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Electrochemical design and characterisation of Au_xAg_{100-x} thin films and nanostructures

Vinicius Cruz San Martin

A dissertation submitted to the University of Bristol in accordance with the requirements for award of the degree of Doctor of Philosophy in the Faculty of Science, School of Physics, April 2021

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Abstract

Recent research suggests that Au_xAg_{100-x} alloy films and alloy derived nanostructures (e.g. ordered arrays, nanoporous structure) with controlled geometry, composition and distribution can exhibit a range of new optical phenomena. The controlled electrodeposition of alloy nanostructures is desirable as it could provide pathways for the development of many new applications.

Electrodeposition of Au and Au_xAg_{100-x} alloys is commonly based on cyanide baths. In this work, Au_xAg_{100-x} alloys with different compositions have been electrodeposited using less toxic thiosulphate solutions. Alloys of different compositions (from Au₄₇Ag₅₃ to Au₂₂Ag₇₈) were obtained from solutions with different $Au^+:Ag^+$ ion ratios by constant potential deposition. The XPS analysis of films of different thicknesses (range 20 nm-100nm) showed that the composition of electrodeposited films was homogenous and consistent during growth. In addition to that, the design of nanopatterned alloy structures on transparent substrates for potential plasmonic applications has been demonstrated.

The electrodeposited Au_xAg_{100-x} alloys were used to obtain nanoporous gold (NPG) by selective electrochemical Ag dissolution. The potential at which Ag dissolution takes place, known as critical potential, changed to more positive potentials with the increase of Au content as expected. The resulted porous structures of Au were characterised electrochemically by surface area measurements using Pb underpotential deposition (UPD). It was observed that repeated cycling of Pb UPD on the NPG led to changes in the surface porosity. Following up on the studies of surface-alloying during Pb UPD on Au in our group, Pb UPD was then explored as a 'tool' to alter the size of porosity. Repeated potential cycling of Pb UPD on NPG resulted in 'coarsening' of the porous structure. The study has shown changes in porosity size depending on the number of potential scans, scan rate and the initial size of Au ligaments (i.e. initial alloy composition). Monitoring of the evolution of the NPG structures with cycling was done using electrochemical and surface characterisation.

Surface characterisation of alloys using UPD processes is one of the goals of electrochemical surface science. The electrodeposited Au_xAg_{100-x} alloys were analysed by Pb UPD and Cu UPD processes. Pb UPD has been studied extensively in the past on both pure Au and pure Ag surfaces. The main peaks of Pb UPD characteristic for pure Ag shifted towards more positive values with higher Au content in the alloys. Also, Pb UPD voltammograms on Au_xAg_{100-x} showed an unusual peak in the most negative cathodic direction (around 0.03 V vs Pb/Pb²⁺). A systematic study of Pb UPD on pure Ag films electrodeposited from three different solutions (thiosulphate, perchlorate solution, and surfactant mediated growth (with Pb UPD as mediator)) confirmed that the peak is related to the Ag compound and thiosulphate. In contrast to Pb, Cu is a metal that forms the UPD layer on Au but not on Ag. Cu UPD voltammograms showed similar shifts in the peaks potentials towards more positive values with the increase of Au content in the alloys. The charges measured for the Cu UPD layer (in both sulphate and perchlorate background solutions) decreased with the increase in the alloy's Ag content. The observations and measurements followed a general trend observed on bulk alloys of different composition previously reported.

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Finally I would like to thank my parents, sister, family and friends; which have always helped and encouraged me during my research. Without your continuous support and motivation, this work would not have been possible. I declare that the work in this dissertation was carried out in accordance with the requirements of the University's Regulations and Code of Practice for Research Degree Programmes and that it has not been submitted for any other academic award. Except where indicated by specific reference in the text, the work is the candidate's own work. Work done in collaboration with, or with the assistance of, others, is indicated as such. Any views expressed in the dissertation are those of the author.

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List of abbreviations

AFM	Atomic Force Microscopy
BCFN	Bristol Centre for Functional Nanomaterials
BET	Brunauer-Emmett-Teller
CA	Chronoamperometry
CE	Counter Electrode
CV	Cyclic Voltammetry
DTL	Displacement Talbot Lithography
FCC	Face-Centre Cube
HER	Hydrogen Evolution Reaction
IMFP	Inelastic Mean Free Path
IPCE	Incident Photon-to-Current Conversion Efficiency
LHE	Light-Harvesting Efficiency
LSV	Linear-sweep Voltammetry
MEMS	Micro-electro-mechanical System
ML	Monolayer
MSE	Mercury Sulphate Electrode
NPG	Nanoporous Gold
RE	Reference Electrode
SEM	Scanning Electron Microscopy
SERS	Surface-Enhanced Raman Spectroscopy
SHE	Standard Hydrogen Electrode
SLRR	Surface Limited Redox Replacement
SMG	Surfactant Mediated Growth
STM	Scanning Tunnelling Microscopy
UPD	Underpotential Deposition

WE	Working Electrode
XPS	X-Ray Photoelectron Spectroscopy
XRR	X-Ray Reflectivity

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1 Chapter - Introduction

1.1 Applications of Au, Ag and Au_xAg_{100-x} alloys

Silver (Ag) and gold (Au) are noble metals of particular interest for future plasmonic, catalytic and (bio)sensing applications due to their unique optical properties and coupling with light in the visible range.¹⁻² Recent studies suggest that Au_xAg_{100-x} alloy nanostructures of different geometry, composition and size can exhibit interesting new optical phenomena.³⁻⁴ While most of the research so far has been devoted to understanding the effects of single-metal nano particles' size and shape, there is a newly emerging interest in exploring alloys' optical and plasmonic properties.⁴

Throughout history, gold (Au) and silver (Ag) have been used and appreciated in different decorative applications worldwide. From the mask of Tutankhamun, over the Hall of Mirrors in the Palace of Versailles in France to the baroque altarpiece inside of "San Francisco Javier" Temple in Tepotzotlán, Mexico, gold has been treasured for its value, radiance, and chemical (corrosion) stability. As the most malleable metals, Au and Ag have been extensively used in jewellery. Au and Au_xAg_{100-x} alloys in the form of very thin leaves have been used in paintings and decorations of walls of churches and historical buildings around the world. Colloidal gold nanoparticles have been used in stained glass windows for centuries and have been of interest from Faraday⁵ to modern times in molecular detection and quantum photonics.⁶

Because of its excellent chemical stability, gold has been used in surface coatings as protection from corrosion. The biocompatibility of gold has been well known and used in many different biomedical applications^{2, 6}. Gold is commonly used in microelectronics in packaging for bonding and connectors because of its good properties, such as 310 W/mK and 0.022 $\mu\Omega$ m for thermal conductivity and electrical resistivity at 20 °C respectively, gold is commonly used in microelectronics in packaging for bonding and connectors.⁷⁻⁸ Electrodeposition of gold has been one of the preferred fabrication methods used in microelectronic circuits and micro-electro-mechanical systems (MEMS) for electrical connections, structural layers, adsorber layers and bonding pads on devices.⁸⁻⁹

Silver is another very important noble metal that readily alloys with Au. It has been used for decorative purposes in jewellery, cutlery, cosmetics, and different surface coatings for optical applications. It has been studied extensively due to its antimicrobial ¹⁰⁻¹² and antifungicide¹³⁻¹⁵ properties. Silver is not as stable chemically and biocompatible¹⁶⁻¹⁷ as Au due to oxide formation on the surface. One way to improve stability and avoid oxide formation is by alloying with more noble, chemically stable metals such as Au.

Au and Ag mixing (alloying) has been of great interest as a model system of random solid solution over the whole range of compositions.^{3, 18} The formation of nanoporous gold (NPG) by selective dissolution of Ag from Au-Ag alloys has been central in the theory of dealloying and understanding of the processes during nanoporosity formation.¹⁸⁻¹⁹ The NPG is an important metamaterial with a high surface area that has been explored in applications for sensing, plasmonics, functional electrodes in fuel cells and batteries.²⁰⁻²¹

Many different deposition techniques have been used to produce Au-Ag alloys. The common ways to make bulk samples such as ingots, foils and wires include casting Au and Ag metals followed by cold-rolling and wiredrawing²²⁻²³. The advanced applications of Au-Ag alloys of current interest in sensing and microelectronics require a high control of morphology, crystal structure, and composition on nano-and micrometre length scales, often with complex geometries (such as patterned electrodes, high aspect arrays, nanorods, thin films, etc.)⁷. The growth of Au, Ag and Au-Ag nano-alloys and microstructures via evaporation, spray-pyrolysis, sputtering, and chemical reactions have been explored ²⁴⁻²⁷. However, these methods have limitations regarding the uniform and void-free growth of complex geometries (high aspect ratio features), difficulties of processing in an industrial setting that include low deposition rates, a lot of wasted material, and high cost. Electrodeposition on the other hand is a powerful technique suitable for microfabrication because of its versatility, selectivity, easy control and low cost.^{9, 28-29}

As noble metals with very high metal/metal ion equilibrium potentials, Au and Ag electrodeposition are usually done from solutions with complexing agents^{9, 29}. The most stable and common in industrial processing, are cyanide complexes used in electroplating (under controlled potential or current) and electroless plating.^{9, 29} Due to the well-known toxicity of cyanide to human health and environment, development and applications of

cyanide-free solutions and conditions are of great interest. Free cyanide ions $(CN)^{-}$ also present an issue in the nanoelectronics processing because of the incompatibility with the photoresists used in the circuit patterning, causing their damage and undesired lifting from the substrates.

The goal of 'green' electrodeposition of pure Ag and pure Au has advanced over the last few decades by developing new plating baths based on thiosulphate and sulphite complexes as they are less harmful complexes suitable for microelectronics applications^{7-8, 30-34}. While electrodepositions of pure Au and pure Ag from the thiosulphate solutions have been explored, no reported studies systematically explored electrodeposition of Au-Ag alloys. The control of composition, structure and thickness of alloys would be interesting for designing nanostructured materials that would be useful in a whole range of applications.

1.1.1 Optical and plasmonic properties of Ag, Au and AuAg alloys

The development of new plasmonic materials has been actively pursued due to their broad application potential in bio-sensing^{6, 35}, photovoltaics³⁶⁻³⁷, and catalysis³⁸. These materials use the strong interaction between light and the free electron oscillations on the surface of metals, leading to an electric field enhancement^{1, 39-42}.

Metals are, in general, highly reflective for low frequencies of electromagnetic (EM) radiation up to the visible light. At higher frequencies (near-infrared and visible light regions), light penetrates significantly. At ultraviolet frequencies, metals exhibit dielectric character and allow light propagation with different degrees of attenuation dependant on the electronic band structure. For example, for noble metals such as Au and Ag, transitions between the electronic bands lead to strong adsorption in this part of the EM spectra. These dispersive properties of metals can be explained by the complex dielectric function⁴³:

$$\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$$
 Eq. 1.1

The $\varepsilon(\omega)$ at optical frequencies can be experimentally measured by reflectivity and determination of the complex refractive index function:

$$\tilde{n}(\omega) = \sqrt{\varepsilon} = n(\omega) + i\kappa(\omega)$$
 Eq. 1.2
 $\varepsilon_1 = n^2 - \kappa^2$ and $\varepsilon_2 = 2n\kappa$ Eq. 1.3

where *n* is the refractive index, and κ is the extinction coefficient. κ determines the optical adsorption of EM wave propagating through the metal, which means that the imaginary part of the dielectric function describes the adsorption of light inside the material. On the other hand, the real part quantifies the lowering of the velocity of light due to the polarisation of the material.

The electrons in metals have resonance modes (of frequency ω_p) that we call plasmons^{39, 42}. *The plasma model* (also called the Drude model) is used to describe the optical properties of metals. In the model, a gas of free electrons moves in the field of positive ion cores. The details of the crystal lattice potential and electron-electron interaction are neglected. The assumption is that some aspects of the band structure are incorporated in the effective optical mass of each electron. The model will be described below.

The electrons can ne be considered to oscillate in the electromagnetic field, and their motion is damped with characteristic collision frequency $\gamma = \tau^{-1}$ (of the order of 100 THz), where τ is known as the relaxation time of the free electron gas (~10⁻¹⁴ s) at room temperature. The equation of motion for an electron movement of plasma gas subjected to external electric field *E* is given by

$$m\frac{d^2x}{dt^2} + m\gamma\frac{dx}{dt} = -eE$$
 Eq. 1.4

where m is the mass of the electron and e is the charge of the electron.

If $E(t) = E_0 e^{-i\omega t}$, i.e. we consider harmonic time dependence of the field, the solution of the equation that describes the oscillations of the electron as:

$$x(t) = \frac{e}{m(\omega^2 + i\gamma\omega)}E(t)$$
 Eq. 1.5

The polarisation is the dipole moment per unit volume, is then

$$P = -nex = -\frac{ne^2}{m(\omega^2 + i\gamma\omega)}E$$
 Eq. 1.6

It is known that the dielectric displacement field is related with the polarisation by

$$D(\omega) = \varepsilon_0 E(\omega) + P(\omega) = \varepsilon_0 \varepsilon_r(\omega) E(\omega) \text{ Eq. 1.7}$$

Then, the relative dielectric function can be defined as

$$\varepsilon_r(\omega) = 1 + \frac{P(\omega)}{\varepsilon_0 E(\omega)} = 1 - \frac{ne^2}{\varepsilon_0 m(\omega^2 + i\gamma\omega)} = 1 - \frac{\omega_p^2}{(\omega^2 + i\gamma\omega)}$$
 Eq. 1.8

The real and imaginary components in Eq. 1.1 are:

$$\varepsilon_1(\omega) = 1 - \frac{\omega_p^2}{\gamma^2 + \omega^2}$$
 and $\varepsilon_2(\omega) = \frac{\omega_p^2 \gamma}{\omega(\gamma^2 + \omega^2)}$ Eq. 1.9

where the plasma frequency $\omega_p{}^2\,$ of the free electron gas is defined as

$$\omega_p^2 = \frac{ne^2}{\varepsilon_0 m} \qquad \qquad \text{Eq. 1.10}$$

In the range of frequencies of $\omega < \omega_p$ we can consider the following case:

a) for the negligible damping, i.e. frequencies close to ω_P , the dielectric function is real:

$$\varepsilon(\omega) = 1 - \frac{\omega_p^2}{\omega^2}$$
 Eq. 1.11

b) for considerable damping, i.e. for the low frequencies, the dielectric function is predominantly imaginary (ε_2 " ε_1) and the metals in this region are adsorbing.

$$n \approx \kappa = \sqrt{\frac{\tau \omega_p^2}{2\omega}}$$
 Eq. 1.12

For the transverse waves in the frequency regime of $\omega < \omega_p$, the propagation of transverse waves is forbidden, and only longitudinal waves can occur.

II) In the range of frequencies $\omega > \omega_p$, the transverse waves can propagate. This is the transparency regime. The dispersion relation of the travelling wave with the wave vector k is given as:

$$\omega^2 = \omega_p^2 + k^2 c^2$$
 Eq. 1.13

Volume plasmons - Following the analysis above, it can be concluded that the plasma frequency ω_p has a specific meaning. First, we can see that at the low damping limit, Eq. 1.10 $\varepsilon(\omega_p) = 0$. Such excitation corresponds to a collective longitudinal mode of electrons motion. From Eq. 1.7, we can see that the electric field is a pure depolarisation field in this case. This can be understood as the electric field created by a collective longitudinal oscillation of the electron gas versus a fixed positive background of ion cores. For the collective displacement *u* of the electron cloud (*Ne*) create the dipole establishing the electric field $E = Neu/\varepsilon_0$ so the electrons experience a restorative force (-NeE), and their motion can be described by equation

$$Nm^* \frac{d^2 u}{dt^2} = -NeE = -\frac{N^2 e^2}{\varepsilon_0} u \qquad \text{Eq. 1.14}$$
$$\frac{d^2 u}{dt^2} + \omega_p u = 0 \qquad \text{Eq. 1.15}$$
$$\omega_p = \frac{ne^2}{m^* \varepsilon_0}. \qquad \text{Eq. 1.16}$$

Therefore, the frequency ω_p can be recognized as the natural frequency of free electron cloud. These oscillations are called 'volume plasmons' distinguished from 'surface plasmons' that we will describe in the next section.

Surface Plasmons - When light (EM wave) interacts with the metal surface, it couples with the electrons plasma oscillations, resulting in *surface plasmons* that can propagate at the interface between the dielectric and conductor.

We can consider the case of a metal surface in contact with a dielectric media of dielectric constants ε_m and ε_d respectively. For the propagating electromagnetic wave at the surface (in the x-direction), only transversal magnetic modes (TM) will exist, as illustrated in Fig. 1.1 a). The electric and magnetic components of the TM wave will be harmonic solutions for both media^{39, 43-44}. The conditions for these fields are that the magnetic component in the y-direction (*Hy*) and the electric component in z-direction (*Ez*) are the same value at the surface for both media. Also, it is known that⁴⁴

$$k_{xm}^2 + k_{zm}^2 = \left(\varepsilon_m \frac{\omega}{c}\right)^2$$
 Eq. 1.17

where c is the speed of light and k_{xm} and k_{zm} are the x and z components of the wave vector in the metal, respectively⁴⁴. Analogously, a similar expression can be obtained for the wave vectors components in the dielectric media. Including the harmonic solutions in Maxwell's equations, and considering the boundary conditions and Eq. 1.16, it can be obtained⁴³⁻⁴⁴

$$\frac{k_{zm}}{\varepsilon_m} + \frac{k_{zd}}{\varepsilon_d} = 0 \qquad \text{Eq. 1.18}$$

As the wave vector along the x direction needs to be the same in both media, k_x , then the following dispersion relation for the surface plasmon (SP) moving along the surface can be obtained^{39, 43-44}

$$k_x = k_{SP} = \frac{2\pi}{\lambda} \left(\frac{\varepsilon_m \varepsilon_d}{\varepsilon_m + \varepsilon_d}\right)^{1/2}$$
 Eq. 1.19

Looking at the dispersion relation for the optical frequencies, the real part of ε_m is negative. Considering an imaginary component of both dielectric constants is small, then k_{SP} is purely real if the real part of ε_m is smaller than $-\varepsilon_d$ ⁴⁴. The coupling of light with the oscillating electrons has resonance modes (frequency ω_{Sp}) that we call surface plasmons^{39, 42}. In the case of the metal surface, the incident light forms a quantized oscillation of plasma, called *surface plasmon polariton*.

The electric field decays exponentially with the distance from the surface, as seen in Fig. 1.1 b), with the decay in the metal side being faster than on the dielectric side. The plasmons' exponential decay indicates that they are bounded to the surface and do not emit any electric field far from it³⁹. The penetration depth in the dielectric and metal are given by the inverse of the imaginary components of k_{zm} and k_{zd} :⁴³⁻⁴⁴

$$\delta_d = \frac{\lambda}{2\pi} \sqrt{\frac{\varepsilon_d + Re(\varepsilon_m)}{-\varepsilon_d^2}} \quad \text{Eq. 1.20}$$
$$\delta_m = \frac{\lambda}{2\pi} \sqrt{\frac{\varepsilon_d + Re(\varepsilon_m)}{-Re(\varepsilon_m)^2}} \quad \text{Eq. 1.21}$$

Another characteristic of surface plasmon polaritons is the propagation length that corresponds to the distance where the intensity is reduced to 1/e of the maximum value obtained from^{1, 39, 43-44}

$$L_{\chi} = \frac{\lambda}{2\pi} \frac{(Re(\varepsilon_m))^2}{Im(\varepsilon_m)} \left(\frac{\varepsilon_d + Re(\varepsilon_m)}{\varepsilon_d Re(\varepsilon_m)}\right)^{3/2} \qquad \text{Eq. 1.22}$$

Because metals contain many electrons and have a low dispersion at frequencies lower than ω_p , plasmons are sustained⁴⁵. Plasmon frequency will depend on the material used, such as the composition, size and shape of particles⁴⁶⁻⁴⁷. Plasmons can be manipulated depending on the material used, the size and shape of the material to match a wavelength^{6, 37, 48-49}.



Fig. 1.1. a) Surface plasmon polaritron formed at the surface of a metal and b) electric component of a surface plasmon with distance from the surface³⁹. The electric field in the direction perpendicular to the surface decays exponentially, which indicates that the plasmon stays at the surface. Figure adapted from Ref³⁹.

In the case of metallic nanoparticles, the incident light has a wavelength bigger than the size of particles, which results in the displacement of the free electrons forming a dipole. As illustrated in Fig. 1.2, the attractive Coulomb force between the electrons and nuclei acts as a restoring force resulting in the electron cloud's oscillations. In this case, the oscillation of the electron cloud is referred to as *localized surface plasmons (LSP)*. These plasmons oscillate at the interface of a nanoparticle conductor and a dielectric ^{39, 42, 45, 47}. Considering the simplest case of spherical particles of radius R smaller than the wavelength of the incident light, as in Fig. 1.2, then the electrostatic potential in spherical coordinates for this case is divided in the section inside and outside of the particle and can be written as⁴⁴

$$\phi(r,\theta,\varphi) = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} a_{lm} r^{l} Y_{lm}(\theta,\varphi), for \ 0 \le r \le R \text{ Eq. 1.23}$$

$$\phi(r,\theta,\varphi) = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} b_{lm} \frac{1}{r^{l+1}} Y_{lm}(\theta,\varphi), for \ r \ge R \text{ Eq. 1.24}$$

where $Y_{lm}(\theta, \varphi)$ the spherical harmonic function. Using the boundary conditions that the potential at the centre of the particle and infinity is zero, that the potential and the derivative $\varepsilon \frac{\partial \varphi}{\partial r}$ must be the same at the radius R, then the dispersion relation can be obtained⁴⁴

$$\frac{\varepsilon_m}{\varepsilon_d} + \frac{l+1}{l} = 0 \qquad \text{Eq. 1.25}$$

where *l* is a positive integer.

Considering the metal dispersion, according to Drude

$$\omega_l = \omega_p \left(\frac{l}{\varepsilon_d(1+l)+l}\right)^{1/2}$$
 Eq. 1.26

The case of l = 1 corresponds to a dipole mode, which corresponds to the spherical particle. In this case, the electric field outside the particle can be seen as⁴³⁻⁴⁴

$$E_{out}(x, y, z) = E_0 \hat{z} - \left(\frac{\varepsilon_m - \varepsilon_d}{\varepsilon_m + 2\varepsilon_d} R^3 E_0\right) \left(\frac{\hat{z}}{r^3} - \frac{3z}{r^5} (x\hat{x} + y\hat{y} + z\hat{z})\right) \quad \text{Eq. 1.27}$$

When considering electrostatics, the polarisability α can be written then as⁴³⁻⁴⁴

$$\alpha = \frac{\varepsilon_m - \varepsilon_d}{\varepsilon_m + 2\varepsilon_d} R^3 \quad \text{Eq. 1.28}$$

Equation 1.27 shows that α depends on the size of the particle.



Fig. 1.2. Schematic of Localized surface plasmon oscillations. Figure taken from Ref⁴⁹.

Ag and Au are considered the best plasmonic materials in the visible light region due to their low energy loss and high coupling of plasmons^{4, 42, 50}. Silver is a metal that exhibits many advantages over gold, such as higher extinction coefficients in the blue and UV region of the EM spectrum, sharper extinction bands and extremely high field enhancements. Au is the second-best plasmonic material in the visible region. Both Au and Ag have a low imaginary component of dielectric constant, attributed to a very low energy loss^{39, 51}, as illustrated in Fig. 1.3.



Fig. 1.3. Au dielectric function *a*) real and *b*) imaginary components. Ag dielectric function *c*) real and *d*) imaginary components. Figure taken from ⁵¹.

Au and Ag nanoparticles with different sizes and shapes exhibit properties that can be exploited in photovoltaics^{36, 48} and sensors. In Surface Enhanced Raman Spectroscopy (SERS), the Raman signal of an adsorbed molecule could be significantly enhanced due to the surface plasmons.^{1, 6}

1.1.2 Nanoporous gold

Another material of interest that can be obtained from Au-alloys is nanoporous gold (NPG). NPG is a well-known metamaterial derived from the Ag_xAu_{100-x} alloys by selective dissolution of Ag by a process called dealloying. NPG can be described as a bi-continuous structure composed of the interconnected network of solid (Au) ligaments and voids (or pores)^{19, 21, 52} as seen in Fig. 1.4.¹⁹



Fig. 1.4. SEM images of a nanoporous gold film obtained from the dissolution of an $Au_{32}Ag_{68}$ in nitric acid under free corrosion conditions. a) A cross-section and b) a planar view of the bicontinuous ligament-hole structure. Figure taken from Ref ¹⁹.

NPG is an extensively studied material due to its unique structure that can be exploited in many applications. Because the sizes of ligaments and pores are in the nanometer regime, NPG could be used for optical applications such as Surface Enhanced Raman Spectroscopy (SERS)⁵³⁻⁵⁵ or Surface Enhanced Fluorescence⁵⁶. Due to the high surface area, this material has been studied for biosensing⁵⁷ and catalytic^{20, 57-60} applications. Due to high surface stress originating from charge changes at the surface, NPG shows a macroscopic strain that could be used for actuation⁶¹⁻⁶² and sensing⁶¹⁻⁶³. An actuator is a material that can change its physical properties, getting compressed or stretched, due to some energy, such as electric, chemical or heat⁶¹. Different surrounding media can induce compression of the sample, which could be used as a chemical characterisation to identify the electrolyte or gases for chemical actuation.⁶³

The structure of NPG varies due to different factors ^{18-19, 64-65}. The porosity size depends on the composition of the precursor alloy used, the dealloying method used (such as the scan rate used for dissolution) and the temperature at which dissolution takes place¹⁸. The interest in this material rises from the unique structure and ligament size of NPG, which can range from a few nanometres (~5 nm) to 100 nm, which directly affect the material properties (such as the mechanical, photocatalytic, optical and plasmonic properties). Recent work suggests that nanoporous gold electrodes derived from Au-Ag alloys show both propagating and localized surface plasmon resonances⁶⁶.

