to experimental, but still about

twice as long. Linear fit parameters for the singlet ($R^2=0.8334$) and its half-life (63 h) are not as confident, but imply the same second-order rate.

The sample that was exposed to light exhibited different decomposition orders between peaks: first-order in the triplet peak and second-order in the singlet. Integration of these peaks approached closely to zero concentration with the singlet still indicating about 5% remaining. For the covered sample, the decomposition was second-order in both peaks and each did not reach zero concentration even after 26 days. Although the half-life of each sample was similar, the samples that were exposed to light decomposed to a greater extent in 15 days. Therefore light must provide additional energy for the compounds to decompose/deposit gold on the walls of the NMR-tube. It then follows that there is greater selectivity to deposit on glass than on gold film or the ligand does not dissociate from the gold film when protected from light. With these assumptions it is likely that the decomposition rate found by the triplet exposed to light may actually be pseudo-first order. This is because the energy barrier preventing deposition can be overcome therefore continually producing a surface to deposit.

2.3.6 Auttbiip - Summary Conclusions

The order of decomposition found from the exposed sample was first-order in the triplet peak and second-order in the singlet. The experimental concentration midpoint was at 24 h. The calculated half-life for the triplet is 55 h while the singlet is 21 h. The second order rate yields a half-life that is much closer to experimental. It is believed that the rate found for the triplet peak is actually pseudo-first due to the accelerated and near

complete decomposition caused by interaction with light. The sample that was protected from light exhibited second-order decomposition in both peaks. After removing highly fluctuating data near the end of the plots, the data produce stronger second-order assumption with half-lives that more closely match experimental concentration midpoints. The rate slowed with removal of the reactive surface sites on the walls as gold plated out. It is also possible that, under these conditions, gold has a greater selectivity for depositing on glass walls than on the gold film or that, upon gold metal deposition, the ligand does not leave the gold surface. The major decomposition product is protonated ligand, which is believed to be from reaction with silanol moieties on the tube walls, similar to **Agttbip**. The cause of the significant fluctuation in the data points is unknown. The experimental midpoint of concentration is similar for both light and dark samples.

Exposed to light 2.55 t

Protected from light 2.55 t

Figure 2.3.4: Linear fit graphs for the determination of order of decomposition for Auttbp by triplet at 2.55 ppm.

a)		Auttbip Exposed to Light		
	Peak(ppm)	Triplet 2.55 ppm		
	Order(R^2)	Zero (0.5995)	First (0.9686)	Second (0.5612)
	rate, k	0.0062 mM/s	0.0141/s	0.0396/mMs
	$t_{1/2}$, theoretical	278 h	55 h	2 h
	Experimental midpoint	24 h	24 h	24 h

b)		Auttbip protected from Light		
	Peak(ppm)	Triplet 2.55 ppm		
	Order(R^2)	Zero (0.6775)	first (0.8113)	second (0.9872)
	rate, k	0.0049 mM/s	0.0093/s	0.015/mMs
	$t_{1/2}$, theoretical	102 h	76 h	67 h
	Experimental midpoint	24 h	24 h	24 h

Table 2.3.5: Summary of order determination by linear fit of Auttbip from triplet at 2.55 ppm when a) exposed to light and b) protected to light.

a)

	Auttbip Exposed to Light		
Peak(ppm)	Singlet 1.33 ppm		
Order(R ²)	Zero (0.5896)	first (0.9297)	second (0.9691)
rate, k	0.0060 mM/s	0.0131/s	0.0345/mMs
t _{1/2} , theoretical	294 h	98 h	21 h
Experimental midpoint	24 h	24 h	24 h

b)

	Auttbip protected from Light		
Peak(ppm)	Singlet 1.33 ppm		
Order(R ²)	Zero (0.6166)	first (0.7222)	second (0.8334)
rate, k	0.0045 mM/s	0.0081/s	0.0160/mMs
t _{1/2} , theoretical	111 h	86 h	63 h
Experimental midpoint	24 h	24 h	24 h

Table 2.3.6: Summary of order determination by linear fit of Auttbip from singlet at 1.33 ppm when a) exposed to light and b) protected to light.

2.4 Conclusions

For **P2Au** exposure to light increases the decomposition rate in the monitored peak and is found to be first-order. This is exhibited as a large difference in the half-life of illuminated **P2Au** which is 200 h shorter in experimental data and 324 h shorter in the fitted data. The decomposition of **P2Au** when protected from light is found to be zero-order as the rate does not change when decomposing on the walls of the NMR tube or on the subsequent gold film. Illuminating the sample appears to quicken decomposition. This occurs to the point where the NMR tube walls are covered with a gold film and light can no longer interact with the solution. The rate then slows which produces a graph that appears first-order. This indicates that decomposition begins on the NMR tube wall. After saturation of silanol surface sites, the rate is determined by deposition of gold on gold and/or removal of physisorbed precursor.

The silver precursor shows zero-order decomposition in all peaks and both exposed/covered environments. This is seen as the highest linear fit parameter is for the zero-order plots. There is a doubling in the rate of thermolysis when the sample is exposed to light in both peaks in the fitted data. The experimental data does not wholly corroborate this because the fluctuation in the data does not provide much precision when determining the time for the experimental midpoint concentration. The rate order has similar implications as **P2Au** whereby reduction at a surface is the rate limiting step and there is no noticeable selectivity between glass and silver surfaces. The only substantial product shown in NMR is protonated ligand.

The decomposition of **Auttbip** is second-order. This is observed in both peaks when protected from light, but only one peak when exposed. **Auttbip** shows a three-fold increase in decomposition rate with respect to the singlet. The triplet peak of **Auttbip** also indicates faster thermolysis when illuminated but because of the rate difference they cannot be objectively compared. The calculated half-life also shortens with the illuminated sample. Comparable to the silver analogue, the experimental concentration midpoint is not precise because of fluctuating data points. As light hastens decomposition it also provides enough energy to almost complete decomposition. This affects the calculated rate such that the triplet peak appears first order. The singlet peak is also affected as there is less difference between first and second order assumptions. The second-order rate must be caused by reaction with particular surface sites on the wall of the NMR tube. The rate slows as it is dependent on the decreasing population of glass surface sites. The ligand either does not dissociate from the surface or there exists selectivity towards glass over the growing gold film.

Under these conditions the order of reactivity determined by decomposition time for the gold precursors is: **Agttbip** < **P2Au** < **Auttbip**. **Agttbip** required a higher temperature of 120°C before significant decomposition was observed. The fitted data indicates that light accelerates decomposition of each precursor. The ttbip ligand displays greater stability in solution than the carbene as the only discernable product in the NMR of **P2Au** is the protonated HMDS ligand. The appearance of protonated ligand in both iminopyrrolidines must be due to reaction with silanol groups on the glass NMR tube walls. The exact mechanism of this reaction is unknown.

3 Chapter: CVD of Antimony Containing Films

Antimony (III) oxide is used as a catalyst in the manufacturing of plastics⁴¹ and a favourable component in fire retardant material.⁴² Antimony has found much use in V-VI semiconductors such as Sb_2Te_3 films and wires which have desirable thermoelectric properties.⁴³ Other such semiconductor alloys of Sb_2S_3 and Sb_2Se_3 exhibit band gap values that make them suitable for photovoltaic devices.⁴⁴ Interest in transparent conducting oxides has led to studying films of tin oxides doped with antimony by both solution⁴⁵ and vapour deposition methods.⁴⁶ Antimony is shown to improve electrical properties when used as a dopant in tin oxide as well as increasing the film's physical stability.⁴⁷

Although routes to produce antimony containing thin films exist,^{48,49} other potential antimony precursors may provide better deposition characteristics. These characteristics could be lower temperature deposition, production of different crystalline phases or perhaps films of fewer impurities. Two potential precursors were obtained from the Burford Group from the University of Victoria;⁵⁰ **1** trichlorobis(trimethyl phosphine) antimony (III) (Figure 2.4.1) and **2** trichlorotris(trimethyl phosphine) antimony (III) (Figure 2.4.2). By XRD **1** is a networked solid while **2** is a crystalline powder.

3.1 Thermogravimetric Analysis

3.1.1 Experimental

Thermogravimetric analysis is a technique whereby mass loss is measured against an increase in temperature. A mass of sample was placed on a tarred TGA pan. An auto-sampler places the sample and pan on the balance which is enclosed by a furnace. The furnace is then ramped at a rate of 10°C/min up to a temperature of 400°C. The mass loss of sample is plotted against temperature. The program controlling the TGA and recording data also calculates the derivative curve for the data. Volatility is taken as the temperature where 0.5% mass is lost.

This method aids the development of volatile precursors with greater thermal stability. By testing families of ligands on a metal center one can select a precursor with sufficient volatility and stability. The same experiment has been employed to select the ligands used in the previous chapter. Copper tertbutyl-imino-2,2-dimethylpyrrolidinate proved to be more robust than others tested with a residual mass close to zero and no increase in residual mass with greater initial mass loading.³⁴ This led to the silver and

gold analogues which displayed greater residual mass, but produced their respective films by CVD.³⁸ Furthermore, the copper equivalent of **P2Au** (1,3-diisopropyl-imidazolidin-2-ylidene copper(I) hexamethyldisilazide) displayed a lower residual mass than a similar, but unsaturated compound. The P2Cu precursor was able to produce films by plasma enhanced ALD while the unsaturated compound did not.

