A study of material condensation on liquid substrates

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A STUDY OF MATERIAL CONDENSATION ON LIQUID SUBSTRATES

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**A thesis submitted to the Nanyang Technological University
in partial fulfilment of the requirement for the degree of
Doctor of Philosophy**

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ANANTHA P

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ABSTRACT

This thesis aims to establish the influence of a liquid substrate on material deposition. The influence of a liquid substrate is explored by a comparative study with an amorphous solid counterpart. Simultaneous gold vapor deposition onto both silicone oil and amorphous carbon was carried out and the morphologies were found to be highly dissimilar. A uniform distribution of condensate following the conventional growth mechanism was observed on the solid substrate. However, on the other hand, low coverage with large empty regions were prevalent on the liquid substrate. This thesis deduces that the effect is due to structural differences between the two substrates. The magnitude of the response of the liquid to the depositing atoms causes the depositing atoms to undergo either desorption or diffusion. The resulting morphology is related to the affinity of the condensing species and momentum transfer accompanying deposition.

In the case of gold vapor deposition, weak interacting forces, combined with higher atomic mass of gold, leads to additional desorption events, giving rise to low coverage condensate on the liquid substrate. Delayed secondary nucleation, along with multilayer growth, is also observed. Therefore, under weak binding forces, a liquid substrate prefers condensate growth over coverage. Furthermore, this mechanism is verified by simulating via the kinetic Monte Carlo technique, the nucleation and growth on a liquid substrate. The simulated morphologies under liquid substrate conditions match well with experimentally observed morphologies. The deposition of copper on the surface of silicone oil resulted in monodisperse nanoparticles uniformly distributed over the surface. This distinct morphology is attributed to differences in the response of the liquid substrate (additional desorption / diffusion events).

A novel phenomenon called shared coarsening, for synthesis of uniformly sized particles on a 2D surface is proposed for particle growth on liquid surfaces. It is the simultaneous coarsening of a smaller particle by several similarly sized larger particles, resulting in monodispersity. Increased diffusion mobility of adatoms on the liquid surface along with an appropriate spatial distribution of the particles is critical for shared coarsening. Thus, a facile nanoparticle synthesis approach has been developed.

A condensate – substrate interaction model has been developed which defines the morphological outcome. Deposition of silver and aluminum onto silicone oil has been studied. The effects of the condensate mass on the perturbation of the liquid molecular arrangement, along with their affinity towards the substrate are discussed. The limitation of a molecular liquid substrate to provide particle stability is overcome by fabrication of highly monodispersed gold nanoparticles on the surface of an ionic liquid. The ionic liquid yields shared coarsening, resulting in spherical particles with uniform size distribution. Thus our model and experiments were utilized to synthesize novel monodispersed nanoparticles.

In summary, vapor condensation onto liquid substrates was studied by determining the effect of the kinetics of nucleation and growth on condensate morphology. The new concepts introduced, along with the synthesis method developed here are thus a step forward to understand and exploit material condensation on liquid substrates.

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Chapter 1 Introduction – Condensation on Liquid Surfaces

1.1 Background

Liquid surfaces play a significant role in everyday life. The interaction between liquid surfaces and vapor molecules forms the basis of macroscopic phenomena, such as the formation of cloud condensation nuclei¹, air-sea gas exchange² etc. Even stratospheric ozone layer depletion is a consequence of the interaction of these two phases. Many industrial processes, such as distillation, desiccation and the manufacture of surfactants also involve gas-liquid interactions^{3,4}.

The use of a reflective liquid in liquid mirror telescopes is also a revolutionary concept utilizing the liquid surface. It was first noted by Isaac Newton that when a liquid is made to rotate, its free surface forms a circular parabolic shape. This shape is put to use in telescope mirrors to focus starlight⁵. The most common liquids conventionally used for this purpose were mercury and low melting alloys of gallium. Only recently was the use of an ionic liquid (with silver thin film deposited onto it) successfully demonstrated as the basis for a lunar telescope (Figure 1.1). The liquid does not evaporate even under vacuum conditions and provides long term stability to the silver film.

Figure 1.1: A Liquid Mirror Telescope (left hand side) showing a liquid mirror of 6 m diameter of a large zenith telescope located at the University of British Columbia. The image on the right hand side shows the image captured using this telescope – showing numerous galaxies [Reference⁵].

Other solids such as polymers have also been deposited onto liquid substrates for the encapsulation and replication of liquid substrates⁶. These solid- on- liquid deposition techniques provide opportunities to develop novel fabrication techniques utilizing the unique liquid surface structure. Conventional physical or chemical vapor deposition techniques, combined with processes such as dip coating, facilitates fabrication of 3D patterns. These processes would be difficult to realize without the help of liquid substrates/liquid sacrificial layers. Therefore an in-depth understanding of the influence of the liquid upon the condensing species is essential to realize its potential applications.

The liquid surface energy and the wetting characteristic at the solid - liquid interface is of importance in this study^{7,8}. The molecular level interaction between the solid and liquid interface results in consequences observable at the macroscopic scale. The liquid surface molecules behave differently at the interface as compared to their bulk, due to the net inward attractive force. This net inward force on the liquid surface behaves as an elastic skin and constantly tries to decrease its area. This way of describing surface free energy of a liquid was first put forward by Young in 1805⁹. These surface tensions generate forces

acting along the interface and the contact angle is determined by the surface tensions of three pairs of materials and is dependent on the relative values of surface tension between solid – vapor (γ_{SV}), solid – liquid (γ_{SL}) and liquid – vapor (γ_{LV}).

At solid-liquid interfaces, the work of adhesion is quantified as wetting. This is directly related to the liquid contact angle of the solid and is represented through the well-known Young-Dupre equation and predicts^{10,11}:

Complete wetting: $\gamma_{SV} > \gamma_{SL} + \gamma_{LV}$ (1)

Zero wetting: $\gamma_{SL} > \gamma_{SV} + \gamma_{LV}$ (2)

It is to be noted that, the work of adhesion drives the restructuring at the interface in the absence of chemical reactions. Therefore the work of adhesion is a critical driving force for the densification and ordering at the interfacial liquid. The relative surface energies for the materials discussed in this thesis are given in Table 1.1(a) and Table 1.1(b)

Table 1.1: (a) The surface energy value for condensate materials tabulated¹² is an average of the values along (111), (100) and (110) planes. (b) The surface tension values of the two primary liquids is tabulated according to reported literature¹³.

(a)	Condensate Material	Surface Energy(mJ/m ²)	(b)	Liquid Substrate	Surface Tension (mN/m)
	Gold	1536		Silicone Oil	30.9
	Copper	2118		Poly Phenyl Ether	49.9
	Silver	1203			
	Aluminum	1272			

The liquid surface tension is affected by several parameters such as presence of impurities, temperature changes or the modification of the bonding characteristics of surface molecules with various chemicals⁷ In most liquids, as temperature increases

surface tension decreases. Impurities such as surfactants, have significant influence on surface tension as they segregate to the surface and resist stretching. The surface tension of surfactant solutions depends on the number of surfactant molecules at the interface. When a particular surfactant is considered, the higher the surfactant molecules concentration, the lower is the surface tension [crude oil].

The role of substrate during the growth of metallic islands and thin films has been previously investigated. Considering the wetting characteristics of the condensate, epitaxial thin film growth is known to occur in three different modes¹⁴. They are (a) layer – by – layer (2D) growth (Frank-van der Merwe mode) which corresponds to complete wetting; (b) island (3D) growth (Volmer – Weber mode), which corresponds to a incomplete wetting angle (dewetting) and (c) layer – by – layer and island growth (the Stranski–Krastanov (SK) mode), which corresponds to an intermediate wetting scenario. The interaction between the adatoms and the substrate is critical to these modes of growth. A strong interaction between the condensate atoms and substrate leads to the layer- by layer growth mode with high crystalline quality of the thin film. Weak interfacial bonding results in 3D growth and a large lattice mismatch (or large interfacial energy) in a system gives rise to SK growth mode.

The Volmer – Weber growth mode is particularly relevant to this study. According to this model, island growth occurs to maximize exposed substrate area, thereby minimizing surface energy. The condensate atoms are more strongly bound to each other than to the substrate. The growth on liquid substrate is reported to be a two-stage process – which involves the formation of condensate islands and their subsequent growth. The growth of islands and their aggregation mechanism on liquid substrates has been reported

extensively.

In this study, therefore, the focus is on vapor deposition onto liquid substrates. An analysis of the importance of the liquid structure on condensate growth, occurring in the initial stages is provided. In particular, studies of interactions between metallic vapor and the liquid surface, is investigated in detail. The synthesis of metallic nanoparticles and a study of condensate growth on liquid substrates are described. Thus, the main objective of this thesis is to establish the role played by the liquid substrate during material condensation. The motivation of this work is now discussed.

1.2 Motivation

The condensation of water vapor onto a cold surface and their subsequent self-arrangement into ordered arrays is known as breath figures^{15,16}. The concept of breath figures is widely utilized for the fabrication of ordered porous polymeric thin films¹⁷⁻¹⁹. Water vapor is condensed onto an evaporating solution of a volatile liquid and dissolved polymer. The condensed water droplets self assemble into close packed structures. Upon complete evaporation this ordered assembly of water droplets leaves behind a porous polymeric thin film. This formation technique has been utilized for the synthesis of a variety of novel patterns such as nanorings^{20,21}, functionalized surfaces²², hierarchical structures^{23,24}, etc.

Our porous polymeric films, synthesized via the breath figure technique, are shown in figure 1.2. A variety of polymers such as mono-carboxy terminated polystyrene (PS_m), Poly(methyl methacrylate) (PMMA), etc. were dissolved in organic solvents such as toluene, carbon disulphide (CS₂), chloroform, etc. A variety of pore sizes in the range of 0.8 μm -5 μm in diameter were obtained. The pores are ordered into hexagonal arrays

with large domains, with domain size of the order of tens of μm . Figure 1.2(c) shows the formation of a hierarchical structure of polystyrene (PS) colloids dispersed in pores, obtained via the breath figure technique.

Figure 1.2: Scanning Electron Micrographs showing films of (a) the ordered porous polymer (PSm in CS_2 – 1wt %) (b) PMMA obtained from its solution in toluene and (c) PS colloids dispersed in pores of PSM; all obtained via the breath figure synthesis technique.

A number of mechanisms discussing the formation of these structures have been reported. A summary of the three main proposed mechanisms is presented. Francois et al²⁵ suggest that condensed water droplets touch the solution surface and their subsequent polymer encapsulation is responsible for their non-coalescent nature. Shimomura et al^{26,27} claim that the submerging behavior of the water droplets into the organic solution arising from Marangoni and thermocapillary forces leads to the final stage of ordering of the droplets²⁸. Finally the popular mechanism of Srinivasarao et al suggest a mechanism of water droplets levitating over the surface seconds before they sink in the last stage¹⁷. However, all these theories agree on the polymer bagging effect in the final stage¹⁶, which results in the formation of mesoporous polymeric films.

An in-situ video captured using an in house set-up, showed the arrangement of condensed water droplets on the surface of a liquid solution of carbon disulphide and monocarboxy-

terminated polystyrene (Figure 1.3). It was observed that ordered water droplets grow at a uniform rate, maintaining their monodispersity in sizes (Figure 1.3a and 1.3b) and coalesce only in the last stages. The first two optical micrographs (snapshots from the video captured *in-situ*) of Figure 1.3 show the water droplets arranged in a close packed structure on the liquid surface. Figure 1.3c shows the late stage coalescence of the water droplets, leaving behind the porous polymer with the water droplet “imprints”. This led us to investigate the role played by the liquid on the kinetics of vapor condensation, in particular the influence of the substrate on nucleation and growth. From the study of breath figure formation on paraffin oil¹⁵ the uniformity of the water droplet sizes was attributed to the liquid surface. A nucleation and growth mechanism has been put forward by Beysens et al²⁹. Further, even when water vapor was condensed onto a pure organic liquid (without dissolved polymer), formation of monodisperse water droplets was still observed, in agreement with the literature³⁰.

Figure 1.3: Formation of Breath Figure Arrays - Video frames taken at (a) 22s; (b) 40s; (c) 77s after introducing water vapor onto a drop of 1wt% monocarboxy-terminated polystyrene in carbon disulfide solution.

Therefore this unique method was utilized and a new method for the formation of arrays of ring- like structures of CdSe nanoparticles was developed¹⁹ in this study. The nanoparticles were dispersed in a volatile organic solvent and a drop of it was cast on a solid substrate.

Water vapor introduced over it resulted in condensation of water droplets (breath figures) on the liquid surface. Further assembly of dispersed nanoparticles at the water-solvent interface resulted in the formation of arrays of CdSe nanoparticle rings (figure 1.4). The rings were in the size range of 1.5 to 2 μm .

Figure 1.4: (a) Optical micrograph and (b) Scanning Electron Micrograph of CdSe nanoparticle rings along with a magnified image (inset).

These results of water vapor condensation obtained onto liquid surfaces motivated us to think about the possible outcome of depositing metal vapor onto a liquid substrate. Would it give rise to the formation of uniform nanoparticles? Would the condensate morphology be different from its solid substrate counterpart? Thus the current study of material condensation onto liquid substrates was initiated to explore these questions. The main objectives and scope of this work are now discussed further.

1.3 Objectives & Scope

The main focus of this thesis is to investigate condensate growth dynamics on a liquid substrate up to the thin film formation stage. The primary objectives are:

1. Investigate the influence of liquid substrate on condensate morphology

First, a comparative study of metal vapor deposition on a liquid substrate and a counterpart solid substrate is presented. Differences in condensate morphologies are related to increased vapor deposition time and variation in flux of the condensate. Distinct condensate characteristics of low non uniform coverage and increased multi layer growth found on liquid substrates are attributed to the liquid structure. A model considering the influence of the liquid structure on growth kinetics is described.

2. Model the effect of liquid substrate structure on nucleation and growth

Direct experimental observations of the influence of the greater number of degrees of freedom of the liquid substrate on growth kinetics are challenging. Hence, the kinetic Monte Carlo simulation technique is adopted to investigate the effect of different substrate conditions. Simulation variables, such as substrate molecular frequency and adsorption probability, are used to differentiate solid and liquid substrate properties. Time resolved condensate coverages are generated at varying substrate conditions and are correlated with experimental results. Low condensate coverage resulting from liquid substrate conditions (high molecular frequency and low adsorption probability) aid in verifying the initial hypothesis from experimental observations.

3. Study the emergence of monodispersed particles in a 2D particle growth environment

A novel growth mechanism called ‘shared coarsening’ is developed to obtain monodisperse particles under 2D growth conditions. The effect of surface diffusion kinetics and substrate adsorption probability is examined. First via simulation study, conditions to obtain a narrow particle size distribution were optimized. The proposed

shared coarsening model and the conditions giving rise to monodispersed particles are discussed. Further, uniform sized copper nanoparticles are synthesized on the liquid surface, serving as an experimental example of the proposed mechanism.

4. Evaluate the importance of condensate – liquid substrate interaction

The key parameters responsible for the type of condensate microstructure obtained on the liquid substrate are identified. The deposition of two other types of vapor, namely silver and aluminum, with varying mass and binding energy onto the liquid is investigated. The two main consequences of (a) low, non-uniform condensate coverage and (b) uniform coverage of spherical nanoparticles with narrow size distribution are demonstrated. Conclusions are made related to utilizing liquid substrates.

5. Fabrication of highly monodispersed nanoparticles on a liquid substrate

Lastly, the final objective is to utilize the effects of the liquid structure (established in the earlier chapters) to demonstrate an one step facile synthesis technique for monodisperse nanoparticles. Physical vapor deposition of metal on ionic liquid is utilized in this study. The use of ionic liquid to provide higher stability for particles (compared to molecular liquids) was explored. An environmentally friendly, short alkyl chain length PMIM(I) ionic liquid was utilized as the substrate.

1.4 Significant Findings & Innovative Aspects

The main focus of this work was to investigate the influence of the liquid substrate on condensate nucleation and growth. Firstly, our comparative study of simultaneous vapor deposition onto a liquid as well an amorphous solid substrate revealed distinct condensate

growth morphologies. Randomly distributed, low condensate coverage was observed on the liquid substrate unlike the uniform coverage obtained on the solid surface. A novel liquid substrate effect was deduced, based on the effects of structural differences among the two substrates on condensate morphology. The entropic response of the liquid structure to the perturbation to its structure causes additional desorption of condensate atoms, resulting in low coverage. This response of a non-rigid substrate is likely for minimally interacting condensate-substrate binding energies, due to its additional degrees of freedom.

Secondly the growth of monodispersed copper nanoparticles was observed upon physical vapor deposition onto the surface of a molecular liquid (silicone oil). Formation of uniformly sized particles was attributed to the occurrence of shared coarsening – an innovative growth mechanism introduced in this study. The mechanism involves the simultaneous coarsening of a secondary nuclei by several primary nuclei, resulting in the growth of the latter at the expense of the smaller particles. This was observed to be the result of the geometrical arrangement of the particles (resulting from exclusion zone model) and is critical to diffusion kinetics on the growth surface. Based on these condensate-substrate interactions, a generic model was developed for varying condensate mass and condensate-substrate affinity.

Lastly, the original knowledge developed was utilized to maintain particle monodispersity on liquid substrates. Uniformly sized nanoparticles formed on molecular liquid surfaces undergo coarsening or coalescence with growth, resulting in polydispersity. To prevent coalescence and introduce shared coarsening (to maintain particle uniformity), ionic liquid substrates were used. The synthesis of uniformly sized Au nanoparticles with improved

particle stability was demonstrated using the novel physical vapor approach on liquid substrates.

1.5 Organization of the Report

This thesis comprises 7 more chapters related to the study of liquid substrates:

Chapter 2 - Literature review: It provides the background information on the structure of liquids relevant to the current study along with a review of research utilizing a liquid substrate for vapor condensation.

Chapter 3 – Materials & Methods: The materials utilized in this work along with experimental methods are presented in this chapter.

Chapter 4 – Results & Discussion - **Liquid Substrate Effect on the Condensate:** A comparative study of metal vapor deposition onto a liquid as well as a solid substrate is presented. A condensate growth model emphasizing the influence of the liquid substrate is proposed.

Chapter 5 – Results & Discussion - **Simulation of Nucleation & Growth on Liquid Surfaces:** The proposed growth model on liquid substrates is modeled using the kinetic Monte Carlo simulation technique.

Chapter 6 – Results & Discussion - **Shared Coarsening on Liquid Surfaces:** The growth of uniform nanoparticles, arising from the effect of a proposed novel phenomenon termed as shared coarsening, is described. Simulation and experimental results are presented.

Chapter 7 – Results & Discussion - Importance of Condensate – Substrate Interaction:

The condensate – substrate interaction is further studied by deposition of additional metals, verifying the effect of the liquid substrate. In addition, the fabrication of highly monodispersed gold nanoparticles (NPs) by metal vapor deposition onto ionic liquids (IL) is presented.

Chapter 8 – Conclusion & Future Work: A summary of the current work along with recommendations for future work are discussed.

Chapter 2 Vapor Deposition onto Liquid Surfaces

2.1 Introduction

The interaction of gas molecules with liquid substrates can result in a variety of outcomes, depending on the energy exchange between the two interacting materials. The intermolecular forces, which define the liquid properties, also play a critical role. A variety of techniques have been utilized to characterize the liquid structure as well as to understand vapor-liquid interactions. These examples establish the importance of the liquid-vapor interface. The objective is to understand the atomistic processes, with a focus on the influence of liquid structure on these processes. In particular, metal vapor condensation onto liquid surfaces is reviewed. Thus the liquid structure and the various models describing it are briefly discussed, followed by methods to study the liquid substrate.

The areas discussed in this chapter include: (1) liquid structure and gas-liquid interface characteristics with respect to a variety of liquid substrates (2) analysis of the structure of the liquid surface and its interaction with gas molecules/atoms at the liquid-vapor interface; (3) methods of metal vapor deposition onto liquid surfaces. This chapter highlights the gap in liquid substrate studies for metal vapor deposition and also examines models for growth on liquid substrates.

2.2 Liquid Vapor Interface:

2.2.1 Structure of a liquid:

A liquid is a homogeneous, coherent but irregular arrangement of atoms/molecules³¹. Most of its unique properties arise from its distinctive interatomic/ intermolecular forces.

Liquid atoms/molecules, unlike in solids, possess additional degrees of freedom of motion. A degree of freedom can be defined as a parameter to characterize the state of a system^{31,32}. A difference between a solid, liquid and gas phase is their degrees of freedom for translational particle movement. Molecules in the solid state do not possess degrees of freedom for free molecular motion and each direction of motion is occupied by intermolecular forces. In the liquid state, molecules have two coordinates of free space for molecular motion. Therefore they show two-dimensional movement – but are still influenced by intermolecular force³³. The structure of a liquid is further analyzed using a variety of models.

The early liquid structure studies assumed that these structures were largely dependent on the repulsive forces between atoms (r^{-12}). The initial hard sphere model did have a characteristic nearest neighbor distance even in the random liquid structure. The most significant feature, was the variation in coordination number (5 – 11), unlike the fixed 12 nearest neighbors in a regular closed packed crystalline solid. Nonetheless, some of the property of translational invariance can still be observed in liquids. Close packing in a liquid implies high degree of uniformity in the density of the assembly. For instance, any compact volume of the liquid containing a couple of hundred atoms can be exchanged for a similar volume from another region, without causing any significant disturbance. Therefore the material is known to be statistically homogeneous over several orders of length. It may thus be represented approximately as a continuous medium^{34,35}.

Further, dense random packing of spheres was modeled as an arrangement of polyhedral holes with atoms at vertices¹⁹. The expansion of these holes between atoms and a gradual shift towards lower coordination numbers was suggested to occur with an increase in

temperature. Eventually, the intrinsic liquid coherence is lost on approaching the boiling point, where the transition to a gas occurs. The change in atomic arrangement is illustrated in Figure 2.1 and is critical in analyzing liquid/vapor interfacial structures.

Figure 2.1: Coherent Liquid – Incoherent Gas: Illustration showing the atomic arrangement transition from a close packed liquid structure to a gas, close to the critical point. The liquid vapor interface is indicated by the dotted line [Reference³¹]

The atomic structure of a liquid was conventionally characterized using X-ray diffraction techniques and is represented by the radial distribution function. To understand the structure of a liquid, the radial distribution function was studied with increasing temperature, from solid to liquid (Figure 2.2). The absence of long range order in a liquid is clearly seen in comparison to an FCC solid, as well as a solid held at a temperature slightly below its melting point³¹. The liquid phase between the crystalline and gaseous state is characterized by short range order and high density. According to the density distribution functions, the atoms have the form of hard spheres in the liquid. As per the

linear model, the function oscillations are accentuated with increase in concentration. The first and maximum peak (Figure 2.2c) correspond to a distance equal to the diameter of the atom. In addition, these theoretically predicted patterns for a collection of hard spheres are found to be true for monatomic liquids^{35,36}.

Figure 2.2: Liquid vs Solid Structure and Absence of long range order - Radial density distribution functions obtained from x-ray studies and neutron scattering studies for (a) Close packed FCC solid at low temperature, (b) solid below melting point (T_M) (c) for a liquid (d) The pair potential for two molecules in a liquid with its density distribution as shown in (c) [Reference³¹]

On the other hand, amorphous structures are characterized by a distribution function $P(x)$ for X-rays. There is no clear distinction between the function corresponding to highly compressed gases and liquids, or between vitreous solids and liquids. The distribution function $P(x)$ varies progressively with degree of condensation and with degree of organization of the samples³⁶.

2.2.2 Comparison between a dielectric liquid and metallic liquid:

A comparison of a dielectric liquid and a metallic liquid transition zone structure is shown in Figure 2.3³⁷. The nature of the interatomic interactions at the two surfaces is fundamentally different. Molecular liquids display van der Waals (VDW) type of bonding. On the other hand there is metallic bonding at liquid metal surfaces. In high density metallic liquids, interactions between the quantum Fermi fluid of free electrons and the charged ion cores of the classical liquid result in a complex interplay of forces. Apparent oscillations across the liquid-metal density profile indicate atomic layering at the interface^{37,38}. Also, the difference between metallic interaction at the liquid surface and the dispersive forces present in the vapor above it induces distinct liquid metal interfacial properties. Thus the study of metallic liquids and the characterization of their interface is intriguing and challenging³⁹.

