Mechanics of Compliant Nanoporous Gold

By

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Abstract

Compliant nanoporous gold is investigated with regards to its elastic modulus and deformation mechanisms. Samples are fabricated by dealloying AgAu alloys at elevated temperature and reduced dealloying potential compared with conventional methods in the literature. This procedure minimizes cracking and shrinkage that is typical from other dealloying methods. Furthermore, samples are found to be more compliant while immersed in water. Samples were tested in cyclic compression using a piezoelectric compression rig. Testing showed that the wet samples become stiffer upon drying and the effect is reversible with short drying times. This is attributed to microstructural effects as the ligament network becomes more connected as a result of drying, effectively shifting the dominant deformation mode from three-point bending to cantilever bending. At longer dry times, the effect is irreversible due to contact weld formation. Preliminary results on sputter deposited AgAuPt alloys show altered dealloying kinetics and crack formation.
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1 Introduction:

1.1 History of nanoporous gold

The removal of a less noble metal from an alloy has been practiced for many centuries with the earliest example being a ceremonial dagger recovered from the Royal Tombs of Ur in Mesopotamia dating to the 3rd millennium BC [1]. The process commonly involved purifying gold or silver alloys and has been referred to since as gold colouration, depletion gilding, selective dissolution and dealloying.

Ancient Latin, Greek, Hebrew and Syriac texts refer to a material known as Corinthian Bronze which was prized above silver and nearly above gold [1]. The famed Gate of Nicanor from the Temple of Jerusalem is thought to be made of Corinthian Bronze. Figure 1-1 shows a 2nd century Syrian depiction of the gate which was an object of fascination for ancient Jewish authors. Corinthian Bronze was an alloy containing varying amounts of gold, silver and copper. It would take on a colour characteristic of its predominant alloying element: white for silver rich, yellow for gold rich and bronze for copper rich. It was the gold rich alloys which were of primary interest because they could be depletion gilded to produce a gold surface that was more durable than plating techniques. This durability was due to depletion gilding producing a graded concentration of gold in the surface layer rather than the abrupt interface of a plating technique.
Figure 1-1. Depiction of the Gate of Nicanor found in a 2\textsuperscript{nd} century Syrian synagogue [1]

Depletion gilding has also been attributed to the natives of pre-Columbian Central America, who developed methods for enriching the gold content in the surface of copper-gold alloys. One method was to form copper oxide by heating in air and then remove the oxide by chemical dissolution. The other method involved a slow removal of copper in a corrosive bath [2]. Both of these procedures left a “spongy” gold layer that was densified by burnishing.

The spongy gold layer was black in appearance and upon further exposure to a pickling solution turned from black to white and eventually to a light brown. Burnishing gave it the characteristic shiny yellow colour of pure gold. The initial black layer described was in all likelihood a layer of nanoporous gold.
Nanoporous gold (np-Au) is a random, continuous network of nanoscale ligaments which is formed by the electrochemical removal of silver from silver gold alloys. The porosity or void space in the material is also continuous. The ligament and pore structure is shown below in Figure 1-2. Nanoporous gold with pores and ligaments as small as 5 nm has an extremely high specific surface area of up to 20 m²/g. This makes it very similar to naturally occurring zeolites which have porosity in the 1-2 nm range and a specific surface area of up to 100 m²/g [3]. This makes it an attractive material for applications such as sensing, actuating and catalyzing. It is produced by dealloying, the electrochemical removal of a less noble metal in an alloy system. Typically a gold-silver starting alloy in varying compositions is used, where the gold-silver ratio is determined on the lower range by the continuum percolation limit for this system (~16 at% Au, below which the porous structure falls apart) and the upper range is determined by the parting limit for this system (~45 at% Au, above which Ag atoms cannot percolate to form the porous structure) [4,5].
1.2 Formation of nanoporous structure

Dealloying can be conducted under either controlled potentiostatic conditions or at the free corrosion potential. Electrolytes used with silver gold alloys in literature \([6,7,8,9]\) are generally nitric acid and perchloric acid in various concentrations. There are two processes at work during dealloying: selective dissolution of the less noble metal and surface diffusion of the more noble metal. The initial silver-gold alloys exist as solid solutions. The dissolution of silver atoms and surface diffusion of gold atoms work in tandem to create the coral-like nanoporous structure. Once the initial structure has formed, it coarsens due to the Gibbs-Thomson effect, which relates the surface curvature to a change in free energy \([10,11,12]\). The equation for the Gibbs-Thomson effect is shown below. As the radius of curvature
decreases, the change in free energy increases which provides the driving force for particle growth.

$$\Delta G = \frac{2\gamma V_m}{r}$$  \hspace{1cm} (Equation 1-1)

Where:
- $\Delta G$ = change in free energy (J/mol)
- $\gamma$ = surface energy (J/cm$^2$)
- $V_m$ = molar volume (cm$^3$)
- $r$ = particle radius (cm)

### 1.3 Applications

Most research regarding applications of nanoporous gold aim to utilize the high surface area to volume ratio of the material in order to improve performance of devices such as sensors, actuators and catalysts. For example, Kim et al have demonstrated the potential of nanoporous gold as a sensor for metal ion detection [13]. Weissmuller et al have shown that nanoporous gold can achieve charge induced reversible strains of the same magnitude as piezoceramics [14]. Zeis et al have found that nanoporous gold performs favourably as a catalyst in the oxygen reduction reaction due to the increased density of step edges [15]. One of the advantages that nanoporous gold has is that the ligament size and porosity can be tuned through the dealloying conditions and starting alloy composition. This means that the electrical conductivity, optical absorption, and magnetic interactions can be tuned for different applications.
1.4 Size dependence of mechanical properties

More recently, several groups [6,7,8,9] have investigated the mechanical properties of nanoporous gold. As will be discussed in the following section, the mechanical properties of nanoporous gold show a dependence on the ligament size as this decreases towards the nanometer size. The behaviour of the material approaches the limits of classical continuum descriptions. Individual ligaments can be thought of as nanowires, however, the mechanics of the overall structure are complicated by the random nature of the ligament network. The properties of the bulk nanoporous material are governed by this nanostructure.

1.5 Brittle and compliant nanoporous gold

Generally, nanoporous gold is known to be macroscopically brittle even though the individual ligaments are ductile. In this work, compliant nanoporous gold is investigated. This is based on a result first reported by Senior and Newman [4]. It was found that by tailoring the dealloying conditions, a compliant nanoporous gold product would be made instead of the brittle material reported by other groups [6,16]. In this thesis, the compliant nanoporous gold of Senior and Newman has been replicated and is investigated. Figure 1-3 below shows a nanoporous gold sample bending under its own weight in water.
1.6 Dealloying of ternary precursor alloys

Ternary starting alloys consisting of silver, gold and platinum are investigated in this thesis. It is expected that small amounts of platinum will limit the surface diffusion of gold atoms and subsequent coarsening in the material since platinum has a much lower surface diffusion rate compared with gold [17]. This will result in a nanoporous gold that has a finer microstructure and greater stability against coarsening. Work involving platinum and nanoporous gold has been reported in the literature [17,18] and will be discussed in Chapter 2.
1.7 Objectives

The objectives of this thesis are as follows:

1) To develop a model for understanding the compliant behavior of nanoporous gold that is obtained when the starting alloy composition and dealloying conditions are controlled. Specifically, this thesis aims to determine how the microstructure of nanoporous gold contributes to the compliant behaviour and how the testing environment affects this.

2) In addition, nanoporous gold with small amounts of platinum is investigated to determine the how the addition of varying amounts of platinum affects the dealloying process and nanoporous structure in terms of ligament size and morphology.
2 Literature Review:

Much has been added to the literature regarding nanoporous gold in recent years. The material initially drew interest for its expected potential as an ideal material in sensors, catalysts or actuators. However, it was not until more recently that interest has turned to the unique mechanical behaviour exhibited by nanoporous gold which is the focus of this thesis. The following review of literature will reflect this focus. First, introductory material regarding dealloying will be presented. Next, material regarding the mechanical behaviour of nanoporous gold and the modelling of this behaviour will be discussed. Following that, material regarding deformation in nanoporous gold will be presented. Finally, work regarding thin film deposition as it relates to nanoporous gold will be discussed.

2.1 Dealloying of binary alloys

As was discussed briefly in Chapter 1, nanoporous gold is formed from the dealloying of silver-gold alloys. Dealloying requires both the dissolution of silver and the surface diffusion of gold. The process was first reported by Forty, who proposed the model for dealloying [2]. Forty dealloyed 50:50 AgAu alloys at the free corrosion potential using 50% aqueous nitric acid and evaluated the resultant structure using energy dispersive x-ray analysis. Based on the observation of gold rich islands and silver rich channels, he proposed that dealloying is a layer by layer process whereby the surface diffusion of gold reveals more silver atoms for dissolution [2]. This process is shown schematically in Figure 2-1.
Erlebacher et al later created Monte Carlo simulations that took into account the kinetics of dissolution, surface diffusion and mass transport through both the bulk material and electrolyte. They assumed that the process which determined the final morphology was confined to the interface between the alloy and electrolyte since mass transport through the dissolving alloy phase is too slow to be significant. The simulation was successful in reproducing the characteristic experimental trends in terms of the morphology and kinetics [19].

Shown below in Figure 2-2 is the simulated evolution of an artificial pit in an Au$_{10}$Ag$_{90}$ alloy. The surface is passivated with the exception of the circular pit region in the center. Cross sections of the yellow line across the pit are shown below each of the images. Initially, there is a flat, close packed (111) surface of silver gold alloy in which a single Ag atom is dissolved. The silver atoms surrounding the vacancy created are less coordinated and more susceptible to dissolution than the other silver atoms on the surface. Within a very short time, the entire terrace of silver atoms on the surface becomes stripped leaving relatively few gold atoms which are essentially adatoms since they have no lateral coordination, only the atoms from the layer below. These gold atoms diffuse across the surface and agglomerate to
form locally passivated regions. The formation of passive regions exposes further alloy surfaces which are susceptible to dissolution and the layer by layer stripping and diffusion continues. Early on in the process, there are islands which are gold rich on the surface but have the starting alloy composition below. As dealloying progresses, these islands become undercut from below, further increasing the surface area.

The other process central to the formation of nanoporosity by dealloying is coarsening, or the coalescence of gold atoms. Erlebacher et al considered the gold adatoms and the electrolyte interfacial monolayer to be a solution which meant that the solubility of the gold could be determined. It was found that the concentration of gold adatoms was significantly higher than the solubility of gold in electrolyte, which provides the driving force for gold adatoms to condense onto nearby clusters of gold atoms [19].
Figure 2-2. Simulated evolution of dealloying in Au$_{10}$Ag$_{90}$ at (a) 0 s, (b) 1 s, (c) 10 s and (d) 100 s. Cross sections of yellow line are shown below each image, from Erlebacher et al [19]

Pickering was the first to generalize the electrochemical behaviour of binary alloys [20]. Figure 2-3 shows the electrochemical behaviour of 4 different binary alloys composed of metal A and metal B. Metal A is the more active element and metal B is the nobler element. The numbers represent different alloy compositions, with the noble metal content increasing from alloy 1 to alloy 4. The electrochemical behaviour of pure metal A is shown in curve a. The plateau in region b is a passivation-like behaviour in the alloy with a limited
current. The current is due to the dissolution of metal A and is limited as the surface becomes enriched with metal B. This region is larger for greater amounts of B in the alloy. The area labeled $E_C$ is designated as the critical potential. Here there is a significant increase in the anodic current with increased applied potential, shown in region c. Note that the critical potential increases with increasing noble metal content since the dissolution must occur through the larger enriched layer. In region d, there is oxidation of the more noble metal B.

Figure 2-3. *Schematic polarization curves for binary alloys, adapted from Pickering [20]*

Applying a potential below the critical potential results in noble metal surface enrichment only. The porous dealloyed structure is produced when the applied potential is greater than $E_C$. This was termed Type I dealloying by Pickering. Type II dealloying occurs when the applied potential is so large that both elements are oxidized. Generally, the critical potential is defined by reaching a threshold current density greater than $1 \text{ mA/cm}^2$ [4]. As
was briefly introduced in Chapter 1, the upper limit for gold concentration in dealloying silver gold alloys is determined by the parting limit, which is defined by ASTM as the minimum concentration of noble metal above which parting (or dealloying) does not occur [21]. In other words, the parting limit is the concentration of noble metal at which the transition from Type I dealloying and Type II dealloying occurs for a given acid solution [21]. The lower limit for gold concentration is determined by the continuum percolation threshold of ~16% for a 3-dimensional lattice [5]. At concentrations of gold below this threshold, the clusters of gold atoms are not connected and the structure falls apart during dealloying. Zallen provides a more in-depth discussion on continuum percolation in Ref [5].

Maier et al have investigated stress corrosion cracking in AgAu alloys in 1 M perchloric acid [22]. The results of interest are the polarization curves obtained for various AgAu alloy compositions which demonstrate the behaviour idealized by Pickering. Figure 2-4 shows polarization curves for low gold content alloys while Figure 2-5 shows high gold content alloys. It is clear from this work that there is a transition between curve 1 and curve 2 (dealloying of silver) when the gold content is increased from 2.2% Au to 5% Au. In the sample with 40% Au, it is seen that the current decreases near 1.4 V versus NHE (normal hydrogen electrode) before increasing at higher potentials. This is attributed to oxidation of gold followed by oxygen evolution.
Figure 2-4. Polarization curves for AgAu alloys with low Au content, from Maier [22]

Figure 2-5. Polarization curves for AgAu alloys with high Au content, from Maier [22]
Sieradzki et al have conducted a study further investigating the dealloying critical potential as a kinetic phenomenon which is dependent on alloy composition, electrolyte composition as well as the potential sweep rate [23]. It was found that the critical potential was affected by the concentration of silver ions in the electrolyte. As seen in Figure 2-6, increasing the concentration of silver ions resulted in a higher critical potential, which in turn increases the dealloying rate.

![Graph showing electrochemical behaviour of Au28Ag72 in x M AgClO4 and 1 M HClO4, from Sieradzki et al.](image)

**Figure 2-6.**  *Electrochemical behaviour of Au28Ag72 in x M AgClO4 and 1 M HClO4, from Sieradzki et al [23]*

### 2.1.1 Structure of nanoporous gold

The final dealloyed structure, namely the ligament and pore size, can be controlled by altering the dealloying conditions. There are four main variables which can be changed:
applied potential, electrolyte temperature, electrolyte composition and initial alloy composition. Each of these factors affects the silver dissolution rate and gold diffusion rate, which are also dependent on each other.

Increasing the applied potential increases the silver dissolution and gold surface diffusion, but at sufficiently high potentials there is monolayer gold hydroxide formation. The formation of gold hydroxide inhibits surface diffusion, resulting in a finer microstructure as reported by Senior and Newman [4]. Sieradzki et al and Erlebacher have reported a similar link between increased potential and decreased length scale [23,24].

