Electric field assisted adsorption of nanocolloidal gold particles: Characterisation and deposition kinetics

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Electric field assisted adsorption of nanocolloidal gold particles: Characterisation and deposition kinetics

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1 Introduction

1.1 Summary

In this thesis, I describe the deposition and characterisation of nanocolloidal gold films. The films are assembled under the influence of either electrostatic attraction or externally induced electrical fields. Colloids are commonly defined as particles with a size between 1 nm and 10 μm, dispersed into a continuous medium. Both the particles and the continuous medium can be solid, liquid or gaseous. This thesis deals with aqueous suspensions of gold particles, which are an example of the important class of solid particles dispersed in a fluid medium.

In this chapter, I give an overview of the history of colloid science and point out some applications of nanoparticles. Then, I will present a very short introduction into colloid chemistry, focusing on the stability of colloidal suspensions. In addition, I will describe a few techniques for deposition of nanocolloidal films. Finally, the content of this thesis is shortly introduced.

1.2 Background

Although few people realise, colloidal systems are nearly everywhere, both in nature and in man made entities. An example of natural origin is milk, which is a suspension of small fat particles and proteins in water. Smoke consists of small solid particles in air. An ancient example of a man-made colloidal suspension is Egyptian ink, which consists of small particles of carbon stabilised in water by gum Arabic. Another example is the metallic luster observed in glazed ceramics from Mesopotamia from as early as the 8th century \[1\]. Objects made of lustered glass show different colours depending on the way the glass is illuminated. This behaviour is caused by metal nanoparticles embedded in the glass. Suspensions of gold nanoparticles played a role in medieval alchemy, and today some people claim that these suspensions can heal several diseases.

Although people have been using colloidal systems for centuries, systematic research on colloids was only initiated in the middle of the 19th century\(^1\). In 1845, Selmi investigated suspensions of sulphur, Prussian blue and casein (the most important protein in milk) and concluded that they consisted of small particles suspended in water. Sixteen years later Graham, who introduced the word ‘colloid’,

\(^1\)An overview of the history of colloid science is given by Derjaguin [2] and by Jirgensons and Straumanis [3].
identified several colloidal suspensions by analysing diffusion constants of the suspended particles [4]. Another early pioneer is Faraday, who investigated colloidal gold suspensions and concluded that the gold was present in the solvent in the metallic state [5]. Faraday and Tyndall [6, 7] were the first to explore the optical properties of colloidal gold suspensions.

Direct evidence for the particulate nature of colloidal suspensions became available when in 1903 Zsigmondy and Siedentopf invented the ultra-microscope [8, 9]. This microscope uses the Tyndall effect to observe colloids against a black background. When the particles are illuminated from one side, scattered light is observed perpendicular to the incident beam.

At this time a lot of properties of colloidal suspensions were being investigated. Migration and Brownian motion of colloidal particles were studied by Smoluchowski [10], Einstein [11] and Perrin. An example that is relevant for the work described in this thesis is the work done by Mie [12] and Gans [13, 14] who gave a thorough description of the scattering of light by small particles, such as colloids. Although many properties of colloidal suspensions were known at this time, the interactions that keep suspensions stable were still unknown. Colloid stability was explored by Schulze [15] and Hardy [16], who discovered that addition of salts to colloidal suspensions causes them to precipitate. The theory of the stability of colloidal suspensions was developed more or less simultaneously by Derjaguin and Landau [17] and by Verwey and Overbeek [18]. This theory is referred to as the DLVO theory, after the initials of its developers. Although this theory surely has it limitations, it is still the starting point for the description of many experiments involving colloidal stability.

Nanocolloidal particles have potential applications in very different fields, encompassing the entire area of nanotechnology. Some of these take advantage of the huge surface to volume ratio of the particles. This holds for instance for metal nanoparticles that are used as catalyst [19, 20]. Another example is detection of chemical or biological compounds present in solutions or gasses [21–23]. Magnetic nanoparticles are applied for liquid bearing [24] in for instance hard disks, and can be employed as medium for information storage. The properties of semiconductor nanoparticles are strongly dependent on their size, which is employed for applications in light emitting devices [25, 26]. Many more applications can be found in reviews such as the book ‘Colloids and Colloid Assemblies’ edited by Caruso [27].

1.3 Colloid chemistry

For the reader who is not familiar with colloids, I will give a short introduction into colloid chemistry. For a more extensive introduction the reader is referred to textbooks [28]. One of the distinct properties of colloids is that they have a huge surface to volume ratio. A sphere of $1 \text{ cm}^3$ of some material, has a surface of $4.8 \text{ cm}^2$. When we divide this large sphere into many small spheres with a radius
of $1\,\mu\text{m}$ preserving the volume, the total surface increases to $0.62\,\text{m}^2$. When we decrease the particle radius to $5\,\text{nm}$ the total surface of the particles amounts to $124\,\text{m}^2$!

Many colloidal particles are lyophobic\(^2\), which means that they have a large surface free energy, and this is thermodynamically very unfavourable. Consequently, they tend to reduce their total surface by fusing together. This process is referred to as coalescence and is accelerated by the attractive Van der Waals forces. If this process is not prevented or at least slowed down considerably, the colloidal suspension is unstable, and the particles will precipitate from the suspension as large flocks.

Three mechanisms for stabilisation of colloidal suspension are known. The surface of the particles can be coated with a surfactant. The lyophobic part of the molecule will attach to the surface of the particle, while the lyophilic part will be exposed to the solvent. In this way, the particle is made more lyophilic, which reduces the surface free energy, thus stabilising the suspension. A second method is capping the particle surface with a steric stabiliser. The stabiliser acts as a spacer and prevents the cores of the particles from coalescence. For gold nanocolloids, alkanethiols are often used for this purpose.

The last mechanism is stabilisation by a nett charge at the particle surface. The presence of a charged particle in a solution containing ions locally modifies the distribution of both co-ions (ions with the same charge as the particle), and counter ion (ions with an opposite charge). This redistribution of charge is governed by two thermodynamic factors. The electrostatic interaction between the ions and the particle favours accumulation of counter ions at the particle surface and depletion of co-ions. Accumulation of all counter ions close to the surface would result in a very inhomogeneous distribution of the counter ions, which is thermodynamically unfavourable. Similarly, complete depletion of co-ions is also unfavourable. The result is therefore a diffuse cloud of ions around the particle that consists predominantly of counter ions. The charge of the particle and the counter charge in the diffuse ion cloud together constitute the electrical double layer of a charged particle. When two similarly charged colloids approach each other, the diffuse part of their double layer starts to overlap. Since the diffuse part of the double layers consist mainly of counter ions, this overlap results in an increase of the electrostatic energy of the system and therefore in a repulsive force. This force stabilises the particles in the solution.

The electrical double-layer at the interface between a charged particle and the solvent is described by the DLVO theory already mentioned in the previous section. The relation between the electrostatic potential and the distribution of charge is described by the Poisson equation

\[ \nabla^2 \psi = \frac{\rho}{\varepsilon} \]  \hspace{1cm} (1.1)

\(^2\text{In case of aqueous suspensions the word hydrophobic is used.}\)
where $\psi$ is the electrostatic potential, $\rho$ is the charge distribution and $\varepsilon$ is the dielectric constant of the surrounding medium. The charge distribution is described by the Boltzmann equation

$$\rho = \sum_i n_i^0 z_i e \exp \left( -\frac{z_i e \psi}{kT} \right)$$  \hspace{1cm} (1.2)

The summation extends over all ion species in the solution, $n_i^0$ and $z_i$ are the bulk number concentration and valence of species $i$, $k$ is the Boltzmann constant and $T$ the absolute temperature. The Boltzmann equation states that positive ions are predominantly present in places where the electrostatic potential is low, while negative ions are dominant in areas where the potential is high. Combining equations 1.1 and 1.2 yields the Poisson–Boltzmann equation:

$$\nabla^2 \psi = \frac{1}{\varepsilon} \sum_i n_i^0 z_i e \exp \left( -\frac{z_i e \psi}{kT} \right)$$  \hspace{1cm} (1.3)

This equation cannot be solved analytically in spherical coordinates and is therefore linearised by expanding the exponential up to the linear term. This approximation is referred to as the Hückel approximation and yields:

$$\nabla^2 \psi = \kappa^2 \psi$$  \hspace{1cm} (1.4)

where the Debye screening constant $\kappa$ is defined as

$$\kappa = \sqrt{\frac{2e^2 N_A I}{\varepsilon kT}}$$  \hspace{1cm} (1.5)

in which $N_A$ is Avogadro’s number. The ionic strength $I$ is defined as

$$I = \frac{1}{2} \sum_i z_i^2 c_i$$  \hspace{1cm} (1.6)

with $c_i$ the molar concentration in moles per $m^3$ or in millimoles per liter. Solving the linear Poisson–Boltzmann equation in spherical coordinates yields

$$\psi (r) = \psi_0 \frac{\exp \left(-\kappa \left(r - a\right)\right)}{r/a}$$  \hspace{1cm} (1.7)

where $r$ is the distance from the centre of a spherical particle, $a$ is the particle radius and $\psi_0$ is the surface potential of the particles. This solution is valid for relatively low potentials, for higher potentials this solution is a far field approximation that holds when a suitable effective far field surface potential is used for $\psi_0$. 

4
1.4 Self-assembly of nanocolloidal films

An illustration of the electrical double layer is shown in figure 1.1, where we calculated the properties of the double layer around a particle with a diameter of 10 nm and a surface potential of +25 mV. The particle is suspended in a solution with an ionic strength of 10 mM containing only monovalent ions. This hold for instance for a 10 mM solution of NaCl. The Debye screening length $1/\kappa$ is 3 nm under these circumstances. The figure shows that the double layer potential drops to zero in approximately 3 times the screening length. The accumulation of the negatively charged counter–ions and the depletion of the positively charged co–ions is also clearly illustrated. At a distance of 10 nm from the particle surface, the ion concentrations have reached their bulk values and the nett charge density has vanished.

1.4 Self-assembly of nanocolloidal films

With the growing interest in nanotechnology, research on nanocolloids has increased strongly. A comprehensive overview of the recent developments in colloid science
1 Introduction

Figure 1.2: Film of 6 nm sized silver particles dropcasted on thin chip of HOPG on a TEM grid. The imaged area is 200 × 150 nm.

would therefore be a respectable work in itself. For this reason I have limited myself to shortly pointing out a few developments that are related to the topic of this thesis: deposition and self-assembly of colloidal films.

The most straightforward way to self-assemble colloidal particles is by controlled drying. If a drop of a suspension is cast onto a substrate, the solvent will evaporate. When only a thin film of the solvent is left, strong capillary forces act on the particles. If the particles are mobile on the surface, these forces will result in the formation of a densely packed colloidal film. This procedure can be influenced by the temperature, vapour pressure and the choice of the solvent. It is possible to deposit particles of very different composition, such as silica [29], CdSe [30], cobalt [31], Ag$_2$S [32, 33], silver [29, 34] and gold [35]. In many cases long range ordering can be achieved [35]. An example of a film of dodecythiol stabilised silver particles drop casted on highly oriented pyrolytic graphite (HOPG) is shown in figure 1.2. These particles are synthesised using a reverse micelle method [36, 37]. A disadvantage of self-assembly by evaporation is that it requires volatile, often harmful organic solvents, which makes application for large scale production purposes undesirable.

Layer-by-layer self-assembly is a very popular deposition technique that is employed to deposit films of very different materials, including nanocolloidal particles.
When a colloidal films is grown, a substrate is immersed first in a solution containing nanocolloidal particles and then in a binder solution. When this procedure is repeated several times, 3-dimensional colloidal films are assembled. The binder can be a polyelectrolyte [23, 38], in which case the binding is provided by electrostatic and Van der Waals forces. Alternatively, covalent binding [21, 22, 39–41] can be employed. Using layer-by-layer self-assembly, it is possible to grow relatively thick and dense films, which makes the study of the optical properties of interacting particles possible [23, 39, 41]. Films grown in this way generally do not show ordering, which is a disadvantage for some applications.

An other technique we want to mention is Langmuir-Blodgett deposition. It is a technique that is already quite old and can be applied to a wide variety of materials, including colloids. In case of assembly of colloidal films, a suspension of hydrophobic particles in an apolar solvent is carefully spread over water. As the particles are insoluble in the water phase, they self-assemble into a film at the water–air interface when the solvent evaporates. The film is transferred onto a substrate that was immersed in the water prior to evaporation of the solvent by slowly removing the substrate from the suspension. This technique has been applied
to a wide variety of colloids, including gold particles stabilised with an alkanethiol or alkylamine \[43, 44\]. Figure 1.3 shows a film made of 13 nm gold particles, grown at a water–oil interface using a modified Langmuir–Blodgett technique \[42\]. After assembly, the film has been transferred onto an oxidised silicon wafer.

### 1.5 This thesis

In this thesis, we investigate two other techniques for assembly of nanocolloidal gold films. These are adsorption of particles on an oppositely charged substrate and deposition driven by an externally applied DC voltage. Three aspects are highlighted: (i) the kinetics of the deposition process, (ii) the morphology of the deposited films and (iii) optical characterisation of the films. For these studies, we need measurement techniques that allow us to observe colloidal particles that have been adsorbed onto a surface. Since the particles are so small, techniques conventionally used in colloid science, such as optical microscopy, ultra-microscopy and confocal microscopy, cannot be applied. Therefore we use two non-imaging optical reflection techniques: single wavelength reflectometry and spectroscopic ellipsometry. The latter is widely used to investigate interfaces and processes occurring at interfaces \[45–47\]. Spectroscopic ellipsometry is a very versatile technique that can provide a lot of information on the sample that is analysed.

Chapter 2 describes the suspensions and measurement methods that have been used. The synthesis and characterisation of the colloidal gold suspensions are reported. Furthermore, an introduction into ellipsometry and reflectometry is presented, including a description of the measurement procedures. A description of the experimental setups is given.

Obtaining quantitative information from ellipsometry spectra usually involves fitting a model to the measured data. In case of single wavelength reflectometry, a calibration curve relating the optical signal to the relevant film parameter has to be calculated. In either case the optical response of the substrate with the film has to be known. This is the topic of chapter 3. In this chapter we show that conventional models describing the optical response of heterogeneous films are inadequate for the description of colloidal monolayers. An alternative theory, developed by Bedeaux and Vlieger \[48, 49\] provides an accurate quantitative description of the optical response of colloidal gold films, and enables us to accurately determine the number of colloids present on a substrate from the ellipsometry spectra.

Optical modelling can be quite complicated, or even impossible. Sometimes, required knowledge of the optical properties of the sample is not available. For instance, when the optical properties of a substrate are unknown it is not possible to construct a model. In chapter 4 we present a method that allows analysis of series of ellipsometry spectra in these situations. This method, referred to as principal component analysis (PCA), is a statistical analysis method to obtain the number of colloids on a surface from series of similar ellipsometry spectra. PCA
is also useful for obtaining an overview of the trends in data without modelling of the spectra. We apply PCA to several sets of spectra, including spectra of gold nanocolloids on a silicon substrate. Comparing the results of PCA with optical modelling described in chapter 3 shows that PCA is a useful complementary tool for analysis of ellipsometry spectra.

One of the important advantages of optical techniques such as ellipsometry and reflectometry is that they can easily be integrated in a wide variety of experimental setups. This enables in-situ observation of many surface processes including the adsorption of nanocolloids. In chapter 5, adsorption of gold nanocolloids on chemically modified silicon wafers is studied using single wavelength reflectometry. In these experiments, electrostatic attraction between the positively charged substrate and negatively charged particles is the driving force for deposition. The adsorption kinetics are studied under well-defined mass transport conditions, and the morphology of the deposited films is analysed.

Deposition of nanoparticles using purely electrostatic interactions has several disadvantages. Therefore we have investigated the deposition of gold nanocolloids under influence of an externally applied DC voltage. In chapter 6 we show measurements of the dependence of the deposition rate on the applied field and propose a deposition mechanism that explains the observed behaviour. We observe the adsorption process using spectroscopic ellipsometry and analyse the measured spectra using PCA. The morphology of the films is analysed and compared to the morphology of films that are deposited on a chemically charged substrate.
References


1 Introduction


2 Experimental techniques

2.1 Introduction

This chapter deals with experimental aspects that are not described in the later chapters. In section 2.2 the synthesis and characterisation of the used nanocolloidal gold suspensions are described. In section 2.3, a short overview of spectroscopic ellipsometry is presented. This section also describes the rotating polariser ellipsometer that is employed in the Solid State Physics group and treats some important issues for spectroscopic ellipsometry measurements in the attenuated total reflection setup. Finally, section 2.4 describes the single wavelength reflectometer used for the studies of the adsorption kinetics of gold colloids, including error sources that can be important in some situations.

2.2 Gold suspensions

2.2.1 Synthesis and particle size

For the experiments described in this thesis two different types of gold nano-particle suspensions are used. Most experiments are performed using citrate stabilised gold particles that are synthesised by reduction of $\text{AuCl}_4^-$ with citrate. The synthesis of these particles is well known [1]. For a typical synthesis, 100 mL of 1 mM HAuCl$_4$ (from Aldrich) is heated to 100°C. Then 10 mL of 38.8 mM trisodiumcitrate (from Aldrich) is added. The light yellow solution immediately turns colourless, and then slowly changes colour to dark blue/black and after a few minutes burgundy red. As shown in figure 2.1(a), the resulting suspension contains spherical particles. In figure 2.1(b) the distribution of the particle size is shown. The mean particle diameter is 12.7 nm, with a spread of 7.7% [2]. From the particle size and the initial concentration HAuCl$_4$ follows that the particle concentration is approximately $7.4 \times 10^{18}$ per m$^3$. The suspension has an ionic strength of approximately 14.3 mM, mostly due to sodium chloride and citrate. The $\zeta$-potential of these colloids is approximately -85 mV [3, 4]. Because the surface charge is negative, the particles are unsuitable for electrophoretic deposition at low DC voltages in an aqueous environment. The reason is that in a suspension containing chloride, gold is oxidised at an anodic voltages as low as 1 V, under formation of $\text{AuCl}_4^-$. Therefore, positively charged particles have to be employed for DC electrophoretic deposition.

Octadecylamine ($\text{C}_{18}\text{H}_{37}\text{NH}_2$) stabilised gold nano-particles are used for the electrophoretic deposition experiments described in chapter 6. Because of the amine
2 Experimental techniques

(a) TEM image showing the crystalline domains in the particles

(b) Distribution of the particle diameters with an average size of 12.7 nm and a standard deviation of 7.7%

Figure 2.1: Citrate stabilised gold nanocolloids
group in the stabiliser, these particles are expected to have a positive surface charge. The particles are synthesised using the recipe described by Aslam et al. [5]. Typically, 100 mL of an aqueous solution of 1 mM HAuCl$_4$ is heated to 60°C. Then 190 mg molten octadecylamine is slowly added, resulting in an octadecylamine concentration of 7 mM. Due to the formation of a gold–octadecylamine complex, the solution immediately obtains a bright yellow colour. The temperature is increased to 85°C. After a few minutes, the solution turns colourless, indicating the reduction of AuCl$_4^-$.
2 Experimental techniques

(a) TEM image showing that the particles consist of a small number of domain

(b) Distribution of the particle diameters with an average size of 8.6 nm and a standard deviation of 13%

Figure 2.2: Octadecylamine stabilised gold particles
and polydispersity. This is demonstrated in figure 2.4. In this figure the absorption spectra of gold colloids of several sizes are shown. The full line shows the absorption spectrum of colloids, calculated using the bulk dielectric function. Around 520 nm the plasmon resonance peak is clearly visible. This peak originates from collective motion of conduction electrons in gold under influence of the electromagnetic wave. At a wavelength of 520 nm, which corresponds to a photon energy of 2.4 eV, the frequency of the electromagnetic wave matches the resonance frequency of the particles, which yields a strong interaction between the radiation and the particles.

In bulk gold the electron mean free path is 42 nm, which means that electrons can typically move 42 nm without being scattered by the atom cores. But in gold particles with a diameter that does not exceed this distance, significant scattering of the electrons is caused by the surface. This scattering results in a suppression of the motion of the electrons and therefore in a lower plasmon resonance peak. This is exactly what we observe for the dashed and dash-dotted curves that show the spectra of nanocolloidal gold particles stabilised with citrate and octadecylamine, respectively. In these spectra the plasmon resonance peak is much weaker than for the larger particles. The peak of the octadecylamine stabilised particles is lower than the peak of the citrate stabilised particles, in agreement with their relative size.

The finite size of the particles also results in a small redshift of the plasmon
2 Experimental techniques

Figure 2.4: UV/Vis absorption spectra of colloidal gold particles. The full line shows the calculated spectrum of large particles, whereas the dashed and dash-dotted lines show the measured spectra of nanocolloidal gold particles stabilised with citrate and octadecylamine, respectively.

resonance peak, which can be seen from figure 2.4. Another difference in the spectra is that the peaks of the suspensions described above are also broader than the peak of the large particles. Partly, this is caused by the finite size of the particles but another important cause is the polydispersity of suspensions. The presence of larger particles, for instance due to coagulation, will result in a broad tail on the red side of the peak, and this allows us to detect degradation of a suspension.

2.3 Spectroscopic ellipsometry

2.3.1 Introduction

Spectroscopic ellipsometry is a widely used experimental technique for the characterisation of surfaces and processes at surfaces.

In an ellipsometry experiment, light with a known polarisation state is reflected at or transmitted through an interface, which causes a change of the polarisation. This is illustrated in figure 2.5. The incident light wave can be decomposed into two components with the polarisation direction, parallel or perpendicular to the plane of incidence. The later plane is defined by the direction of the incident light beam
2.3 Spectroscopic ellipsometry

Figure 2.5: Reflection of linearly polarised light at an interface. The dark grey wave is polarised parallel to the plane of incidence, the light grey line represents the perpendicularly polarised wave. After reflection the relative amplitudes have changed and a relative phase shift \( \Delta \) has occurred. The angle of incidence is \( \theta \).

and the normal of the sample surface. The polarisation of the incident beam is characterised by the ratio of the amplitudes of both components, and their mutual phase.

Depending on the setup, the polarisation of the reflected or the transmitted light is measured. Due to interaction with the sample, both the ratio of the amplitudes and the mutual phase of the two components change. This change is therefore represented by a complex number

\[
\rho \equiv \frac{r^p}{r^s} \equiv \tan(\psi) \cdot \exp(i\Delta)
\]  

(2.1)

where \( r^p \) and \( r^s \) are the amplitude reflection coefficients for parallel and perpendicularly polarised light. The modulus, \( \tan(\psi) \) represents the change in the ratio of the amplitudes, and \( \Delta \) represents the relative phase change. Ellipsometry measurement can be performed at a single wavelength or over a larger part of the electromagnetic spectrum. In the later case, much more information is gathered, allowing extraction of more parameters of the sample.

One of the benefits of ellipsometry is that it is quite sensitive. For instance, using spectroscopic ellipsometry, the thickness of an oxide layer on a silicon wafer can be
measured with an accuracy better than 1 nm. Secondly, an ellipsometry setup can be integrated relatively easily in a wide variety of experimental setups, enabling in-situ observation of many different processes [6–8].

Obtaining quantitative information from ellipsometry spectra requires modelling of the optical response of the sample that is used. The most common model regards a sample as a stack of flat, planar films on a substrate. In this case, the optical response can be calculated using the Fresnel equations:

\[
\begin{align*}
    r^p &= \frac{n_{i+1} \cos \theta_i - n_i \cos \theta_{i+1}}{n_{i+1} \cos \theta_i + n_i \cos \theta_{i+1}} \\
    t^p &= \frac{2n_i \cos \theta_i}{n_{i+1} \cos \theta_i + n_i \cos \theta_{i+1}} \\
    r^s &= \frac{n_i \cos \theta_i - n_{i+1} \cos \theta_{i+1}}{n_i \cos \theta_i + n_{i+1} \cos \theta_{i+1}} \\
    t^s &= \frac{2n_i \cos \theta_i}{n_i \cos \theta_i + n_{i+1} \cos \theta_{i+1}}
\end{align*}
\]

(2.2a) (2.2b) (2.2c) (2.2d)

where we assume that light enters from medium \(i\) into medium \(i+1\). The quantities \(t^p\) and \(t^s\) are the amplitude transmission coefficients for parallel and perpendicular polarised light. Furthermore we need to take into account the phase change of the light passing through film \(i\):

\[
\Delta_i = \frac{2\pi}{\lambda} d_i n_i \cos \theta_i
\]

(2.3)

where \(\lambda\) is the wavelength of the light in vacuum, \(n_i\) and \(d_i\) are the refractive index and thickness of film \(i\), and \(\theta_i\) is the angle of the light in the film. When the sample consists only of a substrate and a single film, evaluation of the total reflection coefficient of the sample is relatively straightforward. For more complex samples, consisting of multiple layers, the total reflection coefficient can be calculated more easily using the Abelès matrix formalism. This formalism is described extensively by Azzam and Bashara [9] and is summarised in chapter 3.

When this model is used to calculate the optical response of a sample, the refractive indices of all layers in the stack, including the substrate and the ambient medium, have to be known. For a lot of materials the refractive index has been tabulated, but for many other films the optical properties are a-priori unknown. This holds for instance for films consisting of a mixture of two or more materials. In this situation the optical constants can sometimes be calculated using an effective medium theory. In effective medium theories the dielectric function of a material is calculated from the dielectric functions of the constituent materials and their volume fractions. This approach gives often good results, but in case of colloidal metal films not, as will be shown in chapter 3.