Figure 2.3: Dielectric vs Metallic Liquid - Difference in inter atomic interactions between a dielectric and metallic liquid shown at the liquid - vapor interface [Reference³⁷]

Liquid surface structures have been analyzed by both experimental and simulation

techniques. They have been probed by x-ray scattering studies using synchrotron radiation sources⁴⁰, along with advanced optical techniques and / or molecular beam scattering. Measurements have been made for both metallic and molecular liquid surfaces^{41,42}. A short review of the occurrence of layering in metallic liquids is discussed, followed by a review of scattering studies at the gas-liquid interface.

2.2.3 Layering at Metallic Liquid Surfaces:

The existence of atomic layering at the liquid-vapor interface was first predicted by Rice et al⁴³. The first experimental evidence came from measurements across the surfaces of mercury and gallium⁴⁴. According to their results when a peak in the reflectivity measurements at high momentum was seen, transfer was observed, which indicated the presence of atomic layering. A significant peak was identified for the case for metals with high surface tension. However, for low surface tension metals only a minor effect was observed³⁷. The presence of capillary waves due to thermal excitation causes additional difficulty for density profile fitting, especially for low surface tension metals. This is because these waves cause dampening of the intrinsic structure of the liquid and these waves cannot be easily measured. In the case of Sn⁴⁵ and Bi⁴⁶ the distance between the first two layers from the surface was observed to be smaller in comparison to the spacing of subsequent layers.

Water has been reported not to display any signs of layering at its free surface⁴². On the other hand, molecular and dielectric liquids display promising results for layer formation. This has been reported for the isotropic liquid tetrakis (2-ethylhexoxy)silane⁴⁷. These studies show that liquid surfaces may not display a monotonic density profile.

2.3 Processes at Liquid Interface:

2.3.1 Scattering Studies at the Gas – Liquid Interface:

The molecular beam scattering technique is widely used to investigate liquid surfaces^{3,48}. More importantly it is used to explore the various modes of interaction of gas atoms, which either (a) scatter from or (b) which are accommodated onto or (c) even dissolve/react with the liquid. Several studies⁴⁹ have been reported which explore the influence on energy transfer due to critical parameters such as E_{inc} (incident energy), angle of incidence (θ_{inc}), mass of the gas (m_{gas}) and surface (m_{surf}) molecules, temperature (T_{liq}) and attractive forces. Various gas species, such as Ne/Ar/Xe, CH₄, NH₃ and D₂O have been directed towards liquids such as glycerol^{50,51}, squalene⁵² and perfluorinatedpolyethers⁵³ or even onto concentrated sulphuric acid^{54,55}. Metallic liquid surfaces such as indium, gallium, bismuth^{52,56} etc. were also studied using this technique. Furthermore, even protic gases like water, alcohols, and carboxylic acids have been directed towards liquid surfaces⁵³. All these interactions provide insight into the liquid structure.

An experimental set up (Figure 2.4) used to carry out molecular beam scattering is discussed. A mono-energetic atomic or molecular beam generated from a pinhole nozzle via supersonic expansion is directed onto a liquid surface. The nozzle temperature and appropriately chosen carrier gases are utilized to tune the incident energy. The liquid film is brought to the top using a rotating wheel installed inside the chamber. A razor blade was used to scrape away the surface to result in a 0.2 mm fresh layer⁵⁷. The atoms/molecules striking the clean surface could either get trapped at the interface momentarily prior to dissolution/desorption or bounce directly off the surface. A mass

spectrometer is used to record the direction and velocity of the scattered or desorbed species along with identifying the species. Figure 2.4 shows the set-up used by Nathanson et al⁴⁰.

Gases having short arrival times have high velocities and recoil energies, they also transfer minimum energy. On the contrary, almost complete energy transfer to the liquid phase is expected from gases arriving at prolonged times with low velocities. Thus the arrival time and the velocity of the gas species is a prime indicator of the energy transfer characteristics.

Figure 2.4: Molecular Beam Scattering - Set-up utilized for molecular beam scattering experiments carried out for liquid substrates [Reprinted with permission from reference⁵⁷. Copyright © 2006, American Chemical Society]

The pathway taken by the colliding atoms or molecules was largely divided into two limiting processes, i.e., direct inelastic scattering (IS) and trapping desorption (TD)⁵⁸ (Figure 2.5). For example, consider the molecular scattering of D₂O molecules from liquid

glycerol⁵⁹. When the IS pathway is chosen, D₂O molecules appear to be impulsively scattered, undergoing one, or only a few, hard sphere like collisions with the protruding functional groups of OH/CH_x. These possess high recoil energies, with only a part of their energy transferred. Further, it is important to note that, during this process, the impact energy is transferred to the hindered vibrational, torsional and translational motions of the liquid molecules⁶⁰. Such an observation was first put forward during the scattering of neon atoms from the surface of liquid squalene⁵⁷. In addition, the difference between the incident and final translational energies of the neon atoms is equivalent to the energy lost. Trapping desorption (TD), on the other hand, allows multiple collisions, which drains away most of the kinetic energy, causing it to be trapped on the surface. Referring back to the D₂O/glycerol system, TD is favored when collision occurs at either the soft or the rough sites of the glycerol molecules. When it is in this trapped state, the atom could momentarily be dissolved into the liquid phase. However, thermal motion of the liquid molecules at the surface propel the atoms to undergo desorption⁶¹. Also, attractive forces which bind the gas molecule to the surface enhance this large scale energy transfer process⁶². In a relatively less soluble gas species and liquid system, it is more likely that greater numbers of atoms will desorb back, probably without penetrating the bulk liquid. The path chosen by the incoming gas atoms cannot be completely traced only by the velocity distribution. Nevertheless, several parameters critical to the kinematics of gas-liquid collisions have been identified. These are discussed further as they aid in understanding other gas-liquid interactive systems as well.

Figure 2.5: (a) The possible outcome of collision with a liquid surface is illustrated along with (b) the hard sphere behavior and collision between gaseous species and surface [(a) Reprinted with permission from reference⁴⁸. Copyright © 2000, American Chemical Society, (b) Reprinted with permission of Annual Reviews from Reference⁴⁸. Copyright ©]

Nathanson et al formulated guidelines to predict scattering and trapping probabilities. These rules have originated from interactions at the gas-solid interface. The very first determining factor is the point of contact of the gas species with the liquid surface group. The angle of deflection X on colliding with the protruding segments of the liquid (behaving as hard spheres) defines the amount of impulsive energy transfer. Secondly, the ratio of mass of the gas species to the mass of the surface molecule ' μ ' is critical to energy transfer. The energy transfer is predicted to be higher when the mass ratio is higher. Hence efficient energy exchange is said to take place during head on collisions of heavy gaseous atoms with low-density liquids. The energy transferred was modeled according to the method of Harris et al⁶³:

$$\frac{\Delta E}{E_{inc}} = \frac{E_{inc} - E_{fin}}{E_{inc}} \approx f(\mu, \theta_{inc}^{loc} \text{ or } X) \cdot \left[1 + \frac{V - 2RT_{liq}}{E_{inc}} \right] \quad (2.1)$$

Here, V is the potential well depth, other parameters are as shown in Figure 2.5. The term f is expressed as:

$$f(\mu, \theta_{inc}^{loc} \text{ or } X) = \frac{4\mu}{(1+\mu)^2} \cos^2 \theta_{inc}^{loc} \quad (2.2)$$

The energy transfer process shown in equation 2.1 involves both kinematic and energetic terms. The kinematic terms consists of the momentum transfer, which is dependent on $f(\mu, \theta_{inc}^{loc})$. The acceleration of the incoming molecule is determined by the V/E_{inc} term. As the velocity of the gas molecule is relatively higher when it approaches the surface, the net effect of surface thermal motions is to provide momentum to the gas molecule, thus reducing energy transfer. However, as incident energy E_{inc} increases, these effects have minimal contribution to energy transfer. The outcome of most gas-liquid collisions is found to be in good agreement with equation 2.1⁴⁶.

The collective interactions of surface molecules also play a key role in these collision effects. Firstly, surface roughness brought about due to an increase in temperature causes incoming species to undergo multiple bounces. This increases trapping along with scattering events^{64,52}. Using simulation studies, Benjamin et al also suggested collective interactions between solvent molecules to trap an incoming species⁶⁵. The ‘like traps like’ rule was introduced, as an increase in trapping probability was observed with higher solubility of gas molecules in the liquid⁵⁰.

To summarize, findings from the molecular beam technique provide broad understanding of energy transfer processes along with chemical reactions occurring a gas/liquid interfaces. A short review of studies utilizing a liquid-liquid interface for material growth

is presented. The interface between two liquids was considered to be defect free, without permanent preferential nucleation sites⁶⁶, similar to the liquid – gas interface.

2.3.2 Material Growth at the Liquid-Liquid Interface

The absence of permanent preferential nucleation sites at the liquid – liquid interface makes it an interesting growth environment to be studied⁶⁷. This interface has been utilized for deposition of various metallic films (gold, copper, silver)⁶⁸. Rao et al have successfully demonstrated interfacial reduction of metals at the water/toluene interface for formation of metallic films. Schiffrin and Cheng have utilized an applied potential to control formation rate of gold nanoparticles at the liquid–liquid interface⁶⁹. Gold nanoparticles formation resulted due to reduction of the organic phase AuCl_4^- by aqueous $\text{Fe}(\text{CN})_6^{4-}$ ⁶⁶. Deposition studies of metallic nanoparticles at membrane supported liquid–liquid interfaces have utilized polarization measurements across this interface^{70–74}. This methodology is considered to be intermediate between the cases of solution phase metal reduction and conventional electrodeposition⁷¹. Although chemical growth methods are mostly employed here, kinetics of overlap of diffusion fields in both liquids and occurrence of nucleation at the interface is intriguing and has been modeled⁶⁶. Liquid–liquid interfaces have been extensively studied for self assembly of preformed nanoparticles driven by reduction in interfacial energy⁷⁵. Studies related to oxide growth on metallic liquid surfaces also discuss the effect of a defect free liquid surface. Thus, the studies reviewed describe deposition, aggregation and growth of condensates on liquid substrates. Firstly, growth of an oxide layer on metallic liquid surfaces is reviewed. In addition, the influence of the liquid structure on oxidation is highlighted.

2.3.3 Oxidation of Metallic Liquids:

Basic processes such as- adsorption/desorption, diffusion and nucleation occurring on a metallic liquid have been studied *via* surface oxidation. These studies are related to the current study. The difference between oxidation on a solid and liquid metallic surface of tin was identified by Noack et al³⁹. Utilizing low energy electron loss spectroscopy (LEELS) and Auger spectroscopy changes in oxide growth rate, continuity and / or stoichiometry were reported for tin at varying temperatures. With exposure of liquid tin (close to its melting point) to oxygen, growth of a continuous solid oxide (primarily SnO) was reported, unlike that of the SnO₂ enriched surface on single crystal or polycrystalline tin⁷⁶. The rate of oxidation of solid tin is significantly enhanced by the presence of a large number of surface defects⁷⁷. When an area displays a defect free surface, it has been reported to be insensitive to oxygen exposure, the rate of oxidation is low under such conditions. A study by Pershan et al⁴⁰ on the oxidation of Sn reported the requirement of a threshold oxygen pressure for the occurrence of homogeneous nucleation on an oxide free surface⁷⁶ of liquid tin. With respect to absence of defects on the free surface of the liquid metal, a threshold oxygen pressure for occurrence of homogeneous nucleation was anticipated. Below a pressure threshold (oxygen exposure of 50×10^{-6} Torr for 1 s) negligible oxidation was observed, indicating liquid tin resistance to oxidation⁷⁶. Such observations were first made for Sn, and were not reported from oxidation studies of other metallic liquids, such as gallium or indium. X-ray scattering technique results on the surface oxide of liquid Ga⁵² indicated formation of a uniform layer preventing further oxidation, the layer was amorphous in structure. In the case of liquid In, a rough oxide film with negligible x-ray reflectivity signals was reported⁷⁸.

Oxidation of liquid gallium surfaces from simulation studies were found to display fractal like patterns (Figure 2.6) and were investigated experimentally^{79,80,81}. Growth of the oxide with time was observed using Secondary Ion Mass Spectroscopy (SIMS) micrographs acquired *in situ*. The formation of the fractal-like oxide pattern was attributed to the DLA (Diffusion Limited Aggregation) mechanism under non-equilibrium conditions. Changes in oxide patterns to smooth boundary patterns were observed, separated by uniform gaps of un-oxidized liquid. This could be due to (a) impurities confined to the liquid only, promoting the reordering of the oxide or (b) interfacial tension or (c) reduction in oxide sticking probability⁸². Thus the diffusion–aggregation process is modified on a liquid surface. Spatial and temporal scaling property studies of oxide growth show that oxide aggregation on liquid gallium bears a close resemblance to reaction-limited cluster-cluster aggregation. More importantly, the requirement of more than one unique length scale to describe microstructural evolution of a system has been suggested.

Figure 2.6: Oxidation of Liquid Gallium - Oxide clusters obtained on the surface of liquid gallium showing the various aggregation stages with time [Reference⁸⁰]

The unique oxide patterns on metallic liquids and the difference of these patterns from their solid substrate suggest the strong influence of the properties of the liquid. The conclusions drawn from these studies are mostly specific to oxidation of metallic liquids

only. Nevertheless, differences in growth dynamics on any liquid surface can be expected to be distinct from the primary stages of adsorption/desorption. This suggests the necessity to develop a more general model of condensate growth on liquid surfaces. Thus, a solid–liquid comparative study, such as the one developed in this study, is highly beneficial to realize the potential uses of a liquid substrate. A physical vapor deposition technique is employed in the current research work. Importantly, deposition of metallic vapor onto molecular and ionic liquid surfaces was studied. The studies reviewed below highlight current progress in this field.

2.4 Physical Vapor Deposition onto Liquid Surfaces:

The formation of metallic thin films is strongly influenced by the surface characteristics of the substrate. The structural properties of thin films change significantly with changes in substrate properties, such as surface energy, roughness, temperature and structure (or phase). The structure-property relationships result in a change in metallic thin film properties (electrical, optical, mechanical, etc.), leading to several investigations to employ liquid surfaces for film formation⁸³. The pioneering studies carried out by Ye et al⁸³ demonstrated the fabrication, utilizing RF-magnetron sputtering, of rough metallic films on the surface of silicone oil. The films displayed distinct microstructural (percolation structures & rough thin films) and electrical properties (non-linear dc I - V characteristics of metallic rough films). Condensate growth observed in their study on liquid substrate, begins with the formation of percolation structures (random fractals) followed by gradual growth of the metallic clusters and their interconnection on contact, resulting finally in a continuous rough thin film displaying a unique growth morphology. A difference in film thicknesses on the two substrates was reported. The film thickness

was much smaller than to the film deposited on a glass surface ($d > 5000 \text{ \AA}$). The liquid surface was reported to require a minimum incident power below which film formation would not occur, unlike the observations made on glass substrates. At low incident RF power conditions ($< 30 \text{ W}$), a majority of the sputtered products are expected to be independent metal atoms (Ag), given the lower Ar ions energy. It was put forward that evaporation or the penetration of these independent atoms on striking the liquid surface, was not difficult. On the other hand, on increasing the incident power, Ag atomic clusters are in majority in the sputtered products. Therefore an increase in deposition rate was observed due to (a) interaction between the atoms in the Ag clusters and (b) reduced mean free path of the cluster compared to individual atoms. Therefore a second evaporating effect and a penetrating effect of the depositing atoms (generated under low incident power conditions) were proposed to result in smaller deposition rate in the initial stages. Furthermore, during the early deposition time this study also proposes a high increase in local temperature of the oil surface due to the strong strikes of the Ag atoms. Combined influence of rise in temperature and the interaction with the liquid surface is proposed to cause both the second evaporating effect and the penetration effect. Although the anomalous deposition rate relies heavily on the nominal film thickness, the role of the liquid (or any other material properties) in causing such an effect or the dynamics of metallic atoms on the liquid surface contributing to formation morphology have not been investigated in detail. This is identified as one of the important science gap in vapor deposition on liquid substrate studies.

The electrical property investigation of the rough Ag films formed on the surface of the liquid displayed random resistance fluctuation. It was proposed that the increase in

temperature with an increase in breakdown current (I_c) caused liquid dynamic viscosity to be reduced. As a consequence an unstable shift between the clusters was observed (due to melting of the links between the percolation structures), resulting in the random resistance fluctuation. As this behavior was not observed for other percolation films, the behavior was attributed to both the microstructure and the liquid substrate effect.

Various condensed structures, ranging from metallic clusters⁸⁴ to percolation structures⁸³ to stress free buckling films⁸⁵ were fabricated on liquid substrates. The condensate morphology on liquid surfaces displayed fractal like structures. The non-lattice/liquid substrate condition was modeled considering the difference in island/cluster diffusion properties. This was carried out by varying the diffusion step length and/or the island/cluster rotation angle⁸⁶. The island fractal dimensions were found to be independent of diffusion step length, rotation and mobility of the islands. These simulated morphologies were correlated with the experimental results obtained of silver islands on silicone oil⁸⁷. Importantly, the silver island *morphologies* were similar to aggregates obtained on solid substrates^{88–90} with the average sizes reported to be the only difference. Therefore it was indicated in this study that fractal dimension is not the suitable parameter to distinguish aggregation mechanism⁸⁶.

On the other hand, a theoretical model modifying the fractal growth model shows that fractal aggregation dynamics are strongly influenced by deposition flux and cluster rotation on the surface of liquids⁹¹. The nucleation and growth of Ag clusters on silicone oil displaying fractal morphology with increase in growth time was discussed. Microstructural evolution, i.e., deposition, diffusion, rotation and aggregation (DDRA) model of clusters on liquids was put forward. These studies are discussed in detail in

chapter 5. Other studies of metal deposition on oils reported bands or ordered structures on the liquid surface^{92,93}. The formation mechanism is related to the compressive stress relaxation arising from almost freely sustained films. Band formation was observed for a range of metals such as copper, gold, etc^{92,93}. Experimental studies on the formation of a variety of metallic thin films on liquid substrates, resulting in improved electrical and optical properties have also been reported⁹⁴. Therefore liquid substrates have been put to developmental use for the fabrication of metallic thin films and particles. The understanding of the influence of the liquid on their growth on liquid substrates however is still ambiguous.

2.4.1 Formation of Metallic Nanoparticles:

One of the most sought after applications of metal vapor deposition onto liquid surfaces is nanoparticle synthesis. A vast range of liquids have been employed for this fabrication technique, ranging from simple molecular liquids such as silicone oil or liquid polyvinyl phenylene, vegetable oils such as castor oil⁹⁵ or canola oil and a variety of ionic liquids. The approaches and formation mechanisms for molecular liquids are reviewed next. Ionic liquids, which generate particles with highest stability among liquid substrates, are discussed later.

This field of study was initiated by Wagener and Gunther⁹⁶, a modified VERL (vacuum evaporation on running liquids) technique was employed to fabricate magnetic colloidal suspensions on a low vapor pressure liquid. Silicone oil and mineral oil were employed. Although the liquids did not provide sufficient particle stability to prevent agglomeration, a promising method was successfully demonstrated. A variety of metallic particles have been synthesized on various types of molecular and ionic liquids⁹⁷. Sputtering and thermal

evaporation vapor deposition methods have been utilized. An increase in sputtering voltage resulted in larger particle sizes. Molecular liquids such as canola oil⁹⁸ or castor oil⁹⁹ aid in synthesizing biocompatible nanoparticles. The formation mechanism of these nanoparticles was described by Dupont et al (Figure 2.7)⁹⁹. Three different mechanisms were discussed, describing (I) atomic aggregation / clustering of particles on the liquid surface followed by nucleation and growth in the bulk; (II) nucleation and growth of particles at the liquid surface and particles to sink into the bulk according to its mass and (III) particle nucleation and growth both to occur in the liquid bulk only. The particle sizes reported were not highly mono-disperse. The limitation of this process could be the use of sputtering techniques, which can also deposit gold *clusters* onto the liquid surface. This alters the formation dynamics and thus the influence of the liquid substrate cannot be easily deduced.

Figure 2.7: Formation mechanisms of gold nanoparticles after sputtering of gold vapor onto the surface of liquid [Reprinted with permission from Reference⁹⁹. Copyright © 2010, American Chemical Society]

A more recent report related to metal vapor deposition discusses the influence of surface coordination and voltage variation on silver nanoparticle formation on three different liquids⁹⁸. The mechanism is illustrated in Figure 2.8.

Figure 2.8: Particle formation mechanism on various liquids, effect of surface coordination and voltage [Reprinted with permission from Reference⁹⁸. Copyright © 2011, American Chemical Society]

The variation in distinct final morphologies obtained on three different liquids is associated with different fatty chain compositions⁸¹. The surface composition of the liquid surface is populated with non-polar moieties of the oil (given the bulk chemical composition and polarity of the gas phase). The surface of castor oil with hydroxyl groups on ricinoleic acid-derived fatty chains displays highest coordination ability (stabilizing NPs against coalescence) resulting in the formation of stable Ag nanoparticles. Canola oil, composed mostly of unsaturated aliphatic chains, displays lower coordination ability. CCT (Caprylic/Capric Triglycerid) oil with least surface coordination has highest probability of thin film formation under low voltage sputtering conditions, due to its saturated alkyl chains. Thus this study reveals the effect of liquid surface composition on the morphology during sputtering. The surface functionalities of ionic liquids (ILs) can be altered with ease utilizing, e.g., nitrile, acid, alcohol functionalization. Therefore a broad

variety of ILs have been used for studies of physical vapor deposition onto liquids and are reviewed further.

2.4.2 Ionic Liquids for Nanoparticle Synthesis

The formation of metallic nanoparticles by physical vapor deposition on liquids was first reported by Kuwabata et al¹⁰⁰. They synthesized gold nanoparticles in 1-ethyl-3-methylimidazolium tetrafluoroborate (EMI.BF₄). Sputtering was utilized for deposition. The importance of Ionic Liquids (IL) was highlighted. Following this study, a variety of metallic¹⁰¹ as well as alloy nanoparticles¹⁰² have been synthesized. The study by Dupont et al reported that IL surface composition was the critical parameter to determine the size of the Au nanoparticles when the number of fluorinated groups of IL is increased⁹⁹. A review article summarizes studies related to sputtering onto liquid substrates by this same group¹⁰³.

A study carried out by Mudring et al proposed another mechanism for nanoparticle formation on ionic liquids using the thermal evaporation technique, which is relevant to our current technique (Figure 2.9)¹⁰⁴. A particle nucleation and growth mechanism occurring in the bulk of the liquid is reported (Figure 2.9). Short alkyl chains of methylimidazolium salts, having perfluorinated counter ions, provided better particle stability than longer alkyl chain length cations or high coordination strength anions. Again, particle size was attributed to the type of IL and metal used. The same deposition method was utilized again for generation of metal-metal oxide nanocomposites. Besides, synthesis and stabilization of metallic colloids- Cu/ZnO has also been reported to be stabilized by [C₄mim][Tf₂N] ionic liquid.

Figure 2.9: Mechanism for NPs synthesis on ionic liquids [Adapted from Reference¹⁰⁴]

As discussed earlier, most current studies do not highlight the influence of inherent liquid structure during deposition. Here we consider condensation dynamics from the first atomistic processes and analyze these processes with reference to the liquid structure. Vapor deposition of elements is utilized to minimize other factors. Groups working on metal vapor deposition onto molecular liquid surfaces are summarized in Table 2.1. The current method is also included to highlight similarities and differences in approach.