Increasing the electrolyte temperature increases both the dissolution rate and surface diffusion increasing the pore size and spacing as first reported by Pickering and Kim [25]. This was used by Senior and Newman as a means to compensate for dealloying at a lower potential so as to avoid the formation of a gold hydroxide monolayer [4]. Qian and Chen have conducted work investigating dealloying at low temperatures using the reduced dissolution and diffusion as a means to produce a finer porosity [26]. By dealloying in 70% nitric acid at -20°C, it was possible to obtain nanoporous gold with a ligament size of ~5 nm as seen in Figure 2-7.
The anion species in the electrolyte as well as the concentration can affect the dealloying process. Dursun et al have shown that the presence of halides in electrolyte can have a significant effect on the critical potential and resultant pore size [27]. The authors found that the addition of halides increased the surface diffusion which resulted in a larger pore size. It was also found that the critical potential decreased with the addition of halides with stronger halides having a more drastic effect as seen in Figure 2-8. Increasing the concentration of electrolyte has the same effect of increasing diffusion and resulting in a coarser structure. Nanoporous gold dealloyed in nitric acid tends to have larger pores, premature fracture as well as increased ligament ripening after dealloying. Alloy composition does not directly affect the gold diffusion but increased gold content inhibits the dissolution of silver due to enrichment [4,28].
Figure 2-8. Effect of halides in electrolyte on critical potential, from Dursun et al [27]

An interesting feature of nanoporous gold formed by dealloying is that the crystal lattice of the starting alloy is still present in the dealloyed material. This observation was first noted by Forty and Durkin who reported that the pore and ligament size is much smaller than the grain size [29]. The observation has since been confirmed by several other techniques including electron diffraction, focused ion beam microscopy, high-resolution TEM, and electron backscatter diffraction [30,16,31].
2.1.2 Shrinkage and defects due to dealloying

It is well documented in literature that as-dealloyed nanoporous gold typically exhibits severe cracking caused by the dealloying process \([4,6,16]\). Parida et al investigated the large volume shrinkage of up to 30% in silver gold alloys during dealloying and found that accelerated corrosion observed at higher potentials resulted in the largest change in volume \([16]\). Samples dealloyed under these conditions were found to have many lattice defects, resulting in extensive macroscopic cracking. In comparison, the starting alloys and samples dealloyed at a slower rate with a lower potential are found to have significantly fewer defects. This suggests that the defects and subsequent macroscopic cracking from aggressive dealloying procedures are generated from the dealloying \([32]\). Only two approaches in literature are known to result in crack-free nanoporous gold. The first was conducted by Senior and Newman using elevated temperature and reduced potential \([4]\). The second was conducted by Sun and Balk using a multistep, galvanostatic and free corrosion approach \([33]\).

The work of Newman and Senior investigated potentiostatic dealloying at various potentials and temperatures to determine the effect on the dealloying process and resultant structure \([4]\). It was found that dealloying for 30 s at 1.1 V versus saturated calomel electrode (SCE) and 20°C resulted in extensive transgranular fracture as seen in Figure 2-8. In contrast, dealloying for 120 s at 1 V (versus SCE) and 20°C resulted only in intergranular fracture as seen in Figure 2-9. Finally, dealloying for 120 s at 0.92 V (versus SCE) and 60°C resulted in a nanoporous sample with no visible cracking as seen in Figure 2-10.
Figure 2-9. \( \text{Au}_{23}\text{Ag}_{77} \) dealloyed at 1.1 V and 20°C showing transgranular cracking (marker: 20 µm), from Senior and Newman [4]

Figure 2-10. \( \text{Au}_{23}\text{Ag}_{77} \) dealloyed at 1 V and 20°C showing intergranular cracking (marker: 20 µm), from Senior and Newman [4]
Figure 2-11. $\text{Au}_{23}\text{Ag}_{77}$ dealloyed at 0.92 V and 60°C showing no macroscopic cracking, from Senior and Newman [4]

While most of the work in the literature investigates dealloying at the free corrosion potential or under potentiostatic control, Sun and Balk found that by initially dealloying under galvanostatic conditions (current of ~200 mA with voltage of ~500 mV), a more dilute nitric acid (for up to 70 hours) before switching to free corrosion in 70% stock nitric acid, crack-free nanoporous gold could be formed [33]. In addition, there was no observed volume change which is a direct contrast with up to 30% shrinkage observed by Parida et al when a more aggressive potentiostatic dealloying procedure was used (1 M perchloric acid, potential not specified) [16]. The authors point to the work of Rosler who used a similar galvanostatic approach to etch two phase Ni-base superalloys and found no volume contraction [34]. It is thought that the galvanostatic dealloying approach results in a constant current and thus constant Ag dissolution. Also, since Au is not expected to oxidize at the potentials used, the surface diffusion of gold acts to relax tensile stresses which evolve during dealloying.
2.2 Scaling equations

Nanoporous gold is generally modelled as an open celled foam. Gibson and Ashby have derived scaling equations to describe these properties with respect to relative density, which is the ratio of the foam density, $\rho^*$, to the density of gold, $\rho_S$. Equation 2-1 and Equation 2-2 show the Gibson and Ashby relationships for strength and elastic modulus respectively. In the strength equation, $\sigma_S$ refers to the strength of the solid material and $\sigma^*$ refers to the strength of the foam. Similarly, in the elastic modulus equation, $E_S$ refers to the elastic modulus of the solid material and $E^*$ refers to the elastic modulus of the foam. $C_1$ and $C_2$ are constants. These equations are developed from a generalized unit cell shown in Figure 2-11 as well as data obtained from mechanical tests of foams with macroscopic porosity.

$$\frac{\sigma^*}{\sigma_S} = C_1 \left( \frac{\rho^*}{\rho_S} \right)^{1.5} \quad \text{(Equation 2-1)}$$

$$\frac{E^*}{E_S} = C_2 \left( \frac{\rho^*}{\rho_S} \right)^2 \quad \text{(Equation 2-2)}$$

Where: 
- $\sigma^*$ = strength of foam (MPa)
- $\sigma_S$ = strength of solid material (MPa)
- $\rho^*$ = density of foam (g/cm$^3$)
- $\rho_S$ = density of solid material (g/cm$^3$)
- $E^*$ = elastic modulus of foam (GPa)
- $E_S$ = elastic modulus of solid material (GPa)
This model presented by Gibson and Ashby has been found to predict the behaviour of foams very well at the macroscopic scale. However, it has not been as useful in predicting the behaviour of nanoporous gold. At the nanoscale, the ligament size can have a more pronounced effect on the strength of the material. Hodge et al have developed a modified scaling equation for the strength of nanoporous gold which takes into account the effect of ligament size [35]. This is shown below in Equation 2-3. Here, \( k \) is material dependent coefficient similar to that used in the Hall-Petch equation and \( L \) is the ligament size in nm. \( C_S \) is a constant.

\[
\sigma^* = C_S \left[ \sigma_S + kL^{-0.5} \right] \cdot \left( \frac{\rho^*}{\rho_S} \right)^{1.5} \quad (Equation \ 2-3)
\]

Where:
- \( \sigma^* \) = strength of foam (MPa)
- \( \sigma_S \) = strength of solid material (MPa)
- \( \rho^* \) = density of foam (g/cm\(^3\))
- \( \rho_S \) = density of solid material (g/cm\(^3\))
- \( k \) = material dependent coefficient
- \( L \) = ligament size (nm)

**Figure 2-12.** Generalized open cell foam unit cell
This equation assumes a Hall-Petch type relation (increasing strength with decreasing grain size) between decreasing ligament size and increasing strength. The causes for the increased strength cannot simply be accounted for by the causes of strengthening in nanocrystalline materials. The increase in strength surpasses that expected from having nanocrystalline ligaments. The following section and further discussion in this thesis will address the factors which contribute to strength in nanoporous gold.

2.3 **Strength of nanoporous gold**

It has been observed by several groups that the strength of nanoporous gold approaches the theoretical shear strength of gold when the ligament size decreases below 10 nm. Much of this is attributed to the absence of dislocations in individual ligaments at small scale lengths, making the ligaments behave similarly to dislocation free nanowires. Several different approaches have been taken to measure the strength of nanoporous gold and these methods will be discussed in the following section.

The properties of nanoporous gold depend strongly on the relative density, defined as the density of the nanoporous material divided by the density of the solid material. Generally, relative density is predicted by the starting content of gold in the starting alloy. The dealloying conditions also play a large role in the final structure as discussed previously. Since it is difficult to draw direct quantitative comparisons between results presented in the literature, these findings are meant to provide a qualitative comparison.
One of the earlier studies on the mechanical strength of nanoporous gold was completed by Biener et al. [6]. In this study, nanoporous gold with 42% relative density was tested in compression using nanoindentation. The dealloying in Ref [6] was conducted potentiostatically at 1 V (vs. saturated calomel electrode) in 75% nitric acid at room temperature. Dealloying was allowed to proceed for 2-3 days until there was no weight loss in the material. This resulted in a nanoporous gold with ligaments on the order of 100 nm. The nanoindentation showed that nanoporous gold had yield strength of 145 MPa, which translates to a ligament yield strength of approximately 1.8 GPa.

Volkert et al conducted mechanical testing on columns of nanoporous gold which were fabricated by focused ion beam (FIB) [9,36]. Dealloying was carried out in 1 M perchloric acid under potential control and at ambient temperature. The applied potential was not specified, but the procedure was referenced to a study conducted by Kramer, who did not report a value for the potential used either. Kramer investigated surface stress induced bending of nanoporous gold cantilevers [37]. The columns were then compressed using a flat punch on a nanoindententer. In this work, the nanoporous gold had a relative density of 33% and ligaments of about 15 nm. The diameter of the columns increased following compression and was used to determine that the columns had a Poisson’s ratio of 0.2. The columns showed an abrupt change from elastic to plastic behaviour at about 100 MPa, which corresponds to a ligament yield strength of 1.5 GPa.

A study by Lee et al investigated the mechanical properties of nanoporous gold that was fabricated into dog-bone shaped specimens using electron beam lithography [7]. The dealloying here was conducted in 70% concentrated nitric acid (~16 M) for 45 minutes at ambient temperature. The relative density was found to be 35.2% and the average ligament
size was measured as 32 nm. The specimens were deflected and yielded using a nanoindenter with a Berkovich tip. The ligament yield strength was calculated from the results and reported as 1.45 GPa.

In summary, it can be said that the published results regarding the strength of nanoporous gold are fairly consistent. Different measurement techniques have yielded similar findings, namely, that the ligament strength of nanoporous gold approaches the theoretical shear strength of gold when the ligament size is decreased into the nanoscale range. Figure 2-12 shows a summary of some of the results that have been reported regarding the strength of nanoporous gold.

Figure 2-13. Yield strength of nanoporous gold, adapted from Biener et al. [6]
2.4 Elastic modulus of nanoporous gold

There has been less attention given to the elastic modulus of nanoporous gold in comparison to the strength of nanoporous gold. Generally, elastic modulus values are reported as an afterthought in studies focusing on the strength. When interpreting these results, it is important to remember that elastic modulus of nanoporous gold is dependent on the relative density. In this section, results from the previously discussed studies will be presented along with a study dedicated to the scaling of elastic behaviour with ligament size in nanoporous gold.

The nanoindentation experiments of Biener et al discussed in Section 2.3 measured the Young’s modulus of nanoporous gold to be $11.1 \pm 0.9 \text{ GPa}$ [6]. This value was obtained by using the standard nanoindentation deconvolution methods developed by Oliver and Pharr [6,38]. The authors noticed that the surface of the nanoporous gold had become sintered and appeared as a solid layer about 10-20 nm thick. However, this layer did not seem to influence the results as the elastic modulus measurements did not change with depth. Recall that the ligament diameter was reported as 100 nm and the relative density was 42%. The material was noted to deform by densification of ligaments as the damage to the material was localized in the area where the nanoindenter tip made contact as shown in Figure 2-13. Another important observation here is that there are no indications of sink-in or pile-up, which are problems that are generally associated with nanoindentation [38].
The compression of micro-columns conducted by Volkert et al yielded similar results regarding elastic modulus. However, it was also observed that the elastic modulus was a function of strain. The elastic modulus was determined from unloading curves to be 7 GPa at 2% strain and 12 GPa at 36% strain. This was likely caused by ligament contact during compression since the relative density was quite high (36%). In addition, it was observed that the column diameter increased during loading which indicates a non-zero Poisson’s ratio. This is typical for open cell foams with larger relative densities [39]. Therefore, true stress and true strain were used in the subsequent measurements and calculations. Another important observation was that a region of “early plasticity” was observed during the initial loading of samples. This was attributed to sample surface roughness or non-planarity between the columns and the indenter punch. Figure 2-14 shows one of the focus ion beam (FIB) fabricated columns.
The elastic modulus measured by Lee et al from the deflection of the freestanding, dog-bone shaped specimens was 8.8 GPa. However, nanoindentation of nanoporous gold adhered to a silicon substrate resulted in an elastic modulus of $13.2 \pm 3.4$ GPa, higher than what is predicted by applying the Gibson and Ashby scaling equation. Using a relative density of 35.2%, the predicted modulus was $9.91 - 10.31$ GPa. The increased modulus was thought to be an effect of the underlying substrate. The elastic modulus for the dog-bone shaped specimens was determined by comparing the force-displacement data with an analytical model of a center-loaded double cantilever beam [7]. The elastic modulus of samples directly adhered to the substrate were determined from continuous stiffness measurements as well as standard nanoindentation deconvolution analysis methods [7,38]. Figure 2-15 below shows SEM images of the specimens as well as the nanoporous structure.
A study conducted by Mathur and Erlebacher used a buckling based technique to determine the elastic modulus of nanoporous gold. The nanoporous gold is adhered to a thick, compliant polydimethylsiloxane (PDMS) and then loaded in a custom built compression rig. When a load is applied, the substrate buckles due to imbalance between the energy to bend the sample and deform the substrate. If a smooth sinusoidal waveform is assumed for the buckles, then the elastic modulus can be related to the buckling wavelength, film thickness, and Poisson’s ratios of the two materials. Samples were made with ligament sizes from 3-40 nm. The nanoporous gold with a ligament diameter below 10 nm was produced by dealloying Au35Ag65 in 70% nitric acid at an applied potential of 1 V in a two electrode configuration with a graphite counter electrode. To create nanoporous gold with ligaments greater than 10 nm in diameter, the samples were simply coarsened at room
temperature in acid. The measured elastic moduli for the samples are shown below in Figure 2-16.

![Figure 2-17](image)

**Figure 2-17.** Elastic modulus versus ligament diameter, adapted from Mathur and Erlebacher [8]

Here we see that the elastic modulus increased with decreasing ligament diameter. This was a surprising finding and it was initially thought that there was a thin stiff oxide layer had formed on the surface. A brief cathodic bias of 0.5 V was applied for 5 s in nitric acid to remove any oxide layer, but this did not prove to change the mechanical response. Another possible explanation for the increased modulus was an increase in density due to shrinkage as reported by Parida et al [16]. However, the magnitude of change from this explanation could not account for the change in modulus that was recorded. It was also
proposed that surface stress effects from a thin film may be contributing to the mechanical behaviour, but the extent and nature of the effect is not clear. Finally, the authors proposed that the most probable cause of the increased stiffness was microstructural effects from the fine nanoporous structure. Thinking of the material as a truss with identical beams, nanoporous gold with a large number of fine beams will have a greater moment of inertia than nanoporous gold with a smaller number of thicker beams [8]. For samples with ligament size greater than 12 nm, the elastic modulus was found to lie in the 6-12 GPa range. Samples with ligament size less than 12 nm saw the elastic modulus rise almost 4 times to a maximum of 40 GPa for the samples with 3 nm ligament size.

One of the most relevant studies to this thesis was conducted by Senior and Newman investigating dealloying conditions that result in highly compliant nanoporous gold. A starting alloy of Au$_{23}$Ag$_{77}$ was selected and dealloyed under potentiostatic conditions at a temperature of 60°C. The electrolyte used was a 0.77 M perchloric acid. Further details regarding the dealloying procedure will be discussed in Chapter 3. Senior produced nanoporous gold with 3 different starting alloys: Au$_{20}$Ag$_{80}$, Au$_{23}$Ag$_{77}$, and Au$_{28}$Ag$_{72}$. Critical potentials were determined for each of these alloys and the dealloying procedure tailored along with the dealloying temperature to determine which conditions would minimize the extensive cracking that is reported by other groups using a free corrosion approach [4,6,16]. It was found that the effects of internal stress induced by the dealloying procedure are reduced by lowering the applied potential and increasing the electrolyte temperature. Senior and Newman also reported that at higher applied potentials there was the onset of gold hydroxide formation. In fact, for the Au$_{28}$Ag$_{72}$ sample, it was found that the potential
required to dealloy the material was higher than the potential for the onset of monolayer gold hydroxide formation [4].