Figure 3.1.1: Mass loss vs. temperature of 1 by TGA

Figure 3.1.2: Mass loss vs. temperature of 2 by TGA

3.1.2 Results and Discussion

Preliminary results by TGA were promising for both **1** and **2** as CVD precursors. Each compound volatilized in a single event shown as a smooth curve in the TGA plot (Figures 3.1.1, 3.1.2). The residual mass can serve to indicate whether the thermal event is either volatility or decomposition. A zero residual mass suggests the precursor is wholly volatile, while any other mass can indicate decomposition. A precursor is most unsuitable when the residual mass obtained is on the order of the percent mass of the metal intended for deposition. This suggests that the metal-containing species itself is not volatile and the metal is left behind not able to volatilize. For each of the trials of **1** and **2** the residual mass is below the atomic percent of antimony in either precursor. This indicates that the thermal event includes volatility of the metal center. Also, **2** displays a

slower onset of mass loss as seen by the gradual slope of **2** (Figure 3.3.2) vs. that of **1** (Figure 3.3.1). This shows that volatilization of **2** has greater sensitivity to the temperature ramp and therefore may afford greater control of volatilization with temperature.

Performing multiple trials with increasing mass also helps determine thermal stability. Since the temperature is ramped at a constant rate, greater initial sample masses lead to more of the sample being exposed to higher temperatures for both compounds. The TGA traces show an increase in remaining mass with increasing sample weight, which is undesirable (Figure 3.1.4). This means that a greater percent of the initial precursor sample will decompose at higher temperature when using a higher sample mass. The trend for both compounds is similar, but the increase in residual mass of **2** is not as great at higher temperatures. The greatest amount of **2**, (46.69304 mg) shows a residual mass of 4.8%; while a lower mass of **1**(42.60509 mg) produced a larger residual mass of 5.8%. This would suggest **2** is a better candidate for deposition because of its lower residual mass. Figure 3.1.3 shows the onset of volatility of **2** for higher mass loadings occurs at lower temperatures than for **1**. The lower onset is beneficial as less temperature is required for volatilization.

Figure 3.1.3: Onset of volatility for compounds 1, and 2.

Figure 3.1.4: Residual mass from TGA trials with different mass loadings.

Figure 3.1.5 and 3.1.6 are graphs of the derivative of mass loss (with respect to temperature) vs. temperature. The derivative of weight change curves of **1** can indicate fragmentation or multi-step decomposition, highlighted as inflections or additional, shallow peaks in these higher-order curves. Inspection of Figure 3.1.5 shows inflection points before and after the absolute max for all curves becoming more pronounced with larger mass samples. This is with exception to the lowest mass loading as it is quite small and there is expected to be more uncertainty in its measurement. One can see upon comparison, the graph of precursor **2** (Figure 3.1.6) also has inflection points near the beginning of the traces, but appears smoother and decreases smoothly to zero after the absolute maximum. The trace demonstrates the potential of **2** as a more suitable precursor. Greater masses of **2** give similarly smooth traces and relates to a greater thermal stability. As more of **2** is exposed to higher heat the thermal profile remains since additional peaks do not appear. Additional peaks would suggest occurrence of a different thermal event. This is not the case with **1** which exhibits change in curve shape with greater sample masses.

Figure 3.1.5: Derivative of weight change for 1

Figure 3.1.6: Derivative of weight change for 2

These precursors do not exhibit the excellent stability seen in previously developed precursors of copper.⁴⁰ However gold and silver precursors have displayed greater residual mass and been used for successful deposition.³⁸ The experiment with antimony compounds **1** and **2** indicate fundamental properties that give the possibility of a successful and more easily handled candidate for deposition. The residual mass from both antimony compounds is below the atomic percent of antimony in the compound. This indicated that some antimony is thermally promoted to the gas phase allowing for transport to the deposition chamber. This along with the smooth derivative curve of **2** expresses the compounds thermal stability as it volatilizes in a single event with greater mass.

3.2 CVD trials

3.2.1 Experimental

The CVD trials were performed both with and without entrainment of moist air. Both experimental designs are depicted in Figure 3.2.1. A Variac potentiometer was used to control heating tape to resistively heat the precursor container, or bubbler, through the use of heating tape. The heating tape was wrapped around the bubbler while an attached thermocouple was used to monitor its temperature. The deposition chamber was a steel tube within a tube-furnace. The temperature of the tube-furnace was monitored by the output on the furnace as well as a secondary thermocouple connected to the center of the tube. It was found that with a bubbler temperature of 100°C much of the starting precursor material was volatilized. Although no repeatable deposition was obtained, the

white film deposition was routinely found at furnace temperatures between 300°C and 400°C. Moist air was introduced by attaching a tube from a Schlenk adaptor of a 500 mL round-bottom Schlenk flask to the bubbler. The round bottom flask was filled half-way with distilled water and a rubber septum capped the round-bottom flask (Figure 3.2.1). A metal needle was pierced through the rubber septum so that its tip was below the water line. With the inclusion of moist air there was an attempt to keep the pressure around 100 mTorr through the Schlenk valve of the round-bottom and a ball valve between the round-bottom and bubbler. Otherwise the system was reduced to below 10 mTorr by an Edwards rotovane pump. Substrates in these trials consisted of glass and silicon slides placed side by side, or just one of these substrates. Slides were prepared by sonicating in isopropyl alcohol for thirty minutes, rinsing with deionized water and being placed in a (4:1 of $\text{H}_2\text{SO}_4\text{:H}_2\text{O}_2$) piranha solution for twenty minutes. The slides were then rinsed with deionized water, then hexanes and left in a 110°C oven until further use. The tube furnace and slides were preheated to deposition temperature under low flow of nitrogen. A measured amount of precursor in a vial was prepared in a dry box and quickly placed in the attached bubbler under low flow of nitrogen. Heating tape was wrapped around the bubbler, fixed with a type K thermocouple and the system placed under vacuum. The trial began by quickly heating the bubbler to the selected temperature.

3.2.2 Results and Discussion for CVD Trials of 1

There were 10 CVD trials using **1** (Figure 3.2.1). Trials 5 through 9 produced a deposition on the bottom of glass and silicon slides with moist air and without. Within these trials slides closest to the bubbler showed evidence of some deposition. A white film that was easily removed was observed only on glass slides placed close to the bubbler while silicon slides appeared discoloured (Figure 3.2.2). This white film was characterized for composition by EDX for trial 9 (Figure 3.2.3). The EDX spectrum shows an amount of antimony that is less than 10% of the composition of the film. The majority of the film was copper and chlorine. The chlorine content is likely precursor contamination: 30% by mass of either compound. The copper seen by EDX is an artifact originating from inadequate cleaning of the aluminum slide-holder which was used in a previous deposition using a copper precursor.

CVD trial #	Deposition time	Moist air?	Bubbler (°C)	Furnace (°C)	Mass (mg)	Remaining mass (mg, %)	Pressure (mTorr)	Deposition?	Substrates
1	3hr	n	200	450	40	-	-	no	Si, SiO ₂
2	3hr	n	120	150	37	17	-	no	Si, SiO ₂
3	16hr	n	120	250	41	5	-	no	Si, SiO ₂
4	18hr	y	80	300	47	1	-	no	SiO ₂
5	3hr	y	100	300	59	21	150	yes	SiO ₂
6	18hr	y	100	300	39	29	100	yes	SiO ₂
7	18hr	y	100	400	36	1	110	yes	Si, SiO ₂
8	21hr	n	100	300	41	4	-	yes	Si, SiO ₂
9	16hr	n	100	300	27	0.6	-	yes	Si, SiO ₂
10	14hr	n	100	300	-	-	-	no	Si

Table 3.2.1: CVD trials attempted with precursor 1

Figure 3.2.2: Deposition on the bottom of Si and white deposition on glass slide

An atypical deposition was found after CVD trial 5. A silicon slide that was left in the deposition chamber for CVD trials 3, 4 and 5 produced a rainbow pattern as seen in Figure 3.2.4a. This slide likely fell off the slide-holder and onto the tube furnace during trial 3. The rainbow-coloured deposit was characterized by SEM and EDX, Figure 3.2.4b and 3.2.4c, respectively. Compositional analysis by EDX indicates a film of mainly antimony with significant amounts of chlorine and oxygen. The SEM image shows growth that is not continuous and appears to be island-like. The size and structure of the deposits are unknown. The slide in Figure 3.2.4a had been exposed to multiple experiments and displayed characteristics of a successful deposition. After the discovery of this slide the amount of precursor used during deposition trials was thought to be too low. This was further explored during depositions of **2**.

Figure 3.2.3: composition of white film on glass slide from experiment CVD9

3.2.3 Results and Discussion for CVD Trials of 2

Using deposition parameters similar to **1**, CVD was attempted with compound **2**. These trials can be seen in Table 3.2.2. During these trials the amount of precursor was increased to see if it would improve coverage. Unfortunately only 4 trials were performed, of which only one trial produced a deposition seen in Figure 3.2.5. The slide with the exhibited deposition was closest to the bubbler, as in the trials for **1**. Conversely, the area of deposition on this slide was furthest from the bubbler. This deposition was not characterized.