Another situation where the conditions for application of the Fresnel equations
2.3 Spectroscopic ellipsometry

do not hold is when the interface between two media is rough. In this case, often an extra film with smooth interfaces can be defined, which incorporates the roughness. The thickness of this film is approximately equal to the roughness of the film, while its refractive index can be estimated using an effective medium theory.

In both situations, the Fresnel equations can still be applied. Whether this approach yields correct results depends on the materials involved. As will be extensively discussed in chapter 3, the approach described above does not hold for films consisting of nanocolloidal metal particles. One of the causes is that these films are not isotropic, which is a prerequisite for description of their dielectric function using an effective medium theory. A second cause is that colloidal metal particles have strong electromagnetic interactions with the substrate and with other particles. Nanocolloidal metal films are much better described using the thin island film theory [10, 11]. This theory describes the colloidal particles as excess polarisabilities at the substrate–medium interface. In this way, both the anisotropic nature of these films and the interactions are taken into account.

2.3.2 The rotating polariser spectroscopic ellipsometer

Spectroscopic ellipsometry measurements can be performed in several setups. All setups have in common that they consist of a light source, a polariser in the incident beam, a second polariser behind the sample, often referred to as the analyser, and a detector. The monochromator can be integrated in the incident or the outgoing beam. Sometimes a compensator is used to shift $\Delta$ to more easily measurable values.

Before fast digital measurements became popular, the nulling ellipsometer was the most widely spread setup. In this ellipsometer, the polariser, analyser and a compensator are rotated until the signal on the detector is minimal, hence its name. The ellipsometric angles $\psi$ and $\Delta$ can then be determined from the angles of the polariser and analyser. Since the nulling ellipsometer is the most accurate type, it is still used. The main disadvantage of the nulling ellipsometer is its relative slowness. Therefore, most ellipsometers nowadays are of the rotating element type. This class offers high a measurement speed and a high accuracy. Characteristic for this class of ellipsometers is that one of the optical elements is rotating. Most often, this is the polariser or the analyser, but in some cases, the compensator is rotating. Due to the rotation, the signal observed on the detector typically shows a sinusoidal time-dependence with a frequency that is two times the rotation frequency $\omega$ of the rotating element. The spectroscopic quantities $\tan(\psi)$ and $\cos(\Delta)$ are calculated from the Fourier coefficients of the signal at $2\omega$. A more extensive discussion of the different types of ellipsometers is given by Thomkins [1].

A nulling ellipsometer can also be used in the off null mode. In this situation the analyser angle is fixed close to the null position, and the signal intensity is measured as function of time. This measurement mode is fast, but does not easily allow exact determination of the ellipsometric angles.
2 Experimental techniques

and McGahan [12] and Azzam and Bashara [9]. The ellipsometer that is used for the experiments described in this thesis is of the rotating polariser type. This setup is described shortly below. A much more elaborate description is given by Bijlsma [13], De Nijs [14] and Wentink [15].

The incident side of this setup consists of a xenon light source that emits a wide spectrum of light, a diaphragm followed by a lens and a second diaphragm that creates a well-defined beam, a filter and a rotating polariser. The polariser creates linearly polarised light with a polarisation direction that is modulated by the rotation of the polariser. After reflection at the sample, the light is generally elliptically polarised. The outgoing side of the setup consists of an analyser at a fixed angle, that creates again linearly polarised light. A grating monochromator selects the wavelength at which the measurements are done. This type of monochromator transmits not only light with the required wavelength $\lambda_0$, but also light with wavelength $(n+1)\lambda_0$ with $n$ a positive integral number. These components are eliminated by the filter on the primary side. Finally, the light is detected by a photomultiplier tube.

For a perfect ellipsometer, the detected signal can be described as:

$$I(t) = I_o \{1 + \alpha \cos(2\omega t) + \beta \sin(2\omega t)\}$$

(2.4)

where $\omega$ is the rotation frequency of the polariser. The signal consists of a DC component and an AC component with a frequency that is twice the rotation frequency of the polariser. From the Fourier coefficients $\alpha$ and $\beta$, the values of $\tan(\psi)$ and $\cos(\Delta)$ can be calculated by inverting:

$$\alpha = \frac{\cos(2A) - \cos(2\psi)}{1 - \cos(2A) \cos(2\psi)}$$

(2.5a)

$$\beta = \frac{\sin(2A) \sin(2\psi) \cos \Delta}{1 - \cos(2A) \cos(2\psi)}$$

(2.5b)

In this equation, $A$ is the angle of the analyser with respect to the plane of incidence. From the second equation follows that using a rotating polariser ellipsometer only $\cos(\Delta)$ is measured. It is therefore impossible to obtain the sign of $\Delta$.

2.3.3 Measuring with the rotating polariser ellipsometer

Equations 2.5 show that the analyser angle with respect to the plane of incidence has to be known for the calculation of $\psi$ and $\cos(\Delta)$. But it is a-priori unknown which angle $A_0$ of the polariser coincides with the plane of incidence. Therefore this angle has to be determined before the measurements.

Additionally, equation 2.4 describes the ideal rotating polariser ellipsometer. In practice two deviations from the ideal situation occur. First, the signal measured by an imperfect ellipsometer contains more Fourier components than included in
equation 2.4:

\[
I(t) = I_0 \left\{ 1 + \sum_i \alpha_i \sin(i\omega t) + \beta_i \cos(i\omega t) \right\}
\]  

(2.6)

where \( i \) is an integral number and \( \alpha_i \) and \( \beta_i \) are the Fourier coefficients of the corresponding component. These extra components are caused by residual polarisation of the light source and alignment errors of components of the setup, including the sample.

The second deviation is that the measured signal is somewhat delayed and the AC component is slightly attenuated. The signal can therefore be described as

\[
I(t) = I_0 \{ \alpha_m \sin(2\omega t) + \beta_m \cos(2\omega t) \} = I_0 \{ \eta \alpha \sin(2\omega t - \Phi) + \eta \beta \cos(2\omega t - \Phi) \}
\]  

(2.7)

where \( \alpha_m \) and \( \beta_m \) are the measured Fourier coefficients, \( \eta \) is the attenuation factor and \( \Phi \) the phase lag. Rewriting equation 2.7 yields:

\[
\sqrt{\alpha_m^2 + \beta_m^2} \cos(2\omega t - \xi_m) = \eta \sqrt{\alpha^2 + \beta^2} \cos(2\omega t - \xi - \Phi)
\]  

(2.8)

with \( \xi_m = \frac{\beta_m}{\alpha_m} \) and \( \xi = \frac{\beta}{\alpha} \). This equation defines the relation between the theoretical and the actual measured Fourier coefficients.

Because of the issues described above two procedures have to be executed before a measurement. First, the setup has to be aligned such that the undesired Fourier coefficients are minimised. Secondly, the values of \( A_0 \), the attenuation factor \( \eta \) and the phase shift \( \Phi \) have to be determined. The latter procedure is referred to as calibration of the ellipsometer.

In a well-aligned ellipsometer the Fourier coefficients of the \( 2\omega \) component are typically 40 dB larger than the other components. Nevertheless, small errors will always occur, which will affect the values of \( \tan(\psi) \) and \( \cos(\Delta) \) that are obtained. Fortunately, these errors are in a first order approximation odd functions of the angle between the analyser and the plane of incidence. They can therefore be reduced by doing a two zone measurement, which means that the Fourier coefficients are measured at two positions of the analyser, \( A_0 + A \) and \( A_0 - A \). When the values obtained at these positions are averaged, the obtained values of \( \tan(\psi) \) and \( \cos(\Delta) \) are very accurate, provided that the errors are not too large.

For the calibration of the ellipsometer, two different procedures exist: residue- and phase calibration. Using either method, first \( A_0 \), the analyser angle coinciding with the plane of incidence, is determined. When \( A = A_0 \), equation 2.5 reduces to \( \alpha = 1 \) and \( \beta = 0 \). Consequently, once \( A_0 \) is known, \( \eta \) and \( \Phi \) can be obtained by measuring the Fourier coefficients at \( A = A_0 \). Residue calibration is based on equating the absolute values of both sides of equation 2.8, whereas for phase calibration the phases are equated. The two methods are more or less complementary: at some spots in the \( \psi-\Delta \) plane residue calibration is accurate, while at other spots
phase calibrations yields better results. Since calibration can be performed at all photon energies, it is in most situations possible to perform an accurate calibration, although there are places in the $\psi-\Delta$ plane where neither method yields an accurate result. A detailed discussion on the calibration of a rotating polariser ellipsometer is given by De Nijs [14, 16].

### 2.3.4 Ellipsometry in an attenuated total reflection setup

The ellipsometry measurements done during the electrophoretic deposition experiments described in chapter 6 are performed in an attenuated total reflection (ATR) setup. Figure 2.6 shows the propagation of the incident and reflected beam in this setup. A transparent sample is mounted on the long side of a triangular prism. The incident beam enters the prism at one of the short sides, and after reflection at the substrate, leaves the prism again at the other side. In this way, light propagates from the backside through the sample to the substrate–solution interface, where it is totally reflected. This means that there is no propagating wave in the solution. Nevertheless, an exponentially decaying wave exists in the solution, and this evanescent wave probes the adsorbing particles. The big advantage of this setup for electrophoretic deposition experiments is that it does not impose constraints on the electrode geometry employed. A second advantage is that the light is not absorbed by the solution, which is important since the gold particles strongly absorb light around 2.4 eV, exactly the energy where the change in the ellipsometric spectra upon adsorption of particles is most pronounced.

In addition to the reflection $\rho$ at the substrate, the light is also refracted at the air–glass and finally at the glass–air interface, which results in additional polarisation contributions. The total reflection coefficient $\rho'$ is related to $\rho$ by:

$$\rho' = \frac{t_{ag}^p \cdot \rho \cdot t_{ga}^p}{t_{ag}^s \cdot t_{ga}^s}$$

(2.9)

where $t_{ag}^p$ and $t_{ga}^p$ are the Fresnel transmission coefficients at the air–glass and the glass–air interface, respectively for parallel and perpendicular polarised light.

When we rewrite the Fresnel’s equations for transmission we find [9]:

$$t_{1,2}^p = \frac{2 \cos \theta_1 \cdot \sin \theta_2}{\sin (\theta_1 + \theta_2) \cdot \cos (\theta_1 - \theta_2)}$$

(2.10a)

$$t_{1,2}^s = \frac{2 \cos \theta_1 \cdot \sin \theta_2}{\sin (\theta_1 + \theta_2)}$$

(2.10b)

Applying these equations to the air–glass and the glass–air interface an inserting them into equation 2.9 yields:

$$\rho' = \frac{1}{\cos (\theta_a - \theta_g)} \cdot \rho \cdot \frac{1}{\cos (\theta_g - \theta_a)} = \frac{\rho}{\cos^2 (\theta_a - \theta_g)}$$

(2.11)
2.3 Spectroscopic ellipsometry

The angles $\theta_a$ and $\theta_g$ and the incident angle $\theta_i$ can be calculated from $\theta_{\text{top}}$, the top angle of the prism, the alignment angle of the cell $\Delta \theta$ and the refractive index of the prism. The definition of all these angles is shown in figure 2.6. Using elementary goniometry, we find:

$$\theta_a = \frac{\theta_{\text{top}}}{2} - \Delta \theta$$

$$\theta_i = \frac{\pi - \theta_{\text{top}}}{2} + \theta_g$$

The angle $\theta_g$ is related to $\theta_a$ by Snell’s law. Since $\theta_g$ depends on the refractive index of the prism, and the latter is a function of the photon energy of the light, the incident angle $\theta_i$ also varies slightly with the photon energy. When the prism is made of BK7 glass and we assume $\theta_{\text{top}} = 90^\circ$ and $\Delta \theta = 0$, the incident angle $\theta_i$ decreases from $72.92^\circ$ to $72.37^\circ$ between $1.5$ eV and $3.5$ eV.

When performing ellipsometry experiments in the ATR setup, a few precautions have to be taken. Although it is quite easy to obtain low values of the unwanted Fourier coefficients, this does not mean that the differences between the two zone measurements are low. When the cell is not properly aligned, the angle $A_0$ can shift as much as 2 or 3 degrees as a function of the photon energy. This shift is caused by the fact that the light path is not perpendicular to the sides of the prism. If the prism is slightly rotated around the normal of the long side, the light will also be refracted upwards or downwards when it enters the prism. Because the sides of the prism are not parallel, this change of the direction of the beam will not be reverted when the light leaves the prism. Therefore, the direction of the light after the cell is affected. Since the refractive index of the prism varies with the photon energy, the deflection of the beam also depends on the photon energy, which explains the variation in the observed value of $A_0$. Therefore, the cell has to be aligned such that the long edge of the long side of the prism is horizontal. The alignment of the cell can be verified by performing a calibration at a few energies. If the alignment is done carefully, $A_0$ will not vary more than 1 degree between 1.8 and 2.6 eV. A second problem is that neither residue-, nor phase calibration yield an accurate
value of $A_0$ when the cell is filled with water. The calibration therefore has to be performed before the cell is filled.

## 2.4 Reflectometry

### 2.4.1 Introduction

In chapter 5 single wavelength fixed angle optical reflectometry is used to observe the growth of the thin colloidal gold films. Therefore a brief review of the technique is given here. Reflectometry differs from ellipsometry by the fact that not the amplitude ratio and the phase difference, but only the intensities of the parallel and perpendicularly polarised components are measured. These are related to the intensity reflection coefficients $R_p$ and $R_s$ by:

\begin{align}
I_p &= I_0^p R_p \\
I_s &= I_0^s R_s
\end{align}

A consequence of this method is that the information on the phase difference between the two components is lost. The benefit of this setup is that it is relatively simple, which makes this type of measurements inexpensive and easy to implement.

When single wavelength reflectometry is done on samples with a low reflection coefficient for parallel polarised light, the measured data depend strongly on a few instrumental parameters. This will be analysed in the paragraphs 2.4.3 and 2.4.4.

### 2.4.2 The reflectometer

The setup we used consists of a helium neon laser, the deposition cell, a band filter transmitting light with a wavelength of 632.8 nm, a beam splitter cube and two silicon detectors for the detection of the intensities of parallel and perpendicularly polarised light. Both the laser and the detection system are mounted on a goniometer. The setup is more extensively described by Dijt et al. [17]. The goniometers enable adjustment of the angle of incidence. In most situations this angle is fixed to a value close to the Brewster angle where the sensitivity of the setup is maximal. For silicon samples in water, the Brewster angle is approximately 70°.

The laser can be moved in the plane of incidence in the direction perpendicular to the incident beam using a micrometer screw. The cell used for the deposition experiments is described in more detail in chapter 5. It is designed for deposition experiments under well-defined flow conditions in a single point, referred to as the stagnation point. Due to design constraints imposed by the desired flow, the light is not transmitted at perpendicular angles through the cell walls. Therefore, the angle of incidence deviates from the angle between the arms of the goniometer.
Since we want to measure deposition in the stagnation point, the laser has to be pointed at this spot. This is achieved by adjustment of the position of the cell in two directions: perpendicular to the plane of incidence and along the normal of the sample. We make use of the fact that in early stages of deposition the highest deposition rate occurs in the stagnation point and that the reflection coefficient \( R_p \) increases monotonically with the amount of adsorbed colloids. A short (2 minutes) deposition experiment is performed. After deposition a density profile exists in the colloidal film with the maximum at the stagnation point. The position of the cell is then adjusted until the maximum intensity on the detector for p-polarised light is observed.

The intensities of parallel and perpendicularly polarised light are measured simultaneously. In order to eliminate fluctuations in the intensity of the laser, the ratio of the reflected intensities is calculated:

\[
S \equiv \frac{I^p}{I^s} = \frac{I^p_0}{I^s_0} \cdot \frac{R^p}{R^s}
\]  (2.14)

Other authors only use \( R_p \) \cite{18}, and therefore need to use a stabilised laser and detector. The intensities of the incoming beam \( I^p_0 \) and \( I^s_0 \), which enter equation 2.14, are determined by the polarisation direction of the incoming beam. Since the optical information on the samples is contained in the reflection coefficients \( R^p \) and \( R^s \), \( I^p_0 \) and \( I^s_0 \) have to be eliminated. This is done by defining:

\[
Y \equiv \frac{S - S_0}{S_0} = \frac{R^p R^s_0}{R^s R^p_0} - 1
\]  (2.15)

where \( S_0 \) is the quotient of \( R^p_0 \) and \( R^s_0 \), the reflection coefficients of the samples before deposition. The function \( Y \) only depends on the optical properties of the sample and can therefore be used to relate a measured signal to the amount of deposited material. For this purpose, \( R^p_0 \) and \( R^s_0 \) are calculated as a function of the amount of adsorbed material, using a suitable model. For the adsorption experiments described in chapter 5, a model consisting of a silicon substrate with a silicon oxide film of known thickness in a water ambient is used. The colloidal gold film, located at the substrate-medium interface, is described using the thin island film theory \cite{10, 11, 19, 20}. This model is described in more detail in chapter 3.

Since only the ratio \( \frac{I^p}{I^s} \) is measured, at a single wavelength, only one parameter from the sample can be determined. Therefore, if one wants to measure the deposition of gold colloids on silicon wafers, one has to assume fixed values for the angle of incidence and the thickness of the oxide layer, which makes these quantities possible error sources. If the optical response of the sample depends strongly on either of these parameters, large errors can result. Fortunately, dependence of the optical signal on the thickness of the oxide film is quite weak, even for very thin films, such as the 1.5 nm thick native oxide that exists on silicon wafers exposed to...
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Figure 2.7: Influence of small deviations in the angle of incidence on the calibration curve $Y(\varphi)$. In the inset $S(\varphi)$ is plotted. It shows that a strong dependence of $S_0$ on the angle causes the variation in the calibration curves. The black line indicates curves calculated for $\theta = 70^\circ$, while the dashed and dashed-dotted lines are for $69.5^\circ$ and $70.5^\circ$, respectively. The thickness of the oxide film is 5 nm.

air. But the influence of the angle of incidence on the calculated calibration curves can be very strong, depending on the thickness of the oxide film.

2.4.3 Influence of the angle of incidence

Figure 2.7 shows a few calibration curves, plots in which the optical signal $Y$ is plotted as a function of the coverage defined as $\varphi = \pi a^2 \cdot N$, where $a$ is the particle radius and $N$ the number of particles per unit area. The figure makes clear that for a substrate with an oxide layer of 5 nm, an error in the angle of incidence of only $0.5^\circ$ can result in more than a factor 2 in the optical signal. For thinner oxide films, this situation is even worse, but for an oxide film of 50 nm, the difference is only 5%. As shown by the inset in figure 2.7, the cause for the large deviations for thin oxides, is the large variation in $S_0$.

Although the mounting mechanism of the deposition cell is designed to enable reproducible positioning, the cell can not be aligned with an accuracy better than a few tenths of a degree. This cell is therefore not especially suitable for measurements on silicon substrates with thin oxides. The situation can be improved
somewhat by doing the measurement at angles further away from the Brewster angle. Although the change of $S_0$ upon variation of the angle of incidence is approximately as large as at the Brewster angle, $S_0$ is much larger, which makes the error in $Y$ significantly smaller. In this way, part of the sensitivity of the setup is sacrificed, but this can be done without serious consequences, because the optical contrast of the gold colloids with water is so high that accurate measurements do not require a very sensitive setup.

### 2.4.4 Influence of the beam splitter alignment

A second source of errors is the alignment of the beam splitter cube. The beam splitter works optimal if the light enters the cube at an angle of $90^\circ$. When the alignment is imperfect, a small portion of the perpendicular polarised light will be
transmitted into the detector for parallel polarised light and vice versa. When a sample is used for which \( r^p \) is much smaller than \( r^s \), the intensity of the parallel polarised light is very low. A small fraction of the perpendicular polarised light that is transmitted in the wrong direction by the beam splitter can then significantly influence the signal observed on the detector for p-polarised light. This situation can arise for silicon samples with a very thin oxide film when measurements are performed close to the Brewster angle.

When we define the alignment error of the beam splitter cube \( \alpha \) as the angle between its normal and the incoming beam, we can write down the following equations for the transmitted electrical fields:

\[
E^p = E^0 \{ r^p \cos P \cdot \cos \alpha + r^s \sin P \cdot \sin \alpha \} \quad (2.16a)
\]

\[
E^s = E^0 \{ r^s \sin P \cdot \cos \alpha + r^p \cos P \cdot \sin \alpha \} \quad (2.16b)
\]

\[
\frac{E^p}{E^s} = \frac{\rho + \tan P \cdot \tan \alpha}{\tan P + \rho \tan \alpha} \quad (2.16c)
\]

where \( P \) is the angle of the polariser. For a perfectly aligned beam splitter, i.e. \( \alpha = 0 \), this yields:

\[
\rho = \tan P \cdot \frac{E^p}{E^s} \quad (2.17)
\]

Combining equations 2.16(c) and 2.17 yields for an imperfect aligned beam splitter:

\[
\rho' = \tan P \cdot \frac{E^p}{E^s} = \frac{\rho + \tan \alpha \cdot \tan P}{1 + \rho \cdot \frac{\tan \alpha}{\tan P}} \quad (2.18)
\]

A few calculated calibration curves are shown in figure 2.8. The figure shows that the error can be as large as 34% for silicon samples with 5 nm oxide close to the Brewster angle. For samples with an oxide layer of 25 nm, the error is only a few percent. Furthermore the error increases with increasing polariser angle \( P \). This is understood from equation 2.16(a): making \( P \) as small as possible minimises the contamination of \( E^p \) with of the perpendicular polarised light. As with the error due to misalignment of the cell, the influence of the beam splitter misalignment can be reduced by moving away from the Brewster angle, since this will increase \( r^p \). Still, if one wants to measure accurately on samples with a low \( r^p \), the alignment of the beam splitter has to be accurate.
References


2 Experimental techniques


3 Optical characterisation of thin colloidal gold films using spectroscopic ellipsometry

3.1 Summary

Spectroscopic ellipsometry and scanning electron microscopy (SEM) experiments are employed to characterise nanocolloidal gold films, self-assembled at APTES-derivatised Si/SiO$_2$ surfaces. Optical properties of gold nanoparticle assemblies are investigated \textit{ex situ} after drying. Quantitative optical characterisation of these highly inhomogeneous systems is not unambiguous. Conventional effective medium approximations are not applicable to these systems. To enable an accurate analysis, extinction measurements on colloidal suspensions are performed. The limited particle size in relation to the electron mean free path leads to a modification of the dielectric function at longer wavelengths. Quantitative results are obtained using the thin island film theory, which treats the nanoparticles as polarisabilities at the Fresnel interface. When the isolated single particle approximation is used for the calculation of the polarisabilities, quantitative agreement between the coverages determined from optical spectra and results from SEM images is found only close to 20\% coverage. At lower coverages the optical results seem to overestimate the actual nanoparticle density, whereas at higher coverages an underestimation is observed.

Therefore, lateral particle-particle interactions and image dipole effects have to be included in the calculation of the polarisabilities. We show that for silicon substrates with an oxide layer smaller than the particle diameter, the image dipole strength has a value between the values for an uncovered silicon substrate and a silicon oxide substrate. Therefore, an effective image dipole has to be taken into account. Although the distribution of the colloids on the sample surface is used for the calculation of the optical response, it turns out that the shape of the distribution has only a minor effect on the spectra.

3.2 Introduction

A prerequisite for studying colloidal systems is the ability to characterise them unambiguously under relevant conditions. Among the large number of methods available for characterisation of colloids and their superstructures, electron microscopy
(SEM/TEM) is by far the most popular [1–14]. For both very small and relatively large particles this is the most employed *ex situ* technique. The use of scanning probe microscopy (AFM, STM, MFM) among colloid scientists is increasing, but also with this technique experiments are typically performed *ex situ* [10, 15]. In fact, only optical methods have been employed *in situ*. Imaging techniques such as conventional [12, 13, 16] or confocal [1, 17] microscopy are used for large colloids. For sizes much smaller than the wavelength of light, such as with gold nanoparticles, only non-imaging (lateral averaging) *in situ* experiments are available. These include primarily UV/Vis absorption spectroscopy [1, 2, 6, 9, 14, 15], but also optical waveguide lightmode spectroscopy [18], and reflection techniques as reflectometry and ellipsometry [19–21].

The major advantage of ellipsometry as compared to reflectometry is its sensitivity to very small perturbations at an interface [22, 23]. Additionally, owing to the non-invasive character, ellipsometry is a powerful *in situ* technique to study a large variety of surface processes [24], such as the deposition, growth and drying processes of (nano)colloidal particles at a solid-liquid interface [19–21, 25]. Spectroscopic ellipsometry has also been used to study *in situ* electrochemical processes [26–31], protein adsorption [25, 29, 30, 32] and the CO$_2$ sorption behaviour in inorganic materials [33, 34].

In this chapter we investigate the optical properties of colloidal gold films by means of spectroscopic ellipsometry. Gold particles are deposited from a colloidal gold suspension on silicon substrates covered with a thin layer of oxide. To enhance the affinity for the gold nanoparticles, the surface is derivatised with 3-aminopropyltriethoxysilane (APTES). The amino end groups serve as anchor sites for the gold particles [9, 10, 15]; due to the strong bonding of the particles the surface mobility is negligible and the deposition is governed by Random Sequential Adsorption (RSA), see [35] and chapter 5. A higher degree of ordering has been achieved by electrophoretic deposition [11, 12], which was shown to be very successful with much larger particles [13, 16].