The increased interest in nanoporous plasmonics⁵⁴ suggests that optimising the plasmonic properties of nanoporous metals for SERS depends on the structure and size of metal ligaments and pores of the NPG structures. In the most recent work by Jalas et al., optical transmission of light from the NPG can be tuned by electrochemical processes that affect the ligament size.⁶⁷ There is still a lack of clarity and disagreement in the literature on what NPG structure parameters give rise to different plasmonic responses^{53-54, 68}. Moreover, there is very little knowledge about the effects of different electrochemical surface processes on porosity. Understanding this will enable easier tuning of the porosity scale, impacting a broad range of future optical and sensing applications of NPG.

1.2 Au_xAg_{100-x} alloys characterisation

1.2.1 Au_xAg_{100-x} alloys Phase diagram

Au and Ag have a range of similar physical properties. Both metals have the face centre cubic (fcc) crystal structure and lattice parameter of 4.08 Å ^{3, 69}. The difference in electronegativity of 0.61 is high between Au and Ag, which might increase the alloys' ordering and avoid phase separation⁶⁹.

The Au–Ag system has complete solid solubility over the whole range of compositions and has one of the simplest phase diagrams. The enthalpy of mixing for the bulk alloy is negative $\Delta H_{mix} = -48 \text{ meV}/\text{atom}$, which suggests that no additional energy is required to form an

alloy. Also, the excess in entropy of solid solutions is $\Delta S_{mix} = -11.12 \text{ meV/atom}^{69}$. The bulk phase diagram of Au_xAg_{100-x} alloys is known as isomorphous. The temperature at which the solid-liquid phase transition occurs increases for more Au rich bulk alloys⁷⁰, as shown in the phase diagram in Fig. 1.5 a). The phase diagram changes depending on the sample size, as seen in Fig. 1.5 b). The transition between the solid and liquid phase shifts towards lower temperatures for samples with nanometric features.

Following the regular solid solution model, the phase diagram can be calculated and constructed.^{3, 71} The most recent computational calculations of the phase diagram can be constructed to show the effects of nanoscale size⁷² and shape^{3, 72}.



Fig. 1.5. Phase diagrams of Au_xAg_{100-x} *, for: a) bulk alloys ⁷⁰. The figure is taken from Ref ⁷⁰, b) nanophase Au-Ag alloys of different sizes calculated using Fact Sage Module. The figure is taken from Ref ⁷².*

1.2.2 Dealloying of Au_xAg_{100-x} alloys and formation of NPG

Formation of NPG structure is obtained by dealloying of a bimetallic alloy. Different dissolution methods can be used to form NPG structures, such as chemical and electrochemical. Chemical dissolution of alloys can be done by immersing the alloy in acid such as nitric acid for a given amount of time. Electrochemical dissolution can be done during a potential sweep or at constant potential/current. During a potential sweep, the dissolution of the less noble metal is monitored. The potential at which dissolution of the less noble metal takes place is called the critical potential^{18, 73-74}. The dealloying critical potential for bulk alloys depends on the alloy composition, and it is a kinetically determined morphological transition.⁷³ The illustration of a typical current/potential behaviour during electrochemical sweep is shown in Fig. 1.6. At low potentials, below the critical potential, there is a passivation-like behaviour.⁷⁴⁻⁷⁵ After a critical potential is reached, the current increases steeply, and the less noble metal dissolves from the alloy.



Fig. 1.6. Schematic of the current/potential behaviour of selective dissolution of a less noble component from an alloy. The critical potential is associated with the transition of the current. Two dashed vertical lines illustrate that defining a critical potential is not sharply defined. The figure is taken from Ref⁷³.

The bimetallic alloy composition affects the critical potential, shifting the potential towards more positive values when the composition of the more noble metal increases⁷³, as seen in Fig. 1.7. The value of the critical potential is also affected by the electrolyte composition and scan rate. The lower scan rates result in a more positive critical potential value, as well as a better-defined measurement. The critical potential is also more negative for the lower concentration of metallic ions in the solution.^{19, 73}



Fig. 1.7. Linear sweep voltammetries of Ag dissolution in 1 M AgClO₄ + 1 M HClO₄ of different Au_xAg_{100-x} alloys⁷³. The critical potential shifts towards more positive values with a decrease of Ag content. Figure taken from ⁷³.

Another electrochemical method to determine the critical potential is to consider the current behaviour at different potentials. Instead of applying a potential sweep, the potential is maintained fixed, and the current is measured over time. To determine the critical potential, several potential values are selected. The experimental measurements and the simulations show that the current transients have a distinctly different shape below and above the critical potential, as illustrated in Fig. 1.8.⁷⁴



Fig. 1.8. Dissolution curves of $Au_{0.25}Ag_{0.75}$ alloys by fixing the dissolution potential and measuring the current evolution through time. Figure taken from Ref ⁷⁴.

1.2.3 Formation of Au_xAg_{100-x} alloys

Au_xAg_{100-x} alloys could be prepared using different growing techniques. Smelting of the pure metals in various ratios and cooling to obtain the alloys is a standard metallurgical method to obtain bulk alloys. Thin alloy films can be prepared using physical vapour deposition techniques such as electron beam evaporation⁷⁶ or sputtering deposition of both metals.⁴ Another alternative is induction heating or in situ thermal annealing following thin Ag films' evaporation onto Au substrates or vice versa.⁷⁷⁻⁷⁸ The formation of the homogeneous thin film alloys is driven by interdiffusion of Ag and Au that takes place at relatively low temperature (~150°C) on polycrystalline films and multilayers.⁷⁷⁻⁷⁸

Many applications such as sensors or nano-optics require specific shapes and sizes of particles usually obtained in combination with lithography and electrodeposition. Electrodeposition of Au usually is done in industry by using cyanide-based baths⁷⁹. Au and Ag electrochemical (electro/electroless) deposition from cyanide complex baths have been extensively used in the electronics industry, particularly for metallisation of microelectronics components on different substrates templated geometries. For example, the most exploited baths (some of them still in active industrial use) are alkaline cyanide electrolytes using $[Ag(CN)_2]^-$ and $[Au(CN)_2]^-$ complex in solutions with excess free cyanide.^{9, 29} Alloy

electrodeposition from these solutions on n-type Si(111) was studied by Marquez et al.⁸⁰ Their study showed the potential dependent composition of alloys. Moreover, their kinetic study showed that using a two-step potential (with the second step being in the charge transfer regime), the homogeneity of films could be improved.⁸⁰

The voltammetric behaviour and interfacial chemistry of gold-silver alloy electrodeposition from alkaline cyanide baths have been investigated in detail with FTIR and SERS studies.⁷⁹⁻ ⁸² In the case of deposition using Au and Ag cyano-complexes in cyanide-free solutions, alloys of different compositions varying from 13% to 75% of Au for different deposition potentials have been reported⁷⁹. Different structures such as macrocrystalline, globular, cauliflower and dendritic have been observed at different potentials. A SERS study showed specific spectral features of $C \equiv N$ bonds only present on alloys, different from those observed during depositions of pure Au or Ag solutions⁷⁹. Electrodeposition of Au, Ag and Au-Ag alloys has also been explored from citrate⁸³ and pyrophosphate-baths⁸⁴⁻⁸⁵ in the presence of organic and inorganic additives as an alternative to the high cyanide baths. In these solutions, cyanide was used as a stable complex form of gold or silver (no free cyanide ions). In the case of pulse plating deposition of Au-Ag alloys from pyrophosphate-baths, alloy compositions between 36% and 44% mole Au have been reported by varying the pulse and pause times, with more Au-rich alloys obtained for a higher pulse time⁸⁶. If the current and the pulse time are controlled, alloys between 46% and 70% mol Au have been reported, with alloys containing more Au for the cases of higher current values applied⁸⁶. The alloys electrodeposited from pyrophosphate-baths using brightener additives such as polyethyleneimine (PEI) and KSeCN alloys showed structural dependence in the type and concertation of additives on the grain size measured by X-ray diffraction⁸⁵. It was also shown that alloys' composition could vary from ca. 26 wt% Au for lower current densities to ca. 75 wt%⁸⁵ for higher current densities.

A 'greener' electrodeposition of pure Ag and pure Au based on thiosulphate and sulphite complexes have been explored activly^{7-8, 30-34}. In contrast to the cyanide-based solutions, no systematic studies of Au-Ag alloys deposition from these solutions have been conducted. The aspects of electrodeposition of alloys from the thiosulphate solutions will be presented in Chapter 3.

1.2.4 Properties and characterisation of Au_xAg_{100-x} alloy thin films

There is an increased interest in manipulating metals' dielectric functions by alloying and understanding how materials' optical properties depend on alloy concentration. In several recent studies, the dependence of the optical constants for noble metal alloys films on alloys of varied composition has been reported and debated.^{4, 76, 87-88}

Au_xAg_{100-x} is a model system that has been studied a lot. The results have shown different optical properties compared to pure metals and a deviation from a simple linear combination (average) of their values. Systematic measurements of optical constants on evaporated films of different compositions and thicknesses (from 30 nm to 300 nm) were studied using spectroscopic ellipsometry and custom-designed optical setups for simultaneously measured transmission and reflectance of light.

Fig. 1.9 shows the change of the real component of the dielectric function obtained from two different methods, from surface plasmon polariton (SPP) and ellipsometry (Ellip.). It can be seen that both methods of measurement show similar values of the real component of permittivity, and the change follows a non-linear trend with Au_xAg_{100-x} alloy composition⁴. The optical constants' measurements have been in agreement with the calculations based on the fitting of ellipsometry measurements. Different studies disagree on the trends of measured values, which could be attributed to the deposited films' differences in quality and structure (roughness). ^{4, 76, 87-88}


Fig. 1.9. The real component of the dielectric function ε_1 of Au_xAg_{100-x} alloys at 637 nm. The real component was obtained from two different methods, surface plasmon polariton excitation (SPP) and ellipsometry (Ellip.). Thin films were prepared using co-deposition sputtering. Figure taken from Ref⁴.

In terms of photovoltaics application, it has been shown that the alloys incident photon-tocurrent conversion efficiency (IPCE) is better than the pure gold by 3.1 times⁴⁸, which is similar to Ag as demonstrated in Fig. 1.10. The peak for light-harvesting efficiency (LHE) Ag values are around 400 nm, for Au₅₀Ag₅₀ alloy is about 550 nm. In contrast, for Au, it is near 650 nm. This illustrates that alloys of different compositions can be identified from the peak wavelength position, and the percent of the light that can be harvested (used) is around 50 to 60%.



Fig. 1.10. Incident photon-to-current conversion efficiency (IPCE) for Ag, Au₅₀Ag₅₀, Au nanoparticles and single-layer graphene as a control device for photovoltaic applications⁴⁸. The inset corresponds to the light-harvesting efficiency (LHE) of the samples, which corresponds to the ratio of absorbed to incident light as a function of the wavelength. Figure taken from Ref⁴⁸.

1.3 Underpotential deposition applications in thin film growth and surface characterisation

Underpotential deposition (UPD) is an electrochemical phenomenon where a metal electrodeposits epitaxially 1-2 monolayers (ML) on top of a foreign substrate at the potentials positive from the Nernst equilibrium potential for bulk deposition⁸⁹⁻⁹¹. Some of the main characteristics of the UPD processes include:

i) potential dependant deposition with adsorption like behaviour;

ii) substrate structure dependant nature (i.e. sensitivity to the surface crystal structure)

iii) interaction of anions in the solution with the substrate and the UPD layer; anions can coadsorb and play an important role on the monolayer structure.⁹² The formation of a UPD ML proceeds at stages often detected as peaks in the CV. Fig. 1.11 illustrates the Cu UPD on Au(111) in sulphate solution that proceeds in two steps. This is one of the most studied and well known UPD systems in which a pseudomorphic ML of Cu is formed on Au(111) assisted by sulphate co-adsorption. The most positive peak labelled A in Fig. 1.11 a) is the formation of a low-density phase of 2/3 ML known as honeycomb or $(\sqrt{3} \times \sqrt{3})R30^{\circ}$ phase.^{89-90, 93} The second peak, labelled B in Fig. 1.11 a) is a deposition of additional 1/3 ML and the formation of (1×1) structure of Cu ML. The coverage-potential isotherm is shown in Fig. 1.11 b) from which it can be observed that the low-density phase is stable between the potentials of its formation and the start of the second stage.



Fig. 1.11. A) CV of Cu UPD on Au(111) in 0.05 $M H_2SO_4 + 1 mM CuSO_4$ with a scan rate of 1 mV/s and b) adsorption isotherm for the Cu UPD on Au(111) with the schematics of Cu structure at different stages of ML of formation. Peak A corresponds to the formation of a honeycomb low-density phase and B to a (1 x 1) structure of 1 ML of Cu. The image is taken from Ref⁸⁹.

Due to the unique aspects of surface interactions between the UPD metal and substrate, structure and chemical sensitivity UPD processes have been exploited as a tool for surface characterisation and thin film growth.

The UPD voltammograms vary depending on the surface crystal structure, which can be used to identify the surface orientation⁹⁰. The charge of a metal deposited in the UPD region on top of a substrate can be used to obtain its electrochemical active surface area⁹⁴⁻⁹⁶, which can be used as an alternative to other methods for surface area measurements. For example, Pb UPD on Au has been used for measuring the area of NPG as a better alternative to Brunauer-Emmett-Teller (BET) gas adsorption technique⁹⁷, and Cu UPD has been used to evaluate the active area of Pt catalytic surfaces for fuel cells applications.⁹⁶ During the sample preparation for BET, annealing is applied to remove any adsorbed molecules and clean the surface⁹⁸. However, for nanoporous gold, the annealing affects the initial surface area^{54, 99}. Also, some considerations are made for calculating the surface area using BET, such as forming a uniform monolayer of the adsorbed molecules, which could be different for molecules adsorbed on pores at the surface than inside the bulk porous films¹⁰⁰. For these reasons, the BET is not the most reliable technique for surface area measurements of NPGs⁹⁷.

The UPD metals have been used as mediators and sacrificial layers for the epitaxial growth of thin films. Some of the methods include the Surface Limited Redox Replacement (SLRR)¹⁰¹⁻¹⁰³, Surfactant-Mediated Growth (SMG)¹⁰⁴⁻¹⁰⁵ and Defect Mediated Growth (DMG)^{101, 106-107}. In the case of SLRR, a UPD layer of Cu or Pb is formed on top of the substrate, which is then replaced by a more noble metal (such as Pt, Au, Pd) spontaneously by galvanic displacement at the open circuit. The process can then be repeated to obtain films of different thicknesses¹⁰¹.

In the case of SMG, the growth of metal is assisted by using foreign UPD metal which serves as a surfactant layer¹⁰⁴. The UPD metal forms a floating layer on top of the depositing metal. The SMG method has been demonstrated for quasi-2D growth of ~200 ML of Ag films on Au (111)¹⁰⁴ and epitaxial growth of Cu on Ru(0001)¹⁰⁵ using the Pb UPD surfactant layer.

In the case of DMG, electrodeposition of a growing metal is assisted by a mediator UPD metal that is periodically, reversibly deposited and stripped from the surface ¹⁰⁶⁻¹⁰⁷. This

method uses UPD metal as a mediator to manipulate the kinetics of growth. In each cycle of UPD metal deposition, a new population of nuclei on the surface is formed, assisting faster growth and merging into a continuous layer. The DMG has been used in the deposition of epitaxial films of Ag on Au(111)¹⁰⁶, Cu on Au(111)¹⁰⁷ and Ru(0001)¹⁰⁵.

Surface characterisation of alloys using electrochemical processes has been an area of interest of the electrochemical community.^{65, 108-110} The UPD voltammograms depend on the nature of the substrate. Several studies in the past focused on understanding the aspects of UPD formation on alloy surfaces and the correlation with the alloy composition. For example, Fig. 1.12 shows Cu UPD stripping from bulk Au-Ag alloys of different compositions.¹¹⁰ Cu is known to form a UPD layer on Au electrodes but not on Ag electrodes. The results have shown that the charge associated with the UPD decreased with increasing Ag atomic fraction in the alloy.¹¹⁰



*Fig. 1.12. Cu UPD stripping waves from Au-Ag alloys of different compositions. Scan rate 20 mV/s. Figure adapted from Ref*¹¹⁰.

In the studies of Cu UPD on Pt-Pd¹⁰⁸ and Pt-Ru¹⁰⁹ alloys where Cu forms UPD layers on both metals, making correlations with the alloy composition is more challenging. The voltammograms change, and the peaks shift due to the UPD metal interacting with the surface of the alloy locally ¹⁰⁹⁻¹¹⁰.

1.4 Aims and thesis overview

The main goals of the PhD project included:

1) Development of Au_xAg_{100-x} films of different compositions by electrodeposition from thiosulphate solutions. The effect of electrodeposition potential in solutions with different $Au^+:Ag^+$ thiosulphate complexes on the structure and composition of alloys was explored. The electrodeposited alloys' structure was examined by a range of surface characterisation techniques (such as XPS, SEM and AFM), and the details will be described in Chapter 3.

2) Characterisation of the alloys via dealloying and forming NPGs nanostructures with tuneable porosity using the Pb UPD process. The electrodeposited alloys of different compositions were used to form NPG by selective dissolution of Ag. The electrochemical process of Pb underpotential deposition (UPD) was used to characterize and modify the NPG structures. The Pb UPD on Au is a process of epitaxial Pb-monolayer formation accompanied by the top-surface Pb-Au surface-alloying. In Chapter 4, it will be shown that repeated cycles (deposition and dissolution) of Pb UPD can lead to surface coarsening, i.e., porosity length scale changes similar to the effect of thermal annealing. The changes in the NPGs porosity were explored by a different number of Pb UPD cycles with different scan rates.

3) Electrochemical characterisation of Au_xAg_{100-x} films using UPD processes. Chapter 5 includes systematic studies and a comparison of Pb UPD and Cu UPD processes (in sulphate and perchlorate solutions) on electrodeposited Au_xAg_{100-x} alloys. In the case of Pb UPD, the changes of the main voltammetry peaks were monitored and compared to the Pb UPD on pure Au and Ag substrates. Since Cu forms the UPD layer on pure Au but not on Ag, a more quantitative correlation was obtained between the alloy-surface composition and the UPD measurements. Because anions play an important role in the Cu UPD formation studies, the sulphate and perchlorate solution were used for comparison. The effect of Au_xAg_{100-x} composition on the voltammetric peaks positions and deposition charge was explored.

2 Chapter - Experimental Methods

2.1. Electrochemical methods

2.1.1. Electrochemical cell

All electrochemical experiments were done in three-electrode cells, as illustrated in Fig. 2.1. The cell includes a working electrode (WE), counter electrode (CE) and reference electrode are (RE). The reactions of interest occur on the WE. A potentiostat establishes the potential difference between the WE and the RE, whereas the current is measured through the CE¹¹¹.



*Fig. 2.1. Three-electrode cell diagram with a working (WE), counter (CE) and reference electrodes (RE) in a solution and connected to a potentiostat*¹¹¹.

A Pt wire was used as CE for all experiments. CE was cleaned by nitric acid, rinsed with Milli-Q water and annealed with a butane torch until it was flaming red. Reference electrodes used in this work included commercial mercury sulphate electrode (MSE) and pseudo reference electrodes of Ag, Pb or Cu wires used in the solutions containing their metal ions. The details will be specified at the beginning of each chapter accordingly. MSE was cleaned

by rinsing with Milli-Q water before the experiments. The metal wire pseudo-RE were cleaned by etching in dilute nitric acid (1: $1 = HNO_3$: H₂O) and rinsing with Milli-Q water.

WEs used in this work included Au-films on glass substrates and layers on top of it such as electrodeposited Ag, AuAg alloys, and NPG obtained by dealloying.

The three electrodes were connected to a CompactStat.h (Ivium Technologies) potentiostat controlled by IviumSoft software.

All solutions were prepared using Milli-Q with a resistance of 18.2 M Ω and salts with high purity (99.99% Sigma Aldrich or Alfa Aesar) specified in each chapter. All solutions were deaerated for a minimum of 30 min using N₂ before the experiments. During experiments, nitrogen flow above the solution was used to maintain an oxygen-free environment.

2.1.2. Chronoamperometry (CA)

Chronoamperometry is an electrochemical technique in which the current is measured over time after the potential of the working electrode is stepped from a potential E_1 , where there is no electrolysis, to a potential E_2 , at which the reaction of interest takes place at the electrode surface, as seen in Fig. 2.2 a).¹¹² The potential is maintained constant, and the current is measured for an established amount of time.



Fig. 2.2. a) Potential step in CA method. b) Concentration profile of electroactive species as a function of distance from the electrode at different times. c) Current-transient registered during the CA potential step illustrated in a). The figure is taken from Ref.¹¹²

A general case of a solid electrode in contact with the solution containing the oxidised form (Ox) of a redox couple (Ox/Red, Eq. 2.1) initially with concertation C_0^* can be used to describe the current-time response following the potential step.

$$Ox + ne \leftrightarrow Red$$
 Eq. 2.1

Initially, the applied potential E_1 is positive from the equilibrium potential, E^0 , for the redox couple Ox/Red, and only Ox species are present in the solution. In the CA method, the potential is then stepped at a time t_0 to the potential E_2 significantly more negative than the equilibrium potential E^0 . At the moment of the potential step, the concentration of the electrode Ox species will immediately reduce to zero from its initial bulk value C_0^* , and diffusion of Ox species from the bulk of the solution will start. Assuming the transport of Ox species toward the electrode is diffusion controlled, the concentration gradient of Ox species will be formed (Fig. 2.2 b). With time the diffusion layer will extend further and further away from the electrode, as shown in Fig. 2.2 b). The current under diffusion-controlled conditions is directly proportional to the concentration gradient, $\partial C_0(x, t) / \partial x$, at the electrode (x = 0). As the concentration profile for Ox decreases with time, the current will decrease too.¹¹²

For the case of the planar electrode, the current-time dependence can be described by Cottrell Equation, given by

$$i(t) = \frac{nFAD_0^{1/2}C_0}{\pi^{1/2}t^{1/2}}$$
, Eq. 2.2

where *n* is the number of electrons exchanged in the reaction, *F* is Faraday's constant 96485 *C/mol*, *t* is the time (*s*), *A* the area of the electrode (cm^2) , D_0 is the diffusion coefficient of Ox species (cm^2/s) , C_0 is the bulk concentration of electroactive species (mol/cm^3) . It should be mentioned that the current contribution due to the double layer (capacitive current) also contributes to the total current measured by. However, its decay is much faster (of the order $\sim 1/t$) and becomes significant for transients over short times.¹¹² CA method is often used to study diffusion processes and adsorption.

In the thesis, the CA method was used for the electrodeposition of Au_xAg_{100-x} alloys in Chapter 3.

2.1.3. Linear sweep voltammetry (LSV)

The linear sweep voltammetry (LSV) is a technique that measures the current as the potential is changed linearly with time. Typically the LSV starts at an initial potential E_i , then the current is measured as the potential is changed at a constant scan rate until it reaches the final potential, as shown in Fig. 2.3 a).¹¹²⁻¹¹⁴

In the case of a reversible electrode reaction described by Eq. 2.1, the concentration of the reaction species at the electrode, $Ox(C_0)$ and $Red(C_R)$, will depend on the magnitude of applied potential (*E*) and will follow the Nernst equation:

$$E = E^0 - \frac{RT}{nF} \ln\left(\frac{c_R}{c_O}\right) \qquad \text{Eq. 2.3}$$

where E^0 is the equilibrium potential for the redox couple Ox/Red at standard conditions measured against SHE, *R* is the universal gas constant 8.31 *J/mol K*, *n* is the number of electrons exchanged in the reaction, *F* is Faraday's constant. For illustration, a standard current response is illustrated in Fig. 2.3 b).



Fig. 2.3 a) Potential change during LSV starting at E_i . b) Corresponding current-potential response. C) Concentration profiles of the reaction species Ox (C_0) and Red (C_R) for potentials beyond the peak. Figure adopted from Ref¹¹².

At the open circuit potential, the net current detected will be near zero. If a negative potential sweep is applied going from E_i to more negative potentials than the equilibrium potential E^0 , the reduction current will start to increase as the potential gets closer to $E^{0'}$. As the

potential passes E^0 , the surface concentration of Ox species at the surface will drop almost to zero as the mass transport of Ox species toward the electrode reaches its maximum rate. As the depletion of Ox species around the electrode sets in, the current will drop, thus forming a peak as shown in Fig. 2.3 b). On the other hand, if the potential is swept from more negative values to more positive ones, the oxidation reaction will be more favourable, and a similar process will follow and be registered as anodic current. The magnitude of the current detected during LSV will vary depending on the scan rate used; an increase in the scan rate will result in a higher current detected¹¹³⁻¹¹⁴.

The LSV method was used for Ag dissolution from alloys (dealloying) as described in Chapter 4. Measured LSV curves of Ag dissolution at the very slow scan rate were used to evaluate the critical potential for alloys and estimate the amount of dissolved Ag. LSV was also used in the NPG surface area measurements where the Pb UPD monolayer was dissolved and integrated current normalised to measure the active area change (Chapter 4). The LSV characterisation of Pb UPD and Cu UPD processes on Au_xAg_{100-x} alloys was also used in Chapter 5.

2.1.4. Cyclic voltammetry (CV)

The cyclic voltammetry is similar to the LSV, but in this case, measuring the current between the potential limits is done in both directions¹¹²⁻¹¹⁵. Oxidation and reduction peaks of electrochemical processes can be obtained on the same voltammogram, allowing to relate peaks of the opposite reactions occurring at the surface.

A CV of the reaction of ferrocenium (Fc⁺) and ferrocene (Fc) is shown in Fig. 2.4 as an example. In the diagram, the current of the cathodic peak is marked by $i_{p,c}$ and that of the anodic peak by $i_{p,a}$. The potential between these two peaks is marked $E_{1/2}$, which is an experimental estimation of the Nernst potential for the ferrocenium (Fc⁺) / ferrocene (Fc) reaction ¹¹⁵.