CVD trial #	Deposition Time	Moist air?	Bubbler temp(°C)	Furnace temp (°C)	Mass (mg)	Pressure (mTorr)	Deposition ?	Substrates
11	16 hr	no	100	200	103	-	no	Si, SiO ₂
12	19 hr	no	100	200	90	-	no	Si, SiO ₂
13	16 hr	no	110	250	74	-	yes	Si, SiO ₂
14	18hr	yes	100	250	67	100	no	Si, SiO ₂

Table 3.2.2: CVD trials of 2

Figure 3.2.5: Silicon slide after experiment CVD13 with 2

3.3 Conclusion

According to TGA traces, the thermally driven volatilization of compounds **1** and **2** show results that are acceptable for CVD precursors. They seemingly volatilize in a single step whereby the TGA profile of **2** is most acceptable as it shows a slower onset of volatilization that begins at a lower temperature. The residual mass gain with increasing amounts of starting material of **2** is not ideal as it infers some thermal instability. This can be acceptable as it appears that most of either compound is volatilizing and successful depositions have occurred with precursors with much greater residual masses.

After multiple CVD trials these compounds have not provided practical nor repeatable depositions. The white film on glass produced by experiment CVD9 was characterized by EDX to contain antimony, but in amounts much lower than other elements such as oxygen or chlorine. Following experiment CVD5 a film was obtained that spanned most of the slide and contained greatest amount of antimony. This slide was left in the furnace for trials CVD3-5 and thus did not properly represent film growth characteristics of **1**. Even after multiple trials the film was not continuous and indicated poor nucleation capabilities on silicon by SEM. The inclusion of moist air did not aid in producing any film with either precursor.

Through these trials, compounds **1** and **2** have not provided predictable depositions of continuous films. Films that were produced by these compounds and characterized exhibited high concentration of impurities, particularly chlorine. The deposition temperatures used in these experiments may not have been suitable for

chemisorption of the antimony-containing precursor. Another possibility for poor film growth may be a long nucleation delay on glass and silicon substrates. A long nucleation delay may explain the results for the film recovered after CVD5. These compounds have not provided film growth characteristics suitable for CVD precursors.

4 Chapter: Royal Canadian Mint Contract Work

4.1 Introduction

Work in this area had already been previously established.⁵¹ Deposition on bronze circulation coins was initially achieved using a custom-built ALD tool and a previously reported aluminum precursor.⁵² Thicknesses of alumina producing interference colours were investigated by ellipsometry and film adhesion degradation was related to cleanliness of the coins. Laminate films of alumina and titania were produced and a ‘triple pulse’ program (discussed below) was created to increase film uniformity at 250°C. Thicknesses of 1200Å were found to produce coins that were indistinguishable to uncoated coins by sight and feel. Results from this work were considered throughout the following experiments.

4.1.1 Alumina

Crystalline alumina is known for its hardness and used as an insulating anti-wear coating for microelectromechanical systems.⁵³ Processes to grow alumina by ALD have been explored thoroughly, leading to the benchmark process of trimethyl alumina (TMA) and water. TMA is an excellent precursor for the deposition of alumina by ALD. It reacts with water even below room temperature and is a viable ALD precursor until about 300°C.⁵⁴ At this temperature TMA begins to decompose to carbon-rich aluminum films.⁵⁵ Although the film can be made crystalline by annealing the underlying substrate may not endure the process. In considering the safety aspect of this potentially industrial method, TMA can pose a high personal risk since it is pyrophoric. But proper handling can limit this liability and thus industrial processes can exploit the benefits of this well-

known process. The high linear growth rate per cycle of alumina and its reproducibility increases its value in application to industry. Another feature of alumina by ALD is the low temperature of deposition. Although density is known to decrease with decreasing temperature, alumina depositions have taken place on plastic substrates at 33°C and do not deform or destroy this thermally sensitive substrate.⁵⁶ Alumina ALD is well behaved and a widely studied system.

The hardness of alumina films is generally characterized by nano-indentation.⁵⁷ In this technique a particular type of atomic force microscope (AFM) tip made of very hard material is pressed into the deposited layer. Two common tips are used: a Berkovich tip, shaped like a three-sided pyramid or Vickers tip, a four-sided pyramid. Surface displacement is measured against the loading force of the tip. Essentially nominal hardness is defined as the maximum indentation load divided by the cross-section area of the indenter at the maximum indentation depth.⁵⁸ The hardness is recorded as pressure at which the tip penetrates the surface. Young's modulus (E) can be determined from a nanoindentation test with the maximum indentation load and depth, and the work done during loading and unloading processes.⁵⁸ One may be able avoid substrate effects by lowering depth of displacement, whereas some soft substrate effects can be adjusted for mathematically.⁵⁹

Very thin films of alumina with thicknesses of only 2-3nm grown on graphene via TMA and water have exhibited Young's modulus of 154 GPa.⁶⁰ Films of 100 nm have shown to have hardness (H) values of 6.79 GPa with Young's modulus of 202.7 GPa.⁵⁹ A

2006 literature survey⁵⁷ identifies a Youngs modulus and nanohardness of $100 < E < 272$ GPa and $8 < H < 9.6$ GPa respectively for evaporated, chemical deposited, and vapor deposited alumina. A recent study⁶¹ specific of ALD Al_2O_3 identified E and H values of 220 and 10.5 GPa, respectively, using an analytic model to account for the film/substrate geometry. The modulus for ALD alumina is less than that of bulk because of its amorphous nature.⁶²

4.1.2 Titania

Deposition of titania is also another well studied process by ALD. A common precursor is titanium (IV) tetrachloride. This precursor can react with water at reasonable temperatures to form conformal thin films of titania. Unfortunately, lower temperature depositions produce chlorine impurities at higher concentrations.⁶³ A chlorine impurity at as low as 3% can create an electron ‘sink’ and be detrimental to electronic applications.²⁸ Another disadvantage are hydrochloric byproducts which can corrode metal substrates as well as the reactor. Another well-known precursor is titanium IV isopropoxide. It is less thermally stable,⁶⁴ but the carbon impurities are not corrosive and better step coverage can be achieved.⁶⁵

Titania can be deposited as an amorphous film or with crystalline domains of anatase or rutile. Evidently the temperature range for each phase is also dependent on precursor, alkoxide based precursors yield amorphous material while crystalline material is produced at lower temperatures with halide based precursors.⁶⁵ The phase and morphology can be controlled by temperature.⁶⁶ Generally with titanium tetrakis

(isopropoxide) (TTIP) and water, below 150°C smooth and continuous amorphous titania is formed. At 200°C films are remain amorphous but decorated with tiny crystalline domains of 2-3 nm. At 250°C the layer is rough and bumpy with increased intensity of different characteristic planes of anatase. As deposited nanoparticles are crystalline and mostly show anatase.

Other characteristics are controlled by temperature such as the grain size of crystalline domains decrease with decreasing temperature. This also has an effect on elastic modulus as it decreases with reduction of grain size. As grain size decreases below 20 nm, there is not a large decrease in elastic modulus. The decrement below grain sizes about 10 nm, however, is relatively large.^{67,27} Porosity of films also plays important part on elasticity of titania films. Below 20 nm the effect of porosity on elastic modulus is more dominant than grain size as lower porosity yields greater elastic moduli. The Hall-Petch relation suggests that the yield strength of a material should increase with decreasing grain size.⁶⁷

4.1.3 Corrosion: Mechanical Characteristics of Coating Materials

Note: all studies referenced in this section use titanium (IV) chloride as a titanium precursor. Because of the corrosive nature of byproducts, it is not suggested as a precursor to prevent corrosion.

Using ALD to deposit thin films of alumina and titania for protection against mechanical and chemical attack is not novel. The protection of stainless steel is important in industry. Studies have shown that ALD layers exhibit corrosion resistance similar to or even better than conventional or thicker coatings.^{68 69 70}

Alumina films alone show limited protection from chemical attack by concentrated salt solutions.⁶⁹ The porosity of alumina can contribute to poor resistance, but increasing layer thickness decreases porosity.⁶⁹ Unfortunately increasing layer thickness also promotes delamination.⁶⁹ Alumina is amphoteric as it is reactive with both acid and base. This makes it unsuitable as a primary coating for resistance to this kind of corrosion.⁷¹ An advantage of alumina is that it adheres well to steel substrates and only shows delamination at higher loads.⁶⁹

Titania films of similar thickness to alumina show greater resistance to concentrated salt solutions.⁶⁹ Amorphous titania has been shown to afford better protection than bare steel substrates⁷² while lower temperature deposition of amorphous titania contains higher hydroxyl content and does not give greatest corrosion resistance.⁷¹

The weak points of corrosion for crystalline titania films lie in the grain boundaries and films of titania do not adhere well to steel as they show higher instances of delamination.⁶⁹

Multilayers of both alumina and titania however exhibit corrosion and wear characteristics that add the benefits of both films. Alumina serves as an adhesion layer and also fills in grain boundaries of any previous titania deposition. Delamination occurs to a lesser extent with multilayers. Multilayer films with similar overall thickness, but an increased number of layers perform even better. Electrochemical corrosion testing also points to the benefits of multilayers. These studies show better resistance than single layers and greater amounts of layers with similar thickness yield greatest resistance.⁶⁹

4.2 Protection of Numismatic Silver

Silver is a precious metal which oxidizes to Ag_2O in air (oxygen radicals) at standard temperatures and pressures. It also corrodes in air due to the presence of sulfur. This forms an undesirable black oxide finish that is aesthetically unappealing and detrimental for the sale of silver. Over time some oxidation can be aesthetically pleasing to consumers and is known as patina.