Table 2.1: Summary of some prominent groups studying metal vapor deposition onto liquid surfaces

Group	Substrate & Condensate	Deposition Type	Morphology	Highlights
Ye GaoXiang [China] ^{84,86,91,94} & M. Wuttig [Germany] ^{105,106}	Silicone Oil Canola Oil	Au, Ag, Cu Sputtering & Thermal Evaporation	Thin Films, Fractal aggregates , clusters	Pioneering studies; Stress Patterns
E. F Borra & S. P Worden [Canada & USA] ⁵	Ionic Liquid	Ag Sputtering or Vacuum Evaporation	Thin films	Basis for lunar telescope (liquid mirrors)
J. Dupont [Brazil] ^{66,69,70,103}	Castor Oil, Canola Oil, ILs	Au, Ag Sputtering	Particles	Co-ordination mechanism for NP synthesis
A.V Mudring [Germany] ⁹¹	ILs	Au, Cu Thermal Evaporation	Metal-Metal Oxide Nano-composites	Long term particle stability
Current Method:	Silicone Oil, PPE, ILs	Au, Ag, Cu, Al Thermal Evaporation	Up to thin film growth	Shared Coarsening for NP synthesis

2.5 Chapter Summary:

After reviewing current studies related to metal vapor deposition on liquid substrates, the need for an in depth understanding of the influence of the liquid structure is apparent. This enables us to predict the type of condensate microstructure for a given material system, along with processing parameters such as temperature, pressure, energy input etc. Thus, a study considering film formation from an atomic level offers numerous potential applications. The focus of this thesis is on film formation on liquids and the changes

brought by the influence of the liquid structure. The two main factors are (1) condensate – substrate binding energy and (2) mass of condensing species. Utilizing different material systems and observing differences in their morphological features result in a variation in these two factors. A simulation technique was used to provide analysis for other parameters to be investigated. This is a step forward for novel uses of liquid substrates in materials science & engineering. Several fabrication techniques with improved control over condensate characteristics – such as thin film properties or control over particle size and shape could be developed by an in depth understanding of physical vapor condensation on liquid substrates.

Firstly, experimental techniques were used to observe condensate morphologies on both liquid and amorphous solid substrates. Based on these observations and keeping the liquid structure in mind, the mechanisms were deduced. Next, computer simulations were carried out and compared to the experimental results. The synthesis of mono-disperse nanoparticles on liquid substrates was also investigated by considering a range of diffusion kinetics on the liquid substrate. Novel experimental results and modeling by shared coarsening, resulting in particle monodispersity, are put forward. Furthermore, highly monodisperse gold nanoparticles were also synthesized on an environmentally friendly ionic liquid, which is an interesting and potentially important application of this method.

Chapter 3 Materials and Methods

The experiments carried out involved deposition of metallic vapor onto various substrates. The types of metals and liquids utilized along with their important material properties are reported in this chapter. The details of vapor deposition and sample preparation techniques, along with various characterization methods, are discussed.

3.1 Types of Substrates

Molecular liquids, ionic liquids and amorphous carbon are the three major types of substrates utilized for comparison in this study. The majority of the deposition conditions involve use of silicone oil to observe the resulting morphology. A simple molecular liquid - PPE (Poly Phenyl Ether) is also used for comparison. The amorphous carbon substrate is utilized as the main reference to compare the growth stage on solid substrate and thus identify differences in growth mechanisms between solid and liquid substrates.

3.1.1 Silicone Oil:

Silicone oil ([1,1,3,5,5-Pentaphenyl-1, 3,5-trimethyltrisiloxane]) is the liquid substrate (Dow Corning) utilized for metal vapor deposition. The liquid is chosen for its exceptional stability even under ultra-high vacuum conditions. The liquid displays an extremely low vapor pressure of 2×10^{-8} Torr. In addition it also offers high thermal stability making it the most suitable substrate for thermal vapor deposition conditions. The basic properties of the liquid are listed in Table 3.1.

The molecular structure of silicone oil [$C_{33}H_{34}O_2Si_3$] is shown in figure 3.1. Each of its molecules consists of 5 bulky phenyl groups attached to 3 silicon atoms. The tetravalent silicon is strongly bonded to 2 oxygen atoms, thus making up the backbone structure of

the molecule. In addition 3 methyl functional groups are also attached to each of the silicon atoms.

Figure 3.1: Molecular Structure of silicone oil as shown in 2D and 3D (optimized structure) formats.

3.1.2 Amorphous carbon and other liquid substrates:

The approach employed for vapor deposition on amorphous carbon substrates is described. Holey carbon copper grids used to prepare transmission electron microscope (TEM) samples are directly utilized (TED Pella Inc). Thus we can simultaneously deposit the vapor onto two grids side by side – one coated with liquid and the other with the reference copper grid. The holey carbon coating was reported to be deposited using a thermal evaporation technique. Its structure was found to be a mixture of sp² and sp³ bonding. This is relevant when we consider the binding energy characteristics of the substrate. The structures of the other liquids (PPE and ionic liquids) utilized are as shown in Figure 3.2.

Figure 3.2: *Liquid Structures* - 2 dimensional structures of (a) Poly Phenyl Ether (m-Bis(m-phenoxyphenoxy)benzene); (b) PMIM(I) (1-Methyl-3-propylimidazolium iodide); (c) BMIM(PF6) (1-Butyl-3-methylimidazolium hexafluorophosphate); (d) BMIM(BF4) (1-Butyl-3-methylimidazolium tetrafluoroborate)

Poly Phenyl Ether (m-Bis(m-phenoxyphenoxy)benzene) with five aromatic rings was used in this study. It is a clear liquid with high thermal stability (453 C) and exceptionally low vapor pressure (4×10^{-10} Torr) and was utilized as purchased from SPI suppliers. These physical properties make PPE to be suitable for being used a liquid substrate for metal vapor deposition under vacuum conditions. In addition, is a simpler molecular liquid compared to silicone oil and offers a linear structure and lower molecular weight (PPE: 446.49; Silicone Oil: 484). Therefore vapor deposition onto a second molecular liquid was also carried out thus enabling a comparative study as well.

3.2 Sample Preparation:

During sample preparation, 1 μ L of the liquid is coated onto the holey carbon copper grids. The reference, uncoated plain holey carbon copper grids are the amorphous solid substrates which are directly used for deposition. The liquids and the copper grids are stored in a dry box prior to sample preparation to reduce moisture absorption. The entire procedure is carried out inside the clean room, thus minimizing the influence of humidity and reducing the probability of contamination. Both the amorphous carbon substrate and the liquid coated grid are carefully placed into the vacuum chamber holder, along with the reference plain holey carbon grids.

3.2.1 Thermal Evaporation of Metallic Vapor onto Liquid Substrates:

Metal vapor generation is carried out using a physical vapor deposition system. It consists of purely physical forces and the underlying principle involves high temperature vacuum evaporation to be achieved through electrical heating of the source. Subsequent vapor condensation occurs onto the cold substrate. The vapor generated is reported to be in

atomic form given its subtle vaporization methodology unlike other physical vapor deposition techniques such as sputtering. A JEOL vacuum evaporator (model: JEE – 420) – a high vacuum deposition system, has been employed in this study and is customized to our requirements (Figure 3.3). The key specifications of the system are given as follows. It consists of a glass bell jar of 250 mm (height) and 250 mm (outer diameter). The system operates with an automatic vacuum system and is fitted with a diffusion pump (420 L/s with water cooling baffle) and a rotary pump with 100 L/ min capacity. The system heat power supply specifications are 10 V AC and 50 A.

Four different types of metals, i.e., gold, silver, copper and aluminum of 99% purity grade were utilized for deposition. The substrate samples are placed horizontally below the vapor generation source. The desired metal of ~2-3 mg is placed in the tungsten crucible (above the sample surfaces) for thermal evaporation. The chamber is evacuated prior to evaporation and its pressure is maintained at 7.5×10^{-7} Torr with the aid of the diffusion pump. The chamber is allowed to degas for 4 – 5 h. The evaporation currents made use of are in the range of 20 A – 30 A.

Next the metal is deposited onto the liquid samples under vacuum conditions. The generated gold atoms undergo random scattering events with each other, followed by deposition on the samples. This is unlike conventional directional vapor deposition onto samples placed above the vapor source. The non line-of-sight set-up of deposition is possible here due to the lack of ultra-high vacuum conditions in the customized chamber. The vapor deposition rate and time are the key variables used to study differences in microstructure.

The flux rate was determined by correlating the mass of evaporated gold at various input

current. For example, an emission current of 22 A was utilized to obtain a low deposition rate of gold. A deposition time of 20 s at 22 A current resulted in the evaporation of 15 mg of gold. Thus the evaporation rate (f) is calculated to be 2.3×10^{18} atoms/s. According to the set-up used in our system, the source to substrate distance (r) is 4.5×10^{-2} m. Given the atomic flux $F = f / (4 \pi r^2)$, the final deposition rate is equivalent to 9.04×10^{19} atoms/($s \cdot m^2$).

To study vapor pressure effects the deposition rate was varied from an extremely low deposition rate (9.04×10^{19} atoms/($s \cdot m^2$)) to intermediate rate (2.26×10^{20} atoms/($s \cdot m^2$)) to a high deposition rate of deposition (1.92×10^{22} atoms/($s \cdot m^2$)). The time of metal deposition is varied from a minimum of 10 s to a maximum of 60 s up to the condensate film formation stage. This time control is highly efficient to observe the various growth stages for the different material systems.

Figure 3.3: Deposition Set-Up - Schematic of the thermal evaporation chamber showing the position of the samples, placed below the metal vapor source.

Silicone oil has been the choice of liquid for vapor phase deposition studies on liquid

substrates. Its primary advantages of high thermal stability and low vapor pressure makes it highly suitable for vacuum processes with promising applications. In addition, this molecular liquid is relatively inert in nature and provides for weak transverse interaction between the liquid substrate and the solid (metallic) film. A lack of strong chemical interaction between the substrate and metallic vapor is of advantage to evaluate condensate nucleation and growth on a liquid. This interesting property has allowed the fabrication of a variety of microstructures ranging from branched aggregates^{105, 107}, compact clusters, ramified islands¹⁰⁸ to ultra thin films or wedge shaped thin films to even ordered patterns on its surface^{109, 110}. Despite these observations, the underlying formation mechanism has not been studied in depth. Therefore, silicone oil is utilized as the primary liquid substrate in this thesis work to explore the liquid substrate effects on the condensate.

Furthermore ionic liquid was the choice of liquid due to (1) negligible vapor pressure and (2) the expected high particle stability owing to the liquid composition at the surface. The technique offers the advantage of fabricating stabilizer free particles. In addition, this characteristic of the ionic liquid also enables is to test the shared coarsening mechanism in this study, providing a material system with high condensate substrate affinity. Therefore ionic liquid is a suitable choice as the second model liquid in this work. Thus both liquids investigated in this study were chosen in consideration of the nature of their surface chemical composition.

3.2.2 Liquid dissolution technique:

The characterization of the condensate formed on the liquid substrate is not straightforward. Liquid samples require additional processing steps to remove liquid

without disturbing the microstructure of the deposit. This is necessary as the liquid limits the characterization techniques which can be used. Copper grids can be directly used for Transmission Electron Microscope (TEM) characterization once the liquid is removed. Hence, after deposition, the liquid coated grids are gently removed and immediately introduced over an acetone vapor environment. Since the carbon support layer is holey, the acetone vapor gently dissolves most of the liquid. This novel technique of sample preparation where a vapor is introduced only at the bottom surface of the sample causes minimal disturbance. Further the samples are free of the liquid and are suitable to be characterized using TEM.

This microscopy technique involves a beam of electrons to be transmitted through ultra-thin specimens, interacting with it and result in constructing an image. This technique aids us to observe the detailed microstructure of the condensate and also capture high resolution images. Imaging of the holey carbon copper grids with metal condensate (post liquid dissolution) was carried out using a JEOL 2010 TEM operating at 200 kV. The instrument utilizes a gentle LaB6 electron source and is suitable for observing the metallic condensate microstructure. The images captured were analyzed using the image analysis software Image J to measure particles sizes, condensate coverage and particle number density.

In addition, it is to be noted that the TEM images captured with the oil present also show similar condensate morphologies, thus confirming no-disturbance from this vapor dissolution technique. The images with the liquid are shown in Appendix I (section A1), for both gold and copper vapor deposit. After completion of removal of the liquid (20 – 30 s), the condensate is left behind on the carbon support. Thus, this technique is common to

all the samples and enables the major characterization technique i.e., TEM, to be used to characterize the deposits on the liquid surfaces.

The functional groups of the liquid substrate – silicone oil was characterized using FTIR (Fourier Transfer Infrared) spectroscopy. This technique aids in identifying the individual functional group vibrational frequencies. Furthermore, the identification of copper and its oxidation was verified using XPS (X-ray Photoelectron Spectroscopy) elemental analysis technique. Copper films deposited onto both the solid and liquid substrates were analyzed. To sum up the metal vapor is deposited on a liquid substrate as well as on an amorphous carbon substrate placed by its side in the same run. The deposition conditions (rate and time) are described above and controlled in the customized vacuum chamber. Sample preparation prior to and post deposition are critical. The following results and discussion chapter begins with a description of the deposition of gold vapor onto silicone oil and the study of the growth of the deposit with respect to the influence of the liquid structure.

Chapter 4 Liquid Substrate Effect on the Condensate Morphology

4.1 Introduction:

It is known that condensate morphological properties are directly influenced by the growth mechanism. The development and growth of metallic condensate on liquid substrates has been investigated earlier^{48,100,2}. Moving forward it is essential to further examine the role played by the liquid structure to improve this method. For this, a direct liquid – solid comparative study is carried out, focusing on differences in condensate coverage. The differences due to the liquid substrate are analyzed and changes in growth kinetics identified. The foremost distinction of a liquid substrate relative to its solid counterpart, as reviewed earlier, is its constantly changing internal structure. It is well known that these effects are enhanced on its surface and this gives rise to many distinct liquid properties. This behavior of the liquid arises from its intermolecular forces. Thus it is likely that the interaction of the condensing vapor with the liquid surface is influenced by the liquid structure.

4.2 Background:

A limited number of studies discuss the influence of the liquid substrate on the deposited atoms or molecules and the role of the liquid in altering the dynamics of condensation. As discussed in chapter 2 (section 2.4), although a variety of low vapor pressure liquids have been successfully used to synthesize metallic nanoparticles/thin films^{101,104,111}, the influence of the inherent properties of the liquid, owing to its structure/state, on the condensation kinetics has not been adequately explored. The theoretical study by Philips et al.¹¹² discusses the influence of the degrees of freedom of a liquid against an opposing

force with respect to collisional energy exchange. The collision of a fast, low mass atom onto a liquid surface is predicted to cause a parabolic downward displacement at the liquid surface. The opposing force from the energy transfer causes the atom to scatter away upon retraction. Comparative studies of oxidation of solid substrates and metallic liquids are also relevant here. As discussed in section 2.3.3, morphological differences in oxidation have been reported to be a consequence of structural differences between the substrates⁸⁰. The response of the liquid substrate with respect to its structure was noted in earlier studies. In our study the liquid's response upon deposition of a slow, heavy atomic species is discussed at the atomic scale.

Figure 4.1: The statistical response of the liquid substrate (reproduced from reference⁹⁶) showing the retraction (parabolic in shape) in the surface degrees of freedom of the liquid molecules on collision with the incoming atom (not drawn to scale).

The formation of ramified aggregates, post-deposition, of silver on silicone oil, reported by Wuttig⁸⁹, draws attention to room temperature aggregation behavior of metallic clusters on liquids. The formation of fractal structures (after 3 or 30 h of deposition) has been shown at various deposition rates, indicating cluster/aggregate mobility on the liquid surface. Silver atoms and aggregates perform random walk diffusion on the liquid surface, resulting in large aggregates. The Brownian motion of the clusters post deposition is

dependent on their deposition rate (which influences the cluster size distribution) and a two-stage (early and late time) growth mechanism⁸⁹. Post stage 1 a high deposition rate results in formation of small compact clusters with high mobility. On the other hand, low deposition rate gives rise to a small number density of large clusters, which requires a relatively longer time to aggregate. The second stage is observed at a much later time scale (hours or days), taking into account changes in size, shape and density of clusters. It is at this stage that diffusion and aggregation of clusters is prominent (size of the order of μm), resulting in formation of fractal structures. The focus of the current work is to analyze condensate growth and coverage at low deposition rates obtained on a liquid surface during early deposition times (first 60 s). A low deposition rate was chosen in order to be able to study condensate growth at various time stages. At this deposition rate, a thin film like morphology was observed at and above 60 s. Therefore the growth stages up to thin film formation time are examined in detail. Given the low deposition rate combined with the low energy of the depositing atoms (due to thermal evaporation technique), the formation of fractal structures at late growth stage is not observed.

A comparative study of a liquid substrate, as well as a counterpart amorphous solid substrate onto which metallic vapor is deposited was conducted. The deposition of metallic vapor onto the liquid surface under vacuum conditions is employed, as described earlier in the experimental section. The kinetic energy of the thermally generated vapor atoms is of the order of $\sim 0.1 \text{ eV}^{113}$. Gold vapor is chosen given its exceptionally inert characteristics. It is thermally evaporated onto silicone oil which is the liquid substrate utilized here. Amorphous carbon is the solid substrate onto which simultaneous deposition is carried out. The scope of this study involves physical interaction forces only -

emphasizing aspects of substrate structure with the most influence over condensation dynamics. Throughout this chapter, comparisons are made between growth morphologies obtained on solid and liquid substrates. Initially, low deposition rate is employed to give rise to slow growth of the condensing metal, enabling us to observe a number of morphologies at useful time scales. Eventually, the effect of utilizing higher deposition flux is also investigated.

The observations demonstrate that condensate coverage on the liquid surface is considerably lower and non-uniform in distribution, unlike that on the solid surface. The time resolved images reveal distinct growth kinetics to have occurred on the liquid substrate. The binding energies between the depositing species and the substrates were calculated to be similar for both substrates. Furthermore, given that other influencing parameters were alike, differences in inherent structure were deduced to play a major role in defining the growth mechanism. In particular, perturbation of the internal degrees of freedom of the liquid upon binding with the depositing species is deduced to cause additional desorption events. The consequence of this unique behavior of the liquid substrate is the low condensate coverage.

Before addressing the issue of surface coverage, the silicone oil is assumed to be in film form and not as droplets on the holey carbon grid. This is verified indirectly by observing, through an optical microscope the morphology of gold clusters formed on the oil surface (Figure 4.2). The deposition rate in this case is higher (2.26×10^{20} atoms/ (s*m²)) and much later growth stage is captured (after one minute of deposition). The cluster coverage is continuous and indirectly verifies the absence of droplets.

Figure 4.2: (a) Gold vapor deposited onto holey carbon copper grid – deposited at a higher deposition time of ~1 minute; (b) Shows the higher magnification optical image of the gold islands on top of silicone oil surface.

Furthermore the contact angle of silicone oil on the holey carbon copper grid (Figure 4.3) supports this contention. Silicone oil readily wets the copper grid and expected to follow the Wenzel Effect – as the liquid flow occurs even on the microscopic mesh structures. The type of wetting behavior observed here acts as secondary evidence for the liquid to exist in film form. The silicone oil contact angle with the copper grid is seen to be 14.2° and it recedes to $\sim 7.5^\circ$ implying very good liquid wettability onto the structured surface.

Figure 4.3: Contact angle of silicone oil with holey carbon copper grid is shown in (a) at contact and (b) after 5 s.

4.3 Results & Discussion:

4.3.1 Deposition of Gold onto Silicone Oil:

The time resolved growth morphologies obtained upon simultaneous gold vapor deposition onto both substrates are shown in figure 4.4. The gold vapor is thermally generated in the customized vacuum evaporator. A low gold vapor flux of 9.04×10^{19} atoms/(s*m²) is maintained to clearly differentiate the growth morphologies. The various growth stages captured with increase in deposition time (10, 20 and 45 s) on both silicone oil and amorphous carbon during the course of film formation are compared. The growth morphologies observed on amorphous carbon substrate is as expected and in agreement with conventional film growth stages on a solid substrate¹¹⁴. After 10 s of deposition the formation of 2 nm gold particles, uniformly distributed all over the carbon surface, can be observed. The subsequent stage, captured after 20 s of deposition, shows that particles have grown to larger sizes, 10 – 12 nm in diameter. The cluster shapes indicate the occurrence of liquid like coalescence among the particles, which resemble images previously reported in literature¹¹⁴. The condensate distribution continues to remain uniform all over the carbon surface. The stage after 45 s of deposition displays the formation of a nascent thin film with 75% substrate coverage.

The time dependent condensate morphologies obtained on the liquid substrate placed next to the solid substrate differ from the solid substrate morphologies at all deposition times. After 10 s of deposition the surface is seen to be completely empty apart from a few large (5 – 9 nm), irregularly shaped particles which are randomly distributed on the substrate. The apparent low condensate coverage of 2 – 3% is significantly different from the coverage on the solid substrate. While a higher number of gold particles appears to have

formed (5 – 10 nm in size) after 20 s of deposition, non- uniform distribution is still prevalent (S20, Figure 4.2). The gold condensate coverage at this stage is only slightly over 10% (Figure 4.3). Particle aggregation along with non-uniform multilayer growth can be identified.

Figure 4.4: TEM images of gold vapor deposited onto amorphous carbon (C - Upper row) and Silicone Oil(S - Lower row) at the same flux for 10, 20 and 45 seconds.

Even after 45 s of deposition, only a highly granular discrete particle network is observed. The coverage at this stage is 55%, quite different from the 75% coverage of thin film structures observed on the solid carbon substrate. The coverage, quantified by analyzing the images captured from several deposition batches under constant deposition flux, is shown in the coverage v/s time plot (figure 4.5). The coverage values were averaged by sampling 100 nm^2 areas from the images. Although both cases exhibit non linear growth

coverage, a distinct time lag for the liquid substrate is evident. It appears that silicone oil maintains a nearly constant coverage between 20 to 45 s, followed by a rapid increase in coverage unlike the gradual rise in coverage observed on amorphous carbon.

Figure 4.5: Coverage of gold deposited onto amorphous carbon and silicone oil at the same flux and captured at various time scales, averaged over sampling 100 nm² areas of the images.

The highly non uniform coverage observed on the liquid surface naturally raises a series of related questions. Is the liquid surface responsible for inducing the difference in coverage? What are the forces impeding the growth of clusters from forming a continuous film? Are these exclusive to the chosen material system?

To address the issue of surface coverage, the condensation process starting from atomic scale interactions with the substrate is considered. According to the experimental conditions the impingement rate or the arrival flux (J_i) of the gold atoms and time duration of deposition (t) is the same for both substrates, as they are placed within the same system. Adsorption of gold atoms onto the substrate denotes the first interaction between vapor and substrate. Other interaction modes such as possible collision/backscattering of

atoms or their penetration/implantation, is considered to be negligible in this system. This is due to the minimal kinetic energy of the thermally generated atoms deposited. Atoms generated from thermal vapor deposition are reported to possess kinetic energies in the range of 0.1 – 0.25 eV. However, sputtered atoms have higher kinetic energies in the range of 2 – 7 eV¹¹³, allowing for higher backscattering or penetration probability. Therefore, here given the purely physical interaction forces between substrate and adsorbate, the gold adatom (adosorbate) coverage (Θ) at early time, on a substrate having a residence time of " τ ", is given by equation 4.1, according to the classical Langmuir adsorption isotherm¹¹⁵.

$$\Theta = [1 - (C_s/C_{0s})](J_i \cdot \tau) P \quad (4.1)$$

$$\tau = (1/v_D) \exp(-\Delta H_{ad}/k_B T) \quad (4.2)$$

C_s and C_{0s} are the number of adsorbed atoms and the total number of available sites for adsorption, respectively, under gas pressure P . The mean residence time τ of the adsorbates plays a critical role in defining subsequent growth morphology. It is an exponential function of temperature (T) and the heat of adsorption (or binding energy), ΔH_{ad} of the vapor atoms to the substrate surface. As the variation in temperature is not considered in the current system, binding energy of the gold atoms with the two substrates is evaluated next.