The voltammogram in Fig. 2.4 starts at a potential A, and the potential shifts towards more negative values, making the reduction of Fc^+ to Fc more favourable. As the potential increases, the amount of Fc^+ reduced increases and thus, the current increases. The equilibrium potential is at point B, where the concentration of Fc^+ and Fc are equal at the surface and oxidation and reduction reactions occur at the same rate. The amount of Fc⁺ at the surface depends on the mass transport from the bulk to the surface, and the amount of Fc at the surface continues to increase, thus forming the peak at C, which is labelled as $i_{p,c}$. The previous factors reduce the amount of Fc⁺ that reaches the electrode surface, thus the detected current decreases until point D, where the potential scan direction is reversed. After D, the Fc at the surface oxidises to Fc⁺, and the inverse process takes place. Point E is at the equilibrium potential, and point F is at the anodic peak labelled as $i_{p,a}$.¹¹⁵

In general, the current at the peak, i_p , for the reduced (R) or oxidised (O) species depends on the scan rate v_s as given by the Randles-Sevcik equation¹¹³⁻¹¹⁴

$$|i_p| = 0.4463 n FAC_{O/R} \left(\frac{n F v_s D_{O/R}}{RT}\right)^{1/2}$$
, Eq. 2.4

where T the temperature and R the universal gas constant 8.31 J/mol K.

In this work, CV was used to characterise all surfaces such as Au substrates (described in section 2.2.1) and UPD characterisations of NPG and alloys in Chapter 4 and Chapter 5, respectively.



Fig. 2.4. Cyclic voltammetry of ferrocenium (Fc^+) and ferrocene (Fc) with a concentration in mM range and a scan rate of 100 mV/s. From the voltammogram, the peak for cathodic ($i_{p,c}$) and anodic ($i_{p,a}$) currents can be obtained, as well as $E_{1/2}$. Image is taken from ¹¹⁵.

2.1.5. Underpotential deposition (UPD)

As mentioned in Chapter 1, underpotential deposition is a phenomenon that occurs for some metal/substrate combinations. The metal ions in solution electrodeposit epitaxially¹¹⁶ on top of a metal substrate as a monolayer at the potentials more positive than the Nernst equilibrium potential¹¹³. In order to determine epitaxial growth, the crystalline structures of the substrate and the foreign metal on top of it need to be compared by means of in-situ scanning probe microscopes such as AFM and STM¹¹⁷⁻¹¹⁸ or by X-ray crystallography¹¹⁹.

Some examples of UPD systems include Ag on Au(hkl), Cu on Au(hkl), Pb on Ag(hkl) and Au(hlk), and there are several reviews and books where a list of many fundamental aspects and studied systems can be found.^{90-91, 120-122} The UPD process is characterised by unique CV features (peaks) depending on the metal/substrate combination, substrate crystallinity and the ions in solution^{90, 120}. As an example of the differences depending on substrate crystallinity, Pb UPD on Ag(hkl) single crystal orientations is illustrated in Fig. 2.5¹²³. For the measurement of charge and coverage, the concentration twin-layer thin layer method was

used, where MSE is used as a reference and a melted Pb electrode was used as a constant generator of Pb^{2+} ions by applying a constant potential negative from the Nernst equilibrium potential.



Fig. 2.5. Pb UPD on a) Ag(111), b) Ag(100) and c) Ag(110). Pb UPD varies depending on the crystalline structure of the substrate. Solid lines represent the global current measured from the Ag substrate, while dashed lines are the current detected by a melted lead electrode embedded with Araldite into PVC-holders. $E_{Pb/Pb}^{2+}=-900$ mV vs MSE. 0.5 M NaClO₄ + 5 mM HClO₄ with scan rate of 0.42 mV/s. Images were taken from Ref¹²³.

Another UPD system relevant to mention is Ag UPD on Au(hkl)¹²⁴⁻¹²⁷. Ag UPD on Au substrate used in this thesis was recorded in 0.1 M HClO₄ + 1 mM AgClO₄ solution with a scan rate of 50 mV/s and is shown in Fig. 2.6. The CV agrees with the results in the literature and illustrates the quality of or Au (111) textured substrates. There has been a lot of discussion in the literature for this system, and it has been argued that ~2ML monolayers form in contrast to other UPD systems.



Fig. 2.6. Ag UPD on Au(111) films in a 0.1 M HClO₄ + 1 mM AgClO₄ solution with scan rate 50 mV/s.

Well-established UPD processes on single metal surfaces of Au and Ag have been used in this work for surface characterisation and surface area measurements. However, this thesis includes studies where UPD processes were used as a surface modification tool, which will be described and discussed in Chapter 4. The characterisation of Au_xAg_{100-x} alloys using Pb and Cu UPD processes will be described and discussed in Chapter 5.

2.2. Sample Preparation

2.2.1. Au substrate preparation and characterisation

Au thin films on Schott Nexterion glass slides (15 nm Au with 5 nm Ti adhesion layer) were evaporated in a high vacuum at room temperature. Schott glass slides were cleaned in before the Au evaporation. Two cleaning procedures have been used: 1) Immersion in piranha solution for 1 hour. After this, the slides were rinsed thoroughly with Milli-Q water and left to dry in an oven the day before Au evaporation.

2) Plasma cleaning - Glass slides were cleaned using oxygen plasma for 8 min at 100W on the evaporation side.

Au evaporated on glass slides cleaned using the two procedures were analysed electrochemically by CVs in 0.1 M H_2SO_4 , and the results showed good quality and no differences between them.

Prior to the electrochemical experiments, Au-film substrates were cleaned in H_2SO_4 for 5 min, rinsed with Milli-Q water and dried using nitrogen. Before experiments were done, the substrate was flame annealed for 20 s using a butane/propane torch.

The Au substrate quality surface was characterised by CV in 0.1 M H₂SO₄ solution. Formation of the Au surface oxide (Au-O) at the surface of metals occurs as a monolayer level before deeper oxidation of Au (Au₂O₃) formation and O₂ evolution take place¹²⁸⁻¹³⁰. The process observed is the surface oxidation and reduction of Au in the potential region between 0 and 1 V vs MSE, as seen in Fig. 2.7. The anodic peaks in the voltammogram give a qualitative assessment of surface crystal structure. If the peak around 0.8 V vs MSE is pronounced, the surface has dominant (111) orientation ¹³¹⁻¹³². The cathodic peak was integrated to obtain the charge on the reduced surface oxide. The electrochemical active surface area (ECASA) was then obtained by normalising the integrated charge with the 440 μ C/cm² for a ML of Au(111) surface oxide ¹³¹⁻¹³².



Fig. 2.7. CV of Au oxidation/reduction in 0.1 M H₂SO₄ with scan rate 50 mV/s.

2.2.2. ITO preparation

Indium-Tin Oxide (ITO) samples were prepared by immersing the substrate in acetone and sonicating for 10 min. After this, the ITO was rinsed with Milli-Q water and sonicated for another 10 min in ethanol. The sample was then rinsed with Milli-Q water and dried with N_2 gas. The area of the sample was masked with Kapton tape and measured by calliper.

2.2.3. Solutions preparation aspects

Ag_xAu_{100-x} alloys were prepared using 0.1 M Na₂S₂O₃ + 2 mM Au(I)Na₃(S₂O₃)₂ + 2 y mM AgClO₄ solution, where y was changed to obtain different alloy compositions. For preparing the deposition solution, first AgClO₄ was added to Na₂S₂O₃, and the obtained solution was added carefully to Au(I)Na₃(S₂O₃)₂ while vigorously mixing to avoid precipitation. One important aspect to consider is that the ratio of the concentrations [Na₂S₂O₃]/[AgClO₄] must be higher than unity to avoid precipitation of Ag due to the formation of silver sulphite as a consequence of chemical reaction.

For illustration, the preparation of a 1:1 Au⁺:Ag⁺ ion ratio solution will be described. Three stock solutions of 0.5 M Na₂S₂O₃, 10 mM AgClO₄ and 0.15 M Na₂S₂O₃ + 5 mM Na₃Au(S₂O₃)₂ were prepared. The Au thiosulphate stock solution was prepared by dissolving 0.245 g of Na₃Au(S₂O₃)₂ salt with 30 ml of 0.5 M Na₂S₂O₃ in a 100 ml volumetric flask, adding the remaining volume with milli-Q water. First, 10 ml of AgClO₄ from the stock solution was mixed with 4 ml of thiosulphate stock solution. This was then added drop by drop and stirred to 20 ml of Au thiosulphate stock solution. Finally, 16 ml of Milli-Q water were added to have a 50 ml solution of 0.1 M Na₂S₂O₃ + 2 mM AgClO₄ + 2 mM Na₃Au(S₂O₃)₂.

2.3. Structural and chemical characterisation

During this project, several surface science techniques were used to characterise the samples. For structure and morphology, Scanning Electron Microscopy and Atomic Force Microscopy were used. To obtain chemical composition, X-ray Photoemission Spectroscopy was used. The principles of these techniques will be explained below.

2.3.1. Scanning electron microscopy (SEM)

A scanning electron microscope is an instrument that, similarly to optical microscopes, allows to obtain images of samples. However, the latter ones have limitations of resolution because of the wavelength of the light used. SEM takes advantage of the wave-particle duality to target smaller sizes using electrons, which wavelength λ will depend on the momentum they have p and Planck's constant $h = 6.626 \times 10^{-34} Js$ by¹³³

$$\lambda = \frac{h}{p}$$
, Eq. 2.5

A diagram of a scanning electron microscope is presented in Fig. 2.8. Electrons are generated usually by heating a wire, and they are accelerated due to a potential difference. After this, the beam of electrons is aligned with a set of lenses to focus the beam and reduce the stigmatism of the image. When these electrons interact with the atoms in the sample, they

release secondary electrons. The secondary electrons are then detected to create an image of the surface, generally by scanning horizontal lines until the complete image is taken¹³³.



*Fig. 2.8. Diagram of an SEM with a display. Electrons are obtained by the electron gun, which is then focused with lenses on the specimen. These electrons interact with atoms and excite secondary electrons from them, seen by the detector and transmitted into the display. Image obtained from*¹³³.

The incident beam has a region inside the sample where they can interact, as shown in Fig. 2.9 by the pear-shaped region. Suppose the incident beam has high energy. In that case, images of smaller resolutions can be obtained, but the problem is that the volume of interaction inside the sample is bigger. Not all the electrons from the interaction volume can be detected, as they need to have enough energy to leave the sample. Backscattered electrons occur when there is an elastic collision of electrons, which might occur at half of the penetration depth in the sample. These electrons have the same energies as the incident electrons. However, these are affected by the atomic weight of the sample a variant, in contrast, can be used to identify different elements at the surface¹³³. Depending on the type of detector in the instrument, images can also be obtained from backscattered electrons.



*Fig. 2.9. Interaction volume inside the sample of the incident electron beam. An increase in potential applied to the incident electron beam increases the penetration depth. Image modified from*¹³³.

In this thesis, SEM images of alloys were taken in a Vegas Tescan using an electron beam voltage of 20 KV and a magnification of 10 Kx. Dr. Andrei Sarua did the training for operating this system. Some of the SEM images of NPG were taken by Dr. Jean Charles Eloi, School of chemistry, UOB, using a Field Emission Gun Scanning Electron Microscope (SEM) with a 15 KV electron beam and a magnification of 100 Kx at the School of Chemistry. The analysis of SEM images was done using the software ImageJ.

2.3.2. Atomic force microscopy (AFM)

Atomic Force Microscopy is a scanning probe microscopy technique that uses a cantilever with a fine tip to scan the surface of a sample¹³³⁻¹³⁴, as shown in Fig. 2.10. The principle is to scan the surface topography with the aid of a laser that hits the cantilever on the tip side. The cantilever bends depending on the interaction with the surface as it moves in x and y directions. The bending of the cantilever deflects the laser beam from the cantilever surface and deflection is detected by photodetector, which sends a signal to the piezoelectric device to adjust the height of the sample and adjust the laser position at the photodetector. The change in height at different positions of the surfaces gives a 3D map of the surface.¹³⁴

Different modes can be used for AFM imaging. The most used are contact and tapping modes. In contact mode, the tip is in contact with the surface. As the cantilever moves over the surface, the force is maintained constant by adjusting the height. In tapping mode, the tip vibrates near its resonant frequency at a distance from the sample surface. As the surface is probed, the feedback loop keeps the amplitude of oscillations constant by adjusting the height with the piezoelectric.



Fig. 2.10. Atomic force microscope diagram. The laser on the cantilever is deflected depending on the distance of the tip with the sample. The height adjustment compensates for the deflection due to a piezoelectric device. A 3D image of the surface of the sample can then be obtained. Image obtained from ¹³³.

AFM images were taken using a NanoSurf Easy Scan atomic force microscope, and the images were analysed using Gwyddion software. Dr Massimo Antognozzi did training for AFM microscope. Some of the AFM images were taken by Dr Robert Harniman from the School of Chemistry.

2.3.3. X-ray Photoemission spectroscopy (XPS)

The electrons from an element have binding energy B_E , related to their atomic orbitals. Electrons that are closer to the nucleus have bigger binding energies compared to the ones that are in the outer orbital. If a source of X-rays is used with the photons having a minimum of energy equivalent to the binding energy, then a free electron is obtained, and the atom becomes ionised, as shown in Fig. 2.11 a)^{113, 135}. If the energy of the incident photon hv is higher than the B_E, then the electron in the orbital is emitted with a kinetic energy K_E. Thus, the binding energy can be obtained from

$$B_E = hv - K_E - W$$
, Eq. 2.6

where W refers to the work function of the spectrometer used. The spectra for each element are unique, so this technique can be used for the chemical analysis of samples¹³⁵.

After the photoelectron has been obtained from the element, the atom becomes ionised. In order to neutralise electrically, the atom can take a free electron. There might be some cases where an inner orbital electron has been photoemitted, forming a hole. Then an electron from an outer orbital might jump to fill the hole, and because of the energy conservation, another electron will be emitted from the atom^{113, 135}, as shown in Fig. 2.11 b) and c). The previously mentioned process is called the Auger effect. The resulting Auger electron depends strictly on the energy difference between orbitals, whereas for the photoemitted electron, its kinetic energy depends on the incident photon's energy. For this reason, photoemitted electrons can be differentiated from Auger electrons by changing the source of the incident photon, where the position of Auger peaks will be invariant. Photoelectrons are used for chemical analysis, and Auger can be used for imaging and chemical analysis.

To calculate the composition of the materials, the intensity measured on the XPS can be expressed as

$$I = J\rho\sigma K\lambda$$
, Eq. 2.7

where *I* is the photoemission line area, *J* is the photon flux, ρ is the element concentration in the material (which gives the atomic percentage and thus the stoichiometry), σ is the crosssection, λ is the electron attenuation length, and *K* is a parameter which includes instrumental factors¹³⁵. The value for λ corresponds to the depth of analysis, which depends on the inelastic mean free path (IMFP). λ is affected by the energy of incident X-rays¹³⁵. The value of σ corresponds to the probability of emitting an electron, depending on the element, the orbital of the emitted electron analysed and the incident energy¹³⁵.



Fig. 2.11. A) Photoemitted electron from the K-shell of an element after an incident photon of X-ray. B) Electron from the upper shell $L_{2,3}$ that fills the hole generated by the photoemitted electron. C) Auger electron from $L_{2,3}$ shell emitted due to the energy conservation. Image modified from ¹³⁵.

To calculate the electron attenuating length (λ), the free software QUASES-IMFP was used, selecting each element and including the energy of incident X-rays. The XPS parameters of cross-section and asymmetry for each element can be obtained from graphs in databases such as https://vuo.elettra.eu/services/elements/WebElements.html, taking into consideration the energy of incident X-rays used¹³⁶. The asymmetry factor is related to the difference in intensity of photo emitted electrons depending on the emission angle because the emission of photoelectrons is non-isotropic, generally considering the random orientation of atoms or molecules¹³⁶⁻¹³⁷.

I can be obtained by integrating the area beneath the elemental peaks and using a background subtraction method. The method used for background subtraction for XPS is Shirley, and it is obtained after selecting two points that have no contribution from the peaks to be fitted. B_n is the n-th iteration of Shirley background, k_n is the iterative value of scattering factor, E is kinetic energy and I the intensity¹³⁵. Each iteration must fulfil that the k_n selection allows the iteration to pass through (E_{left},I_{left}) and the outside selected region background must be 0 for $E_{right} \leq E$ and $I_{left} - I_{right}$ for $E \leq E_{left}$.¹³⁵

$$B_{1}(E) = k_{1} \int_{E}^{E_{right}} dE' [I(E') - I_{right}], \quad \text{Eq. 2.8}$$

$$B_{2}(E) = k_{2} \int_{E}^{E_{right}} dE' [I(E') - I_{right} - B_{1}(E')], \dots \text{ for } E_{left} \le E < E_{right}, \quad \text{Eq. 2.9}$$

$$B_{n}(E) = k_{n} \int_{E}^{E_{right}} dE' [I(E') - I_{right} - B_{n-1}(E')], \quad \text{Eq. 2.10}$$

The chemical composition of alloys was done using an X-ray Photoemission Spectrometer at the Nano-ESCA facility in the Bristol Centre for Quantum Information. An angle of 25° with respect to the normal and Al-K α (1486.6 eV) was used as an X-ray source. Some measurements and training for using the equipment were done by Dr Mattia Cattelan. Analysis of XPS spectra to obtain the chemical composition of samples was done using the software Igor Pro taking into account the values for cross-section, attenuation length and asymmetry.

3 Chapter - Electrodeposition of Au_xAg_{100-x} alloys from thiosulphate solutions

The development of a new environmentally friendly (cyanide-free) electrodeposition route to fabricate Au_xAg_{100-x} alloys is desirable for the range of their possible applications in sensing and plasmonics. A study of electrodeposition of Au_xAg_{100-x} alloys from thiosulphate solutions on Au substrate will be presented in this chapter. Thin-film alloys (50 nm - 100 nm thickness) of different compositions were electrodeposited by variation of $Ag^+:Au^+$ concentrations in the solution. The structure of the deposited alloys was explored as a function of the electrodeposition potential and film thicknesses. The characterisation of alloys morphology was done by Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM). The chemical composition of the electrodeposited alloys was determined using X-Ray Photoemission Spectroscopy (XPS).

3.1 Introduction

Au_xAg_{100-x} alloys are materials of interest due to their excellent optical properties suitable for application in plasmonic devices, sensors, catalysis, and photovoltaics^{24, 138-144}. Growth of Au-Ag alloys could be done using different deposition techniques such as evaporation, spraypyrolysis, sputtering, electrodeposition, and chemical reactions^{24-27, 79, 85, 145-146}. Electrodeposition has many advantages over other methods. It is an ambient condition (temperature, pressure) and a low-cost process that can be easily scaled on samples of different shapes and length scales (from nanoscales to microscopic scales).²⁸

The electrodeposition community in recent years has actively pursued electrodeposition of Au and Ag from non-cyanide-based solutions motivated by the need for more environmentally friendly fabrication methods in the microelectronics and optoelectronics industry.^{7-8, 30-34} Studies of Au electrodeposition from sulphite, thiosulfate and mixed sulphite-thiosulphate solutions have been reported ^{7-8, 30-34}. Also, the mechanism and kinetics of Ag electrodeposition from thiosulphate solutions has been well characterised in the past due to its importance in plating and photography.¹⁴⁷⁻¹⁴⁹

The general mechanism of Au(I) electrodeposition from a solution containing a metal complex is illustrated in Fig. 3.1. As the negatively charged complex ion approaches the cathode electrode, the ligands around the metal become distorted. The complex becomes polarised, resulting in the removal of ligand ions in the Helmholtz double-layer, which is then followed by a metal deposition.³³



Fig. 3.1. Schematic diagram of gold deposition process from the Au(I) complex. Figure adapted from Ref ¹⁵⁰.

Of particular interest for our study is the electrodeposition from the thiosulphate solutions where the reduction of gold thiosulphate takes place by reduction reaction: ³²

$$Au(S_2O_3)_2^{3-} + e^- \leftrightarrow Au + 2S_2O_3^{2-}, \quad \text{Eq. 3.1}$$

The stability constant is $\beta = \frac{[Au(S_2O_3)_2^{3^-}]}{[Au][S_2O_3]^2} = 10^{26}$ for this complex^{7, 32}, the standard potential for gold thiosulphate has been reported as 0.15 V vs SHE³².

Electrodeposition of Ag from thiosulphate solutions has also been studied in the past.¹⁴⁷⁻¹⁴⁹ The reduction reaction for silver thiosulphate is represented by reaction:

$$Ag(S_2O_3)_2^{3-} + e^- \leftrightarrow Ag + 2S_2O_3^{2-}$$
, Eq. 3.2

which has a stability constant of 4.2×10^{13} for the complex¹⁵¹ and a standard potential of 0.016 V vs SHE.

A second reduction path has been mentioned to occur following the next reaction¹⁴⁸

$$AgS_2O_3^- + e^- \leftrightarrow Ag + S_2O_3^{2-}$$
, Eq. 3.3

There are two different pathways that this reaction can take place in order to obtain metallic silver¹⁴⁸.

$$Ag(S_2O_3)^- + e^{-\frac{k_1}{2}} [Ag(S_2O_3)^-]^-$$
$$\beta_{11} \downarrow \uparrow \qquad \qquad \downarrow \uparrow \beta_{11}^- \quad , \qquad \text{Eq. 3.4}$$
$$Ag^+ + S_2O_3^{2-} + e^{-\frac{k_0}{2}} Ag + S_2O_3^{2-}$$

The linear sweep cannot determine the path that is followed but by analysing the surface to determine Ag and $[Ag(S_2O_3)^-]^-$ content in the surface¹⁴⁸.

The electrodeposition of Au_xAg_{100-x} alloys from thiosulphate solutions was recently demonstrated by McCurry et al.¹⁴⁶. In the work of McCurry et al., AuAg alloy deposition was conducted at the constant potential for a selected range of different molar ratios of Ag⁺:Au⁺ ion complexes in 0.1 M $Na_2S_sO_3$ background solutions using Au(I)Cl and AgClO₄ as sources of Ag and Au. The solutions with low concentrations of Au and Ag in the (10⁻⁴ M range) have been used, and the growth was conducted at the -0.15 V vs Ag/Ag⁺ reference electrode under the mass transport-controlled reduction for both Au⁺ and Ag⁺ ions on Au and Glassy Carbon substrates. Deposited alloys had compositions ranging from 77:23, 74:26, and 70:30 Ag: Au for the solution compositions 2:1, 3:2, and 1:1, respectively. The study reported no traces of S in the deposit as measured by the EDX method.¹⁴⁶ The AuAg alloys were then used as a precursor for creating NPG electrodes by dealloying to create porous supports for Pt deposition and electrocatalytic studies.

The electrochemical aspects and details of the Au and Ag co-deposition in McCurry et al.¹⁴⁶ work from the thiosulphate solutions were not explored. Considering the complexities and interest in developing new plating baths for Au-Ag, dependence on the potential of deposition or solution composition has not been reported. This chapter presents a systematic study of the Au-Ag alloys electrodeposition at constant potentials in thiosulphate solutions. Solutions containing different concentrations ratios of Ag^+ : Au⁺ complexes were examined. Freshly prepared solutions were used for the deposition to avoid solution instabilities or spontaneous metal reduction in the solution. The concentrations range was selected to avoid Au thiosulphate solution instabilities by ageing. The films of different thicknesses were deposited to measure alloy composition's homogeneity and consistency throughout the film. The several selected deposition potentials were explored, and SEM, AFM and XPS were used to examine the films' structure.

3.2 Experimental

3.2.1 Electrodeposition Solutions

Electrodeposition of Au_xAg_{100-x} alloys was conducted from thiosulphate-based solutions. Stock solutions of 0.5 M Na₂S₂O₃, 10 mM AgClO₄ and 0.15 M Na₂S₂O₃ + 5 mM Na₃Au(S₂O₃)₂ were utilised to obtain the deposition solutions by mixing them in different ratios before the electrodeposition. The selected range of compositions was based on varying the Ag content in solution while keeping Au ions concentration constant. The solutions compositions are presented in Table 3.1 with the labels (notation) used in the rest of the thesis.

Table 3.1. Solutions used for electrodeposition of Au, Ag and Au_xAg_{100-x} alloys and the thiosulphate background solution.

Solution composition	Label
0.1 M Na ₂ S ₂ O ₃	S_0
$2 \text{ mM AgClO}_4 + 0.1 \text{ M Na}_2\text{S}_2\text{O}_3$	S_1
$2 \text{ mM Na}_3 \text{Au}(\text{S}_2\text{O}_3)_2 + 0.1 \text{ M Na}_2 \text{S}_2\text{O}_3$	S_2
$2 \text{ mM Na}_{3}\text{Au}(S_{2}O_{3})_{2} + 1 \text{ mM AgClO}_{4} + 0.1 \text{ M Na}_{2}S_{2}O_{3}$	$\mathbf{S}_{2,1}$
$2 \text{ mM } Na_3Au(S_2O_3)_2 + 2 \text{ mM } AgClO_4 + 0.1 \text{ M } Na_2S_2O_3$	$\mathbf{S}_{1,1}$
$2 \text{ mM } Na_3Au(S_2O_3)_2 + 4 \text{ mM } AgClO_4 + 0.1 \text{ M } Na_2S_2O_3$	$\mathbf{S}_{1,2}$

3.2.2 Experimental conditions

All experiments were done using a three-electrode electrochemical cell. The solutions were deaerated by purging oxygen-free nitrogen for at least 20-30 min before the experiments. The electrode potential was controlled using an Ivium Compactstat potentiostat. Au substrates were used as working electrodes (WE), a Pt wire as the counter electrode (CE) and Ag/Ag⁺ or MSE was used as reference electrodes (RE). Potentials are referenced against MSE unless otherwise stated.