An unambiguous optical characterisation of colloidal systems and assemblies is not straightforward [36]. In this chapter we present *ex situ* ellipsometry spectra on samples after drying. The spectra are compared to SEM measurements on these samples, enabling the determination of the accuracy of ellipsometry experiments. This provides a basis for evaluating the analysis strategies for optical spectra.

To enable an accurate optical analysis, we first discuss the single-particle polarisability. The agreement between measured and calculated extinction coefficients of the colloidal gold suspension can be improved substantially by using a simple modification of the effective dielectric function of bulk gold in terms of the limited electron mean free path in the nanoparticles [37].

The measured ellipsometry spectra are compared to simulations using conventional effective medium approximations such as the Maxwell-Garnett and the Bruggeman approximation. Both methods fail because the thin film cannot be de-
scribed, even in a diluted state, as a 3D isotropic medium. Considerably better results are obtained with the 'thin island film' theory established by Bedeaux and Vlieger [38–40]. In the latter approach, the particles are described as excess polarisabilities at the substrate-ambient interface. When only the single particle polarisability of the colloids is considered (bare dipole approximation), the correspondence between the measured and simulated spectra is quite good for spectra measured on samples with a surface coverage between 10 and 20%. At lower coverages the simulations overestimate the change in the spectra, while at higher coverages an underestimation is observed.

During the seventies, Yamaguchi et al. showed that the strength of the dipole induced by the electromagnetic field is modified by an image dipole [41]. The influence of lateral interaction between dipoles was analysed by Haarmans and Bedeaux [42, 43] and Barrera et al. [44] in the early nineties. Especially the influence of densely packed square and hexagonal distribution of metal particles was considered. This work was used specifically for the analysis of deposited metal films, and recently also for hexagonal closed packed 5 nm silver colloids [45]. Both the lateral particle-particle interactions and the image dipole effect can be included in the thin island film theory in a quite natural way. In this chapter we will show that taking into account both image dipoles and lateral interaction up to quadrupole order results in a good agreement between calculated and measured spectra up to 40% surface coverage.

Analysis of the contribution of the image dipoles shows that the thickness of the oxide layer on the silicon has noticeable influence on the spectra. When the thickness of this layer is smaller than the particle diameter, the strength of the image dipole is bound between values for a silicon and for a silicon oxide substrate. Introduction of an effective image dipole strength allows an accurate quantitative description of the image dipole contribution to the spectra.

When lateral interactions and image charges are taken into account the spatial distribution of the particles has to be included in the model. We consider both an isotropic distribution and an experimentally determined distribution. As we describe in chapter 5, the latter exhibits a preferred nearest neighbour distance that scales with the coverage. This can be explained by the electrostatic repulsion between the particles. It turns out that the distribution of the particles on the surface has little effect on the spectra [46], provided that the surface coverage is below 40%.

### 3.3 Transmission spectroscopy

An accurate, quantitative optical characterisation of thin colloidal gold films is only possible if the dielectric function of the individual particles is known. Owing to their small size the optical properties of nanoparticles are markedly different from those of bulk material. Therefore, we first study the optical properties of single
colloidal particles in suspension by means of optical absorbance spectroscopy. The extinction coefficient $\sigma_{\text{ext}}$ of our as-prepared colloidal gold suspension, calculated from absorbance measurements\(^1\), is shown in figure 3.1 as a function of photon energy. The maximum at 2.4 eV, often referred to as the surface plasmon resonance, results in a red colour of the suspension, in good agreement with previous work. Upon dilution of the suspension, the entire extinction spectrum scales linearly with the particle concentration, which indicates that the multiple particle effects, such as secondary scattering, are negligible. Since the particles are much smaller than the wavelength of the light, the extinction is dominated by absorption, and scattering can be neglected [47].

The response of spherical particles in a colloidal suspension to an electro-magnetic field can be calculated exactly using Mie theory. However, as the particles are much smaller than the wavelength, the optical properties can be analysed in the quasi-static regime (also referred to as the Rayleigh regime). In this approximation ($a \ll \lambda$) the extinction cross section is due to dipolar absorption only; the scattering cross section and higher multipolar contributions (such as quadrupole

\(^1\)The extinction coefficient $\sigma_{\text{ext}}$, defined by $I/I_0 = \exp(-\sigma_{\text{ext}}z)$ with $I/I_0$ the attenuation of the light intensity at depth $z$ in the suspension, is determined from the optical absorbance $A$ given by $A = -\log I/I_0$, using the known optical path length $l = 10^{-2}$ m.
3.3 Transmission spectroscopy

extinction and scattering) are strongly suppressed in this size regime [37]. The extinction coefficient in the quasi-static approximation is given by:

\[ \sigma_{\text{ext}} = \frac{2\pi \sqrt{\varepsilon_1 N}}{\varepsilon_0 \lambda} \text{Im} (\alpha) \]  

(3.1)

with \( N \) the particle number density, \( \lambda \) the wavelength of the light and \( \varepsilon_1 \) the dielectric function of the medium in which the colloids are suspended. The single-particle polarisability \( \alpha \) is related to the dielectric function through the Clausius-Mosotti relation:

\[ \alpha = 3\varepsilon_0 V \frac{\varepsilon - \varepsilon_1}{\varepsilon + 2\varepsilon_1} \]  

(3.2)

where \( V = \frac{4}{3} \pi a^3 \) is the particle volume, \( \varepsilon_0 = 8.85 \times 10^{-12} \text{Fm}^{-1} \) is the permittivity of vacuum and \( \varepsilon \) is the complex dielectric function of the particle. The bulk dielectric function for gold\(^2\) [48] is shown in figure 3.2 by the dashed lines. In figure 3.1 the dashed line shows the calculated extinction using the aforementioned bulk optical properties of gold. Qualitatively, the features of the measured spectrum are reproduced. The extinction maxima are at the same energy, but the calculated peak is considerably higher and markedly narrower. Nevertheless, the difference between measured and calculated extinction is negligible on the high energy side of the spectrum. A similar decrease of the height and broadening of the peak for gold nanoparticles with a size below approximately 30 nm has been observed before [14]. Surprisingly, however, these spectra are often only compared qualitatively and merely the position of the surface plasmon resonance is considered.

The differences between calculated and measured extinction can be accounted for by considering the limited electron mean free path due to the small particle size [37, 49]. Within the classical electrical conductivity theory, the overall relaxation frequency for bulk material \( \Gamma_\infty = \sum \Gamma_i \) is composed of contributions \( \Gamma_i \) due to interactions with phonons, electrons, impurities and lattice defects. Assuming that only electrons near the Fermi surface (with Fermi velocity \( v_F \)) contribute to the conductivity, the mean free path \( \ell_\infty \) is related to \( \Gamma_\infty \) through \( \Gamma_\infty = \frac{v_F}{\ell_\infty} \). For gold \( \ell_\infty \) amounts to 42 nm. As our colloidal particles are markedly smaller than this, the effective mean free path is considerably reduced. Following Matthiessen’s rule, the additional scattering of conduction electrons gives rise to an extra term in the relaxation frequency:

\[ \Gamma(r) = \Gamma_\infty + A \frac{v_F}{\ell} \frac{\varepsilon_1}{\varepsilon} \]  

(3.3)

in which \( A = 4/3 \) is a theory-related constant. This size-dependent relaxation frequency leads to an alteration of the dielectric function \( \varepsilon(\lambda, a) = \varepsilon_{\text{bulk}}(\lambda) + \)

\(^2\)The bulk dielectric function of gold was determined using spectroscopic ellipsometry on a 1.5 \( \mu \)m thick gold film on mica. The results are in agreement with literature data [48].
Figure 3.2: Real and imaginary parts of the complex dielectric function of gold. The dashed lines refer to bulk values, while the solid lines depict the modified dielectric function, as described in the text.

\[ \Delta \varepsilon(\lambda, a) \] which, in turn, now also becomes size-dependent. The correction \( \Delta \varepsilon(\lambda, a) \) of the dielectric function due to intrinsic size effects can be expressed in terms of a difference of two Drude expressions \([49]\):

\[
\Delta \varepsilon = \frac{\omega_p^2}{\omega} \left( \frac{1}{\omega + i \Gamma_{\infty}} - \frac{1}{\omega + i \Gamma(a)} \right) \quad (3.4)
\]

where \( \omega = 2\pi c/\lambda \), with \( c \) the speed of light. As this simple model only takes into account free electron effects, the correction is largest at low energies.
With the size-dependency of the dielectric function $\varepsilon(\lambda, a)$, and thus the polarisability $\alpha$, we are able to calculate the modified extinction, employing equations 3.1 and 3.2. The plasma frequency $\omega_p$ and the Fermi velocity $v_F$ are not known for these small particles. With the bulk values $\hbar\omega_p = 8.8\, \text{eV}$ and $v_F = 1.39 \times 10^6 \, \text{ms}^{-1}$ the best fit upon varying $a$ (shown by the solid line in figure 3.1) yields a particle radius $a = 4.2\, \text{nm}$. This value is lower than the physical nanoparticle radius of 6.6 nm. Several reasons for this discrepancy can be envisaged. First of all, the TEM images reveal that the gold nanoparticles generally consist of multiple crystalline domains. This enhances scattering of electrons and decreases the electron mean free path even further, compared to the bulk value. Furthermore, the radius obtained by fitting is very sensitive to $\omega_p$ and $v_F$, the exact values of which are not known for these small particles. The shift of the surface plasmon resonance of nano colloidal gold suspensions with varying dielectric constant of the solvent [50] yields a plasma frequency $\hbar\omega_p = 9.9\, \text{eV}$. The best fit with this value inserted into equation 3.3 yields $a = 5.3\, \text{nm}$. The sensitivity to the precise value of $v_F$ is comparable.

The modified dielectric functions are shown in figure 3.2 by the solid lines. As mentioned above, the correction is largest at low energies and much more pronounced for $\text{Im}(\varepsilon)$. The calculated extinction coefficient using this modified dielectric function yields a broader, but also lower peak. At low energies, between 1.5 eV and 2.5 eV, the tail of the extinction is much higher compared to what is calculated using the bulk dielectric function, in agreement with experimental observations.

Finally, we also attempted to determine the dielectric function from the extinction using a Kramers-Kronig (K-K) transformation. The extinction measurement together with the inverse of equation 3.1 provides the imaginary part of the particle polarisability. As the imaginary and real parts of the polarisability are K-K consistent, the real part can be calculated. However, as the extinction is measured over a limited wavelength range and extrapolation of the spectrum is not obvious, especially at short wavelengths, the K-K transformation does not yield accurate results, especially at the edges of the spectral range. Qualitatively, results similar to those shown in figure 3.2 are obtained.

In the next part of this chapter we will only use the modified dielectric functions, as shown in figure 3.2 by the solid lines, to describe the optical properties of our colloidal particles.

### 3.4 Spectroscopic ellipsometry

In this section we briefly review the principles of reflection of polarised light and the Abéès method for calculation of the reflection properties of surfaces. Additionally, we describe possible ways to treat the optical properties of random colloidal films, such as effective medium approximations.
3 Optical characterisation of thin colloidal gold films

The complex reflection coefficient $\rho$ obtained from ellipsometry is defined as:

$$\rho \equiv \frac{r^p}{r^s} \equiv \tan(\psi) \cdot \exp(i\Delta)$$  (3.5)

where $r^p$ and $r^s$ are the reflection coefficients for the parallel and perpendicular polarisations, respectively [22]. For a single interface $r^p$ and $r^s$ represent the Fresnel reflection coefficients. Historically, the complex quantity $\rho$ is expressed in the two angles $\psi$ and $\Delta$. The absolute value $|\rho| = |r^p/r^s|$ is represented with $\tan(\psi)$, while the phase change between the two polarisation directions is related to $\cos(\Delta)$. In fact, $\tan^2(\psi)$ is the quantity we measure in the reflectometry experiments, described in chapter 5. However, the analysis of the reflective properties of (very) thin layers indicates that the largest effects are in $\cos(\Delta)$. Although the actual ellipsometry measurement is relatively simple, the analysis of the results is often complicated [22, 23]. A model is required for the system under consideration, which can then be used to simulate or fit the results.

The optical response of a multilayered structure with known dielectric functions can be simulated using the Abéis matrix algorithm. Details of the original method are described by Azzam and Bashara [23]. Two types of matrices are employed. One describes the transition from medium $m$ to medium $m + 1$, and is defined as:

$$I_{m,m+1} = \frac{1}{t_{m,m+1}} \left( \begin{array}{cc} 1 & r_{m,m+1} \\ r_{m,m+1} & 1 \end{array} \right)$$  (3.6)

with $r_{m,m+1}$ and $t_{m,m+1}$ the Fresnel reflection and transmission coefficients.

Another matrix describes the light passage through the medium and involves the phase factors:

$$L_m = \left( \begin{array}{cc} e^{-i\Delta_m} & 1 \\ 1 & e^{i\Delta_m} \end{array} \right)$$  (3.7)

where $\Delta_m = (2\pi/\lambda)d_m n_m \cos(\theta_m)$ with $\lambda$ the wavelength of the light in vacuum (in nm), $d_m$ the thickness of layer $m$ (in nm), $\theta_m$ the angle of the light and $n_m$ the refractive index of medium $m$. The angles in the various media are related through Snell’s law: $n_m \sin(\theta_m) = n_{m+1} \sin(\theta_{m+1})$.

For our system consisting of a colloidal gold layer ($m = 2$) and a silicon dioxide film ($m = 3$) on a silicon substrate ($m = 4$), in contact with the ambient (air or aqueous solution; $m = 1$), a matrix product is defined as:

$$A = I_{1,2} L_2 I_{2,3} L_3 I_{3,4}$$  (3.8)

and the overall reflection coefficient is calculated from $r = A_{21}/A_{11}$. For both the parallel and perpendicular polarisations the reflection coefficients $r^p$ and $r^s$ can be obtained by inserting the appropriate Fresnel coefficients in equation 3.6 and the ellipsometric quantity in equation 3.5 can be calculated.
3.4 Spectroscopic ellipsometry

To model ellipsometry spectra, the dielectric function of inhomogeneous media is often treated in terms of an effective medium approximation \[37\]. For two types of spherical inclusions (with \(\varepsilon_a\) and \(\varepsilon_b\)) in a host matrix (with \(\varepsilon_h\)) the effective dielectric function \(\varepsilon_{\text{eff}}\) is given by:

\[
\frac{\varepsilon_{\text{eff}} - \varepsilon_h}{\varepsilon_{\text{eff}} + 2\varepsilon_h} = f_a \frac{\varepsilon_a - \varepsilon_h}{\varepsilon_a + 2\varepsilon_h} + f_b \frac{\varepsilon_b - \varepsilon_h}{\varepsilon_b + 2\varepsilon_h}
\]

(3.9)

where \(f_a\) and \(f_b\) are the volume fractions of the materials with dielectric functions \(\varepsilon_a\) and \(\varepsilon_b\), respectively. Replacing \(f_b\) by \(1 - f_a\) and substituting \(\varepsilon_h = \varepsilon_{\text{eff}}\) gives the effective medium approximation established by Bruggeman, while inserting \(\varepsilon_h = \varepsilon_b\) corresponds to the Maxwell-Garnett approximation.

As we will show later, these effective medium approximations yield unsatisfactory results. Another method for treating the optical properties of particulate films is provided by the thin island film theory as originally described by Bedeaux and Vlieger \[38–40\]. If the constituent entities are small compared to the wavelength of the light, they can be described in terms of excess optical susceptibilities. Recently, an elaborate review has been published by Koper \[21\] and an application of the theory to a reflectometry experiment has been described by Böhmer et al. \[19\].

For a film of identical small spherical particles the susceptibilities have been calculated by Haarmans and Bedeaux \[43\]. The optical response to an electromagnetic field is in good approximation described in terms of polarisabilities along the surface and normal to the substrate, respectively:

\[
\gamma = \phi 4a \varepsilon_a \frac{\varepsilon - \varepsilon_a}{\varepsilon + 2\varepsilon_a}
\]

(3.10a)

\[
\beta = \phi 4a \varepsilon_a \frac{\varepsilon - \varepsilon_a}{\varepsilon + 2\varepsilon_a}
\]

(3.10b)

where \(\varepsilon\) and \(\varepsilon_a\) are the dielectric functions of the spheres (gold in this case) and the suspending medium (air/water), \(\phi\) is the surface coverage defined as \(\phi = N\pi a^2\), \(N\) is the number of particles per unit area, and \(a\) the particle radius. The reflection and transmission coefficients depend on the polarisation of the light and are for s-polarised light:

\[
r_s^s = \frac{X^s}{1 - X^s}
\]

(3.11a)

\[
t_s^s = \frac{1}{1 - X^s}
\]

(3.11b)

with:

\[
X^s = \frac{i\pi \gamma}{\lambda n_1 \cos \theta_1}
\]

(3.11c)
and for p-polarised light:

\[
\begin{align*}
\tau_p^p &= \frac{X_p}{1 - X_p} - \frac{Y_p}{1 - Y_p} \\
\tau_t^p &= 1 + \frac{X_p + Y_p - 2X_pY_p}{(1 - X_p)(1 - Y_p)}
\end{align*}
\]

(3.12a) (3.12b)

with:

\[
\begin{align*}
X_p &= \frac{i\pi\beta n_1^3 \sin^2 \theta_1}{\lambda \cos \theta_1} \\
Y_p &= \frac{i\pi\gamma \cos \theta_1}{\lambda n_1}.
\end{align*}
\]

(3.12c) (3.12d)

The Abelès film matrix for such a particulate film in terms of these reflection and transmission coefficients is given by:

\[
F = \frac{1}{t_\ell} \begin{pmatrix}
1 & -\tau_\ell \\
\tau_\ell & t_\ell^2 - \tau_\ell^2
\end{pmatrix}
\]

(3.13)

and for our system the modified overall matrix becomes:

\[
A' = FL_F I_{1,3} L_3 I_{3,4}.
\]

(3.14)

The layer matrix \(L_F\) is identical to \(L_m\) in equation 3.7, but with a phase factor \(\Delta = \frac{2\pi}{\lambda} h n_1 \cos(\theta_1)\), where \(h\) is the height of the excess susceptibilities above the Fresnel interface. Often, the distance \(h = r\) between the bare substrate and the particle centres is used. Note that the film matrix \(F\) is different from the interface matrix \(I_{m,m+1}\) as for an interface \(r_{m,m+1} = -r_{m+1,m}\), which is obviously not true for the reflection coefficients \(\tau_\ell^s\) and \(\tau_\ell^p\) of a thin film.

### 3.5 Ellipsometric spectra of nanocolloidal gold films

In figure 3.3 SEM images for different fractional coverages \(\varphi\) are shown. Tuning of the surface coverage of gold colloids on the silicon/siliconoxide substrate is achieved by varying the ionic strength of the solution by adding inert ions to the solution, see refs [51, 52] and chapter 5.

Figure 3.4 shows ellipsometry spectra of samples before and after gold colloid deposition. After immersion in the suspension (typically for 10 hours) the samples are dried in a nitrogen gas flow. The deposition of colloidal gold particles has a marked effect on the ellipsometry measurements. As expected for a thin layer of deposited material, the change in \(\cos(\Delta)\) is much more pronounced than the change...
Figure 3.3: SEM images of three samples with different coverages of gold colloids. The fractional surface coverages $\varphi$, determined by counting the particles, amount to 10\% (a), 18\% (b) and 28\% (c). The scan size in all images is $700 \times 700$ nm$^2$. 
3 Optical characterisation of thin colloidal gold films

Figure 3.4: Ellipsometry spectra for (dry) samples with different gold colloid coverages, measured in air. The solid lines represent the spectrum of a bare silicon / silicon oxide substrate (for which $\varphi = 0$), while the broken lines correspond to samples for which the SEM images are shown in figure 3.3. The coverages are 10\% (dashed lines), 18\% (dash-dotted lines) and 28\% (dash-dot-dotted line).
3.6 Simulation of spectra

A logical way to obtain quantitative information from spectroscopic ellipsometry data is to calculate the ellipsometry spectra using a specific model for the system to be analysed. In this approach the particle surface density can be used as a fitting parameter. The primary question which interests us is: is it possible to accurately determine the particle coverage using spectroscopic ellipsometry?

The obvious problem in simulating the optical response of any system is the choice of the dielectric function of an unknown material, the colloidal gold film in our case. Using a homogeneous gold film with a thickness equivalent to the amount of colloidal gold yields spectra, which are totally different from the measurements.

The dielectric function $\varepsilon_2$ of the colloidal layer can be mimicked using an effective medium approximation [37] in combination with the surface coverage $\varphi_{SEM}$ determined from SEM images. The volume fraction $f$ needed in equation 3.9 for spherical particles is related to the surface coverage through $\varphi = \frac{3}{2} f$. With the Abelès matrices in equations 3.6 and 3.7 the optical response of our multi-layered sample can be calculated and compared to the experimental spectra. In figure 3.5 the experimental ellipsometry result of a colloidal gold film with coverage $\varphi = 18\%$ is compared to calculations using the Bruggeman (dashed line) and Maxwell-Garnett (dash-dotted line) effective medium approximations. A thickness of 13.3 nm was used for the colloidal film with a volume fraction $f = 0.12$. In both simulations considerable differences are observed in comparison to the experimental data. This is most clearly visible in $\cos(\Delta)$. Apart from being much lower, the calculation using the Bruggeman effective medium approximation exhibits a much broader peak in $\cos(\Delta)$ and the features in $\tan(\psi)$ also extend to markedly longer wavelengths. The Maxwell-Garnett approximation yields a peak in $\cos(\Delta)$, which is in qualitative agreement with the experimental result, but is much too low. Increasing the volume fraction $f$ (corresponding to a higher coverage) results in an increase in $\cos(\Delta)$, but with both the Bruggeman and the Maxwell-Garnett approximation the spectra never approach the experimentally obtained results.

---

3 We assume that the colloidal film has a thickness $2a$. The volume fraction $f$ is then $\frac{4 \pi a^3 \cdot N}{2 \pi a} = \frac{2}{3} \pi a^2 \cdot N$, with $N$ the number of particles per unit area. As $\varphi$ equals $\pi a^2 \cdot N$ this yields $f = \frac{2}{3} \varphi$. 

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3 Optical characterisation of thin colloidal gold films

Figure 3.5: Calculated ellipsometry spectra for a silicon/siliconoxide sample with 18% gold coverage. The Bruggeman (dashed lines) and Maxwell-Garnett (dash-dotted lines) effective medium approximations (equation 3.9) were used to model the dielectric function $\varepsilon_2$ of the colloidal film with a fill fraction $f = 0.12$. The solid lines represent a calculation using the Thin Island Film theory, with a surface coverage equal to that obtained with SEM. The open circles represent the ellipsometry data for a film with $\varphi = 18\%$ (corresponding to the dash-dotted lines in figure 3.4).
3.6 Simulation of spectra

Figure 3.6: Surface coverage $\varphi_{\text{film}}$, obtained by fitting the experimental spectra to the thin island film theory, as a function of the coverage $\varphi_{\text{SEM}}$ determined from SEM images. The straight dashed line has a slope of 1 while the dash-dotted line is just a guide to the eye.

Considerably better results are obtained using the thin island film theory developed by Bedeaux and Vlieger [38–40]. The two main features of this theory are that the film under consideration (i) has a thickness that is small compared to the wavelength of the light and (ii) is discontinuous. The optical characteristics of such films are almost always described by an effective dielectric function and an optical thickness. The precise determination of this thickness for optically thin films is often unclear, owing to the strong correlation of the thickness and the refractive index. Bedeaux and Vlieger describe the optical properties of thin island films in terms of excess polarisation and magnetisation densities, positioned at a certain dividing plane. Usually, this dividing plane is taken to coincide with the physical substrate-ambient interface.

The solid lines in figure 3.5 show $\cos(\Delta)$ and $\tan(\psi)$, calculated using the Abelès matrix for a particulate film in equation 3.13 and inserting a coverage $\varphi = 18\%$ in equation 3.10. Clearly, the measured features both in $\cos(\Delta)$ and $\tan(\psi)$ are reproduced much better than with the Bruggeman or Maxwell-Garnett effective medium approximations (dashed and dash-dotted lines, respectively). Note that, as mentioned in section 3.3, we used a modified dielectric function for the gold. With the bulk values a much higher peak in $\cos(\Delta)$ is calculated and the agreement between experiment and simulation is considerably worse.
Instead of merely calculating the spectra on the basis of the known surface density of nanoparticles, we can also fit the experimental spectra to the thin island film theory with the coverage $\varphi_{\text{film}}$ as a fitting parameter. The resulting coverages $\varphi_{\text{film}}$ are shown in figure 3.6 as a function of the coverage $\varphi_{\text{SEM}}$ determined by SEM. The straight dashed line with slope 1 indicates perfect agreement between the coverage determined by ellipsometry and the coverage obtained from the SEM measurements. Figure 3.6 shows that between 10 and 20% the agreement between the both methods is quite good. Below 10% the optical analysis using the thin island film theory leads to an overestimation, while above 20% a strong underestimation is observed.

From these results we conclude that the bare dipole approximation, although it gives a good qualitative description of the spectra, is an oversimplification of the real situation. To obtain an accurate quantitative description of the optical response of nanocolloidal gold films, electromagnetic particle-particle and particle-substrate interactions have to be included in the model.