As introduced previously in Section 2.1, gold hydroxide formation has the effect of reducing the surface diffusion of gold which hinders the initial coarsening of ligaments. This in turn prevents interior silver atoms from being exposed and dissolved. As a result, the ligament structure is finer and the sample behaves in a brittle manner macroscopically. In addition, the surface diffusion relieves stresses generated by dealloying, meaning that hydroxide formation will prevent this stress relief, resulting in more cracking. The highly compliant sample made from Au23Ag77 that Senior and Newman produced had a lower residual silver content than the other alloys. The mechanical integrity of these samples was said to be associated with ligaments bridging grain boundaries [4]. Figure 2-17 shows the compliant nature of the nanoporous gold that was produced.

Figure 2-18. Compliant nanoporous gold, from Senior and Newman [4]
In summary, it can be said that the elastic modulus of nanoporous gold is generally well predicted by the scaling equations developed by Gibson and Ashby. An exception is the nanoporous gold with very small ligament size used in the work of Mathur and Erlebacher, which showed an increased elastic modulus [8]. Another exception is the compliant nanoporous gold developed by Senior and Newman [4]. However, the modulus of this material was never measured or reported. Table 2-1 shows a summary of the dealloying conditions used by the works which have been discussed in this section.

Table 2-1. Summary of dealloying conditions and resulting ligament sizes

<table>
<thead>
<tr>
<th></th>
<th>Alloy composition</th>
<th>Electrolyte</th>
<th>Dealloying conditions</th>
<th>Ligament size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biener [6]</td>
<td>Au_{42}Ag_{68}</td>
<td>75% nitric acid</td>
<td>Potentiostatic, 1 V (vs. SCE)</td>
<td>100</td>
</tr>
<tr>
<td>Volkert/Kramer [9,37]</td>
<td>Au_{25}Ag_{75}</td>
<td>1 M HClO4</td>
<td>Potentiostatic, unspecified potential</td>
<td>15</td>
</tr>
<tr>
<td>Lee [7]</td>
<td>Au_{37.4}Ag_{62.6}</td>
<td>70% nitric acid</td>
<td>Free corrosion</td>
<td>20-40</td>
</tr>
<tr>
<td>Mathur and Erlebacher [8]</td>
<td>Au_{35}Ag_{65}</td>
<td>70% nitric acid</td>
<td>Potentiostatic, 1 V (vs. graphite counter electrode)</td>
<td>3-12</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>70% nitric acid</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Free corrosion</td>
<td>12-40</td>
</tr>
<tr>
<td>Senior and Newman [4]</td>
<td>Au_{20}Ag_{80},</td>
<td>0.77 M HClO4</td>
<td>Potentiostatic, various potentials, 20°C and 60°C</td>
<td>Not reported, varied</td>
</tr>
<tr>
<td></td>
<td>Au_{23}Ag_{77},</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Au_{28}Ag_{72}</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 2-18 is a summary of the elastic modulus results from the previously mentioned groups plotted against relative density. The black line is the predicted behaviour by the Gibson and Ashby scaling equation. Note that for the work of Mathur and Erlebacher, only the results from nanoporous gold with ligament size greater than 12 nm were included. Also, it should be noted that most of the work in literature has been with higher relative densities. The compliant nanoporous gold produced by Senior and Newman had a relative
density in the 23% range. One of the motivations for this thesis is to determine the elastic modulus of nanoporous gold in this lower relative density region.

![Graph](Image)

Figure 2-19. Elastic modulus versus relative density [6,7,8,9]

2.5 Deformation and fracture in nanoporous gold

One of the earlier studies on nanoporous gold was conducted by Li and Sieradzki, who observed a microstructurally driven ductile-brittle transition in the material [40]. This investigation confirmed an earlier theoretical model by Kahng et al which predicted such a transition for network materials [41]. In the work of Li and Sieradzki, ductile fracture and brittle fracture are defined by the nature of the damage introduced to the sample during fracture. In ductile fracture, there are many separated or distributed microcracks that are
developed during fracture. In brittle fracture, there are few of these microcracks prior to fracture.

A starting alloy with a composition of Au$_{24}$Ag$_{76}$ was dealloyed in 1 M perchloric acid at 1 V (vs. SCE) for 12 hours. Samples were cut into 2 mm x 2 mm x 30 mm beams prior to dealloying. The resulting microstructure following dealloying had a ligament size of about 3 nm. Samples were coarsened by annealing for 10 minutes at temperatures ranging from 100 °C to 800 °C. Samples were deformed by 3 point bending with attention given to the load at fracture, load point displacement at fracture and fracture energy. The results are shown below in Figure 2-19. Here, $P_f$ is the fracture load in kg x 10$^{-3}$, $\delta_f$ is the displacement at failure in $\mu$m and $W$ is the fracture energy in J x 10$^{-7}$. N/A is the number of pores per $\mu$m$^2$ of sample area. It is clear that at higher values of N/A (i.e. more pores, finer ligament size) there is a decrease in displacement at failure and fracture energy.

![Figure 2-20](image.png)

*Figure 2-20. Fracture load, displacement at failure and fracture energy versus pores per 1 $\mu$m$^2$ [40]*
2.6 Deposition techniques and thin films of nanoporous gold

Magnetron sputtering is the deposition method utilized in this work and hence this section will address the technique. An excellent overview of magnetron sputtering is given in Chapter 8 of Ref [42]. A brief summary will be given here as well as work in literature regarding sputtering as it relates to the work conducted in this thesis.

2.6.1 Sputter deposition

Sputtering is the process of atomic erosion by which an atom is removed from a surface by the impact of another particle colliding with the surface. The removed atoms are contained in a charged plasma which can then be directed electrically towards a substrate. This is sputter deposition. Magnetron sputtering involves the generation of a static magnetic field directly below the cathode in order to contain secondary electrons produced by sputtering. This creates a denser plasma, increases the degree of ionization and results in a more efficient sputtering rate, which is the amount of material deposited with respect to power applied [42].

One of the difficulties with depositing thin films is the stress or interfacial strain created by lattice mismatch. This can encourage delamination of the film. To remedy this, generally it is desired to minimize the mismatch through selecting an appropriate substrate, using interlayers or depositing at elevated temperatures. The mechanical integrity of thin film depositions is crucial for nanoporous gold applications since dealloying introduces more stress in the film that can increase problems associated with delamination.
The grain structure of the sputter deposited film is dependent on the argon pressure and film temperature during deposition. Thornton has presented a comprehensive explanation of this relationship in Ref [43]. In Zone 1, at low temperatures and pressures (like those used in this work) the material is organized as narrow columns with domed tops and voided boundaries. In Zone 2, the surface is smoothed and the boundaries are dense. At the highest temperatures of Zone 3, equiaxed grains are formed. Zone T is a transitional zone where the films are much denser than those in Zones 1 and 2 [43]. This morphology is caused by adatoms diffusing from one grain to another as they land on the nucleating grains as well as the immobility of grain boundaries at this temperature [44].

Figure 2-21. Structure zone model for sputter deposited films, from Thornton [43]
2.6.2 Crack-free thin films of nanoporous gold

Sun et al successfully deposited silver gold alloys for dealloying on silicon substrates by using several interlayers. A 10 nm tantalum layer followed by a 10 nm gold layer was deposited onto the substrate to improve the adhesion of the silver gold alloy deposition [45]. Tantalum was known to improve adhesion between gold and silicon while the gold interlayer was known to improve the adhesion and stability of nanoporous gold. Au$_{30}$Ag$_{70}$ alloys were deposited to thicknesses of 45 and 75 nm.

Samples were dealloyed in 70% nitric acid for 10 minutes and showed no signs of cracking [45]. Samples were then subjected to various annealing treatments to investigate the effect on stress within samples. It was found that samples would anneal and collapse at long annealing times. The authors suggest that the thickness of gold available reached a critical value while the ligament thickness increased, resulting in an instability [45].

It was also determined that dealloying always creates a tensile stress in the film regardless of whether the film had compressive or tensile stresses prior to dealloying. Although the tensile stresses were quite high relative to the intrinsic stresses from deposition, they were not enough to cause cracking in the samples. The tensile stress is not well understood but is likely related to volume contraction during dealloying, as was reported by Parida et al [16]. However, it was noted that the sample thickness did not decrease following dealloying [45].
2.6.3 Depositing silver gold alloys with a composition gradient

Lu et al used magnetron sputtering to investigate nanoporous gold produced from a silver gold alloy with a composition gradient of 22-45 at% Au [46]. In this work, alloys were deposited on silicon substrates for measurement of surface stresses by wafer curvature. Alloys were also deposited on polyimide substrates for compositional and microstructural analyses. The silicon substrates were coated in 50 nm of amorphous silicon oxide followed by 50 nm of amorphous silicon nitride. The polyimide samples utilized a 20 nm Au interlayer to improve adhesion of the final nanoporous film. Also, the edges of samples were coated in lacquer to prevent delamination. Samples were deposited to thicknesses of 400 and 1600 nm. Dealloying in this work was conducted in 32.5% nitric acid.

The authors found that dealloying would cause microcracks (200-1200 nm in length) in the area with composition ranging from 22-26 at% Au. In the area with a higher Au content, the porosity and amount of microcracks were found to decrease. However, in these high Au content areas, there were islands of undealloyed material as well. Figure 2-22 illustrates the microcracking and islands of undealloyed material. Also, when no interlayer is used, it was found that samples would break into pieces 3-5 mm in size, but these pieces would have no microcracks in them. Another observation was that the pores showed anisotropy in the out of plane direction as seen in Figure 2-23. This elongated pore structure was typical for samples with Au content below 26 at% [46].
Figure 2-22. Microcracks from 22-26 at% Au region (left) and islands of undealloyed material from higher Au content region (right), from Lu et al [46]

Figure 2-23. Cross-sectional view of dealloyed layer from 26 at% Au region showing anisotropic pore structure, from Lu et al [46]
2.6.4 Evolution of structure in thin films of nanoporous gold

Another study involving sputter deposited thin films of nanoporous gold was conducted by Sun and Balk. Here, glass slides and silicon wafers were used as substrates. The glass slides were deposited with 10 nm of gold to counteract the tendency of films to flake off during dealloying. The silicon substrates were coated with 10 nm of amorphous silicon oxide followed by 50 nm of silicon nitride and finally 10 nm each of tantalum and then gold to further improve adhesion. Dealloying in this work was conducted in 70% nitric acid [47].

It was found that the samples on glass slides commonly delaminated from the substrates more easily than samples on silicon. The only difference between the sample groups was the presence of a tantalum interlayer between the gold interlayer and substrate. This suggests that the quality of the interface between the gold and substrate is important in preventing delamination. The authors claimed that the tantalum interlayer is crucial to the stability of the nanoporous gold films.

In this work by Sun and Balk, it was found that dealloying resulted in a decrease in thickness from 382 nm to 331 nm. This is contrary to what was reported by Sun et al previously using thinner films [45]. The stress in the films was measured using wafer curvature and was found to decrease as a result of dealloying; a surprising finding given that there is considerable volume contraction.

Another interesting observation was that microcracks tended to form along grain boundaries. The authors suggested that this was due to preferential dealloying in these regions. Short dealloying times (10 seconds to 100 minutes) revealed that these grain...
boundary microcracks form very quickly, within the first minute of dealloying. It is believed that these microcracks play an important role in the evolution of stress in the films. Calculations indicate that the stress relaxation can be accounted for by film cracking. Thermal cycling up to 100 °C and 200 °C revealed that the change in film stress was minimal. This is likely because the extensive cracking caused by the dealloying procedure is able to accommodate the expansion and contraction. Figure 2-24 shows the evolution of grain boundary cracking during dealloying.

![Figure 2-24. Grain boundary microcracks after (a) 1 min (b) 10 min and (c) 100 min of dealloying, from Sun and Balk [47]](image)

### 2.7 Dealloying of ternary alloys

The first known publication regarding dealloying from ternary precursors was conducted by Snyder et al. A starting alloy of Au$_{30}$Ag$_{64}$Pt$_{6}$ was dealloyed using 2 procedures. The first procedure involved floating samples in concentrated (70%) nitric acid. The second procedure involved a neutral 0.1 M silver nitrate solution and an applied potential of 0.8 V
(vs. Hg/HgSO₄). Pore size varied with the majority being in the 4 nm range and 50% of the pores being less than 10 nm in diameter [17].

The double layer capacitance of samples was measured following varying lengths of immersion in concentrated nitric and compared with nanoporous gold samples made with a starting alloy of Au₃₅Ag₆₅. It was expected and found that the specific capacitance of the nanoporous gold decreased from 6 F/g to 2 F/g due to coarsening (shown in Figure 2-25). However, the Pt-stabilized nanoporous gold did not see a change in capacitance. In addition, even after annealing for 3 hours at 400 °C, the pore size of the Pt-stabilized nanoporous gold remains less than 10 nm. It is believed that the less mobile platinum atoms are pinning the step edges and inhibiting the surface diffusion of gold [17].

![Figure 2-25. Change in capacitance versus time for AuAg(Pt) and nanoporous gold, from Snyder [17]](image-url)
3 Experimental Methods

The experimental methods in this thesis can be divided into two groups of experiments. The first group of experiments revolves around nanoporous gold formed by the dealloying of bulk alloys. These samples were tested in a custom built compression rig that is described below. The objective here was to develop an understanding of the compliant behaviour that can be observed in nanoporous gold dealloyed under specific conditions. The second group of experiments utilized nanoporous gold dealloyed from magnetron sputtered alloy films. The advantage to using sputtering was that alloy compositions could be carefully controlled. In addition, small amounts of platinum were added to some of the alloys. Preliminary electrochemical experiments were conducted on sputter deposited samples and SEM images were obtained following dealloying. The objective of these experiments was to determine the effect of platinum on the dealloying process and nanoporous gold structure.

3.1 Bulk alloy experiments

3.1.1 Alloy composition

Two alloy systems were investigated in the bulk alloy experiments. The first was Ag$_{77}$Au$_{23}$, which will be referred to as “Au23”. This alloy was selected to reproduce the compliant nanoporous gold first reported by Senior and Newman [4]. The second alloy system was Ag$_{72}$Au$_{28}$, which will be referred to as “Au28”. This alloy was selected to provide a comparison with an alloy with a higher starting gold content. This also allows an intermediate gold content compared with work found in the literature with a gold content.
above 35 atomic percent. Both alloys were obtained from Goodfellow Metals (Cambridge, UK). The Au23 alloys were received as rolled sheets 200 microns in thickness and the Au28 alloys were received as rolled sheets 100 microns in thickness. The alloy compositions were confirmed using the energy dispersive x-ray spectroscopy.

### 3.1.2 Annealing

Since the alloys were received as-rolled, it was necessary to anneal the samples to relieve internal stresses and allow for recrystallization. Samples were heated to 975°C for 1 hour in flowing hydrogen (hydrogen, 2.5% argon balance) and then allowed to cool in the furnace. Hydrogen was used because it was found by Senior that annealing in air led to significant oxide formation while annealing in argon led to some oxide formation. In both air and argon annealing, it was found that the grain size distribution and morphology varied between surface and interior grains. In comparison, annealing in hydrogen led to equiaxed grains with a more even grain size distribution. Annealing was carried out in alumina crucibles lined with tantalum which acted to prevent oxide formation on the samples. Following annealing, samples were cleaned with acetone, rinsed with Type I water and finally cleaned with ethanol.