Au_xAg_{100-x} alloys were electrodeposited on Au films evaporated on glass slides. The Au substrates were evaporated 20 nm Au films on top of 5 nm Ti as an adhesive layer on glass slides. As described in Chapter 2, all substrates were cleaned before alloy electrodeposition in conc. $H_2S_2O_4$ for 5 mins. The Au substrates were rinsed in plenty of MilliQ water and 'flash-annealed' (brushed with the butane torch flame) for 20 s. The hydrophilicity of the water droplet was then used to confirm the surface cleanliness. Following that, the Au substrate structure and the area measurements were confirmed by AuO surface oxidation/reduction in the perchlorate solution described in Chapter 2.

In order to determine the conditions for electrodeposition of alloys, cyclic voltammetry and linear sweep voltammetry were done in each solution. After this, different potentials were

selected for each solution to electrodeposit alloys (constant potential deposition). Several potentials have been selected in order to explore their effect on the composition of the electrodeposited alloys and structure.

The deposition charge controlled the thickness of electrodeposited alloys (the thickness), and it ranged from 20 up to 100 mC/cm². Based on Faraday's law, 100 mC/cm² was roughly corresponding to ~100 nm thickness of the alloy. Different thicknesses were selected in order to study the homogeneity and consistency of the composition through the sample.

3.2.3 Methods of structural characterisations

Electrodeposited samples morphology and structure were characterised by atomic force microscopy and scanning electron microscopy. SEM images of samples were taken by a Vega3 TESCAN, with a 20 kV potential and WD of 15 mm. AFM images were taken using a Bruker Multimode VIII atomic force microscope utilising peak force feedback control.

X-ray photoemission spectroscopy was used for composition and chemical characterisation. XPS measurements were taken at the Nano-ESCA facility in the Bristol Centre for Quantum Information. Igor Pro software was used to fit the peaks to obtain the Au_xAg_{100-x} thin films composition comparing Ag 3d and Au 4f peaks because these are the most intense peaks for each element. The photoelectron emission line analysis area for Au is for energies between 80 and 91 eV, whereas for Ag is between 365 and 379 eV and a Shirley background, corresponding to the red line in Fig. 3.7 b) and c), was used. Parameters for the cross-section of photoelectron production σ , Asymmetry, electron attenuation length λ , and the area mentioned previously for each metal were taken into consideration in Igor Pro software to obtain a more reliable value of the stoichiometry of alloys than only considering the ratio of the fitted areas for the metals. In

Table 3.2, the parameters for each metal are given.

Table 3.2. Parameters of Au and Ag used to obtain composition of alloys using Igor Pro software.

Parameter	Au	Ag
σ [Mbarn]	0.2511	0.2476
Asymmetry	1.032	1.21
λ[Å]	18.98	15.98

3.3 Results and discussion

3.3.1 Au and Ag electrodeposition using a thiosulphate solution

Before the electrodeposition of Au_xAg_{100-x} alloys, pure Ag and Au electrodeposition from the same background solutions was examined. Cyclic voltammetry and linear sweep voltammetry experiments in solutions S₀, S₁ and S₂ were conducted in the potential region between -0.3 V and -1.3 V, as shown in Fig. 3.2 a) and b). The linear sweep voltammetries in Fig. 3.2 b) clearly show the potentials at which deposition takes place for each solution. For the silver-containing solution, the potential is more positive than for the Au containing solution.

The observed equilibrium potential for Ag deposition from S_1 solution is around -0.65 V. Closer inspection of Ag electrodeposition at a shorter potential range showed that Ag electrodeposition starts in the underpotential range, as shown in Fig. 3.3. A comparison of voltammograms in S_0 and S_1 was made to confirm that the peak at about -0.35 V is related to Ag thiosulphate reduction, as shown in Fig. 3.3 a). Different negative potential limits were taken to identify the bulk Ag deposition potential and determine more precisely equilibrium potential (~ -0.65 V), as presented in Fig. 3.3 b).



Fig. 3.2 a) CVs on Au substrate in different thiosulphate solutions. b) LSV obtained from the CVs in a) showing the cathodic peaks for each solution. Scan rate of 50 mV/s.



Fig. 3.3. CVs of a) background solution S_0 and Ag containing solution S_1 , and b)Ag UPD on Au substrate with different negative potential limits in solution S_1 . Scan rate 50 mV/s.

The electrodeposition from different alloy solutions is shown in Fig. 3.4. From the LSV curves, it can be observed that behaviour is similar for the different solutions, with a loop

with a maximum of current at a potential of -0.88 V. The potential at which the current starts increasing has a trend of moving towards more negative potentials for solutions that have more Au content. The potentials at which deposition start in different solutions are between those for pure Ag and pure Au. The current drop and the nucleation loops are due to Ag and Au's electrodeposition based on the comparison with the background solution current that shows very low values through the whole potential range, as shown in Fig. 3.4 b). The current density in solution $S_{1,2}$ shows higher values than $S_{1,1}$ and $S_{2,1}$ as this is the solution with the highest Ag ions concentration.



Fig. 3.4 a) CVs on Au substrate in different alloy deposition solutions. b) LSVs obtained from the CVs in a). The two potentials marked on the graph, -0.79 V and -0.94 V, are used later in the analysis. Scan rate of 50 mV/s.

3.3.2 Electrodeposition of Au_xAg_{100-x} alloys at different potentials from solution $S_{1,1}$

A more detailed study of the electrodeposition of thin films using different potentials from solution $S_{1,1}$ was conducted. Alloy films were deposited at potentials of -0.7V, -0.79V, -0.94V, -1.04 V and -1.14 V, as indicated in Fig. 3.5.



Fig. 3.5. Linear Sweep Voltammetry in solution $S_{1,1}$ *with the different potentials selected for analysis. Scan rate: 50 mV/s.*

The constant potential deposition transients at selected potentials are shown in Fig. 3.6. The deposition currents are very close, reaching stable values within 100 s. The steady current values range between $75 - 110 \,\mu$ A/cm² (average 95 μ A/cm²) without any specific trend with the deposition potential. The samples deposited at all potentials looked very shiny and mirror-like, except the ones deposited at the potential of -1.14 V, where the fuzzy reflection suggested a rougher deposit structure. The electrodeposited alloys were rinsed and dried with nitrogen and subjected to further analysis.



Fig. 3.6. Current transients of electrodeposition by constant potential step in solution $S_{1,1}$ with different deposition charges and deposition potentials.

3.3.3 Chemical composition characterisation

The chemical composition of the films was determined using X-ray Photoelectron Spectroscopy (XPS). A survey of each sample was obtained as presented in Fig. 3.7 a). The Ag 3d and Au 4f doublet peaks presented in Fig. 3.7 b) and c) respectively were selected for the composition analysis.



Fig. 3.7. Binding energy spectra corresponding to a) full elemental survey, b) Au 4f doublet peaks and c) Ag 3d doublet peaks. An X-ray source of Al-K α (1486.6 eV) was used to obtain the spectra.
When looking at the XPS spectra in more detail, the peak of S $2p_{3/2}$ can be distinguished; however, the peak intensity is very low compared to the double peaks of Au 4f, as seen in Fig. 3.8 a). Furthermore, the same peak has been observed in the spectra of all samples deposited from different solutions, as presented in Fig. 3.8 b). When calculating the alloys' composition considering the sulphur peak, the at% of S for all alloys is less than 5% and does not significantly affect the at% ratio of Au and Ag. For this reason, the chemical composition of films will be used in the rest of the thesis as determined by the Au and Ag measurements only.



Fig. 3.8. XPS spectra of a) S $2p_{3/2}$ peak and the double peak of Au 4f from S_{1,1} and b) S $2p_{3/2}$ peak of Au_xAg_{100-x} alloys deposited from different solutions. Potential of deposition of -0.79 V vs MSE.

The compositions of alloys deposited in $S_{1,1}$ solution at different potentials are given in Table 3.3. The analysis was done for films deposited with different thicknesses (for 50 mC/cm² and 100 mC/cm²), and the measurements gave similar composition values, as shown in Table 3.3. It can be concluded that alloy composition did not change much with deposition potential, suggesting a mass transport control of electrodeposition.

Table 3.3. Chemical composition of Au_xAg_{100-x} alloys electrodeposited from $S_{1,1}$ solution at different selected potentials. Films were deposited using 100 mC/cm².

$E_{dep} \left[V \right]$	$(X_{Ag} \pm 2) at\%$	$(Y_{Au} \pm 2) at\%$
-0.7	68	32
-0.79	68	32
-0.94	62	38
-1.04	65	35
-1.14	68	32

Further surface characterisation of samples was done by SEM as presented in Fig. 3.9. It can be seen that the samples look homogeneous and flat for the deposition potentials between -0.7 and -0.94 V. As the potentials are more negative from -1.04, the sample shows some instability during the formation of the alloy. The pH of the thiosulphate solution was measured, and a value of 6.3 was obtained. Hydrogen evolution reaction (HER) occurs at 0 V vs SHE at standard conditions for samples grown on Au substrate, and it shifts according to the Nernst equation with pH as E_{HER} = 0 V -0.06pH V. Then, the potential at which HER starts in our thiosulphate solution is at -0.38 vs SHE or -1 V vs MSE. Thus, during deposition at -1.04 and -1.14 V vs MSE, the contribution from the HER could explain the non-uniform films deposited at this potential. Considering the previous results, the following samples deposited were limited to potentials below -1.00 V, at -0.79 and -0.94 V.



Fig. 3.9. SEM images of Au_xAg_{100-x} alloys deposited using $S_{1,1}$ at different potentials. 10 kx image magnification was used. Potentials of each sample are a) -0.7, b) -0.94, c) -1.04 and d) -1.14 V vs MSE.

3.3.4 Electrodeposition of Ag_xAu_{100-x} alloys at a fixed potential from different solutions

Following the analysis described in the previous section, two deposition potentials were selected for further study in all solutions. Alloy deposition in each solution was conducted at -0.79 V and -0.94 V vs MSE (or at an overpotential of ~0.15 V and ~0.3 V from Ag/Ag⁺ equilibrium, respectively). Electrodeposition was conducted by chronoamperometry starting from the (open circuit potential) potential of ~ -0.34 V for 10 s, followed by a potential step to the desired deposition potential. The measured deposition charge controlled the length of the deposition. Two different values were selected for examination, 50 mC/cm² and 100 mC/cm².

In Fig. 3.10 a), current transients for samples of different thicknesses deposited at selected potentials in $S_{2,1}$ solution are shown. Similar plots were obtained for all other solutions just different levels of the steady-state current were measured (-50 μ A/cm², -100 μ A/cm² and

-170 μ A/cm² for the solutions S₂₁, S₁₁ and S₁₂, respectively). In Fig. 3.10 b), the representative deposition transient for films deposited at E_{dep}=-0.79 V vs MSE with Q=100 mC/cm² in three different solutions are selected. The results indicate that the deposition is diffusion-controlled, and the current level (as expected) depends on the total ion concentration in the solution. Using the Cottrell equation for the representative transient presented in Fig. 3.10 b), the Cottrell plot was obtained and shown in Fig. 3.10 c). The slope is related to the diffusion coefficient for each solution. The diffusion coefficient for each solution is obtained and presented in Table 3.4. As it can be seen, the diffusion coefficient decreases with solutions more Au-rich.



Fig. 3.10. Current transients of electrodeposition by the constant potential for a) $S_{2,1}$ with different deposition charges and deposition potential, and b) deposition charge of 100 mC/cm^2 and at a deposition potential of -0.79 V but different solutions during deposition. C) Cottrell plots obtained from b) to obtain the diffusion coefficients.

Solution	Diffusion coefficient [cm ² /s]
S _{1,2}	$(8.2 \pm 0.4) \times 10^{-5}$
S _{1,1}	$(3.9 \pm 0.8) \times 10^{-5}$
S _{2,1}	$(17.0 \pm 0.3) \times 10^{-6}$

Table 3.4. Diffusion coefficient from Cottrell plots.

The samples' compositions are listed in Table 3.5. It can be observed that electrodeposited films are more Ag-rich, and gold content increases for a higher Au-to-Ag ratio in the solution. The alloy compositions are similar for different deposition potentials from the same solution, corroborating that the deposition is in the diffusion-controlled regime. All films are Ag-rich alloys and have compositions different from the ion ratios in the deposition solutions. This result agrees with the previously reported work of McCurry et al.¹⁴⁶. Although ions' concentrations for our solutions were in the millimolar range, which is one order of magnitude higher than their work, the compositions of alloys deposited from the S_{1,1} solution is the same (very close) to those reported from solutions with 1:1 ratio of Ag: Au ions.¹⁴⁶ The reason for growing alloys with compositions not matching the ratio of ions present in the solution could be related to Au and Ag thiosulphate complexes' relative stability. For example, Au(I)-thiosulphate stability constant is $\beta_{Au} = 1.3 \times 10^{26}$ and for Ag(I)-thiosulphate, $\beta_{Ag} = 4.2 \times 10^{13}$ which suggest that Ag deposition is a lot easier than for Au under given conditions.^{7, 151}

SEM was also used to characterise the surface of the electrodeposited alloys. The images (not shown) show a similarly smooth and homogeneous surface morphology as those obtained in $S_{1,1}$ illustrated in Fig. 3.9. For closer morphology examination, AFM images of the selected sample are shown in Fig. 3.11. As can be corroborated, the surface looks homogeneously distributed for the different samples and potentials of deposition. Better defined and possibly smaller grains can be observed for samples grown from $S_{2,1}$ compared to the other samples from $S_{1,1}$. Grain sizes from c) can be seen to be less than 100 nm in diameter.

Solution used	Edep [V]	(X _{Ag} ±2) at%	(Y _{Au} ±2) at%
S _{2,1}	-0.79	52	48
S _{2,1}	-0.94	54	46
S _{1,1}	-0.79	68	32
${f S}_{1,1}$	-0.94	62	38
S _{1,2}	-0.79	78	22
S _{1,2}	-0.94	77	23

Table 3.5. Composition of electrodeposited alloys measured by XPS for different deposition solutions and potentials.



Fig. 3.11. AFM images of samples deposited at -0.79 V for a) $S_{2,1}$, b) $S_{1,1}$ and deposited at -0.94 V for c) $S_{2,1}$, d) $S_{1,1}$. Images from courtesy of Dr Robert Harniman at the School of Chemistry.

3.3.5 Optical characterisation of electrodeposited alloys

As a part of the preliminary study of alloys optical properties, ellipsometry measurements were conducted on electrodeposited alloys from $S_{2,1}$ and $S_{1,2}$ solutions. The measurements were done by MSci students Akash Dasgupta¹⁵² and Christian de Podesta¹⁵³ as part of their Final year Project. The ellipsometry measurements were compared to pure Au and Ag⁵⁰ films, as shown in Fig. 3.12. From the imaginary component measurements, the samples show one peak around 300 nm, similarly to the case of pure Ag; however, the value increases with more Au content. For wavelengths higher than about 500 nm, the imaginary part of the dielectric constant for the alloys increases instead of remaining low for Ag's case, even reaching higher values than Au. For the real component, it can be seen that the wavelength at which the permittivity begins to become negative shifts towards higher wavelengths with more Au content in the alloy. A region of interest for plasmon coupling for the alloys would be between 400 and 600 nm, where the imaginary component is low and the real component is negative.



Fig. 3.12. Imaginary and real components of permittivity of Au, Ag^{50} , $Au_{47}Ag_{53}$ and $Au_{23}Ag_{77}$ alloys were obtained from ellipsometry. Image is taken from Ref ¹⁵².

3.3.6 Electrodeposition of AuAg alloy nanostructures

Electrodeposition of AuAg alloys is an active area of research due to their potential applications in photonics and sensors. The work has been explored in collaboration with the MSc student Jing Ren Wong¹⁵⁴, who extended the study presented in previous sections on Au-Ag electrodeposition to ITO substrates patterned with Au. Substrate patterning was done at the University of Bath by the Displacement Talbot Lithography (DLT) technique¹⁵⁵ in collaboration with Dr Andrei Sarua.

DTL is a recently developed non-contact photolithography method¹⁵⁶⁻¹⁵⁸ to create periodic patterns of sub-micron features (such as holes, nano-dashes, fishnets and other motifs) for large scale metamaterials production exploiting the Talbot effect. The Talbot effect is a formation of periodic images of the grating when illuminated with the monochromatic, collimated light of wavelength λ (usually near infrared to deep ultraviolet range). The Talbot length for a grating of periodicity p, is defined as $2p^2/\lambda$, which is the distance behind the grating at which the grating images repeat. At distances that correspond to the integer fractions of the Talbot length ($2p^2/n\lambda$, where n is an integer) the sub-images of the grating can be formed with the multiple frequencies of the grating periodicity.

A schematic illustration of the DLT method is shown in Fig. 3.13^{156} . In this approach, the position of the wafer with the photoresists (distance *d*) is varied by one Talbot length during the exposure.¹⁵⁹ The resulting structures will create the mask-pattern that will have double the frequency of the grating, Fig. 3.13. This method has benefits in cost of production compared to other lithographic techniques (such as e-beam lithography, focused ion beam or nanoimprinting)¹⁵⁹. Other benefits are that periodic patterns could be uniformly printed over large areas and non-planar surfaces.



Fig. 3.13 a) Schematic diagram illustrating the DTL process. The photoresist-coated substrate is moved towards the mask by one Talbot length during the exposure. B) and c) Application of the DTL method to a periodic pattern with hexagonal symmetry. (b) Schematic view of the mask pattern. (c) SEM image of a pattern of 300 nm-diameter holes with 600 nm period obtained by a DTL exposure and transferred into a silicon wafer by reactive ion etching. Figure adapted from Ref ¹⁵⁶.

The electrodeposition of all thin films was conducted on Indium-Tin Oxide (ITO) substrates. The linear sweep voltammetry of deposition in thiosulphate-based solutions with different Au⁺: Ag⁺ ratios are presented in Fig. 3.14. It can be seen that the potentials at which the deposition starts taking place for all the solutions are shifted towards more negative values compared to the depositions shown in Fig. 3.2 b) and Fig. 3.4 b) on gold substrates, which could be attributed to the difference of Fermi level at the surface of the two different substrates. XPS was used to determine the composition of the electrodeposited alloys. Table 3.6 summarises the composition of Au_xAg_{100-x} films electrodeposited at -0.97 V on ITO substrate using solutions with different Au⁺: Ag⁺ ratios in solution. Comparing these compositions with the ones obtained in Table 3.5 shows that the values are very similar, with a variation between 2 and 3 %, which would suggest that the composition would be similar independent of the substrate used for each solution.



Fig. 3.14. LSVs in solutions with different $Au^+:Ag^+$ ratios (as labelled) using thiosulphatebased solutions on ITO substrate using a scan rate of 50 mV/s.

Table 3.6. Composition of electrodeposited alloys from different solutions at -0.97 V on ITO measured by XPS.

Solution	(X _{Ag} ±2) at%	(Y _{Au} ±2) at%
S _{2,1}	53	47
S _{1,1}	66	34
S _{1,2}	75	25

Based on the results that the Au_xAg_{100-x} alloy electrodeposition on ITO occurs at more negative potentials than those electrodeposited on Au, the Au-patterned ITO substrates (such as one presented in Fig. 3.15 a) were used for alloy deposition. Fig. 3.15 b) shows pure Ag electrodeposition from S₁ solution, resulting in very small grains with different sizes and not homogeneously distributed. However, the alloy deposition from the S_{2,1} solution, as shown in Fig. 3.15 c), results in smooth and homogeneous layers throughout the surface.



Fig. 3.15. SEM images (50 kX magnification) of a) Au-ITO substrate with the hexagonal pattern created by DTL and subsequent Au evaporation. b) Electrodeposited Ag on Au-ITO substrate for 10 min from solution S_1 . c) Electrodeposited Au-Ag alloy on Au-ITO substrate for 10 min from solution $S_{2,1}$.

3.4 Conclusions

In this work, Au_xAg_{100-x} alloys with different compositions have been electrodeposited from thiosulphate-based solutions. Different alloy compositions were grown by changing parameters such as deposition potentials and complex-ion ratios in the solution. The results have shown that the composition of alloys was independent of the potential of deposition and thickness. Uniform and smooth films were obtained at deposition potentials positive than the Hydrogen Evolution Reaction (HER). Alloys of different compositions were obtained from solutions with different Au⁺: Ag⁺ ions in the solution ranging from Au₄₇Ag₅₃ to Au₂₂Ag₇₈. Using the XPS analysis on films of different thicknesses (range 50 nm -100nm), the composition of electrodeposited films was shown to be homogenous and consistent during growth. In addition to that, the design of nanopatterned alloy structures on transparent substrates for potential plasmonic applications has been demonstrated. A preliminary study

of the optical behaviour of electrodeposited alloys illustrated the potential for future studies of fundamental importance. The electrodeposition method developed could be used for the development of nanostructures for optical and sensor applications.

4 Chapter - Electrochemical Design of Nanoporous Gold with Tuneable Porosity

Selective dissolution of Ag from Au_xAg_{100-x} alloys was used to obtain the interconnected bicontinuous structure of nanoporous gold (NPG). NPG is an important metamaterial well known for its excellent mechanical, plasmonic, and catalytic properties that depend on porosity's length scale. The pore and ligament size generally depend on the parent alloy composition, the method of dealloying (chemical or electrochemical) and the post-treatment. Besides thermal treatments commonly used for this purpose, there has been an increased interest in using electrochemical methods to fine-tune the porosity. The work presented in this chapter aims to demonstrate and explore Pb underpotential deposition cycling as a new effective tool for tuning the porosity structure of NPG.

4.1 Introduction

NPG is a bicontinuous 3D structure made of interconnected Au ligaments and pores²¹. NPG is a material obtained by dealloying Au alloys, such as Au-Ag, and Au-Cu alloys. NPG formation has been explained as the result of two processes; the dissolution of the less noble element and the accompanied diffusion of Au to form ligaments, allowing the further dissolution of Ag into the bulk material⁷⁴. NPG has been an extensively studied nanomaterial because of its wide-ranging applications.⁵² Due to the high surface area of NPG, it can be used as a catalyst support^{20, 58-59}. Also, covalent adsorbate-metal interactions affect the strain at the surface, which can be used for actuation applications⁶¹⁻⁶². Free electrons of Au allow the formation of surface plasmons, which can be used in enhanced spectroscopies, such as Surface Enhanced Raman Spectroscopy (SERS)¹⁶⁰ or Surface Enhanced Fluorescence (SEF)⁵⁶. Surface-enhanced spectroscopies can be used as sensors for molecular detection⁵⁶.

NPG mechanical and optical properties depend on ligament and pore sizes^{54, 64}, and for many desired applications, precise control of morphology is essential. Porosity size depends on several factors, such as the composition of parent alloy^{65, 97}, the temperature during dealloying¹⁶¹, and the dealloying method used^{18, 64, 162}. Porous samples could be obtained by dealloying chemically or electrochemically. Electrochemical dealloying could be done by two methods: 1) at a constant potential/current and 2) by a linear sweep of the potential. In the second case, it has been shown that the porous structure is affected by the scan rate⁷³. Pore sizes may vary from a few nanometres to 10-15 nanometers^{64, 97, 163}. Post-treatment of the NPG is commonly used to modify the length scale of porosity further up to a few hundred nanometres. The ligament and pore size of NPG is most commonly modified by thermal treatment (annealing ^{54, 163-165}, electrical treatment ¹⁶⁶⁻¹⁶⁷, chemical¹⁶⁴, and photothermal¹⁶⁸). The most recent interest in modifying NPG structures includes electrochemical protocols¹⁶⁹⁻¹⁷¹ as possible methods for fine-tuning NPG porosity. The reported electrochemical methods include electrochemical etching¹⁷⁰ and electrochemical annealing with potential cycling involving Au oxidation-reduction processes¹⁶⁹.

Different ways to measure the area of NPG include gas adsorption^{126, 163, 172}, and electrochemical methods such as impedance measurements^{163, 173}, and UPD metal electrodeposition^{97, 174}. The most recent study by Liu et al. ⁹⁷ demonstrated that Pb UPD on the Au process could measure the NPG surface area more accurately than Brunauer-Emmett-Teller (BET) gas absorption⁹⁷.

Pb UPD on the Au system is a well-known UPD system that has attracted much attention due to its surface stress behaviour.¹⁷⁵⁻¹⁷⁶ Recent in situ surface stress and Scanning Tunnelling Microscopy (STM) studies on Au(111)¹⁷⁶ (the work in our Surface Physics research group) have shown that in this process, surface alloying takes place. The potential cycling in this system resulted in significant restructuring of the Au surface, i.e. formation of Au ad-island and holes¹⁷⁶.

In this chapter, the aim was to explore Pb UPD as a tool for changing the length scale of the NPG porosity. Following the methodology and conditions described in Chapter 3, Au_xAg_{100-x} alloys of three different compositions were electrodeposited on Au substrates. The alloys were dealloyed (Ag was selectively dissolved) electrochemically using potential

sweep to create NPG films. The NPG samples with different length scales (size) of porosity were then characterised by electrochemical methods (Pb UPD) and SEM. The surfaces of NPGs were subjected to repeated Pb UPD cycles (different number of cycles with fast and slow scan rates). Monitoring the Pb UPD cyclic voltammetry changes suggested gradual coarsening of the porous structure for all NPGs with an increasing number of UPD cycles. SEM was used to characterise the initial NPGs structures and those after Pb UPD cycles. The charge of the Pb UPD monolayer was used to measure the NPGs area and monitor changes. Moreover, we explored the effect of Au oxidation red/oxidation pre-treatment on asdealloyed NPGs structure. The work demonstrated that Pb UPD could be used as an effective tool for tuning the porosity structure of NPG.

4.2 Experimental Conditions

4.2.1 Electrodeposition conditions

Au_xAg_{100-x} alloys were prepared using 0.1 M Na₂S₂O₃ + 2 mM Au(I)Na₂S₂O₃ + 2 y mM AgClO₄, where y was modified to obtain different alloy compositions. For preparing the deposition solution, first AgClO₄ was added to Na₂S₂O₃, and the obtained solution was added carefully to Au(I)Na₂S₂O₃ while vigorously mixing. Each solution prepared will follow the label system proposed in Chapter 3. Ag wire was used as a reference electrode (RE). The RE was cleaned first in HNO₃, thoroughly rinsed with Milli-Q water and dried using nitrogen.