### 3.7 Optical particle-particle and particle-substrate interactions

The influence of image dipoles on the optical response of small particulates on a surface was considered by Yamaguchi et al. [41] and Bedeaux and Vlieger [38]. The influence of the lateral distribution on the optical response was considered by Haarmans and Bedeaux [42]. In their treatment, they model the optical response of the particles in terms of excess dipoles at the interface. The magnitude of the dipole is given by the one particle polarisability along the interface and perpendicular to the interface, $\gamma$ and $\beta$, respectively. Without image dipole and lateral interaction, the bare polarisabilities are defined as in equation 3.10.

Note that an essential difference between the thin island film theory and for instance the description by Barrera et al. [44] is that (i) the thickness of the layer in the thin film theory is simply given through the influence of the particle radius $a$ on the strength of the polarisability and (ii) the anisotropic response due to the finite thickness of the layer is embedded in the thin island film theory by the different reaction of the electromagnetic field, especially due to the presence of a surface on which the colloids are adsorbed, on the polarisabilities $\gamma$ and $\beta$. The optical properties of the colloids are embedded in the dielectric function of the non-interacting spherical particle. This dielectric function can, for instance, be experimentally obtained from an extinction measurement of the colloid solution, see section 3.3 and ref. [53].

The incorporation of image dipole effects and lateral interaction with neighbouring particles leads to a modification of these one particle polarisabilities. Haarmans and Bedeaux [40, 43] have shown that these changes are adequately described by
an expansion of the potential distribution up to quadrupole order. The optical response is thus described as the response of an ensemble of non-interacting particles with effective polarisabilities $\gamma$ and $\beta$ given by [20]:

\[
\gamma_{qu} = \varphi \frac{4a \varepsilon_a}{3} \frac{\delta (1 + \delta L_1 p)}{(1 + \delta L_p) (1 + \delta L_1 p) + \delta^2 \Lambda_p}
\]

\[
\beta_{qu} = \varphi \frac{4a}{3 \varepsilon_a} \frac{\delta (1 + \delta L_1 z)}{(1 + \delta L_z) (1 + \delta L_1 z) + \delta^2 \Lambda_z}
\]

Here, $\delta = \frac{\varepsilon_a - \varepsilon_s}{\varepsilon_a + \varepsilon_s}$ is the dielectric contrast between the particles and the ambient medium. $L_p$ and $L_z$ represent the dipolar correction terms and $L_1 p$, $L_1 z$, $\Lambda_p$ and $\Lambda_z$ are the quadrupole depolarisation factors. It is instructive to see what happens when the dielectric contrast between the particles and their ambient medium vanishes, i.e. when $\delta \to 0$. The fractions containing the correction terms in equations 3.15a and 3.15b reduce then to $\delta$, so $\gamma_{qu}$ and $\beta_{qu}$, reduce to $\gamma$ and $\beta$ for the bare dipole approximation (equations 3.10a and 3.10b). This means that the particle–particle and the particle–substrate interactions vanish when the dielectric contrast becomes small. Using:

\[
B_{sa} = \frac{\varepsilon_a - \varepsilon_s}{\varepsilon_a + \varepsilon_s}
\]

with $\varepsilon_s$ the dielectric function of the substrate these correction terms are given by [40]:

\[
L_p = \frac{1}{3} \left( 1 + 2 \sqrt{\frac{\pi}{5}} I_2 (\varphi) + 2 \sqrt{\frac{\pi}{5}} B_{sa} I_2 r (\varphi) \right)
\]

\[
L_z = \frac{1}{3} \left( 1 - 4 \sqrt{\frac{3}{\pi}} I_2 (\varphi) + 4 \sqrt{\frac{3}{\pi}} B_{sa} I_2 r (\varphi) \right)
\]

\[
L_1 p = \frac{2}{5} \left( 1 - \frac{8}{3} \sqrt{\pi} I_4 (\varphi) + \frac{8}{3} \sqrt{\pi} B_{sa} I_4 r (\varphi) \right)
\]

\[
L_1 z = \frac{2}{5} \left( 1 + 4 \sqrt{\pi} I_4 (\varphi) + 4 \sqrt{\pi} B_{sa} I_4 r (\varphi) \right)
\]

\[
\Lambda_p = \frac{8}{35} \pi \left( I_3^2 (\varphi) - B_{sa}^2 I_3^2 r (\varphi) \right)
\]

\[
\Lambda_z = \frac{24}{35} \pi \left( I_3^2 (\varphi) - B_{sa}^2 I_3^2 r (\varphi) \right)
\]

The integral quantities $I_l$ and $I_{lr}$, with $l = 2, 3, 4$, take into account the spatial distribution of the nanoparticles on the surface, in terms of the correlation function.
The influence of the particles is thus given by:

$$I_l = 2\phi \sqrt{\frac{2l+1}{4\pi}} \int_2^\infty \frac{g(r)}{r^l} P_l^0(0) \, dr$$

(3.18)

The integrand is normalised to the radius $a$. Since we are dealing with non-overlapping particles, the minimum nearest neighbour distance is $2a$. $P_l^0$ is the Legendre polynomial, and as $P_3^0(0) = 0$, this gives $I_3(\phi) = 0$. The integral that describes the influence of the image dipoles is given by:

$$I_{lr} = \frac{(-1)^l \sqrt{\frac{2l+1}{4\pi}} P_l^0(1)}{2l+1} + 2\phi (-1)^l \sqrt{\frac{2l+1}{4\pi}} \int_2^\infty \frac{rg(r)}{(r^2 + 4)^{l+1}/2} P_l^0 \left( \frac{2}{\sqrt{r^2 + 4}} \right) \, dr$$

(3.19)

For an isotropic, i.e. a purely statistical distribution of nanoparticles $g(r)=1$ for $a>2$. The integrals $I_l$ and $I_{lr}$ in equations 3.18 and 3.19 can be evaluated analytically [43]:

$$I_2(\varphi) = -\sqrt{\frac{5}{4\pi}} \frac{\varphi}{2} \tag{3.20a}$$
$$I_2r(\varphi) = \sqrt{\frac{5}{4\pi}} \left( \frac{1}{8} - \frac{\varphi}{4\sqrt{2}} \right) \tag{3.20b}$$
$$I_3(\varphi) = 0 \tag{3.20c}$$
$$I_3r(\varphi) = \sqrt{\frac{7}{4\pi}} \left( -1 + \frac{\varphi}{\sqrt{2}} \right) \tag{3.20d}$$
$$I_4(\varphi) = \frac{3}{64\sqrt{\pi}} \varphi \tag{3.20e}$$
$$I_4r(\varphi) = \frac{1}{32} \sqrt{\frac{9}{4\pi}} \left( 1 - \frac{3\varphi}{8\sqrt{2}} \right) \tag{3.20f}$$

In figure 3.7 $\gamma$ and $\beta$ are shown for both the bare dipoles and the modified values with up to quadrupole interactions taken into account. The dielectric function of the gold nanocolloidal particles was obtained as described previously [53]. The strength of the image dipoles was evaluated by inserting the silicon dielectric function in equation 3.16. Due to the incorporation of the image dipole effect, the slopes of the curves in the limit of zero coverage are different from those obtained using the bare dipole approximation. This explains the deviation between the optically and SEM determined coverages in the low coverage regime that was observed in section 3.6. Above 20%, $\gamma$ shows an underestimation by the bare dipole model,
3.7 Optical interactions

Figure 3.7: Real and imaginary part of $\gamma$ and $\beta$ at 2.4 eV (517 nm) for 13.3 nm gold colloids on silicon. The calculations are done using the bare dipole approximation (dashed line) and the full thin island film theory taking into account the influence of lateral interactions of colloids and their image dipole up to quadrupole order, both for an isotropic particle distribution (solid line) and a distribution with a preferred nearest neighbour distance (dash-dotted line), see section 3.9 and chapter 5.
3 Optical characterisation of thin colloidal gold films

Figure 3.8: The value of the real part of $B_{\text{eff}}$ at 2.4 eV as a function of thickness $d$ of the SiO$_2$ layer, normalised to the colloid radius $a$. Shown are curves for air (solid line) and water (dashed line) as ambient medium. The limit for $d = 0$ is equal to the value for an ambient-Si interface and the limiting value (indicated with dotted lines) for a large oxide thickness is equivalent to an ambient-SiO$_2$ interface. The vertical dotted line indicates the value of $d/a$ for 13.3 nm colloids on an oxide film of 1.8 nm.

while for $\beta$ an overestimation is noted. These two effects cancel each other for a coverage of about 20% and this results in a good correspondence between the optical and SEM determined coverage. The image dipole effect is especially noteworthy since Si has a relatively high dielectric function compared to many oxide materials commonly used as substrates. In this case $B_{sa} = -0.89$ at a photon energy of 2.4 eV, i.e. a wavelength of 517 nm, while the value of $B_{sa}$ for quartz for instance is almost 3 times smaller.

3.8 Contribution of the image dipole

Gold colloids with a diameter of 13.3 nm were deposited on naturally oxidised silicon. The silicon oxide interface is covered with an approximately 0.3 nm thick layer of APTES, which gives a total layer thickness of 1.8 nm. As this layer is only a fraction of the particle radius $a$, the image dipole contribution has to be reconsidered [46]. The strength of an image dipole contribution $B_{sa}$ for a dipole
3.8 Contribution of the image dipole

placed at distance $a + d$ above a homogeneous substrate falls of as $\left(\frac{a}{a+d}\right)^3$:

$$B(d) = -\frac{\varepsilon_s - \varepsilon_a}{\varepsilon_s + \varepsilon_a} \left(\frac{a}{a + d}\right)^3 = B_{sa} \left(\frac{a}{a + d}\right)^3$$  \hspace{1cm} (3.21)

with $\varepsilon_s$ and $\varepsilon_a$ the dielectric functions of the substrate and ambient, respectively. In the evaluation of the image dipole, usually the dielectric properties of the outermost layer on which colloids are deposited are used. However, this no longer holds when the thickness of the layer is equivalent to or smaller than the radius of the colloid, such as in the present case. The nanoparticles have a radius three times larger than the thin layer on which they are deposited. The strength of the image dipole contribution is thus expected to be bound between the value for a silicon substrate and that for a silicon oxide substrate, i.e. between $B_{sa} = -0.89$ and $B_{sa} = -0.365$, respectively, when the spectra are measured in air. For image dipoles, the value $B_{sa}$ is treated as a reflection coefficient [54]. An expansion with reflection and transmission coefficients of both interfaces, combined with the attenuation factor given by the thickness of the layer $d$ yields an effective image dipole strength [46]:

$$B_{\text{eff}}(d) = \frac{B_{la} + B_{sl} \left(\frac{a}{a+d}\right)^3}{1 + B_{la}B_{sl} \left(\frac{a}{a+d}\right)^3}$$  \hspace{1cm} (3.22)

where $B_{la}$ and $B_{sl}$ represent the image dipole strengths for thin layer-ambient and substrate-thin layer interfaces. The value of $B_{\text{eff}}$ is plotted as a function of the SiO$_2$ layer thickness in figure 3.8. The real part of $B_{\text{eff}}$ is considered only as the imaginary part is negligible at a photon energy of 2.4 eV. The rapid change of $B_{\text{eff}}$ with thickness leads to a considerably reduced value of the image dipole contribution already for thin oxide layers. When spectra are measured with the sample immersed in water, the effect of image dipoles is reduced, as shown by the dashed curve in figure 3.8. This reduction is quite small for very thin oxide layers, but increases strongly as the oxide thickness increases: for thick oxides films the reduction amounts to a factor of 4.

The influence of a thin silicon oxide layer on the polarisabilities $\gamma$ and $\beta$ is shown in figure 3.9. Especially for $\beta$ a marked difference is observed both in the real and imaginary parts. The most substantial difference is observed in the imaginary part of $\beta$ in the 10 – 30% coverage range.

Measured ellipsometric spectra for three different coverages are shown in figure 3.10. We analysed the experimental ellipsometry spectra by fitting them to the thin island film theory. The optical response of the colloidal film in terms of the polarisabilities $\gamma$ and $\beta$ in equations 3.15a and 3.15b, respectively, is calculated using the Abeles matrix method, as described in section 3.4 and in refs. [19, 53]. Note that in this chapter we follow the definition of the polarisabilities $\gamma$ and $\beta$ as used
by Bedeaux and Vlieger [40]. Sometimes [19, 21, 53] slightly different definitions are used. The surface coverage $\varphi$ is the only free parameter in our fitting procedure. For all the models used in this work, i.e. the bare dipole and the models that include the various image dipole effects and lateral distributions, the quality of the fit is approximately equal. Especially the plasmon peak at 2.4 eV is very sensitive, not only for the coverage, but also for the size distribution and agglomeration of particles. The resonance energy shifts and simultaneously the peak broadens when two or more metal particles coagulate [37]. In this analysis we only consider the spectra that did not show such broadening effects. A one to one correspondence between broadening and coagulation in AFM and SEM pictures was found. The absence of such features in the presented spectra shows that we are able to deposit
Figure 3.10: Experimental ellipsometric spectra for different coverages of gold colloids on SiO$_2$/Si. The coverages, as determined from the SEM pictures in figure 3.3, are 10\% (circles), 18\% (squares), and 28\% (triangles). The solid lines represent fit results using the thin island theory, taking into account the effective image dipole and an isotropic lateral distribution of the nanocolloids.
non-coagulated citrate stabilised gold colloids up to a coverage of 35%.

The influence of the image dipole contribution was evaluated in three different ways. Using the aforementioned fitting procedure, the optical coverage was determined from the spectra for both (i) a Si and (ii) a SiO$_2$ substrate for the evaluation of the image dipole contribution. The optical coverage was also determined with (iii) a $B_{\text{eff}}$, equation 3.22, for an oxide layer with a thickness of 1.8 nm. Figure 3.11 shows the resulting optical coverages for the three aforementioned cases, as a function of the coverage determined using SEM. It is clear that if only SiO$_2$ or Si is considered as a substrate in the calculation of the image dipole contribution, optically an overestimation, respectively underestimation results. The correction made by incorporating $B_{\text{eff}}$, yields a one to one correspondence between the optically and SEM determined coverages.

### 3.9 Influence of the lateral particle distribution

Experimentally we found that the correlation functions which describe the lateral distribution of gold nanoparticles after deposition for various saturation coverages...
scale with respect to the nearest neighbour distance \( L \), see chapter 5. The scaled correlation function \( g(r) \) is shown in figure 3.1 on page 91. However, at coverages well below saturation, the distance distribution will not be this pronounced. Initially, i.e. far below the set saturation coverage, the colloids will be randomly distributed. In the series of experiments presented here, the coverage was not achieved by controlling the ionic strength, but by limiting the deposition time. Nevertheless, for coverages above 10\%, the scaled distribution function in figure 5.8 accurately represents the actual distribution. The coverage was found to scale in a coverage range of 10–35\% as:

\[
\varphi = \frac{\pi}{L^2}
\]  

(3.23)

i.e. the coverage of a square lattice with lattice parameter \( L \), see section 5.4.4 and ref. [51].

With this correlation function, the integrals \( I_l \) and \( I_{lr} \) in equations 3.18 and 3.19 related to the lateral distribution and the image dipole of this lateral distribution, respectively, can be evaluated, with the inter-particle distance \( L \) as parameter [46]. Only for \( I_l \), a substantial difference was found between the isotropic distribution and the preferred distance distribution. The difference only becomes significant for coverages above 5\%. The coverage dependent \( I_l \) is used to calculate the parallel and perpendicular polarisabilities \( \gamma \) and \( \beta \), as depicted in figure 3.7.

The comparison of calculated values of \( \gamma \) and \( \beta \) for an isotropic distribution and the distribution over a square and hexagonal lattice, led Bedeaux et al. [40, 42, 43] to the conclusion that below 40\% hardly any difference between these distributions can be observed using ellipsometry. The optical coverage determined using (i) the bare polarisability (equations 3.10a and 3.10b), (ii) the isotropic distribution and (iii) the preferred lateral distribution is shown in figure 3.12. The failure of the bare dipole approximation is obvious from this graph in both the low coverage (overestimation below 15 \%) and for the high coverage region (underestimation above 25 \%). A significant difference between the isotropic distribution and the preferred lateral distribution is not observed [46]. This supports the conclusion of Bedeaux et al. [40, 42, 43] that below 40\% the details of the lateral distribution are of no importance.

### 3.10 Conclusion

We have presented a detailed study of the optical properties of colloidal gold films assembled on naturally oxidised silicon treated with APTES. Knowledge of both the single particle diameter and its polarisability is a prerequisite for a quantitative analysis of the surface coverage using ellipsometry.

Crystalline metal colloids with grains that are smaller than the electron effective mean free path have optical properties different from the bulk material. Especially at long wavelengths differences between colloids and bulk optical response can not
Figure 3.12: The coverage as determined with spectroscopic ellipsometry, analysed taking into account the lateral distribution and image dipole effects as a function of the coverage determined with SEM. The lateral distribution was evaluated for an isotropic distribution (squares) and the preferred lateral distribution (triangles). The result for the bare dipole approximation is also shown (circles), with the dash-dotted line as a guide to the eye.

be neglected. The standard experimental procedure of an absorbance measurement provides an experimentally determined extinction coefficient. This can function as a benchmark for the modification of the bulk dielectric function that takes the limited electron mean free path into account.

The standard analysis procedure of ellipsometric spectra of samples, such as our gold nanoparticle-on-silicon assemblies, involves an effective medium approximation for the dielectric function of the adsorbed colloid layer. The commonly used Maxwell-Garnett and Bruggeman approaches, however, lead to highly inaccurate results.

The thin island film theory developed by Bedeaux and Vlieger, which treats the deposited colloids as excess polarisabilities, allows an accurate calculation of the optical properties. Even when the most simple form of this theory is used, i.e. when optical particle-particle and particle-substrate interactions are ignored, an accurate qualitative description of the optical response of colloidal gold films is possible. However, quantitative agreement with results from SEM measurements is only obtained for values of the surface coverage around 20\%.
This shows the necessity to include particle-particle interactions and image dipole interaction with the substrate in the description. It is shown that the specific lateral distribution has little influence on the optical spectra for coverages up to 40%. The image dipole contribution has a pronounced effect because naturally oxidised Si substrates are used. The thickness of the oxide layers is smaller than the colloid radius. This implies that a modified image dipole is required, the strength of which lies between the strength due to a bare Si substrate and the strength due to a SiO\textsubscript{2} substrate. When an effective image dipole strength is used, a good quantitative agreement between the surface coverages determined from SEM measurements and from spectroscopic ellipsometry is obtained.
References

3 References


3 Optical characterisation of thin colloidal gold films


4 Application of principal component analysis to ellipsometric spectra

4.1 Summary

A Principal Component Analysis (PCA) is applied to several sets of ellipsometric spectra. The relation between the first coefficient obtained from PCA and the film thickness or the coverage of a substrate with colloids is explored. In many cases a linear relation is found, but in case of gold colloids that have a large optical contrast with the ambient medium, there is a non-linear dependence on the surface coverage. It is shown that calibration of the coefficients allows extraction of quantitative information from the ellipsometric spectra. When calibration is performed using least squares fits to a small number of spectra, fitting of all other spectra is avoided. When an other experimental technique such as AFM and SEM is used for calibration, PCA can extend the applicability of spectroscopic ellipsometry to areas where quantitative information is required but optical modelling is impossible or inconvenient.

4.2 Introduction

Principal Component Analysis is a statistical technique aimed at reducing a large set of correlated variables to a small number of uncorrelated principal components. Once the components are known, the original variables can be constructed from the components, using a small number of coefficients. These coefficients can then be used to characterise the original variables.

PCA is used in many fields of, especially applied, research and industry in combination with measurement methods such as Fourier transformed IR spectroscopy [1], time of flight mass spectroscopy [2, 3], Raman spectroscopy [4, 5] and many others. A recent overview on the application of PCA in chemometrics is presented by Geladi [6].

One of the benefits of PCA is that it yields a certain degree of understanding of the data even when an adequate model is not available. Secondly, PCA can simplify the handling of a large number of variables. For example, plotting a few components is much more convenient than plotting all original variables. Another strength of the technique is that a large set of measurements can be analysed at once. PCA can therefore be used to get a quick insight in global trends in data.
before further analysis, or to replace analysis of every single measurement. A last advantage of PCA is that it can be applied when an adequate model is available but involves too many variables to be determined by a fit. This situation can arise, for example, in transmission spectroscopy and reflectometry.

The major drawback of the statistical nature of PCA is that the principal components can not be assigned an interpretation beforehand. Often it is non-trivial to relate a component to physical quantities. Secondly, the value of the coefficients is largely determined by the number of variables and the variance in the individual variables, so quantitative interpretation requires calibration.

We demonstrate the power of PCA by applying it to ellipsometric spectra obtained either from measurements or from calculations. In an ellipsometry experiment, the change of polarisation of an incident light beam upon reflection at or transmission through an interface is measured. In case of reflection ellipsometry, this change is expressed with a complex quantity $\rho$ (see chapter 3):

$$\rho = \frac{r_p}{r_s} = \tan(\psi) \cdot \exp(i\Delta) \quad (4.1)$$

Since PCA is usually applied to real valued variables, application to ellipsometric spectra requires extension of PCA to include complex numbers.

Spectroscopic ellipsometry is a versatile tool for the investigation of surface phenomena. Measurements can easily be performed in a wide variety of setups and environments. A more extensive discussion is found in the chapters 2 and 3. The main problem is that quantitative analysis of the data is often not straightforward and sometimes even impossible. We demonstrate that in these cases PCA can be used to obtain quantitative information from large numbers of spectra. The first component is related to either the thickness of a film or to the coverage of a substrate with particles. We will show that PCA yields quantitative information when the coefficients are calibrated. Calibration can be done by determining the values of the film thickness or surface coverage for a small number of measurements, using either a different analysis procedure or another experimental technique.

We analysed (i) measured spectra of multi-layers composed of oppositely charged polyelectrolytes, (ii) calculated spectra of 15 nm silica colloids, and (iii) both measured and calculated spectra of 13 nm gold colloids. In all cases the optical response of the films can be adequately modelled in terms of the film thickness or surface coverage and the dielectric functions of the constituent materials [7–9]. This enables us to get a general idea about the relation between the coefficients obtained from PCA and physical quantities such as the coverage of a substrate with colloids or the thickness of a film. This knowledge can be used to make an educated guess about the relation between the coefficient and the physical quantity of interest in situations where this relation is unknown.
4.3 Formalism

In PCA, the original correlated variables are transformed to an equally large set of uncorrelated principal components. These are constructed such that the first components account for as much of the total variance in the original variables as possible. Often, a small number of components accounts for nearly all variance and the other components can be neglected. The variance not accounted for by the first components is either caused by physical factors of minor importance or just by noise. Discrimination between these two cases can be made by inspection of the second component. A more elaborate description of PCA can be found in text books on multivariate analysis [10].

The principal components $y_i$ can be written as a linear combination of the original variables $x_j$:

$$y_i = \sum_j a_{i,j} x_j$$  \hspace{1cm} (4.2)

where both $x_i$ and $y_i$ are row vectors. Rewriting equation 4.2 in matrix terms yields:

$$y_i = a_i \cdot X$$  \hspace{1cm} (4.3)

In this equation $a_i$ is a row vector and $X$ is a matrix of which the rows are the original variables $x_i$. The vectors $a_i$ have to be constructed to maximise the variance of $y_i$ and to ensure that all $y_i$ are uncorrelated. Therefore, Lagrange multipliers are used to maximise $\text{var}(y_i)$ under the condition that $y_i^T \cdot y_j = \delta_{ij}$. It can be proved that $a_i$ is an eigenvector of $\Sigma$, the correlation matrix of $X$ and that $\text{var}(y_i)$ equals an eigenvalue of $\Sigma$. The first principal component that accounts for most of the variance in the original spectra is constructed from the eigenvector corresponding to the largest eigenvalue. The second component that accounts for most of the remaining variance is constructed from the eigenvector corresponding to the second largest eigenvalue. This procedure can be repeated until all required components have been calculated.

In practice, the components are calculated using a matrix formalism. The covariance matrix $\Sigma$ is calculated from the data matrix $X$. Then the coefficient matrix $A$ is constructed using the vectors $a_i$, the eigenvectors of $\Sigma$, as columns. The principal components are now calculated using:

$$Y = A^* X$$  \hspace{1cm} (4.4)

where the components are stored in the rows of $Y$.

In this paper we are more interested in the coefficients that can be regarded as the importance of a component $y_i$ for the original variables. Inversion of equation 4.4,
4 Application of principal component analysis to ellipsometry

yields $\mathbf{X} = \mathbf{A}\mathbf{Y}$ from which we can see that the coefficients of the $i$-th component are in $i$-th column of $\mathbf{A}$.

The importance of the first $m$ coefficients is defined as the fraction of the total variance they account for. Since the variance of a component is equal to the value of the corresponding eigenvalue of the covariance matrix, the importance of the first $m$ components equals:

$$ I = \frac{\sum_{i=1}^{m} \lambda_i}{\sum_i \lambda_i} \quad (4.5) $$

Variables often differ very much in their variance. If no precautions are taken, variables with a large variance will dominate the components and variables with a small variance will have only a small influence. This can be avoided by using the correlation matrix instead of the covariance matrix. When this is done and one wants to calculate the principal coefficients of the original data, the obtained coefficients must be multiplied with the variance of the original variables. This procedure is used throughout this paper to prevent domination of the components by spectra from samples with a high surface coverage, or a thick film.