### 3.1.3 Dealloying

Two dealloying procedures were used for the bulk alloy samples in this study. The first will be referred to as low potential dealloying and the second will be referred to as high potential dealloying.
The low potential dealloying procedure was based on the work of Senior that produced highly compliant nanoporous gold \[4\]. During low potential dealloying, dilute perchloric acid (0.77 M) was used as the electrolyte. The dilute perchloric acid was produced by diluting 60% perchloric acid (EMD Chemicals, ACS grade) with Type I water. The electrolyte was first deaerated by purging nitrogen at ~5 psi for at least 15 minutes before being heated to 60°C. Dealloying was carried out potentiostatically at 513 mV versus mercury/mercurous sulfate electrode (MSE, saturated). Dealloying was allowed to proceed until the current dropped to a negligible value (< 200 nA/cm²) which typically took approximately 6 hours.

The high potential dealloying procedure is based on the work of Parida and Kramer \[16,37\]. This procedure provided a good comparison because it also utilizes perchloric acid. Generally, nitric acid is favoured in literature because it affords a simpler free corrosion dealloying procedure rather than a potential controlled procedure. However, nitric acid dealloying results in a coarser structure \[4\]. During high potential dealloying, samples are dealloyed in 1 M perchloric acid at ambient temperature. The electrolyte was produced by diluting 60% perchloric acid (EMD Chemicals, ACS grade) with Type I water. This solution was also deaerated for at least 15 minutes with nitrogen. The potential is held at 643 mV and dealloying is allowed to proceed until the current drops below 200 nA/cm², typically after 2-3 hours.

A custom glass cell was used for both dealloying procedures. The cell has a built in water jacket to help stabilize the temperature of the electrolyte. A platinum counter electrode and mercury/mercury sulphate reference electrode were used in all experiments. The cell is shown in Figure 3-1.
Samples were connected to a potentiostat (Gamry Instruments, Femtostat) through an insulated 20 gauge copper wire. The samples were cut into strips approximately 3 mm by 20 mm using a razor blade and the dimensions were measured using an optical microscope and ruler. All bulk samples were mounted in epoxy (Leco, 811-563-101 epoxy and 812-518-Haz hardener) to isolate the soldered electrical connection and copper wire from the electrolyte. Samples were soldered to a copper wire, which was punched through a plastic holder that was used to contain the epoxy. Lacquer was applied to the bottom of the plastic holder to prevent the flow of epoxy through the hole. Following dealloying, samples were rinsed and then submerged in Type I water until further testing. Figure 3-2 shows a schematic of the mounted sample.
3.1.4 Mechanical Testing

Samples were tested using a novel high speed, piezoelectrically-driven compression rig that was originally developed by Nunnari, Farnood and Kortschot to test the mechanical properties of paper [48]. The primary components of the compression tester are a piezoelectric actuator (PZT PI-841.40, Physik Instrumente) and load cell (ICP 208C02, PCB Piezotronics) mounted in a load frame. Samples are compressed over a platen in the out of plane direction while the load applied and displacement are recorded to a computer. A 6 mm glass hemisphere is adhered to the end of the piezoelectric actuator using epoxy. A glass disc is placed between the glass hemisphere and the sample to create an even force distribution over the sample. A schematic of the compression testing is shown below in Figure 3-3.
3.1.5 Calibration of compression rig

The compression rig is calibrated with respect to load, displacement and compliance. For load calibration, known weights (obtained by measuring with a balance) were used to compare the recorded load with the equivalent load applied by the weights. The load cell is piezoelectrically driven, which has an inherent decay in the signal. The decay rate is insignificant compared to the test rate. The calibration results are shown below in Figure 3-4. It was found that there was a 5% increase in load that needed to be applied to match the results from the load cell with the equivalent loads calculated from the known weights.
Displacement calibration was conducted by using the actuator to measure the known thicknesses of different plastic shim stock sheets (McMaster-Carr, USA). It was found that the measured thicknesses (average of 4 measurements) fell within the manufacturer’s specifications for the plastic sheets. The results from displacement calibration are shown below in Figure 3-5.
The compliance of the micro compression tester was calibrated by measuring the stiffness of a glass cover slip placed over a custom aluminum block. The stiffness values were compared to stiffness values obtained by testing the same glass cover slip using a strain gauge (Mitutoyo, 543-182 Digital Gauge) loaded with different weights. The micro compression tester was run at 3 different test speeds: 0.1 Hz, 0.5 Hz, and 1 Hz. It was found that the initial measurement at the lowest speed (0.1 Hz) resulted in a lower measured stiffness, resulting in a larger standard deviation. The test was run twice at this speed to determine whether the effect was reproducible. The strain gauge was loaded with 50 g and 100 g weights. The compliance of each system was measured without the glass cover slips and subtracted from the measured displacements. Five measurements were taken for each speed on the micro compression tester and ten measurements were taken for each weight on the strain gauge.

![Graph showing measured versus actual thickness with error bars]

**Figure 3-5. Displacement measurement calibration**
Table 3-1. Compliance calibration

<table>
<thead>
<tr>
<th>Test speed (Hz)</th>
<th>Stiffness (N/µm)</th>
<th>Standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>0.0181</td>
<td>0.0029</td>
</tr>
<tr>
<td>0.5</td>
<td>0.0183</td>
<td>0.0009</td>
</tr>
<tr>
<td>1</td>
<td>0.0195</td>
<td>0.0003</td>
</tr>
<tr>
<td>0.1</td>
<td>0.0183</td>
<td>0.0034</td>
</tr>
</tbody>
</table>

b) Strain gauge

<table>
<thead>
<tr>
<th>Weight (g)</th>
<th>Stiffness (N/um)</th>
<th>Standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>0.0169</td>
<td>0.0002</td>
</tr>
<tr>
<td>100</td>
<td>0.0179</td>
<td>0.0001</td>
</tr>
</tbody>
</table>

The readings from the strain gauge are lower, likely caused by friction and geometry leading to non-linearity in the system. For the micro compression tests, the samples were loaded to a displacement of approximately 50 µm and a load of about 1 N. For the strain gauge, the displacement was approximately 31 µm for the 50 g weight (0.49 N load) and 57 µm for the 100 g weight (0.98 N load).

3.1.6 Interpretation of results

Samples were tested in cyclical compression with increasing loads for each cycle. The rationale for this approach was to investigate the cumulative effects of damage in the material. Figure 6 shows a typical stress-strain curve that is calculated from the load-displacement data collected. The three regions labeled are considered to represent elastic loading (1), plastic deformation (2) and inelastic unloading (3). Only loading moduli are considered in this work because the nonlinear behaviour of the unloading portion is not clearly understood. It is likely that the nonlinearity is a product of the machine compliance as
well as the sample response, but it is not trivial to determine how much of the response is caused by each factor due to the nature of the piezoelectric actuator. The compression rig determines loading and unloading by extension of the actuator rather than load applied. None of the conclusions in this thesis would be changed by using unloading moduli rather than loading moduli as the differences between compliant and stiff samples could still be distinguished.

The loading modulus is determined from each cyclic loading curve by visual inspection and identification of the linear area. The transition between the elastic loading and plastic deformation is not always clearly defined; therefore, the slope is typically determined from the portion of the curve that is further from the transition. An example of the modulus that would be selected in this example is shown by the black line overlaid on Figure 3-6.

![Figure 3-6. Typical stress-strain curve](image)
3.1.7 Sample drying

Au23 samples were tested in three conditions: wet, dry and rewet. These conditions are summarized in Table 3-2. All samples were immediately rinsed and left submerged in Type I water following dealloying. Wet samples were tested in this condition within 2 days. Dry samples were either dried in air at ambient conditions or flowing nitrogen at ~ 5 psi. Initially, it was suspected that drying in air would lead to oxidation of residual silver, which could be prevented by drying in nitrogen. This does not appear to be the case as there was no significant difference in the response. Rewet samples are samples that had been dried in either air or nitrogen and then immersed in Type I water.

Table 3-2. Treatment of Samples

<table>
<thead>
<tr>
<th></th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wet</td>
<td>Rinsed and left in Type I water</td>
</tr>
<tr>
<td>Dry</td>
<td>Rinsed with Type I water and dried in either ambient conditions or flowing nitrogen for varying periods of time</td>
</tr>
<tr>
<td>Rewet</td>
<td>Same as dry, but re-immersed in Type I water following varying periods of time</td>
</tr>
</tbody>
</table>

The behaviour of rewet samples depended on the extent of drying that occurred prior to rewetting in addition to the length of rewetting time. Figure 3-7 shows the change in weight of a sample measured using a microgram balance as it dried. Samples showing reversible low modulus behaviour were typically dried to no more than 600 seconds. This suggests that there is a significant amount of water remaining in the samples upon drying. Upon drying, samples begin to stiffen and curl for reasons that will be discussed in Chapter 4. If the sample is rewet within a short amount of time (< 10 minutes), the material will
revert to the compliant behaviour. If the sample is allowed to dry for a longer time, the change is irreversible. The amount of drying required for the change to be irreversible was not determined because humidity was not controlled in this work.

![Sample drying in ambient conditions](image)

**Figure 3-7. Sample drying in ambient conditions**

### 3.2 Sputtered alloy experiments

#### 3.2.1 Alloy composition

Three alloy systems were investigated during the sputtered alloy experiments. The compositions were selected to match the noble metal content of the Au23 alloys investigated during the bulk alloy experiments. Each of the sputter targets had a purity of 99.9999% as given in Appendix A. Samples were sputtered to a thickness of 100 nm. The base pressure of the system was in the $10^{-7}$ Torr range. The compositions are summarized below in Table 3-3.
Table 3-3. *Sputtered alloy compositions*

<table>
<thead>
<tr>
<th>Sample name</th>
<th>at% Ag</th>
<th>at% Au</th>
<th>at% Pt</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au23</td>
<td>77</td>
<td>23</td>
<td>0</td>
</tr>
<tr>
<td>Au22Pt1</td>
<td>77</td>
<td>22</td>
<td>1</td>
</tr>
<tr>
<td>Au18Pt5</td>
<td>77</td>
<td>18</td>
<td>5</td>
</tr>
</tbody>
</table>

### 3.2.2 Sputtering conditions

The magnetron sputtering system used in this thesis is briefly described here and further details can be found in Appendix A. The system consists of a vacuum chamber containing 3 sputtering guns. Two of the sputtering guns use a DC power source while the third uses a RF power source. The vacuum chamber is accessible by a load lock, which also contains an etching electrode which is used to clean the surface of the substrates. The samples are transferred to a manipulator which is rotated to ensure even deposition. The manipulator also has the capability to heat the sample holder.

Initially, silicon substrates were used in this work, but it was found that samples would delaminate from the substrate during dealloying. Several approaches to remedy this were unsuccessful. The use of a thin gold interlayer of 20 nm was expected to improve adhesion through moving the interface mismatch from between the nanoporous gold and silicon to between a pure gold interlayer and the silicon substrate. The difference was not significant. Post deposition annealing was also attempted but also showed little effect. The substrates had been cleaned with isopropanol and then sputter etched for 10 minutes. The sputter etching process is described in Appendix A. In order to improve adhesion of samples, air cleaved mica (using a razor blade) was tested as a replacement for silicon as the substrate.
The mica was expected to give better adhesion since gold is known to grow epitaxially on mica [49]. The substrates were cleaned with isopropanol and then sputter etched for 10 minutes. A gold interlayer of 20 nm was also used to prevent delamination of the sputtered film. However, there was not a significant improvement and the samples still delaminated during dealloying. As a result, silicon was used as the substrate for ease of handling since it was difficult to determine which side of the substrate the deposit was on for very thin slices of cleaved mica. In order to counteract the delamination, Amercoat 90 HS (PPG Protective and Marine Coatings, USA), which is an epoxy-phenolic based coating intended to protect tanks in petrochemical and chemical applications.

Sputtering was conducted under a pressure of 10 mTorr of argon gas. A stainless steel mask was used to produce circular samples with a diameter of 3 mm. Calibration of the sputter rates for each target was conducted using an optical profilometer and the results are shown in Appendix B along with calculations of the sputtering powers used for each source to fabricate the alloy systems.

3.2.3 Electrochemistry of sputtered samples

The dealloying procedure used for the bulk alloys could not be used with the sputtered films since the samples were too small to make an isolated solder connection to. Instead of using the custom electrochemical cell of Figure 3-1 used for the bulk alloys, the samples were placed in approximately 100 mL of electrolyte. The electrolyte was 0.77 M perchloric acid and ambient temperatures were used for all experiments. Electrical contact to the sample was made by a gold wire held in contact with the sample. Platinum was used as
the counter electrode. Dealloying was conducted at ambient temperature while potential scans were taken for each sample to determine an ideal critical potential for dealloying. Polarization curves were obtained using a potentiostat (Gamry Instruments, Femtostat) to sweep from 0 V to 1.5 V at a rate of 1 mV/s. Dealloying was conducted potentiostatically at 250 mV (near the onset of the critical potential) with the intention of using a slow dealloying rate to minimize the shrinkage and prevent delamination. Figure 3-8 shows the set up for sputtered sample dealloying.

Figure 3-8. Sputtered sample dealloying set up
4 Results and Discussion

4.1 Bulk alloy experiments

The results of the bulk alloy experiments focused on the elastic properties of the nanoporous gold samples tested under compression. Sample stress-strain curves will be presented first in order to show the difference between several sample groups. SEM micrographs will be used to provide further information regarding the material behaviour. Finally, all of the elastic modulus results will be presented in order to better understand the synergy existing between the data sets.

This chapter will also elaborate on the ideas and questions that are raised from the results obtained in this work. The focus will be on the nature of deformation in nanoporous gold and the factors which contribute to the elastic response of nanoporous gold.

4.1.1 High potential dealloying versus low potential dealloying

A comparison between the two dealloying methods employed in this study is shown below in Table 4-1. Recall that the low potential dealloying was expected to result in a compliant, crack-free nanoporous gold while the high potential dealloying was used to provide a comparison to the results presented by other groups in literature [16,37]. Only the 28 at% Au samples were used for the dealloying procedure comparison since no groups in literature performed mechanical testing with lower gold content starting alloys.
Table 4-1. **Dealloying conditions**

<table>
<thead>
<tr>
<th></th>
<th>Low potential dealloying</th>
<th>High potential dealloying</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrolyte</td>
<td>0.77 M perchloric acid</td>
<td>1 M perchloric acid</td>
</tr>
<tr>
<td>Temperature</td>
<td>60°C</td>
<td>Ambient (~20°C)</td>
</tr>
<tr>
<td>Applied potential</td>
<td>513 mV vs. MSE (saturated)</td>
<td>643 mV vs. MSE (saturated)</td>
</tr>
</tbody>
</table>

Testing by compression revealed that the dealloying procedure resulted in a drastic change in material properties. Figure 4-1 shows stress strain curves for two samples which were dealloyed using the different procedures. Loading was increased with each cycle to demonstrate the cumulative effects of loading. Note that the samples become stiffer with subsequent loading. It is evident from these results that the sample dealloyed at the lower potential is more compliant than the sample dealloyed at high potential.
Recall that Senior reported gold hydroxide formation at higher applied potentials such as those used in the high potential dealloying procedure [4]. This is likely the reason for the increased stiffness that results from the high potential dealloying. Investigating SEM micrographs reveals that the high potential dealloying creates a finer microstructure as was predicted since hydroxide formation impedes surface diffusion. Figures 4-2 and 4-3 show the differences between the microstructures of the samples. The high potential dealloying procedure results in ligament thicknesses on the order of 10 nm while the low potential dealloying procedure results in ligament thicknesses on the order of 40 nm.