Au_xAg_{100-x} alloy thin films of ~100 nm thickness were electrodeposited at a constant potential of -150 mV vs Ag/Ag⁺, which corresponds to -0.79 V vs MSE following the protocols as described in Chapter 3. The thickness was controlled by a constant deposition charge of Q=100 mC/cm² corresponding to ~100 nm thickness. After deposition, samples were rinsed in Milli-Q water, dried in nitrogen and kept in a desiccator until their use. Most of the samples presented here were de-alloyed and examined right after they were electrodeposited.

4.2.2 Selective dissolution of Ag from alloys conditions

Ag from the alloys was dissolved in 0.1 M HClO₄ + 1 mM AgClO₄. The Ag wire was used as RE. Linear sweep voltammetry (LSV) with a scan rate of 0.2 mV/s was used for dealloying,

Samples were then carefully rinsed by leaving samples for 5h in Milli-Q water.

4.2.3 Au oxidation-reduction on nanoporous gold

After the dealloying step, 7 cycles in the AuO oxidation-reduction region with a scan rate of 50 mV/s were applied on the NPG using a solution of 0.1 M HClO4. The RE used for this experiment was the mercury sulphate electrode (MSE). MSE was rinsed using Milli-Q water before the experiment.

4.2.4 Pb UPD for surface area measurement measuring and surface modification A solution of 0.1 M HClO₄ + 1 mM Pb(ClO₄)₂ was used for surface area measurements on NPG and the surface modification. A Pb wire was used as RE in these experiments.

4.2.4.1 Pb UPD conditions for surface area measurements

To measure the sample's surface area, a Pb UPD monolayer was formed on top of the samples by applying a step potential at 0.01 V vs Pb/Pb²⁺ for 5 min. After this, the potential was swept from 0.01 to 0.8 V vs Pb/Pb²⁺ at a scan rate of 10 mV/s to remove the Pb layer completely. The anodic (dissolution) current of Pb UPD was measured to obtain the charge by integration, which was then used to estimate the surface area.

4.2.4.2 Multiple cycles for surface modification

Cyclic voltammetry of the Pb UPD, from 0.01 to 0.8 V vs Pb/Pb²⁺ with scan rates of 10 mV/s and 100 mV/s, was applied repeatedly to observe surface changes. After each tenth cycle, the surface area was measured by a Pb UPD LSV, as mentioned in the previous section.

4.3 Results and Discussion

Three Au_xAg_{100-x} alloys of different compositions were selected as parent alloys for NPG formation and further study. The alloys were electrodeposited following the methodology developed and described in Chapter 3. For completeness, a summary of the parent alloys characterisation will be presented first.

4.3.1 Characterisation of electrodeposited alloys

As described in Chapter 3, for all electrodeposited alloys, chemical and morphological characterisation were done using X-ray Photoelectron Spectroscopy (XPS) and Atomic Microscopy (AFM), respectively. The composition of the electrodeposited alloys and the solutions used are shown in

Table 4.1 and illustrated in Fig. 4.1. The composition analysis by XPS methods was done by comparing the peak intensities of Ag3d 5/2 and 3/2 with Au4f 7/2 and 5/2, as described in Chapter 3. The mean grain sizes of the alloys were obtained from the AFM images shown in Fig. 4.2. Au₃₃Ag₆₇ mean grain size of 109 ± 10 nm was measured, Au₂₂Ag₇₈ was 105 ± 10 nm, and Au₁₆Ag₈₆ of 110 ± 10 nm.



Fig. 4.1 Composition of electrodeposited Au-Ag alloys as measured by XPS. The horizontal axis includes the ratios of Ag: Au ions in the deposition solutions.

<i>Table 4.1.</i>	Chemical	composition	of electro	odeposited	Au_xAg_{100-x}	samples	obtained	from	XPS
measurem	ents.								

Electrodeposition Solution	$X_{Ag} \pm 2$, at%	$Y_{Au} \pm 2$, at%
S _{1,1}	67	33
S _{1,2}	78	22
S _{1,3}	84	16



Fig. 4.2 AFM images of a) Au₃₃Ag₆₇, b) Au₂₂Ag₇₈ and c) Au₁₆Ag₈₄ electrodeposited alloys.

4.3.2 Dealloying of Au-Ag alloys

Following the deposition and characterisation of alloys, Ag was removed electrochemically using linear sweep voltammetry. Depending on the parent alloy's composition, the Ag dissolution potential shifts to more positive values than pure Ag.⁷³ More Au in the alloy results in a more positive potential shift. This is observed for the electrodeposited alloys, as shown in Fig. 4.3. The critical potential, *Ec*, is shown as the dotted line in the figure. Determining the exact value of *Ec*, has been challenging as this is not very exact value but a range of potentials⁷³⁻⁷⁴. Here the second derivative of the current density was used, and the critical potential was selected as the inflexion point where there was a change in the slope. As shown for the dissolution wave of the Au₃₃Ag₆₇ sample in Fig. 4.4, the second derivative cross zero and shows a peak at the potential of ~0.3 V.



Fig. 4.3 Linear sweep curves for pure Ag and different electrodeposited alloys in a 0.1 M $HClO_4 + 1 \text{ mM AgClO}_4$ solution using a scan rate of 0.2 mV/s. For each alloy, the critical potential is shown with the dotted line.



Fig. 4.4. Ag dissolution current density for sample Au₃₃Ag₆₇ and the second derivative used to obtain the critical potential, Ec. For this dissolution current wave, the Ec value selected is around 0.3 V.

The dissolution charge Q_{meas} was measured to determine the amount of Ag removed from the films. This was done by integrating the current density of the dissolution waves for each sample shown in Fig. 4.3. Considering that the total alloy deposition charge was 100 mC/cm² and the Ag composition for each film was determined by XPS measurements, we estimated the charge of Ag expected in each film, Q_{film} . The difference between the measured and estimated (deposited) values is calculated and presented in Table 4.2. It can be observed that the difference in charges is for all samples less than 10 mC/cm². The small amount of remaining Ag, which can be thought of as trapped in the remaining NPG structure, has been shown in other works as well¹⁷⁷⁻¹⁷⁸ with percentages ranging ~3 -5 % similar to those obtained in our results.

Table 4.2. Estimated charge of Ag deposited in the films (Q_{film}) and measured charge (Q_{meas}) of Ag dissolution for alloys electrodeposited from different solutions.

Electrodeposition	$Q_{film} \pm 2$	$Q_{meas} \pm 1$	$\Delta Q = Q_{film} - Q_{meas}$
Solution	$[mC/cm^2]$	[<i>mC/cm</i> ²]	$[mC/cm^2]$
S _{1,1}	67	65	2
S _{1,2}	78	70	8
S _{1,3}	84	77	7

4.3.3 Surface characterisation of starting surface after Ag dissolution of alloys

Following the dealloying, a porous structure is obtained and then characterised electrochemically. In the rest of the chapter, each NPG sample will be labelled according to Table 4.3. The as-dealloyed NPG surface area was measured using Pb UPD following the work by Liu et al.⁹⁷. The results of LSV of Pb UPD dissolution from different NPGs are presented in Fig. 4.5 and compared to the flat Au substrate.

Electrodeposition Solution	Parent alloy	NPG label
S _{1,1}	Au ₃₃ Ag ₆₇	NPG _{67/33}
S _{1,2}	Au ₂₂ Ag ₇₈	NPG _{78/22}
S _{1,3}	Au ₁₆ Ag ₈₄	NPG84/16

Table 4.3. The alloys and corresponding NPGs after Ag dissolution.



Fig. 4.5. Linear sweep voltammetries of Pb UPD in 0.1 M HClO₄ + 1 mM Pb(ClO₄)₂ solution used to measure the surface area of flat Au substrate and three NPGs obtained from different parent alloys. Scan rate of 10 mV/s.

Integrating the current from the linear sweeps shown in Fig. 4.5, the charge Q_i for each NPG sample is obtained and presented in Table 4.4. The charge was then normalised, i.e. divided by the charge of Pb UPD measured on flat Au substrate $Q_{Au} = 312 \pm 6 \,\mu C/cm^2$. This was used to obtain the factor of surface area increase compared to the flat Au. It can be observed that the area for all NPG structures is significantly larger than the flat Au, and the largest area was measured for NPG_{67/33}. These results agree with the literature measurements and show that NPG_{67/33} has the smallest pore and ligament sizes. ⁹⁷

Sample	$Q_i \pm 10$ [μ C/cm ²]	Q_i/Q_{Au}
NPG _{67/33}	5200	16.7
NPG _{78/22}	2610	8.4
NPG _{84/16}	1830	5.9

Table 4.4. Pb UPD charge measured on as-dealloyed NPG samples (Qi) and comparison with the charge measured on flat Au surface $Q_{Au} = 312 \pm 6 \,\mu C/cm^2$.

SEM measurements further confirmed the structure of the NPG samples. The SEM images of as-de-alloyed samples are shown in Fig. 4.6. It can be observed that the pore sizes increase with Ag content in the parent-alloy in agreement with literature⁹⁷. For the NPG_{84/16} sample shown in Fig. 4.6 c), cracks at the surface could be observed. This agrees with the observed cracking in the bulk alloy samples due to dealloying induced strain and a significant volume reduction during the dealloying process¹⁷⁹⁻¹⁸⁰. The size of the pores in between the cracks are larger than the other two samples, as expected.



Fig. 4.6. SEM images of as-dealloyed samples for a) NPG_{67/33}, b) NPG_{78/22} and c) NPG_{84/16}.

4.3.4 Surface modification on Au after multiple cycles using Pb UPD

The voltammogram in Fig. 4.7 shows Pb UPD on a flat Au (111) surface. Starting from the potential of bare Au at 0.8 V, the potential is swept negative to form a complete Pb monolayer at 0 V. The in-situ STM images show the formation of small islands and holes in the Pb monolayer suggesting the exchange of Pb and Au atoms during the monolayer formation.

During the reversed potential sweep, the surface shows additional Au islands and holes formed at the surface. These morphology changes have been attributed to surface alloying of Pb with Au during the potential cycle ^{175-176, 181-183}. The anodic peak at the most positive potential has been associated with the dealloying process of the low coverage of Pb in the top Au layer. Considering that there are morphological changes at the surface of flat Au after cycling in the Pb UPD region, repeated potential cycling was further explored as a tool for electrochemical annealing and NPG structure modification. A similar approach has been used in the past where potential cycling in the Au oxidation region resulted in coarsening and electrochemical annealing of NPG.¹⁶⁹



Fig. 4.7. Pb UPD on Au (111) surface and STM images at different stages of the UPD process in 0.1 M HClO₄ + 1 mM Pb(ClO₄)₂ solution using a scan rate of 10 mV/s. STM images are taken from Ref ¹⁷⁶.

4.3.5 Surface modification of NPG samples using Pb UPD

After the area of the as-dealloyed NPG sample was measured, multiple potential cycles of Pb UPD were applied. After each 10th cycle, the surface area was measured by LSV to follow the evolution and changes with the number of CV cycles. Scan rates of 10 mV/s and 100 mV/s were used.

The evolution of the area with the number of cycles for sample NPG_{78/22} is shown in Fig. 4.8 for illustration. Similar curves (not shown) have been obtained for all alloys. It can be observed that with each cycle, the Pb UPD voltammogram current is reduced for both scan rates. The voltammograms show better-defined peaks for slower scan rates compared to the faster scan rates as expected.^{65, 97, 146}



Fig. 4.8. Changes of the voltammograms of Pb UPD in 0.1 M HClO₄ + 1 mM Pb(ClO₄)₂ solution on NPG_{78/22} samples with the number of cycles. Selected CVs are shown for scan rates a) 10 mV/s and b) 100 mV/s.

The area measurements were conducted every 10 cycles. A plot of integrated Pb UPD stripping charges with respect to the number of CV cycles is presented in Fig. 4.9 a) for all porous samples. It can be observed that the charges for all samples decrease similarly. The changes follow a trend similar to those observed during thermal annealing, where the structure of Au gradually coarsens. The NPG area changes are also presented in Fig. 4.9 b) as a relative area change, i.e. normalised to the initial NPG area. It can be observed that faster changes occur after initial cycles, and the fastest changes have been observed on NPG_{67/33} samples with the smallest pores and ligaments.



Fig. 4.9. a) Total charge of the Pb UPD in 0.1 M $HClO_4 + 1 \, mM \, Pb(ClO_4)_2$ solution measured on different NPG samples vs the number of CV cycles. b) The reduction of surface area normalised to the initial NPG area. The results show repeated potential cycling with a scan rate of 100 mV/s for all samples.

A similar trend of surface area changes has been observed using CV cycles with slow (10 mV/s) and fast scan rates (100 mV/s), as shown in Fig. 4.10. However, much faster changes were obtained using slower scan rates. This could be explained by the slow kinetics of the surface alloying process and slower electrochemical annealing compared to the Au surface diffusion process involved. The effect of the scan rate on the porosity change can be observed on SEM images in Fig. 4.10 c) and d).



Fig. 4.10. a) Relative area change of as-dealloyed NPG_{67/33} samples after multiple Pb UPD cycles with different scan rates. SEM images of b) as-dealloyed sample and samples after 200 cycles with scan rate c) 100 mV/s and d) 10 mV/s.

As already noted earlier, some amount of Ag was considered trapped in the structure following dealloying. Ag may be removed during initial CV cycles, and this may contribute to the NPG porosity evolution. To examine this hypothesis and explore the effect of residual

Ag removal, the surface of dealloyed samples was first treated by Au oxidation/reduction cycles before multiple Pb UPD cycles were employed. This will be illustrated in the next section on the $NPG_{67/33}$ samples.

4.3.6 The effect of oxidation/reduction on the initial NPG surface

It has been shown that NPG features can be modified by thermally annealing the sample, which coarsens the structure^{54, 163-165}. Another technique that can lead to coarsening of the structure is known as electrochemical annealing¹⁶⁹. The process of electrochemical annealing involves multiple cycling of Au in the gold oxidation region. The formation of AuO on the surface is often used as a surface area measurement method, as mentioned in Chapter 2. Au surface oxide (AuO) reduction results in the formation of Au ad-atoms that are redistributed by surface diffusion to the lowest energy surface structure. Sharma et al. combined the oxidation of Au protocol with the effect of different anions in the solution and showed changes in surface area between 20% to about 60% ¹⁶⁹.

In this thesis, Au surface oxidation-reduction was used for the area measurements of flat gold substrates.^{96, 128} In this study, it was also used to 'treat' the as-dealloyed NPG sample, following the approach often used on bulk de-alloyed samples to remove remnant Ag. ¹⁷⁷ For illustration, the results will be presented and discussed for NPG_{67/33} samples.

The as-dealloyed NPG_{67/33} sample was immersed in a solution containing 0.1 M HClO₄ solution, and several cycles of Au oxidation (Au ox/red cycles) were applied as shown in Fig. 4.11 a). It can be observed from the graph that the area of the voltammograms gets reduced after each cycle until it reaches the seventh cycle, after which the cycles stop changing. Following these observations, seven Au ox/red cycles were selected as a pre-treatment for all samples before multiple cycles of Pb UPD application. The surface area was measured from the reduction peak of AuO for the initial and seventh cycles. The area measured by integration of current shows that the as-dealloyed sample has the associated charge of 9970 \pm 10 μ C/cm² whereas the one after Au oxidation/reduction cycles is 7200 \pm 10 μ C/cm².

The SEM images of the NPG_{67/33} sample before and after applying the seven cycles are shown in Fig. 4.11 b) and c), respectively. The pores in Figure c) are more easily resolved and

interconnected. The redistribution of Au atoms could explain the reduction of the surface area during the cycling in the gold oxidation region, which coarsens the structure and releases Ag atoms that may have remained in the structure after the dealloying process.



Fig. 4.11. a) Cyclic voltammograms of 10 cycles in 0.1 M HClO₄ solution on NPG_{67/33} sample with a scan rate of 20 mV/s. SEM images of b) as dealloyed NPG_{67/33} sample and c) NPG_{67/33} sample after the 7th cycle of Au ox/red.

The surfaces of NPG_{67/33} samples treated by Au ox/red cycles were then examined with Pb UPD cycles in the same way as described in the previous section. The respective structures were then examined by SEM. The SEM images of the samples following 200 Pb UPD cycles with different scan rates are shown and compared to those without Au ox/red cycles pre-

treatment in Fig. 4.12. The SEM images show the more open structure and larger pores for samples treated with Au ox/red cycles. This is expected and suggested by area measurements.

The relative area change of the Au ox/red treated samples is measured and shown in Fig. 4.13, with a similar trend to the as-dealloyed samples. This result confirms that electrochemical annealing by Pb UPD has the general effect that can be applied as a tool for tuning porosity. The surface changes are independent of remnant Ag in the initial NPG structure.



Fig. 4.12. SEM images of a) as-dealloyed NPG_{67/33} sample and as-dealloyed NPG_{67/33} sample after 200 Pb UPD cycles with b) scan rate 100 mV/s and c) scan rate 10 mV/s. For comparison, the images of d) NPG_{67/33} samples after the 7 Au ox/red cycles and after 200 cycles of Pb UPD with e) scan rate 100 mV/s and f) scan rate 10 mV/s.



Fig. 4.13 Comparison of the relative surface area change of $NPG_{67/33}$ samples versus the number of Pb UPD cycles using a scan rate of 100 mV/s in 0.1 M HClO₄ + 1 mM Pb(ClO₄)₂ solution. As-dealloyed samples are black data points, and pre-treated with Au ox/red cycles are red.

Furthermore, the analysis of SEM images for each sample has been conducted to obtain the ligament width ($w_{ligament}$) and the pore radius (r_{pores}) and the results are shown in

Fig. 4.14 a). The ligaments were measured from the images as presented in

Fig. 4.14 b) using Gwyddion software. The size distribution was obtained from a set of values, as shown in

Fig. 4.14 c). After that, a filter was applied to the original image using ImageJ software to select the holes in each image as illustrated in

Fig. 4.14 d), and the pore size distribution is shown in

Fig. 4.14 e). The summary of the ligament width and pore radius obtained from different samples is presented in Table 4.5. From the table, it could be confirmed that the increase in ligament width and pore radius follows multiple cycles in the Pb UPD region on as-dealloyed and the initial AuO pre-treated samples.



Fig. 4.14. Analysis of SEM images used to obtain ligament and pore sizes. A) Selected SEM image, b) an example of ligament measurements, c) distribution of $w_{ligament}$ obtained of 12.7 nm with SD of 3.3 nm, d) an example of the method used for hole identification by applying a filter mask and e) distribution of r_{pores} measured from image d) of 8.6 nm with SD of 3.2 nm.

Table 4.5. A table containing the ligament width and pore radius with standard deviations obtained from the SEM images of $NPG_{67/33}$ samples after different treatments.

Sample	Ligament width [nm]	SD of ligament width [nm]	Pore radius [nm]	SD of pore radius [nm]
Initial as-dealloyed	12.7	3.3	8.6	3.2
As-dealloyed after 200 cycles of Pb UPD with 100 mV/s	13.2	3.4	13.2	6.1
As-dealloyed after 200 cycles of Pb UPD with 10 mV/s	20.1	5.3	15.5	9.0
Initial after Au ox- red cycles	9.7	3.0	11.1	7.1
Au ox-red sample after 200 cycles of Pb UPD with 100 mV/s	16.6	3.7	12.4	6.1
Au ox-red sample after 200 cycles of Pb UPD with 10 mV/s	19.6	4.4	16.8	8.9

4.4 Conclusions

The study of fabrication of NPG structures using all electrochemical approaches has been presented. NPGs have been obtained by electrochemical selective dissolution of Ag from electrodeposited Au-Ag alloys of different compositions. The measured values of critical potential shifted more positive for alloy films with more Au content, agreeing with the bulk alloy values. Different porous structures were obtained depending on the parent alloy used. The Pb UPD was used to obtain the surface area of porous samples, which showed higher values than flat Au.

The application of multiple cycles of Pb UPD showed that the surface of the porous structures could be changed and coarsened. Different scan rates during Pb UPD cycling were used, and more significant area changes were obtained for slower scan rates. The pre-treatment of NPG porous structures with Au ox/red cycles increased the initial NPG surface area. However, the effect of repeated Pb UPD cycles was the same as on non-treated samples. This confirmed the applicability of Pb UPD based electrochemical annealing as a tool for fine-tuning the NPG surface porosity. This is the first report of the electrochemical annealing method induced by surface alloying of Pb with Au that could have implications and use on other Au nanostructured surfaces.

5 Chapter - Electrochemical characterisation of Au_xAg_{100-x} alloys using underpotential deposition

The electrodeposited Au_xAg_{100-x} alloys were analysed by Pb UPD and Cu UPD processes in this chapter. Pb UPD has been studied extensively on both pure Au and Ag surfaces and was selected as one of the UPD systems to explore. The second metal was Cu that is well known to form UPD on Au but not on Ag. In the case of Cu, two background solutions were studied, sulphate and perchlorate, as the role of anions is essential and affects this metal monolayer formation. The changes of the UPD voltammetric peaks were monitored and correlated to the alloy compositions.

5.1 Introduction

The underpotential deposition (UPD) involves a formation of an epitaxial monolayer of a metal (M) on a foreign substrate (S) at potentials that are more positive than the Nernst equilibrium potential for bulk metal M deposition. This process takes place only on certain metal/substrate combinations.^{89-91, 120, 122} The structure of the voltammograms (peaks) are influenced by the interaction between the metal M and substrate S, crystal structure of the substrate and ions present in the solution.^{89-91, 120, 122}

Over the last few decades, understanding of different UPD system has been exploited in many ways. The most advanced applications include mediation and manipulation of thin-film growth kinetics in Surfactant-Mediated Growth (SMG)¹⁰⁴⁻¹⁰⁵ and Defect Mediated Growth (DMG)^{101, 106-107} methods. The most recent work used UPD layers as sacrificial to deposit noble metals (such as Pt, Au, Pd) spontaneously by galvanic displacement at the open circuit ¹⁰¹.

Processes of metal UPD on foreign substrates have been often used as analytical tools in electrochemical surface science to characterise surface crystal structure and measurements of active surface area. The surface composition sensitivity of UPD processes has not been understood and explored enough. The research in the area of UPD metals on alloys could help in the development of new tools for surface characterisation that would be particularly useful in catalysis^{65, 108-109} and corrosion.¹⁸⁴⁻¹⁸⁵

Surface characterisation of alloys using UPD has been explored in the past.^{65, 108-110} Because the UPD characteristic peaks depend on the substrate's nature, there have been very few studies in the past focused on understanding the aspects of UPD formation on alloy surfaces and the correlation with the alloy composition. ¹¹⁰ One such example is Cu UPD formation on Au-Ag alloys explored by McCall et al ¹¹⁰ where it was shown that the charge associated with the Cu UPD decreased with increasing Ag atomic fraction in the alloy.¹¹⁰ In the studies of Cu UPD on Pt-Pd¹⁰⁸ and Pt-Ru¹⁰⁹ alloys where Cu forms UPD layers on both metals, the correlations with the alloy composition have been primarily qualitative. ¹⁰⁹⁻¹¹⁰

In this chapter, Pb UPD and Cu UPD (in sulphate and perchlorate solutions) were used to analyse electrodeposited Ag and Au_xAg_{100-x} alloys. The shape of characteristic Pb UPD peaks on Ag and Au surface is different, and the positions are well separated (~50 mV) to allow comparison of changes with alloy composition. In the case of Cu UPD on alloys, two background solutions were studied as the role of anions affects this metal monolayer formation. More quantitative measurements showed the differences and similarities with the previously reported results.¹¹⁰

5.2 Experimental Section

5.2.1 Sample preparation

Au_xAg_{100-x} alloys were electrodeposited from thiosulphate solutions following the protocols and compositions as described in Chapter 3. The same labels and annotations will be used in this chapter. The alloys' deposition conditions were: i) limited deposition by total deposition charge of 50 mC/cm² and ii) electrodeposition at a constant potential of -0.79 V vs MSE (or -0.15 V vs Ag/Ag⁺). Pure Ag films were also electrodeposited for comparison using different experimental conditions and solutions. The details of the solutions are presented in Table 5.1.

Ag grown in perchlorate solution (0.1 M HClO₄ + 1 mM AgClO₄, S_{perch}) was used as a reference sample for comparison with films deposited from thiosulphate-based solution, S1. Both samples were electrodeposited at the same overpotential of -0.15 V vs Ag/Ag⁺. The Ag films were grown for different thicknesses corresponding to the deposition charge of 5 mC/cm², 10 mC/cm², 20 mC/cm² and 50 mC/cm².

Solution S_{surf} was used for growing epitaxial Ag films by SMG method using Pb UPD as a surfactant. Ag film was deposited at -0.125 V vs Ag/Ag⁺, following the conditions as described by Brankovic et al.¹⁰⁴. For the SMG deposited Ag films, growth is much slower, and for comparison, Ag films were grown for different deposition times.

Solution	Label	Method	Deposition Potentials vs <i>Ag/Ag</i> ⁺
$0.1 \text{ M Na}_2\text{S}_2\text{O}_3 + 2 \text{ mM AgClO}_4$	S_1	Const. Pot.	-0.15 V
0.1 M HClO ₄ + 1 mM AgClO ₄	$\mathbf{S}_{ ext{perch}}$	Const. Pot	-0.15 V
10 mM HClO ₄ + 0.1 mM AgClO ₄ + 10 mM Pb(ClO ₄) ₂	$\mathbf{S}_{\mathrm{surf}}$	SMG	-0.125 V

Table 5.1. Different solutions and conditions used to electrodeposit pure Ag films. The labels were used in this chapter.