A process to protect silver from tarnishing has already been developed and is currently used by the Royal Canadian Mint. It involves a thin coating of lacquer on finished coins. The details of this coating are a trade secret, thus we knew only that it was prone to incorporate defects that required stripping of the lacquer before re-coating. Thus

the vacuum and chemical nature of ALD would be ideal to coat silver coins while minimizing defects and lowering rejection rates.

Much interest is invested into the ability to deposit coatings on metal surfaces. These films would act as a passivation layer to protect the metal substrate. An ideal coating would be clear, transparent and would not impact the visual appeal, feel or the purpose of the coated material. The conformal nature of ALD as well as its high degree of thickness control would afford minimal amount of coating. The ALD process and transparent nature of alumina and titania thin films should produce defect-free substrates. The goal of this project was to develop an industrial-level process to coat coins.

4.3 Experimental

Silver numismatic coins produced by the Mint contained 99.99% silver whereby the remaining composition was not known. The tool used to perform depositions of alumina and titania was a PicosunTM P-series ALD system. The tool was modified to best suit deposition on coins through utilization of racks. Thicknesses of deposited films were measured *ex-situ* on silicon witness slides using a J. A. Woollam Co. Alpha-SE ellipsometer. The refractive index used to output thickness values were $n = 1.73$ for alumina and $n = 2.45$ for titania.

Three particular methods to clean the substrate coins were employed. For safety reasons and to protect trade secrets the tools used were operated by Mint technicians where details of the procedures were not disclosed. One such tool was the Ebner furnace.

The parameters were: 250°C for 30 minutes, program #2. Another was the Finnsonic tool; an automated ultrasonic multi-solvent based cleaning apparatus. There was also a method to clean coins via hydrogen scrubbing. This included a heated furnace that was pressurized with 5% hydrogen in nitrogen. This technique effectively burns off organic material and forms a chemically reduced surface on the substrate. Hydrogen scrubbing was performed *ex-situ* for 1 or 2 hours at a temperature of 150°C. Coins were then allowed to cool to less than 40°C before being removed where they were immediately used or vacuum sealed for future use.

The general sulfur/adhesion test began by applying Scotch tape across the top portion of the coin, pressing firmly then quickly removing the tape. The coins were then placed on a rack, to keep the coins out of solution and held up-right in a glass desiccator. The bottom of the desiccator was filled with approximately 500 mL of water and 0.14 g disodium sulfide. To initiate generation of hydrogen sulfide: about 1 mL of diluted hydrochloric acid was added to the solution below, the lid placed on the desiccator and the solution was stirred by a magnetic stir bar. Coins were left in the desiccator for 2 hours. Glass slides were used as blanks by applying Scotch tape to see if residue from the tape affected the glass. No such affect was seen.

The inspection protocol to select defect-free coins was performed by trained quality control staff at the Mint. These inspections took place before deposition and after to attain rejection rates. The method of inspection could be best described as a quick glance of each face. The defects included but were not limited to scratching, haze and

any discolouration. Rejection rates could vary with the same inspector as well as with other quality control staff. The process of doubly inspecting coins was implemented to ensure pristine coins were used in depositions and that aesthetically defective coins did not produce a false rejection rate. The process of doubly inspecting coins required bringing separate trays of uncoated coins to a quality control staff member. When a sufficient number of defect-free coins were selected for a single deposition, the coins were collected on a single tray and brought back to the same inspector. This would continue until each coin was inspected twice and enough coins to complete a deposition were selected.

To ensure complete surface saturation and uniform coatings pulse parameters were optimized for this application (Figure 4.3.1). Multiple short pulses give better uniformity than longer pulses of equal time since the head-space in a bubbler is regenerated in the purge step between subsequent pulses of the same precursor. The standard triple pulse program to deposit alumina begins with two similar 0.1 s pulses of the metal containing precursor, TMA, which are separated by a 0.5 s interval. This particular tool utilizes a constant flow of nitrogen which acts to purge the precursor molecules from the deposition chamber during this interval. The final metal precursor pulse is of the same 0.1 s interval, but is followed by a 10 s purge. This long purge is to prevent unwanted deposition as residual precursor may react in the gas-phase with the next reactant gas. Water is then pulsed into the chamber in three similar pulses that mirror the previous precursor. Bubblers for TMA and water were kept at room temperature. The bubbler for TTIP was heated to 125°C and the lines leading to the

deposition chamber were heated to 160°C to prevent condensation. The growth rate of alumina was previously determined to be 1.26 Å/cycle and titania 0.47 Å/cycle.

	Leading Double Pulse (s)				Lagging Single Pulse (s)		Leading Double Pulse (s)				Lagging Single Pulse (s)	
	TMA	purge	TMA	purge	TMA	purge	H ₂ O	purge	H ₂ O	purge	H ₂ O	purge
Alumina	0.1	0.5	0.1	0.5	0.1	10.0	0.1	0.5	0.1	0.5	0.1	10.0
	TTIP	purge	TTIP	purge	TTIP	purge	H ₂ O	purge	H ₂ O	purge	H ₂ O	purge
Titania	1.0	0.5	1.0	0.5	1.0	10.0	1.0	0.5	1.0	0.5	1.0	10.0

Table 4.3.1: Parameters for the triple-pulse program used to deposit alumina and titania on bronze tokens.

4.4 Results and Discussion

4.4.1 Numismatic Haze

Since these coins are collectable there is a requirement for very low rejection rate – less than 2%. ALD does not inherently cause defects due to deposition *in vacuo* although high purity silver (99.99% Ag) produced a ‘haze’ after deposition of 150 cycles of TMA and water at 250°C. This was aesthetically undesirable and considered a reject. The haze was not clearly characterized and was thought to be from oxidation or contamination due to lack of cleaning. It was found from a ‘dry run’ such that the precursor valves remained closed and no precursor was being introduced, that heating to 250°C caused the haze to form on the coins. Dust also was found to cause problems as scratches on the mirror-like surface and sometimes as particles incorporated into films.

This is what led to greater scrutiny and the double inspection to select pristine coins before deposition.

The determination of a rejection rate was carried out visually by inspection staff. It was clear that inspection techniques needed to be learned and understood in order to better understand the rejection process and what makes an acceptable coin. Because of the subjective nature of a visual inspection process steps were taken to ensure coins were considered defect-free before deposition. This would include previously self-inspecting coins and working with only one inspector who would be required to double-check coins before deposition. The double check was required as about 4% of coins that initially passed would be rejected the second inspection. After deposition the same staff member would be called upon to examine the coins.

Attempts to pre-clean coins in solvent were tried. First was sonication in acetone. The purity of acetone was an issue as haze-like deposits formed on coins as the solvent evaporated. This method was quickly discarded. Another procedure was to use the Finnsonic tool, an automated ultrasonic solvent based cleaning apparatus. Even with this sophisticated cleaning apparatus coins still produced haze after deposition. It could therefore be stated that hazing of the coins was not produced by surface contaminants which would be removed from this apparatus, such as the mineral oil used in stamping the coin. Nitrogen gas ‘flushes’ were performed to help remove any residual oxygen or water from the deposition chamber to prevent their oxidative effects. These nitrogen flushes were undertaken by increasing the flow of nitrogen to the deposition chamber to a

set pressure then reducing this flow to achieve a <10 mbar pressure. This was performed as the chamber was slowly heated. As well, an overnight bake-out whereby the chamber was heated to 500°C for 18 hours was performed. These attempts had no effect on preventing the haze from occurring. Three tests were then performed to determine the cause of the haze and to prevent it from forming. As coins are pressed a mineral oil is used on the die. A special set of coins were pressed where the oil from the die was removed with isopropyl alcohol (Ag10). Regardless of this step, the subsequent coins produced a haze after deposition. Another method (Ag11) to prevent haze was to pretreat the coins in a separate furnace equipped with hydrogen gas, a so called hydrogen-scrub. At first the coins were placed on the bottom of the furnace with one face down. After deposition only one face of each coin had haze. Although it was not known which face was up, it seemed apparent that the face-down side formed haze while the face-up was free from haze after deposition (Ag14). Coins were placed in a rack so they stood on edge and not on their face (Ag18). This produced coins that, after deposition of 150 cycles of alumina at 250°C were considered 'borderline passable'. These hydrogen scrub parameters were tried on future depositions. The third test (Ag11) used an Ebner furnace was to pretreat the coins with parameters that were not completely disclosed: 250°C for 30 minutes, program 2. Regardless of this attempt haze still formed on the coins.