4.3.2 Binding Energy Calculation:

The binding energy of the gold atom with the liquid substrate is calculated from first principles. Density Functional Theory (DFT) via CASTEP simulation tool from Materials Studio (Accelrys)¹¹⁶. Similar calculations have been reported for the binding energy of gold and ionic liquids¹¹⁷. CASTEP is a quantum mechanics-based program which employs the density functional theory plane-wave pseudopotential method. It aids in calculations that explore the properties of crystals and surfaces in materials for studies related to structural properties, surface chemistry, optical properties and density of states.

4.3.2.1 DFT Calculation Details:

The DFT exchange-correlation potential utilizes the Generalized Gradient Approximation (GGA) method with the PW91 functional electronic and geometry structures¹¹⁸. The approximation was chosen due to the weak interactive forces between silicone molecules. The total self-consistent threshold energy was set to be 2×10^{-5} eV/atom. A reciprocal space pseudopotential representation was utilized and the plane wave basis set cut-off was 300.00 eV. The eigen-energy convergence tolerance was set to 0.1×10^{-5} eV and the fermi energy convergence tolerance was 0.1×10^{-6} eV. A Gaussian smearing scheme was utilized with a smearing width of 0.1 eV. The structures were geometry optimized with forces, displacement and tolerance set equal to 0.05 eV/Å, 0.002 Å and 2×10^{-6} eV/atom, respectively.

It is to be noted that, here the binding energy value is only of the electronic energy, the vibrational contribution was not taken into account. This is because the entire structure was refined to obtain a stable geometry using the CASTEP code via an iterative procedure. The BFGS¹¹⁹ (Broyden Fletcher Goldfarb Shanno) geometry optimization

scheme was adopted. This BFGS minimizer provides the advantage of performing cell optimization along with optimization at a fixed external stress. The optimized geometry bears close similarity to the system at equilibrium with minimum energy, hence it is assumed to be sufficient for the current calculation.

The gold atoms were found to have weak binding energies with all the functional groups of silicone oil; (Table 4.1). Binding energy calculations under several configurations were calculated as shown in Table 4.1. The Au atom was placed close to the (1) methyl functional group (2) benzene ring (a) Perpendicular to the H atom of benzene ring (b) equidistant from two H atoms of the benzene ring (c) atop the benzene ring; (3) Si atom and (4) oxygen atom. The configurations of 2(c) and methyl functional group offer low binding of 0.094 eV and 0.12 eV respectively. The oxygen site offers the strongest binding energy of -0.55 eV. The binding with the silicon and benzene ring shows a small difference of 0.04 eV. Moreover, it is interesting to find that these binding energy values are of the same order as that of gold binding with amorphous carbon. The binding energy values for amorphous carbon range from -0.52 to -0.65 eV, as reported in the literature using simulations^{120,121}. Although both substrates offer similar weak binding force for gold atoms, the resulting morphological differences observed is remarkable.

Table 4.1: The binding energy values of gold onto the (a) various functional groups of silicone oil and (b) various configurations of binding with H atom of Benzene ring are as shown, obtained from DFT calculations.

(a) Au atom binding with		Binding Energy (eV)	(b) Various configurations at Au atom binding with H atoms of Benzene ring	Binding Energy (eV)
Methyl		-0.1223		-0.4105
Silicon		-0.4466		-0.4138
Oxygen		-0.5522		-0.0948

When two substrates offer similar (weak) bond strengths and yet display dissimilar condensate morphology and coverage, differences in desorption kinetics along with changes in surface diffusion and nucleation characteristics can be anticipated. The changes in desorption kinetics introduced by the substrate structure is examined next. A novel growth mechanism occurring on a liquid surface with weak binding forces is proposed.

4.3.3 Effect of the Substrate Structure:

During condensation, incoming atoms lose the velocity that they possess in the vapor state in order to be successfully bound to a substrate (adsorption). On being adsorbed, the energy transferred (E_{TS}) results in generation of surface phonons in the rigidly bound solid substrate. The inter-atomic carbon-carbon binding is strong enough not to be disturbed by this energy transfer and thus easily accommodates gold atoms. A similar amount of

energy transfer is expected at both the substrates, given the simultaneous deposition of thermally generated, low energy incident atoms (~ 0.1 eV), their binding energies are of the same order. However, completely different consequences are observed on the liquid substrate.

Each silicone oil molecule comprises three groups of CH_3 functional groups attached to each silicon atom. The presence of 'Si-O-Si' bonding along with five phenyl groups provides the molecule with an extremely large number of vibrational modes. CH_3 group alone is reported to have stretching and bending modes for C-H at higher excitation energies and numerous other modes¹²² at lower energies such as torsional, wagging etc. The Si-O-Si bond torsional modes of vibration at low excitation energies, along with the Si- CH_3 modes, provide pathways to convert energy transferred on adsorption into internal modes of vibration. Simultaneously, these modes of degrees of freedom can serve as intramolecular relaxation modes after excitation, among which vibrational modes are reported to occur very rapidly¹²². Thus energy transferred on adsorbing gold is converted into excitations. Simultaneously, the vibration frequency of the complete molecule is also significantly altered. In this case again, backscatter or penetration of the adatoms was considered to be negligible due to the low kinetic energy of the deposited atoms, along with the weak binding forces between the condensate atoms and substrate. Hence we propose the following mechanism to occur on the liquid surface.

The energy transferred to the liquid changes the center of mass of the liquid molecule, altering its nearest neighbor configuration. This effect is plausible given the weak inter molecular van der Waals' binding forces between liquid molecules. This results in a significant localized disturbance, which is equivalent to perturbing the internal degrees of

freedom of the molecule and its functional groups. The binding of the gold atom with the liquid molecule limits the number of accessible degrees of freedom and reduces entropy. Given the tendency to maximize its entropy, the liquid would ‘collectively’ act against the bonded state. Consequently it uses the fastest route for restoration, i.e, to cause the gold atoms to break the ‘weak’ bond. This collective action of the liquid molecules can make the gold atoms desorb back into the vapor phase.

Such collective action from the liquid molecules can result in either desorption or diffusion of atoms, depending on the magnitude of the response energy. This energy is a function of the mass of the incoming species and its binding energy with the liquid molecule. In this material system the heavy mass gold atom enables efficient momentum transfer¹²³ by allowing the normal energy component to be successfully lost to the liquid substrate. The binding energy, which accounts for the minimum activation energy required to completely break the bond, is also low. This analysis combined with the observed morphology, enables us to deduce increased desorption. Furthermore, the magnitude of such a response energy can be estimated to be equivalent to ‘ $n \cdot (k_B \cdot T/2)$ ’, where n is the number of compromised accessible modes, each of which carries an equivalent energy of $k_B \cdot T/2$.

According to classical equations, the first order desorption rate constant equation and the life time of an adsorbate are as given below:

$$k_{\text{des}} = (A) * \exp(-E_{\text{des}}/RT_s) \quad (4.3)$$

$$\tau = \frac{1}{k_{\text{des}}} = \frac{1}{A} \exp(E_{\text{des}}/RT_s) \quad (4.4)$$

The desorption rate constant (k_{des}) is directly related to the pre exponential factor (A) and exponentially to the activation energy of desorption (E_{des}), k_B is the Boltzmann constant

and T_s the temperature. On a non rigid substrate (or a liquid), the desorption rate is extremely sensitive to changes in the pre exponential function A , which could be the vibration frequency of the atoms or the total number of degrees of freedom of the liquid molecule. In addition, when the activation energy for desorption is low, ' A ' is said to govern desorption.

The solid substrate's degrees of freedom are much fewer, limited to vibrational modes only, clearly different from its liquid counterpart. Conventionally ' A ' for solid substrates is known to be in the range of 10^9 to 10^{16} . The pre exponential factor for the amorphous carbon substrate is estimated to be $\sim 10^{12}$ at room temperature. A residence time of $\sim 10^{-6}$ s can be estimated as ' $A = k_B T/h$ ', according to transition state theory. For the liquid molecule, Si-CH₃ and Si-C₆H₆ functional groups alone have individual vibrational frequencies of $\sim 10^{13}$ from FTIR measurements (see section A2 in Appendix I). The liquid molecules can access a higher number of rotational and translational degrees of freedom (lacking in the rigid solid substrate), along with vibrational modes of their local clusters. As the pre exponential factor includes the total number of degrees of freedom, the value of A is expected to be higher, in the range of 10^{13} to 10^{15} or higher. The total partition function (q_{total}) of a molecule is a product of the partition functions for all its degrees of freedom, given by¹²⁴:

$$q_{total} = q_{trans} \cdot q_{rot} \cdot q_{vib} \cdot q_{elec} \quad (4.5)$$

where q_{trans} , q_{rot} , q_{vib} and q_{elec} represent the partition functions for the translational, rotational, vibrational and electronic degrees of freedom. Therefore this corresponds to a higher value of A for a liquid molecule. The activation energy of desorption is of the same

order as the condensate/substrate binding energy. In the current system this activation energy is of the same order for both amorphous carbon and silicone oil. Thus the term $\exp(-E_{\text{des}}/k_B T)$ is equal to 1.7×10^{-7} . ‘A’, being the critical parameter determining the morphology, results in variations in desorption rates, as calculated for various E_{des} (eV) values.

Table 4.2: Calculated desorption rates and adatom residence times for varying values of A – the pre exponential factor.

Pre exponential Factor (A)	Desorption Rate			Residence Time (s)
	$E_{\text{des}} = 0.2$	$E_{\text{des}} = 0.4$	$E_{\text{des}} = 0.8$	at $E_{\text{des}} = 0.4$
10^{10}	4.36×10^6	1.7×10^3	3.63×10^{-4}	5.26×10^{-4}
10^{12} (solid)	4.36×10^8	1.7×10^5	3.63×10^{-2}	5.26×10^{-6}
10^{14} (liquid)	4.36×10^{10}	1.7×10^7	3.63	5.26×10^{-8}

A linear increase in desorption rate is seen with increasing values of the pre exponential factor. Therefore for a liquid substrate with low binding energies, higher desorption rate is expected, along with shorter residence time on the liquid substrate, unlike that on amorphous carbon. In addition, calculations from the experimental coverage results indicate that after 10 s of deposition additional desorption of $\sim 15 \times 10^8$ atoms/cm² from the surface of the silicone oil can be expected at the given deposition rate. Thus a larger number of atoms ($\sim 12.6290 \times 10^{14}$ atoms/cm²) are available for growth on the carbon surface. In addition, the liquid surface has been reported to require a higher incoming flux (condensate species) to achieve threshold for nucleation. This was observed in a study of

metal vapor deposition on liquids *via* the sputtering technique. Therefore our proposed model is consistent with reported literature.

The difference in binding energy was referred to be ‘small’ in context of the observed vastly different (a) condensate coverage and (b) condensate morphology obtained on the two substrates. It is to be noted that, both the substrates offer weak physical forces of binding only. It can be observed from the plots in Figure 4.6, that binding energy values less than 0.5 eV do not alter the residence time significantly at a given pre-exponential factor value. Due to this reason, the difference in binding energies of the condensate to the substrate (~ 0.2 eV) is considered to be small and negligible in our current system.

In addition, although the nature of binding with the condensate atoms is similarly weak for both the substrates, the observed distinctions in morphology and coverage indicate can thus be attributed to the pre-exponential factor A . The continuously decreasing adatom residence time with increasing pre-exponential factor value is shown, highlighting its effect on particle growth kinetics.

Figure 4.6: The change in residence time (seconds) with binding energy (eV) at varying pre-exponential factor A (10^{10} , 10^{12} , 10^{14} , 10^{16}) are shown. It can be noticed that a significant change in residence time is observed only at 0.6 eV and the trend is the same for all the pre-exponential factor values.

To summarize this section, the heavy mass gold atom can cause substantial perturbation to the liquid structure. The effective reduction in the liquid molecule's degrees of freedom causes the liquid structure to collectively respond against this perturbation. This response causes additional desorption events on the liquid surface. This effect is realized due to the weak binding energy between the gold atom and silicone oil molecule, allowing for the small activation energy to be overcome. Consequently the liquid

system is expected to require a longer time to achieve equilibrium. Therefore, distinct nucleation and growth kinetics on the liquid substrate are expected, as discussed below.

4.3.4 Nucleation & Growth - Gas-phase transport model:

In this section the mechanism by which an increase in desorption rate results in low condensate coverage on the liquid surface is discussed. The effect of the liquid on nucleation and growth is considered. Nucleation occurs when adsorption/desorption equilibrium is attained and a critical number of atoms accumulate together on the surface. Due to increased desorption events on the liquid surface the time required to achieve this equilibrium is delayed compared to the amorphous carbon surface. The increase in 'A', which in turn results in an increased desorption rate or increased surface adatom mobility, is absent on the amorphous carbon. Therefore, the adsorbed atoms are more stable and higher concentration of adatoms can be found on the surface. This allows nucleation to happen earlier, leaving gold nuclei uniformly distributed over the carbon surface. After nucleation, growth occurs either by direct capture from the vapor or through surface diffusion, maintaining uniform distribution throughout the surface. Concurrently, accumulation of adatoms on residual empty carbon surface continues and results in secondary nucleation over time. Further growth occurs by conventional coarsening and coalescence.

On the liquid surface, a higher number of desorbed gold atoms contribute to a gradual increase in the *local* gold vapor pressure due to increased concentration of atoms in the vapor. This gradual rise in supersaturation results in nucleation in a few random places. The lower concentrations of adatoms with limited residence time and diffusion mobility generally collide with their nearest adatoms only to achieve the critical cluster

size for nucleation. Consequently, primary nuclei are spaced at relatively large distances from each other. This non uniform distribution of the nuclei is maintained for longer time scales, resulting in low condensate coverage. Also, with a lower net number of atoms adsorbed on the liquid surface, the adatoms traverse larger diffusion lengths prior to formation of nuclei. Thus, the incubation time for nucleation is larger on a liquid surface.

After nucleation, these nuclei act as preferential sites for vapor condensation, while the uncovered surface continues to remain uncovered. Gold nuclei offer an adsorption coefficient of unity for gold vapor atoms. Given the higher rates of desorption, nucleation is difficult on the liquid surface. Thus, once the nuclei are formed, a vapor atom is more likely to be captured by the nuclei directly rather than to cluster to form a new nucleus. The continuously increased number of desorbed atoms from the liquid surface is an additional source for supply to the growing nuclei via *gas phase transport*. In addition, interatomic binding strength of gold adatoms (-1.26 eV for isolated metal pair) is comparatively stronger than the binding of gold with the substrate.

Hence Volmer-Weber type growth mode is expected, with 3D island growth. The higher density of islands at certain regions promotes early aggregation or coalescence/coarsening events. This causes condensate surfaces to have higher surface roughness and greater multilayer growth, as observed in the TEM micrographs (Figure 2.1 - S20, S45). The change in mean particle size and the density v/s time plots (Figure 4.7) clearly illustrates this behavior. Therefore, this is another key difference in growth on liquid and solid substrates.

Figure 4.7: Change in mean particle size and density with deposition time is shown for (a) amorphous carbon and (b) silicone oil.

For condensate growth on amorphous carbon substrate, the initially high particle number density continuously decreases with time (Figure 4.7). Dynamic coalescence through the cluster diffusion mode can be expected. However, on the liquid substrate the initially extremely low particle density continues to remain so even with increasing time. At the same time, the mean particle size increases continuously. During the entire deposition period up to 60 s, the density changes from ~ 13 to $\sim 30 \times 10^{10}$ particles/ cm^2 . Therefore multilayer growth of the low density particles can be expected, in accordance with our proposed mechanism. This can also be identified from the optical microscope micrograph of gold clusters/islands formed on the surface of silicone oil (Figure 4.8).

Figure 4.8: Gold deposited onto silicone oil at higher deposition rate, illustrating multilayer growth

In addition, this characteristic of the liquid surface, i.e., to prefer growth of the condensate compared to surface coverage can result in suppression/delay in secondary nucleation. On a liquid surface, clusters growing via direct capture of the vapor flux act as preferred sites for vapor deposition. The growth of these clusters occurs at the expense of secondary nucleation. Thus gold atoms prefer to bind with existing gold clusters rather than to the liquid surface, leading to a more granular morphology compared to a continuous film on the surface. These combined distinct condensation characteristics on the liquid surface are responsible for (a) the observed low coverage and (b) granular film morphology with uneven film thickness. In the next section, the effect of varying the deposition rate is investigated.

4.4 Effect of Deposition Rate:

The deposition rate was substantially increased to observe its influence on condensate coverage and morphology. The differences in growth kinetics are discussed with respect to the experimental observations (Figure 4.9). The low coverage trend on the liquid surface continues to exist at various time scales, even with increased deposition rates. After 8 s of vapor deposition, tiny particles uniformly distributed all over the carbon substrate are seen. However, on silicone oil, low density particles with apparent multilayer growth can be observed. The particle size range is also large, varying from 2 nm to 100 nm (aggregated particles cluster). Although slightly higher particle density can be seen at 10 s, empty areas were observed. Only after a deposition for 15 s is there a thin film like structure visible on the liquid substrate. The film thickness is not uniform and the population of clusters / particles still make up the majority of the condensate morphology (coverage is still incomplete). On the other hand, the carbon surface displays a nearly continuous and almost complete condensate coverage on its surface after ~15 s of deposition. Thus it can be said that the liquid substrate induces low condensate coverage even at high deposition rates. The mechanism is discussed further considering the response of the liquid.

Figure 4.9: TEM images showing the timeline of morphological changes observed at high vapor supersaturation conditions 1.92×10^{22} atoms/ (s*m²). Time resolved images (8, 10 & 15 s) are captured depicting the various growth stages.

The liquid's response to vapor deposition causes additional desorption events compared to the amorphous carbon surface, which leads to low coverage. A higher deposition rate indicates a larger number of atoms arriving onto the liquid surface. This improves adatom collision probability due to increased surface concentration. However, it aids only in faster nucleation stage and does not alter the overall kinetics. Given a larger number of atoms the later stages display an increased coverage. Thus the morphologies obtained do resemble the initial morphology from a lower deposition rate. Nevertheless the gas phase transport mechanism continues to be prevalent. This can be observed from the minimal increase in particle density with time as shown in Figure 4.10b. On the other hand under

the same conditions, a large particle density can be seen after only 8 s of deposition on the carbon surface (Figure 4.10a). Another observation is that, in the initial stages of deposition (8s, 10s) the mean particle size of the particles grown on silicone oil is much larger than the particles grown on the carbon surface, even though their number density is low. Therefore, gas phase transport, resulting in multilayer growth even at high deposition rate conditions, is also verified.

Figure 4.10: Change in mean particle size and density v/s time plots for morphologies obtained under high vapor flux of deposition of gold on (a) a-carbon and (b) Silicone Oil.

To verify the entropy effect experimentally it would be required to lower the temperature of the liquid to restrain its molecular degrees of freedom. However, on freezing the silicone oil, several undesirable effects emerge. Firstly, effective supersaturation is a rapidly varying function of substrate temperature. As even a small variation in substrate temperature can lead to changes of several orders of magnitude in supersaturation, freezing the liquid to -14°C (solid structure) will cause a large number of adatoms to be adsorbed onto the substrate. Following this, the resulting morphological changes would be a consequence of the very high ΔT effect, rather than structural changes in the substrate.

Further, the residence time is exponentially dependent on the ‘heat of adsorption’ (equation 4.2). The difference in heat of adsorption accompanying binding onto the ‘frozen’ silicone oil substrate can also substantially alter the adsorption/desorption kinetics. Thus freezing the liquid to observe structural effects would require extremely stringent atomic vapor flux control for uniform deposition onto both the substrates maintained at different temperatures. Therefore the nucleation and growth of condensate (in the first minute of deposition) was modeled and the critical parameters resulting in a similar morphology (obtained on liquid substrate) was demonstrated (Chapter 5), verifying the effects of additional desorption events. In addition, gold vapor deposition onto another molecular liquid substrate, offering similar material characteristics (low binding energy on gold vapor deposition) was also utilized to verify the liquid substrate effect. A low condensate coverage observed with similar morphologies aids in verifying the entropy effect arising from the liquid. .

4.5 Deposition of Gold onto a simple Molecular Liquid – PPE:

The simpler molecular liquid used here is PPE (Poly Phenylene Ether), whose characteristics were described in chapter 3. Gold vapor was deposited simultaneously onto three different substrates in the same run. PPE and silicone oil were used for the liquid substrate comparison given their differences in functional groups (see Figure 3.1 (a) and 3.2 (a)). The use of amorphous carbon as the solid substrate was maintained. The vapor flux was maintained at 2.26×10^{20} atoms/(s*m²) for a deposition time of 15 s. From Figure 4.11 we can observe that low condensate coverage is seen on both the liquid surfaces (~40% coverage on SiOil & ~43% PPE). The reference amorphous substrate on the other hand, displays the usual, uniform coverage (80%). The binding energy (calculated using

CASTEP as described earlier) of gold with PPE is also of the same order (Table 4.3) as that with silicone oil and amorphous carbon. The average binding energy of gold atoms with PPE was also found to be of the same order of -0.4 eV, thus confirming the proposed mechanism on an additional liquid substrate as well.

Table 4.3: Gold binding energy values with PPE calculated using DFT calculations via Accelrys – Materials Studio software.

PPE – Functional Group	CH ₃ group	Benzene Group	O- attached	Average
Binding Energy (eV) with Gold atom	0.4	0.37	0.43	0.4

Figure 4.11: TEM images of gold condensate morphologies obtained by simultaneously depositing gold vapor onto liquids Poly Phenyl Ether (PPE), Silicone Oil and amorphous carbon for 15 seconds at constant deposition flux.

4.6 Chapter Summary:

Gold vapor deposition onto silicone oil surface gives rise to low condensate coverage which is highly non uniform in distribution. By comparison with an amorphous carbon substrate, this coverage difference can be attributed to the non rigid structure of the liquid substrate, most influential at two specific stages during condensation.

First, adsorption/desorption dynamics are altered due to the higher degrees of freedom among liquid molecules given their weak intermolecular forces. An increased rate of desorption is deduced to occur, caused by the liquid in an attempt to maximize its entropy. Further the increased desorption rate affects nucleation and growth, leading to the observed low coverage of condensate by the occurrence of low density, non-uniform nuclei. The other stage where the liquid substrate effect is most prominent is during growth, suppressing/delaying secondary nucleation. The non-accommodating nature of the liquid surface causes stronger bonding between gold atoms. Hence gold atoms prefer to grow on existing nuclei, rather than to increase coverage on the liquid surface. Thus the condensate morphology on the liquid surface exhibits multilayer growth. These interactions are valid for minimally interacting condensate-substrate systems and for heavy mass incoming species at slow deposition rates. Nevertheless, this liquid substrate effect could be applicable to a variety of systems and provides useful insights to predict the morphology for systems offering higher vibration modes.

In the subsequent chapter vapor deposition onto liquid substrates is modeled using kinetic Monte Carlo simulations. The proposed mechanism of the liquid causing additional desorption events of the weakly bonded gold atoms is validated.

Chapter 5 Simulation of Nucleation & Growth on Liquid Surfaces

5.1 Introduction

The unique morphological features observed during gold vapor deposition onto silicone oil demonstrate the influence of the liquid substrate. However, it is challenging to quantify the influence of the structure of a solid/liquid substrate experimentally. To overcome this, nucleation and growth on the liquid surface have been modeled to investigate the characteristics of surface kinetics. The two main variables considered to differentiate solid and the liquid substrates are (a) molecular frequency and (b) binding energy. The change in morphology on varying these two parameters is mapped pictorially. Time resolved condensate morphologies are generated and analyzed to support our hypothesis of additional desorption effects occurring at a liquid substrate.

5.2 Background

Initial vapor deposition experiments onto a liquid surface have been reported to result in fractal aggregates^{107,125}; percolation structures⁸³ or thin films^{94,126,127}. Modeling studies have been carried out to reveal the effects of deposition parameters, such as deposition flux or cluster diffusion on condensate growth⁹¹, post-deposition dynamics of ramified clusters and thin film growth¹⁰⁸. Simulation studies model non-equilibrium growth of thin films and aggregates considering classical models, such as Diffusion Limited Aggregation (DLA)¹²⁸, Cluster Cluster Aggregation (CCA)^{129,130} and Deposition Diffusion Aggregation (DDA)^{131–134}. DLA is an idealized process where the diffusion of matter/condensate to the aggregate is the rate limiting step and atoms irreversibly combine to form clusters¹²⁸. It generally results in monolayer growth under low deposition flux parameters. The CCA

model developed allowed all clusters to diffuse, irrespective of their sizes. Upon contact they were “made” to stick together. However the model does not consider continuous deposition of particles into the system - they are assumed to be all injected at once.