If we would apply PCA directly to ellipsometric spectra, we would find that there are at least two important components, because the substrate spectrum and the change of the optical response of the sample upon adsorption of another material are independent. To simplify the interpretation of the results of the principal component analysis, we apply the method therefore not to the spectra themselves but to the optical invariant that can be considered as the change in the spectra upon adsorption. This procedure has been developed by Lekner Kooij et al. [7], Lekner [11].

The change of the reflection properties of a surface upon adsorption of a film can be described using a finite number of invariants $J_i$:

$$ \frac{\rho_{\text{film}}}{\rho_0} - 1 = \alpha J_1 + \ldots \quad (4.6) $$

In this equation $\rho_{\text{film}}$ and $\rho_0$ are the complex reflection coefficients as defined by equation 4.1 of a sample with and without a film, respectively. The energy dependent prefactor $\alpha$ depends on the dielectric functions of the substrate and the ambient, the wavelength and the reflection angle, but is independent of the thickness and dielectric function of the film. When the film is sufficiently thin the expansion in equation 4.6 can be truncated after the first term. Since this truncation is valid in all cases described in this paper, we will simply use the quantity $J = \frac{1}{\alpha} \left( \frac{\rho_{\text{film}}}{\rho_0} - 1 \right)$ as invariant.
Figure 4.1: Ellipsometric spectra of poly(ferrocenylsilane) films on silicon substrates with a 1.4 nm oxide layer. The films consist of 0 (solid), 4 (dashed), 7 (dash-dotted) and 11 bilayers (dash-dot-dotted).
4.4 Polyelectrolyte multilayer films

Polyelectrolyte multilayer films are grown using layer-by-layer self-assembly [12]. A well-defined number of bilayers is deposited by alternating immersion of the substrate (silicon in our case) into aqueous solutions of poly(ferrocenylsilane) (PFS) polyanions and polycations. Poly(ferrocenylsilanes) are a class of organometallic polyelectrolytes with ferrocene units in the main chain. From an application point of view, this makes them an interesting class of materials, as they are, for example, resistant to reactive ion etching, and also exhibit electroactivity.

Figure 4.1 shows spectra of PFS films composed of an increasing number of bilayers. The spectra were measured using the homebuilt spectroscopic ellipsometer at a fixed incident angle of 70°. To avoid problems with reproducibility, the measurements were performed after deposition of every bilayer on the same sample without realignment and recalibration of the ellipsometer. The spectra show little variation in \( \tan(\psi) \) and significant increase in \( \cos(\Delta) \), which is characteristic for thin dielectric films. PFS films show little absorbance and have a dielectric function that is assumed to be nearly constant in the visible part of the spectrum. Since this holds for nearly all films consisting of organic materials such as polymers and proteins, PFS films can be considered as a model system for this class of materials.

After performing the principal component analysis, it turned out that the first component accounts for 99.88% of the variance in the spectra. From inspection of the second component we find that the remaining variance represents experimental noise. Therefore, we can conclude that the first component is a good representation of the invariant and the second and higher components can be safely neglected. The imaginary part of the first coefficient was smaller than the real part by at least a factor of 20, thereby suggesting that the real part of the first coefficient is a good measure for the number of bilayers. This is confirmed by figure 4.2(a) that shows a linear relation between the number of bilayers and the real part of the first coefficient. It is even more interesting to compare the value of the first coefficient to the thickness of the film obtained by fitting a four layer model to the data. The model includes the silicon substrate, an oxide layer of 1.4 nm, the PFS film with unknown thickness and the air ambient. The refractive indices of silicon and silicon oxide are well known, while for PFS a constant value of 1.687 was assumed. This value was determined previously by single wavelength ellipsometry [12].

Figure 4.2(b) shows that there is a perfect linear relation between the fitted thickness of the film and the first coefficient. Since there is only one significant component, this implies that the first invariant should be proportional to the film thickness. The first invariant of a film can be evaluated analytically using the following expression [7, 11]:

\[
J = \int_{-\infty}^{\infty} \frac{(\varepsilon_a - \varepsilon_f(z))(\varepsilon_f(z) - \varepsilon_s)}{\varepsilon_f(z)} \, dz
\]  
(4.7)
4.4 Polyelectrolyte multilayer films

**Figure 4.2:** Real part of the first coefficient plotted as function of (a) the number of bilayers and (b) the film thickness obtained from fitting the individual spectra. The circles and the diamonds denote experiments using two different samples.
In this equation \( \varepsilon_a \) and \( \varepsilon_s \) are the dielectric functions of the ambient and the substrate. The film is represented by a dielectric profile function \( \varepsilon_f (z) \), that varies from \( \varepsilon_s \) in the substrate to \( \varepsilon_a \) in the ambient medium and can have any value in between. When we assume that the film has sharp interfaces and a dielectric function that is uniform in the direction perpendicular to the surface, equation 4.7 reduces to:

\[
J = d \left( \varepsilon_a - \varepsilon_f + \varepsilon_s - \frac{\varepsilon_a \varepsilon_s}{\varepsilon_f} \right) \quad (4.8)
\]

where \( d \) is the film thickness. This explains the observed proportionality between the first coefficient and the film thickness. Equation 4.8 is not limited to dielectrics as used in this section. Therefore, we can also expect a linear dependence of the first coefficient on the surface coverage for continuous metal films. This makes PCA a useful tool for analysis of, for example, films consisting of metal alloys. The dielectric functions of alloys are generally unknown and hard to model since they can vary a lot over the spectrum and include absorption. An alternative analysis technique, such as PCA, can yield important extra information in these situations.

We can conclude that for uniform films the first coefficient is proportional to the film thickness. When the thickness of one of the films is determined using another measurement technique, PCA can be applied to obtain quantitative information from a collection of measured spectra, without modelling of the data.

### 4.5 Nanocolloidal silica films

Ellipsometric spectra of nanocolloidal films are, in general, more difficult to model than uniformly stratified films. Therefore, it is interesting to investigate spectra of colloidal films using PCA. As we have shown in chapter 3, the frequently used effective medium theories are inadequate to model the optical response of nanocolloidal films, because these films are not isotropic in three dimensions. We calculate spectra of colloidal films using the matrix formalism formulated by Abelès [13] and the thin island film theory developed by Bedeaux and Vlieger [14, 15]. This theory describes the optical response of a film in terms of the effective individual polarisabilities of the particles, which are influenced by both the substrate and the other particles at the interface. In this way electromagnetic particle-substrate and particle-particle interactions are taken into account. Using this approach, the ellipsometric spectra of gold colloids on silicon have been described very accurately as demonstrated in chapter 3. When particle-particle interactions are taken into account, a spatial distribution of the particles has to be assumed. We assume that the particles are randomly distributed on the surface. In reality there is a preferred minimum distance between the particles (see chapter 5), but this has little effect on the spectra, provided that the surface coverage is below 40%, which is shown in chapter 3.

The model used for calculation of the spectra consists of a silicon substrate with
Figure 4.3: Spectra of 15 nm silica colloids on silicon with 10 nm oxide in water, calculated using the thin island film theory. The surface coverages are 0\% (solid line), 20\% (dashed line) and 40\% (dash-dotted line).
4 Application of principal component analysis to ellipsometry

Figure 4.4: Real part of the first coefficient as a function of the surface concentration, for calculated spectra of 15 nm silica colloids on silicon. The points indicated with diamonds are calculated using water as ambient medium. For the points indicated with circles and squares air was used as ambient medium. Particle-particle interactions were taken into account for the circles and are neglected for the squares.

10 nm of oxide with silica colloids at the interface with the ambient, which is either air or water. The bulk dielectric function of silicon oxide is used for the particles. Figure 4.3 shows the spectra of nanocolloidal silica films in water with a coverage of 0%, 20% and 40%. The surface coverage is defined as:

$$\varphi = \pi a^2 \cdot N$$

where $a$ is the particle radius and $N$ is the number of particles per unit area. From the figure it is clear that $\tan(\psi)$ is barely affected by the adsorption of silica particles. The change in $\cos(\Delta)$ is more pronounced, but shows no distinct features. This is due to the fact that the dielectric function of silica shows little variation (2.11 – 2.21) between 1.5 and 4 eV. This is also reflected in the importance of the first component: it accounts for 99.98% of the variance in the spectra. Due to the nearly constant dielectric function of silica, the shape of the invariant does not change with increasing coverage, so all spectra can be represented with one single component.

Figure 4.4 shows the real part of the first coefficient plotted as a function of the surface coverage. The imaginary parts of the coefficient are more than one order of
magnitude smaller than the real parts, so they are ignored. The points indicated with diamonds were calculated with water as the ambient medium. The dependence of the first coefficient on the surface coverage is perfectly linear. This shows that the first coefficient can be a good measure for the amount of adsorbed material, even for the optically more complicated colloidal films. When the ambient is air, the dependence of the real part of the first coefficient on the particle coverage is not perfectly linear, as shown in figure 4.4 with the circles. The slope of the line decreases slowly with increasing surface coverage. This decrease is caused by particle-particle interactions whose importance increases when the dielectric contrast, defined as $\frac{\varepsilon_p - \varepsilon_a}{\varepsilon_a}$, increases [16]. In this equation, $\varepsilon_p$ and $\varepsilon_a$ are the dielectric functions of the particle and the ambient, respectively. The dielectric contrast of silica particles in water is only approximately 0.2, whereas the contrast in air is 1.1, which explains the larger influence of particle-particle interactions in case of silica colloids in air.

This explanation for the decrease of the slope is supported when we apply PCA to spectra of silica colloids in air that were calculated while neglecting the interactions. The result of this analysis is indicated with squares in figure 4.4. The relation between the coefficient and the surface coverage is again perfectly linear. Summarising, we can conclude that the value of the first coefficient is proportional to the coverage of the surface with particles. Only when the dielectric functions of the particles and the ambient are quite different, a slight deviation from the linear behaviour is observed.

4.6 Nanocolloidal gold films

Metals have a much larger dielectric contrast with water or air, so particle-particle interactions in nanocolloidal metal films are expected to be very strong. Additionally, the dielectric function of gold particles strongly depends on the photon energy. It is therefore interesting to analyse spectra of colloidal gold films using PCA. Figure 4.5 shows spectra of 13 nm gold colloids on silicon with 10 nm oxide in a water ambient, represented by solid lines. The spectra are calculated using the thin island film theory as described in Bedeaux and Vlieger [15], Wormeester et al. [16] and chapter 3. All interactions have been taken into account. Because the electron mean free path in gold is larger than the particle size, a modified dielectric function has to be used, as described by Kooij et al. [7] and in chapter 3. The values of the surface coverage used in the calculations are 0 %, 4 %, 10 %, 20 % and 40 %, where the first value corresponds to the spectrum that is lowest in both $\tan(\psi)$ and $\cos(\Delta)$, and the last to the uppermost spectrum.

Figure 4.5 shows that a clear peak develops around 2.4 eV. This peak is associated with the plasmon resonance of the gold particles and is also observed in transmission spectroscopy as shown in chapter 3, figure 3.1. Plasmon resonance occurs when the amplitude of the collective oscillation of electrons due to the ex-
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Figure 4.5: Spectra of 13 nm gold colloids on silicon with 10 nm oxide in water, calculated using the thin island film theory, indicated with solid lines. The surface coverages are, from bottom to top: 0%, 4%, 10%, 20% and 40%. The dashed lines indicate the reconstructions of the spectra from the first component only.

ternal electromagnetic field is maximal. Close observation of figure 4.5 reveals that the shape of the peak changes with increasing surface coverage. This change of the peak shape results in a somewhat lower efficiency of the first principal component: 99.57%, as compared to the value of 99.98% that was observed for the silica colloids. The remaining variance is due to a change of the shape of the plasmon resonance peak, which is caused by particle–particle interactions. This becomes clear when we insert \( J_1 = c_1 Y_1 \) in equation 4.6 and truncate the expansion after the first invariant. We can than reconstruct \( \rho \) from the first component only. The spectra resulting from this reconstruction are plotted in figure 4.5 using dashed lines. The figure shows that the exact shape of the peaks and the low energy tail of the spectra are not reproduced very well, especially at higher surface coverages.

From the large dielectric contrast we can expect a very non-linear dependence of the first coefficient on the surface coverage. This is confirmed by figure 4.6, in
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Figure 4.6: Real part of the first coefficient as function of the surface concentration, for calculated spectra of 13 nm gold colloids on silicon in different media: air (circles) and water (diamonds). The points represented by triangles are measurements of samples in an air ambient. Solid lines are the fits as described in the text.

which the real part of the first coefficient is plotted as a function of the surface coverage, both for films in water (indicated with diamonds) and in air (indicated with circles). The decrease of the slope of the curves is now much stronger than in case of silica colloids, making it impossible to fit them with a straight line. The relation between the surface coverage and the coefficient is very complex so if one wants to use a function to fit this relation, one has to make a more or less arbitrary choice. The following function turns out to fit the data well and is used for calibration of the coefficients:

\[ y = a (1 - \exp(-bx)) \]  

(4.10)

Since the proportionality constant \( a \) depends on the variance in the invariants and the number of spectra analysed, it has little physical significance. It has a different value for every series of spectra. The parameter \( b \) is related to the influence of particle-particle interactions and has in both cases a value of 0.0310. Therefore, we assume that it is a kind of system constant whose value depends predominantly on the dielectric function of the particles. Apparently, the dielectric contrast between the particles and the ambient medium is so large that the exact
value of the dielectric function of the medium does not influence the value of $b$.

Also shown in figure 4.6 is a series of coefficients obtained from measured spectra of nanocolloidal gold films. The gold particles used in these experiments had a diameter of 13 nm and were stabilised with citrate, so they have a negative surface potential. The films were deposited on silicon substrates with a native oxide layer of approximately 2 nm. Since silicon oxide also has a negative surface charge at normal pH, the samples were functionalised with 3-aminopropyltriethoxysilane to induce a positive surface charge and thus an attractive interaction between the particles and the substrate. The coverage of the samples was obtained using scanning electron microscopy (SEM). Figure 4.6 shows that the dependence of the real part of the first coefficient is very similar for the measured and calculated data. The value of $b$ equals 0.034 for the measured data, which is quite close to the value for the calculated data. This agreement between measured and calculated data reflects the fact that the surface coverage obtained by fitting the optical model agrees very well with the surface coverage measured with SEM, which is shown in chapter 3.

PCA was also applied to spectra measured during deposition of citrate stabilised gold colloids on a silicon substrate with 2 nm native oxide. One spectrum was measured every three minutes for a period of more than five hours, so over a
hundred spectra were collected. In figure 4.7 the time dependence of the surface concentration during deposition is shown. The values of the first coefficient were converted to surface concentrations using equation 4.10. To apply this equation the values of both $a$ and $b$ have to be known. For $b$ a value of 0.034 was used, as obtained from the SEM experiments described in the previous paragraph. The final surface concentration was 8.9 %, determined by counting particles in an AFM image. From this final surface concentration, the value of $a$ was calculated. In this way the coverage was calculated for all measured spectra. The values of $a$ and $b$ could also be obtained by fitting a few spectra, since the optical model of this system is available, but we have chosen to demonstrate how to obtain quantitative information from ellipsometric spectra using PCA without optical modelling of the system.

4.7 Conclusions

We have shown that PCA is a useful tool to analyse large numbers of ellipsometric spectra. Its benefits are that it can even be applied when an optical model is not available, when the dielectric function of one of the components of the samples is unknown or when analysis of all individual spectra is inconvenient. The main problem with PCA is establishing a relation between the values of the coefficients and the relevant physical properties, the film thickness or surface coverage in this work. When PCA is applied to the first optical invariant, often only one component is relevant. In this case calibration can be achieved by comparing the values of the first coefficient for a few samples to known values of the physical properties obtained from other experimental methods. In most cases there is a linear relation between the first coefficient and the physical quantity of interest and calibration using only one measurement suffices. When PCA is applied to spectra of colloidal films with a strong optical contrast with the medium, the relation between the first coefficient and the coverage is non-linear. In this case more measurements are required to investigate the relation between the surface coverage and the first coefficient. Once this relation is known, calibration of the coefficient for a particular series of spectra requires only a single measurement. This makes PCA a convenient tool to analyse series of spectra obtained from similar samples or from a single sample during a deposition process. In this way the applicability of spectroscopic ellipsometry is extended to areas where quantitative information is required but optical modelling is impossible or inconvenient.
4 Application of principal component analysis to ellipsometry

References


5 Ionic strength dependent nanocolloidal gold deposition

5.1 Summary

The deposition kinetics of the irreversible adsorption of citrate-stabilised, nanocolloidal gold particles on Si/SiO$_2$ surfaces, derivatised with 3-aminopropyltriethoxysilane (APTES), is investigated in situ using single wavelength reflectometry. A well-defined flow of colloids towards the surface is realised using a stagnation point flow geometry. The saturation coverage after prolonged deposition can be analysed in terms of random sequential adsorption (RSA) and depends on the ionic strength of the solution, in good agreement with DLVO theory. The spatial distribution of particles on the surface is determined from atomic force microscopy (AFM) images using radial distribution functions. The obtained particle distribution is in qualitative agreement with results from RSA simulations. AFM measurements after prolonged experiments indicate that for higher coverage, the formation of particle clusters gives rise to a deviation from DLVO behaviour. The dynamics of the deposition process are at first mass transport limited. Surface blocking effects determine the adsorption kinetics in the final stage. The entire deposition process can be adequately described in terms of a generalised adsorption theory, which combines the effects of mass-transport and the actual adsorption onto the surface.

5.2 Introduction

The deposition kinetics of colloidal particles are influenced by many factors. Obviously, particle size, shape and polydispersity as well as surface heterogeneity’s are important. But also electrostatic and/or steric particle-particle interactions, particle-substrate interactions, forced convection and the presence of external fields (shear, electric, magnetic) can have a profound effect on the adsorption process and the resulting distribution of particles on the surface. Both reversible and irreversible deposition of a large number of colloidal systems have been investigated, but the scope is primarily limited to relatively large particles, which can be directly observed by optical microscopy.

For particles with dimensions well below the diffraction limit of (visible) light, such as proteins [1] or nanocolloidal particles [2, 3], it is difficult to monitor the deposition process in a truly in situ manner. Obviously, analysis can be done
after deposition using many techniques, e.g. electron microscopy (SEM/TEM) or scanning probe microscopy (STM, AFM), but the influence of drying effects and reorientation upon change of ambient may hinder proper analysis in terms of real deposition parameters.

As mentioned above, electrostatic interactions (particle-particle, particle-surface) may have a pronounced influence on deposition processes. In case of strong attractive interaction between particle and substrate, the deposition will be highly irreversible. Additionally, low lateral mobility results in a random spatial distribution of particles, as has been adequately described by the random sequential adsorption (RSA) model [4–7]. In principle, electrostatic interactions are relatively short ranged due to screening by counter ions in the solution. Therefore, for large particles in the micrometer range, particle-particle interactions are frequently neglected and particles are treated as hard spheres [6, 8]. However, when the colloid or protein dimensions decrease into the low-nanometer range, the extent of the electric double layer becomes of the same order of magnitude as the particle radius. The spatial distribution after irreversible deposition of such small entities will obviously be affected by repulsive interactions resulting from double layer overlap. We will show that for nanocolloidal gold particles, with double layer thicknesses of the same order of magnitude as the particle radius, the average minimum inter-particle distance is tunable via the ionic strength. Despite the large contribution of the double layer, the spatial distribution can still be analysed in terms of the RSA model [6–8], but now by taking an increased effective particle diameter into account [5, 8, 9], which depends on the ionic strength of the suspension from which the particles are deposited.

In this chapter we study the irreversible deposition characteristics of colloidal particles with dimensions in the low-nanometer range using optical reflectometry in a stagnation point flow geometry\(^1\) [10]. As mentioned above, considerable effort has been devoted to (irreversible) deposition of micrometer sized particles. For these large particles the RSA model adequately describes the overall deposition kinetics. However, for considerably smaller particles in the 10–100 nm range, this relatively simple model fails. Böhmer and coworkers [11] presented a detailed study of the deposition kinetics of such small particles. The initial deposition rate as well as the characteristics in the saturation regime were in agreement with the RSA model. However, they were unable to quantitatively analyse their results over the entire coverage range. Here we show that the generalised adsorption model, as described in detail by Adamczyk and coworkers [4, 5, 8, 12, 13], is in perfect agreement with deposition transients of particles in the low-nanometer range over the entire coverage range. Also, quantitative analysis of our results indicates that the adsorption rate, which strongly depends on particle size, is in good agreement with similar experiments using particles of very different nature [13] (i.e. various proteins) but of roughly the same size.

\(^1\)In many publications, this setup is also referred to as a radial impinging jet cell.
5.3 Experimental

For the deposition experiments citrate stabilised gold particles are used. Details on the synthesis and characterisation of these particles can be found in chapter 2. Sodium chloride (from Merck) is used to vary the ionic strength of the solution. Silicon substrates with a well-defined oxide thickness are cleaned ultrasonically in water and derivatised for 30 min in a 10% solution of 3-aminopropyltriethoxysilane (APTES, obtained from Merck) in methanol (Merck).

The experiments are performed in a stagnation point flow setup, shown in figure 5.1. In this setup, a flow of the suspension is directed to the sample. The flow hits the surface at a perpendicular angle and spreads in all directions along the surface. The flow velocity vanishes at the centre of the flow at the surface of the sample. In this point, which is referred to as the stagnation point, transport of the particles is governed by diffusion. The benefit of this setup is that it offers very well-defined deposition conditions. In the experiments described in this chapter the ow was approximately 1.0 ml min\(^{-1}\). The adsorption process in the stagnation point can be conveniently observed using single wavelength reflectometry.

The stagnation point flow cell and the reflectometer are homebuilt at Philips Research [14]. The setup consists of a He-Ne laser, the stagnation point flow cell, a beam splitter and two photo diodes for detecting the intensities \(I_p\) and \(I_s\) of the parallel and perpendicular components of the reflected light. A more extensive description of the setup is given in chapter 2 and by Dijt et al. [14]. The intensity ratio \(S \equiv \frac{I_p}{I_s} \equiv \frac{I_p^0 R_p}{I_s^0 R_s}\) is measured, where \(I_p^0\) and \(I_s^0\) are the initial intensities and \(R_p\) and \(R_s\) are the intensity reflection coefficients. The polarisation of the light source is eliminated by calculating \(Y \equiv \frac{S}{S_0} - 1\), where \(S_0 = \frac{I_p^0}{I_s^0}\) is the value of \(S\).
before deposition. The angle of the incident beam can be adjusted and is set to $70^\circ$ with respect to the normal of the sample surface.

For the reflectometry experiments, substrates cut from p-type silicon (100) wafers with a deposited oxide layer of either 25 nm or 45 nm are used. When the oxide layer is too thin, $R_p$ is very small and the initial sensitivity of the setup is low. With too thick oxide layers, the reflectometer signal flattens and even decreases above a certain surface concentration. This is shown in figure 5.2, where the reflectometer signal $\frac{R_p}{R_s}$ is shown as a function of the surface coverage. These curves are calculated using the simple dipole approximation of the thin island film theory \[2, 15\]. Details on the applied model and the calculation are presented in chapter 3. The figure shows that for both very thin and very thick oxides, single wavelength reflectometry has serious sensitivity problems. The 45 nm oxide curve is used as calibration to convert the reflectometer signals to absolute surface coverages.

AFM images are obtained using a Molecular Imaging PicoSPM. The large tip-sample interaction in normal contact mode will inevitably lead to a displacement of the particles on the substrate \[16, 17\]. Therefore, measurements are performed in intermittent contact mode, also often referred to as ‘tapping\textsuperscript{TM}-mode’ \[18\]. The resonance frequency of the cantilevers (Nanosensors) is approximately 65 kHz.
5.4 Results

5.4.1 Description of the experiments

In figure 5.3 typical reflectometry transients, obtained during colloidal gold deposition in the stagnation point flow cell at various ionic strengths, are shown. The silicon samples used for these experiments had a 45 nm thick oxide layer. After dilution of the as-prepared colloidal gold suspension by a factor of 4, the particle number density amounts to $1.85 \times 10^{18} \text{ m}^{-3}$, while the minimum ionic strength is 3.6 mM. The ionic strength of the solution is varied by adding 0 to 15 mM NaCl, which corresponds to Debye screening lengths from 5.1 nm to 2.2 nm. For $t < 0$ only water flows through the cell, and a constant base line is measured. At $t = 0$ the gold suspension is injected in the cell. When the flow is switched back to water at $t = 38$ min (not shown in figures 5.3 and 5.4), no significant decrease of the surface coverage is observed, indicating the absence of particle detachment.