Since the appearance of haze seemed to be brought on by increased heat, depositions at reduced temperatures were performed. Temperatures of 80°C were first tried with normal 150 cycle coatings of alumina. It was observed by ellipsometry that this did not change the thickness of deposition. Unfortunately coatings at this

temperature did not adhere well and failed the Scotch tape test. Temperatures of 150°C provided results that were aesthetically pleasing (Ag17) and also passed adhesion tests. Through further experimentation with deposition temperatures it was found that temperatures above 227°C and extended flushing produced haze on 99.99% silver. Depositions then were performed at temperatures of 220°C to prevent temperature overshoot, for greater adhesion, density and to prevent haze. To further insure this temperature limit was not surpassed, a slow temperature ramp was used. There is an unfortunate drawback to this approach to reduce haze. Lowering temperature of deposition affects essential film characteristics that are important for most applications. Properties such as adhesion and film density decrease with decreasing deposition temperature which would directly affect wear of the coatings. A slower temperature ramp would increase the deposition time which is not desirable in a time-constrained industrial process. Also, the temperature of 250°C was initially selected as the precursor pair of TTIP and water begins to form domains of crystalline anatase titania. The anatase form of titania has the benefit of greater density and hardness over the amorphous phase.

Since high temperature was found to effect haze, and it was believed the haze was the result of residual water or air in the deposition chamber, there was an attempt to “bake-out” the chamber. This entailed loading the coins and opening the chamber to vacuum with temperature set to 150°C overnight before deposition at 250°C (Ag29). This proved to reduce the occurrence of haze, but with this particular deposition one was considered ‘borderline hazy.’

4.4.2 Tests of ALD Coatings on Numismatic Silver

The corrosion tests show that ALD coatings protect coins and out-perform lacquer. These trials began by comparing coated and unprotected coins exposed to hydrogen sulfide. ALD coins of 150 cycles of alumina showed superior corrosion resistance. The lacquer showed brown tarnishing that may be due to reaction of the lacquer to the hydrogen sulfide. The uncoated coins became purple while the lacquered coins became dark brown in appearance (Figure 4.4.1).

Figure 4.4.1: Hydrogen sulfide tests show better protection by ALD as the coating is intact and the coin un-tarnished. The lacquer on the coins show reactivity to the hydrogen sulfide and the uncoated coins become much darker.

4.4.3 Adhesion tests (Ag21 vs. Ag25)

To form a visual indication of film adhesion, a Scotch-tape adhesion test was performed before coins were placed into the sulfur chamber. Some coins with the ALD coating were scratched in a cross-hatched pattern with a diamond tipped pen (Figure 4.4.2). This was done to see if the resulting squares would be removed. Coatings of 150 cycles of alumina at 150°C (Ag21) showed some tarnishing in the form of small black spots underneath where the tape had been. The scratches made with the diamond-tipped pen also became black, but none of the resulting squares were removed. In these tests the ALD coated coins outperformed lacquered and uncoated coins, although some of the alumina was removed with tape. This is evident as tiny black spots on the coin underneath where the tape had been. These spots were not due to tape residue as glass slides treated similarly did not show any of the spots. All ALD coated coins showed black tarnishing on the edges of the coins which was thought to be because they are handled at the edges to prevent damage to the face.

A thicker coating Ag25 (200 cycles alumina, 150°C) showed better results. After the sulfur chamber, the areas under where the tape had been had fewer black spots. These coins still had tarnishing marks along the edges, possibly from handling. A bilayer deposited at 220°C of 106 cycles of titania on top of 150 cycles of alumina was also tested (Ag30). Results for adhesion of this bilayer were similar to coins without titania. Unfortunately there were tests where almost all of the ALD coated coins (Ag37, 39) failed adhesion tests. Experiments Ag37 (200 cycles alumina, 150 cycles titania 220°C) and Ag39 (200 cycles alumina, 220°C) had most of the area under the tape blackened by

sulfur exposure indicating removal of the ALD layer(s). This is thought to be because of a change in the tape used for this test and the likely possibility of low uniformity between tape batches. Regardless this later resulted in not using tape to test for adhesion.

Figure 4.4.2: Ag 21 cross hatch, tape and H₂S. The scratched surfaces clearly indicates corrosion from sulfur.

4.4.4 Humidity and Adhesion (tape and sulfur)

In this study, adhesion and corrosion (as described above) were tested after the coins were subjected to a humidity chamber to determine the durability of the ALD coatings. The humidity chamber consisted of a large desiccator with water in the bottom where coins would sit on a rack, above the water at room temperature for 24. The 24 hour test was performed on coins from Ag21 (150 cycles alumina 150°C). Results showed slight signs of humidity exposure as small white spots. The humidity however did not affect the adhesion test. The results for adhesion after humidity were similar as the adhesion test alone on Ag21. Coins that had been subjected to cross-hatching, then humidity/adhesion again did not have the square pieces removed from the tape. They

were tarnished at the scratches, which was likely because the cross-hatching procedure inherently breaks the coating layer. Uncoated coins became a dark purple brown during this test. The same minor black tarnishing was seen on the ribbed edges of the coins and is again thought to be because of handling. The bilayer with titania (Ag30: 150 cycles alumina 106 cycles titania, 220°C) performed worse. More of the area under the tape had black spots indicating that parts of the coating had been removed. This may be caused by a difference in applied pressure during the adhesion test.

4.4.5 Brine solution and Adhesion

This test was the most harsh and also showed greater variability of results (Figure 4.4.3). Coins from Ag21 (200 cycles alumina, 150°C) were placed in a 2% w/w NaCl solution for 2 hours and then subjected to the adhesion test. The salt-water bath left white deposits and left the mirrored sections of coins foggy. It also weakened the alumina layer as much of the area under the tape was removed for some coins. After the adhesion test, about half the coins had large areas under the tape removed which became black with tarnish. While the remaining half resembled adhesion test results without brine solution. The cross-hatching technique was also tried and the same results were obtained, with half of the coins exhibiting heavy tarnishing.

These results led to producing coins at higher deposition temperatures in order to achieve greater adhesion. A set of coins with the same thickness of 150 cycles of alumina were produced at a temperature of 250°C (Ag29). They showed similar results to previous adhesion tests which were not placed in brine solution, but were not suitable because of the formation of haze at this temperature. Coins from Ag30 (150 cycles of alumina and 106 cycles of titania, 220°C) showed similar results to Ag29 which is likely due to similar deposition temperatures.

4.4.6 New Tests

The previous set of tests of humidity or brine solution with tape was considered quite harsh by the Mint project manager. Further testing of coatings was not to include tape before introducing coins to sulfur. The first of these new tests was to place coins in the humidity chamber then expose them to sulfur. They were performed on Ag33 (200 cycles alumina, 220°C) and Ag35 (200 cycles alumina, 500 cycles titania, 220°C) and

Ag37 (200 cycles alumina, 150 cycles titania, 220°C). The differences in layer thickness of titania was to see if it afforded any extra protection from tarnishing. Similar white spots and smudging were observed on all coins. One particular coin of Ag37 (Figure 4.4.4) became unusually tarnished. Otherwise no straightforward conclusion could be reached on the effect of layer thickness of titania on film appearance. These trials also helped indicate the maximum deposition temperature before haze appeared. A deposition temperature of 223°C for Ag34 was selected, but it overshot this temperature and haze was observed. The bake out performed on Ag29 in attempt to deposit at higher temperatures did not produce haze-free coins.

Figure 4.4.4: Ag-37 coin with unusual sulfur damage

4.4.7 Humidity Duration Test

The titania coins seemed to have a slightly greater instance of unappealing marks after humidity testing. A humidity duration test was implemented where coins placed in

a humidity chamber were inspected after 8, 24, 48 and 72 hours. Coins used here were Ag38, Ag40, Ag41 and uncoated coins.

The batch of Ag41 was coated with 200 cycles of alumina and 150 cycles of titania at 220°C. The remaining coated coins had only alumina layers deposited at 220°C, but Ag38 had 200cycles whereas Ag40 had 500. After 8 hours very few, but noticeable white marks appeared on all coins. The uncoated coins showed brown tarnishing near the contact points with the holder. After 24 hours more, haze and white marks visible on mirrored parts of the coin on Ag38, Ag40 and Ag41. It was apparent that the uncoated coins exhibited a greater amount of haze on the mirrored parts. The coins after 48 and 72 hours all followed the same trend, but one of Ag41 after 72 hours showed small brown spots indicating a slight tarnish. All coins in this experiment showed some degree of aesthetic degradation, with the uncoated coins and one of Ag41 showing effects of brown tarnishing. This tarnishing along with variably poor results previously with titania in the humidity chamber led to the exclusion of titania from future coatings because of its apparent degradation under these conditions.

4.4.8 Hydrogen Furnace and Final Products

The hazing was found to not be part of any contamination on the silver surface, and eliminated by lowering temperature. A cleaning process was devised whereby coins would be put through the Finnsonic cleaning system to remove any residual oils then subjected to a hydrogen scrub. The dual cleaning was to provide an ultimately clean

surface to test adhesion and quality of the coating. After being treated in the Finnsonic the coins were placed for one hour in the hydrogen furnace at 150°C. Ten coins were deposited with 200 cycles of alumina (200H1) and ten were deposited with 300 cycles alumina (300H1). These coins were tested against lacquered and uncoated coins as well as a previous deposition, Ag22 (150 cycles alumina 150°C). The corrosion tests involved 24 hours in the humidity chamber followed by 2 hours in the sulfur chamber (Figure 4.4.5).