5.2.2 UPD measurements on Au, Ag and alloys samples

All UPD measurements were done in a three-electrode cell, using Pt as a counter electrode, the pseudo-reference electrodes were Pb wire for Pb UPD in perchlorate solution and a Cu wire for solutions containing Cu ions. Samples were rinsed after alloy deposition with Milli-Q water and immediately used for the Pb UPD measurements to avoid prolonged exposure to air.
Pb forms a UPD layer on top of Au and Ag, which is why we were interested in looking at this system for our alloys characterisation^{176, 186-187}. Cyclic voltammograms were taken between 0.0 V and 0.8 V vs Pb/Pb²⁺ with a scan rate of 10 mV/s in 0.1 M HClO₄ + 1 mM Pb(ClO₄)₂. For the case of Pb UPD on Ag (111), the range of potential scans was narrower compared to that of Au¹⁸⁸ in order to avoid silver oxide formation.

Cu UPD was explored using two different solutions, $0.1 \text{ M H}_2\text{SO}_4 + 1 \text{ mM Cu}(\text{SO}_4)_2$ and $0.1 \text{ M HClO}_4 + 1 \text{ mM Cu}(\text{ClO}_4)_2$. For sulphate-based solution, the potential range explored was from 0.0 V to 0.4 V vs Cu/Cu²⁺ with a scan rate of 20 mV/s. In the perchlorate-based solution, the potential range varied from -0.04 V to 0.4 V vs Cu/Cu²⁺ with a scan rate of 20 mV/s.

5.3 Results and discussion

5.3.1 Pb underpotential deposition on perchlorate-based solutions

The first system studied was the Pb deposition in a perchloric-based solution, known to start by UPD monolayer formation on both Ag and Au.

5.3.1.1 Pb UPD on Au and Ag

The process of Pb UPD on Au(111) has been extensively studied in the past ^{175-176, 181, 183, 186-191}. Cyclic voltammetry of Pb UPD on Au film substrates is shown in Fig. 5.1 a with labelled characteristic peaks associated with the monolayer formation on a single crystal surface of Au(111).^{176, 181, 186-187} Each set of peaks presents a stage of monolayer formation and anodic dissolution. In the cathodic direction, three stages/peaks are visible and labelled C1-C3. On the reversed scan, the associated anodic peaks show asymmetry.¹⁸⁶⁻¹⁸⁷ The CV of Pb UPD with different potential limits was used in the past to establish the cathodic and associated anodic peaks as shown in Fig. 5.1 b (Figure taken from ref ¹⁷⁶). The first cathodic peak, C1, and associated anodic A1 mark the initial stage of Pb UPD formation/dissolution. This stage was associated with Pb deposition at the step edges based on the in-situ STM studies.^{175, 183} The second cathodic peak, C2, covers a broad potential region. Its anodic counterpart, A2, is at the most positive potentials. Such asymmetric peaks behaviour is unusual. This stage has

been associated with the surface alloying/dealloying of Pb with Au, as mentioned and exploited in Chapter 4. The in-situ STM studies observed the formation of Au ad-islands and vacancies formation on the top surface layer¹⁷⁶ and illustrated in Fig. 4.7. The third cathodic peak, C3, is the final stage of the Pb monolayer completion, during which the surface alloy transitions to a Pb hexagonal incommensurate overlayer on Au. The anodic counterpart labelled A3 is a double peak associated with the dissolution of the Pb overlayer phase from the two energetically different surface sites, such as steps and terraces. The splitting of the main anodic peak A3 is characteristic of high-quality Au(111) surfaces. The studies in our group and the literature have shown that on samples with more polycrystalline nature (such as non-annealed Au) A3 is usually a single peak.



Fig. 5.1. a) CV of Pb UPD on Au thin film substrates in a solution of 0.1 M HClO₄ + 1 mM $Pb(ClO_4)_2$. Scan rate of 10 mV/s.(b) Cyclic voltammetry of Pb UPD with different potential limits used to establish cathodic and associated anodic peaks. The figure is taken from Ref ¹⁷⁶.

Pb UPD on Ag was conducted on the Ag films electrodeposited from three different solutions (Table 5.1), and the results are shown in Fig. 5.2.

Electrodeposition at constant potential of -0.15 V vs Ag/Ag^+ from S_1 and S_{perc} solutions were used to make Ag films of different thicknesses controlled by deposition charge. In order to determine the efficiency of deposition, Ag dissolution was conducted by linear sweep voltammetry with a scan rate of 20 mV/s as presented in Fig. 5.2 a1) and b1). The comparison of the dissolution charge Q_{diss} with the target deposition charge Q_{target} , is shown in Fig. 5.2 a2) and b2). The efficiencies determined by the slope of the curves were $k = 0.98 \pm 0.01$ for deposition of Ag in solution S_1 and $k = 0.94 \pm 0.01$ for deposition in solution S_{perc} . The results show very high efficiency and a good control of Ag film thickness.

Following the electrodeposition from S_1 and S_{perc} solutions, and before LSV dissolution, all Ag films were rinsed with MilliQ water and immediately examined by Pb UPD in Pbcontaining solution. CVs were recorded with a scan rate of 10 mV/s, and the results are presented in Fig. 5.2 a3) and b3). It can be observed that all voltammograms show a very sharp peak at 0.15 V vs Pb/Pb²⁺, which is characteristic for Pb UPD on Ag (111) with two side shoulders linked to the roughness and defects of the Ag surface.¹⁸¹ From both voltammograms, the areas under the CVs change slightly with a thickness attributed to the increase in the films roughness (surface area).

The most notable difference is the presence of a very pronounced cathodic peak for all samples deposited in the S_1 solution. Compared with the films deposited in the S_{perc} solution, it can be concluded that this peak is not associated with the Pb UPD process. However, it could be associated with some other surface reduction processes.



Fig. 5.2. Linear sweep voltammetry of Ag dissolution in 0.1 M HClO4 + 1 mM AgClO4 solution for films grown in a1) S_1 and b1) S_{perc} . Scan rate 10 mV/s/. The integrated charges of Ag dissolution vs targeted deposition charges for samples deposited from a2) S_1 and b2) S_{perc} . Cyclic voltammograms of Pb UPD on Ag samples grown with different deposition charges (thickness) in 0.1 M HClO4 + 1 mM Pb(ClO4)₂ solution with a scan rate of 10 mV/s.

For Ag, Pb UPD was limited to a narrower potential range from 0 until 0.3 V vs Pb/Pb²⁺ compared to Au. Potentials more positive than that showed on S₁ films another anodic peak which could be associated with silver oxide formation as seen in Fig. 5.3. As CVs in this region did not show clear Pb UPD peaks, the upper potential limits for the voltammograms of pure Ag and the Au_xAg_{100-x} alloys was varied to obtain the complete measurement of the monolayer and to avoid this oxidation peak. The reduction peak nature was not explored further (due to time restrictions), but it is associated with Ag deposition from thiosulphate solution.



Fig. 5.3. Pb UPD in 0.1 M HClO₄ + 1 mM Pb(ClO₄)₂ solution on pure Ag sample deposited in S1 solution over a different range of potentials. Scan rate 10 mV/s

In addition to Ag films electrodeposition at a constant potential, Ag films were also grown by the SMG method following Brankovic et al., who used Pb UPD as a surfactant layer to promote the epitaxial growth of Ag ¹⁰⁴. For this case, the thickness via total charge measurement could not be used, so the deposition time was varied to form films of different thicknesses. Cyclic voltammetry of Pb UPD on Ag films deposited via SMG after different deposition times are shown in Fig. 5.4. As shown, the voltammograms are very similar independent of time of deposition. This can be attributed to the Ag epitaxial deposition, i.e. 2D growth following the substrate surface morphology, as no contribution due to roughness was observed.



Fig. 5.4. Pb UPD cyclic voltammograms on Ag thin films grown via SMG from S_{surf} for different deposition times. Scan rate of 10 mV/s.

The three different samples of Ag films of similar thickness (~10 mC/cm²) were compared, and CVs of Pb UPD are shown in Fig. 5.5. It can be seen that the peak at 0.15 V vs Pb/Pb²⁺ is common for all the samples, which is related to Pb UPD on Ag(111). The comparison also confirms that the Ag film grown from the S₁ solution exhibit a cathodic peak around 0.03 V vs Pb/Pb²⁺ characteristic only for thiosulphate growth solution.



Fig. 5.5. Pb UPD cyclic voltammograms in 0.1 M HClO $_4$ + 1 *mM Pb*(*ClO* $_4$)₂ *solution, on Ag thin films grown using three different solutions and methods. Scan rate of 10 mV/s.*

5.3.1.2 Pb UPD on Au_xAg_{100-x} alloys

Voltammograms of Pb UPD on pure Ag, pure Au and Au-Ag alloys are shown in Fig. 5.6 a). For analysis, the most prominent peak position was taken from the linear sweeps and shown in Fig. 5.6 b). The pronounced UPD peak position was plotted as a function of composition in Fig. 5.6 c). The potential of the Pb UPD prominent peak shifts towards more positive values with the increase of Au content in the film. One important thing to mention is that the peak position shift does not follow a linear trend with alloy composition, which is noted for other UPD systems. Also, considering a silver-rich composition of alloys, the features of the UPD resemble the Pb UPD on the Ag surface.

Also, the anodic charge was integrated to obtain the coverage of Pb at the surface and is presented in Table 5.2. Pb forms UPD on both Au(111) and Ag(111), and the charge of a full Pb UPD has a value of $\sim 310 \pm 10 \,\mu C/cm^2$. Both metals have the same crystal structure and lattice parameters, and therefore a similar charge as the pure metals is expected for the alloys. It can be observed that alloys show a lower Pb UPD charge than Ag and Au samples. A possible reason for that could be the narrow potential range of Pb UPD scans that does not extend enough to dissolve a complete Pb monolayer.



Fig. 5.6. a) Cyclic voltammograms and b) Linear sweep voltammograms of Pb UPD on Au, Ag (deposited from S_1) and Au_xAg_{100-x} alloys of different composition in 0.1 M HClO₄ + 1 mM Pb(ClO₄)₂ solution recorded with a scan rate of 10 mV/s. c) Potential of the main Pb UPD peak as a function of alloy composition.

Au cont. [%]	$Q \pm 10 \ [\mu C/cm^2]$
100	301
47	226
32	295
23	243
0	311

Table 5.2. Charge integrated from the Pb UPD LSVs for the Au_xAg_{100-x} alloys obtained from Fig. 5.6.

5.3.2 Cu underpotential deposition in sulphate-based solutions

A similar comparison was made using another UPD system, which is Cu. Cu UPD was studied using two background solutions, using sulphuric and perchloric acid. Because Cu does not form UPD on Ag, measurements are expected to be influenced by Ag and Au distribution and composition in the Au_xAg_{100-x} alloys.¹¹⁰

In the sulphuric-based solution, Cu UPD on Au and alloys was explored by cyclic voltammetry and the linear potential sweep in the same potential range. The samples were first characterised by cyclic voltammetry. Then the potential was stepped to 0.01 V for 180 s, and the linear sweep voltammetry was recorded. Two prominent peaks in Cu UPD cyclic voltammetry and on the linear sweeps are shown in Fig. 5.7 a) and b) respectively.^{89-90, 93} The position of both peaks was recorded for each alloy composition and presented in Fig. 5.7 c). As it can be seen, the peak position increases in potential value with Au content in the film. The trend that both peaks follow is similar, and it is not linear, the same as in the case of Pb UPD. The peaks from linear sweep voltammetry were integrated to obtain the charge of Cu UPD for each alloy. The results are shown in Fig. 5.7 d) and summarised in Table 5.3. The theoretical charge value is $440 \,\mu \text{C/cm}^2$ for Cu UPD on Au(111)⁹⁰. From Fig. 5.7 d), it can be seen that the trend for the charge is not linear, and it follows a similar trend of peak positions in Fig. 5.7 c).



Fig. 5.7. A) Cyclic voltammetry and b) linear sweep voltammetry of Cu UPD on Au and Au_xAg_{100-x} alloys in 0.1 M H₂SO₄ + 1 mM CuSO₄ solution. Scan rate of 20 mV/s. c) Cu UPD peak positions and d) charge for Au_xAg_{100-x} versus Au composition.

The results can be compared with the previous work of McCall et al.¹¹⁰ Modelling UPD formation on ideally mixed random alloy, ideally ordered alloy and phase segregated alloy McCall et al.¹¹⁰ showed that in the case of phase segregated and ordered alloys, linear dependence with composition is expected.¹¹⁰ In their work, a randomly mixed binary alloy model, was developed using the percolation theory.¹⁹² The components in the alloy were considered organised in clusters of different sizes related to the composition of the alloy. The model considers average clusters size and considers the blocking effect of Ag on neighbouring Au atoms.

The average cluster size (diameter), ξ was given as

$$\xi = \frac{1+q}{1-q}a$$
, Eq. 5.1

where q is the fraction of Ag in the alloy and a is the nearest neighbour distance between the atoms. For an alloy containing a fraction of Aq, q, number of $\xi - size$ clusters is given as q/ξ^2 . For alloys rich in Au (q < 0.5), the model predicted Cu coverage as a function of q (or p = 1 - q, a fraction of Au) as:

$$\theta_{Cu} = 1 - \pi \frac{q}{\xi} = 1 - \pi \frac{(1-p)p}{2-p}$$
 Eq. 5.2

For alloys rich in Ag (q > 0.5), the model predicted coverage of Cu given by:

$$\theta_{Cu} = \frac{(\xi^2 - 2)p}{\xi^2} = p \frac{4p - (1-p)^2}{(1+p)^2}$$
 Eq. 5.3

The models' predictions of Cu UPD coverage as a function of Au content in the alloy are illustrated in Fig. 5.8, taken from Ref¹¹⁰.



Fig. 5.8. Predicted trends of Cu UPD coverage (normalised charge density) for three models of binary alloys: randomly mixed, ideal ordered and phase-separated. Points on the graph present measured Cu coverage on Au-Ag polycrystalline bulk samples from the study McCall et al.¹¹⁰ Figure taken from Ref¹¹⁰.

From the linear sweep voltammetry in Fig. 5.7, the stripping charges for the Au_xAg_{100-x} alloys were measured and presented in Table 5.3. The results show that the Cu UPD charge on

alloys follows qualitatively the same trend as predicted by the cluster model. The normalised experimentally measured Cu UPD coverage (θ_{exp}) and that predicted by Eq. 5.3 (θ_{model}) are shown in Table 5.3 for comparison. There is a significant discrepancy. The normalised charge of Cu UPD on alloys shows higher values than those predicted by the model. Some of the possible reasons for this could be:

1) not considered the total surface area of the alloy samples in charge density evaluation. The measured values presented in the table were normalised to Au substrate surface area;

2) the alloy surface could be Au enriched by the removal of Ag atoms on the top layer. During sample handing (after deposition), such as rinsing and transferring to Cu solution, Ag might become oxidised. During Cu UPD cycles, the Ag oxide could be reduced and removed/redistributed on the top surface layer in the process.

3) The distribution of Ag and Au in the alloy might vary for different alloys due to codeposition experimental conditions that could favour more segregated alloys in the case of higher Ag concentration in the solution.

Further studies to distinguish and confirm the possible effects are needed.

Table 5.3. Charge integrated from the Cu UPD anodic peak for the Au_xAg_{100-x} alloys in 0.1 M $H_2SO_4 + 1$ mM CuSO₄ obtained from Fig. 5.7.

Au cont. [%]	$Q \pm 10$ [$\mu C/cm^2$]	$\theta_{ex} = Q/Q_{Au}$ (Normalised charge)	θ _{model} (Eq 5.3.)
100	440	1	
47	350	0.80	0.35
32	336	0.76	0.15
23	302	0.69	0.05

5.3.3 Cu underpotential deposition on perchlorate-based solutions

Similarly, cycling in the Cu UPD region on different alloys was done using a 0.1 M HClO_4 + 1 mM Cu(ClO₄)₂ solution. The cyclic voltammograms in the Cu UPD region are shown in Fig. 5.9 a). The dissolution of the Cu UPD charge for each sample is measured by the linear sweep voltammogram to obtain the relation with the film's composition, as shown in Fig. 5.9 b). The integrated charge of Cu UPD on each alloy is presented in Fig. 5.9 c) and in Table 5.4. The UPD charge increases as the Au content in the film increases, which is similar for Cu UPD on the sulphate-based solution. The charges measured for this system are slightly smaller compared to those measured in sulphate solutions.



Fig. 5.9. A) Cyclic voltammograms and b) linear sweep voltammograms of Cu UPD on Au and Au_xAg_{100-x} alloys in a 0.1 M HClO₄ + 1 mM Cu(ClO₄)₂ electrolyte. Scan rate 20 mV/s. c) Cu UPD charge on each Au_xAg_{100-x} alloy as a function of composition.

Table 5.4. Charge integrated from the Cu UPD anodic peak for the Au_xAg_{100-x} alloys in 0.1 M HClO₄ + 1 mM Cu(ClO₄)₂ solution obtained from Fig. 5.9.

Au cont. [%]	Q ± 10 [μC/cm ²]	$ heta_{exp} = Q/Q_{Au}$ (Normalised charge)	θ _{model} (Eq 5.3.)
100	440	1	
47	340	0.77	0.35
32	270	0.61	0.15
23	210	0.48	0.05

Besides the discrepancy between the measured normalised Cu UPD coverage and those predicted by the model based on the alloy compositions, there are also slight differences in the measured coverage of Cu UPD in solutions with different background ions. It is well known that Cu UPD stability is affected by anion adsorption, and the results suggest some effect on the alloys. Further studies to quantify and confirm the effects are needed.

5.3.4 Cu UPD and Pb UPD subsequent measurements

Since we have shown and used in Chapter 4 the Pb UPD process to modify the surface of NPG, we need to explore if there is any effect on the surface structure/composition of the alloys. The comparison was made on a sample of $Au_{47}Ag_{53}$ alloy electrodeposited at a potential of -0.15 V vs Ag/Ag⁺ with a thickness of 50 mC/cm².

Case 1 - The as-deposited alloy was rinsed and analysed first in the Cu containing solution looking at the Cu UPD with scan rate 20 mV/s, then rinsed with Milli-Q water and after that immersed in the Pb containing solution to obtain the Pb UPD linear sweep voltammetry. After this, the sample was rinsed again, and the second linear sweep voltammetry was taken from the Cu UPD solution. Both linear sweeps are shown in Fig. 5.10.

Peaks for Cu UPD before and after Pb UPD have very similar positions (slightly shifted closer). However, it can be seen that there are some changes in the alloy surface as the peaks change intensity. This could be explained by the effect of surface alloying/dealloying with Pb during the UPD process. Following repeated cycling, alloying and dealloying could redistribute Au and Ag atoms at the surface.

Case 2- The second sample of the same alloy composition was analysed first by Pb UPD following the electrodeposition. After that, the sample was examined by Cu UPD cycles and then again by Pb UPD. In this case, the Pb LSVs before and after Cu UPD showed no changes. It can be concluded that Cu UPD does not affect the surface structure, i.e. no surface alloying taking place during Cu UPD.



Fig. 5.10. Linear sweep voltammetry of $Au_{47}Ag_{53}$ taken in 0.1 M $H_2SO_4 + 1$ mM CuSO₄ solution with a scan rate of 20 mV/s. The Cu UPD immediately after electrodeposition (black curve) and after the sample was examined by Pb UPD (red curve).

5.4 Conclusions

Different Au_xAg_{100-x} alloys were electrodeposited from thiosulphate-based solutions and analysed by different UPD systems. For the case of Pb UPD on alloys, it can be seen that the voltammogram peaks for alloys shift non-linearly from more negative for more Ag-rich films

to more positive for samples that contain more Au content. The Pb UPD charge values measured on alloys were slightly lower than those on pure metals. The narrow potential range of Pb UPD scans on alloys was used to avoid any Ag oxidation contributions. A more detailed study of Ag oxidation on alloys would be useful to make more accurate measurements of Pb UPD charge. The more accurate Pb UPD charge measurements could also be used to evaluate the 'real area' of the alloy samples.

For the case of Cu UPD on a sulphuric acid solution, the voltammograms and linear sweep also show a non-linear shift in peak potential towards more positive values with an increase in Au content film. By integrating the charge of Cu UPD, it was obtained that it decreased for more Ag-rich films. The reduction of Cu coverage showed a non-linear trend with alloy composition. In the case of Cu UPD on a perchlorate-based solution, similar results were observed. The voltammograms showed two peaks, as in the case of the sulphate-based solution, and this is in agreement with previous results on this system. From the analysis, the charge of Cu UPD decreases with an increase in Ag content on the alloy and a lower charge was measured for the perchlorate-based solution. Comparison with the cluster model for Cu UPD on AuAg alloys, the results showed qualitative agreement. The differences in the measured values were noted and could not be explained without additional studies.

The linear sweep of Cu UPD on $Au_{47}Ag_{53}$ alloy before and after examination with Pb UPD showed changes in peak intensities. The surface structure or composition changes could be attributed to the surface alloying with Pb, as mentioned in Chapter 4. On the other hand, the effect of Cu UPD on the alloys of the same composition showed no surface change.

6 Chapter - Conclusions and Future Work

6.1 Summary of main results and conclusions

Electrochemical growth of Au_xAg_{100-x} thin films is of interest for the design of nanostructures for plasmonic and sensors applications. The thesis includes studies of controlled electrodeposition of alloys with different composition, their electrochemical and structural characterisation, and their use in the design of NPG with electrochemically tunable porosity. The main results of this thesis are summarised below.

1) Electrodeposition of Au_xAg_{100-x} thin films with different compositions was explored using a thiosulphate-based solution. The aim was to develop less toxic conditions than those typically used in industry. It was shown that for the selected composition of Ag and Au ions in the solution, the grown alloys' composition was independent of applied potential during deposition below HER potential (-0.38 V vs SHE). The composition of films was varied by altering the ratio of the Au⁺: Ag⁺ ions in solution. Compositions of electrodeposited films were Ag-rich and ranged from Au₄₇Ag₅₃ to Au₂₂Ag₇₈. Using XPS analysis on films of different thicknesses (range 20 nm -100nm), the composition of electrodeposited films was shown to be homogenous and consistent during growth. In addition to that, the work demonstrated application on the formation of nanopatterned samples for potential plasmonic applications and fundamental studies of optical properties of alloy nanoparticles on transparent substrates.

2) NPG samples were obtained by electrochemical dissolution of Ag from Au_xAg_{100-x} thin films. The critical potentials of dealloying obtained by linear sweep voltammetry showed to shift to more positive potentials as the Ag content in the parent alloy increased, which was in agreement with observations on bulk alloys. The surface area of the dealloyed samples was obtained by measuring the charge of Pb UPD. The NPG's porosity level was dependent on the parent alloy, with a bigger mean pore size for samples derived from alloys with higher Ag content. Surface modifications of porous samples were done using Pb UPD multiple cycles. The Pb UPD on Au is a system with Pb-Au surface alloying that affects surface atoms redistribution. It was shown that repeated cycling of Pb UPD on NPG caused coarsening, i.e. affected the surface in the same way as 'thermal annealing'. The surface area of NPG decreased with the number of Pb UPD cycles, reflected by the increased size of ligaments and pores. Another factor that influenced the surface modification was the scan rate during cycles of Pb UPD. Slower scan rates showed a more prominent effect on the surface coarsening with the number of cycles. In addition, using Au ox/red cycles after dealloying showed an impact on the initial porosity size. The use of Au ox/red cycles on the as-dealloyed NPG_{67/33} samples demonstrated a better-defined porous structure (observed by SEM), which was reflected in a decrease in surface charge measured by Pb UPD (from 3870±10 to 510±10 μ C/cm²) almost eight times. The as-dealloyed samples treated by seven Au ox/red cycles followed the same surface area changes after Pb UPD cycles.

The results on Pb UPD based modifications of NPGs are new. These results show that using electrochemical methods, it is possible to create nanostructures of NPG with desired pore/ligament size ranging from 5 nm - 50 nm.

3) Surface characterisation of metals and alloys using UPD processes has been an attractive electrochemical surface science area. Pb UPD in perchlorate solution and Cu UPD in sulphate and perchlorate solutions were used to analyse electrodeposited Ag and Au_xAg_{100-x} alloys. Pb UPD has been well studied in the past on both pure Au and Ag surfaces. Pb UPD systems have characteristic prominent peaks that are separated ~50 mV. The study has shown that the prominent peak positions of Pb UPD shifted towards more positive values with higher Au content in the alloy. Also, Pb UPD voltammograms on Au_xAg_{100-x} alloys showed an unusual peak in the most negative cathodic direction (around 0.03 V vs Pb/Pb²⁺) associated with Ag grown in thiosulphate solutions. This compound's nature has not been determined. Still, we showed that it could be related to the detected S in the samples. A systematic study of Pb UPD on Ag films electrodeposited in three different ways has confirmed this. Ag thin films were electrodeposited in thiosulphate solution, perchlorate solution and via surfactant mediated growth (with Pb UPD as mediator).

Ag films electrodeposited in perchlorate solution have shown Ag-(111) characteristic peaks during Pb UPD, reflecting the structure with high roughness and an increased number of defects in the film. Epitaxial Ag films grown using the surfactant-mediated method were used for comparison to eliminate the effects of roughness and imperfections. Ag films produced by these two methods did not show an unusual reduction peak. The presence of a cathodic peak at 0.03 V vs Pb/Pb²⁺ was detected only for Ag samples grown in thiosulphate solutions confirming the hypothesis.

In contrast to the Pb UPD, Cu is a metal that forms UPD only on Au and not on Ag. Cu UPD voltammograms showed a similar shift in the peaks potentials towards more positive values with a higher Au content in the alloy films. The charge measured for the Cu UPD on the alloys (in both sulphate and perchlorate background solutions) decreased for a higher Ag content in the film. The observations and measurements followed a general trend observed on bulk alloys of different compositions previously reported.

6.2 Future work

A few project directions were explored that could not be pursued further because of the time limitations, and Covid 19 restricted access to the facilities and laboratory. However, promising preliminary results were obtained, and they will be presented here as possible directions for future work.