Figure 4-1. Stress strain curves for Au28 dealloyed under high and low potential

Figure 4-1. Stress strain curves for Au28 dealloyed under high and low potential
Figure 4-2. SEM micrograph showing Au28 dealloyed under high potential

Figure 4-3. SEM micrograph showing Au28 dealloyed under low potential
Investigating crack propagation in the samples, one can see that both materials demonstrate sharp crack propagation. The fine microstructure from the high potential dealloying created a highly constrained ligament network which prevented any yielding before crack propagation as seen in Figure 4-4. The low potential Au28 sample had areas with similar fracture behaviour but the edges of the cracks were much rougher, indicating more yielding had occurred as highlighted by Figure 4-5.

Figure 4-4. SEM micrograph showing sharp crack propagation in Au28 dealloyed under high potential
4.1.2 Au23 versus Au28 (low potential dealloying)

Comparing the effects of starting alloy composition revealed that using lower starting noble metal content resulted in a more compliant nanoporous gold product. Figure 4-6 shows the stress strain curves obtained for Au23 and Au28 samples both dealloyed using the low potential conditions. This is an expected result since a sample with less noble metal content will have more void space. These are essentially two different materials that cannot be compared. However, the results are shown together here to highlight the magnitude of the change in modulus with changing bulk composition. Note that the Au28 sample shown here is the same sample discussed in Figure 4-1.
Recall that as discussed in Chapter 2, the continuum percolation threshold for a 3-dimensional lattice was 16% [5]. However, nanoporous gold has a very narrow distribution of ligament sizes (few very thin or very thick ligaments) as was first reported by Li and Sieradzki [40]. This raises lower limit threshold for continuity between the ligaments, as was noted in the work of Senior and Newman [4].

SEM micrographs reveal that the Au23 sample had ligaments on the order of \(~30\) nm compared with the \(~40\) nm ligaments of the Au28 sample. Although reducing ligament size is expected to increase the stiffness, the sample with smaller ligaments was observed to be
more compliant. Again, this is because the void space in Au23 is greater than that in Au28. Figure 4-7 shows the ligament structure for the Au23 sample.

![SEM micrograph of Au23 dealloyed under low potential](image)

*Figure 4-7. SEM micrograph of Au23 dealloyed under low potential*

The samples were cracked in bending in order to examine the interior of the material. Investigating crack propagation behaviour in the Au23 samples revealed that the material appeared to tear rather than crack abruptly in the fashion the Au28 samples did. This correlates well with the highly compliant behaviour that is observed macroscopically and measured using compression. Figures 4-8 and 4-9 show examples of crack propagation in Au23 samples. As the crack front progresses across the material, ligaments seem to bend, twist and yield in order to accommodate the stress applied. Figure 4-9 shows that ligaments become entangled. This suggests that there are weaker areas in the material that break first.
while other areas densify, making them stronger and alloying the material to accommodate larger strains.

*Figure 4-8.* SEM micrograph of Au23 showing crack propagation and ligament entanglement (low magnification)
4.1.3 Au23 wet versus dry behaviour

In this work, it was observed that the behaviour of the nanoporous gold was dependent on its environment. Figures 4-10, 4-11 and 4-12 show a silver-gold alloy, a wet dealloyed sample and a dry dealloyed sample respectively. The change in colour following dealloying is due to the material’s interaction with visible light since the porosity is on the nanoscale [50]. Following drying, the sample curls. This effect will be discussed later in this section. Recall that the nanoporous gold only shows the highly compliant behaviour while wet, but not dried.
Figure 4-10.  Silver-gold alloy prior to dealloying

Figure 4-11.  Dealloyed sample (rinsed and left in water)

Figure 4-12.  Dealloyed sample (dried in air)
Compression testing revealed that the increased compliance observed while the sample is wet can be measured as shown in Figure 4-13. The sample from the curve labeled “wet” was rinsed and kept immersed in Type I water following dealloying prior to being placed inside a droplet of water on the platen on the compression tester. The sample labeled “dry” was rinsed in Type I water following dealloying and allowed to dry in ambient conditions on a precision wipe (Kimberly-Clark, USA) for a minimum of 15 minutes prior to being tested.

Rewetting samples following a short drying time (<10 minutes) would revert the sample to the low modulus behaviour of wet samples. Macroscopically, it was observed that samples which had curled would relax and uncurl. Rewetting following longer dry times had no effect as the samples remained curled and exhibited the same higher modulus behaviour of the dry samples. Furthermore, sample thickness was measured using the compression tester, but it was found that the differences were negligible as seen in Figure 4-14.
Figure 4-13. Stress strain curves for Au23 tested dry and wet

Figure 4-14. Thickness of Au 23 samples
4.1.4 Summary of modulus results

Figure 4-15 shows all of the elastic modulus results from Au23 samples plotted as a function of the initial permanent strain. Initial permanent strain is defined here as the amount of permanent, unrecovered strain that is accumulated by the sample from each test cycle leading up to the present one. As described in the preceding sections, the elastic modulus was seen to increase as more strain was applied. Generally, the elastic modulus results fall into two distinct groups. The first group exhibits low modulus behaviour and is represented by the wet samples and rewet samples with short dry times. These samples have elastic moduli in the range of 15 to 500 MPa depending on the amount of permanent strain. The second group exhibits high modulus behaviour and is represented by the dry samples and rewet samples with long dry times. These samples have elastic moduli ranging from 50 MPa to 1 GPa depending on the amount of permanent strain applied.
Figure 4-15. Elastic modulus results for all Au23 samples

4.2 Deformation in nanoporous gold

4.2.1 Open cell foams and nanoporous metals

As discussed in Chapter 2, nanoporous gold is typically modelled as an open cell foam with nanoscale dimensions. Open cell foams generally show compressive stress strain curves similar to the schematic shown below in Figure 4-16. Initially, there is a linear region that is caused by the linear bending of cells. Upon further loading, there is a plateau region that is associated with the plastic yielding of hinges. This region typically extends to 70-80% strain.
Finally, when cell ligaments come into contact with one another, there is densification. This causes a drastic increase in the stress required to further deform the material.

![Schematic compressive stress strain curve for open cell foam, adapted from Gibson and Ashby [51]](image)

Figure 4-16. Schematic compressive stress strain curve for open cell foam, adapted from Gibson and Ashby [51]

In contrast, nanoporous gold samples with lower relative densities (such as the ones studied in this thesis) show a very different mechanical response. Figure 4-17 shows a series of curves obtained from cyclic compressive stress strain testing. The strain extends to about 13% (recall that the samples were 200 µm thick) and the sample becomes stiffer with each subsequent cycle, suggesting that there is immediate densification upon loading. This is a plausible explanation because with pore size being on the order of nanometers, very small amounts of strain could cause ligaments to touch, thus increasing the stiffness. In addition, recalling the work of Biener et al, it was observed that nanoporous gold deformed by densification during nanoindentation as the damage to the material was limited to the area in contact with the indenter [6].
Another important question is whether the Gibson and Ashby models for open cell foam can adequately describe the elastic modulus for nanoporous gold. As was seen in Chapter 2, the strength cannot be accurately described by scaling laws without incorporating terms which consider the ligament size. Consider the two unit cells below in Figure 4-18. On the left is the unit cell used to derive the Gibson and Ashby scaling laws. On the right is a unit cell that has been modified so that it has the same ligament size, but a different relative density.

Figure 4-17. Example of cyclic compressive stress strain curves
4.2.2 Deformation modes

In the Gibson and Ashby model, the unit cell is loaded in compression from the top and bottom. As a result, the loading is similar to a beam loaded in three-point bending. However, this assumes that the entire material has a structure similar to the rigid, cage-like structure of the open cell foam unit cell. In nanoporous gold, particularly samples with lower relative densities, it can be expected that there are mixed deformation modes. Rather than the mechanical behaviour being dominated by three-point bending, it is perceivable that there is a greater influence from the more compliant cantilever bending mode among other more complex torsional loadings.
The stiffness of a beam in bending is given by Equation 5-1 shown below. Stiffness is defined by the force F required to achieve a given deflection δ. The term $C_1$ is a constant and depends on the loading. For a beam in three-point bending as shown above, $C_1$ has a value of 48. For a cantilever in bending, $C_1$ has a value of 3 [52]. This is the most likely origin of the drastic changes in the elastic response observed in nanoporous gold.

$$S = \frac{F}{\delta} = \frac{C_1EI}{l^3}$$  \hspace{1cm} (Equation 4-1)

Where:
- $S$ = stiffness (N/m)
- $F$ = force (N)
- $\delta$ = deflection (m)
- $C_1$ = constant
- $E$ = elastic modulus (N/m$^2$)
- $I$ = second moment of area (m$^4$)
- $l$ = length (m)

### 4.3 Elastic modulus of nanoporous gold

As discussed in the previous section, the elastic modulus of nanoporous gold is heavily influenced by the microstructural aspects of the ligament structure. This likely accounts for the finding that the elastic modulus of Au23 was significantly lower than that of Au28. There are also influences that arise from the small scale length that should be considered as well.
Recall that with the Au23 samples, it was possible to measure a lower elastic modulus while samples were tested in the wet state. Drying and subsequent rewetting showed that there was a time-dependent drying limit before which the low modulus behaviour could be obtained again. The following sections will address this behaviour as well as the factors which can influence the elastic modulus in nanoporous gold.

### 4.3.1 Surface effects

The small scale length is what sets nanoporous gold apart from macroporous metallic foams. As a result, nanoporous gold has a much larger fraction of its atoms residing at or near the surface rather than the bulk. Surface atoms behave differently than bulk atoms since they are not surrounded by as many nearest neighbour atoms. Bulk atoms are known to exert a stress constraint on the uncoordinated surface atoms [53]. In addition, the surface atoms are exposed to the atmosphere and this interaction can potentially affect the surface stress state in the material. Several atomic simulations investigating the elastic properties of nanoscale structures have shown that elastic modulus can change when a material dependent critical length scale is reached [53,54]. Most of the simulations are based on the work of Gurtin et al who presented a model which considers the effect of surface elasticity [55].

Surface stresses arise from the stretching of an existing surface so that the density of atoms on the surface is altered but not the number of atoms at the surface. By contrast, surface free energy is the energy associated with creating a new surface through a process such as cleavage. A comprehensive description of surface stress with regard to nanostructured materials is given by Cammarata in Ref [56].
The work of Feng et al considered the effect of surfaces on the macroscopic elastic properties in an open cell foam unit cell. The model in this study predicted an increase in elastic modulus as ligament size decreased below 10 nm. However, the extent of change was dependent on the defined value of surface elasticity, which the authors conceded may be positive or negative [57]. This model was used to reproduce the results of increased elastic modulus with decreasing ligament size that was first reported by Mathur and Erlebacher [8].

While it was established in the preceding section that stiffness is dependent on the mode of deformation, simulations on nanowires have shown that the measured elastic modulus can also be affected. A study conducted by He and Lilley has shown that nanowire cantilevers have a lower elastic modulus compared to fixed end beams as well as simply supported beams. This is a result of how surface stresses interact with the material based on the boundary conditions. In cantilevers, a positive surface stress acts in the same direction as a positive curvature (towards more bending), increasing the displacement and resulting in a more compliant response. However, in simply supported beams and fixed end beams, a positive surface stress acts in the opposite direction as a positive curvature, decreasing the displacement and resulting in a stiffer response. Reversing the sign on the surface stress has the opposite effect of making cantilevers behave with a stiffer response [53]. Figure 4-20 below shows the response for several loadings when the surface stress is zero (solid black line), positive (blue dashed line) and negative (red dotted line).
Figure 4-20. Displacement versus position for (a) cantilever, (b) simply supported and (c) fixed end beams, from He and Lilley [4]

4.3.2 Effects of testing environment

One of the more intriguing findings that has been quantified in this thesis is the measurement of a reduced elastic modulus for samples tested wet compared with dry samples as seen in Section 4.1.3 comparing wet and dry Au23 samples. It was initially suspected that there was a chemical change at the surface of the material caused by airborne contamination, a reaction with oxygen, or possibly the presence and/or absence of water. However, as will be seen in the discussion that follows, the evidence strongly suggests that the phenomenon is physical in origin.

Since samples which had undergone rewetting following longer dry times did not show the compliant behaviour, it seems that the compliant behaviour is not caused by the presence
of water. Furthermore, drying in flowing nitrogen and flowing air yielded no discernable differences in behaviour. In addition, the limited reversibility (only reversible with short dry times) is difficult to explain by any type of chemical change in the material. Instead, it is more likely that the compliant behaviour is present in the as-dealloyed material while submerged in water and is subsequently lost during drying.

As discussed in Chapter 2, the dealloying process has several effects on the stress state and defect structure in nanoporous gold. The first is that dealloying imposes a residual stress on the material that is dependent on the rate of dealloying [16]. Faster dealloying rates (through higher applied potential) results in extensive transgranular macroscopic cracking. At intermediate dealloying rates, this cracking is found to be intergranular. At slow dealloying rates (through lower applied potential) there is no visible cracking when dealloying occurs at elevated temperatures [4]. Crackfree nanoporous gold can also be produced when the initial dealloying is conducted galvanostatically at a lower rate prior to dealloying at the free corrosion potential in a stronger electrolyte [33]. It is likely that the stress produced by dealloying can be mitigated when the dealloying procedure is sufficiently slow. Another factor may be the formation of hydroxide. This has the effect of impeding gold diffusion which is known to be a stress relief mechanism in dealloyed materials through the reorganization of the dealloyed material in the lateral (from surface diffusion) and to some extent, vertical direction [4].

It was observed that samples curled macroscopically upon drying. This is an indication that the water was having an effect on the stress state within the material. Water atoms are weakly adsorbed onto the surface of the gold ligaments and bound to each other through hydrogen bonding. This creates a resistance against the movement of ligaments and
counteracts the residual stress caused by dealloying. When the water is removed, the stresses are allowed to act on the material and cause ligaments to impinge on each other. This effect causes the modulus to increase. Another possible effect of drying is the capillary force of water moving through the ligament network. Regardless of the mechanism, it is clear that removing water from the nanoporous gold causes the material to become stiffer.

This effect is reversible when the sample is submerged into water as the water relaxes the surface stress allowing ligaments to return to their original positions. However, at longer dry times, the effect is irreversible due to formation of contact welds. Contact welding or cold welding is the welding of metals under ambient conditions, usually requiring very high applied loads. Conversely, contact welding can occur with very low applied loads in vacuum conditions provided that the surfaces are flat, ductile and atomically clean. However, it has been reported that contact welding occurs in thin gold films (20 nm) at ambient temperatures and pressures [58]. Shown below is a SEM micrograph which shows apparent contact welding between ligaments in a Au23 sample.
4.3.3 Summary of bulk alloy results

In summary, compliant nanoporous gold is obtained by dealloying silver-gold alloys with lower starting gold concentrations. The compliant nature comes from the ligament network being less connected when there is more void space in the material, shifting the dominant deformation mode from three-point bending to cantilever bending. This is related to the continuum percolation threshold since the gold concentration is approaching a lower limit.
The elastic modulus is even lower when the samples are tested wet because water plays a role in relieving residual stresses from the dealloying process. When the water is removed, these stresses cause the ligaments to impinge on each other, which increases the number of contact points and creates a stiffer microstructure. Water may also exert capillary forces on the ligaments during drying. These mechanisms account for the dramatic rise in modulus when the samples are dried. This process becomes irreversible at longer drying times due to the formation of contact welds between ligaments.