**Figure 5.3:** Deposition of gold colloids on silicon with 45 nm oxide at different ionic strengths in a reflectometry experiment using the stagnation point flow geometry. The ionic strength is varied by adding NaCl. The ionic strengths of the solutions are 3.6 mM (solid line), 6.1 mM (dashed), 8.6 mM (dash-dash-dotted), 13.6 mM (dash-dotted) and 18.6 mM (dash-dot-dotted). The coverage is calculated from the reflectometer signal using the thin island film theory (see figure 5.2).
5 Ionic strength dependent nanocolloidal gold deposition

5.4.2 Initial deposition kinetics

Two distinct regimes are observed in the measured curves in figure 5.3. At longer deposition times, the deposition process leads to a saturation at coverage values, which show a clear dependence on the ionic strength. This will be discussed in section 5.4.3. For short times the deposition rate is similar for all ionic strengths. This implies that initially the deposition process is limited by the supply of colloidal particles to the surface. The hydrodynamics of colloid deposition in a stagnation point flow cell has been discussed by Dabros and Van de Ven [19] and also by Adamczyk and coworkers [10]. The initial particle flux towards the surface is in good approximation given by:

\[ j_0 = 0.776 \left( \frac{D^2 \pi \nu \text{Re}}{R^2} \right)^\frac{1}{3} c_0 = k_c \cdot c_0 \]  \hspace{1cm} (5.1)

where \( c_0 \) is the bulk particle concentration, \( D \) is the diffusion coefficient of the nanocolloidal particles, \( R = 0.64 \text{ mm} \) is the radius of the inlet tube and \( \nu \text{Re} \) is the average flow velocity, with \( \text{Re} \) the Reynolds number and \( \nu \) the kinematic viscosity.
vicecosity of the fluid. The dimensionless flow parameter \( \bar{\tau} \) depends on the Reynolds number and the cell geometry parameter \( h/R \). The value \( \bar{\tau} = 4.2 \) used in the present case is obtained from the work of Dabros and Van de Ven [19] using \( Re = 8.3 \) and \( h/R = 1.7 \). Adamczyk et al. give an analytical expression for \( \bar{\tau} \) for \( h/R = 1.6 \), from which a value of 5.6 is calculated [10]. The mass transfer coefficient \( k_c \) will be discussed in a later section.

Analysis of the initial deposition rate is performed on the deposition curves shown in figure 5.4. The data from figure 5.3 were measured while the laser spot was not correctly aligned with the stagnation point. Outside the stagnation point, the supply of particles is smaller, which results in a lower deposition rate. This makes the deposition curves from figure 5.3 unsuitable for analysis of the initial deposition kinetics. Since the final coverage is not affected by this misalignment, these data can be safely used to analyse the saturation coverage.

These measurements shown in figure 5.4 were obtained during deposition of gold colloids on silicon samples with a 25 nm oxide layer. The observed initial adsorption rate \( d\varphi/dt = \pi a^2 j_0 = 0.080 \text{ min}^{-1} \), has an experimental error of about 9%, but does not vary with the ionic strength. Assuming that the sticking probability is 1, the particle diffusion coefficient can be calculated from the initial deposition rate using equation 5.1. Inserting the known values for particle density and cell
geometry parameters, we find \( D = 44 \, \mu m^2 s^{-1} \). We now compare this result to the diffusion coefficient obtained using the Stokes-Einstein relation:

\[
D = \frac{kT}{6\pi\eta a}
\]

(5.2)

where \( kT \) is the thermal energy and \( \eta \) is the dynamic viscosity of the fluid (for water, \( \eta = 1.00 \times 10^{-3} \, \text{kg m}^{-1} \text{s}^{-1} \)). With a particle radius \( a = 6.7 \, \text{nm} \) the Stokes-Einstein relation yields a diffusion coefficient \( D = 32 \, \mu m^2 s^{-1} \). Our experimentally determined value is about 50% higher than this value. It is somewhat surprising that our result is larger than the value calculated from the Stokes–Einstein equation. Equation 5.1 is an approximation [10], which is valid in the infinitely small stagnation point in the centre of the cell, whereas an elliptical area of about \( 1 \times 2 \, \text{mm}^2 \) is probed in the experiments. Therefore we would expect a somewhat lower result.

We compared our results with literature results obtained from experiments with PS-latex particles by Böhmer et al. [11] and from experiments with silica particles by Hayes et al. [20]. Figure 5.5 shows the diffusion coefficients as a function of particle size. The literature data are indicated with circles, and our result with a star. The Stokes–Einstein relation is indicated with a line. It is clear that our results are in good agreement with literature data. We can conclude that the diffusion coefficient does not depend on the composition of the particles, which is to be expected since hydrodynamic drag is only determined by the particle geometry.

### 5.4.3 Saturation surface concentration

We now turn to the saturation regime of the deposition curves in the figures 5.3 and 5.4. For higher ionic strengths, the maximum attainable coverage increases. This is in agreement with the DLVO theory [21, 22]. This theory describes the accumulation of ions near charged interfaces, in this case the colloid-solvent interface, which results in a double layer around every particle. When the double layers of two particles overlap, the average distance between the ions decreases, which results in an increase of the free energy. The resulting repulsive force prevents coagulation of the particles, and also defines the distance of closest approach of two particles. When particles adsorb on a surface, this distance determines the maximum attainable coverage [9].

More quantitatively, the double layer interaction potential \( U_{pp}^{dl} \) in units \( kT \) is described by [7, 23]:

\[
\frac{U_{pp}^{dl}(\tau)}{kT} = \frac{C_{pp}}{\tau} \exp \left[-\kappa a (\tau - 2)\right]
\]

(5.3)

where \( \tau = r/a \) is the particle-particle distance scaled by the particle radius \( a \), \( \kappa \) is the Debye screening parameter and \( C_{pp} \) the particle-particle interaction coefficient.
5.4 Results

Figure 5.6: Experimentally determined saturation coverage $\varphi_{\text{meas}}$ from the reflectometry measurements as a function of the coverage $\varphi_{\text{calc}}$ calculated from the ionic strength using DLVO theory. The circles and squares indicate measurements performed on samples with an oxide thickness of 45 nm and 25 nm, respectively. The line shows the situation where the measured and calculated coverage are identical.

Defined as:

$$C_{pp} = \frac{4\pi \varepsilon_0 \varepsilon_r k T a}{e^2} \left( \frac{y_p + 4\gamma \Omega \kappa a}{1 + \Omega \kappa a} \right)^2$$

with $\gamma = \tanh \left( \frac{y_p}{4} \right)$, $\Omega = \frac{y_p - 4\gamma}{2\gamma^3}$ and $y_p$ the dimensionless surface potential. This yields an interaction potential that is valid for a large range of $\kappa a$, provided that $\pi$ is larger than about $\frac{1}{a + \frac{\kappa a}{2}}$. Assuming a constant surface potential, the distance $\pi kT$ between particles when their interaction energy drops below $\frac{1}{2} kT$ can be determined numerically as a function of $\kappa a$, i.e. as a function of the ionic strength. The choice for the interaction energy is justified by the fact that particles have an average thermal energy of $\frac{1}{2} kT$, which competes with their electrostatic repulsion upon approaching each other.

In figure 5.6, the measured saturation coverage, obtained from figures 5.3 and 5.4, is plotted as a function of the calculated coverage. The latter is obtained by calculating the doublelayerdoublelayer thickness $\Delta a = \frac{1}{2} kT - a$ using equations 5.3 and 5.4. For this calculation the surface potential of the particles is taken as $-85 \text{ mV}$ [24, 25]. From the effective double layer thickness $\Delta a$, the saturation
coverage $\varphi_\infty$ is obtained from:

$$\varphi_\infty = \frac{\varphi_{RSA}}{(1 + \frac{\Delta a}{a})^2}$$

(5.5)

in which $\varphi_{RSA} = 54.7\%$ represents the jamming limit for irreversible random deposition of hard spheres [4, 6, 7].

The data in figure 5.6 exhibit a good qualitative agreement between the experimental and calculated data. However, one series of experimental data is systematically too low, while the other is systematically too high. The scatter within the individual series is relatively small. This suggests that a systematic error is causing the discrepancy with the calculated data. For samples with an oxide layer that is thinner than 100 nm, the sensitivity of the reflectometer depends strongly on the measurement angle. For the samples we used, an error of $1^\circ$ can cause a deviation as large as we observe here. Unfortunately, the construction of the setup does not allow a very precise fixation of the cell in the reflectometer, and consequently the reflection angle is not very well-defined. A misalignment of $1^\circ$ is a realistic estimate of the accuracy that can be achieved. Therefore we attribute the observed discrepancy mainly to misalignment of the cell.

A second, minor cause of the discrepancy might be the breakdown of the Hückel approximation at high coverages. The linear approximation of the Poisson-Boltzmann equation underestimates the potential drop near the particles. When a far field potential is used, as it is here, the potential at short distances is overestimated. This results in an overestimation of the distance where the particle-particle interaction drops below $\frac{3}{2}kT$, and consequently leads to an underestimation of the surface concentration. This effect will become important when $r < a + \frac{3}{2} \frac{1}{n}$, which is approximately 10 nm for the highest ionic strengths. This value corresponds to a surface coverage of 25%, which indicates that this issue can only play a roll at the highest surface concentrations obtained here.

A last possible explanation for the deviation at higher ionic strengths may be the formation of clusters on the sample surface. A cluster has a larger volume on a relatively small area, thereby accounting for a larger optically determined surface concentration. Unfortunately, single wavelength reflectometry does not enable us to investigate this issue. Therefore, the spatial distribution of particles in the gold films are studied using AFM.

**5.4.4 Spatial distribution of the deposited particles**

In figure 5.7 four typical AFM images are shown for colloidal gold assemblies at maximum coverage. Saturation of the coverages is obtained after 5-6 hours, which is primarily determined by diffusion of nanoparticles to the surface. Generally, however, deposition is performed overnight ensuring that indeed the surface particle density has reached its maximum value. The ionic strength in figures 5.7(a), (b),
5.4 Results

(a) $I = 4.2 \text{ mM}$
(b) $I = 7.2 \text{ mM}$
(c) $I = 8.9 \text{ mM}$
(d) $I = 18 \text{ mM}$

Figure 5.7: AFM images of the colloidal gold layers deposited from solutions with different ionic strength. All images represent an area of $1 \times 1 \mu\text{m}^2$. 
5 Ionic strength dependent nanocolloidal gold deposition

(c) and (d) amounted to 4.2 mM, 7.2 mM, 8.9 mM and 18 mM, respectively, and was varied by adding NaCl to the colloidal suspension. Identical results are obtained with other inert salts such as KNO$_3$.

The as-prepared suspension was diluted 5 times, thus lowering the intrinsic ionic strength. However, this also lowers the concentration of colloidal particles in suspension to $1.5 \times 10^{18}$ m$^{-3}$ and consequently the deposition rate. Care was taken that all measurements were performed with the same concentration of nanoparticles in suspension.

The AFM images in figure 5.7 were obtained after removal of the samples from the colloidal suspension, careful rinsing with water and finally drying. The fact that after deposition no decrease of the surface concentration is observed, indicates that desorption of weakly bound particles upon gently rinsing is negligible. The adherence of the particles to the substrate is good, as multiple re-immersion, rinsing and drying steps do not lead to a measurable change in the morphology. AFM images were measured at least at four different positions on the surface to ensure that the coverage is homogeneous over length scales exceeding the relatively small scan range.

The gold nanoparticles deposited from the diluted suspensions with a low ionic strength show only a few small clusters and there is a preferred minimum distance between the particles, in agreement with the ‘soft particles’ approximation. In contrast to the low ionic strength situation, the layers deposited with a high ionic strength exhibit considerable coalescence and a number of larger clusters consisting of several individual particles are observed. The inhomogeneous spatial distribution indicates that clustering of particles may play a role at higher ionic strengths and thus at higher coverages. To which extent this happens during the deposition experiments in the stagnation point flow setup is unsure. On one hand, these experiments last much shorter, so slow coagulation will not affect the experiments too much. But on the other hand, the maximum ionic strength is higher, and therefore, coagulation can be much faster than in case of the ex-situ experiments.

To obtain more quantitative information, radial distribution functions were calculated from the AFM-images in figure 5.7(a)-(c). The film in figure 5.7(d) is too dense to accurately discern all individual particles. The particles in the other images are manually marked, after which their positions are determined using Scion Image (Beta 4.0.2, Scion Corporation). The radial distribution function (also referred to as the pair correlation function) is obtained from these positions by calculating:

$$g_i'(r) = \frac{\delta n(r)}{N \cdot 2\pi r \cdot \delta r}$$

for every particle $i$, where $\delta n(r)$ represents the number of particles within a ring of width $\delta r$ at a distance $r$, $N$ represents the overall surface density of particles. The total radial distribution function $g(r) = n^{-1} \cdot \sum g_i'(r)$ is found by averaging over all $n = N \cdot A$ particles ($A$ represents the surface area in the image which equals 1 $\mu$m$^2$).
Figure 5.8: Radial distribution functions of 13 nm gold colloids on silicon deposited at an ionic strength of 4.2 mM (solid line), 7.2 mM (dashed line) and 8.9 mM (dash-dotted line)
in figure 5.7). The results obtained from the three AFM images in figure 5.7 are shown in figure 5.8(a). These exhibit a maximum corresponding to the minimum inter-particle separation, which is determined by the ionic strength of the solution. At approximately 50% larger distance a shallow minimum is observed.

When the distance \( r \) is normalised by the square root of the average area per particle \( r_0 = 1/\sqrt{N} \) all curves scale onto a single radial distribution function \( g(r/r_0) \), as is shown in figure 5.8(b). This indicates that the spatial distribution of nanoparticles in this range of ionic strengths is universal and that the same mechanism determines the nanoparticle organisation on the surface, irrespective of the ionic strength. Obviously, for considerably lower coverages, at which the inter-particle interactions can be neglected, this is no longer valid. In that case, the statistical distribution of nanoparticles results in a Boltzmann distribution.

To the left of the maxima in figure 5.8, a clear shoulder is observed, which is most pronounced for the lowest ionic strength. This shoulder is due to the few nanoparticle clusters on the surface (the bright regions in figure 5.7). The particles are touching and/or stacked on top of each other. Therefore, the rise of \( g(r) \) with distance \( r \) is already observed well below the smallest average nearest-neighbour distance \( r = 2a \) for touching particles. Also, a size dispersion may lead to a lowering of the onset of \( g(r) \). A similar effect has been observed with colloidal suspensions having larger size dispersions [26].

The features in the radial distributions, such as the maximum at \( r_0 \), followed by the shallow minimum near \( \frac{3}{2}r_0 \), are in good agreement with results of RSA simulations assuming soft-colloidal particles [4, 26–28], i.e. with an electrical double layer in the order of or larger than the particle radius. Also, the results in figure 5.8 are similar to what others have measured using larger particles.

### 5.5 Discussion

The deposition kinetics of colloidal particles [5, 12, 13, 29] can be described in terms of the adsorption rate \( d\varphi/dt \) by:

\[
\frac{d\varphi}{dt} = \pi a^2 \cdot j_0 \cdot B(\varphi)
\]

(5.7)

where \( \pi a^2 \) is the geometrical particle surface area and \( j_0 \) represents the limiting deposition flux for uncovered surfaces. The quantity \( B(\varphi) = j(\varphi)/j_0 \), with \( j(\varphi) \) the actual deposition flux for a given coverage, is usually referred to as the overall kinetic blocking function [5, 12, 13, 30]. This designation is somewhat misleading since \( B(\varphi) = 1 \) for low coverages, while in the limit of saturating coverages \( B(\varphi) \to 0 \), so in fact \( B(\varphi) \) represents an effective, coverage dependent available surface. More correctly, it is also referred to as the ‘available surface function’. However, to be consistent with the work by Adamczyk and coworkers, we will adopt the former
5.5 Discussion

Figure 5.9: Deposition curves from figure 5.3 (3.6, 6.1, 8.1, 13.6 and 18.6 mM) and figure 5.4 (8.6 and 13.6 mM) scaled using transformations from equation 5.8.

designation of the blocking function. The function $B(\varphi)$ depends not only on the coverage, but also on many additional factors such as particle–particle interactions, the mechanism of particle transport and the reversibility of particle adsorption.

In principle, the overall kinetic blocking function can only be determined empirically from the particle deposition rate as a function of time, i.e. curves similar to those presented in figure 5.3. If we assume that all deposition transients for our system (nanocolloidal gold particles irreversibly deposited on APTES-derivatised siliconoxide surfaces) are characterised by a single, coverage dependent overall kinetic blocking function $B(\varphi/\varphi_\infty)$, where $\varphi_\infty$ is the saturation coverage defined in equation 5.5, the general adsorption equation 5.7 can be rewritten in terms of the dimensionless variables:

$$\overline{\varphi} = \frac{\varphi}{\varphi_\infty}$$  \hspace{1cm} (5.8a)

$$\overline{t} = \frac{t}{\tau} = \frac{\pi a^2 \cdot j_0 t}{\varphi_\infty}$$  \hspace{1cm} (5.8b)

to yield:

$$\frac{d\overline{\varphi}}{d\overline{t}} = B(\overline{\varphi})$$  \hspace{1cm} (5.9)

The result of this scaling, applied to deposition curves in the figures 5.3 and 5.4, is shown in figure 5.9. It is clear from figure 5.9 that all curves collapse to a single
curve, verifying that indeed a single overall kinetic blocking function $B(\varphi/\varphi_\infty)$ governs the deposition process, irrespective of the ionic strength.

A theory that is more specifically applicable to adsorption of colloidal particles that are irreversibly deposited under forced convection, has been extensively described by Adamczyk and coworkers \cite{5, 12, 13, 31}. A similar model was also described by Faruolo and Bafaluy \cite{32}. In this generalised adsorption model, the deposition is considered to consist of two processes as is schematically shown in figure 5.10. The adsorption process can be described by:

$$\frac{d\varphi}{dt} = \pi a^2 \cdot k_a c(\delta_a) \cdot B(\varphi) \quad (5.10)$$

and is governed by a rate constant $k_a$ and a particle concentration $c(\delta_a)$ at distance $\delta_a$ from the surface \cite{4}. The available surface function $\overline{B}(\varphi)$, also often referred to as the generalised blocking function, describes the transport resistance of the adsorbed layer to adsorbing particles; effectively it is equal to the overall sticking probability. In fact, equation 5.10 is similar to equation 5.7. In equation 5.7, the actual adsorption process is taken into account by the overall kinetic blocking function $B(\varphi)$ considering a constant supply of colloidal particles, while in equation 5.10 the adsorption process is considered and the supply of colloidal particles is described by the time-dependence of $c(\delta_a)$.

Within the adsorption layer of thickness $\delta_a$, convection effects can be neglected. The thickness $\delta_a$ is comparable to the range of specific interactions, in principle electrostatic interactions, the extent of which is governed by the double layer
thickness. For our nanocolloidal particles, this implies that $a$ is of the same order of magnitude as the particle radius. The adsorption rate constant $k_a$ contains a barrier term in the particle-substrate interaction energy, which represents the repulsive electrostatic interaction of an adsorbing particle with the already adsorbed particles.

The supply of colloidal particles to the outer edge of the adsorption layer, at a distance $a$ from the surface, is described by the rate constant $k_c = j_0/c_0$, where $j_0$ is equal to the particle flux [4, 5, 11–13]. For the well-defined flow conditions in our stagnation point flow setup, equation 5.1 yields:

$$k_c = 0.776 \left( \frac{D^2 \alpha V_m}{R^2} \right)^{\frac{1}{3}} \tag{5.11}$$

For the irreversible adsorption of particles at uniformly accessible surfaces, Adamczyk derived an expression for the kinetic overall blocking function, given by [5, 12]:

$$B(\varphi) = \frac{K B(\varphi)}{1 + (K - 1) B(\varphi)} \tag{5.12}$$

where $K = k_a/k_c$ represents the coupling between adsorption and diffusion processes. In the case of strong particle-particle interactions, $B(\varphi)$ can be approximated by the RSA available surface function $B_0(\varphi)$ [5, 12, 30]. It is not possible to evaluate $B_0(\varphi)$ analytically, but a good approximation is given by [5, 29]:

$$B_0(\varphi) = \left( 1 + 0.812 \frac{\varphi}{\varphi_\infty} + 0.426 \left( \frac{\varphi}{\varphi_\infty} \right)^2 + 0.0716 \left( \frac{\varphi}{\varphi_\infty} \right)^3 \right) \left( 1 - \frac{\varphi}{\varphi_\infty} \right)^3 \tag{5.13}$$

With this expression the overall kinetic blocking function $B(\varphi)$ can be calculated, using equation 5.12, which now only depends on the maximum coverage $\varphi_\infty$ obtained after saturation and the coupling constant $K$.

In practice, $K \sim 1$ for micrometer large particles [5, 12]. However, our colloidal particles are markedly smaller, which leads to a significant increase of the value of $K$. This can be understood by considering that from equation 5.2 $D$ is inversely proportional to the particle radius $a$. Therewith the convective flux, expressed by the rate constant $k_c$ in equation 5.11, varies as $a^{-2/3}$. Assuming a parabolic potential distribution around the adsorption barrier with magnitude $\phi_b$, the adsorption rate constant can be approximated by [12]:

$$k_a = \frac{D}{a} \left( \frac{\phi_b}{\pi kT} \right)^{\frac{1}{3}} \exp \left( -\frac{\phi_b}{kT} \right) \tag{5.14}$$

However, this equation is only valid for large barrier heights. A more accurate
formula is given by Adamczyk and Szyk [33]:

\[ k_a = \frac{D}{2a} \frac{1}{1 + \frac{1}{2} \ln \left(1 + \frac{\Delta a}{a}\right)} \]  

(5.15)

where \( \Delta a \) represents the extent of the repulsive interactions, i.e. the effective thickness of the double layer. In both cases, with equation 5.2, we obtain for the coupling constant \( K = k_a/k_c \sim a^{-4/3} \), i.e. for smaller particles \( K \) is expected to become considerably larger than 1.

In figure 5.11 the coverage dependence of the overall kinetic blocking function is plotted for different values of \( K \). A large value of \( K (\gg 1) \) implies that the adsorption rate is considerably larger than the convective supply of particles. Thus, up to relatively large coverages the deposition is transport limited, which is expressed by the considerable \( \varphi \)-range over which \( B(\varphi) \approx 1 \). Only near the saturation coverage, \( B(\varphi) \) drops rapidly to 0. In the opposite case when \( K \sim 1 \), corresponding to pure RSA, the adsorption itself becomes rate-limiting. Accordingly, for low \( K \) values, \( B(\varphi) \) exhibits a sharp decrease already at low coverages.

From the deposition curves in figures 5.3 and 5.4, it is obvious that for a large
coverage range the deposition is dominated by mass transport of particles to the adsorption layer. The deposition rate \( d\varphi/dt \) only decreases upon approaching the saturation coverage. This indicates that for our system of nanocolloidal gold particles, irreversibly deposited in a stagnation point flow geometry, \( K \) is considerably larger than 1. The blocking function can be calculated by scaling and differentiation of a measured deposition transient, using equations 5.8 and 5.9. Application of this procedure to the 10 mM data from figure 5.3 yields the dotted curve in figure 5.11. This curve is close the the \( K = 50 \) curve, which confirms that \( K \) is considerably larger than 1.

To obtain more quantitative information, we fitted the generalised adsorption model, expressed by equations 5.7, 5.12 and 5.13, to deposition transients from the figures 5.3 (series 1, indicated with circles) and 5.4 (series 2, indicated with squares). The saturation coverage \( \varphi_\infty \), the coupling constant \( K \) and the initial deposition rate \( \pi a^2 j_0 \) are used as fitting parameters. The results obtained by this fitting procedure are shown in figure 5.12. Over the entire coverage range there is a perfect correspondence between the measured and calculated deposition curves. The calculated initial deposition rate \( d\varphi/dt = \pi a^2 j_0 \) amounts to 0.032 min\(^{-1}\) for series 1 and to 0.080 min\(^{-1}\) for the series 2, while the saturation coverages \( \varphi_\infty \) are identical to the values given in figure 5.6.

The fits yield a coupling constant \( K = 40 \pm 9 \) for series 1, while for series 2 a value of \( K = 45 \pm 4 \) is obtained. From the coupling constant and the initial deposition rate we can calculate the adsorption constant and the energy barrier for
Table 5.1: Deposition parameters obtained from the fits shown in figure 5.12.

<table>
<thead>
<tr>
<th></th>
<th>series 1 (circles)</th>
<th>series 2 (squares)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D$ [$\mu$m$^2$s$^{-1}$]</td>
<td>12</td>
<td>44</td>
</tr>
<tr>
<td>$K$</td>
<td>$40 \pm 9$</td>
<td>$45 \pm 4$</td>
</tr>
<tr>
<td>$k_c$ [m s$^{-1}$]</td>
<td>$2.0 \times 10^{-6}$</td>
<td>$4.7 \times 10^{-6}$</td>
</tr>
<tr>
<td>$k_a$ [m s$^{-1}$]</td>
<td>$7.9 \times 10^{-5}$</td>
<td>$2.1 \times 10^{-4}$</td>
</tr>
<tr>
<td>$\phi_b$ [kT]</td>
<td>3.1</td>
<td>3.3</td>
</tr>
<tr>
<td>$\phi_b$ [meV]</td>
<td>76</td>
<td>84</td>
</tr>
</tbody>
</table>

adsorption. Values of these parameters are listed in table 5.1. From the values of $k_c$ calculated from equation 5.11, we obtain values for the adsorption rate constants $k_a = 7.9 \times 10^{-5}$ m s$^{-1}$ and $k_a = 2.1 \times 10^{-4}$ m s$^{-1}$, for series 1 and 2, respectively. Using equation 5.15 with $\Delta \alpha = 2$ nm, we obtain a value of $k_a = 2.9 \times 10^{-4}$ m s$^{-1}$, which is close to the value determined experimentally from series 2. The value we obtain from the first series is significantly too low. Since the adsorption constant $k_a$ is calculated from the mass transport constant $k_c$, an error in the latter affects the value of $k_a$ that is obtained. During the experiments of series 1, the laser was aligned inaccurately, resulting in a too low initial deposition rate. As a consequence, the obtained value of $k_c$ is too low, and hence also $k_a$. Calculation of the adsorption barrier height $\phi_b$ from the obtained adsorption rate constants, using equation 5.14 and the diffusion coefficients obtained from either series, yields a value of 3.1 kT or 76 meV for the first series and 3.3 kT or 84 meV for the second series. Within the accuracy of these experiments, which is determined by the accuracy of the measured value of the coupling constant $K$, these values are identical. This can be explained by the equations 5.14 and 5.11. From equation 5.14 we see that $\phi_b$ depends on $k_a D$. Since $k_a$ is determined from $k_a = K k_c$ and $D \propto k_c^{3/2}$ (equation 5.11), $k_a D$ depends only weakly on the mass transport rate constant $k_c$. Furthermore, $k_a$ drops very fast with increasing $\phi_b$, so a relatively small difference in $\phi_b$ can cause a large difference in $k_a D$, which is exactly what we observe here.