1) One of the main goals of the thesis was controlling the electrodeposition of Au_xAg_{100-x} alloys of different compositions. Using the selected range of Ag^+ and Au^+ ion concentrations in the thiosulphate solution, we could not obtain Au-rich alloys by conventional electrodeposition at constant potentials. To deposit more Au-rich alloys, we made a few attempts using the surfactant mediated growth (SMG) method¹⁹³. In this method, deposition potential is selected to be positive from the Ag/Ag+ reversible potential, i.e. in the underpotential deposition regime for Ag on Au. A 'surfactant' UPD layer of Ag was expected to form during Au overpotential deposition. The potential of deposition was chosen to correspond to a full Ag ML on Au. The expectation was to achieve either epitaxial growth of pure Au (if Ag UPD efficiently floats on the surface) or Au-rich alloy by incorporating some Ag during deposition.

The range of Au_xAg_{100-x} alloys electrodeposited from thiosulphate solutions (as discussed in Chapter 3) was limited by the ratio between Ag⁺ and thiosulphate ions in the solution. If the ratio between the concentrations of thiosulphate and Ag⁺ in solution is higher than 1.0, then the system is stable and soluble. However, if the ratio is smaller than 1, then silver sulphide Ag₂S is formed, and it precipitates. A solution of 0.26 M Na₂S₂O₃ + 2 mM AuNa₃(S₂O₃)₂ + 20 mM AgClO₄ was prepared to have 10 times higher Ag⁺ to Au⁺ ion ratio compared to the previous solutions. The higher ratio was to avoid the formation of Ag₂S and to have a higher ratio of the UPD mediator versus deposited metal, similar to the conditions used in the SMG method published in the literature.¹⁹³ The potential of deposition was 0.05 V vs Ag/Ag^{+,} and the length of deposition was 2400 s. The deposition of an alloy film was achieved, and the XPS characterisation showed an alloy of Au₅₂Ag₄₈ (very close to 50:50 composition). The resulting alloy had a composition very close to the one obtained from the solution S_{2,1}, and the cyclic voltammetry of Pb UPD on this alloy was similar, as shown in Fig. 6.1.

The results showed that the SMG growth protocol could be used to deposit Au-Ag alloys. However, to form different alloy compositions, it might be necessary to vary deposition potential at different Ag UPD coverages to confirm the deposit's incorporation mechanism. It would also be interesting to explore the effect of Ag^+ concentration and Au because similar deposition (at the constant potential in the Ag UPD region) could be obtained with less Ag in the solution and increasing the rate of Au deposition.



Fig. 6.1. Comparison of Pb UPD CVs on different Au_xAg_{100-x} alloys. Sample deposited using the SMG method was included and compared to the samples described in Chapter 5. Solution 0.1 M HClO₄ + 1 mM Pb(ClO₄)₂, scan rate 10 mV/s.

2) In chapter 5, it was shown that Ag films electrodeposited from the thiosulphate solutions might have some sulphur traces. That was based on the Pb UPD characterisation and the presence of an unusual reduction peak at 0.03 V vs Pb UPD.

To better understand the Ag deposits structure, we conducted preliminary X-ray reflectivity (XRR) examination of films electrodeposited from thiosulphate solution and SMG grown Ag with Pb UPD meditator. The XRR technique is a non-destructive method that can distinguish the structure of the film by looking at the interference of the reflected x-rays from the film and substrate, probing the surface roughness, thin-film thickness and density. The technique is based on the low angle reflection and refraction of X-rays. ¹⁹⁴

The experiments and analysis were done in collaboration with Dr Ross Springell from the Interface Analysis Centre at the University of Bristol. The measurement taken on the Ag film (~20 nm) grown by the SMG method is shown in Fig. 6.2. The figure shows oscillations known as Kiessig fringes that can be used to evaluate the thickness of the film $t = \frac{2\pi}{Q}$ in Å, where Q is the momentum transfer wavevector.



Fig. 6.2. X-Ray reflectivity (XRR) measurements of Ag film grown by surfactant-mediated growth. Measurements were obtained by courtesy of Dr Ross Springell, who collected and analysed the data.

The results were fitted using GenX software. The best fit estimated 14 ± 1 nm thickness of the film, with a roughness of 2.7 nm ± 0.3 nm. The measurements confirmed the estimated thickness reasonably close to the expected value. However, the XRR results for Ag film grown (~100 nm thickness) in the thiosulphate solution (not shown here) were harder to interpret, and it was harder to fit the data. The 'best fit' estimated thickness of 60 nm \pm 6 nm with the roughness of 120 nm \pm 10 nm and suggested the presence of diffused interface that could be associated with Au-Ag alloying at the substrate surface. Because the XRR samples were of different thicknesses, the comparison was difficult and inconclusive. New Ag films about the same thickness (~20 nm) were grown in thiosulphate and perchlorate solution at the constant potential. However, the reflectivity measurements were not completed. These preliminary results were promising, and completing the XRR studies on Ag films grown under different conditions could help understand the results obtained in Chapter 5 and provide additional information about the film quality.

3) One of the primary motivations for the project work was to develop nanostructured alloy samples for optical and plasmonic applications and measurements. The preliminary studies of alloy samples' optical analysis were done by MSci students Christian De Podesta¹⁵³ and

Akash Dasgupta¹⁵² during academic 2019-2020 during their final year MSci project. During the project, I worked with the students and provided training and assistance with making the samples. Au and Au-Ag were electrodeposited on ITO transparent substrates using different solutions and following the same deposition conditions. The SEM images presented in Fig. 6.3 illustrate grown nanoparticles from thiosulphate solutions uniformly distributed samples at two different deposition potentials.



Fig. 6.3. Radius distribution of two sets of $Au_{0.23}Ag_{0.77}$ samples electrodeposited on ITO at different potentials. Radius values were obtained from the SEM images on the right of each histogram. Figure taken from Ref¹⁵².

The optical transmission spectra from the same samples are shown in Fig. 6.4 a). The comparison shows that although they have different geometries, i.e., height to radius ratios – hr and radius – r, the optical transmission peaks positions were similar. As expected, the transmission for Au-Ag alloy shown in Fig. 6.4 b) is blue-shifted compared to pure Au nanoparticles with a peak of around 590nm.



*Fig. 6.4. Optical transmissions from two samples a) deposited in the same solution but different deposition potentials. b) Au and alloy, grown at the same deposition conditions. Figure adapted from Ref*¹⁵².

Completing a systematic study of optical properties of different alloys electrodeposited in thiosulphate solutions on ITO substrates is required. Electrodeposition of alloys on patterned samples with a set geometry would provide new knowledge and understanding of composition and geometry's role in the plasmonic and optical behaviour.

7 References

Murray, W. A.; Barnes, W. L., Plasmonic Materials. *Advanced Materials* 2007, 19 (22), 3771-3782.

2. Jain, P. K.; Huang, X.; El-Sayed, I. H.; El-Sayed, M. A., Noble Metals on the Nanoscale: Optical and Photothermal Properties and Some Applications in Imaging, Sensing, Biology, and Medicine. *Accounts of Chemical Research* **2008**, *41* (12), 1578-1586.

3. Guisbiers, G.; Mendoza-Cruz, R.; Bazan-Diaz, L.; Velazquez-Salazar, J. J.; Mendoza-Perez, R.; Robledo-Torres, J. A.; Rodriguez-Lopez, J. L.; Montejano-Carrizales, J. M.; Whetten, R. L.; Jose-Yacaman, M., Electrum, the Gold-Silver Alloy, from the Bulk Scale to the Nanoscale: Synthesis, Properties, and Segregation Rules. *ACS Nano* **2016**, *10* (1), 188-98.

4. Gong, C.; Leite, M. S., Noble Metal Alloys for Plasmonics. ACS Photonics 2016, 3
(4), 507-513.

5. Michael, F., X. The Bakerian Lecture. —Experimental relations of gold (and other metals) to light. *Phil. Trans. R. Soc.* **1857**, *147*, 145-181.

6. Anker, J. N.; Hall, W. P.; Lyandres, O.; Shah, N. C.; Zhao, J.; Van Duyne, R. P., Biosensing with plasmonic nanosensors. *Nature Materials* **2008**, *7*, 442-453.

7. Green, T. A.; Liew, M. J.; Roy, S., Electrodeposition of Gold from a Thiosulfate-Sulfite Bath for Microelectronic Applications. *Journal of The Electrochemical Society* **2003**, *150* (3), C104.

8. Green, T. A., Gold electrodeposition for microelectronic, optoelectronic and microsystem applications. *Gold Bulletin* **2007**, *40* (2), 105-114.

9. Kohl, P. A., Electrodeposition of Gold. *Modern Electroplating* **2010**, 115-130.

10. Mijnendonckx, K.; Leys, N.; Mahillon, J.; Silver, S.; Van Houdt, R., Antimicrobial silver: uses, toxicity and potential for resistance. *BioMetals* **2013**, *26* (4), 609-621.

11. Silver, S.; Phung, L. T.; Silver, G., Silver as biocides in burn and wound dressings and bacterial resistance to silver compounds. *Journal of Industrial Microbiology and Biotechnology* **2006**, *33* (7), 627-634.

12. Zheng, K.; Setyawati, M. I.; Leong, D. T.; Xie, J., Antimicrobial silver nanomaterials. *Coordination Chemistry Reviews* **2018**, *357*, 1-17.

13. Kim, S. W.; Kim, K. S.; Lamsal, K.; Kim, Y.-J.; Kim, S. B.; Jung, M.; Sim, S.-J.; Kim, H.-S.; Chang, S.-J.; Kim, J. K., An in vitro study of the antifungal effect of silver nanoparticles on oak wilt pathogen Raffaelea sp. *J Microbiol Biotechnol* **2009**, *19* (8), 760-764.

14. Kim, K.-J.; Sung, W. S.; Moon, S.-K.; Choi, J.-S.; Kim, J. G.; Lee, D. G., Antifungal effect of silver nanoparticles on dermatophytes. *J Microbiol Biotechnol* **2008**, *18* (8), 1482-1484.

15. Lee, K.-J.; Park, S.-H.; Govarthanan, M.; Hwang, P.-H.; Seo, Y.-S.; Cho, M.; Lee, W.-H.; Lee, J.-Y.; Kamala-Kannan, S.; Oh, B.-T., Synthesis of silver nanoparticles using cow milk and their antifungal activity against phytopathogens. *Materials Letters* **2013**, *105*, 128-131.

16. Ahamed, M.; AlSalhi, M. S.; Siddiqui, M. K. J., Silver nanoparticle applications and human health. *Clinica Chimica Acta* **2010**, *411* (23), 1841-1848.

Teodoro, J. S.; Simões, A. M.; Duarte, F. V.; Rolo, A. P.; Murdoch, R. C.; Hussain,
 S. M.; Palmeira, C. M., Assessment of the toxicity of silver nanoparticles in vitro: A mitochondrial perspective. *Toxicology in Vitro* 2011, 25 (3), 664-670.

 Graf, M.; Roschning, B.; Weissmüller, J., Nanoporous Gold by Alloy Corrosion: Method-Structure-Property Relationships. *Journal of The Electrochemical Society* 2017, *164* (4), C194-C200.

19. Erlebacher, J.; Aziz, M. J.; Karma, A.; Dimitrov, N.; Sieradzki, K., Evolution of nanoporosity in dealloying. *Nature* **2001**, *410*, 450.

20. Wittstock, A.; Biener, J.; Baumer, M., Nanoporous gold: a new material for catalytic and sensor applications. *Phys Chem Chem Phys* **2010**, *12* (40), 12919-30.

21. Biener, J.; Nyce, G. W.; Hodge, A. M.; Biener, M. M.; Hamza, A. V.; Maier, S. A., Nanoporous Plasmonic Metamaterials. *Advanced Materials* **2008**, *20* (6), 1211-1217.

22. Barnes, A.; Senior, N. A.; Newman, R. C., Film-Induced Cleavage of Ag-Au Alloys. *Metallurgical and Materials Transactions A* **2008**, *40* (1), 58-68.

23. Senior, N. A.; Newman, R. C., Synthesis of tough nanoporous metals by controlled electrolytic dealloying. *Nanotechnology* **2006**, *17* (9), 2311-2316.

24. Sánchez-Ramírez, J. F.; Pal, U.; Nolasco-Hernández, L.; Mendoza-Álvarez, J.; Pescador-Rojas, J. A., Synthesis and Optical Properties of Au-Ag Alloy Nanoclusters with Controlled Composition. *Journal of Nanomaterials* **2008**, *2008*, 1-9.

25. Szymonski, M.; Bhattacharya, R. S.; Overeijnder, H.; Vries, A. E. d., Sputtering of an AgAu alloy by bombardment with 6 keV Xe + ions. *Journal of Physics D: Applied Physics* **1978**, *11* (5), 751.

26. Kumar, N.; Alam, F.; Dutta, V., Deposition of Ag and Au–Ag alloy nanoparticle films by spray pyrolysis technique with tuned plasmonic properties. *Journal of Alloys and Compounds* **2014**, *585*, 312-317.

27. Gromov, D. G.; Dubkov, S. V.; Savitskiy, A. I.; Shaman, Y. P.; Polokhin, A. A.; Belogorokhov, I. A.; Trifonov, A. Y., Optimization of nanostructures based on Au, Ag, AuAg nanoparticles formed by thermal evaporation in vacuum for SERS applications. *Applied Surface Science* **2019**, *489*, 701-707.

28. Schwarzacher, W., Electrodeposition: A Technology for the Future. *The Electrochemical Society Interface* **2006**, *15* (1), 32-33.

29. Schlesinger, M., Electroless and Electrodeposition of Silver. *Modern Electroplating*,2010; 131-138.

30. Bozzini, B.; Fanigliulo, A., An in situ spectroelectrochemical Raman investigation of Au electrodeposition and electrodissolution in KAu(CN)2 solution. *Journal of Applied Electrochemistry* **2002**, *32* (9), 1043-1048.

31. Estrine, E. C.; Riemer, S.; Venkatasamy, V.; Stadler, B. J. H.; Tabakovic, I., Mechanism and Stability Study of Gold Electrodeposition from Thiosulfate-Sulfite Solution. *Journal of The Electrochemical Society* **2014**, *161* (12), D687-D696.

32. Sullivan, A. M.; Kohl, P. A., Electrochemical Study of the Gold Thiosulfate Reduction. *Journal of The Electrochemical Society* **2019**, *144* (5), 1686-1690.

33. Liew, M. J.; Roy, S.; Scott, K., Development of a non-toxic electrolyte for soft gold electrodeposition: an overview of work at University of Newcastle upon Tyne. *Green Chemistry* **2003**, *5* (4), 376-381.

34. Osaka, T.; Kodera, A.; Misato, T.; Homma, T.; Okinaka, Y.; Yoshioka, O., Electrodeposition of Soft Gold from a Thiosulfate-Sulfite Bath for Electronics Applications. *Journal of The Electrochemical Society* **1997**, *144* (10), 3462-3469.

35. Sujith, A.; Itoh, T.; Abe, H.; Yoshida, K.; Kiran, M. S.; Biju, V.; Ishikawa, M., Imaging the cell wall of living single yeast cells using surface-enhanced Raman spectroscopy. *Anal Bioanal Chem* **2009**, *394* (7), 1803-9.

36. Atwater, H. A.; Polman, A., Plasmonics for improved photovoltaic devices. *Nat Mater* **2010**, *9* (3), 205-13.

37. Chou, C. H.; Chen, F. C., Plasmonic nanostructures for light trapping in organic photovoltaic devices. *Nanoscale* **2014**, *6* (15), 8444-58.

38. Haruta, M.; Yamada, N.; Kobayashi, T.; Iijima, S., Gold catalysts prepared by coprecipitation for low-temperature oxidation of hydrogen and of carbon monoxide. *Journal of catalysis* **1989**, *115* (2), 301-309.

39. Barnes, W. L.; Dereux, A.; Ebbesen, T. W., Surface plasmon subwavelength optics. *Nature* **2003**, *424*, 824.

40. Schuller, J. A.; Barnard, E. S.; Cai, W.; Jun, Y. C.; White, J. S.; Brongersma, M. L., Plasmonics for extreme light concentration and manipulation. *Nat Mater* **2010**, *9* (3), 193-204.

41. Boriskina, S. V.; Ghasemi, H.; Chen, G., Plasmonic materials for energy: From physics to applications. *Materials Today* **2013**, *16* (10), 375-386.

42. Maier, S. A., *Plasmonics: Fundamentals and Applications*. Springer: New York, 2007

43. Sadrolhosseini, A. R.; Noor, A. S. M.; Moksin, M. M., Application of surface plasmon resonance based on a metal nanoparticle. In *Plasmonics - Principles and Applications*, Kim, K. Y., Ed. InTech: 2012; pp 253-282.

44. Zalevsky, Z.; Abdulhalim, I., *Integrated nanophotonic devices*. Elsevier: United Kingdom, 2014.

45. Maier, S. A., *Plasmonics: Fundamentals and Applications*. Springer: United States of America, 2010.

46. Haes, A. J.; Haynes, C. L.; Van Duyne, R. P., Nanosphere lithography: self-assembled photonic and magnetic materials. *MRS Online Proceedings Library Archive* **2000**, *636*, D4.8.1.

47. Maier, S. A.; Atwater, H. A., Plasmonics: Localization and guiding of electromagnetic energy in metal/dielectric structures. *Journal of Applied Physics* **2005**, *98* (1), 10.

48. Li, X.; Jia, C.; Ma, B.; Wang, W.; Fang, Z.; Zhang, G.; Guo, X., Substrate-induced interfacial plasmonics for photovoltaic conversion. *Scientific Reports* **2015**, *5* (14497), 1-10.

49. Kelly, L. K.; Coronado, E.; Zhao, L. L.; Schatz, G. C., The Optical Properties of Metal Nanoparticles: The Influence of Size, Shape, and Dielectric Environment. *J. Phys. Chem. B* **2014**, *107* (3), 668-677.

50. Johnson, P. B.; Christy, R. W., Optical Constants of the Noble Metals. *Physical Review B* 1972, 6 (12), 4370-4379.

51. Babar, S.; Weaver, J. H., Optical constants of Cu, Ag, and Au revisited. *Applied Optics* 2015, 54 (3), 477-481.

52. Seker, E.; Reed, L. M.; Begley, R. M., Nanoporous Gold: Fabrication, Characterization, and Applications. *Materials* **2009**, *2* (4), 2188-2215.

53. Kucheyev, S. O.; Hayes, J. R.; Biener, J.; Huser, T.; Talley, C. E.; Hamza, A. V., Surface-enhanced Raman scattering on nanoporous Au. *Applied Physics Letters* **2006**, *89* (5), 053102.

54. Qian, L. H.; Yan, X. Q.; Fujita, T.; Inoue, A.; Chen, M. W., Surface enhanced Raman scattering of nanoporous gold: Smaller pore sizes stronger enhancements. *Applied Physics Letters* **2007**, *90* (15).

55. Dieringer, J. A.; Wustholz, K. L.; Masiello, D. J.; Camden, J. P.; Kleinman, S. L.; Schatz, G. C.; Van Duyne, R. P., Surface-enhanced Raman excitation spectroscopy of a single rhodamine 6G molecule. *J Am Chem Soc* **2009**, *131* (2), 849-54.

56. Lang, X. Y.; Guan, P. F.; Zhang, L.; Fujita, T.; Chen, M. W., Size dependence of molecular fluorescence enhancement of nanoporous gold. *Applied Physics Letters* **2010**, *96* (7), 073701.

57. Zhu, C.; Du, D.; Eychmuller, A.; Lin, Y., Engineering Ordered and Nonordered Porous Noble Metal Nanostructures: Synthesis, Assembly, and Their Applications in Electrochemistry. *Chem Rev* **2015**, *115* (16), 8896-943.

58. Fujita, T.; Guan, P.; McKenna, K.; Lang, X.; Hirata, A.; Zhang, L.; Tokunaga, T.; Arai, S.; Yamamoto, Y.; Tanaka, N.; Ishikawa, Y.; Asao, N.; Yamamoto, Y.; Erlebacher, J.;

Chen, M., Atomic origins of the high catalytic activity of nanoporous gold. *Nat Mater* **2012**, *11* (9), 775-80.

59. Jia, C.; Yin, H.; Ma, H.; Wang, R.; Ge, X.; Zhou, A.; Xu, X.; Ding, Y., Enhanced Photoelectrocatalytic Activity of Methanol Oxidation on TiO2-Decorated Nanoporous Gold. *The Journal of Physical Chemistry C* **2009**, *113* (36), 16138-16143.

60. Ding, Y.; Chen, M.; Erlebacher, J., Metallic Mesoporous Nanocomposites for Electrocatalysis. *J Am Chem Soc* **2004**, *126*, 6876-6877.

61. Biener, J.; Wittstock, A.; Zepeda-Ruiz, L. A.; Biener, M. M.; Zielasek, V.; Kramer, D.; Viswanath, R. N.; Weissmuller, J.; Baumer, M.; Hamza, A. V., Surface-chemistry-driven actuation in nanoporous gold. *Nat Mater* **2009**, *8* (1), 47-51.

62. Kramer, D.; Viswanath, R. N.; Weissmüller, J., Surface-Stress Induced Macroscopic Bending of Nanoporous Gold Cantilevers. *Nano Letters* **2004**, *4* (5), 793-796.

63. Jin, H.-J.; Weissmüller, J., Bulk Nanoporous Metal for Actuation. *Advanced Engineering Materials* **2010**, *12* (8), 714-723.

64. Chen, A. Y.; Shi, S. S.; Qiu, Y. D.; Xie, X. F.; Ruan, H. H.; Gu, J. F.; Pan, D., Poresize tuning and optical performances of nanoporous gold films. *Microporous and Mesoporous Materials* **2015**, *202*, 50-56.

65. Kamundi, M.; Bromberg, L.; Fey, E.; Mitchell, C.; Fayette, M.; Dimitrov, N., Impact of Structure and Composition on the Dealloying of AuxAg(1–x) Alloys on the Nanoscale. *The Journal of Physical Chemistry C* **2012**, *116* (26), 14123-14133.

66. Yu, F.; Ahl, S.; Caminade, A.-M.; Majoral, J.-P.; Knoll, W.; Erlebacher, J., Simultaneous Excitation of Propagating and Localized Surface Plasmon Resonance in Nanoporous Gold Membranes. *Analytical Chemistry* **2006**, *78* (20), 7346-7350.

Jalas, D.; Shao, L. H.; Canchi, R.; Okuma, T.; Lang, S.; Petrov, A.; Weissmuller, J.;
Eich, M., Electrochemical tuning of the optical properties of nanoporous gold. *Sci Rep* 2017, 7, 44139.

68. Chew, W. S.; Pedireddy, S.; Lee, Y. H.; Tjiu, W. W.; Liu, Y.; Yang, Z.; Ling, X. Y., Nanoporous Gold Nanoframes with Minimalistic Architectures: Lower Porosity Generates Stronger Surface-Enhanced Raman Scattering Capabilities. *Chemistry of Materials* **2015**, *27* (22), 7827-7834.

69. Ozoliņš, V.; Wolverton, C.; Zunger, A., Cu-Au, Ag-Au, Cu-Ag, and Ni-Au intermetallics: First-principles study of temperature-composition phase diagrams and structures. *Physical Review B* **1998**, *57* (11), 6427-6443.

70. White, J. L.; Orr, R. L.; Hultgren, R., The thermodynamic properties of silver-gold alloys. *Acta Metallurgica* **1957**, *5* (12), 747-760.

71. Manzoor, A.; Pandey, S.; Chakraborty, D.; Phillpot, S. R.; Aidhy, D. S., Entropy contributions to phase stability in binary random solid solutions. *npj Computational Materials* **2018**, *4* (1).

72. Park, J.; Lee, J., Phase diagram reassessment of Ag–Au system including size effect. *Calphad* **2008**, *32* (1), 135-141.

73. Sieradzki, K.; Dimitrov, N.; Movrin, D.; McCall, C.; Vasiljevic, N.; Erlebacher, J., The Dealloying Critical Potential. *J. Electrochem. Soc.* **2002**, *149* (8), B370-B377.

74. Erlebacher, J., An Atomistic Description of Dealloying: Porosity Evolution, the Nature of the Critical Potential, and Rate Limiting Behavior. *Journal of The Electrochemical Society* **2004**, *151* (10), C614-C626.

75. Wagner, K.; Brankovic, S. R.; Dimitrov, N.; Sieradzki, K., Dealloying below the Critical Potential. *J. Electrochem. Soc.* **1997**, *144* 3545.

76. Peña-Rodríguez, O.; Caro, M.; Rivera, A.; Olivares, J.; Perlado, J. M.; Caro, A., Optical properties of Au-Ag alloys: An ellipsometric study. *Optical Materials Express* **2014**, *4* (2), 403-410.

77. Kirsch, R. G.; Poate, J. M.; Eibschutz, M., Interdiffusion mechanisms in Ag-Au thinfilm couples. *Applied Physics Letters* **1976**, *29* (12), 772-775.

78. Wonnell, S. K.; Delaye, J. M.; Bibolé, M.; Limoge, Y., Activation volume for the interdiffusion of Ag-Au multilayers. *Journal of Applied Physics* **1992**, *72* (11), 5195-5205.

79. Bozzini, B.; Pietro De Gaudenzi, G.; Mele, C., A SERS investigation of the electrodeposition of Ag–Au alloys from free-cyanide solutions. *Journal of Electroanalytical Chemistry* **2004**, *563* (1), 133-143.

80. Márquez, K.; Staikov, G.; Schultze, J. W., Electrochemical Deposition of Ag, Au and Ag-Au Alloys on n-Si(111). *Transactions of the IMF* **2002**, *80* (3), 73-78.

81. Márquez, K.; Ortiz, R.; Schultze, J. W.; Márquez, O. P.; Márquez, J.; Staikov, G., In situ FTIR monitoring of Ag and Au electrodeposition on glassy carbon and silicon. *Electrochimica Acta* **2003**, *48* (6), 711-720.

82. Bozzini, B.; Gaudenzi, G. P. D.; Mele, C., A SERS investigation of the electrodeposition of Ag–Au alloys from free-cyanide solutions – part II. *Journal of Electroanalytical Chemistry* **2004**, *570* (1), 29-34.