The DDA model developed by Jensen et al^{131,132} has been widely incorporated for growth on both solid as well as liquid substrates. This model considers continuous random deposition onto the substrate, enabling deposition, diffusion and aggregation to be differentiated. Thus, a large range of morphologies (fractal structures) with a characteristic length scale were developed. The characteristic length scale (L_1) is defined as the ratio of diffusion constant to the particle flux raised to the power of 0.25¹³³. This model has also been reported to closely match experimental results obtained during thin film growth¹³⁴ by Molecular Beam Epitaxy [MBE]. The effect of small island diffusion has also been modeled. The time and length scales used to define the obtained morphologies correlated well with experimentally controllable factors, such as deposition flux and diffusion constant. Therefore, the model is highly beneficial for studies of nanostructure morphology. It is from an understanding of island growth provided by these models on solid/crystal surfaces that growth on non-lattice substrates was developed.

One of the limiting factors of these models was that the rotation behavior of clusters was not considered during modeling. The experimental results from Ye et al demonstrated the rotation of large clusters, (formed during deposition of silver clusters on silicone oil) at a late growth stage¹²⁵. The rotation angle was noted to be random on the liquid surface in addition to distinct diffusion behavior of the islands. Lu et al used these results to model, using the help of Monte Carlo technique⁸⁶, growth of fractal islands on a non-lattice substrate. The first stage was modeled by randomly depositing disc shaped compact

clusters of the same size onto a liquid substrate (2D – non-lattice square) with periodic boundary conditions.

The second stage of growth, involving deposition, diffusion and rotation of compact clusters resulting in the formation of ramified islands, was simulated. The model involved diffusion of islands with variable diffusion lengths and their random rotation about their centre of mass. Upon completion of the simulation leading to the formation of ramified islands, their fractal dimensions were determined and found to be independent of the following parameters: (1) diffusion step length; (2) rotation angle¹⁰⁸; (3) diameter of the initially formed discs and (4) mobility.

Following this study, the DDRA (Deposition Diffusion Rotation Aggregation) model for non-lattice substrate was developed and the experimentally obtained morphology was simulated for various deposition flux rates and diffusion lengths. The maximum rotation angle of a cluster was given by⁹¹:

$$\theta_m = \theta_0 s^{-\gamma_\theta} \quad (5.1)$$

Where θ_0 is equivalent to 2π (radian) and γ_θ is indicative of the dependence of the maximum rotation angle on the cluster mass s . Thus, with the help of the DDRA model, the last stages of deposition and late stage growth on liquid substrates were simulated to reproduce the experimentally obtained morphology. In this study the very first stages of deposition (adsorption/desorption), diffusion and collision of atoms, leading to nucleation and growth of particles/clusters on a liquid substrate, were systematically simulated. The processes occurring within the first minute of deposition are considered and their morphologies are mapped.

The modeling of nucleation and growth of thin films is particularly challenging as it

involves various time and length scales, which span several orders of magnitude. Here the focus is on atomic motion which occurs at length scales of the order of a fraction of a nanometer, the corresponding time scales reflect the vibrational frequency of the substrate¹³⁵. Four elementary atomistic processes are considered during stochastic simulation of thin film growth (Figure 5.1). The model is implemented using the Kinetic Monte Carlo (KMC) method¹⁴. The first process involves random approach of single atoms or molecules onto the substrate surface. Their lateral positions are determined by the minimum energy of their Potential Energy Surface (PES). Secondly, transfer of the energy of the monomer/single atom to the bulk occurs. The third surface diffusion process is caused by uncorrelated sequences of jumps of the monomer from one minima of the PES to another. The process of desorption which gives the adatom the chance to detach from the surface, is the fourth atomistic process, critical to the current model. The rate at which these processes (except the first one) occur is directly related to the substrate molecular frequency (the pre-exponential factor ‘A’ discussed in the previous chapter).

Figure 5.1: Schematic of the atomic processes, showing the clustering of adatoms leading to formation of critical sized nuclei.

The adatom mobility on the surface is defined by the process of random walk surface diffusion. This involves only partial bond breaking for atoms to move from one minima to the other on the PES and eventually equilibrate at the right position. Desorption, on the

other hand, involves complete breaking of the bond formed on adsorbing onto the surface, causing the adatom to return back to the vapor phase. Here, the difference in activation energies for diffusion and desorption was set at relatively low values since only weak physical forces are present in our material system. Nucleation is set to begin on the substrate surface (heterogeneous nucleation) followed by growth, with direct attachment of atoms or with the surface diffusion of atoms. This results in thin film formation if sufficient time is provided for growth. The main difference between the solid and liquid substrate is found to be the difference in the distinct degrees of freedom (also referred to as molecular frequency) possessed by substrate atoms/molecules.

5.2.1 Kinetic Monte Carlo Simulation technique

The Kinetic Monte Carlo [KMC] method is developed from the Monte Carlo method, which uses random numbers during simulation¹³⁶. It is often used for analyzing processes involving diffusion, nucleation and growth including thin film growth processes such as CVD, PVD MBE etc^{91,137,138}. The major advantage of the kinetic Monte Carlo technique is that it allows calculation of the time scale and updates it automatically, hence correlating real time with simulation time. In addition, the algorithm considers the rate at which each event occurs. Before the start of a simulation, all events capable of changing the state of the system are considered. The rate of these events is known and a random number determines the probability of its occurrence. After the occurrence of the event, the system time is updated using the *residence time algorithm* given by ' $\log\mu/R$ ' where ' μ ' is a random number and ' R ' is the cumulative function of the state transition rate.

5.3 Simulation Methodology

The key variables utilized are described along with the definitions of the critical parameters. This is followed by detailed discussion of the developed algorithm along with the employed conditions.

5.3.1 Variables for Simulation

The basic distinction between a solid and liquid substrate is the degrees of freedom possessed by the substrate atoms/molecules. The higher degrees of freedom accessed by the liquid molecules are represented by common parameters, such as molecular frequency (Fr) and adsorption probability (AP)¹³⁹. As discussed in chapter 4, this property of the liquid heavily influences growth kinetics on its surface. Thus, to observe the morphological variation in this property, the liquid is assigned higher overall molecular frequency. Molecular frequencies varying from low to high (10^9 to 10^{16} /s), corresponding to a solid and liquid substrate, respectively, are investigated¹¹³. The change in desorption flux and the corresponding change in condensate coverage is also presented.

The second variable is adsorption probability. The adsorption probability is defined as the ratio of atoms adsorbed onto the substrate to the total number of atoms impinging on the substrate. The adsorption probability is utilized to represent condensate – substrate binding energy (which, in turn, strongly affects atom/particle mobility). As seen from the earlier chapter, the concentration of adatoms on the substrate is directly dependent on the binding energy of the substrate surface¹⁴. Thus, a higher adsorption probability (AP) corresponds to a substrate providing higher binding energy.

Secondly, AP is used to verify that higher molecular frequency causes higher desorption

flux, which, in turn, alters condensate coverage on the liquid surface (equivalent to a lower adsorption probability). Thus, growth conditions which result in low condensate coverage are revealed. A variation in degrees of freedom of the condensing phase (molecular deposition) has been reported earlier to alter adsorption probability of the substrate¹³⁹. Here, on the other hand, it is used to represent the influence of the substrate's degrees of freedom. Thus, molecular frequency and adsorption probability are the critical parameters in this simulation. The other interaction forces considered are discussed later.

5.3.2 Kinetic Monte Carlo Simulation Method

The Kinetic Monte Carlo method utilized is run using Matlab. Given the large numbers of atoms, combined with the numerous possible pathways, the initial KMC results indicated that the simulations consumed large storage space and run time. This computer limitation did not allow simulation times to reach realistic times. Due to this, pathway selection and simulations and real time correlations are necessary. Hence, in addition to kMC, modifications e.g., time correlations with arrival of new atoms is employed, resulting in easier pathway selection with predetermined positions. Instead of updating real time using a traditional time algorithm, which involves the rate calculations of all events, real time is updated only with the arrival of a new atom. According to kinetic Monte Carlo simulations, the occurrence of each event is assigned a given probability. That is, all events have the possibility of occurring in a given time frame, but the frequency of occurrence (or event rate) varies, governed by the appropriate classical equation. For example, when substrate molecular frequency is 10^{12} , the arrival rate of a new atom onto the substrate (not necessarily adsorbed) is set to be $5.64 \times 10^4/\text{s}$, the rate of diffusion for a single atom is set to be $6.21 \times 10^6/\text{s}$ and that for desorption of a single atom is $1.94 \times 10^6/\text{s}$.

At any given moment, we consider one of the events (arrival of a new atom / diffusion / desorption) to be occurring. However, within this time frame (1 s), the arrival of a new atom happens 5.64×10^4 times, other events also follow their event rate accordingly. Thus, calculation of the number of atoms arriving on the substrate is sufficient for time update and real time correlation. The time update does not take into account diffusion and desorption times, as these events occur simultaneously with the arrival of new atoms. This algorithm is adequate for the current system and enables us to obtain reliable data without having to utilize large computing memory. Figure 5.2 shows the system flow for the simulation. Figure 5.3 (same color coding) shows the detailed algorithm.

5.3.3 Algorithm – Growth Model

A substrate built with an area of 25 nm*25 nm was utilized in the current simulation. The processes are shown in figures 5.2 and 5.3. At the beginning of each step, a random position is selected to determine the location for the event to take place, leading to state transition of the system. For a given position, several possibilities exist, depending on the condition of the selected site. The site could be empty or it could be occupied by a cluster. Furthermore, this site could be occupied by an atomic cluster (made up of a few atoms) prior to nucleation or it could be a cluster close to the critical nucleation size or even a nuclei. If the randomly selected position is empty, a newly evaporated atom could adsorb onto this site or be present above the substrate. If the position is occupied by a cluster (which is not a nucleus), a newly deposited atom has the possibility to adsorb onto the cluster or just stay above its surface. The cluster may undergo desorption or perform diffusive motion along the substrate surface. If the position is occupied by a nucleus (or by a particle post nucleation) directly, a newly arriving atom could adsorb on it to yield

3D cluster growth. This cluster is also given the probability to diffuse. On the other hand, if the incoming atom is in the periphery of the nuclei/particle, it could adsorb onto the substrate position where it was deposited or it can diffuse and combine with nearby nuclei, resulting in lateral growth.

Figure 5.2: System flow for the current simulation

However at each given position, only one event would be allowed to happen for each iteration and this event is selected by the pathway selection procedure according to the event frequency or event probability. For instance, the probability of adsorption of new atoms depends on the flux and adsorption probability (AP). The occurrence of diffusion and desorption depends on the activation energy for diffusion, substrate molecular frequency, etc. The equations employed to determine the frequency of occurrence and conditions under which these processes take place are discussed in the next section. Coalescence and coarsening were also considered in this simulation. Simulations, with emphasis on diffusion and coarsening dynamics, are investigated in the subsequent chapter.

Figure 5.3: Algorithm for each iteration (in accordance to the growth process) adopted

A. Vapor deposition, diffusion model and Critical Size of Nucleation

To achieve an efficient simulation time, some of the processes were simplified. Surface diffusion causes collision and aggregation of atoms into clusters, eventually giving rise to the formation of critical size nuclei. The number of atoms in these critical nuclei was set to be 10. This was chosen for better simulation efficiency and ease in computation. Gorodetsky and co-workers¹⁴⁰ have reported that nucleation is critical to the free energy and also to the volume mismatch of clusters and their crystal structure. It was reported

that when a cluster consists of 10 atoms, the mismatch could be dramatically reduced and thus could be considered equivalent to that of nucleation. In addition, conventionally, clusters with two or more atoms are considered to be stable i.e., they have higher probability of gaining atoms than losing an atom^{141,142}. Therefore, several cases of growth under low temperatures consider critical cluster size to be 1. However, it is mostly under high deposition temperatures that critical size is larger than 1¹⁴¹. Consistent with nucleation theory, prior to achieving this critical size the clusters were given the possibility of desorption as a whole. However, partial desorption was not allowed, implying stronger binding between condensate atoms compared to binding with substrate surface atoms. Several KMC studies make a similar assumption that clusters after attaining critical nucleation size are stable and not allowed to break up¹⁴³. Thus, desorption is disallowed after nucleation and the cluster is allowed to stay indefinitely on the substrate with its mass conserved. This factor would contribute to the coverage observed from the simulated images. Further, it is these clusters which are involved in coalescence and/or coarsening. To observe the time dependent evolution in morphology, various snap shots were captured at different time scales. These conditions are also in agreement with the experimental conditions. The time algorithm (adapted from the conventional KMC technique), involves the time increment with respect to the atom arrival rate.

5.3.4 Simulation Conditions and Equations

Conventional Arrhenius equations were applied for diffusion and desorption processes and are presented below. For a single atom, surface diffusion processes occur with a frequency of:

$$v_d = v_0 e^{-E_d/(K_B T_s)} \quad (5.2)$$

The mean time for diffusion is

$$\tau_d = 1/v_d = 1/(v_0 e^{-E_d/(K_B T_s)}) \quad (5.3)$$

The diffusion coefficient (D) for a single particle is

$$D = a^2 v_0 e^{-E_d/(K_B T_s)} \quad (5.4)$$

And the distance a monomer travels on a surface in time τ is

$$l = \sqrt{D\tau} \quad (5.5)$$

v_d the diffusion frequency, v_0 the substrate molecular frequency, E_d the activation energy for surface diffusion, a the substrate lattice length, T_s the substrate temperature and K_B is Boltzmann's constant. Some of the previously reported models restricted atomic motion to only four directions⁸⁶. On the other hand, here, random walk was considered and clusters were allowed to move in any chosen direction (360° angular movement), corresponding to a non-lattice substrate surface.

Similar to diffusion, desorption processes also occur with a frequency given by:

$$v_{des} = v_0 e^{-E_{des}/(K_B T_s)} \quad (5.6)$$

The mean time for desorption is

$$\tau_{des} = 1/v_{des} = 1/(v_0 e^{-E_{des}/(K_B T_s)}) \quad (5.7)$$

v_{des} is the desorption frequency and E_{des} is the activation energy for desorption.

For clusters with n atoms, the diffusion energy was calculated by:

$$E_{dn} = E_d + (n - 1)E_b \quad (5.8)$$

where E_b is the lateral binding strength between particles. For clusters with n atoms, E_d is substituted with E_{dn} .

Similarly, for the desorption process,

$$E_{\text{desn}} = E_{\text{des}} + (n - 1)E_{\text{b}} \tag{5.9}$$

For improved efficiency, equations (5.4) and (5.5) were combined and simplified to one equation for each diffusion step to determine the diffusion length, which is

$$L = A/n \tag{5.10}$$

where n is the number of atoms in one cluster and A is a constant of the same order as the lattice length. However, since the substrate surfaces considered in this case are not crystalline, A was taken as 0.4 nm, which is slightly higher than the typical lattice length¹⁴⁴. The relevant energies under which the simulation is carried out along with the range of variable values are listed in Table 5.1.

Table 5.1: *Conditions for simulation* – The values of various parameters utilizing in this substrate along with the variables range are listed.

Conditions for simulation							
Diffusion Energy – E_{d} (eV)	Desorption Energy – E_{des} (eV)	Lateral Bonding – E_{b} (eV)	Flux (atoms/(s.m ²))	Substrate Area (nm*nm)	Source Atom Radius (nm)	Temperature (K)	Critical Nucleation (No. of atoms)
0.32	0.34	0.01	6.37×10^{19}	25*25	0.1	298	10
Variables							
Molecular Frequency 10^9 - 10^{16}				Adsorption Probability 0.001-1			

The vapor deposition flux and substrate temperature were chosen according to the experimental conditions. The lower supersaturation condition was chosen to guarantee minimal vapor dynamics and the other parameters were selected to obtain a simple yet efficient computational method.

5.4 Results and Discussion

5.4.1 Molecular Frequency as the Variable

In this section, the simulated morphologies obtained as a result of varying the substrate's molecular frequency are discussed. During these simulation runs, the adsorption probability of the substrate was set to be a constant of 0.1.

Figure 5.4 shows the simulated images obtained for substrates with different molecular frequencies captured at a constant real time equivalent of ~ 1 s. Figure 5.4a shows the simulated image of the substrate (molecular frequency of 10^9) after 1s deposition time. The subsequent images of 5.4b-5.4h show the morphologies obtained for substrates with molecular frequencies from 10^{10} to 10^{16} . The color coding for the simulated images are as follows: blue dots indicate a conventionally nucleated cluster; red dots indicate a cluster experiencing coalescence. The magenta dots represent cluster/particle formed post coalescence. The green dots indicate a cluster experiencing coarsening. The black dots represent single atoms. It can be observed that, during the same deposition period, higher film coverage is observed on a substrate with lower molecular frequency, indicated by the 68% coverage on the substrate with molecular frequency of 10^9 . As the substrate frequency is increased, film coverage displays a decreasing coverage trend, e.g., 27% and 10.8% coverage displayed for substrate molecular frequencies of 10^{12} and 10^{16} , respectively. The other interesting observation is the changing particle number density obtained on different substrates. At lower frequencies larger particles with lower number densities are obtained. At high frequencies, higher number density particles with relatively narrow size distribution can be observed. This indicates the availability of larger concentration of adatoms available on substrates with low frequencies.

Figure 5.4: The condensate morphology captured at real time = 1s, for varying substrate molecular frequencies. The frequency (Fr) and coverage (C) are as shown with the images.

A. Effect of Time on Condensate Coverage:

The time required for each of these substrates to attain a given condensate coverage is investigated. Figure 5.5b shows that to obtain the same coverage of, say, 50%, the time required increases as the substrate molecular frequency increases. When the substrate molecular frequency is 10^9 (Figure 5.4a), 0.972s is required to reach 50% coverage. On the other hand, when the molecular frequency increases to 10^{16} the time required is 1.29 s (Figure 5.4h) to achieve the same coverage.

The particle size and number of particles for a given coverage depend on the molecular frequency of the substrate. As the molecular frequency increases, coverage morphology shows that a larger number density of smaller particles form the majority of the condensate coverage. On the other hand, for substrates with lower molecular frequencies,

larger size particles are in the majority, but are smaller in number. This can be attributed to the probability of formation of a dimer/critical nuclei. The effect of adatom concentration on particle density is discussed in section 5.4.3.

Figure 5.5: (a) Time required to achieve a given coverage for varying substrate molecular frequencies is shown at $AP = 0.1$ [Reference¹⁴⁵]; (b) Time to achieve a constant 50% coverage for substrates with varying molecular frequencies.

Condensate growth time and evolution is shown in Figure 5.5a from the growth time v/s coverage plot for varying substrate molecular frequencies. For the same period of deposition, substrates with higher molecular frequencies require longer growth time to achieve given condensate coverage. This implies that substrates with higher frequencies display delayed film formation time, whereas faster coverage can be expected for substrates having lower molecular frequencies. These inferences can be correlated with liquid substrate conditions. Liquids possess larger degrees of freedom (equivalent to higher molecular frequencies), hence there is lower coverage or delay in achieving a higher condensate coverage (Chapter 4).

B. Effect of High Frequency:

The influence of higher frequency causing a delay in film formation is discussed in this section. Equation 5.7 gives the mean time of desorption - the time that an atom is permitted to stay on the substrate. The mean time τ_{des} decreases with increasing substrate molecular frequency ν_0 . Thus, it would be easier for atoms to desorb from the substrate surface, resulting in reduced mean residence time on the substrate. Consequently, for the same deposition time relatively higher desorption rate from the substrate surface can be expected. Figure 5.6a – 5.6c show desorption probability results at different frequencies. The images show the effect of randomly chosen desorption events and their probability of occurrence. Initially, the substrate is completely filled with atoms, indicated by blue dots. The red dots indicate unoccupied or empty substrate sites, resulting from desorption. In this case, diffusional processes were not considered. The molecular frequencies used are 10^{11} , 10^{12} and 10^{13} /s. When the molecular frequency is low, a greater number of atoms stay on the surface (majority of the surface is blue (Figure 5.6a)). However, as frequency increases, a greater number of atoms desorb from the surface, leaving behind a nearly empty substrate surface (red).

Figure 5.6: Desorption events for substrates with molecular frequencies of, (a) 10^{11} ; (b) 10^{12} ; (c) 10^{13} . Blue dots indicate the presence of atoms on the substrate and the red dots indicate the unoccupied/empty substrate sites - post desorption [Reference¹⁴⁵]

Furthermore, increase in occurrence of desorption events, which allows for shorter residence time for adatoms, reduces their collisional probabilities with other adatoms on the surface. Hence, this reduction in surface concentration makes the formation of stable configuration atomic clusters more difficult¹⁴⁶. The single atoms are unable to find other adatoms to cluster together and thus undergo desorption with time. This phenomenon leads to an increase in formation time of the atomic clusters, delaying nucleation and growth. Hence, an increase in molecular frequency is one of the factors responsible for the observed delay in formation time of the condensate. However, the non-uniformity in condensate coverage is not as obvious as seen in experiment. This could be due to the pre-set adsorption probability being high for the chosen substrate and only a combination of two factors, i.e., molecular frequency & adsorption probability, will result in non-uniform distribution.

5.4.2 Adsorption Probability as the Variable

In this section, the morphological changes observed due to a change in the adsorption probability of the substrate is presented. The substrate's molecular frequency is set at 10^{12} , a common value for both solid and liquid substrates. Figure 5.7 shows two important observations. As AP decreases (a) longer time is required to attain given coverage and (b) an obvious non-uniformity in condensate coverage. That is, a smaller number of larger size particles are observed at lower AP values. This is associated with a smaller number of available atoms/clusters on a low AP substrate. On the contrary, at higher values of AP, a larger number of atoms available on the surface provide larger collision probabilities, thus uniform distribution is achievable. Therefore, even with smaller growth times a larger number of condensate particles are uniformly distributed at higher AP.

Figure 5.7: The condensate morphology observed at constant coverage of 10%, 50% and 70% for varying adsorption probabilities. The time required to form the given morphology is also shown. The substrate molecular frequency is maintained to be 10^{12} . [Reference¹⁴⁵]

The range of number of atoms in each cluster obtained at different adsorption probabilities at coverage values of 10%, 50% and 70% are shown in Table 5.2. A large variation in cluster size and distribution obtained under varying APs can be identified. At lower adsorption probability, the number of atoms in each cluster lies in a large range, this size range increases as growth proceeds or coverage increases. For instance, at 10% coverage and substrate adsorption probability of 0.001, the clusters contain as few as 10 atoms to as many as 900 atoms. However for an adsorption probability of 1, the clusters only vary

from 10 atoms to less than 60 atoms. Thus, at higher AP, the range of number of atoms in each cluster is narrow, similarly for the particle sizes. Although coverage increases with time at lower adsorption probability, non-uniformity in material distribution broadens quickly. This is due to preferred growth of atoms from the vapor on existing particles, since the substrate exhibits low adsorption probability. Therefore, although empty areas continue to exist, particle growth also continues. This can be correlated to the beginning of multilayer growth at an earlier stage on liquid surfaces, as demonstrated in the earlier chapter.

Table 5.2: Range of number of atoms in a cluster, obtained at varying adsorption probabilities at a given coverage.

Range of number of atoms in a cluster				
Coverage	AP=0.001	AP=0.01	AP=0.1	AP=1
10%	10-900	10-300	10-200	10- (<60)
50%	10-3800	10-2200	10-750	10-350
70%	10-1.8*10 ⁴	10-8000	10-3000	10-(<7500)

The plot shown in Figure 5.8a highlights the role played by the substrate adsorption probability on the change in coverage with time. For a given deposition time, condensate coverage on a substrate is larger at higher adsorption probabilities. On the other hand, at lower adsorption probabilities, greater time is required to achieve the same coverage. This is observed despite the higher number of atoms in each cluster. This verifies preference for multilayer particle growth over increased overall coverage. Thus, at low APs, the time required to achieve larger coverage is higher and smaller number of larger size particles is observed even at higher coverage (Figure 5.7)

Figure 5.8: (a) Time vs coverage plot showing the influence of the varying AP from 0.001 to 1 at a constant molecular frequency of 10^{12} [Reference¹⁴⁵]; (b) Number of atoms desorbed after 0.5 s for AP = 0.001 to 1.