The uncoated coins were badly tarnished across large areas of both faces. Lacquered coins showed the characteristic brown colour from sulfur, again across large areas of both faces. Both hydrogen scrubbed coins showed hazing and some tarnish at the ribbed edges but no tarnishing on either face. The tarnishing on the edges is likely due to handling. Ag22 showed slightly more tarnishing on the ribbed edges as well as some on the face of the coin (Figure 4.4.6).

A)

B)

C)

D)

E)

Figure 4.4.5: Sample of coins after the first of the final sets of corrosion tests. A) 200H1 slight tarnish on edges, haze on mirrored portion. B) 300H1 slight tarnish on edges, haze on mirrored portion. C) Lacquered coin showing brown tarnish from sulfur. D) Ag-22 with black markings similar to other ALD coins. E) Uncoated coin with heavy sulfur damage.

Figure 4.4.6: First trial of the final sets of corrosion tests showing tarnishing along edges.

Although the ALD coated coins performed better than lacquered and uncoated coins in the corrosion tests, the effect of hydrogen scrubbing was further investigated. After Finnsonic treatment, coins were placed in the hydrogen furnace for two hours and the same 200 cycle and 300 cycle alumina thicknesses were compared to the 1 hour hydrogen scrub. Two further trials with 5 each of 200H1, 200H2, 300H1, 300H2 and Ag-22 were performed and gave results identical to the previous trial (Figure 4.4.7). The longer hydrogen furnace times indicate a reduction in tarnishing seen at the edges of the coins. This demonstrates greater adhesion as the edges are where the coins are handled.

Figure 4.4.7: Trial 2 results with coins having longer hydrogen scrubbing times

Because of the reduced tarnishing provided by the hydrogen scrub, the original adhesion test was attempted. Adhesion tests on the 2 hour hydrogen scrub (H2) coins with tape showed variability with respect to how much tarnishing was observed. These tests used the same tape as the tests where Ag-37 and Ag-39 failed. On average the 300H2 coins fared similarly to the original tests performed with Ag-21. They exhibited similar amount of tarnished area and one of 300H2 failed. The 200H2 set fared better than other sets overall. This may be due to delamination that could have occurred at higher deposition thicknesses, but was otherwise unnoticed. Some of these coins had no tarnish at all on either face of the coin.

4.5 Summary Conclusion - Numismatic

The subjective nature of the visual inspection process to determine an aesthetic rejection rate initially hindered furthering of ALD coatings. Multiple inspections by the same inspector on the same batch of coins gave a 'base' rejection rate of 4%. Attempts were made to use the same inspector throughout the duration of the experiment, but this inherent discrepancy was inevitable.

Haze appearing on 99.99% silver coins after deposition was a long standing issue. It was found to be produced when heating the deposition chamber, possibly promoting the formation of silver oxide. The exact nature of the haze is unknown. The heating limit before haze formation was experimentally found to be approximately 227°C. Subsequent depositions were performed at 220°C to prevent temperature overshoot. Use of an *ex-situ* hydrogen scrub appeared to decrease the presence of haze at temperatures of 250°C. Because of the industrial nature of the project the hydrogen furnace was not always available and required a separate operator. Only through an *in-situ* hydrogen scrub could the effectiveness of the reducing atmosphere be fully assessed. The ALD tool used in these experiments could be equipped with a hydrogen generator to create an *in-situ* hydrogen scrub. The end goal was to have a hydrogen equipped tool for production, but the Mint was unwilling to extend testing.

Adhesion tests displayed some variability. The variability is likely related to the test not being standardized; pressure applied to the tape was not measured therefore not exactly reproducible. Tape-based adhesion tests with the initial tape indicated that an increase in layer thickness or deposition at higher temperatures performed better in the following sulfur chamber as fewer tarnishing spots. After the change in tape, depositions with higher temperatures and/or thicker layers clearly failed; however coins that were exposed to the hydrogen scrub passed the adhesion test. Regardless of the inconsistent results with ALD coatings the lacquer coating was never removed by this adhesion test.

The lacquer would however react with the sulfur and become dark brown to the point of severe aesthetic degradation.

Results from coins placed in a humidity chamber revealed that humidity had no effect on adhesion of alumina coatings; however the humidity seemed to produce aesthetic flaws. These flaws occurred more often in coins coated with an outer layer of titania. This led to titania coatings not being considered as an acceptable coating for this application.

Soaking the coins in 2% sodium chloride solution was the harshest test and gave variable results with coatings deposited at temperatures of 150°C. Coatings at higher temperatures of 250°C proved more durable as did laminates of alumina and titania deposited at a temperature of 220°C.

The final corrosion tests included humidity and sulfur experiments on coins deposited with alumina after exposure to the *ex situ* hydrogen scrub. These tests did not initially include adhesion tests using tape. The coins with the longer hydrogen scrubbing times of two hours and thicker 300 cycle alumina depositions showed the greatest results. These coins tarnished at a fewer points along the edges where they were handled than the others coins with less time in the hydrogen furnace and thinner coatings. When subjected to the original adhesion test using newer tape and 2 hour exposure in the sulfur chamber, these coins showed less tarnishing than depositions without hydrogen scrubbing. Thicker coatings provided greater corrosion resistance, but the thinner 200H2 coating yielded a

better result in the adhesion test. This is likely due to delamination occurring with thicker coatings. The hydrogen scrubbing appeared to improve adhesion to the silver substrate. The prevention of haze by lowering temperature is in conflict with the benefits of ALD coatings at higher temperatures. Properties such as density, adhesion and formation of crystalline anatase titania would increase wear resistance. Coatings deposited at higher temperatures performed better than depositions at lower temperatures in all experiments and is believed to be related to the aforementioned benefits. The qualitative testing did not show an improvement when titania was added to form the bilayer. In some cases with humidity, the outer titania layer showed greater aesthetic deterioration the cause of which is unknown.

Baking out the deposition tool to remove condensed water reduced haze but was very time intensive and not a realistic solution in a time constrained industrial application. This study shows results similar to bake-outs with the Finnsonic cleaning and the use of an *ex-situ* hydrogen scrub. It would be beneficial to explore the capabilities of an *in-situ* hydrogen scrub as it also appears to increase film adhesion and to see if the Finnsonic cleaning method is necessary. Clean substrates are crucial for proper adhesion and this will be an on-going problem in this specific industrial setting.

Weak points of the ALD coatings appeared as black tarnish marks where the coins were handled. Multilayers with crystalline titania may be able to withstand friction as anatase titania is harder than its amorphous form. This would require substrate temperatures of at least 250°C which were initially problematic due to the formation of

haze and not further studied because of the poor results with these films in the humidity tests. Although coins coated by ALD protect from sulfur corrosion and do not change colour as do the lacquer coatings, they show aesthetic degradation when exposed to long periods of high humidity. There is an apparent flaw with the sulfur test as the lacquer appears to react with it and produce a brown colour. It is unclear whether the sulfur reaches and reacts with the silver underneath this coating. Regardless, the lacquer coating is not removed by the tape during the adhesion test and otherwise holds up to all other tests.

4.6 Atomic Layer Deposition Coatings for Circulation Coins

4.6.1 Experimental Procedure for ALD Coatings for Circulation Coins

Depositions were run on full baskets of 1500-1600 bronze tokens. Coins were received as 'sheets' of 169 test tokens and 9 of these sheets were dumped into a single basket for approximately 1,521 coins. Coins were dumped into an aluminum basket which consisted of flat side panels and a wire mesh bottom. Depositions were carried out 250°C with two nitrogen flushes performed during the heating period which included a stabilization time of 2 hours. Bubblers for TMA and water were kept at room temperature. The bubbler for TTIP was heated to 125°C and the lines leading to the deposition chamber were heated to 160°C to prevent condensation. The growth rate of alumina was previously determined to be 1.26 Å/cycle and titania 0.47 Å/cycle. The general triple-pulse recipe was discussed in the previous section and shown in Table 4.3.1.

4.6.2 Positional Coins

Positional coins were marked with a punch to indicate placement. The maple leaf on the face of the coins formed a triangle with the orientation of the words on the coins indicating the top of the coin. There were 8 depth positions in the basket: top, top middle, middle, bottom middle and bottom, side top, side middle and side bottom. Except for the ‘side’ positions, each of the positions has 5 coins in a pattern that resembled the fifth side of a die. These coins were placed with their face parallel to the floor. The six ‘side’ coins were placed perpendicular with respect to the other coins with two coins up against each side of the basket. Although care was taken when placing the coins, displacement from intended position was sometimes inevitable.

Figure 4.6.1: Indentations on coins indicating location of positional coins in basket batches.

4.6.3 Placement of Silicon Witness Sides

Silicon witness slides for basket runs B1 and B2 included two silicon witness slides which were initially placed with one on top of the coins in the basket and one in the center. Basket runs B9 and B10 included six witness slides. These slides were placed parallel to the basket floor through the center of the basket. They included a top, top middle, bottom middle, bottom and two side positions. Both side positions were located near the middle of the basket but one side position had the silicon facing the wall of the aluminum basket while the other side had silicon facing inwards towards the coins.