83. Dolati, A.; Ghorbani, M.; Ahmadi, M. R., An electrochemical study of Au–Ni alloy electrodeposition from cyanide–citrate electrolytes. *Journal of Electroanalytical Chemistry* **2005**, *577* (1), 1-8.

84. Hrussanova, A.; Krastev, I., Electrodeposition of silver–tin alloys from pyrophosphate-cyanide electrolytes. *Journal of Applied Electrochemistry* **2008**, *39* (7), 989-994.

85. Akben, K.; Timur, S., A study on gold-silver alloy electrodeposition from pyrophosphate-cyanide electrolyte using polyethylenimine-KSeCN additives. *International Journal of Electrochemical Science* **2018**, *13* (4), 3855-3873.

86. Sánchez, H.; Ozil, P.; Chainet, E.; Nguyen, B.; Meas, Y., Silver-Gold Alloys Prepared by Pulse Plating: Modeling of the Chemical Composition. *Journal of The Electrochemical Society* **1997**, *144* (6), 2004-2012.

87. Hashimoto, Y.; Seniutinas, G.; Balcytis, A.; Juodkazis, S.; Nishijima, Y., Au-Ag-Cu nano-alloys: tailoring of permittivity. *Sci Rep* **2016**, *6*, 25010.

Rioux, D.; Vallières, S.; Besner, S.; Muñoz, P.; Mazur, E.; Meunier, M., An Analytic Model for the Dielectric Function of Au, Ag, and their Alloys. *Advanced Optical Materials* 2014, 2 (2), 176-182.

Kolb, D. M., An atomistic view of electrochemistry. *Surface Science* 2002, 500 (1), 722-740.

90. Herrero, E.; Buller, L. J.; Abruña, H. D., Underpotential Deposition at Single Crystal Surfaces of Au, Pt, Ag and Other Materials. *Chemical Reviews* **2001**, *101* (7), 1897-1930.

91. Oviedo, O. A.; Reinaudi, L.; Garcia, S. G.; Leiva, E. P. M., Underpotential Deposition. From Fundamentals and Theory to Applications at the Nanoscale. Springer: Switzerland, 2016.

92. Budevski, E.; Staikov, G.; Lorenz, W. J., Underpotential Deposition of Metals - 2D Phases. In *Electrochemical Phase Formation and Growth*, 1996; pp 41-148.

93. Vasiljevic, N.; Viyannalage, L. T.; Dimitrov, N.; Sieradzki, K., High resolution electrochemical STM: New structural results for underpotentially deposited Cu on Au(111) in acid sulfate solution. *Journal of Electroanalytical Chemistry* **2008**, *613* (2), 118-124.

94. Shao, M.; Odell, J. H.; Choi, S.-I.; Xia, Y., Electrochemical surface area measurements of platinum- and palladium-based nanoparticles. *Electrochemistry Communications* **2013**, *31*, 46-48.

95. Aldana-González, J.; Olvera-García, J.; Montes de Oca, M. G.; Romero-Romo, M.; Ramírez-Silva, M. T.; Palomar-Pardavé, M., Electrochemical quantification of the electroactive surface area of Au nanoparticles supported onto an ITO electrode by means of Cu upd. *Electrochemistry Communications* **2015**, *56*, 70-74.

96. Łukaszewski, M.; Soszko, M.; Czerwiński, A., Electrochemical methods of real surface area determination of noble metal electrodes–an overview. *Int. J. Electrochem. Sci* **2016**, *11* (6), 4442-4469.

97. Liu, Y.; Bliznakov, S.; Dimitrov, N., Comprehensive Study of the Application of a Pb Underpotential Deposition-Assisted Method for Surface Area Measurement of Metallic Nanoporous Materials. *J Phys Chem C* **2009**, *113*, 12362–12372.

98. Naderi, M., Chapter Fourteen - Surface Area: Brunauer–Emmett–Teller (BET). In *Progress in Filtration and Separation*, Tarleton, S., Ed. Academic Press: Oxford, 2015; pp 585-608.

99. Seker, E.; Gaskins, J. T.; Bart-Smith, H.; Zhu, J.; Reed, M. L.; Zangari, G.; Kelly, R.; Begley, M. R., The effects of post-fabrication annealing on the mechanical properties of freestanding nanoporous gold structures. *Acta Materialia* **2007**, *55* (14), 4593-4602.

100. Rouquerol, J.; Llewellyn, P.; Rouquerol, F., Is the BET equation applicable to microporous adsorbents. *Stud. Surf. Sci. Catal* **2007**, *160* (07), 49-56.

101. Dimitrov, N., Recent Advances in the Growth of Metals, Alloys, and Multilayers by Surface Limited Redox Replacement (SLRR) Based Approaches. *Electrochimica Acta* **2016**, *209*, 599-622.

102. Brankovic, S. R.; Wang, J. X.; Adžić, R. R., Metal monolayer deposition by replacement of metal adlayers on electrode surfaces. *Surface Science* **2001**, (474), L173-L179.

103. Fayette, M.; Liu, Y.; Bertrand, D.; Nutariya, J.; Vasiljevic, N.; Dimitrov, N., From Au to Pt via Surface Limited Redox Replacement of Pb UPD in One-Cell Configuration. *Langmuir* **2011**, *27* (9), 5650-5658.

104. Brankovic, S. R.; Dimitrov, N.; Sieradzki, K., Surfactant Mediated Electrochemical Deposition of Ag on Au(111). *Electrochemical and Solid-State Letters* **1999**, *2* (9), 443-445.

105. Wu, D.; Solanki, D. J.; Joi, A.; Dordi, Y.; Dole, N.; Litvnov, D.; Brankovic, S. R., Pb Monolayer Mediated Thin Film Growth of Cu and Co: Exploring Different Concepts. *Journal of The Electrochemical Society* **2018**, *166* (1), D3013-D3021.

106. Sieradzki, K.; Brankovic, R. S.; Dimitrov, N., Electrochemical Defect-Mediated Thin-Film Growth. *Science* **1999**, *284* (5411), 138.

107. Hwang, S.; Oh, I.; Kwak, J., Electrodeposition of Epitaxial Cu(111) Thin Films on Au(111) Using Defect-Mediated Growth. *Journal of the American Chemical Society* **2001**, *123* (29), 7176-7177.

108. Vidal-Iglesias, F. J.; Al-Akl, A.; Watson, D.; Attard, G. A., Electrochemical characterization of PtPd alloy single crystal surfaces prepared using Pt basal planes as templates. *Journal of Electroanalytical Chemistry* **2007**, *611* (1-2), 117-125.

109. Green, C. L.; Kucernak, A., Determination of the Platinum and Ruthenium Surface Areas in Platinum–Ruthenium Alloy Electrocatalysts by Underpotential Deposition of Copper. I. Unsupported Catalysts. *The Journal of Physical Chemistry B* **2002**, *106* (5), 1036-1047.

110. McCall, C.; Dimitrov, N.; Sieradzki, K., Underpotential Deposition on Alloys. *Journal of The Electrochemical Society* **2001**, *148* (6), E290-E293.

111. Compton, R. G.; Sanders, H. W., *Electrode Potentials*. Oxford University Press: Great Britain, 2002.

112. Bard, A. J.; Faulkner, L. R., *Electrochemical Methods: Fundamentals and Applications, 2nd Edition.* John Wiley & Sons: New York, 2001.

113. Fischer, A. C., *Electrode Dynamics*. Oxford University Press: United States, 2009.

114. Brett, C. M. A.; Brett, A. M. O., *Electrochemistry: Principles, Methods, and Applications*. Oxford University Press: United States, 1993.

115. Elgrishi, N.; Rountree, K. J.; McCarthy, B. D.; Rountree, E. S.; Eisenhart, T. T.; Dempsey, J. L., A Practical Beginner's Guide to Cyclic Voltammetry. *Journal of Chemical Education* **2018**, *95* (2), 197-206.

116. Bewick, A.; Jovićević, J.; Thomas, B., Phase formation in the underpotential deposition of metals. *Faraday Symposia of the Chemical Society* **1977**, *12* (0), 24-35.

117. Obretenov, W.; Schmidt, U.; Lorenz, W. J.; Staikov, G.; Budevski, E.; Carnal, D.; Müller, U.; Siegenthaler, H.; Schmidt, E., Underpotential Deposition and Electrocrystallization of Metals An Atomic View by Scanning Tunneling Microscopy. *Journal of The Electrochemical Society* **1993**, *140* (3), 692-703.

118. Wu, Z.-L.; Zang, Z.-H.; Yau, S.-L., Electrodeposition of Copper at Well-Defined Pt(111) and Rh(111) Electrodes in Sulfuric Acid Solutions: Studying with In Situ Scanning Tunneling Microscopy. *Langmuir* **2000**, *16* (7), 3522-3528.

119. Samant, M. G.; Toney, M. F.; Borges, G. L.; Blum, L.; Melroy, O. R., Grazing incidence x-ray diffraction of lead monolayers at a silver (111) and gold (111) electrode/electrolyte interface. *The Journal of Physical Chemistry* **1988**, *92* (1), 220-225.

120. Kolb, D. M.; Przasnyski, M.; Gerischer, H., Underpotential deposition of metals and work function differences. *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry* **1974**, *54* (1), 25-38.

121. Mayet, N.; Servat, K.; Kokoh, K. B.; Napporn, T. W., Probing the Surface of Noble Metals Electrochemically by Underpotential Deposition of Transition Metals. *Surfaces* **2019**, *2* (2), 257-276.

122. Oviedo, O. A.; Vélez, P.; Macagno, V. A.; Leiva, E. P. M., Underpotential deposition: From planar surfaces to nanoparticles. *Surface Science* **2015**, *631*, 23-34.

123. Bort, H.; Jüttner, K.; Lorenz, W. J.; Schmidt, E., Lead adsorption on silver single crystal surfaces. *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry* **1978**, *90* (3), 413-424.

124. Chen, C. H.; Vesecky, S. M.; Gewirth, A. A., In situ atomic force microscopy of underpotential deposition of silver on gold(111). *Journal of the American Chemical Society* **1992**, *114* (2), 451-458.

125. Garcia, S.; Salinas, D.; Mayer, C.; Schmidt, E.; Staikov, G.; Lorenz, W. J., Ag UPD on Au(100) and Au(111). *Electrochimica Acta* **1998**, *43* (19-20), 3007-3019.

126. Snyder, J. D.; Erlebacher, J. D., Electrochemical measurement of the surface alloying kinetics of underpotentially deposited Ag on Au(111). *Langmuir* **2009**, *25* (16), 9596-604.

127. Rooryck, V.; Reniers, F.; Buess-Herman, C.; Attard, G. A.; Yang, X., The silver upd on gold(111) revisited. *Journal of Electroanalytical Chemistry* **2000**, *482* (2), 93-101.

128. Trasatti, S.; Petrii, O. A., Real surface area measurements in electrochemistry. *Journal of Electroanalytical Chemistry* **1992**, *327* (1), 353-376.

129. Conway, B.; Angerstein-Kozlowska, H.; Sharp, W. a.; Criddle, E., Ultrapurification of water for electrochemical and surface chemical work by catalytic pyrodistillation. *Analytical Chemistry* **1973**, *45* (8), 1331-1336.

130. Conway, B. E.; Angerstein-Kozlowska, H.; Ho, F. C., Electrochemical study of multiple states of chemisorption of atoms at metal surfaces. *Journal of Vacuum Science and Technology* **1977**, *14* (1), 351-364.

131. Zhumaev, U.; Rudnev, A. V.; Li, J.-F.; Kuzume, A.; Vu, T.-H.; Wandlowski, T., Electro-oxidation of Au(111) in contact with aqueous electrolytes: New insight from in situ vibration spectroscopy. *Electrochimica Acta* **2013**, *112*, 853-863.

132. Strbac, S.; Adzic, R. R.; Hamelin, A., Oxide Formation on Gold Single Crystal Stepped Surfaces. *J. Electroanal. Chem.* **1988**, *249*, 291-310.

133. Egerton, R. F., *Physical Principles of Electron Microscopy: An Introduction to TEM, SEM, and AEM*. Springer: United States, 2006.

134. Huang, Q., Nanotechnology in the Food, Beverage and Nutraceutical Industries.Woodhead Publishing Limited: United Kingdom, 2012.

135. Watts, J. F.; Wolstenholme, J., *An introduction to surface analysis by XPS and AES*. John Wiley & Sons Ltd: England, 2003.

136. Yeh, J. J.; Lindau, I., Atomic subshell photoionization cross sections and asymmetry parameters: $1 \le Z \le 103$. *Atomic Data and Nuclear Data Tables* **1985**, *32* (1), 1-155.

137. Carlson, T. A., Basic assumptions and recent developments in quantitative XPS. *Surface and Interface Analysis* **1982**, *4* (4), 125-134.

138. Li, X.; Jia, C.; Ma, B.; Wang, W.; Fang, Z.; Zhang, G.; Guo, X., Substrate-induced interfacial plasmonics for photovoltaic conversion. *Sci Rep* **2015**, *5*, 14497.
139. Sharma, A. K.; Gupta, B. D., Fibre-optic sensor based on surface plasmon resonance with Ag–Au alloy nanoparticle films. *Nanotechnology* **2006**, *17* (1), 124-131.

140. Link, S.; Wang, Z. L.; El-Sayed, M. A., Alloy Formation of Gold–Silver Nanoparticles and the Dependence of the Plasmon Absorption on Their Composition. *The Journal of Physical Chemistry B* **1999**, *103* (18), 3529-3533.

141. Kim, W.-J.; Kim, S.; Kim, A. R.; Yoo, D. J., Direct Detection System for Escherichia coli Using Au–Ag Alloy Microchips. *Industrial & Engineering Chemistry Research* **2013**, *52* (22), 7282-7288.

142. Wang, Z.; Wen, X.; Feng, Z.; Lin, L.; Liu, R.; Huang, P.; Chen, G.; Huang, F.; Zheng, Z., Highly ordered Au-Ag alloy arrays with tunable morphologies for surface enhanced Raman spectroscopy. *Chemical Engineering Journal* **2018**, *345*, 389-394.

143. Wongwisate, P.; Chavadej, S.; Gulari, E.; Sreethawong, T.; Rangsunvigit, P., Effects of monometallic and bimetallic Au–Ag supported on sol–gel TiO2 on photocatalytic degradation of 4-chlorophenol and its intermediates. *Desalination* **2011**, *272* (1-3), 154-163. 144. Sandoval, A.; Aguilar, A.; Louis, C.; Traverse, A.; Zanella, R., Bimetallic Au–Ag/TiO2 catalyst prepared by deposition–precipitation: High activity and stability in CO oxidation. *Journal of Catalysis* **2011**, *281* (1), 40-49.

145. Márquez, K.; Staikov, G.; Schultze, J. W., Electrochemical Deposition of Ag, Au and Ag-Au Alloys on n-Si(111). *Transactions of the IMF* **2017**, *80* (3), 73-78.

146. McCurry, D. A.; Kamundi, M.; Fayette, M.; Wafula, F.; Dimitrov, N., All electrochemical fabrication of a platinized nanoporous Au thin-film catalyst. *ACS Appl Mater Interfaces* **2011**, *3* (11), 4459-68.

147. Hubin, A.; Vereecken, J., Electrochemical reduction of silver thiosulphate complexes
Part I: Thermodynamic aspects of solution composition. *Journal of Applied Electrochemistry*1994, 24 (3), 239-244.

148. Hubin, A.; Vereecken, J., Electrochemical reduction of silver thiosulphate complexes Part II Mechanism and kinetics. *Journal of Applied Electrochemistry* **1994**, *24* (5), 396-403.

149. Vandeputte, S.; Hubin, A.; Vereecken, J., Influence of the sodium nitrate content on the rate of the electrodeposition of silver from thiosulphate solutions. *Electrochimica Acta* **1997**, *42* (23), 3429-3441.

150. Wilkinson, P., Understanding Gold Plating. *Gold Bulletin* **1986**, *19* (3), 75-81.

151. Ivanov, S.; Tsakova, V., Electroless versus electrodriven deposition of silver crystals in polyaniline. *Electrochimica Acta* **2005**, *50* (28), 5616-5623.

152. Dasgupta, A. Gold and Gold-Silver Self-Assembling Nanoplasmonic Arrays - Synthesis, Characterization and Modeling. MSci Thesis University of Bristol, 2020.

153. de Podesta, C. K. Plasmonics in Disordered Au and Au-Ag Alloy Nanoparticles.MSci Thesis University of Bristol, 2020.

154. Wong, J. R. Dynamic Plasmonic Metamaterials Tuned by Surface Electrochemistry.MSc Thesis University of Bristol, 2019.

155. Le Boulbar, E.; Chausse, P. J.; Lis, S.; Shields, P., Displacement Talbot lithography: an alternative technique to fabricate nanostructured metamaterials. *Proc. SPIE, Nanotechnology VIII* **2017**, *10248*, 102480Q.

156. Solak, H. H.; Dais, C.; Clube, F., Displacement Talbot lithography: a new method for high-resolution patterning of large areas. *Opt. Express* **2011**, *19* (11), 10686-10691.

157. Solak, H. H.; Dais, C.; Clube, F.; Wang, L., Phase shifting masks in Displacement Talbot Lithography for printing nano-grids and periodic motifs. *Microelectronic Engineering* **2015**, *143*, 74-80.

158. Wang, L.; Clube, F.; Dais, C.; Solak, H. H.; Gobrecht, J., Sub-wavelength printing in the deep ultra-violet region using Displacement Talbot Lithography. *Microelectronic Engineering* **2016**, *161*, 104-108.

159. Chausse, P. J. P.; Le Boulbar, E. D.; Lis, S. D.; Shields, P. A., Understanding resolution limit of displacement Talbot lithography. *Opt. Express* **2019**, *27* (5), 5918-5930.

160. Lal, S.; Grady, N. K.; Kundu, J.; Levin, C. S.; Lassiter, J. B.; Halas, N. J., Tailoring plasmonic substrates for surface enhanced spectroscopies. *Chem Soc Rev* **2008**, *37* (5), 898-911.

161. Lin, B.; Kong, L.; Hodgson, P. D.; Mudie, S.; Hawley, A.; Dumée, L. F., Controlled porosity and pore size of nano-porous gold by thermally assisted chemical dealloying – a SAXS study. *RSC Advances* **2017**, *7* (18), 10821-10830.

162. Okman, O.; Lee, D.; Kysar, J. W., Fabrication of crack-free nanoporous gold blanket thin films by potentiostatic dealloying. *Scripta Materialia* **2010**, *63* (10), 1005-1008.

163. Tan, Y. H.; Davis, J. A.; Fujikawa, K.; Ganesh, N. V.; Demchenko, A. V.; Stine, K. J., Surface area and pore size characteristics of nanoporous gold subjected to thermal,

mechanical, or surface modification studied using gas adsorption isotherms, cyclic voltammetry, thermogravimetric analysis, and scanning electron microscopy. *J Mater Chem* **2012**, *22* (14), 6733-6745.

164. Hakamada, M.; Mabuchi, M., Microstructural evolution in nanoporous gold by thermal and acid treatments. *Materials Letters* **2008**, *62* (3), 483-486.

165. Hakamada, M.; Mabuchi, M., Thermal coarsening of nanoporous gold: Melting or recrystallization. *Journal of Materials Research* **2011**, *24* (2), 301-304.

166. Dorofeeva, T. S.; Seker, E., Electrically tunable pore morphology in nanoporous gold thin films. *Nano Research* **2015**, *8* (7), 2188-2198.

167. Dorofeeva, T. S.; Seker, E., In situ electrical modulation and monitoring of nanoporous gold morphology. *Nanoscale* **2016**, *8* (47), 19551-19556.

168. Chapman, C. A.; Wang, L.; Biener, J.; Seker, E.; Biener, M. M.; Matthews, M. J., Engineering on-chip nanoporous gold material libraries via precision photothermal treatment. *Nanoscale* **2016**, *8* (2), 785-95.

169. Sharma, A.; Bhattarai, J. K.; Alla, A. J.; Demchenko, A. V.; Stine, K. J., Electrochemical annealing of nanoporous gold by application of cyclic potential sweeps. *Nanotechnology* **2015**, *26* (8), 085602.

170. Dorofeeva, T. S.; Matharu, Z.; Daggumati, P.; Seker, E., Electrochemically Triggered Pore Expansion in Nanoporous Gold Thin Films. *The Journal of Physical Chemistry C* **2016**, *120* (7), 4080-4086.

171. Bhattarai, J. K.; Neupane, D.; Nepal, B.; Mikhaylov, V.; Demchenko, A. V.; Stine,
K. J., Preparation, Modification, Characterization, and Biosensing Application of
Nanoporous Gold Using Electrochemical Techniques. *Nanomaterials (Basel)* 2018, 8 (3),
171.

172. Ji, C.; Searson, P. C., Synthesis and Characterization of Nanoporous Gold Nanowires. *The Journal of Physical Chemistry B* **2003**, *107* (19), 4494-4499.

173. Cattarin, S.; Kramer, D.; Lui, A.; Musiani, M. M., Preparation and Characterization of Gold Nanostructures of Controlled Dimension by Electrochemical Techniques. *The Journal of Physical Chemistry C* **2007**, *111* (34), 12643-12649.

174. Rouya, E.; Cattarin, S.; Reed, M. L.; Kelly, R. G.; Zangari, G., Electrochemical Characterization of the Surface Area of Nanoporous Gold Films. *Journal of The Electrochemical Society* **2012**, *159* (4), K97-K102.

175. Green, M. P.; Hanson, K. J.; Carr, R.; Lindau, I., STM Observations of the Underpotential Deposition and Stripping of Pb on Au(111) under Potential Sweep Conditions. *J. Electrochem. Soc.* **1990**, *137* (11), 3493-3498.

176. Nutariya, J.; Velleuer, J.; Schwarzacher, W.; Vasiljevic, N., Surface Alloying/Dealloying in Pb/Au(111) System. *ECS Transactions* **2010**, *28* (25), 15-25.

177. Krekeler, T.; Straßer, A. V.; Graf, M.; Wang, K.; Hartig, C.; Ritter, M.; Weissmüller,
J., Silver-rich clusters in nanoporous gold. *Materials Research Letters* 2017, *5* (5), 314-321.
178. Zhang, L.; Chen, L.; Liu, H.; Hou, Y.; Hirata, A.; Fujita, T.; Chen, M., Effect of Residual Silver on Surface-Enhanced Raman Scattering of Dealloyed Nanoporous Gold. *The Journal of Physical Chemistry C* 2011, *115* (40), 19583-19587.

179. Parida, S.; Kramer, D.; Volkert, C. A.; Rösner, H.; Erlebacher, J.; Weissmüller, J., Volume Change during the Formation of Nanoporous Gold by Dealloying. *Physical Review Letters* **2006**, *97* (3), 035504.

180. Ma, K.; Corsi, J. S.; Fu, J.; Detsi, E., Origin of the Volume Contraction during Nanoporous Gold Formation by Dealloying for High-Performance Electrochemical Applications. *ACS Applied Nano Materials* **2018**, *1* (2), 541-546.

181. Hamelin, A., Lead adsorption on gold single crystal stepped surfaces. *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry* **1979**, *101* (2), 285-290.

182. Engelsmann, K.; Lorenz, W. J.; Schmidt, E., Underpotential deposition of lead on polycrystalline and single-crystal gold surfaces: Part I. Thermodynamics. *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry* **1980**, *114* (1), 1-10.

183. Green, M. P.; Richter, M.; Xing, X.; Scherson, D.; Hanson, K. J.; Ross, P. N.; Carr,
R.; Lindau, I., In-situ STM studies of electrochemical underpotential deposition of Pb on
Au(111). *Journal of Microscopy* 1988, *152* (3), 823-829.

184. Vukmirovic, M. B.; Dimitrov, N.; Sieradzki, K., Dealloying and Corrosion of Al Alloy 2024-T3. *Journal of The Electrochemical Society* **2002**, *149* (9), B428.

185. Seo, M., Inhibition effect of underpotential deposition of metallic cations on aqueous corrosion of metals. *Corrosion Reviews* **2018**, *36* (1), 17-33.

186. Hamelin, A., Underpotential deposition of lead on single crystal faces of gold: Part I. The influence of crystallographic orientation of the substrate. *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry* **1984**, *165* (1), 167-180.

187. Hamelin, A.; Lipkowski, J., Underpotential deposition of lead on gold single crystal faces: Part II. General discussion. *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry* **1984**, *171* (1), 317-330.

188. Sackmann, J.; Bunk, A.; Pötzschke, R. T.; Staikov, G.; Lorenz, W. J., Combined in situ SPM and EIS studies of Pb UPD on Ag(111) and Ag(100). *Electrochimica Acta* **1998**, *43* (19), 2863-2873.

189. Adzic, R.; Yeager, E.; Cahan, B., Optical and Electrochemical Studies of Underpotential Deposition of Lead on Gold Evaporated and Single-Crystal Electrodes. *Journal of The Electrochemical Society* **1974**, *121* (4), 474-484.

190. Toney, M. F.; Gordon, J. G.; Samant, M. G.; Borges, G. L.; Melroy, O. R., In-Situ Atomic Structure of Underpotentially Deposited Monolayers of Pb and Tl on Au(111) and Ag(111): A Surface X-ray Scattering Study. *J. Phys. Chem.* **1995**, *99*, 4733-4744.

191. Lorenz, W. J.; Staikov, G., 2D and 3D thin film formation and growth mechanisms in metal electrocrystallization — an atomistic view by in situ STM. *Surface Science* **1995**, *335* (Supplement C), 32-43.

192. Sieradzki, K., Curvature Effects in Alloy Dissolution. *Journal of The Electrochemical Society* **1993**, *140* (10), 2868-2872.

193. Brankovic, S. R.; Dimitrov, N.; Sieradzki, K., Surfactant Mediated Electrochemical Deposition of Ag on Au (111) *Electrochemical and Solid-State Letters* **1999**, *2* (9), 443-445.

194. Als-Nielsen, J.; McMorrow, D., *Elements of Modern X-ray Physics*. 2nd ed.; A John Wiley & Sons: Chichester, UK, 2011.