As far as we are aware, the absolute values of the adsorption rate constant $k_a$ and the adsorption barrier height $\phi_b$ have not been determined for colloidal systems with particle sizes in the low nanometer range. However, Adamczyk [13] collected adsorption rate constants for typical proteins (BSA, fibrinogen and IgG), which are of the same order of magnitude as our colloidal particles. Comparison with the $k_a$ values for these proteins$^2$ indicates that our aforementioned values for the irreversible deposition of nanocolloidal gold are in line with other systems of similar dimensions but of very different nature.

$^2$In fact, a dimensionless adsorption constant $\kappa_a$ is given, which is related to the definition used here through $\kappa_a = k_a \cdot \frac{D}{L^2}$ with $L = (\pi a^2 c_0)^{-1}$ and $D$ the diffusion coefficient.
5.6 Conclusions

We have studied the kinetics of irreversible deposition of gold nanoparticles from colloidal suspensions onto silicon/siliconoxide substrates. Using a stagnation point flow geometry, the convective supply of colloidal particles is controlled. Simultaneously, the deposition process is monitored by in-situ single wavelength reflectometry. The absolute coverage, calculated from the reflectometer signal by means of the thin island film theory, is measured as a function of time for different ionic strengths. Two regimes are distinguished, related to two different processes in the adsorption process. Initially, the deposition is merely governed by mass transport limited supply of colloidal particles, and the constant deposition rate is analysed taking into account the cell geometry to obtain a diffusion coefficient for the nanocolloidal particles, which is slightly larger than what is calculated from the Stokes–Einstein relation. The ionic strength of the suspension only affects the deposition process in the saturation regime at higher coverages. For the entire coverage range, the ionic strength dependent saturation coverage is in agreement with calculation using the DLVO theory, although the measured coverages are, depending on the exact reflection angle, slightly smaller or larger than the calculated values.

After prolonged deposition experiments at high ionic strength, formation of nanoparticle clusters is observed using AFM. When present, these clusters will increase the saturation coverage. Whether this plays a role in the in-situ experiments is unsure. From the AFM pictures, radial distribution functions are calculated. These exhibit a maximum corresponding to the minimum inter-particle separation, which is determined by the ionic strength of the solution. These results are in qualitative agreement with simulations based on random sequential adsorption (RSA).

The coupling between diffusion and deposition processes, i.e. the transition from mass transport limitation to the regime where surface blocking effects dominate, is analysed using a generalised adsorption theory. In this theory, the deposition rate is expressed in terms of an overall kinetic blocking function. For the irreversible deposition of particles, the deposition is treated on the basis of the RSA model. For relatively large particles in the micron range, RSA is directly applicable. For considerably smaller particles the aforementioned coupling is more pronounced. Using the generalised adsorption model, the measured deposition curves can be adequately described, and the rate constant for particle adsorption is determined. Comparison with experimental results for proteins of similar dimensions as our colloidal particles, indicates that our results are in line with the adsorption rate constants for these proteins.
References


6 Electrophoretic deposition of gold nanocolloids at low DC voltages

6.1 Summary

Electrophoretic deposition of gold nanoparticles is investigated. During deposition, ellipsometry spectra are recorded and the current flowing through the cell is measured simultaneously. We find that deposition is closely related to the current running through the cell. We argue that the deposition process is driven by an electric field that is constituted by an electrochemical reaction.

The deposited films consist of clusters of particles. Although the clusters generally do not show 2-dimensional ordering, the radial ordering is better than for films grown by electrostatic attraction between particles and a charged surface.

6.2 Introduction

In chapter 5 we have shown that deposition driven by electrostatic attraction between particles in the suspension and a chemically charged substrate results in randomly deposited colloidal films. These films show short ranged local ordering in the radial direction, but no ordering in azimuthal direction, which is a consequence of the irreversibility of the adsorption process. Because of the double layer repulsion, the particles are generally well separated, which implies that the surface coverage is limited. For many applications a higher coverage and a more ordered distribution of the particles would be desirable. Therefore, deposition by electrostatic attraction has to be replaced with a process that allows more control over the growth of the colloidal film.

Using electrophoresis, ordered films of 1 μm large polystyrene latex particles have been made by Böhmer [1] in 1996. In the same year Trau et al. showed well-ordered multilayer films consisting of PS latex particles with a diameter of 2 μm [2]. Since then, much effort has been devoted to electrophoretic deposition of (sub)micrometer sized colloidal particles. This has resulted in well-ordered structures such as 3D colloidal crystals (opals) [3–5] and ordered 2D films of a binary mixture of colloids [6]. The driving force for ordering of these films has been studied by several authors [2, 3, 6–8]. Although the exact mechanism is still unclear, the majority of the authors seem to agree on the fact that electrohydrodynamic flow plays a role [7–11]. Electrohydrodynamic flow is caused by movement of ions.
due to a gradient in the local electrical field. This gradient arises due to variations in the charge distribution around an adsorbed particle. As the flow is a response to the variations in the charge density, it only persists if the variations in the charge distribution persist. Consequently, electrohydrodynamic flow only exists when a current is running.

In contrast to films consisting of relatively large particles, electrophoretically deposited films of nanoparticles are reported less frequently, and films obtained by deposition of these particles generally do not show significant ordering. An early example of an ordered film consisting of nanocolloidal gold particles is presented by Giersig and Mulvaney [12]. Bailey et al. have shown unordered films deposited using electrophoresis on substrates that were pre-patterned using microcontact printing [13]. Another example is from Gao et al. [14], who deposited CdTe nanoparticles on pre-patterned ITO electrodes. An example of EPD of gold particles in a non-aqueous suspension is given by Chandrasekharan and Kamat who deposited unordered 3D films from a toluene based suspension onto an electrode with pre-deposited titania colloids [15]. Inverse opals made by electrophoretic deposition of small particles into voids left between an ordered multilayer film of large particles have been shown by Gu et al. [5].

Summarising the literature results, we can state that electrophoretic deposition of nanoparticles is a known technique, but that in most cases unordered films are obtained. There are several factors that make deposition of ordered films of small particles more challenging. First, for aqueous suspensions of nanocolloids, the thickness of the Debye layer is often comparable to particle size. This means that double layer repulsion plays a role. Secondly, Brownian motion is for small particles much more important than for larger particles and this hampers ordering of the film. The films deposited by Giersig and Mulvaney [12] are the only exception to this rule as far as we are aware. These films show very nice ordering, due to the fact that the particles are mobile even after deposition on the electrode surface. A last important issue is that nanoparticles can not be observed easily, whereas deposition of larger particles is readily observed using conventional microscopy[1–3, 6, 8–10].

In this chapter we will describe deposition experiments where positively charged gold nanoparticles are deposited using an externally applied electric field. Using spectroscopic ellipsometry we are able to observe the adsorption of nanoparticles in-situ. This enables us to study the influence of the applied voltage on the deposition process. Based on the results we propose a mechanism for electrophoretic deposition from an aqueous suspension. Additionally the distribution of the particles on the electrode is analysed from SEM images obtained after deposition.

6.3 Experimental

For electrophoretic deposition experiments, octadecylamine stabilised gold particles with an average diameter of 8.6 nm are used. These particles are synthesised
following the procedure of Aslam et al. [16]. Synthesis and characterisation of these particles are described in chapter 2. As octadecylamine is a weak base, the surface charge of the particles will depend on the pH of the suspension. When hydrogen gas is developed at the cathode, hydroxide ions are produced simultaneously and the pH of the suspension will increase locally. As we do not want the surface charge to vary during the experiment, a pH buffer solution is used as background electrolyte. A mixture of sodium benzoate (from Sigma) and hydrochloric acid (from Merck) with a concentration ratio of 1.65:1 is used to achieve a pH of 4. The concentration of sodium benzoate is typically 10–20 mM. After adding the hydrochloric acid, the ionic strength is equal to the initial sodium benzoate concentration.

The particles are to be deposited onto a transparent sample that serves as the working electrode. The samples are obtained from Ssens in Hengelo, the Netherlands. They consist of a coated round BK7 glass substrate with a diameter of 25 mm. The coating of the substrate is designed to make the optical transmission as uniform as possible in the visible part of the spectrum. The topmost layer is a gold film with a thickness of a few nanometers that acts as the working electrode. Prior to the experiments the samples are cleaned using an acidic piranha solution (a 2:1 mixture of concentrated sulfuric acid and hydrogen peroxide). After this treatment, the gold surface is oxidised and consequently has a negative surface charge. Without further treatment of the sample, this surface charge would cause an electrostatic interaction between the particles and the substrate, resulting in an uncontrolled deposition process. To prevent this, the sample is immersed for an hour in ethanol to reduce the surface oxide. After cleaning and reduction of the surface, a wire is glued to the sample using a two-component silver epoxy glue. This connection is not in contact with the suspension during the experiment.

Electrophoretic deposition experiments are carried out in a cell that allows us to do spectroscopic ellipsometry measurements during adsorption. In figure 6.1
6 Electrophoretic deposition at low DC voltages

A schematic top view of the cell is shown. The sample is mounted on a glass prism. To prevent reflections at the prism–substrate interface, the gap between the substrate and the prism is filled with a refractive index matching fluid. The prism and the sample are attached to the cell using a clamp. A PTFE (teflon) coated o-ring with an inner diameter of 14 mm is used to prevent leaking of the suspension. Consequently, the effective electrode area is 1.5 cm². The cell itself is made of polyetheretherketone (PEEK), a plastic that combines a high chemical resistivity with good mechanical properties. The counter electrode is a platinum plate with a surface of approximately 1.8 cm². The distance between the working- and counter electrode can be varied between 0 and 5 mm. The typical distance is 1–2 mm. A calomel reference electrode is used. This electrode is inserted in a separate compartment that is connected to the main compartment through a narrow channel. An EG&G Princeton Applied Research, PAR-273A potentiostat is used to apply the potential and to measure the current.

Spectroscopic ellipsometry measurements are performed using a homebuilt ellipsometer that is described in chapter 2. The attenuated total reflection (ATR) setup is employed, meaning that the sample is illuminated from the backside through the prism. The incident beam is totally reflected at the substrate–suspension interface so it does not propagate into the suspension. Particles are probed by the exponentially decaying evanescent wave present in the suspension. The benefit of this setup is that the gap between the electrodes can be made arbitrarily small. A second advantage is that the measurements are not affected by absorption of the light in the suspension. More details on the ATR setup can be found in chapter 2.

The cell is attached to a sample stage that can be tilted in two directions: (i) around the normal of the triangular sides of the prism enabling fine adjustments of the angle of incidence and (ii) around the normal of the long side of the prism. This construction allows the cell to be well-aligned for ellipsometry measurements, as explained in chapter 2.

Ellipsometry spectra recorded during adsorption are analysed using a principal component analysis (PCA). As demonstrated in chapter 4, PCA is a statistical technique that allows us to analyse a set of spectra without optical modelling. A set of spectra of gold nanoparticles deposited on the substrate described above can be represented by a single principal component and the corresponding coefficient:

\[ \frac{\rho_i}{\rho_0} - 1 \approx c_i Y \]  (6.1)

In this equation \( \rho_i \) is the \( i \)-th spectrum of the set, \( \rho_0 \) is the spectrum of the substrate before deposition, \( Y \) is the principal component of the set, and \( c_i \) is the coefficient for the \( i \)-th spectrum. Once the components are known, every spectrum of the set is completely characterised by the value of the coefficient \( c_i \). This number is closely related to the coverage of the substrate with particles and is therefore used as the coverage measured in arbitrary units. In this way, trends in the ellipsometry
6.4 Results and discussion

6.4.1 Deposition mechanism

To investigate the deposition process, the applied voltage is increased\(^1\) in small steps during the deposition process. During the experiment the current through the cell is measured and ellipsometry spectra are recorded. In figure 6.2, the results of the experiment are shown. Before an external voltage was applied, an open circuit potential of approximately +0.2 V was observed between the sample and reference electrode. After 24 minutes the voltage was switched to -0.35 V. Subsequently, the voltage was increased with 0.1 V every 35 minutes, up to a voltage of -0.85 V. In the upper graph of figure 6.2 the current is plotted as a function of time. The lower graph shows the time development of the surface coverage, as obtained from the ellipsometry spectra using PCA and calibration of its results using the SEM image in figure 6.7(a).

In the upper graph in figure 6.2, the moments where the voltage is increased are clearly visible. At these moments, a short pulse in the current is observed, which indicates the charging of the double layer. More importantly no significant current is observed as long as the voltage is below -0.65 V. Above this voltage the current increases with increasing voltage. To investigate the cause of the increase of the current, the pH buffer is electrochemically characterised. The dependence of the current on the applied voltage is shown in figure 6.3. The voltages is swept with a scan speed of 20 mV/s from 0 V to -1.2 V and then back to 0 V. This procedure is repeated a few times. When the voltage is swept towards more negative values, no significant current is observed up to -0.5 V. At a more negative voltage the current starts to increase, and a peak in the current is observed. This peak is not observed when an inert electrolyte, such as KCl, is used. Therefore, we attribute the current observed during deposition to the reduction of benzoic acid at the working electrode. If the voltage is lowered to approximately -1.1 V, the onset of hydrogen gas evolution is observed. The current observed in figure 6.3 is significantly larger than in figure 6.2. This is explained by the role of the transport of the reactants to the electrode surface. In the experiment shown in figure 6.2, a static voltage is applied. In this situation, the electrolyte is depleted close to the electrode and the

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\(^1\)Since the deposition is carried out with a negative potential of the working electrode with respect to the calomel reference electrode, we increase the voltage when we make it more negative.
Figure 6.2: Electrophoretic deposition experiment of gold nanoparticles. Initially, the voltage is equal to the open circuit voltage. Subsequently, the applied voltage is varied from -0.35 V to -0.85 V in steps of 0.1 V. The upper figure shows the current as a function of time. The points where the voltage is increased are clearly visible in this graph. The lower figure shows the coverage of the substrate with particles. The data clearly show that a minimum voltage is required for deposition. In the inset, the dependence of the deposition rate on the current is shown.
6.4 Results and discussion

-1.2 -1.0 -0.8 -0.6 -0.4 -0.2 0.0
U [V]

Figure 6.3: Electrochemical characterisation of the background electrolyte, a mixture of sodium benzoate and hydrochloric acid with a total ionic strength of 25 mM. The current is measured as a function of the applied voltage. The peak around -0.8 V indicates the reduction of benzoic acid.

The reactant has to diffuse from an increasingly larger distance towards the electrode. This diffusion driven process limits the reaction and therefore the current. This view is supported by the fact that the increase in the electrochemical current is much smaller when the voltage is increased to -0.85 V than when the voltage is increased to -0.75 V. At a voltage of approximately -0.3 V an oxidation peak is observed. This peak is initially absent, but develops after a few minutes scanning, indicating that the reaction products of the reduction at -0.75 V are oxidised.

When we return to figure 6.2 and focus on the time dependence of the surface coverage we observe that the first point after the start of the experiments already deviates significantly from zero, suggesting that a fast deposition process is running at the start of the experiment. To investigate whether this is true, the ellipsometry spectra measured during deposition are inspected. Figure 6.4 shows an ellipsometry spectrum measured before the start of the experiment, three spectra measured during deposition, and a spectrum measured after deposition. The spectra obtained during the experiment are measured 2, 205 and 220 minutes after insertion of the suspension. Around 2.4 eV a peak that is related to the plasmon resonance of the
Figure 6.4: Ellipsometry spectra measured in-situ in an ATR setup during deposition of 8.6 nm gold colloids (see figure 6.2). The spectra are measured before deposition (dash-dotted line), and 2, 205 and 220 minutes after the start of the experiment (dashed lines). The full line represents the spectrum measured after 4 hours deposition.
gold particles develops when particles adsorb. As can be seen from the graph, the spectrum measured two minutes after the suspension is inserted in the cell already shows a small plasmon resonance peak, which proves that the high initial value of the first coefficient is not an artifact of the analysis. Apparently, a fast deposition process starts to run as soon as the suspension is inserted in the cell. A likely explanation is that the substrate has obtained a negative charge before the suspension is injected. This can happen during the measurement of the initial spectra, which requires approximately 30 minutes. During these measurements, the substrate is in contact with water. The negative surface potential obtained by oxidation results in an attraction between the particles and the substrate. Because of the flow that exists in the suspension after it has been injected, transport of particles towards the surface is very efficient. In combination with the attractive interaction this can result in a fast deposition process.

After initial adsorption, the surface coverage increases only very slowly, even when a voltage as high as -0.65 V is applied. As noted before at these voltages no significant current is observed, which means that the applied voltage is shielded by the electrical double layer at the electrode. Therefore, no electrical field exists in the bulk of the suspension, so the particles do not experience a force that drives them towards the surface of the electrode. Consequently, only particles that enter the double layer by diffusion experience an electric field and adsorb. This still could result in a much faster film growth, but it is known that the double layer potential of a gold electrode in an aqueous electrolyte is much smaller than the externally applied voltage \[17\]. When a voltage is applied, hydroxyl groups at the gold surface accept or donate a proton, thus reducing the double layer potential. The reduction of the double layer potential also depends on the pH of the solution, but is typically 85–90%, which explains the low deposition rate.

When the voltage is increased to -0.75 V, adsorption starts immediately. Upon increasing the voltage 0.1 V further, the deposition rate increases by a factor 1.9. Apparently, a minimum voltage is required for deposition. The value of this minimum is generally between -0.65 V and -0.75 V. This corresponds quite well with the observation made from the upper graph in figure 6.2 that a minimum voltage of approximately -0.65 V is required for a significant current. From this observation we conclude that the deposition rate is closely related to the current flowing through the cell.

Therefore, we conclude that the reduction reaction occurring at the working electrode provides the driving force for deposition. We propose the following explanation. At low voltages, the applied potential is completely shielded by the electric double layer that is formed at the electrode–suspension interface. Consequently, there is no electric field in the bulk of the suspension. This situation is shown in the left part of figure 6.5. When the voltage is increased, the electrochemical reduction reaction starts creating a negative excess space charge near the electrode surface. Due to diffusion and coulombic repulsion, this charge is distributed throughout the
6 Electrophoretic deposition at low DC voltages

Figure 6.5: Schematic representation of the charge distribution in the cell and the resulting potential distribution. The left and the right figure depict the situation without and with electrochemical current, respectively.

bulk of the suspension. In the middle of the cell, the excess charge is compensated by the positive excess charge that is created at the counter electrode. After some time, the amount of charge created at the electrodes is equal to the charge that vanishes in the bulk of the suspension, and from this moment, the charge distribution is more or less stable. The charge distribution constitutes a field gradient that extends throughout the entire suspension, and this field drives the deposition of the particles. A schematic overview of this situation is presented in the right part of figure 6.5. The same mechanism is used by Quinn et al. [18] to analyse the particle flux towards a small electrode. In their paper they detect electrophoretic deposition of latex micro beads on a gold electrode with a diameter of 5 µm using electrochemical detection.

This model can explain the observation made in figure 6.2. When the applied potential is increased from -0.75 V to -0.85 V, more charge is created at the electrode. Therefore, the gradient of charge distribution will increase, which results in a higher electrical field and faster deposition. One observation not yet made is that at -0.65 V, the current has already increased considerably, but still no deposition is observed. Apparently, the electrical field is too weak to overcome the thermal motion of the particles.

The results of a second experiment are shown in figure 6.6. The coverage has been obtained by calibration of the PCA results using the SEM image from figure 6.7(b).
Fifteen minutes after the start of the experiment, the voltage is increased from its open circuit value to -0.75 V. After 65 minutes the voltage was increased further to -0.85 V and 40 minutes later decreased again to -0.75 V. When the voltage is changed to -0.85 V, the deposition rate increases by a factor 1.8, which is in good agreement with the factor 1.9 that was observed in the experiment described above. After switching the voltage back to -0.75 V, the deposition rate decreases again to a value that is within experimental margins equal to the initial value.

After deposition, we try to let the particles desorb by reversing the voltage. When the voltage is switched to +0.4 V an instantaneous increase in the optical
signal is observed. We attribute this change to electroreflection, a change of the dielectric properties of a metal due to modification of the electron density at the electrode surface, which is in turn caused by an applied voltage. After this change we do not observe a decrease of the coverage, not even when the voltage is changed to $+0.7\,\text{V}$. This observation deviates from the results of Giersig and Mulvaney \cite{12} who observe desorption of particles when they reverse the applied potential. An explanation for this difference may be that the Van der Waals forces are much smaller in their situation because they use a carbon coated copper grid as substrate whereas we have a metallic substrate. Therefore, in our situation the particles are expected to be more strongly bound to the electrode. If the interaction between the electrode and the particles is very strong, the particles will be immobile, and this will inhibit the formation of ordered domains in the colloidal films.

6.4.2 Film morphology

After deposition, the films are carefully rinsed and dried. To investigate the morphology of the colloidal films, SEM images are taken. In figure 6.7(a) and (b) the images measured after the experiments described in the previous section are shown. They look quite similar. When these films are compared to the films that are described in chapter 5, a number of important differences are noticed. First, the particle distribution of the films deposited using EPD is more inhomogeneous. Clusters of 20–50 particles coexist with relatively large areas without particles. Close inspection shows that some of these clusters show some azimuthal ordering. These observations indicate the presence of a long ranged attractive force between the particles. The second observation is that on several places a second layer is adsorbed. The pictures also show some dark spots in the image. These are due to organic pollution of the samples, probably originating from the benzoic acid buffer.

Because the majority of the particles is part of a single layer we conclude that the clusters are not formed in the suspension but during deposition. Two interactions can result in long ranged attractive forces required for cluster formation: hydrodynamic forces occurring during deposition and capillary forces acting when films are dried. Electrohydrodynamic forces are known to cause formation of clusters of much larger particles at electrode surfaces \cite{3, 6–8}. In these cases the clusters are imaged in–situ, so drying effects do not play a role. In the present case this is unsure, because the images are made after drying. To be able to estimate the influence of capillary forces, a deposition experiment without applied field is performed. In this experiment, electrohydrodynamic flow does not play a role. A gold surface is oxidised with piranha solution. After cleaning, no measures are taken to reduce the gold surface that is therefore assumed to have a negative surface potential. The sample is rinsed and immediately immersed in a colloidal suspension with an identical composition as used for the EPD experiments. The sample is left overnight in the suspension. Particles are expected to adsorb on this surface due to an attractive electrostatic interaction between the oxidised substrate and the par-
6.4 Results and discussion

(a) SEM image after deposition experiment shown in figure 6.2. The coverage is 41%.

(b) SEM image after the experiment shown in figure 6.6. The coverage is 9%.

(c) Particles adsorbed on an oxidised gold surface

(d) Film deposited at -0.75 V, used for calculation of $g(r)$

Figure 6.7: SEM images of colloidal films. All figures are $750 \times 750 \text{nm}^2$, except the lower right one which is $1 \times 1 \mu\text{m}^2$. 
particles. The resulting film is shown in figure 6.7(c). A small number of particles has adsorbed and the vast majority of them is present as monomers. Only a few small clusters, mainly dimers, are present. The presence of the particles is in agreement with the observation of particle deposition occurring before an external potential was applied.

Since the number of particles on the surface is relatively small, capillary forces are absent on large parts of the surface. They only play a role when a few particles are close together. In figure 6.7(c) we observe a few spots where the distance between two adjacent particles is small. In approximately half of these cases, the particles touch each other, while the other dimers are well separated. This suggests that capillary forces play a role in the formation of the films, but that they are not dominant. This means that the clusters observed in figure 6.7(a) and (b) are mainly caused by electrohydrodynamic flow.

To enable a more quantitative comparison between the films deposited using a chemically modified substrate and electrophoresis, the 2D radial distribution function of a film deposited using EPD is calculated. The radial distribution function \( g(r) \) expresses the probability to find a particle at a distance \( r \) from another particle. Because the films shown in figure 6.7(a) and (b) exhibit a significant number of particles in a second layer, these are not suitable for the calculation of a radial distribution function. Figure 6.7(d) shows a more suitable film with a lower coverage and with only very few particles in a second layer. This film was deposited at a voltage of -0.75 V. Because the contrast between the particles and the substrate is too low, all particles are marked with a small dot. Then the 2-dimensional autocorrelation function of the dots is calculated. This approach offers the additional advantage that the convolution with the particle size is eliminated, which makes the autocorrelation picture much sharper. The autocorrelation function clearly shows two rings corresponding to the first and second preferred inter-particle distances. The radial distribution function is calculated by evaluating all particle-particle distances. The calculated distribution function is normalised by the requirement that its value should be one at infinity and is plotted as a function of the distance divided by the position of the first maximum \( r_o \). The result is shown in figure 6.8(a).