4.6.4 Tests

Thicknesses of deposited films were measured in the same fashion as numismatic coatings, i.e. *ex-situ* on silicon witness slides using a J. A. Woollam Co. Alpha-SE ellipsometer. The refractive index used to output thickness values were $n = 1.73$ for alumina and $n = 2.45$ for titania.

Tumbler tests to gauge wear characteristics consisted of placing coins in a rock tumbler. One coin in each of the 7 positions (top, top middle, middle, bottom middle and bottom, side top and side bottom) were placed in the tumbler and run for 24 hours at ~22 rpm to simulate years of wear. Coatings of 150 Å alumina and 50 Å of titania were used to compare with uncoated coins. ALD coins were run separately from uncoated coins.

Exposure to hydrogen sulfide to test for coverage was performed similar to silver numismatic coins. This sulfur chamber consisted of a desiccator with cut plastic tubing

used to hold the coins up-right. Generation of hydrogen sulfide gas was achieved by placing 0.14 g of disodium sulfide in a small vial and dropping the vial in approximately 500 mL of water in the bottom of the desiccator. A rack was used to keep the coins out of solution and the coins placed in their plastic holders on the rack. About 1 mL of diluted hydrochloric acid was added to the solution below, the lid placed on the desiccator and the solution was stirred by a magnetic stir bar and left for 2 hours.

4.6.5 Basket Depositions

The first basket deposition (B1) consisted of 150 cycles of alumina only. A silicon witness slide was placed on the center of the basket and another on the top of the coins in the basket. Basket batch number two (B2) used the same coins as B1 and differed by an additional leading pulse for a total of four pulses for each metal-oxide layer. These initial tests were to assess penetration depth of the growing film on the silicon slides only. The reused ‘dummy’ coins only served to fill the basket while conserving the supply of coins. This batch also contained 2 silicon witness slides in locations similar to B1. The third and fourth run included 106 cycles of titania in addition to 150 cycles of alumina to form a laminate film. Previously coated dummy coins from the previous batches were again used while uncoated coins in the 8 aforementioned positions were used in the tumbler and sulfur tests. In attempt to prevent black lines from appearing after sulfur treatment, batch six (B6) consisted of an increase in thickness of each metal-oxide layer by 20 Å to 170 Å alumina and 70 Å titania. This was calculated from the previously reported growth rates of 1.26 Å/cycle for alumina and 0.47 Å/cycle for titania. The dummy coins were again re-used with fresh positional coins

and a strong colour gradient was observed. Batch number seven (B7) used an entirely fresh batch of coins and a thickness reduced to 160 Å alumina and 60 Å titania to remove the colour gradient and prevent sulfur lines. No colour gradient was observed. The eighth batch (B8) was to observe if increased pulse times, with the same thickness, afforded a colour gradient. It consisted of increasing pulse time from 0.2 seconds to 0.4 seconds and 1.0 to 2.0 for each of the three pulses of TMA and TTIP, respectively. This batch used all uncoated coins and pulsing was returned to 150 cycles alumina and 106 cycles titania. Batch number nine (B9) consisted entirely of uncoated coins and six silicon witness slides in positions: top, top middle, bottom middle, bottom, side right and side left. There was an increase to 300 cycles of alumina and 200 cycles of titania in order to observe any colour gradient. The precursor pulsing times were kept as per B8. The last batch of circulation coins, B10 were to improve on the deviation in coating thickness. Cycles of each metal oxide were returned to 150 cycles of alumina and 106 cycles of titania, but pulse times were increased. Times were increased for alumina deposition to 0.6 s for both TMA and water, while for titania the pulses for both TTIP and water were increased to 3.0 s.

4.7 Results and Discussion

4.7.1 Thickness Measurements

These circulation tests were run to determine the effectiveness of coating brass coins in batch processes were they were randomly assorted within a basket. These coins were tested for coating efficiency qualitatively by observing a colour change or quantitatively by measure of thickness. The thickness measurement was performed by

ellipsoemetry on the silicon witness slides. Other quality assessments included a tumbler test for wear and a hydrogen sulfide chamber for chemical inertness.

Run	Alumina cycles	Pulse style	Top witness slide (Å)	Bottom witness slide (Å)	Average thickness (Å)	Standard deviation (Å)
B1	150	triple	191	173	182	18
B2	150	quadruple	198	180	189	13

Table 4.7.1: Thickness measurements and coating parameters of the two first trials using only alumina.

The first coatings (B1, B2) were deposited to find parameters that would coat each coin evenly. This began by using the triple pulse style settings to deposit 150 Å of alumina only. These settings produced a thickness deviation of 18 Å on silicon witness slides (Table 4.7.1). This comprises approximately 10% of the coating thickness and would be a large enough deviation to affect reproducibility of the quality tests. Increasing to a quadruple pulse provided only slightly better results with a thickness deviation of 13 Å (Table 4.7.2). These, along with following tests, indicated the initial triple pulse program did not allow for sufficient precursor penetration to coat such a large and disorganized arrangement of coins. Either an increase in pulse time or number of pulses would be required.

Run	TMA pulse length (s)	H ₂ O pulse length (s)	TTIP pulse length (s)	H ₂ O pulse length (s)	Alumina, cyc	<u>Titania,</u> cyc	Number of Si slides	Average thickness (Å)	Standard deviation (Å)
B9	0.4	0.4	1	1	300	200	6	110	10
B10	0.6	0.6	3	3	150	106	6	1145	2

Table 4.7.2: Thickness measurements and coating parameters of the final two trials using both alumina and titania.

Tests of laminate coatings were run with coins placed in certain positions and marked with a punch to dictate their position when later removed from the basket. The rest of the basket was filled with ‘dummy’ coins that were re-used in subsequent depositions in order to have a reasonable mass and surface area to represent a full production run. This was to reduce the amount of coins used per run (1500 coins) and to facilitate locating positional coins among the darker coloured dummy coins. Issues of coating uniformity soon followed as uncoated coins within the basket of dummy coins displayed a colour gradient.

Deviations from uniformity were observed visually when coating thickness was increased by about 20 Å for each layer of titania and alumina. Among the previously coated ‘dummy’ coins, a change in colour in the positional coins was observed. The positional coins near the top and bottom of the basket were darker in colour and the

positioned coins near the center did not change in colour. This would indicate greater coating thickness at the top and bottom of the basket.

To examine the cause of the colour change a second deposition experiment was undertaken with the same 20 Å increase of both alumina and titania but with a complete basket of fresh coins and increased pulse times. This was an attempt to grade uniformity by visual inspection. The pulse time (B8) for TMA was increased from 0.2 sec to 0.4 sec and TTIP was increased from 0.5 sec to 1.0 sec. Purge times were not altered. This produced coins that did not display a colour gradient which was unexpected. The gradient produced in the previous deposition was a product of insufficient precursor infiltration to the center of the basket. An insufficient number of pulses or pulse time would not allow enough precursor into the deposition chamber and would reduce precursor residence time and therefore infiltration into the basket's center. This is due to the random arrangement of coins in the basket causing a very torturous path for a precursor to follow. The amount of precursor was found to be sufficient as the triple pulse program used deposited a uniform coating on a greater number of bronze coins (2744 coins) when they were arranged in racks.⁵¹ Because the only coins discoloured in the previous run were on the top and bottom it is likely that precursor was not reaching the middle of the basket. To be coated evenly a longer precursor resident time would be required to form a saturated monolayer on the most buried of coins. This was provided by increasing the amount of precursor pulse time. Also, the design of the basket prevented flow of precursor to its center since the walls were solid and did not allow for any precursor flow.

To produce a uniform, darker colour change a further increase of coating thickness was deposited on a full basket of fresh coins. With the previous increase in pulse time, approximately 300 Å of alumina and 100 Å of titania was deposited on a fresh basket of coins (B9). These coins were visually uniform in colour as slightly more orange than the coins before coating. Ellipsometry of silicon wafers placed in 6 different locations within the basket gave an average coating of 110 Å with a standard deviation of 10 Å. With improved visual uniformity, the thickness was decreased to the initial 150 Å alumina and 50 Å titania. Pulse times were increased again as well as purge times according to Table 4.7.3.

	Leading Double Pulse (s)				Lagging Single Pulse (s)		Leading Double Pulse (s)				Lagging Single Pulse (s)	
	TMA	purge	TMA	purge	TMA	purge	H ₂ O	purge	H ₂ O	purge	H ₂ O	purge
Alumina	0.6	0.5	0.6	0.5	0.6	10.0	0.6	0.5	0.6	0.5	0.6	10.0
	TTIP	purge	TTIP	purge	TTIP	purge	H ₂ O	purge	H ₂ O	purge	H ₂ O	purge
<u>Titania</u>	3.0	0.5	3.0	0.5	3.0	10.0	3.0	0.5	3.0	0.5	3.0	10.0

Table 4.7.3: Increased pulse parameters for measure of film uniformity (B10)

The accuracy of ellipsometric measurements are questionable as they are much larger than what is expected for the calculated growth rates. Nevertheless the deviation in film thickness was very small with an average of 1145 Å and standard deviation of 2 Å (Table 4.7.2). This was again measured from silicon wafers placed at six different

locations in the basket. In addition each of these pieces was measured six times at different areas of the piece.