5.4.3 Discussion:

The effect of lower adsorption probability, which gives rise to non-uniform condensate coverage and a delay in their growth stages, is discussed. Firstly, consider desorption. Figure 5.8b shows the number of atoms desorbed after 0.5 s for each of the adsorption probability values. The number of desorbed atoms is far smaller at higher adsorption probabilities. This indicates that a smaller number of atoms are available for nucleation on substrates with lower APs. Consequently, it is much more difficult to form stable nuclei as a result of low adatom concentration. However, given the higher concentration of adatoms at higher APs, this is reversed. Thus, irrespective of the reason for lower number concentration of available atoms on a substrate surface (lower binding energy / induced desorption at higher temperature / higher degrees of freedom of the substrate molecules etc.) nucleation and growth kinetics are significantly slowed down. Hence AP plays an important role in defining condensate growth time. The time required to observe the first

nucleation event for varying molecular frequencies confirms the above reasoning (Table 5.3).

Table 5.3: Time required for the appearance of the first nuclei at varying molecular frequencies and constant AP =1.

At Molecular Frequency: (AP = 1)	10^{10}	10^{12}	10^{14}
Time of occurrence of first nuclei (ms)	79.4	104.5	107.7

Furthermore, even after the formation of the first nuclei for a substrate with high AP, large numbers of adatoms would be available on the substrate. This large concentration of adsorbed adatoms throughout the surface ensures greater collision probabilities, leading to secondary nucleation within a short span of time. This minimal time difference between secondary and primary nucleation does not allow primary nuclei to grow at a faster rate. Hence it can give rise to uniform and narrow size distribution of particles on the substrate surface. This is observed for AP =1 at 10% coverage (Figure 5.7). On the contrary, at AP=0.001, a time of ~6.7 s is required to achieve 10% coverage. It indicates delayed occurrence of nucleation and subsequent growth at lower adsorption probabilities. The occurrence of the first nuclei at AP = 0.001 was found to be at ~5 s whereas at AP = 1, the appearance of first nucleus took only 0.1 s. Thus, initial nucleation events are rare and occur at random positions at lower APs. Even subsequently, low AP of the substrate also delays secondary nucleation time. During this longer incubation time for the formation of secondary nuclei, existing nuclei are capable of growth to larger sizes, capturing existing adatoms either from the surface or directly from the vapor. Hence, non-uniformity in condensate coverage is evident at lower APs (Figure 5.7). In addition, the weaker

preference of the depositing species to bind on the substrate, combined with its higher affinity to bind with its own material, would result in multilayer growth. This is indicated by the larger number of atoms in clusters at low AP (Table 5.2), leading to 3D growth of the existing nuclei. Thus, multilayer growth would be preferred, whereas lateral growth, providing larger condensate coverage on the substrate, is slowed down. The rate of growth of existing particles occurs faster than the formation of new particles (secondary nucleation).

A. Comparison of High & Low Adsorption Probabilities:

Figure 5.9 shows the morphological evolution process with time for $AP=0.001$ and $AP=1$. The black dots represent single atoms or pre-nucleation clusters on the substrate surface. At low AP, nucleation density is much lower, unlike the large number of uniformly distributed nuclei seen on the surface with higher AP. The presence of smaller number of nuclei on the substrate allows them to grow larger, at the expense of forming secondary nuclei. Thus, it can be observed that at the second growth stage (row 2 in Figure 5.9); larger particle sizes can be identified on the low AP substrate. In summary, adsorption probability is the other important parameter responsible for delaying condensate growth. More importantly, the condensate distribution is largely dependent on this parameter.

Figure 5.9: Nucleation and growth simulated for (a) $AP = 0.001$ and (b) $AP = 1$ at $Fr = 10^{12}$ with adatom/cluster concentration (represented by black dots).

An additional observation is that coverage rate is more sensitive to AP compared to molecular frequency. With change in molecular frequency both adatom mobility

(diffusion events) and desorption frequency are altered. At higher molecular frequency, desorption has high probability for occurrence, which makes accumulation of adatoms difficult. Besides, diffusion events which are responsible for the clustering of adatoms, are also promoted. The additional desorption events affect the growth morphology only in the initial stages when there are few atoms on the substrate. At late stages, this effect is not evident, as the larger number of adatoms accumulated over time are capable of sustaining growth even with increased desorption events. However, at low AP, the smaller number of adatoms available on the substrate results in higher nucleation barrier due to material limitation. Therefore nucleation events are reduced and only later does the growth of the nuclei play a significant role in coverage. Thus, the effect of lower AP is more prominent during condensate growth.

Conventionally, AP is a function of a variety of factors such as condensate-substrate binding energy, substrate temperature, substrate intermolecular forces, kinetic energy, mass of the incoming species etc. Considering our experimental observations as well, the substrate's degrees of freedom combined with the effective bond strength influences AP on a liquid surface. Thus, deposition of gold on silicone oil experiences lower adsorption probability as a consequence of both lower bond strength and increased desorption events (response from the liquid substrate), resulting in observed lower condensate coverage. Also, the desorption rate is exponentially dependent on binding strength. Thus, considering that AP is equivalent to binding energy, its effect has a larger impact on growth kinetics.

5.5 Correlation of simulated and experimental morphologies:

The above simulation results establish the influence of both molecular frequency and

adsorption probability. By studying their effects independently, more realistic systems were simulated. Considering these results, substrate parameters were defined so as to represent a 'solid' and a 'liquid' and compared with experimental results. As solid surfaces have lower molecular frequencies and higher AP, $Fr=10^{10}$ and $AP=1$ were chosen. On the other hand, liquid substrates, conventionally displaying higher degrees of freedom, were assigned with a higher $Fr=10^{14}$ and lower $AP=0.001$. Figure 5.10 shows the change in particle size and number density with time (simulated growth stages) quantified utilizing morphologies obtained on the representative solid and liquid substrates. It is clearly seen that for the case of the liquid substrate (Figure 5.10b), the change in particle density with time is small, whereas the mean particle size increases continuously. Multilayer growth can be expected to be prevalent from the initial stages itself. *Thus, these simulation results are consistent with experimental observations of liquid substrates favoring condensate growth over coverage.* Also, the particle density change is minimal, implying saturation of the number of particles (in both experimental and simulated morphologies) after the initial nucleation events. These observations are thus in agreement with the DDA model¹³² as well as classical nucleation theory¹¹⁴, which predict cluster density saturation for a given deposition mass.

The solid substrate conditions display conventional growth mode (Figure 5.10a). Multilayer growth can be expected to occur at a very late stage (stage 6), at this stage mean particle size increases whereas number density decreases. Moreover, the simulated results give a more complete picture of growth, compared to the experimental conditions. In the experimental results, the solid substrate displays a high particle density from the first stage of capture. However, theoretically, particle density on a conventional solid

substrate first increases with growth time (Figure 5.10a) and decreases only in the late growth stage following the occurrence of coalescence and coarsening processes.

Figure 5.10: Observed changes in mean particle size and particle density with time (growth stages) for (a) solid substrate (AP=1; Fr = 10¹⁰) and (b) liquid substrate (AP = 0.001; Fr = 10¹⁴) obtained from simulation results.

Furthermore, the evolution in morphologies is also shown for both the substrates (Figure 5.11) and compared to experimental morphologies obtained after 20 s of deposition, for a flux of 2.26*10²⁰ atoms/ (s*m²). The late stage images are similar to the experimental morphologies, with clearly evident large empty areas unlike the solid counterpart, which displays uniformly distributed condensate clusters. As shown earlier, even when AP was

varied independently the number of atoms in each of the clusters under liquid substrate conditions was observed to be larger than the clusters obtained on solid substrate conditions. The differences in formation kinetics on these substrates are thus demonstrated, verifying our hypothesis. In addition, other metal vapor deposition studies on silicone oil also report, under low deposition flux conditions, the formation of discrete, circular clusters in the first growth stage regime¹⁰⁵. The saturation of number density of clusters after the initial nucleation events is associated with two factors, similar to observations made in the current study: (1) the efficiency of the stable clusters to “empty” their surroundings of smaller clusters and adatoms and (2) lower probability for encounter of two large (stable) clusters, since their diffusion is slow. The second factor is also supported by our proposed mechanism that growth of existing nuclei is more likely (suppression of secondary nucleation) in the liquid-condensate material system, due to the gas-phase transport mechanism (section 4.7, chapter 4).

Figure 5.11: Condensate simulation morphologies obtained for a liquid substrate ($Fr = 10^{14}$ and $AP = 0.001$) and a solid substrate ($Fr = 10^{10}$ and $AP = 1$). The final images are compared to the experimentally obtained TEM images of gold deposited onto silicone oil and amorphous carbon surfaces. [Reference ¹⁴⁵]

5.6 Chapter Summary

In conclusion, the nature of a liquid substrate can be modeled using molecular frequency and adsorption probability as variables. While these variables may not be the exclusive ones, they are shown here to be primary, sufficient to describe many of the key features observed empirically. The effect of these parameters on the condensate growth has been investigated. A higher molecular frequency gives rise to low condensate coverage and largely influences initial growth stage. Adsorption probability, on the other hand, has a higher impact on the condensate coverage rate. A non-uniform morphology, with larger cluster sizes formed on substrates with low AP, has been demonstrated. The increase in desorption rate with increase in molecular frequency is clearly shown, consistent with the hypothesized effect of the substrate during condensation. Morphologies obtained from more realistic models of solid and liquid substrates are shown to be in good agreement with the experimental results.

The simulation results not only correlate with our experiment observations for a liquid substrate, it can also be applied to the investigation of other factors such as temperature, which would cause a variation in the substrate structure.

Chapter 6 Shared Coarsening on Liquid Surfaces

6.1 Introduction

Early onset of coarsening which enables particle monodispersity is termed as ‘shared coarsening’. This phenomenon depends on the spatial distribution of the particles. Shared coarsening is demonstrated utilizing a liquid substrate in this study. The influence of the liquid substrate on nucleation and growth during vapor deposition has been established in earlier chapters. The entropy driven effect, due to the perturbation caused by its structure, allows the depositing species to adopt two plausible routes, i.e., desorption and / or diffusion. The effect of increased desorption events, which depends on the condensate substrate-binding energy, has been observed to result in low condensate coverage, enhanced multi-layer growth and delay in secondary nucleation. However, it is known that desorption is an energetically expensive event compared to diffusion. Therefore a suitably chosen material system can result in a large liquid substrate effect on the diffusion kinetics. The subsequent changes in condensate growth and morphology in such a material system were thus investigated via simulation and experimental techniques.

We have observed that thermal evaporation of copper vapor onto silicone oil (discussed in detail later) resulted in the formation of monodisperse copper nanoparticles on the liquid surface, whereas large copper islands, with broad size distributions, were observed on the solid surface (Figure 6.1). The particle size uniformity observed on the liquid substrate, despite the small inter-particle distances led us to further investigate the diffusion kinetics between particles. Subsequently, the formation of these particles was attributed to the novel coarsening dynamics expected to occur under the given conditions. The successful

incorporation of a liquid substrate for the synthesis of monodisperse nanoparticles is highly beneficial, given the number of significant potential applications^{103,147–151}. Hence the formation mechanism leading to growth of uniform size nanoparticles on a 2D surface is discussed for various particle mobility and adsorption probability values of the substrate.

Figure 6.1: Thermal evaporation of copper onto (a) surface of solid a-Carbon and (b) surface of a liquid (silicone oil) shows distinct particle shape and size distribution on the two substrates.

The occurrence of nucleation and growth in the very first minute of deposition has been modeled (chapter 5). Furthermore, as growth proceeds by the incorporation of new atoms, diffusion fields overlap, initiating coarsening. The diffusional geometry influences the arrangement and size distribution of the particles formed, which is important for condensate growth on the liquid surface. It is the interaction between these particles that determines the size distribution. Therefore, coarsening processes become very important. In this thesis, a novel phenomenon called ‘shared coarsening’ is proposed to result in

monodispersed nanoparticles. It is the effect of coarsening experienced by a smaller particle surrounded by several larger particles of the same size. This process leads to monodispersity. The focus is on adatom mobility since it is critical in determining the kinetics of particle formation. Firstly, a kinetic Monte Carlo study of vapor deposition onto a *defect free* ideal surface is reported, the growth of uniformly sized particles in relation to diffusion dynamics is studied. Secondly, a liquid-condensate system with suitable properties is utilized as the substrate for deposition and the shared coarsening mechanism is validated. Copper nanoparticles with a narrow particle size distribution are synthesized experimentally. However, prior to examining the methodology and results obtained, it is necessary to elucidate the mechanism of shared coarsening.

6.2 Background

Coarsening is the continued evolution of a system to reduce its interfacial energy, along with the reduction of its interfacial area, while the volume is conserved^{152,153}. It is generally considered to increase polydispersity and often said to arise from a characteristic difference in particle dimensions. This change in particle size (and shape) introduces a chemical potential gradient into the particle surroundings. This results in inter-particle diffusional transport by the detachment of atoms from one particle and condensation/attachment onto another. Coarsening results in the growth of larger particles at the expense of smaller ones, given the higher chemical potential of the latter, leading to polydispersity¹⁵². Here we identify a mechanism which can enable coarsening to maintain a narrow size distribution, introducing a novel approach to obtain monodispersed nanoparticles under an open system, two dimensional growth conditions. The two dimensional conditions refer to the occurrence of growth on the substrate surface only,

and not in its bulk.

The classical mean field theory of coarsening (the Lifshitz-Slyozov-Wagner (LSW) theory) has been established for sparsely distributed (small volume fraction) spherical particles¹⁵⁴. The LSW theory was developed to model kinetics of precipitate growth from supersaturated solid solutions. It has also been applied to coarsening of grains in liquid-phase sintering^{155,156} and to the coarsening of pores in solid-state sintering^{157,158}. The theory corresponds to a zero volume fraction approximation but has been modified for finite volume fractions in order to correspond to real situations. It predicts the cube of the average particle size $\langle R \rangle$ to be linearly proportional to time 't' and is represented by the following equation¹⁵⁹, with 'k' being the rate constant, $\langle R_0 \rangle$ the average length at time = 0.

$$(\langle R \rangle)^3 - (\langle R_0 \rangle)^3 = kt \quad (6.1)$$

Although many theories of coarsening considering the effect of change in volume fraction have been put forward^{160–163} the LSW cubic law of coarsening kinetics is still widely used. It has been reported from studies that, this theory applies to spherical particles of a liquid or solid phase dispersed in a liquid matrix. Even in such systems there are no stresses present between the dispersed and matrix phases due to volumetric mismatches. It was noted that, even under these systems the ideal limit of zero volume fraction is not attained. And therefore the volume fraction was established to be accounted as the diffusion geometry is strongly influenced by neighboring particles. And following this, the LSW theory also does not discuss particle growth rate to be either dependent on the number of particles or their separation distances in the given system. The influence of the *surrounding particles* on coarsening was first put forward by the communicating neighbor

(CN) growth model of DeHoff¹⁶⁴. The interactions between the particles are treated by introduction of communicating surface elements and a local diffusion length, for both sparse and dense structures. The diffusion length scale appears as the harmonic mean relative to the distance among neighboring particles. Thus, diffusion controlled coarsening is approached using this geometrically general theory. Here we examine the effect of neighboring particles on a 2D surface and how the spatial arrangement of particles can result in monodispersity by coarsening.

6.2.1 Exclusion Zone Model:

Studies of nucleation during electrochemical reactions have shown local inhibition of nucleation rates and exclusion zones^{165–167}. The nearest neighbor particle effects on the spatial distribution and nucleation rates was reported for electrodeposited nuclei undergoing diffusion controlled growth. The exclusion zone model is discussed further. The area swept by atomic clusters to achieve critical size captures all existing single atoms as well as smaller atomic clusters, defining its initial influencing area/diffusion zone. Subsequently, atoms arriving/deposited into this zone will be bound to the corresponding nuclei, with no freedom to wander out of the zone. Thus, from these stages of atomic clustering leading up to the formation of primary nuclei, diffusion zones of the primary nuclei are built up. The denuded zones left behind do not belong to any of the particles formed. These denuded zones are available for the formation of secondary nuclei, i.e., those nuclei formed at the next nucleation event. The diffusion/exclusion zones around the primary nuclei are defined by material properties related to adatom diffusion length and cluster size/volume, concentration of adatoms on the surface and adsorption probability. Depending on adsorption probability values, formation of primary

nuclei is also critical to the process, as their spatial distribution defines denuded zones available for formation of secondary nuclei, assumed to be constant at areas not covered by planar diffusion zones. The covered areas are assumed to have zero nuclei formation rate. The exclusion zone model also reports inhibition of occurrence of nucleation in that exclusion region with a growing diffusion field^{168,169}. Figure 6.2 shows a schematic of the growth stages, along with the final diffusion zone of the primary nuclei formed.

Figure 6.2: *Exclusion Zone Model – formation of primary nuclei:* Illustration of vapor condensation leading up to nucleation. (1) Substrate with randomly deposited single atoms. (2, 3 and 4) Surface diffusion of adatoms results in clustering. (5) On reaching the critical number of atoms in a cluster, the primary nuclei formed are displayed, along with the diffusion zones/ area scanned by them to attain the critical size.

6.3 Special case: Growth on liquid surfaces

The liquid interface, which does not have preferential nucleation sites, is consistent with the exclusion - zone model. Consider an open system with a controlled rate of vapor deposition onto a substrate with uniform surface energy. Atomic vapor adsorption occurs at randomly distributed sites all over the surface. The density of adsorbed atoms (adatoms) is dependent on vapor supersaturation, condensate-substrate binding energy, substrate thermal energy and structure. Here, it is represented statistically by the value of ‘adsorption probability’, defined as the ratio of the “number of atoms adsorbed onto a substrate” to the “total number of atoms impinging on the substrate”.

The adatoms residing on the surface possess a certain ‘mobility’ (related to their diffusion length ‘ l ’ and activation energy for diffusion (DE)) to diffuse on the surface. Random walk collisions - as a result of this diffusion lead to formation of atomic clusters, which eventually form stable nuclei on attaining critical nucleus size. Apart from atoms/clusters themselves, the surface is free of high energy preferential locations, such as defects or contaminants – which otherwise would have caused selective concentration altering the particle size and distribution. A prerequisite condition for the occurrence of shared coarsening is that the condensate-condensate binding energy is to be much stronger than condensate-substrate binding energy, thus providing lower probability for desorption after atomic clustering and prior to nucleation. Given an idealized situation at this stage, it can be expected that the primary nuclei are formed at the same instance of time and are of the same size. The assumption is justified as the liquid surface is defect free, unlike a solid surface which offers preferential nucleation sites that would give rise to a polydisperse system. Therefore during primary nucleation on a liquid surface particle monodispersity is inherently present.

6.3.1 Proposed Mechanism

Consider the growth occurring after nucleation – 1. With increasing time atomic clusters close to critical size which are outside the existing exclusion zones of the primary nuclei capture sufficient atoms to result in secondary nucleation (Figure 6.3 – secondary nucleation). We propose that under two dimensional growth conditions, for appropriate atomic surface mobility and adsorption probability values, secondary nuclei could be coarsened simultaneously by their neighboring primary nuclei. This allows primary nuclei to grow at a similar rate, wherein smaller particles reduce in size and eventually disappear.

This results in improved monodispersity. However, the appropriate distribution of secondary nuclei is essential to obtain uniformly sized particles as the outcome. This condition of what we refer to as “shared coarsening”, could exist in any material. Thus, the defining parameters for shared coarsening are considered, with emphasis on the surface diffusion kinetics needed to induce monodispersity of the particles. The process is illustrated in Figure 6.3.

It begins with primary nucleation, with randomly positioned nuclei on a substrate, followed by a burst of ‘secondary’ nuclei. If the surface diffusion dynamics are appropriate (discussed later), secondary nuclei are formed in the denuded zones, such that they undergo coarsening from an equal number of nearest neighbors. This results in growth of the primary nuclei at a similar rate. This is the condition we refer to as shared coarsening. The larger particles (formed at an earlier time) grow bigger at the expense of these secondary nuclei, which grow smaller with time, and may even disappear due to shared coarsening (Figure 6.3). Eventually, uniformly sized particles themselves come into contact with each other, inducing coalescence and reducing monodispersity. The uniformity in particle size and shape is altered, leading to diffusional growth by Ostwald Ripening (OR). Shared coarsening is more likely to occur at an earlier growth stage, unlike conventional coarsening which is prevalent in the late growth stages. Appropriately chosen parameters can widen the occurrence of shared coarsening.

Figure 6.3: Shared Coarsening - Schematic showing the emergence of monodispersity via the shared coarsening effect followed by continued growth with time.

6.4 Simulation Methodology:

To study shared coarsening, a statistical simulation, adopting the kinetic Monte Carlo (kMC) method, was performed with *surface mobility* of the condensate atoms and their *adsorption probability* with the substrate as key variables. The change in monodispersity obtained by varying the diffusion length (l) at various adsorption probability values was analyzed and the optimum conditions to obtain uniform particle sizes determined. Pathway selection procedure and time algorithm adapted from kMC were used. A substrate with 50 nm*50 nm surface area with no preferential nucleation sites was modeled. The other parameters are the same as in the earlier chapter. The difference is the emphasis on coalescence and coarsening processes. The activation energy for diffusion is taken to be 0.24 eV and desorption energy is set to be 0.35 eV. The vibration frequency (ν_0) is set to be 10^{12} and the temperature (T) is assumed to be 298 K. The diffusion

coefficient ‘D’ plays a key role and is given by:

$$D = l^2 v_0 e^{-E_d/(k_B T_s)} \quad (6.2)$$

where ‘l’, the diffusion length is varied in the range of 0.4 to 1.6 nm to examine the effect of surface mobility on monodispersity. Every nucleus is set to have an attraction zone of coarsening equivalent to the ‘cluster radius + 0.0005*(number of atoms in the cluster)’. Coarsening begins when the edge of another smaller particle’s diffusion zone is tangential to this attractive zone. The atoms of the smaller nuclei diffuse towards the bigger one, given their difference in chemical potential. That is, coarsening is allowed to occur only when the smaller particle enters the diffusion zone of the bigger particle, as shown in the equation below:

Distance between two particles $\leq$

$$\text{Radius of smaller particle} + 0.0005 * (\text{Radius of bigger particle}) \quad (6.3)$$

The coarsening atomic flux is in the direction of the bigger particle within the attractive zone of the larger particle¹⁷⁰. At each instance, atoms of all smaller particles will attach to the bigger particle. The coarsening event is conducted after a certain period of time (500 steps in simulation or 22.12 ms in real time correlation) for ease in computation. Each simulation is run for 100,000 simulation steps (correlated time of ~0.44 seconds) and the morphology is mapped after every 50 steps. The exclusion zone model is adopted in this kinetic modeling method used here. The formation of nuclei in zones screened by existing particles is not allowed. The adsorbed atoms in an exclusive zone are allowed to contribute to the growth of the corresponding particle. This methodology is utilized to analyze the effect of neighboring particles, the effect of which is not seen in conventional coarsening. When the diffusion zone of a smaller particle is tangential with two or more

bigger particle, the atomic flux is shared, in proportion to the size of the particles.

6.5 Conditions to obtain a Narrow Particle Size Distribution (PSD):

The final particle size distribution largely depends on the growth pathways characterized by two critical factors investigated in this diffusion limited coarsening system: (a) adsorption probability (AP) of the substrate, which controls the surface adatom concentration and (b) diffusion length of adatoms, together which define interparticle distances. For each adsorption probability condition, the morphology is investigated to examine its effect on shared coarsening. The conditions giving rise to monodispersed particles were optimized.