Below, the results from this study are shown in comparison with the results found in literature that were previously discussed in Chapter 2. The black line represents the Gibson and Ashby model for elastic modulus of an open cell foam. It is clear that the low potential dealloying results from this thesis cannot be predicted by the scaling equation of Gibson and Ashby. This is likely because the ligament structure in nanoporous gold at lower relative densities is dissimilar to the cage-like unit cell structure that is by Gibson and Ashby used to predict the behaviour of open cell foams as was discussed in Section 4.2.1.
4.4 Sputtered alloy experiment results

Unfortunately due to equipment malfunction, the intended sputtered alloy experiments which were intended (namely, mechanical testing of sputter deposited films) could not be completed during this thesis. However, the preliminary work on sputtered films has revealed several interesting results that will be discussed here.
4.4.1 Heating and interlayer effects on sputter deposited Au23

As discussed in the previous chapter, one of the difficulties encountered in this thesis was the delamination of Au$_2$Ag$_{77}$ alloys from both the silicon and mica substrates that were used. One approach involved using a 20 nm gold interlayer prior to dealloying and then heat treating the sample at 300 °C in order to improve adhesion. It was observed that following heat treatment, there was a bumpy texture on the surface of the film. This sample was compared with a sputtered sample with no heat treatment or interlayer. Both samples were deposited on mica and had the edges protected with Amercoat 90 HS lacquer in order to prevent delamination. The polarization curves for the two samples are shown below.

![Polarization curves for sputtered Au23 sample and sputtered Au23 sample with heat treatment and Au interlayer.](image)

Figure 4-23.
The sample with the heat treatment and interlayer has a much higher initial current and eventually a crack propagates across the sample, breaking the electrical connection after ~500 mV. In contrast, the sample with no interlayer had a much lower initial current and subsequent increase in current after 600 mV, well into the supposed critical potential for this alloy (expected in the 300 mV range). However, the current density is not as high as would be expected for dealloying. The current increase above 1 V is due to oxygen evolution. The causes for these results are discussed in the following section.

4.4.2 XPS depth profile for Au23 samples

An XPS sputter profile was conducted to provide insight into the behaviour of the samples discussed in the previous section. It was found that the sample with no interlayer or heat treatment had a uniform composition (in terms of silver and gold) from the surface to the substrate. However, for the sample with interlayer and heat treatment, it was found that the surface had become silver enriched (or gold depleted) by nearly 10%. Also, this sample had a much higher gold content in the bulk of the film. This is presumably related to the interlayer. For both samples, there is a small amount of carbon contamination at the very surface. Another noted difference is that there is a small amount of oxygen in the sample with no interlayer or heat treatment which increases from 3% at the surface to nearly 20% at the substrate. The sample with interlayer and heat treatment showed very little oxygen until the substrate level is reached in the depth profile.
Figure 4-24. XPS depth profile for sputtered Au$_2$3 sample

Figure 4-25. XPS depth profile for sputtered Au$_2$3 sample (Ag vs. Au)
Figure 4-26.  XPS depth profile for sputtered Au23 sample with interlayer and heat treatment

Figure 4-27.  XPS depth profile for sputtered Au23 sample with interlayer and heat treatment (Ag vs. Au)
This silver enrichment at the surface is likely responsible for the increased initial current seen in Figure 4-23. Since the gold concentration is less than 14% (below the continuum percolation threshold of 16% \[5\]), the material near the surface disintegrates during the initial stages of the scan, potentially injecting a crack into the material. This could be causing stress corrosion cracking (SCC) behaviour similar to that seen in the work conducted by Barnes et al on film-induced cleavage of silver gold alloys \[59\]. The film-induced cleavage mechanism describes how substrate fractures are initiated by a thin surface film of dealloyed, nanoporous material. A review of the relevant SCC mechanisms in silver gold alloys is discussed by Newman in Ref \[60\]. Furthermore, the surface silver enrichment will lead to a higher dealloying rate which results in increased shrinkage and cracking as was discussed earlier in this chapter regarding bulk alloys.

Another factor potentially contributing to the elevated initial current is the surface roughness and grain structure of samples. Sputter deposited films of silver based alloys (including silver gold) are known to have a columnar grain structure under conditions similar to those used in this work \[61,62,63\]. This may lead to surface roughness as well as less coordinated atoms in the grain boundary type area between columns. Increased surface roughness exposes more silver atoms to dissolution while less coordinated atoms will be more easily removed. In addition, it is possible that the atoms in the sputtered film have a more random distribution of atoms compared with a conventional bulk alloy which may show more clustering of like atoms.

There are several possible explanations for the change in composition at the surface and apparent diffusion of the interlayer. Since heat treatment was conducted in air, it is possible that there is some kind of reaction at the surface. However, the XPS signal for
carbon was found in very low levels and only at the surface layer. The XPS survey spectrum revealed very low levels of contamination with possible contaminants being Sulphur and Chlorine. Diffusion of Ag and Au through the bulk of the material is not expected at these temperatures, although it is possible that there is mobility through columnar grain structure of a low temperature and low pressure sputter deposited film.

One possible contribution could be surface segregation in the alloys from the heat treatment. Silver gold alloys have been studied extensively in literature [64,65,66,67,68] and it has been found that silver tends to segregate to the surface, which also has the effect of making a gold enriched monolayer underneath the silver enriched surface monolayer [64]. However, this effect may not be significant since it is only affecting several monolayers at most. There are two main theories to explain surface segregation in alloys. The first theory is known as quasichemical theory and states that the alloy constituent with the lower heat of vaporization will segregate to the surface. The second theory is known as strain theory and states that difference in atomic size is responsible for the surface segregation effect. In this theory, the larger atoms will segregate towards the surface [64]. Although lattice diffusion is not expected at the temperatures used, diffusional transport along grain boundaries has been reported in thin film AgAu alloys at temperatures as low as 200 °C [61].

Regarding the oxygen seen in the Au23 sample without interlayer or heat treatment, the origin of the oxygen is not well understood. However, the effect of oxygen in the alloy may be similar to effect of nitrogen in stainless steels [69,70,71]. Nitrogen is proposed to encourage local passivation in stainless steels by three methods. The first is the consumption of acid in pit nuclei through nitrogen dissolution and the formation of ammonium ions. The second is the enrichment of nitrogen on the passivated surfaces at the film/metal interface
which can cause aggressive anions to desorb upon breakthrough of the passive layer. The third is the enrichment of nitrogen on the active sites of surfaces, which is believed to block kink sites and inhibit pit initiation [70,71]. In the case of the result from Figure 4-23, it is possible that oxygen accumulates on the surface of the forming porosity, inhibiting diffusion (which in turn reduces the amount of silver exposed to electrolyte) and passivating the alloy until the oxygen evolution potential is reached near the end of the scan.

### 4.4.3 Polarization curves for Au23, Au22Pt1 and Au18Pt5

The polarization curves for sputtered alloys on Si substrates are shown below. Note that all samples have an interlayer between the substrate and the deposited alloy. The noise in the graphs is attributed to the gold wire losing contact with the sample surface as the sample begins to dealloy with increasing potential. The initial current is high, similar to the Au23 sample with interlayer and heat treatment previously discussed in Figure 4-23. Each curve shows a shoulder feature near 250-300 mV where the current decreases briefly and then rapidly increases to the 1 mA/cm² range. This occurs near the expected critical potential of 280-430 mV (converted from 650-800 mV versus SCE reported in Ref [4]). However, the current peaks after 400 mV, likely because the sample is becoming depleted of silver. This causes the current to drop until the potential is high enough to remove any remaining silver. Above 1 V, the current increase is due to oxygen evolution.
Figure 4-28.  *Polarization curve for sputter deposited Au23*

Figure 4-29.  *Polarization curve for sputter deposited Au22Pt1*
It is interesting to note that the sample with the most platinum has a much lower current following the main peak at 400 mV. This is possibly caused by platinum atoms pinning the active sites and inhibiting the diffusion of gold. This prevents the electrolyte from reaching silver atoms, which would lead to a higher current. This would explain why the current after 500 mV is lowest for the sample with the most platinum. It was also observed that for all samples there was macroscopic cracking near the sample edges where the sample had been held down by the lacquer. This was especially prevalent in the Au18Pt5 sample where 2 separate edges of the sample become detached and curl up. This behaviour is likely related to the shrinkage that is typical during dealloying [16]. Since there is
conceivably less diffusion in the samples with platinum, these samples would resist volume shrinkage and possibly crack as was seen at the sample edges.

It seems that the elevated initial current is related to the interlayer rather than the heat treatment though further experiments on heat treated samples with no interlayer will be required to confirm this. The interlayer may be altering the initial stages of film growth which leads to a different grain structure in the film. This could have the effect of changing the bond strength which must be broken to remove silver atoms.

### 4.4.4 Dealloying of sputtered alloys

The sputtered alloys were dealloyed at 250 mV (vs. MSE, saturated) and investigated by SEM. The potential used here was much lower than typical potentiostatic dealloying potentials (which are usually well past the critical potential) because a slower dealloying rate was expected to mitigate the cracking and delamination issues that were more problematic for sputtered films. It should be noted that the Au18Pt5 sample became delaminated and curled around the gold contact wire during the dealloying procedure. During removal of the gold contact wire, the sample broke into several pieces. A fragment was placed on a TEM grid for imaging in a SEM.

SEM images of the Au23 sample revealed that the sample had separated from the lacquer, leading to delamination and curling at the edge of the sample. Higher magnification reveals that there is extensive microcracking similar to what was reported by Lu et al as well as Sun and Balk [46,47]. Very fine porosity below 5 nm is formed at this dealloying
potential, appearing like surface texture in Figure 4-33. The grain structure of the sputtered film is also faintly visible with grains about 50-100 nanometers in size.

Figure 4-31. SEM micrograph of sputtered Au23 sample following dealloying at 250 mV (vs. MSE) showing delamination at edge of sample
**Figure 4-32.** SEM micrograph of sputtered Au23 sample following dealloying at 250 mV (vs. MSE) showing macroscopic crack as well as extensive microcracking.

**Figure 4-33.** SEM micrograph of Au23 sample following dealloying at 250 mV (vs. MSE) showing high magnification of microcracks and nanoscale texture on sample surface and cross section.
SEM images of the Au22Pt1 sample were very similar to the Au23 sample, suggesting that the presence of a low Pt concentration does not dramatically alter the dealloying mechanism. The sample showed the same delamination near the edges as well as extensive microcracking. Higher magnification revealed that there was also a nanoscale texture (presumably nanoporosity on the order of a few nanometers) on some but not all of the grains, which were on the order of 50 nm in size as seen in Figure 4-36.

Figure 4-34. SEM micrograph of sputtered Au22Pt1 sample showing delamination of sample near edge
Figure 4-35. SEM micrograph of Au22Pt1 sample following dealloying at 250 mV (vs. MSE) showing microcracks

Figure 4-36. SEM micrograph of Au22Pt1 sample following dealloying at 250 mV (vs. MSE) showing high magnification of microcrack and nanoscale texture
It was not possible to image the surface of the Au18Pt5 sample since it had curled up with the gold interlayer side of the sample facing outward. Images were obtained near the edge of the curled fragment where it was possible to see texture (on the order of 10s of nanometers) on the sample cross section. This suggests that there was either no porosity formed or that the porosity was smaller than the resolution limits of the SEM used. The interlayer is visible in the cross sectional view of Figure 4-38.

*Figure 4-37. SEM micrograph of Au18Pt5 sample following dealloying at 250 mV (vs. MSE) showing cross section*
Figure 4-38. SEM micrograph of Au18Pt5 sample following dealloying at 250 mV (vs. MSE) showing high magnification of cross section and nanoscale texture

It is likely that the microcrack formation is linked to the elevated and increasing current observed during the initial stages of the potential scan. From the higher magnification images, it appears that the microcracks are intergranular in nature, although there may be some transgranular cracking since grains are very small. Since the cracking is formed during dealloying, the surface area is increasing as dealloying progresses. This allows electrolyte to penetrate through the sides of the cracks to remove more silver, resulting in the elevated current which increases as further cracking occurs. The increasing surface area also prevents the passivation that is expected to occur before the critical potential is reached during the potential sweep. The cracking appears to be more severe with increasing platinum concentration as the width of the microcracks is greater although the number of microcracks
is similar. This suggests that while the samples experience the same stress, the Au23 sample can accommodate more strain from cracking than the Au22Pt1 sample.

4.4.5 *Summary of sputtered alloy results*

The preliminary work done here on dealloying of sputtered samples has revealed that there is a nontrivial difference between the sputtered alloys and the bulk alloys. The elevated initial current indicates that silver is more easily removed from the sputtered films. The columnar grain structure of the sputtered film likely contributes to this behaviour since grain boundary atoms are less coordinated and therefore more easily removed by electrolyte. The random nature of atoms from sputter deposition may also play a role. It was also found that oxygen levels in the Au23 film were relatively high when no heat treatment was used (suggesting that the heat treatment removes the oxygen). It is possible that the oxygen in the sample acts similarly to nitrogen in stainless steels and has a passivating effect. However, the oxygen does not seem to affect the polarization curves in Section 4.4.3 since samples show an elevated initial current rather than the low initial current seen in the Au23 sample with no interlayer from Figure 4-23 (which showed the higher oxygen content in the XPS profile).

The addition of platinum does not affect the general shape of the polarization curve until the late stages of the potential sweep in Figure 4-30. This suppressed current after the main peak is likely associated with platinum atoms inhibiting the surface diffusion of gold, which normally reveals more silver atoms for dissolution.

SEM micrographs reveal that that there is very fine porosity with ligament thicknesses well below 10 nm formed at this applied potential. Extensive microcracking is seen in the
dealloyed samples as well as delamination of samples near the edges. The microcracking is the most likely mechanism for the elevated and increasing current during the early stages of the polarization curves. Extensive microcrack formation increases the surface area, allowing more silver to be removed by the electrolyte. The cracking is more severe with increasing platinum content since the platinum inhibits the surface diffusion, making the material less accommodating to the stress developed during dealloying.
5 Conclusions

1) Compliant nanoporous gold has been fabricated from a Au$_{23}$Ag$_{77}$ precursor with ligament size of 40 nm and elastic modulus increasing from 50 MPa to 1 GPa with the amount of permanent strain that has been applied to the material. The elastic modulus of compliant Au$_{23}$ samples tested while immersed in water increases from 15 MPa to 500 MPa with the amount of permanent strain that has been applied to the material. The elastic behaviour of these materials cannot be predicted by the Gibson and Ashby scaling equations.

2) The increase in modulus with permanent strain is associated with ligament impingement, which increases the microstructural stiffness of the material through altering the dominant deformation mode from cantilever bending towards three point bending. The limited reversibility from high and low modulus behaviour during rewetting is dependent on contact weld formation between ligaments at longer dry times. Contact welding is prevented by submerging samples in water.

3) Preliminary experiments have shown that sputter deposited silver gold alloys have a significantly different electrochemical behaviour compared with bulk silver gold alloys. The higher initial current indicates that silver is more easily removed in the early stages of dealloying. There is no plateau region (caused by depletion of silver from the surface atomic layers) that is commonly observed in bulk alloys. The differences are likely linked to the columnar grain structure of sputtered films and the uncoordinated atoms in the intergranular region. During dealloying, sputtered samples tear away from the lacquer, leading to delamination and curling of sample
edges. This behaviour is more severe with increasing platinum content. Also, extensive microcracking is observed throughout the sample surface of all sputtered samples following dealloying. This is creates new pathways for the electrolyte to remove silver atoms, resulting in a faster dealloying. Microcracking is more severe with higher platinum concentrations because the reduced diffusion does not allow the material to accommodate the stress which develops during the dealloying process.
6 Future Work

There are several areas that have been addressed in this thesis which may be of interest for further studies.

First of all, it would be valuable to publish a more comprehensive study on the factors which influence the structure of a dealloyed metal. Namely, it would be of interest to determine how varying the applied potential, electrolyte temperature, electrolyte composition and alloy composition will affect the dealloying process as well as nanoporous structure. Most work in literature exams a very limited set of conditions. Having a greater understanding of how the different factors affect the structure will give researchers more control over the structure and properties of this versatile material.