4.7.2 Sulfur Treatment

Laminate coatings of alumina and titania were produced to test wear and sulfur corrosion against uncoated coins. Coatings with approximately 150 Å of alumina and 50 Å of titania would withstand 2 hours in the sulfur chamber without the drastic colour change seen in the uncoated coins (Figure 4.7.1).

Figure 4.7.1: Before (far left) and after sulfur treatment of ALD coatings of 150 Å of alumina and 50 Å of titania. Notice there is no colour difference between ALD samples (center) while the uncoated coins (right) appear darker.

After sulfur treatment some of the ALD laminate coins would have black marks or lines on the faces. The marks would leave a residue on Scotch tape. They appeared only on the ALD coated coins where the plastic holder was in contact with the coin. In attempt to prevent these lines from appearing, each metal oxide layer was increased by 10 Å. Even after the overall 20 Å increase of each the black marks were still produced after H₂S treatment and only on ALD coins.

These sulfur tests showed reproducible results throughout each deposition. Uncoated coins would change colour to orange. The coins coated in laminates of alumina and titania did not change colour, but did show black marks where the plastic holders contacted the coins. The black marks were not characterized nor were they avoided by increasing layer thickness. Since the black marks only appeared on ALD

coated coins there must have been a reaction between with the titania layer and the plastic tube holders brought about by the hydrogen sulfide. By either adding a final layer of alumina or not depositing titania may give insight into wheather or not the titania coating is responsible for these marks.

4.8 Tumbler Tests

Upon visual inspection of coins after the tumbler: uncoated coins appeared darker while the ALD coated coins do not change colour (Figure 4.8.2). It appears as though the soft plastic of the tumbler is worn down and gently adheres to the sufrage of the uncoated coins. The first trial consisted of running the ALD coated coins first then the uncoated coins, without cleaning the tumbler. For the next trial the tumbler was wiped of all remaining residue and the uncoated coins were run first, then the ALD coated coins run after without cleaning. Similar results were observed as the uncoated coins were considerably darkened by the plastic from the tumbler. The ALD coated coins also showed some plastic residue but not nearly as much as the uncoated coins (Figure 4.8.3).

Figure 4.8.1: Image of both coated and uncoated coins before being placed in the tumbler for 24 hours at 22 rpm. Note: the coins appear identical.

Figure 4.8.2: After 24 hours in the tumbler the ALD coated coins show a dull-ness in the coating brought about by many small indentations. The uncoated coins have the same indentations, but absorb the soft plastic coating of the tumbler walls.

On both coated and uncoated coins many small indentations are seen on the smooth areas. On the coin's embossed face there was no discernable difference between coated and uncoated coins when inspected by eye. Even with the possibility of lack of uniformity of coating throughout the basket there was no difference between basket position and wear. To further this inspection both ALD coated and uncoated coins were gently scrubbed with a paste made of Sparkleen cleaning powder and water to remove residue on the coins. They were then examined with an optical microscope at 12.5x magnification (Figure 4.8.4). The plastic residue left on the coins from the soft plastic wall of the tumbler was removed from the uncoated coins where the coins with ALD coatings appeared unchanged after cleaning. After cleaning the uncoated coins appeared to have much of the bronze surface of the smooth parts removed.

Figure 4.8.3: ALD (left) and uncoated (right) coins after tumbling the uncoated coins first then the ALD coated coins without cleaning the tumbler between. The uncoated coins pick up a similar amount of plastic. The ALD coins do show that some of the plastic adheres to the coin, but not as much as uncoated.

The ALD coating did appear to afford some wear protection on bronze circulation test coins. After cleaning the plastic debris from the tumbler, uncoated coins did appear to have a larger area of the surface removed when examined under microscope (Figure 4.8.4). Also the coatings did appear to reduce the amount of residue left behind by the tumbler. This may be a viable coating to keep part of the aesthetic look and reduce deterioration brought about by handling over time.

4.9 Summary Conclusion - Circulation

The precision of ellipsometric measurements was not reliable between laminate depositions, but they appeared to be accurate with respect to a particular deposition. This is hopefully an indication that the final depositions with increased pulse times were of greater uniformity with a final standard deviation of 1.87 Å. ALD coated positional coins indicate similar results. Since the purge time was not changed from the original setting, precursor trapped in interstitial space between coins would result in CVD growth. Further optimization of number of pulses or pulse length or would be required. The preceding sulfur and tumbler tests show that position did not appear to affect the coatings as each positional coin provided identical results. Sulfur tests indicate protection from chemical attack by the ALD coatings. The exception is the black lines produced after placement in the sulfur chamber, the cause of which is unknown, but likely from contact with the holder. The tumbler tests did indicate an improvement in wear protection after ALD coatings through observation by optical microscope. Although greatest uniformity was not achieved until the last coatings, the ALD laminate coatings produced similar results that were markedly different from uncoated coins. Furthermore the ALD coating appeared to lessen the amount of plastic debris adhered to the coin after the tumbler. This may be a beneficial side-effect of these coatings since they could also be marketed for this reason. The apparent wear protection would need to be further investigated since this study only implemented one method to arrive at this conclusion.

4.10 Conclusions and Future Directions

For protective applications such as those required by the Mint, one should grow alumina films with TMA at temperatures of 200°C or higher for the added benefit of greater density. Titania layers should be grown at temperatures that show high anatase, 250°C or higher with TTIP, to benefit from the hardness of its crystallinity. Use of a hydrogen scrub appears beneficial if not obligatory to produce a clean surface and allow for an increase in deposition temperature. The cost of multilayers on circulation coins must take into consideration the increase in wear resistance and the possible decrease adhesion of particulates. Literature review reveals multilayers should be used for the synergistic benefit of both layering materials, with alumina as the primary layer for adhesion. Thickness should be kept to a minimum with each layer one the order of 10-30nm. It is also very important to first find the optimal deposition of each layer individually.

Appendices

Appendix A: NMR Spectra of Thermolysis Compounds.

Figure 4.10.2: Select NMR spectra taken of Agttbip that had been A) exposed to light over a period of 22 days of that had been A) protected from light for 25 days. Monitored peaks are triplets at 2.5 and 1.6 ppm.

Figure 4.10.3: Select NMR spectra taken of Auttbip that had been A) exposed to light over a period of 15 days of that had been A) exposed to light for 26 days. Monitored peaks are triplets at 2.1 and 1.5 ppm.

Appendix B: Kinetic Decomposition for the Complete Dataset of Autbip

	Auttbip protected from Light		
Peak(ppm)	Triplet 2.55 ppm		
Order(R^2)	Zero (0.3966)	first (0.5418)	second (0.5520)
rate, k	0.0006 mM/s	0.0015/s	0.0042/mMs
$t_{1/2}$, theoretical	833 h	462 h	238 h
Experimental midpoint	24 h	24 h	24 h

	Auttbip protected from Light		
Peak(ppm)	Singlet 1.33 ppm		
Order(R^2)	Zero (0.3782)	first (0.5180)	second (0.5985)
rate, k	0.0005 mM/s	0.0014/s	0.0040/mMs
$t_{1/2}$, theoretical	1000 h	495 h	250 h
Experimental midpoint	24 h	24 h	24 h

Table 4.10.1: Order determination by linear fit using all data points of Auttbip when protected from light.

Appendix C: Deposition Lists

Trial	Alumina	Titania	Pulse style	Other Parameters
1	150	-	triple	
2	150	-	quadruple	
3	150	106	triple	
4	150	106	triple	
6	166	149	triple	Produced orange coins initially believed to be from thickness.
7	158	127	triple	Less coating for thickness investigation.
8	150	106	triple	Doubled pulse length of metal precursors.
9	300	200	triple	Similar pulse parameters as 8.
10	150	106	triple	Doubled pulse times again, water pulse increased to match preceeding metal precursor.

Table 4.10.2: List of depositions on baskets of bronze circulation tokens.

Ag trial	Alumina Cycles	Titania Cycles	Deposition Temperature	Other Parameters
9	150		250	Die cleaned with isopropyl alcohol
10	150		250	20 minute hydrogen scrub at 150°C
11	150		250	Ebner furnace 250°C for 30 minutes, program 2
14	150		250	1 hour hydrogen scrub at 150°C
17	120		150	
18	150		250	1 hour hydrogen scrub at 150°C
19	120		250	
21	150		150	
22	150		150	
25	200		150	
29	150		250	Bake out
30	150	106	220	
33	200		220	
34	200		220	
35	200	500	220	
37	200	150	220	
38	200		220	
39	200		220	
40	500		220	
41	200	150	220	
44	200		220	hydrogen furnace
200H1	200		220	1 hour hydrogen scrub at 150°C
300H1	300		220	1 hour hydrogen scrub at 150°C
200H2	200		220	2 hour hydrogen scrub at 150°C
300H2	300		220	2 hour hydrogen scrub at 150°C

Table 4.10.3: List of depositions on silver numismatic coins.

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