Substrates with low AP give rise to low particle density. A narrow size distribution with higher particle number density is observed when short diffusion lengths are employed. When higher diffusion lengths are employed, a polydisperse system with low particle density is obtained. Given the low AP, their growth with time is minimal and thus particle sizes remain narrow. Nevertheless, due to slow growth rate, monodisperse particles can be obtained even at late stages. On the contrary, high AP substrates display narrow PSD only at early growth stages (Figure 6.4). The large number of adatoms allow for increased collision probability, resulting in high particle density. Again, smaller diffusion length gives rise to a narrower PSD.

Figure 6.4: Standard deviation in particle size v/s time for low and high adsorption probability values

A detailed investigation of the effect of adsorption probability, along with corresponding simulated morphologies is presented in Appendix A4.

6.5.1 Intermediate Adsorption probability – Shared Coarsening Effect: (Balanced state)

Consider the intermediate adsorption probability range, where shared coarsening is pronounced. Figure 6.5 shows the morphological evolution with time for a AP of 0.5 and E_d of 0.24 at $I=8$. Figure 6.5b also shows the particle size distribution normalized with respect to the mean particle size denoted by $\langle R \rangle$, where ‘R’ is the particle radius. In the first image, captured at t_3 , although a large number of particles are in the size range of 2 to 3 nm, the existence of a substantial number of smaller particles indicates a post-secondary nucleation stage. The particle sizes show a standard deviation (σ) of 0.6. With increase in time, i.e., at t_4 , the distribution significantly narrows (FWHM reduces from

0.56 to 0.32), due to shared coarsening. Here particles of smaller size are equally “shared” by larger particles. The bimodal distribution at t_1 (Figure 6.5e), is narrow due to effects similar to shared coarsening. This results in the higher size uniformity observed at stage t_5 . A drop in particle size standard deviation from 0.79 to 0.7 is displayed at this stage (Figure 6.5f). The corresponding PSD are shown for all the time scales.

After the shared coarsening stage, monodispersity is reduced because of particle coalescence. The simulated morphology at t_6 and the emergence of a second peak in the corresponding PSD plots, show that there are a greater number of larger particles (Figure 6.5g). Thus conventional coarsening occurs at late growth, eventually leading to film formation. Thus, the time window for particle size uniformity is short. The coalescence stage, which is responsible for broadening the size distribution, could be delayed on a 2D surface by varying the spatial distribution of the particles. This can be accomplished by tuning adsorption probability and diffusion length of depositing atoms. Here we show that adsorption probability of 0.5 facilitates shared coarsening, resulting in uniform particles. Morphologies for a range of adsorption probabilities and diffusion lengths were also investigated.

Figure 6.5: Effect of Shared Coarsening - Simulated images captured at increasing time steps of t1, t4, t6 and t9 corresponding to 10000, 40000, 60000 and 90000 steps. The continuous PSD evolution with time for AP = 0.5 are shown in e, f & g. The length scale of the simulated images shown is in units of A^0 .

The influence of diffusion length on PSD for a adsorption probability of 0.5 is shown in Figure 6.6. The images captured at a constant time (after 40000 steps) of deposition are compared. Monodispersity occurs at an intermediate growth stage. In the first image (at $l=4$) particles are uniformly distributed over the substrate. The standard deviation is 0.69, and the image is dominated by two different sizes, from primary and secondary/tertiary nucleation events. The interparticle distances are smaller, in accordance with the diffusion length. Although this condition does give rise to monodisperse particles, the higher particle density, combined with smaller interparticle distances leads to early onset of coalescence, causing the monodisperse environment to be short lived. On the other hand, the number of particles obtained at a higher diffusion length is small and large interparticle distances are observed (Appendix I). The average particle size is also large, due to the increased mobility of the particles ($\sigma = 1.45$). As seen at $l=8$, a balance in

diffusion length is critical to produce spatial distribution of particles appropriate to shared coarsening. Although σ is 0.89, the stability of particle size distribution is higher as the particles are not too close to each other. Therefore, for intermediate adsorption probability values, both small as well as intermediate diffusion lengths are suitable to achieve monodisperse particles.

Figure 6.6: The effect of varying diffusion lengths ($l = 4, 8, 16$), PSDs respectively in (a), (b) and (c) are shown with their corresponding simulated morphologies captured after 40000 steps (real time = 0.177 s) at adsorption probability of 0.5. The length scales of the simulated images are shown in units of $\text{\AA}^0$.

A larger diffusion length, which can be interpreted as increasing temperature, gives rise to large particle sizes and smaller number of particles i.e., a reduction in island density with the growth of larger aggregates¹⁷¹. The changes observed due to varying diffusion length can be related to change in surface kinetics due to external factors, e.g., kinetic energy of incident atoms, temperature of the depositing species or substrate temperature. It can also

be correlated to the magnitude of the response of the liquid substrate which can change diffusion length of the adatoms. Therefore, control of these parameters can be used to produce particles with a narrow size distribution.

6.6 Emergence of monodispersity:

As discussed, adsorption probability plays a vital role in changing surface kinetics. Differences in particle size are smaller in the initial stages, prior to secondary nucleation. With the growth of secondary nuclei, the variation in particle sizes increases, resulting in a broader particle size distribution. The size distribution has been compared for various AP values (Figure 6.7). Analysis has been performed using an image analysis software. The various standard deviation vs time plots are shown in Figure 6.8, computed for the particle size distribution obtained at various AP values. Values of $I = 4, 8$ and $E_d = 0.24$ were identified to be optimum parameters to achieve narrow PSD through shared coarsening.

Figure 6.7: Evolution of particle size and distribution with time for varying adsorption probability values of 0.1; 0.5 and 0.8. The diffusion length $l = 4$.

Figure 6.7 shows significantly increasing particle density with increase in adsorption probability, consistent with increasing concentration of adatoms available for nucleation and growth. Comparing AP of 0.5 and AP of 0.8, the average particle size of the latter is much larger. The changing particle size deviation with particle size is quantified in the standard deviation vs time plot. Lower AP yields particles with higher monodispersity (Figure 6.8). More importantly, a decrease in standard deviation with time occurs for the case of AP equal to 0.5.

Figure 6.8: Change in standard deviation in particle size with time for varying adsorption probability and diffusion length values

This trend of improved monodispersity with time, despite relatively close inter-particle distance is novel. This behavior for 2D growth is due to shared coarsening. A smaller particle can be coarsened concurrently by several larger uniformly sized particles and the smaller particles can also reach sizes comparable to larger particles. These effects give rise to monodispersity. The particle size distribution plots for intermediate AP (0.5) and small diffusion length ($L=2$) show increase in particle size uniformity with increasing time (Figure 6.9). The AP effect may not be readily observed in simulated morphologies as coarsening occurs according to iteration steps (one event at a time) and small changes

cannot be captured. In addition, when the particle size deviations for $l=4$ and $l=6$ at adsorption probability of 0.5 are compared, it can be noticed that the saturation their size occurs at different times. The saturation for $l=6$ occurs at later time, indicating the requirement of a longer deposition time to achieve monodispersity for material systems displaying similar characteristics. This indicates that the spatial distribution suitable for the occurrence of shared coarsening is sensitive to diffusion length and adsorption probability parameters. Therefore monodispersity through shared coarsening can be achieved for various material systems by evaluating these critical parameters which aid in identifying its time of occurrence.

Figure 6.9: Simulated particle morphologies for small diffusion length ($l = 2$) and intermediate adsorption probability ($AP = 0.5$) (a – c) shown along with their corresponding particle size distributions (d – f) for increasing time (t_2 , t_4 & t_6).

Now, consider changes arising due to adsorption probability at $l=8$. The particle size deviation appears to be nearly constant from t_3 to t_6 at $AP = 0.1$. The reason is as

discussed in section A4.1 of Appendix I. The opposite effect, for higher adsorption probability, can also be identified. Particle size deviation continuously increases with time. Only in the initial growth stages, i.e., up to time t_3 , is a narrow particle size distribution maintained. Particles grow at a fast rate due to both direct capture and due to surface diffusion, given the abundant number of adatoms in the surroundings. After this stage, a sudden jump in particle size deviation is observed, indicating the start of coalescence; this reduces uniformity in particle sizes. This change in monodispersity is observed at a much later stage (t_7) when the diffusion length is low ($\ell=4$), (Figure 6.8b). Although smaller inter particle distances favor earlier coalescence, the limited mobility of the adatoms delays the event. Thus, as concluded earlier, slow adatom mobility helps to maintain narrow PSD even at higher AP values. Therefore, an additional step to filter out particles of different sizes can increase the efficiency of this method at a later stage as well.

It has been shown till now that shared coarsening is dependent on two main parameters: (a) concentration of adatoms on the surface and (b) adatom mobility on the surface. Now consider a polydisperse system geometry (Figure 6.10) after the secondary nucleation stage. The primary nuclei are black and the secondary nuclei are yellow. A secondary nucleus may be formed in a region not influenced by nearby primary nuclei, as explained in earlier sections. As it grows, the diffusion zone of the secondary nuclei becomes tangential to the diffusion zones of the primary nuclei (1, 2, 3). This is the beginning of the first coarsening event with respect to all the 3 primary particles.

Figure 6.10: Arrangement of primary and secondary nuclei for shared coarsening. The black particles (1, 2, 3) represent primary nuclei, the yellow particles (1*, 2*) represent secondary nuclei. The dotted circles indicate their diffusion zones.

Assume the appropriate adsorption probability and adatom mobility values have given rise to this spatial configuration. The difference in chemical potential due to their sizes causes a flux from the smaller to the bigger particles. The secondary nucleus (1*) is simultaneously “consumed” by the 3 primary nuclei. The diffusion flux is shared; the larger particles grow at a uniform rate due to this coarsening event. DeHoff’s communicating neighbor (CN) theory considers the influence of particle size distribution on the diffusion rate. In the diffusion controlled coarsening model, the rate of particle growth for particles of size ‘r’^{159,164} is given by equation 6.4:

$$\frac{dr}{dt} = K_0 \left\langle \frac{1}{\lambda} \right\rangle \left[\frac{\mu_1}{\mu_2} - \frac{1}{r} \right] \tag{6.4}$$

Here μ_1 & μ_2 are the moments of the size distribution, λ is the characteristic diffusion distance and K_0 is the rate constant, given by:

$$K_0 = 2 \cdot C_0 \cdot D \cdot \gamma \cdot \Omega / \Delta C \cdot RT \tag{6.5}$$

where C_0 is the initial concentration, γ is the interfacial energy and Ω is the volume

fraction. The CN model is consistent with equation 6.1, where the cube of the average radius is expected to vary linearly with time in the late stages (LSW theory). The flux is chosen as the particle growth rate relative to its neighboring particles. Therefore, the model takes into account the geometry of the spatial distribution.

The number of nearest neighbors is also an important parameter to the current system. The dissolution rate of a particle, which is being consumed, is directly proportional to the number of neighbor particles tangential to its diffusion zone. It is assumed for shared coarsening that the neighboring particles have the same size. The classical number density of particles 'N' is given by¹⁷²:

$$N \propto (R/D)^{1/3} \quad (6.6)$$

Here, R is the number of atoms available on a unit area at a unit time. If a system displays reduction in particle number density along with increased size uniformity of the particles, shared coarsening can be expected.

The main parameters of shared coarsening are summarized: 1. The frequency of primary nucleation determines the volume fraction of denuded regions. The extent of *diffusion zones* is a function of time and size of the growing primary nuclei. The combined effect of *adsorption probability* of the growth surface and *diffusion length* of the growth species (adatoms) determines their *spatial distribution* (inter-particle distances and particle number density). With *time*, the formation of *secondary nuclei* in the denuded region occurs. Eventually, overlapping of diffusion zones of the secondary nuclei with the diffusion zones of the larger uniform sized particles facilitate shared coarsening. The larger particles grow at a uniform rate and smaller particles dissolve, leading to improved monodispersity. This mode of coarsening results in particle size uniformity.

6.7 Experimental Correlation - Physical Vapor Deposition:

To experimentally test the proposed shared coarsening mechanism, physical vapor deposition of metals onto a liquid substrate was performed. The liquid surface, being defect-free, does not have preferential sites for vapor adsorption. Hence it is an appropriate surface to test shared coarsening. Pure copper (99.99% purity) was thermally evaporated onto silicone oil at low vapor flux of 9.31×10^{17} atoms/(s*m²). Silicone oil, being non reactive and extremely stable under vacuum conditions (vapor pressure = 3×10^{-10} mm Hg), is appropriate for copper vapor deposition and growth¹⁷³.

Adsorption probability, which experimentally translates to the condensate – substrate binding energy, was calculated *via* Density Functional Theory (DFT) (Table 6.1). It was found that the copper atoms are only weakly bound to the oxygen functional group (-0.55 eV), thus there is a low probability of oxidation from silicone oil. The binding energy with other functional groups is also relatively low indicating minimal interaction between condensing species and the substrate. On the other hand the copper – copper binding energy was found to be much higher than its binding with silicone oil. Thus, the atom clusters can be assumed not to break or desorb as in the case of simulated conditions. Copper deposition is likely to be due to the high adsorption probability onto the surface of the liquid.

Table 6.1: Copper binding energy values with Silicone oil functional groups, calculated using DFT calculations via Materials Studio (Accelrys).

Binding Site at Silicone Oil Molecule	Binding Energy (eV)
Hydrogen	-0.55
Methyl	-0.15
Oxygen	-0.55
Silicon	-1.09
Copper – Copper	-1.38

The first observation was made after 20 s of deposition. It is remarkable to find uniformly sized copper nanoparticles evenly distributed all over the surface. The particles are ~2 - 3 nm in diameter and spherical. The TEM image along with the corresponding PSD histogram can be seen in Figure 6.11d – 6.11f. The condensate coverage is not complete and small empty areas are observed. Another observation is the close proximity of the nanoparticles. Despite the small interparticle distances, the particles remain discrete, without coalescence. The particles are spherical, which would not be the case after coalescence. Vapor deposition was carried out for an additional 5 s. After 25 s particle monodispersity is still observed, with almost complete surface coverage. However, there are regions indicating coalescence, which led to empty regions adjacent to irregularly shaped particles. However, particle monodispersity is still very high (Figure 6.11c). The particle sizes are ~4 – 6 nm in diameter (Standard deviation = 0.89). Also, the substantial decrease in the number of 2 nm particles should be noted. With prolonged deposition time, the empty areas after 20 s deposition are occupied by newly formed particles. Higher particle coverage with improved monodispersity was obtained. The modal particle size increased from 2.5 nm to 4 nm. The beginning of coalescence was captured at 25 s.

Also, coalescence has progressed more in some areas compared to others. The condensate morphology obtained on an amorphous carbon substrate under the same deposition conditions is also shown (Figure 6.11a). Copper clusters, in the size range of 20-30 nm, are observed and the morphology is consistent with growth on solid substrates. The copper particles were anticipated to be oxidized from several possibilities such as exposure of particles to atmospheric conditions; or during silicone oil dissolution in acetone environment. The small particles are shown in the high resolution image (Figure 6.12). The lattice parameter suggests that the particles are copper oxide. The HRTEM images reveal a lattice spacing of 0.23 nm, which matches the (111) plane of cubic Cu_2O and is in agreement with reported values^{174,175}. In addition to confirm this the condensate formed on the liquid and solid surface is characterized separately using XPS to confirm the presence of copper and also its oxidation (Appendix I A3). Both samples show the condensate to be oxidized. Given the nature of our experiments, the copper nanoparticles formed in our experiments are oxidized, this effect is not specific to the liquid substrate.

Figure 6.11: Monodispersed copper nanoparticles formed on the surface of (a) amorphous carbon (20 s); (b) silicone oil after 20s and (c) 25 seconds of deposition along with their respective PSD (d–f). Copper condensate is anticipated to be oxidized as the samples were introduced to atmospheric conditions prior to characterization.

6.7.1 Liquid Substrate Effect:

The observed uniformity in particle sizes can be explained as a consequence of shared coarsening. The binding energy values can be attributed to the intermediate adsorption probability values of the depositing species, providing sufficient adatom concentration on the liquid surface. Higher diffusion mobility is expected from the liquid substrate. Now, consider the earliest interaction of copper atoms with the liquid surface. The range of surface binding energies allows the silicone oil to offer more corrugation in PES (Potential Energy Surface) for the incoming copper atoms. Upon collision with the surface, the copper atom can transfer most of its kinetic energy, becoming immobilized. The energy transfer causes significant perturbation to the liquid structure, causing it to act against the bond which is formed. The relatively higher bond strength between copper

atoms and liquid (as compared to binding energy of gold atoms and silicone oil) is to be kept in mind. The energy transfer¹²³ is a function of mass and binding energy of the condensate atom. Given the combination of the intermediate mass species and its higher binding energy, the magnitude of E_R (the response energy) of the liquid may be insufficient to completely break the bond formed. The effect of E_R is still present, causing adatoms to diffuse on the surface, by allowing the bond be partially broken, allowing the existence of non-equilibrated energy ' E_{parallel} '. The diffusion length is expected to be small, due to the small inter-particle distances. The magnitude of the response from the liquid substrate could thus be slightly less than the binding energy and in the range of 0.4 – 0.5 eV. The adatoms possess high surface mobility, providing higher collisional probability with each other. While performing diffusive motion, the adatoms can retain a few of their bonds with the surface. This is indicative of a non-equilibrated energy ' E_{parallel} ', which facilitates the observed uniform material distribution due to the liquid substrate effect. Thus, a balance between the binding energy and the mass can result in evenly distributed, monodisperse nanoparticles on a non-rigid, dynamic substrate surface. The close proximity of the copper nanoparticles on the liquid surface can induce a dynamic equilibrium between the particles. The diffusing flux is dependent on the number of surrounding particles. Thus, the uniformly sized particles remain apart despite their small interparticle distances. This monodisperse particle size distribution is due to shared coarsening.

The images observed at an earlier time frame (12 s) reveal extremely small particles in (Figure 6.12). The particles occur in low density particle clusters which are widely spaced on the surface. The particles in each cluster have two different sizes (1.9 and 2.6 nm),

indicating a broad size distribution in the initial growth stage. The improved particle uniformity with increasing deposition time can thus be correlated with shared coarsening on the liquid surface.

Figure 6.12: (a) Copper nanoparticles obtained after 12 seconds of deposition time with two distinct sizes. (b) – (g). High resolution images of the particles seen in (a) obtained by varying defocusing values confirming them to be of copper oxide nanoparticles. The source of particle oxidation is not specific to the liquid substrate alone.

The spatial distribution (earlier time frame – Figure 6.12a), wherein smaller particles are surrounded by several larger particles, is the critical configuration leading to shared coarsening. However with increasing time, the particles undergo coalescence. This occurs due to non-uniform adatom concentration developing around the particles. The inner faced edges have a greater chance of capturing atoms from neighboring particles¹⁷⁶ compared to the opposite edge. This difference in growth rates causes a movement in center of mass, resulting in coalescence and loss of monodispersity. Thus, particle spatial

distribution is a key parameter which can facilitate monodispersity for longer duration.

As the particle density observed at 12 s is very low, a higher deposition flux (7.82×10^{18} atoms/(s*m²)) was employed to observe condensate morphology at an earlier time. The particles observed after ~14 s of deposition are shown in Figure 6.13. Broader size distribution can be observed with a majority of the particles being either 4 – 5 nm or 2 – 3 nm in diameter. An increase in deposition time leads to monodisperse particle size distribution due to shared coarsening. The images captured at 20 s of deposition at this higher flux are shown in Figure 6.13.

Figure 6.13: Copper nanoparticles obtained after 12 s of deposition time at higher flux (a & b); Their particle size distribution indicating a polydisperse system is shown (c).

Copper nanoparticles with improved monodispersity are obtained after deposition time of 20 s at a higher deposition flux of 7.82×10^{18} atoms/(s*m²) (Figure 6.14). This uniformity in particles sizes is due to shared coarsening.

Figure 6.14: Copper nanoparticles obtained after 20 s of deposition at higher deposition flux. It is identified to be a post coalescence stage, although a majority of the particles have the same size of 7 nm.

The particle sizes obtained after 20 s of deposition display the maximum uniformity, whereas particles captured before and after this critical time display size deviation (Figure 6.15). Even after 25 s high monodispersity can be observed. The novel observation made on a liquid surface, where a polydisperse system reduces its size dispersity, is unique to shared coarsening.

Figure 6.15: Comparison of the PSDs of copper nanoparticles obtained at various experimental deposition times.

This phenomenon is related to the binding energy values and the mobility of the adatoms. Other materials under 2D surface growth conditions can give rise to uniformity in particle

sizes. The formation of discrete Pt nanoparticles (NP) has been recently reported to have formed on the surface of Al_2O_3 substrate¹⁷⁷ utilizing the sputtering technique. The tunable density of NPs with low (0.1 eV) substrate - condensate binding energy and high condensate-condensate (1-2 eV) binding has been reported. The particle size distribution can be narrowed by increasing adatom mobility for this high particle density distribution. This could be achieved by increasing temperature, which could induce shared coarsening. Shared coarsening is more easily observed on liquid surfaces due to the homogeneous surface conditions. Thus the formation of highly uniform sized metallic nanoparticles on ionic liquids could also be due to this effect¹⁰⁴.

6.8 Chapter Summary:

A novel mechanism of shared coarsening has been proposed to obtain monodisperse nanoparticles on a 2D surface. The combined influence of surface diffusion kinetics and adsorption probability of the substrate dictates the spatial distribution of the particles which are formed. These are critical parameters in inducing the shared coarsening effect. Substrates with low/ intermediate adsorption probability values with short/intermediate diffusion lengths of the adatoms provide optimum conditions to obtain narrow PSD.

Copper nanoparticles with a narrow size distribution are obtained by vapor deposition onto a liquid substrate. The response of the liquid to the perturbation, results in increased adatom mobility, which aids in attaining the appropriate spatial distribution of the nanoparticles formed. For such a spatial distribution shared coarsening results in monodispersed nanoparticles. Binding energy influences two critical stages: (1) initial adsorption probability of the depositing species; the adsorption probability will increase with higher binding energy, allowing sufficient concentration of adatoms on the surface.

(2) larger binding force between the adatom and the liquid molecules (substrate) causes them to adopt relatively short diffusion lengths on the surface. The synergistic effect of these two factors gives rise to the appropriate *spatial distribution* of primary and secondary nuclei. This in turn results in uniformly sized particles due to shared coarsening. Thus, condensate substrate-interaction is primarily responsible for the observed morphology. It is therefore examined further in the next chapter for other materials systems and the liquid substrate effect is summarized.

Chapter 7 Importance of Condensate – Substrate Interactions

7.1 Introduction

Material growth on a substrate begins with the formation of nuclei and clusters, which eventually leads to the formation of nanoparticles or thin films. The control of nucleation and growth behavior requires the understanding of interaction of the growth species with the substrate in consideration. Substrates ranging from crystalline/amorphous solids, polymers, molecular/metallic/ ionic liquids to organic monolayers, etc., have been studied. Their results show that cluster formation and interaction is critical to the morphological outcome. The structure of the liquid substrate during vapor deposition is also shown to play a critical role in defining the morphological features of the condensate, as reported in earlier chapters. The condensate properties are known to be largely dependent on the growth processes through which they arise. The probability of occurrence of these atomistic processes, such as desorption or diffusion, is dependent on the substrate – condensate interaction. The collision of the depositing species and substrate surface can give rise to a number of outcomes which define the *residence time* of the incident atoms. This effect results in a substantial change in morphology and thus the various phenomena need to be differentiated. The distinct influence of the liquid substrate on these atomistic processes is summarized in this chapter. The vapor deposition of silver and aluminum onto silicone oil is analyzed. In addition, a descriptive model for predicting the morphological outcomes based on condensate - substrate properties is also presented.