Secondly, more work needs to be done to investigate the effect of water on the modulus. One of the difficulties encountered in this work was a reliable method of determining the extent of drying that each sample had actually undergone prior to rewetting since there was always water retained in the material when the mechanical behaviour changed. One possible solution would be to conduct testing with humidity control in order to determine a critical relative humidity at which the transition from compliant to stiff response occurs. An experimental setup consisting of the compression tester housed in a glove box, a hygrometer and two separate tubes with flowing air (one at 0% relative humidity and one at 100% relative humidity) could be used to create the various conditions by throttling the flow of the lines. Furthermore, it would be of interest to better understand how the mechanism for how water reduces the modulus of the material. This could include experiments that measured the
modulus in droplets of various liquids. Experimental work could be conducted similar to what was done in this work, substituting other liquids for the water. Another experiment could investigate how different liquids affect the self bending of compliant nanoporous gold. An experimental setup for this could involve a cell which could be connected to two sources and a drain, allowing the sample to be constantly submerged while the liquid is replaced. The purpose of this cell would be to determine if a difference in the amount of bending could be measured by changing the liquid. Also, different ligament sizes and relative densities could be examined to see if the reduction in modulus changes based on the surface area available for interaction.

Finally, it is of interest to investigate the mechanical properties of sputtered alloys with varying amounts of platinum to investigate how the dealloying process and nanoporous structure are altered by the platinum. Unfortunately, due to equipment malfunction and lack of time, the mechanical behaviour could not be investigated in this work and rigorous electrochemistry could not be conducted. Since preliminary experiments suggest that there is a significant difference in the behaviour or sputter deposited alloys compared with bulk alloys, more electrochemistry is required to determine an optimized dealloying procedure for these alloys. This would involve potentiostatic dealloying at several potentials and investigation of the microstructures. One of the difficulties encountered in this work was the fabrication of high quality films that would not be suspect to delamination. Heated substrates may improve the quality of films by allowing diffusion during the deposition, presumably resulting in larger grains which may show dealloying behaviour more similar to the bulk alloys. Another possible strategy would be to deposit the gold interlayer and anneal prior to depositing the alloy. This would increase the grain size and possibly encourage larger grains
in the deposited alloy. Producing high quality films would be of highest priority before any meaningful mechanical work could be conducted since the dealloying behaviour is sensitive to the microstructure.
7 References


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8 Appendix A: UHV Sputtering System

8.1 Introduction and Overview

This chapter outlines and explains the operation of the UHV sputtering system. The following section is meant to provide the reader with an overview of how the system functions. More detailed procedures follow in subsequent sections.

The system is divided into two chambers, the loading arm or load lock chamber and the main chamber. Each chamber is connected to its own turbomolecular (or “turbo”) pump backed by a roughing pump. There is a manual gate valve that can be closed to separate the two chambers when the load lock is brought to atmospheric pressures during sample loading.

Figure 8-1. UHV sputter system (load lock chamber on left and main chamber on right)
8.1.1 Pressure gauges

There are several gauges which monitor the pressure in the system. There is a thermocouple gauge located in the foreline between each roughing pump and turbo pump. These gauges can read pressures between $10^{-3}$ Torr and $9.9 \times 10^{-1}$ Torr. The readout from these gauges is located on the digital gauge control [A] and can be displayed by switching the dial from “OFF” to “UHV”. Channel 1 corresponds to the load lock side and channel 2 corresponds to the main chamber side. The readout corresponds to the thermocouple gauge when the “Ion Tube” light is off.

Figure 8.2. Digital gauge control

Figure 8.3. Thermocouple gauge
There is also an ion gauge located in each of the chambers which reads pressure in the $10^{-8}$ Torr to $10^{-5}$ Torr range. The display can be toggled between the thermocouple gauge and ion tube by pressing the “I/T” button. The readout corresponds to the ion tube when the “Ion Tube” light is on. If the chamber pressure is too high, the ion gauge reading will not be displayed and the digital gauge control will beep several times. The ion gauges can take some time to give an accurate reading as particles and gases can accumulate on the filament or in the area around the ion gauge as it heats when turned on and cools when turned off. The pressure reading will drop slowly and may fluctuate for upwards of 30 minutes depending on the condition of the gauge. Generally, time should be allowed for the reading to drop into the low-mid $10^{-7}$ Torr range before sputtering unless the pressure is known to be lower than the reading.

![Figure 8-4. Ion gauge](image)

There are also pressure transducers located in the load lock and main chambers for monitoring elevated pressures when argon is flowed for sputtering. The readout for the load
lock gauge is located on the console above the 4-Channel Readout [C]. It is labeled “LOADING ARM”. The pressure reading is given in mTorr. The readout for the main chamber is located on the MKS PDR-C-1C Power Supply Readout. The units can be adjusted using the dial and is normally set to mm Hg which corresponds to mTorr.

Figure 8-5. Pressure transducers for main chamber (left) and load lock (right)

8.1.2 Explanation of argon flow in the system

There are two argon tanks connected to the chamber, which will be referred to as the “sputtering tank” and “venting tank”. The sputtering tank (closer to the load lock) is used to form a plasma during sputtering. The venting tank (closer to the main chamber) is used for venting the turbo pumps with Ar when the turbo pumps are shut off.
Both argon tanks are connected to both chambers. The venting tank is connected to the vent valves located between the turbo pumps and the roughing pumps. The vent valves are closed when the turbo pump controllers are turned on and opened when the turbo pump controllers are turned off. The valves should be warm when closed because a voltage is applied to close them. Each vent valve is connected to the controller for the corresponding turbo pump. When a turbo pump is turned off (manually or in the event of a power failure), Ar is vented into the system through the corresponding valve.
Figure 8-7. Vent valve

The sputtering tank flows through separate mass flow controllers (MFCs) to each chamber. Directly downstream from each mass flow controller is a green Nupro valve which is normally in the closed position. These valves should not be used to throttle the flow of argon. During sputtering, a constant pressure of argon is desired. Each chamber controls argon pressure in a different manner.

Figure 8-8. Mass flow controllers and Nupro valves for load lock (left) and main chamber (right)
The main chamber contains a butterfly valve downstream from the sputtering tank. The valve is controlled by the MKS Type 252 exhaust valve controller and can be set to allow a specific pressure in the chamber. Thus for the main chamber, a constant argon flow is set while the valve automatically adjusts to a partially closed position to maintain the correct argon pressure.

The load lock chamber does not have such a valve and as such the method of controlling argon pressure is different. To maintain a specific argon pressure in the load lock, the gate valve directly above the turbo pump is set to an almost closed position to raise the pressure of the load lock chamber. The argon output is dynamically controlled by the MFC in conjunction with the flow rate reading from the 4-channel readout.

Figure 8-9. Gate valve located above turbo pump
8.1.3 Water flow in the system

Water cooling is required for the turbo pumps as well as for the sputter guns. Cooling water is contained in the chiller unit and pumped through the various components of the system. The chiller has 2 water loops. The first is connected by red hoses to the mains water supply. The second is connected by clear hoses to the sputter system and will be referred to as “system water”. Each loop is independent, with the mains water cooling the system water. A manifold distributes the water to the various lines and allows the pressure for individual lines to be throttled back using valves. The manifold has 7 lines with 2 going to the turbo pumps, 1 to the main flange with the sputter targets, and 4 to the flow switches under the main flange.

The flow switches ensure a sufficient flow rate of water is provided to the sputter guns. There is electrical continuity across the switches when the flow is greater than 0.25 gallons per minute (gpm). This satisfies one of the requirements for interlock conditions that allow output power to be provided by the power supplies. Interlock conditions include sufficient water flow, sufficient vacuum and the power direction switch set to the desired output (MAIN or LOADING ARM).

Another important issue is the purity of the system water. Type I water is required because of the high resistivity. If the resistivity is too low, there is a power loss at the cathode due to the low impedance provided by the cooling water to the earth ground. This will result in a decrease of the sputtering rate or an increase in the pressure of argon required to initiate a plasma.
8.1.4 Other components

There is a sample stage attached to a track running along the load lock chamber which is used to transfer samples to the main chamber (Figure 10). The load lock chamber also has a sputter etching electrode which is used to clean the substrate surface (Figure 11). In the main chamber there is a wobble stick which is used to remove the sample from the stage and place it on the manipulator (Figure 12). The manipulator is lowered from the bellows using the hand crank located on the north side of the system (Figure 13). The manipulator can be rotated using the Speed Control Unit [K]. The sputtering targets are located at the bottom of the main chamber. There is a shutter covering each of the sputtering targets as well as a shutter for the sight glass.

Figure 8-10. Sample stage on track (as seen through sight glass looking down)
Figure 8-11.  
*Sputter etching electrode*

Figure 8-12.  
*Wobble stick with safety (white) and screw lock highlighted*
8.1.5 General approach

The general approach for sputtering samples is as follows:

- Close gate valve between main chamber and load lock

- Turn off turbo pump for the load lock. Once the turbo pump has stopped spinning, then turn off mechanical roughing pump and vent load lock to atmosphere

- Load sample and turn on mechanical pump back on, then start the turbo pump on the load lock.

- Flow argon into load lock for sputter cleaning

- Move sample under etching electrode and sputter etch to clean surface

- Turn off argon flow and allow pressure to drop

- Open gate valve and move stage to main chamber
- Move sample to wobble stick and move stage back to load lock chamber

- Move sample aside and lower manipulator to loading height

- Place sample on manipulator, then move wobble stick aside

- Lower manipulator to sputtering height

- Turn on rotation for sample and open shutter for appropriate target(s)

- Sputter desired target(s) onto sample, closing shutter over sight glass once plasma is visible

Once samples have been sputtered, the procedure for removing the samples can be traced backwards from the steps listed above. A more rigorous description of the procedure follows.

### 8.2 Instructions for Operating Sputter System

This section outlines the procedure for operating the sputter system. It is important that the user refers to the manuals for the different components as required for further information.

#### 8.2.1 Loading samples

In order to load samples, the load lock chamber needs to be brought to atmosphere. When venting the chamber, it is important to make sure that the chamber does not become pressurized as the sight glasses can easily crack. Follow the steps below to vent the load lock and load samples:
1) Ensure that the Ar tank connected to the vent valves is open and that there is a small flow of Ar (4 psi or less is sufficient). Rather than venting air into the chamber, Ar is used so that contaminants are not introduced into the load lock upon cycling from vacuum to atmospheric pressure.

2) Turn off the turbo pump on the load lock side and wait for it to stop spinning completely. The individual turbine blades should be visible through the top sight glass. This can take upwards of 15 minutes. Since the turbo pump controller has been turned off, the vent valve connected to the turbo pump is now open and Ar is flowing into the chamber.

3) Turn off the roughing pump on the load lock side. Prop the handle on the load lock door open with a piece of cardboard so that when the pressure in the chamber increases above atmosphere, the door will be popped open.

Figure 8-14. Load lock door handle propped open
4) Set the display on the digital gauge control [A] to the thermocouple gauge 1 to read the pressure in the load lock foreline. It should go off scale in the high pressure direction as the chamber is filled with argon.

5) Once the door is opened, the sample holder can be loaded into the sample stage. Gently place the sample holder into the stage by pinching the screws on the holder and sliding it in place. Be cautious to use only as much force as necessary as the railway can be easily damaged.

6) When the sample holder is secured, the door should be held closed as the roughing pump is turned on. Take care not to inhale the fumes that are emitted from the roughing pump.

7) After the roughing pump has been running for a few minutes, the turbo pump can be activated. The pressure in the foreline will not drop until the turbo is activated as the vent valve is opened when the controller is off.

8) Switch on the ion gauge after several minutes and allow it time to stabilize. This can take some time depending on the cleanliness of the chamber as well as the sample.

### 8.2.2 Sputter etching

The sputter etching process removes oxide layers from the surface of the sample. The electrode is based on the principle that when a high positive voltage is applied to a conductor immersed in a partial pressure of gas that a plasma will be produced. For this etching electrode, an anode plate is positioned above the sample. Due to the high positive voltage on the surface of the anode plate, the positive argon ions in the plasma are accelerated away
from the plate towards the sample holder positioned directly under the electrode. To help confine the ions to a region for cleaning, an anode ring is below the anode plate. As the argon ions collide with the surface of the substrate, material is removed.

8.2.3 Implemented safeguards

To operate the etching electrode or the sputtering guns a number of interlock conditions have to be satisfied in order for the power supplies to supply output power.

The Advanced Energy MDX-1K power supplies have an interlock display light on the front panel that will be illuminated when the interlock conditions have been met. The RF plasma products FR5S power supply will flash an “EXT” signal in the two-line display on the front panel of the power supply if the interlock conditions have not been met. If the interlock conditions have not been satisfied, there will be power to the front panel of each power supply but no output power.

To activate any of the power supplies connected to sputter guns in the main chamber:

- The power direction switch must be turned to MAIN
- The water must be flowing through the appropriate gun(s) at the required rate for the flow sensor to activate (0.25 gpm)
- There must be vacuum in the main sputtering chamber as registered by setpoint #1 on the MKS PDR-C1C gauge readout

To activate the MDX-1K power supply connected to the etching electrode in the loading arm (labeled #1):
- The power direction switch must be turned to LOADING ARM

- There must be vacuum in the loading arm chamber as registered by the Trip Point A on the MKS 623/A Baratron (If Trip Point A has been satisfied, the “G<<R pt.A” LED will be illuminated on the back of the Baratron gauge)

- Note that water flow is not required for the etching electrode

8.2.4 *Sputter etching electrode operation*

**NOTE: Do not touch the etching electrode with power supplied to it. Doing so could result in serious injury or death.**

In order to sputter etch samples the following requirements are assumed:

- That the etching electrode height is adjusted such that the sample holder and sample will not touch the etching electrode when it is positioned under the etching electrode

- That there is a sample mounted to the sample holder and that it is in the loading arm chamber

- That the loading arm chamber is under vacuum with the turbomolecular pump running at full speed

- The manual gate valve between the turbomolecular pump and the loading arm chamber is fully open

- The gate valve between the loading arm and the main chamber is closed
- The MKS type 247 4 channel readout and the MKS type 250C pressure/flow controller are turned on and allowed to warm up for the required time specified in the manual.

Electrode operation is detailed below:

1) Turn the MDX-1K power supply OFF from the backside of the unit. Inspect all of the high voltage cables to see that they are attached securely at their ends and that the cable connections are intact.

2) Turn the power direction switch to LOADING ARM.

3) Turn on the breaker at the back of the MDX-1K #1 power supply. Press the main power switch on the front of the MDX-1K #1 power supply and set the setpoint units to watts and the setpoint value to 0.

4) Check that the interlock light is illuminated on the front panel. If the interlock light is not illuminated refer to the Implement Safe Guard section of the etching electrode guide.

5) Set the argon pressure from the sputtering cylinder (the cylinder connected to the MFCs) to between four and eight pound psi.

6) Set channel 2 on the MKS type 247C 4-Channel Readout to ratio control and set the display to read channel 2. Set the pressure for 29 microns. (On the setpoint potentiometer this would correspond to 2.90 with the full-scale range switch set to 0.1V)

7) Open fully the Nupro valve positioned between the mass flow controller and the loading arm chamber. Do not use this valve to throttle the flow of argon.
8) Close the gate valve between the turbomolecular pump and the loading arm chamber until the lower edge of the gate valve handle is positioned at about 4.125” according to the scale on the gate valve. This is to throttle the argon flow. The gate valve will almost be completely closed.

![Gate valve positioning](image)

*Figure 8-15. Gate valve positioning*

9) Adjust the amount that the gate valve is closed so that the mass flow on the 247C 4-Channel readout is between 4 and 15 sccm to maintain a pressure of 29 microns in the loading arm chamber. This may take a couple of minute to stabilize. (As a check the thermocouple gauge in the foreline should be reading in the low $10^{-2}$ Torr range)

10) Adjust power setpoint on the MDX-1K #1 power supply to 25 watts.