The distance to the first maximum is equal to 10.9 nm. This value agrees very well with nearest neighbour distances observed in figure 6.7(d). From the TEM images presented in chapter 2, we know that the diameter of metallic core of the particles is 8.6 nm, which means that the gap between the surfaces of the particle cores is 2.3 nm. Since the length of the octadecylamine molecule is approximately 1.5 nm, this means that the gap between the metallic cores of the particles is 24% smaller than twice the length of the stabilising molecule. This is in agreement with observations of Giersig and Mulvaney who noticed the same phenomenon for larger gold particles stabilised with several different thiols \[12\]. Since the Debye screening length is 2.8 nm, we conclude from these observations that the double layer repulsion is dominated by electrohydrodynamic attraction.
6.4 Results and discussion

Figure 6.8: Radial particle distribution functions plotted as a function of $r/r_0$, where $r_0$ is the distance of the first maximum. Graph (a) shows the electrophoretically deposited film shown in figure 6.7(d) with $r_0 = 10.9$ nm. The dashed line corresponds with the long distance limit where nearly all correlation has been lost. The arrows mark the positions where peaks are expected if the clusters would be perfectly hexagonal. In the inset the 2D autocorrelation function of the particle distribution is shown. Figure (b) shows the radial distribution of a randomly deposited film with $r_0 = 24$ nm. The inset shows the corresponding AFM image.
6 Electrophoretic deposition at low DC voltages

At distances up to four nearest neighbour distances, a few more maxima are observed, indicating that radial ordering persists up to a distance of a few particle diameters. The height of these peaks is progressively lower because there is only a small number of larger clusters. In figure 6.8(a), the theoretical peak positions for a perfectly hexagonal lattice are indicated with arrows. It is clear that the observed peak positions do not match with the calculated distances, which demonstrates that the azimuthal correlation is lost at larger distances. This is probably a consequence of the fact that the particles are relatively strongly bound to the surface.

For comparison, figure 6.8(b) shows the radial distribution function of a randomly deposited colloidal film. Negatively charged citrate stabilised particles with an average diameter of 13.3 nm are deposited onto a silicon substrate that is derivatised using aminopropyltriethoxysilane. The amine group gives the substrate a positive surface charge. This results in a purely electrostatic attraction between the particles and the substrate, and this attraction drives a random deposition process. This results in randomly deposited films, in which the particle-particle distance and final coverage are determined by the composition of the solution (see chapter 5). Consequently, $r_o$ can be determined from the final coverage. If we compare the radial distribution function of electrophoretic and randomly deposited films, we see that electrophoretic deposition improves the radial ordering in the film. The primary maximum is twice as high, and the ordering persists up to larger distances.

6.5 Conclusions

Using an externally applied voltage, nanocolloidal gold particles have been deposited onto glass substrates with a thin gold layer. The particles have a diameter of approximately 8.6 nm and have a positive surface charge that originates from the octadecylamine stabiliser. The particles are dispersed in an aqueous solution of a mixture of benzoic acid and sodium benzoate.

The mechanism that is responsible for deposition is investigated by measuring the influence of the applied voltage on the deposition process. At low voltages, the current is negligible and no deposition takes place. When a higher voltage is applied, a strong increase in both the current and the deposition rate is observed. We propose that increasing the voltage results in the electrochemical reduction of the benzoic acid. This reaction creates a net space charge in the suspension, thus constituting an electrical field that extends through the entire suspension. This field provides the driving force for deposition of the particles.

The colloidal films that are grown in this way show significant clustering, which indicates the presence of a long ranged attractive force. Although capillary forces play a role during drying of the film, electrohydrodynamic flow is the most important interaction. The radial distribution function is determined from the SEM images of the film and shows that the radial ordering is significantly better than in case of randomly deposited films. In addition to the improved radial ordering, some azimuthal ordering is observed in the clusters.
References

Summary

Introduction

In this thesis, nanocolloidal gold films and their deposition are described. Several aspects are investigated: the deposition process under influence of electric interactions, the morphology of the colloidal films and the optical properties of both the individual particles and the deposited films.

The deposition of particles in the micrometer size regime is frequently studied using optical microscopy. However, this technique cannot be applied to study nanoparticles because their size is well below the diffraction limit of visible light. These particles can be detected using ellipsometry and therefore chapter 3 is devoted to the application of spectroscopic ellipsometry to nanocolloidal films.

The optical properties of nanocolloidal gold particles exhibit a strong plasmon resonance, a feature that arises from collective resonant oscillation of the electrons in the gold. In the UV/Vis absorption spectrum of a nanocolloidal gold suspension this resonance is observed as a strong peak in the absorption around 520 nm. The height of this peak strongly depends on the size of the particles, an effect that cannot be described using the bulk dielectric function of gold. When the dielectric function is modified to include scattering of electrons at the particle surface, an accurate calculation of the absorption spectra can be made. The dielectric function obtained in this way is then used for the calculation of the optical properties of thin films consisting of gold nanoparticles.

Characterisation

The properties of nanocolloidal gold films are investigated using spectroscopic ellipsometry. The measured spectra change strongly with the number of particles per unit area, so in principle it is possible to obtain the surface coverage from the spectra. The surface coverage is defined as $\varphi = \pi a^2 \cdot N$ where $\pi a^2$ is the area occupied by a single particle and $N$ is the number of particles per unit area. Determination of the surface coverage from the measured spectra requires an accurate optical model of colloidal gold films. The models traditionally applied in spectroscopic ellipsometry describe a sample as a stack of films with a well-defined thickness and dielectric function. Obviously, colloidal gold films do not have such well-defined properties.
The traditional model can be extended to inhomogeneous films by introduction of an effective dielectric function. This is done in effective medium theories that describe the optical properties of inhomogeneous films in terms of the dielectric functions and volume fractions of the constituent materials, assuming that the films are isotropic. Frequently, this approach provides satisfactory results. However, effective medium theories fail to describe the optical properties of thin films consisting of metal nanoparticles, since the very limited thickness gives rise to an anisotropy.

The thin island film theory, that was developed by Bedeaux and Vlieger, gives a much better description of the optical properties of colloidal films. This theory does not describe them as a homogeneous films, but as a collection of polarisabilities at the substrate–ambient medium interface, thus taking into account the particulate nature of the films. The most simple implementation of the thin island film theory uses the single particle polarisability to describe the optical response of the nanoparticles. Using this approach the measured spectra can be accurately reproduced. However, the coverage that is obtained by fitting this model to the measured data deviates significantly from the coverage as observed with electron microscopy. Apparently, the isolated dipole approximation fails. This is easily understood because a dipole located at an interface will induce an image dipole in the interface. Moreover, dipoles situated close to each other will mutually influence their dipole moments. These two effects can be taken into account by introducing effective polarisabilities. This yields a perfect correspondence between the coverage measured using ellipsometry and electron microscopy.

Since modelling of ellipsometry spectra can be complicated or even impossible, an alternative analysis method can be very useful. This situation can arise when the optical properties of a sample are unknown. In other situations quantitative analysis is less important than a global view over trends in the data. In chapter 4 it is shown that in these situations a principal component analysis (PCA) offers a way to simultaneously analyse sets of similar spectra without modelling. Such a set typically consists of a spectrum measured on a clean substrate and a number of spectra measured on a film consisting of an increasing amount of material. The growth of the film results in a change in the spectra that is very similar for all of them. PCA can be used to assign a single number to every spectrum expressing the magnitude of this change. This number is referred to as the first coefficient and can be related to the thickness of the film or the surface coverage. It is shown on the basis of a few examples that this coefficient has a one-to-one relation with the thickness of a film or the density of a colloidal film. If quantitative analysis is required, calibration of the first coefficient using a few measurements suffices to obtain quantitative results for all spectra. In case of a polyelectrolyte film grown using layer–by–layer self–assembly, the coefficient is perfectly proportional to the film thickness. For low refractive index colloidal films measured in air, a slight deviation from a linear relationship is observed, originating from the dielectric
contrast between the particles and the surrounding medium. When the contrast is large, as in the case of gold nanoparticles, the relationship between the surface coverage and the first coefficient is non–linear. Although this makes a quantitative interpretation of PCA less straightforward, PCA still offers a quick and convenient overview of a set of data without modelling.

Deposition

Nanocolloidal monolayers can be grown using electrostatic attraction between a substrate and the particles. This method is well–suited for deposition of a single monolayer on a substrate and can be applied to deposit particles on a large surface. Chapter 5 describes the deposition of gold nanoparticles on charged silicon substrates. Citrate stabilised gold nanoparticles with a negative charge and a diameter of 13.6 nm are used in combination with amine derivatised silicon substrates with a positive surface charge. The deposition process consists of two steps: transport of the particles to the substrate, and adsorption. When deposition experiments are performed under well–defined flow conditions, these two steps can be studied more or less independently. This can be achieved using a stagnation point flow setup. In this setup a flow of the colloidal suspension is directed perpendicular to the sample surface. This results in a stagnation point, in which the flow velocity vanishes and diffusion governs the particle transport. Adsorption of the particles can be conveniently observed using single wavelength reflectometry. The adsorption process consists of three stages. Initially, a linear increase of the surface coverage is observed. In this stage, the adsorption rate is determined by the flow conditions in the setup. In the saturation regime the deposition rate is limited by the decrease of the area available for adsorption. In the intermediate stage both factors play an important role.

The entire deposition process can be adequately described using the generalised adsorption model, developed by Adamczyk and coworkers. This model combines transport of the particles towards the substrate with random sequential adsorption (RSA). In the RSA model particles arrive at the surface at a random position. Assuming a hard sphere interaction between the particles, adsorption takes place when the position is at least one particle diameter away from the neighbouring particles. If the distance is smaller, the particle does not adsorb. After adsorption the particles are immobile. Charged nanoparticles with a radius comparable to the thickness of the electrical double layer are obviously soft spheres. Nevertheless, their adsorption can still be described using the RSA concept when an ionic strength dependent effective hard sphere radius is introduced. This effective radius takes into account the thickness of the electric double layer and is therefore larger than the real particle radius. Furthermore, the effective radius increases when the ionic strength of the suspension is decreased. Consequently the saturation coverage of the sample increases with increasing ionic strength.

By adjusting the saturation coverage, the initial deposition rate and the cou-
pling constant describing the balance between mass transport and adsorption, the measured data can be accurately reproduced by a generalised adsorption model. The saturation coverage increases with increasing ionic strength of the solution, in good agreement with the DLVO theory. The initial rate and coupling constant do not depend on the ionic strength. The spatial distribution of the particles on the surface shows little ordering. Only a very short ranged radial ordering is observed. In the radial distribution function this is visible as a weak peak corresponding to the nearest neighbour distance. These observations agree with simulations from the RSA model.

Formation of colloidal films under the influence of an externally applied voltage offers the possibility to influence the deposition process during the experiment. This is not possible when the deposition is driven by a fixed charge of the substrate. Chapter 6 describes the electrophoretic deposition of positively charged gold particles. These particles have a diameter of 8.6 nm and are stabilised in water using octadecylamine. During the deposition experiments the current flowing through the cell is measured and ellipsometry spectra are recorded. The spectra are analysed using a principal component analysis. When the applied voltage is more positive than -0.75 V, the deposition proceeds very slowly. This is due to shielding of the applied potential by surface hydroxyl groups and ions present in the solution. In this situation only a weak electrochemical current is observed. At more negative voltages, the current increases considerably, which indicates the reduction of the background electrolyte at the working electrode. This results in a charge distribution and consequently in an electric field in the bulk of the suspension. This field provides the driving force for electrophoretic deposition. This is indeed observed in the ellipsometry spectra. At voltages more negative than -0.75 V, a strong increase in the deposition rate is observed. Further increasing the voltage results again in an increase of the deposition rate.

After deposition, scanning electron microscopy images of the films are made. The spatial particle distribution of the films differs greatly from the particle distribution of films that have been grown on a chemically charged substrate. The majority of the particles is present in clusters that can contain several tens of particles. The cluster show a strong radial ordering and often they are hexagonally ordered. This distribution indicates the presence of an attractive force between the particles that is strong enough to overcome the double layer repulsion. For much larger particles it has been observed in the literature that electrohydrodynamic flow can cause clustering of particles at an electrode surface. This flow is driven by a local electric field that is caused by inhomogeneities of the charge distribution around a particle at the electrode surface. Unfortunately, it is not possible to directly observe electrohydrodynamic flow around adsorbed nanoparticles. But since all ingredients are present, it is highly probable that electrohydrodynamic flow is indeed the driving force for the observed cluster formation.
Samenvatting in het Nederlands

Inleiding

Dit proefschrift beschrijft onderzoek naar depositie van metaal nanocolloïden. Colloïden zijn kleine deeltjes die gedispergeerd zijn in een continu medium. De grootte van deze deeltjes varieert van 1 nanometer (1 miljoenste van een millimeter) tot 10 micrometer (1 honderdste millimeter). Zowel de deeltjes als het medium kunnen vast, vloeibaar of gasvormig zijn. Alledaagse voorbeelden van colloïdale systemen zijn melk (een oplossing van kleine vet- en eiwitdeeltjes in water), rook (kleine vaste deeltjes in lucht), verf (een complex mengsel van vaste deeltjes in water) en mist (kleine waterdruppeltjes in de lucht). Voor het onderzoek dat in dit proefschrift is beschreven, is gebruik gemaakt van gouddeeltjes met een grootte van ongeveer 10 nanometer, die opgelost zijn in water.

Een van de interessante aspecten van deze deeltjes is dat ze ten opzichte van hun volume een enorm oppervlak hebben. Een bolletje met een volume van $1 \text{ cm}^3$ heeft een oppervlak van $4.8 \text{ cm}^2$. Als dit bolletje wordt opgedeeld in een groot aantal bolletjes met een diameter van 10 nanometer, dan wordt het totale oppervlak $124 \text{ m}^2$. Dit maakt nanocolloïden erg interessant als katalysator. De optische eigenschappen van zulke kleine deeltjes zijn ook sterk afhankelijk van het oppervlak, een feit dat gebruikt kan worden voor toepassingen in bijvoorbeeld sensoren. Een mogelijke toepassing van magnetische nanocolloïden is bijvoorbeeld magnetische dataopslag.

Voor veel toepassingen moeten de nanocolloïden op een oppervlak worden aangebracht. Dit proces wordt depositie genoemd en kan met heel verschillende methodes worden uitgevoerd. In de experimenten die in dit proefschrift zijn beschreven is depositie met behulp van elektrische aantrekkingskracht toegepast. De gebruikte colloïden hebben een elektrische lading, dus is het mogelijk om ze met behulp van een elektrisch veld naar een oppervlak te bewegen. Dit elektrisch veld kan ontstaan doordat het oppervlak waar de deeltjes op aangebracht worden een tegengestelde lading heeft. Een meer flexibele mogelijkheid is om het elektrisch veld te genereren met behulp van een externe spanningsbron. In beide gevallen treedt er een complicatie op. In de oplossing zitten namelijk ook andere geladen deeltjes, ionen. Deze zullen ook door het elektrisch veld aangetrokken worden, met als gevolg dat het

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2 Een dispersie is een oplossing waarin de opgeloste stof niet moleculair verdeeld, maar als grotere deeltjes aanwezig is.
Samenvatting in het Nederlands

elektrisch veld wordt afgeschermd en er geen kracht op de colloïden uitgeoefend wordt.

Karakterisatie

Een belangrijk aspect van het onderzoek is de karakterisatie van de deeltjes, de colloïdale lagen en het hele depositie proces. De deeltjes zijn veel te klein om met een microscoop te zien. Met een elektronen microscoop zijn ze wel te zien, maar omdat elektronenmicroscopie alleen in hoog vacuüm kan worden uitgevoerd, is deze techniek ongeschikt voor het observeren van het depositieproces. Om deze redenen is er gebruik gemaakt van optische technieken: ellipsometrie en reflectometrie. Deze technieken zijn gebaseerd op het meten van de verandering van de polarisatie van licht als het reflecteert aan een oppervlak. Deze verandering bestaat uit twee delen: een amplitude en een fase deel. In geval van ellipsometrie worden beiden gemeten. Bij reflectometrie wordt alleen de amplitude van de verandering gemeten, wat deze metingen veel eenvoudiger maakt. Door deze meting bij een aantal golflengten van het licht uit te voeren wordt een ellipsometrie- of reflectometrie spectrum gemeten.

Met name ellipsometrie is een erg gevoelige techniek, waarmee kleine veranderingen aan een oppervlak waargenomen kunnen worden. Een ander voordeel van zowel ellipsometrie als reflectometrie is dat beiden heel flexibel kunnen worden ingezet, ook voor het observeren van processen die zich in water afspelen. Het nadeel is dat het indirecte methodes zijn. Je kunt geen deeltjes zien, zoals met microscopische technieken, maar alleen een polarisatie verandering meten. Om te achterhalen hoe een laag er werkelijk uitziet, of wat er zich precies afspeelt aan een oppervlak, is het nodig het systeem waaraan gemeten wordt te modelleren. Met een geschikt model is het mogelijk om uit de gemeten spectra de oppervlaktebedekking te bepalen. Deze laatste grootheid is gedefinieerd als de fractie van het totale oppervlak van een substraat dat is bedekt met deeltjes.

Standaard modellen die gebruikt worden in ellipsometrie beschrijven een sample als een substraat met daarop een aantal lagen. Voor berekening van de optische eigenschappen van het sample zijn dan de brekingsindices van alle materialen en de diktes van de afzonderlijke lagen nodig. Omdat een colloïdale laag bestaat uit twee of meer materialen is de brekingsindex niet gedefinieerd. Ook de dikte is niet eenduidig. Toch wordt een colloïdale wordt vaak gemodelleerd als een homogene laag met een eenduidige dikte en een brekingsindex die wordt berekend uit de brekingsindices en de volumefracties van de materialen waaruit de laag bestaat. Deze effectief medium benadering geeft vaak bevreiddende resultaten, maar voor colloïdale lagen van gouddeeltjes op een silicium substraat werkt deze niet.

Deze lagen kunnen wel goed beschreven worden met behulp van de ‘dunne ei-land film’ theorie, die in de jaren zeventig is ontwikkeld door Bedeaux en Vlieger. Dit is een veel complexer model dat fysisch gezien goed aansluit bij de aard van colloïdale lagen. Deze theorie beschrijft de laag daadwerkelijk als een verzameling
van individuele deeltjes op een oppervlak. De meest eenvoudige implementatie van dit model is de geïsoleerde dipool benadering. Deze negeert elektromagnetische interacties tussen de deeltjes en het substraat en tussen de deeltjes onderling. Desondanks komen ellipsometrie spectra die met dit model berekend zijn goed overeen met de gemeten spectra, mits de juiste waarde voor de oppervlaktebedekking wordt gebruikt.

Met behulp van dit model kan de oppervlaktebedekking van een sample bepaald worden uit een gemeten spectrum. De waarde die dan verkregen wordt blijkt alleen rond de 20% overeen te komen met de werkelijke waarde zoals die met elektronenmicroscopie wordt bepaald. Bij een hogere of lagere bedekking treden significante afwijkingen op. De oorzaak hiervan is dat bij de geïsoleerde dipool benadering de deeltje-deeltje en de deeltje-substraat interacties worden genegeerd. Wanneer deze wel in de berekening worden meegenomen resulteert dat over het hele bereik in een erg goede overeenkomst van ellipsometrie en elektronenmicroscopie.

Omdat modelleren erg gecompliceerd kan zijn, is een alternatieve methode voor de analyse van ellipsometrie spectra gewenst. Principal component analysis (PCA) is een statistische methode die gebruikt kan worden voor het analyseren van sets van spectra. Voordeel hiervan is dat er zonder modelleren een inzicht in de trends in een set spectra kan worden verkregen. Deze methode is alleen toepasbaar als de spectra sterk op elkaar lijken. Dit is bijvoorbeeld het geval bij een serie vergelijkbare samples of bij een serie spectra die gemeten zijn tijdens een depositieproces. Van al deze spectra wordt de verandering ten opzichte van het kale substraat berekend. PCA drukt de grootte van deze verandering uit in een enkel getal. Dit getal is een goede maat voor de dikte van een laag of de oppervlaktebedekking van een colloïdale laag.

**Depositie**

De bovenstaande optische technieken zijn gebruikt om de groei van colloïdale goudlagen te bestuderen. Depositie van negatief geladen gouddeeltjes op geoxideerde silicium substraten is geobserveerd met reflectometrie bij één golflengte. Het oppervlak van de substraten is gemodificeerd met een amine verbinding. In waterige oplossing is deze verbinding positief geladen, waardoor de deeltjes elektrostatisch worden aangetrokken door het substraat. Omdat deze aantrekkingskracht vanwege afscherming door de ionen alleen op korte afstand van het substraat merkbaar is, moeten de deeltjes door stroming of diffusie naar het oppervlak bewegen.

Door experimenten uit te voeren onder goed gedefinieerde stromingsomstandigheden kan de adsorptie van de gouddeeltjes bestudeerd worden. De eerste minuten na het begin van de depositie neemt de bedekking lineair toe met de tijd. In deze fase wordt de depositiesnelheid beperkt door de diffusieve aanvoer van deeltjes naar het oppervlak. Na een aantal minuten neemt de depositiesnelheid af omdat steeds minder deeltjes een beschikbare plek op het substraat kunnen vinden. Uiteindelijk
bereikt de bedekking een eindwaarde die hoger is naarmate de concentratie ionen in de suspensie hoger is.

De adsorptie van de deeltjes kan goed worden beschreven met het ‘random sequential adsorption’ (RSA) model. In dit model adsorberen de deeltjes op een willekeurige vrije positie op het substraat, waarna ze zich niet meer kunnen verplaatsen. Daar adsorberen ze alleen als ze geen andere deeltjes raken. Doen ze dat wel dan vindt er geen adsorptie plaats. Dit type interactie tussen de deeltjes wordt harde bollen interactie genoemd. Een tweede kenmerk van RSA is dat de deeltjes na adsorptie immobiel zijn. Het harde bollen concept kan niet verklaren dat de eindbedekking afhankelijk is van de ionenconcentratie. Door het nanodeeltje met zijn elektrische dubbele laag als harde bol te beschouwen, wordt de straal van de ‘harde bollen’ afhankelijk van de ionenconcentratie. Bij een hogere ionenconcentratie is de dubbelelaag dunner en het deeltje effectief kleiner waardoor er meer deeltjes op een substraat kunnen adsorberen. Het gebruiken van deze effectieve grootte in het RSA model resulteert in een goede beschrijving van de bereikte eindbedekking.

Omdat het RSA model alleen de adsorptie van de deeltjes beschrijft, kan het niet het hele verloop van de oppervlaktebedekking in de tijd beschrijven. Het eerste deel van de depositie wordt immers niet bepaald door adsorptie maar door massatransport. Het gegeneraliseerde adsorptie model, dat ontwikkeld is door Adamczyk en medewerkers, koppelt RSA aan transport van de deeltjes naar het oppervlak door diffusie. Met deze uitbreiding kan het hele depositietraject goed beschreven worden.

Depositie van colloïdale films op substraten die geladen zijn door adsorptie of desorptie van ionen uit de vloeistof heeft als nadeel dat het depositieproces nauwelijks beïnvloed kan worden. Dat kan wel als een extern aangelegde potentiaal gebruikt wordt voor depositie. Daarom zijn er experimenten gedaan waarbij positief geladen goud nanodeeltjes met behulp van een extern aangelegde spanning op een goudelektrode zijn aangebracht. Dit proces is met spectroscopische ellipsometrie geobserveerd. De gemeten spectra zijn met PCA geanalyseerd. Tijdens de experimenten is de stroom die door de cel loopt gemeten.

Als er een lage spanning wordt aangelegd vindt er niet of nauwelijks depositie plaats. Er loopt dan ook geen significante stroom door de cel. In deze situatie wordt de aangelegde spanning afgeschermd door een dunne oxidelaag op de elektrode en door de elektrische dubbelelaag. Als de spanning wordt verhoogd neemt de adsorptie sterk toe. Tegelijkertijd wordt er ook een elektrische stroom waargenomen. Verdere verhoging van de spanning zorgt voor een toenemen van zowel de stroom als de depositiesnelheid. Stroom en depositie snelheid zijn blijkbaar aan elkaar gekoppeld. Dit is als volgt te verklaren. De stroom is het gevolg van een elektrochemische reactie die aan de elektrodes lading genereert. Onder invloed van elektrostatische repulsie en diffusie verspreidt deze lading zich door de cel. Het gevolg hiervan is een inhomogene verdeling van lading tussen de elektrodes, die in stand blijft zolang er
stroom loopt. Deze inhomogene ladingsverdeling gaat gepaard met een elektrisch veld dat niet wordt afgeschermd. Dit elektrische veld is de drijvende kracht voor depositie van de gouddeeltjes.

De colloïdale lagen die op deze manier gemaakt zijn, zien er heel anders uit dan de lagen die gemaakt zijn met behulp elektrostatische aantrekking door een geladen substraat. In dat geval liggen de deeltjes los van elkaar op willekeurige plaatsen. Bij lagen die met behulp van een extern aangelegde spanning zijn gemaakt, liggen de deeltjes in clusters die tot enige tientallen deeltjes groot zijn. Deze clusters worden gevormd door op de deeltjes gerichte vloeistofstromingen aan het oppervlak. Deze stromingen zijn het gevolg van inhomogeniteiten van de ladingsverdeling rond geadsorbeerde deeltjes.
List of publications


Curriculum vitae

Dankwoord

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