11) Position the sample holder over the turbo pump. ( Plasma may not ignite if sample holder is positioned under the etching electrode.)

12) Turn on the output power from the MDX-1K #1 power supply. (The plasma light should ignite and then it will ramp up to about twenty-five watts.)
13) Adjust the power to get an actual output of 25 watts.

14) Position the sample under the etching electrode and wait for minimum of ten minutes.
   To assist in lining up the sample, try to position the visible corner of the sample stage with the centre of the electrode.

15) After the etching is finish, turn off the output power to the etching electrode from the MDX-1K #1 power supply.

16) Close the Nupro valve between the mass flow controller and the loading arm chamber.

17) Open the gate valve between the turbomolecular pump and the loading arm chamber fully.

18) Wait for the pressure to drop before transferring the sample into the main chamber.

8.2.5 Sputtering

Once samples have been cleaned and the pressure in the load lock has dropped into the same range (< 1 order of magnitude) as the pressure in the main chamber (should be in the low $10^{-7}$ range or lower), the samples can be transferred to the main chamber for sputtering. The sample needs to be transferred from the wobble stick to the manipulator which is oriented upside down relative to the sample stage.
Note that if the Ag target is to be used, the power selector must be switched back from “LOADING ARM” to “MAIN”. This is because the power supply is shared between the etching electrode and Ag DC filament controller.

The following steps should be followed for sputtering samples. It is assumed that a cleaned sample is in the load lock and mounted in the sample stage:

1) Open the gate valve separating the main chamber and load lock. Make sure that the valve is completely open so that there is sufficient clearance for the sample stage to pass through. Check that the manipulator height is set to 50 so that it is out of the way.

2) Move the sample stage into the main chamber.

3) Remove safety (white plastic device to inhibit movement) from wobble stick and carefully unlock the wobble stick (by turning screw mechanism) while pulling backwards on it. The vacuum from the system will pull the wobble stick into the chamber when the locking mechanism is removed.

4) Transfer the sample holder to the wobble stick by aligning large holes with screw heads on the sample holder then rotating so that screws are pinched. Note that there is a pin in the middle of the sample stage which must be aligned with a hole in the centre of the wobble stick. When the sample holder is securely gripped by the wobble stick, carefully slide the sample holder out of the sample stage. Turn the sample holder upside down, move the sample aside (wobble stick pulled out) and lock the wobble stick (put the safety on as well).
5) Move the sample stage back to the load lock chamber. Position it as far as possible on the turbo pump side so that when the gate valve between the chambers is closed, the stage will not be hit and damaged.

6) Close the gate valve between the chambers.

7) Lower the manipulator from the rest height (50mm) to the loading height (110mm). The heights are marked on the ruler beside the hand crank. When the height is near 100mm, check that the sample holder is positioned so that it will not be hit by the manipulator. It may be necessary to prop the wobble stick in a certain position.

8) When the manipulator is at the loading height, rotate the manipulator using the Oriental Motor Speed Control Unit [K]. When the hex nut is positioned aligned with the marking, the manipulator should be facing the wobble stick, allowing the sample holder to be slid into the manipulator.

Figure 8-16. Aligning manipulator
9) Unlock the wobble stick (remove the safety first) and gently slide the sample holder into the manipulator. When it is in place, rotate the wobble stick so that the screws are unpinched and sample holder is locked in place. Carefully remove the wobble stick from the sample holder. Move the wobble stick aside again (remember to lock it and replace the safety).

10) Lower the manipulator to the sputtering height (130mm)

11) Set display channel on the 4-channel readout [C] to channel 1. Ensure that for channel 1, the control mode switch is set to flow control. Leave the channel in the off position for now.

12) Open fully the green Nupro valve downstream from the MFC on the main chamber. The main chamber pressure may increase if there is residual Ar in the manifold.

13) Set the butterfly valve on the main chamber to auto mode using the Type 252 exhaust valve controller [B]. The set point will be adjusted so that a pressure of 10 mTorr of Ar can be maintained in the main chamber. This corresponds to a set point value of about 0.10 with the input range set to 1V. Since this is near the bottom of the range, it may be necessary to set the input range to 0.1V and select a set point value of about 1.00 (this may be varied to obtain an appropriate pressure. At the time this document was compiled, a value of 1.75 was used).

   a. Phase and gain setting guidelines:
      i. for LOADING, phase set to 0.5 sec and gain set to 50%
      ii. for MAIN, phase set to 9 sec and gain set to 50%

14) Flow Ar into the main chamber by turning on channel 1 on the 4-channel readout [C].
15) Adjust the pressure in main chamber using the set point on the Type 252 exhaust valve controller [B]. An Ar pressure of 10 mTorr in the main chamber is recommended for Au and Ag sputtering. This corresponds to a reading of 0.0010 on the MKS PDR-C-1C Power Supply Readout [D] when the display is set to mm Hg.

16) Set the rotation speed to 3 and rotate the sample using the Speed Control Unit [K].

17) Turn on the power supply breaker switch on the back of the MDX-1K unit(s) that will be used. Remember that the Ag unit shares power with the etching electrode and the power supply switch must be turned from “LOADING ARM” to “MAIN” if Ag is to be sputtered.

18) Turn on the power switch for the MDX-1K unit(s). Allow to warm up for at least 30 minutes and check that the fan on the back of the unit is working. Ensure that the output power is turned off. Set the output units to watts and change the setpoint value to 0.

19) Open the shutter for the desired target(s)

20) When ready to begin sputtering, check that the interlock light is on. Set the setpoint value on the MDX-1K unit(s) to the desired output wattage. Turn on the output power to start sputtering. Plasma should be visible above the targets. Adjust the power to get the desired actual value.

21) Unlock and close the shutter in front of the sight glass so that material is not sputtered onto the sight glass.
22) When the sputtered layer has reached the desired thickness (a function of time and power, needs to be calculated), turn off the output from the MDX-1K unit(s) and trace backwards through the above steps to return the sample holder to the load lock.

23) Trace backwards from the “LOADING SAMPLES” section to vent the load lock and remove the sample holder.
9 Appendix B: Sample Sputter Rate Calculations

9.1 Calibration of Sputter Targets

The silver, gold and platinum targets were obtained from Super Conductor Materials (Suffern, NY, USA) with purity of 99.9999%. Silver and gold were deposited using DC power supplies while platinum was deposited using a RF power supply. Sputter rates for the targets used were calibrated by depositing at an Argon pressure of 10 mTorr using different powers for a fixed time and then measuring the thickness of the deposited layers with an optical profilometer. Deposition rate was plotted against power applied and the results are presented below.

![Figure 9-1. Ag target calibration](image-url)

\[ y = 2.8765x - 78.321 \]
Figure 9-2.  
**Au target calibration**

Figure 9-3.  
**Pt target calibration**
9.2 Sample sputter rate calculation

The required power for each sputter gun can be calculated based on a fixed sputtering time and sample volume. In this sample calculation we will determine the required powers to produce an alloy with 22 at% Au, 77 at% Ag and 1 at% Pt.

9.2.1 Volume of sputtered material

First we must calculate the sputtered volume for each sample. In this case, we will be using a mask with 3 mm holes and we required our samples to be 1000 Å thick. Therefore the volume for each deposited sample will have a volume given by:

\[ V = \pi r^2 \cdot t \]

\[ V = \pi \cdot \left( \frac{3 \, mm}{2 \, 10 \, mm/cm} \right)^2 \left( 1000 \, Å \cdot 10^{-8} \, cm/Å \right) \]

\[ V = 7.0686 \times 10^{-7} \, cm^3 \]

9.2.2 Number of moles for each element

Next we need to calculate the ratio of atoms relative to each other in order to determine the number of moles for each element. If we take the ratios with respect to silver, we get:

\[ \frac{n_{Ag}}{n_{Ag}} = \frac{77}{77} = 1 \quad \frac{n_{Au}}{n_{Ag}} = \frac{22}{77} = 0.286 \quad \frac{n_{Pt}}{n_{Ag}} = \frac{1}{77} = 0.013 \]
Now we will need the molar volumes for each element. Molar volume calculated by molar mass divided by mass density. The molar volumes for silver, gold and platinum are as follows:

\[
MV_{Ag} = \frac{107.87}{10.5} = 10.3 \\
MV_{Au} = \frac{196.97}{19.32} = 10.2 \\
MV_{Pt} = \frac{195.09}{21.45} = 9.1
\]

To calculate the number of moles of silver:

\[
n_{Ag}MV_{Ag} + n_{Au}MV_{Au} + n_{Pt}MV_{Pt} = V
\]

\[
n_{Ag} \left( MV_{Ag} + MV_{Au} \left( \frac{n_{Au}}{n_{Ag}} \right) + MV_{Pt} \left( \frac{n_{Pt}}{n_{Ag}} \right) \right) = V
\]

\[
n_{Ag} = \frac{V}{\left( MV_{Ag} + MV_{Au} \left( \frac{n_{Au}}{n_{Ag}} \right) + MV_{Pt} \left( \frac{n_{Pt}}{n_{Ag}} \right) \right)}
\]

\[
n_{Ag} = \frac{8.0686 \times 10^{-7}}{(10.3 + 10.2(0.286) + 9.1(0.013))} \\
n_{Ag} = 5.378 \times 10^{-8}
\]

The number of moles for gold and platinum can simply be calculated from the ratios:

\[
n_{Au} = n_{Ag} \left( \frac{n_{Au}}{n_{Ag}} \right) = 1.537 \times 10^{-8}
\]

\[
n_{Pt} = n_{Ag} \left( \frac{n_{Pt}}{n_{Ag}} \right) = 6.945 \times 10^{-10}
\]
9.2.3  Sputtered thickness for each element

The sputtered volume of each element is given by multiplying the number of moles by the molar volume. This value can then be divided by the deposited area to obtain the sputtered thickness of each element.

\[
t_{Ag} = \frac{n_{Ag} \cdot MV_{Ag}}{A}
\]

\[
t_{Ag} = \left( \frac{5.378 \times 10^{-8} \text{mol} \cdot 10.3 \text{ cm}^3/\text{mol}}{\pi \left( \frac{3 \text{ mm}}{2} \right)^2} \right) (10^8 \text{ Å/cm})
\]

\[
t_{Ag} = 776.09 \text{ Å}
\]

Similarly,

\[
t_{Au} = 223.91 \text{ Å}
\]

\[
t_{Pt} = 8.98 \text{ Å}
\]

9.2.4  Power required from each source

The power required from each source can be calculated by substituting the thicknesses and sputtering time into the calibration curves.

\[
\text{Ag deposition rate } \left( \frac{\text{Å}}{\text{min}} \right) = 2.88P + 78.32
\]
\[
Au \text{ deposition rate } \left( \frac{\text{Å}}{\text{min}} \right) = 1.92P + 13.56
\]

\[
Pt \text{ deposition rate } \left( \frac{\text{Å}}{\text{min}} \right) = 0.70P + 8.66
\]

Substituting the appropriate thicknesses and 5 minutes of sputtering time:

\[P_{Ag} = 81.2 \text{ W}\]

\[P_{Au} = 16.2 \text{ W}\]

\[P_{Pt} = 14.9 \text{ W}\]

### 9.3 Calculated powers for remaining alloys

Shown below are the calculated power values for the alloys in this thesis based on the procedure outlined in the previous section.

#### 9.3.1 \textit{Au}_23\textit{Ag}_{77}

<table>
<thead>
<tr>
<th>Component</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>at% Ag</td>
<td>77</td>
</tr>
<tr>
<td>at% Au</td>
<td>23</td>
</tr>
<tr>
<td>at% Pt</td>
<td>0</td>
</tr>
<tr>
<td>mols Au/Ag</td>
<td>0.298701299</td>
</tr>
<tr>
<td>mols Pt/Ag</td>
<td>0</td>
</tr>
<tr>
<td>mols Ag</td>
<td>5.32408E-08</td>
</tr>
<tr>
<td>mols Pt</td>
<td>1.59031E-08</td>
</tr>
<tr>
<td>mols Pt</td>
<td>0</td>
</tr>
</tbody>
</table>
Sputtered thickness of Ag (Å): 768.27
Sputtered thickness of Au (Å): 231.73
Sputtered thickness of Pt (Å): 0.00

Sputtering time (min) 5
Ag power required (W) 80.64
Au power required (W) 17.05

9.3.2 Au$_{28}$Ag$_{72}$

at% Ag 72
at% Au 28
at% Pt 0
mols Au/Ag 0.388888889
mols Pt/Ag 0

mols Ag 4.97593E-08
mols Ag 1.93508E-08
mols Pt 0

Sputtered thickness of Ag (Å): 718.03
Sputtered thickness of Au (Å): 281.97
Sputtered thickness of Pt (Å): 0.00

Sputtering time (min) 5
Ag power required (W) 77.15
Au power required (W) 22.27

9.3.3 Au$_{22}$Ag$_{77}$Pt$_1$

at% Ag 77
at% Au 22
at% Pt 1
mols Au/Ag 0.285714286
mols Pt/Ag 0.012987013

mols Ag 5.37827E-08
mols Ag 1.53665E-08
mols Pt \quad 6.98477 \times 10^{-10}

Sputtered thickness of Ag (Å): \quad 776.09
Sputtered thickness of Au (Å): \quad 223.91
Sputtered thickness of Pt (Å): \quad 8.98

Sputtering time (min) \quad 5
Ag power required (W) \quad 81.19
Au power required (W) \quad 16.24
Pt power required (W) \quad 14.91

### 9.3.4 \textit{Au}_{18}\textit{Ag}_{77}\textit{Pt}_5

at\% Ag \quad 77
at\% Au \quad 18
at\% Pt \quad 5

\begin{align*}
mols \text{ Au}/\text{Ag} & \quad 0.233766234 \\
mols \text{ Pt}/\text{Ag} & \quad 0.064935065
\end{align*}

\begin{align*}
mols \text{ Ag} & \quad 5.60652 \times 10^{-8} \\
mols \text{ Ag} & \quad 1.31061 \times 10^{-8} \\
mols \text{ Pt} & \quad 3.6406 \times 10^{-9}
\end{align*}

Sputtered thickness of Ag (Å): \quad 809.02
Sputtered thickness of Au (Å): \quad 190.98
Sputtered thickness of Pt (Å): \quad 46.82

Sputtering time (min) \quad 5
Ag power required (W) \quad 83.48
Au power required (W) \quad 12.81
Pt power required (W) \quad 25.70

### 9.3.5 \textit{Au}_{27}\textit{Ag}_{72}\textit{Pt}_1

at\% Ag \quad 72
at\% Au \quad 27
at\% Pt \quad 1

\begin{align*}
mols \text{ Au}/\text{Ag} & \quad 0.375
\end{align*}
mols Pt/Ag: 0.013888889

mols Ag: 5.02655E-08
mols Ag: 1.88496E-08
mols Pt: 6.98132E-10

Sputtered thickness of Ag (Å): 725.33
Sputtered thickness of Au (Å): 274.67
Sputtered thickness of Pt (Å): 8.98

Sputtering time (min): 5
Ag power required (W): 77.66
Au power required (W): 21.51
Pt power required (W): 14.91

9.3.6 Au$_{23}$Ag$_{72}$Pt$_{5}$

at% Ag: 72
at% Au: 23
at% Pt: 5
mols Au/Ag: 0.319444444
mols Pt/Ag: 0.069444444

mols Ag: 5.23976E-08
mols Ag: 1.67381E-08
mols Pt: 3.63872E-09

Sputtered thickness of Ag (Å): 756.10
Sputtered thickness of Au (Å): 243.90
Sputtered thickness of Pt (Å): 46.79

Sputtering time (min): 5
Ag power required (W): 79.80
Au power required (W): 18.31
Pt power required (W): 25.69