7.2 Background - Influence of the Substrate:

First, the influence of soft matter substrates during vapor deposition and growth is briefly discussed. Soft matter substrates comprise colloidal gels, polymers and liquid crystals where the conformation of the molecules is not fixed or the subunits are loosely bound. This property causes their mechanical properties to be different from simple solid substrates. The basic property of soft matter is their flexibility and their interfacial properties which are structurally different from their bulk. For example, polymers above their glass transition temperatures exhibit continuous rearrangement of their surface by movement of polymer chains within accessible voids between neighboring chains; this phenomenon is called ‘reptation’. This allows the surface to be modified, the chains can move back to the bulk – allowing the surface properties to be “fresh” and effectively unmodified. It has been reported that reconstruction might occur at the soft matter and substrate interface when there is strong chemical affinity. Even under these conditions it was noted that small atomic rearrangements or strain are capable of relaxing efficiently after deposition, indicating that reconstruction could not modify the soft matter surface. The interactions between clusters and soft matter is useful to realize effects such as single electron charging phenomena (Coulomb blockades and staircases), electrochemical charge transfer etc.

Adsorption of atoms from the gas phase onto solid substrates has been well investigated, this process leads to the formation of clusters or thin films. Generally adatoms diffuse and collide until they attain critical nucleus size. Since substrate rearrangements and/or conformation changes are prominent on soft matter substrates, formation of particles or thin films (layers) is known to be difficult. Wet chemical synthesis techniques which

involve reduction of metal salts or reactions with cations or anions have been investigated for formation on soft matter. Here, physical vapor deposition on liquid substrates has been investigated, with relatively weak chemical interactive forces.

The liquid surface is considered as a non rigid, vibrationally and rotationally active surface at the atomic scale. Its surface is assumed to be soft relative to the force of the incoming species, thus efficient energy transfer is expected¹⁷⁸. The initial adsorption probability of the atoms is influenced by the corrugation in the potential energy surface, which acts as preferred sites for adsorption. The energy transfer increases due to these corrugations¹²⁴ as a result of the attractive potential energies. This attractive force is considered to be equivalent to the binding energy E_B of the bond formed. The type of material systems chosen here are dominated by physical forces and adsorption is considered to be of the non-activated type.

As discussed in chapter 4, when gold vapor is thermally deposited onto a liquid substrate with weak binding forces, low non-uniform condensate coverage was observed. The response from the liquid substrate was inferred to result in additional desorption events, unlike the case of its solid counterpart. This was likely, as the gold-silicone oil bond strength is weak. Hence the bond could be broken, decreasing the residence time of the gold atom. Now what would be the consequence if the atom is strongly bound to the substrate? Will the response of the liquid change? What are the consequences of changing the mass of the incoming species? These questions were studied by considering the deposition of two other elements (varying mass and binding energy) onto the same liquid. The resulting morphologies are studied to examine the response of the liquid.

7.2.1 Case I – Desorption: Silver Vapor Deposition

Thermal evaporation of silver (99% purity) onto silicone oil is carried out under the same conditions as gold. Silver atoms, which are lighter than gold, display comparatively higher binding energies with silicone oil functional groups (see Table 7.1). Nonetheless, binding energy values are still low and of the same order on both the solid & liquid substrates. Upon considering these conditions, the morphology observed on the liquid substrate is seen to be in agreement with our proposed mechanism.

The deposition rate was maintained to be of similar order 6.38×10^{19} atoms/(s*m²) as used during deposition of gold. It was also carried out onto an amorphous carbon substrate for comparison. The growth morphologies after 20 s of deposition are as shown in Figure 7.1. The carbon surface displays growth after secondary nucleation. Small Ag spherical nanoparticles, ~ 2 – 3 nm in size, are also seen at the empty regions between the large silver clusters. The larger silver clusters observed after the liquid like coalescence stage are in the size range of 20 – 50 nm and irregularly shaped. The coverage is uniform all over the surface, similar to gold deposition onto the carbon surface.

Very low condensate coverage (less than 10%), with large aggregates of silver particles, are seen randomly distributed on the liquid surface. Multi-layer growth of the condensate structures can also be identified from their texture. The growth morphology of silver on silicone oil appears to be similar to that of gold/silicone oil. This material system falls in the category of depositing heavy mass atoms with weak binding forces onto the liquid/non rigid surface. Hence the additional desorption of silver atoms caused by the liquid's response can be expected to be predominant. According to the observed low condensate coverage the nucleation and growth process is inferred to be similar to gold. Low number

density of clusters is maintained even with increasing time. The cluster mean size also increases accordingly, given the higher binding energy between the silver atoms. Therefore the existence of gas-phase transport attributed to the multilayer growth (as explained in section 4.3.4) is confirmed yet again. Consequently, overall low silver condensate coverage is demonstrated.

Figure 7.1: Silver condensate morphologies as seen on amorphous carbon (top row) and silicone oil (bottom row) after 20 s of deposition time.

Observation of silver deposition on silicone oil has been reported earlier with respect to the formation of silver clusters^{105,106,179}. Post deposition silver aggregates have been shown to cluster with each other within a short period of time. Also, the late growth stage has been reported to follow the cluster-cluster aggregation model.

7.2.2 Case II – Surface Diffusion: Deposition of Aluminum

Next, condensate with very low atomic mass but high binding energy with the liquid substrate was investigated. For this case, aluminum was thermally evaporated onto silicone oil. Mass of an aluminum atom is 4.5×10^{-23} grams, which is substantially lower than that of copper. The binding energy of Al with the liquid is much higher than that of Au/Ag but comparable to Cu (Table 7.1). In accordance with the material properties and the proposed mechanism of nucleation and growth occurring on the liquid substrate, aluminum atoms were expected to be readily accommodated on the liquid surface. The mass of the condensate and the binding energy being high, the deposition was not anticipated to perturb the liquid configuration. Figure 7.2 shows the TEM images of the Al metal condensate onto both amorphous carbon and silicone oil surfaces.

Table 7.1: Condensate – substrate binding energies - The various metal binding energies (eV) with all the functional groups of silicone oil substrate, a-carbon along with the isolated metal pair binding energies are shown.

Substrate	Aluminum	Copper	Silver	Gold	
Silicone Oil	Hydrogen	-0.644	-0.553	-0.145	-0.095
	Methyl	-0.482	-0.148	-0.089	-0.122
	Silicon	-0.670	-0.551	-0.143	-0.447
	Oxygen	-0.694	-1.094	-0.177	-0.552
	Average	0.623	0.586	0.423	0.304
a-Carbon	-1.19 ¹⁸⁰	-0.99 ^{181,182}	-0.4 ¹⁸³	-0.48 ^{120,121}	
Isolated Metal Pair	-0.83	-1.38	-1.03	-1.06

Figure 7.2: TEM images of Aluminum deposited onto amorphous carbon (top row) and silicone oil (bottom row) after 20 s and 40 s of deposition.

The morphology on the liquid surface resembles that of copper condensate. Small particles of similar sizes can be observed. After deposition for 20 s, the liquid substrate displays a high density of 5 nm particles. The deposition rate is maintained to be 1.85×10^{22} atoms/(s*m²). The particles are uniformly distributed on the surface with minimal inter-particle distances, indicating that the Al adatoms have a short diffusion length on the liquid surface. An advanced growth stage is observed on the carbon surface with the formation of large Al clusters of sizes 30 - 50 nm diameter. The cluster shapes indicate growth to be brought about by liquid like coalescence of the Al clusters, as was

the case of gold clusters on the surface of amorphous carbon.

Furthermore, with an increase in deposition time to 40 s a thick aluminum film can be seen on the carbon surface. However on the liquid surface, the particles have grown to large sizes of 10 – 20 nm in diameter. Upon doubling the deposition time, the morphology on the liquid remains granular without the formation of a continuous film. As the Al-liquid binding energy is high, a large number of adatoms are available on the surface. Thus, their collision probability is high, giving rise to high particle density with uniform coverage, similar to the simulated image under high adsorption probability and short diffusion length conditions (Figure Appendix I A4.4). However, the binding energy being substantially lower than its solid counterpart, the growth kinetics are slower on the liquid substrate. Given the absence of surface defects, the saturation density of the number of islands is higher, giving rise to larger number of smaller particles. The probability of formation of grain boundaries/defects increases with increasing time. Thus under the conditions of short diffusion length combined with higher binding (~adsorption probability), a smooth metallic film is not likely. The explanation discussed here is in agreement with studies reporting the formation of rough Al films on silicone oil with high density of stress patterns/defects^{83,184}.

The morphology on the carbon surface seems to be in agreement with the hit-and-stick growth model. The binding energy between the Al atoms and carbon is extremely high relative to the liquid (1.19 eV). Most of the deposited atoms stick to the surface upon deposition and have high stability. This provides adatoms with higher collision probabilities to collide with nearly stationary adatoms (or even slow moving clusters), resulting in fast growth conditions. However, the film formed appears to be of uneven

thickness due to high deposition rate combined with higher adsorption probability.

The formation of uniformly sized Al particles in the early stages is a consequence of shared coarsening. The opportunity window to capture uniform particles is small, given the high particle density and shorter inter-particle distances. The liquid substrate effect may however be subtle in this case. The magnitude of the liquid response energy could be negligible due to the low mass of condensate and thus insufficient to effectively break strong Al bonds, providing longer adatom residence time. In addition, in the case of Al, even with increased deposition time, the morphology remains highly granular. It is shown that the binding energy between the liquid molecules and Al particles is high. This is anticipated to cause the liquid molecules to encapsulate around the large Al particles. This prevents the particles from coalescing with each other, allowing them to be discrete. However, this effect is seen to occur only at late stages. It could be due to the increase in average particle mass (and volume) with time, causing sufficient number of molecules to encapsulate the particle. Thus, given high deposition rate and high chemical affinity of the condensate species, a granular film can be expected. Also, in this material system, another possibility could be that coalescence may not be readily prevalent even at late stages, due to the oxidation of the Al clusters.

7.3 Conclusion of Condensate – Substrate Interaction

The two main morphologies observed in the materials considered here are given below. Other parameters have been maintained to be the same i.e., energy of the incoming atoms (deposition method) and substrate temperature.

Case I: High Mass and Low Binding Energy – Under this condition, low condensate coverage (randomly distributed) are observed on the liquid substrate from the very initial

stages. Both gold and silver deposition resulted in similar observations.

Case II: Low/Intermediate Mass and High Binding Energy – Under these conditions, more uniform coverage of spherical particles is observed. Aluminum and copper with low and intermediate masses respectively belong to this category.

From the results obtained by metal vapor deposition onto liquids it can be concluded that when the substrate-condensate binding energy is weak, mass plays a significant role during deposition on a non-rigid substrate. The mass ratio indicates the amount of energy transfer into the substrate with respect to momentum transfer. However, when the binding energies are strong the magnitude of perturbation may not be sufficient to completely break the formed bond. Therefore depending on the response from the substrate, partial bond breakage to induce surface diffusion of the atoms has been deduced. This is indicated by the uniformly distributed Cu/Al particles obtained on the liquid surface. The pictorial plot of mass ratio (indicative of perturbation effect) vs binding energy is shown in Figure 7.3 and Figure 7.4 for silicone oil and amorphous carbon substrate respectively. Two distinct morphologies can be clearly identified. The increase in adatom residence time on the substrate is the key parameter indicating the type of morphological growth on a given substrate and it is also indicated next to the micrographs.

Figure 7.3: The effects of varying mass and binding energy on *silicone oil*.

Figure 7.4: The effects of varying mass and binding energy on *amorphous carbon*.

The metallic and ionic radii of the various condensate materials are tabulated (Table 7.2). The holes in pentagonal and hexagonal hydrocarbon rings are ~0.14 nm and ~13 nm respectively¹⁸⁵ and are of the same order as metallic radii of the condensates. Therefore based on the size of these atoms, there is no preferred site for attachment for the metal adatoms. In addition, consider the gold atom binding with the benzene functional group as shown in Table 4.1. The DFT calculations show that the metal atom – when placed at the centre of the ring shows negligible bonding strength. Therefore, the liquid molecule (silicone oil) does not offer preferred attachment sites for the adatom.

Table 7.2: The metallic and ionic radii of the condensate materials used in this study are tabulated.

Condensate Material	Metallic Radii (nm)	Ionic Radii (nm)
Gold	0.144	0.099
Copper	0.128	0.068
Silver	0.144	0.089
Aluminum	0.143	0.067

The structural changes induced by deposition onto soft / hard substrates have been previously studied. The depositing species (clusters/atoms) are classified to be soft/hard with respect to their inherent characteristics and the corresponding substrate. A variety of substrates, such as soft polymers, self - assembled monolayers (SAMs), hard metal substrates have been studied to understand the interaction¹⁸⁶. The main parameters considered are: energy between the clusters, energy between the substrate atoms, cluster – substrate energy, temperature and mass of the depositing species. With the knowledge of

these studies, the mass of the depositing species is established to be a critical factor.

Although the liquid substrate's composition remains the same during deposition, it possesses conformational flexibility, which alters growth kinetics. Momentum transfer accompanying deposition of metal atoms is capable of altering the degrees of freedom of the liquid molecule. This, in turn, induces conformational changes with respect to the nearest neighbor configuration of the molecules. Thus condensate mass condensate contributes to the perturbation of the structure. In addition the perturbation is directly related to the momentum transfer arising from the kinetic energy and mass of the depositing species.

Consider the thermodynamic growth mode of the metallic condensate on the liquid substrate. Given the weak condensate substrate interfacial bonding, incomplete wetting characteristic is expected ($0 < \theta$ (wetting angle) < 90). The system energy is maximized by the observed formation of gold clusters (islands) to maximize lowest energy surfaces and thus minimize interfacial energy. Therefore a Volmer – Weber growth mode eventually resulting in multilayer growth. As for the case of higher condensate-substrate affinity, the nucleation density is observed to be significantly higher, resulting in improved surface coverage (arising from improved diffusion events).

Based on these observations an extrapolation of the mechanism discussing the liquid substrate's response aids us in predicting the morphologies for deposition (low kinetic energies) on molecular liquids (Table 7.3) and illustrated in Figure 7.5.

Table 7.3: Morphology Prediction – Table summarizing the outcomes for vapor deposited onto molecular liquid substrates under different conditions along with predictions of the probable outcome for other conditions (**predicted morphologies).

Condensate		Morphology	Comments
Low Affinity	High Mass (Gold/Silver)	<i>Coverage:</i> Low; Non uniform distribution <i>Type:</i> Irregularly shaped clusters; Particle aggregates; Multi-layer growth	Low affinity allows higher chance for desorption ; Delayed secondary nucleation and gas phase transport
	Low Mass**	<i>Coverage:</i> High and uniform; highly dependent on flux <i>Type:</i> Begins with island growth, eventually leading to film formation – conventional process <i>Useful for the formation of films with uniform thickness</i>	No perturbation with high diffusion rates Possible formation of 2D gas, resulting in homogeneous nucleation Delayed secondary nucleation stage, with improved lateral growth
High Affinity	Low Mass (Aluminum)	<i>Coverage:</i> High and uniform <i>Type:</i> Particles ; Granular Film at late stage	Higher diffusion rate causing higher coverage Uniformity in particle size
	Intermediate Mass (Copper)	<i>Coverage:</i> High and uniform <i>Type:</i> Highly mono-dispersed particles; Coalesced particle clusters at late stages	Monodispersity due to shared coarsening effect Influence of liquid structure prominent in diffusion kinetics
	High Mass**	<i>Coverage:</i> Minimal; non uniform distribution <i>Type:</i> High density of particles formed in the bulk liquid	Liquid substrate forced to accommodate impinging atoms Penetration/dissolution into the bulk with minimized lateral or surface interaction

Figure 7.5: Schematic showing the predicted microstructures obtained under various condensate – liquid substrate interaction conditions and properties; I, II and III refer to time sequence during growth.; The deposition of (a) Low mass condensate with low affinity to the substrate; (b) High mass condensate with low affinity to the substrate (c) Low mass condensate with high affinity to the substrate; (d) High mass condensate with high affinity to the substrate; (e) Intermediate mass condensate with high affinity to the substrate.

7.4 One Step Synthesis of Monodisperse Gold Nanoparticles on Ionic Liquids

The fabrication of monodispersed nanoparticles through physical vapor deposition is the main objective of this work. As reported in earlier sections, size dispersity of nanoparticles formed is destroyed by coalescence and coarsening. Previous discussions focused on molecular liquids which were unable to provide the particles with required stability to maintain monodispersity. Due to the limits of this class of liquids it is challenging to achieve particle monodispersity. Therefore a facile synthesis technique which can prevent coalescence and invoke shared coarsening was explored. Hence, ionic liquids, which also display negligible vapor pressure, were chosen for this technique.

Furthermore, given the ionic nature of the liquid, the gold – PMIM(I) material system was expected to fall under the high affinity category (as described in Table 7.3). Therefore, the formation of high density, monodispersed nanoparticles was anticipated, with the ionic liquid offering required particle stability.

Ionic liquids (ILs) have been utilized as substrates for vapor deposition due to their unique physicochemical properties. They are composed of sterically hindered organic salts, consisting entirely of ions. Due to this reason, ionic liquids display high stability (do not evaporate) even under ultra-high vacuum conditions^{187,188}. They possess high chemical and thermal stability at high temperatures and display a large liquid range (up to 300°C)¹⁸⁹. In addition to these exceptional physical properties, highly structured liquids¹⁹⁰ provide electrostatic and steric stabilization for nanoparticles (not seen in molecular liquids – studied in earlier sections) and thus makes them most attractive for their use in this system. The large variety of available ionic liquids (apolar / polar in nature) provide a range of surface functional groups which assist in the fabrication of a variety of nanomaterials. The ionic nature of the liquid also offers high adsorption probability substrate, improving nanoparticle density. They have been incorporated for a variety of applications, such as metallic film deposition in space telescopes⁵ and synthesis of metallic nanoparticles^{102,117,191,192}. The fabrication of nanostructures on ILs by physical vapor deposition techniques has been discussed in chapter 2. These techniques that omit the use of stabilizing agents are highly advantageous.

Here we chose the thermal vapour deposition technique which provide low kinetic energies of deposition (0.1 – 0.25 eV¹¹³) and the depositing species is expected to be of 99 % atoms¹⁹³. These parameters allow us to effectively test our original knowledge on the

formation of monodispersed nanoparticles on liquid substrates. The physical vapor deposition technique of nanoparticle synthesis on a biocompatible IL substrate is the focus of this chapter. The synthesis of gold particles with minimal chemical contaminants and high stability is demonstrated. The effect of liquid structure on particle formation mechanism is also discussed. Interestingly, thermally evaporated gold vapor deposition results in highly monodispersed gold nanoparticles.

7.4.1 Formation of Monodispersed Gold NPs on PMIM(I):

Thermally evaporated gold vapor was deposited onto the surface of 1-Propyl- 3- Methyl Imidazolium Iodide (PMIM-I) ionic liquid for 20 s. The flux rate is maintained at 1.92×10^{22} atoms/ (s*m²). The rest of the conditions are maintained constant. Figure 7.6 shows the TEM micrographs of gold nanoparticles formed on the surface of the IL. The particle size uniformity is very high and is shown in the particle size v/s count histogram (Figure 7.6d) averaged for over 250 particles from large areas. The images (Figure 7.6a – 7.6c) clearly show that particles are spherical in shape and are highly monodisperse in nature. The particle distribution is also uniform, as seen from low magnification images. The modal particle sizes is 4 nm in diameter with the narrow PSD shown, the standard deviation in size is 3.4 nm.

Figure 7.6: *Gold Nanoparticles:* TEM images of highly monodispersed gold nanoparticles obtained from vapor deposition onto PMIM-(I) ionic liquid (c). Their corresponding particle size histogram with a modal particle diameter of 4 nm is also shown (d).

The growth of these uniformly sized nanoparticles is proposed to be as follows. The thermally evaporated gold atoms deposit onto the surface of the liquid with low kinetic energies. Given the characteristic polar nature of the IL, the instantaneous/fluctuating dipole moments are high – resulting in a high potential energy surface. This increases the number of adsorbed gold atoms on the surface and can thus be identified as a substrate

with high adsorption probability. Moreover, the low interfacial energies of most ILs have also been reported to cause an increased adsorption of depositing species and increase in the nucleation rate¹⁹². The high concentration of adatoms with high binding energy with the substrate results in the formation of high density of nuclei on the surface with small inter-particle distances.

The difference between ionic and molecular liquids now comes into play. The coordination ability of the IL is large, providing the particles with encapsulation around their surfaces. Further growth occurs mostly by direct capture of the atoms from the vapor maintaining their uniform size. The gold atoms are stabilized by the short alkyl chains of PMIM (I), which have been reported to provide good stability¹⁰⁴. Thus particle coalescence is delayed in a continuous vapor deposition process. Even if the vapor source is cut off at this stage, the particles can be expected to remain dispersed in the ionic liquid with minimal aggregation for long duration. Furthermore, the particle size distribution was analyzed with respect to their average size (Figure 7.7). The narrow distribution is a result of the shared coarsening effect discussed in chapter 6. A high adsorption probability with short diffusion length condition gives rise to uniformly sized, high density of gold nanoparticles.

Figure 7.7: Plot showing the normalized population of the gold nanoparticles size distribution obtained on PMIM(I) ionic liquid.

The occurrence of shared coarsening is more likely when a thermal evaporation method of deposition is adopted for synthesizing nanoparticles. This allows the majority of the deposited species to remain on the liquid surface rather than penetrate into the bulk. The high adatom density, combined with shorter diffusion length, results in high density of nuclei (both primary and secondary) in close proximity. The particle size distribution becomes narrower with shared coarsening, resulting in a monodisperse system. Particle encapsulation ensures minimum coalescence. Thus ionic liquids provide the best case scenario with their inherent stabilizing property for nanoparticle synthesis. Even at low deposition rates, stable and high density particles can be obtained, serving as an important potential application of this study.

Some reports suggest that when ILs are introduced inside a vacuum system their surface is populated with their alkyl groups^{194,195}. This causes the surface to become highly non polar in nature. Thus, diffusion of gold atoms into the bulk liquid is significantly reduced.

The PMIM(I) cation short alkyl chains behaves as a barrier (non-polar) film, increasing surface diffusion, providing favorable conditions for shared coarsening. Consider the monodispersed copper nanoparticles formed on silicone oil substrate. Figure 6.11c clearly indicates the occurrence of coalescence of the copper particles, when they come in contact with each other. Thus the particle monodispersity generated via shared coarsening is reduced. Nevertheless, we report that the particles formed on the imidazolium IL to be stabilized by their short alkyl chains which coordinate to the nanoparticle surface. These surrounding alkyl chains form a steric barrier around the particles and provide long term stability against coalescence. This particle stability is absent on molecular liquids. Imidazolium ILs have also been reported by other studies to provide high particle stability. On the other hand, an alternate stabilization route by ionic repulsion is also probable on the surface ionic liquids^{196,197}. According to this theory the electropositive nanoparticle surface is surrounded by an electrostatic double layer of anions and cations. Given the ionic character of the liquid, a protective electrostatic and steric shell prevents particle agglomeration and results in monodispersity. This electrosteric stabilization property has been reported to provide long term stability for metallic nanoparticles. Furthermore, the particle stability in this study, allows for a prolonged shared coarsening time window, thus giving rise to highly monodisperse nanoparticles. Therefore this fabrication methodology with a self-stabilizing substrate, eliminates the addition of other chemicals as stabilizing agents.

Another observation (from high resolution images) is the high crystallinity and minimum defects of the gold nanoparticles (Figure 7.8). This is due to growth under minimum stress conditions (liquid substrate). Such a growth mode can be exploited for the growth of

smooth metallic thin films with improved properties. In addition, PMIM-I is an environmentally friendly liquid, thus the synthesized nanoparticles have minimum toxicity and could be utilized for biocompatible applications.

Figure 7.8: High resolution TEM images showing the crystallinity of the gold nanoparticles grown on PMIM(I) ionic liquid.

7.5 Chapter Summary:

The investigation of the interaction between the metallic condensate and molecular liquid substrate has been discussed. The condensate mass and its affinity towards the substrate are varied by utilizing four metallic condensates deposited onto silicone oil (the liquid substrate). Two inherently different morphologies of (1) low, condensate coverage with non-uniform distribution and (2) high, uniform coverage of spherical particles has been identified. The influence of perturbation of the liquid structure due to the condensate mass is most prominent when condensate – substrate affinity is weak. With increasing affinity / binding energy the effect of the perturbation may be insufficient for additional desorption/diffusion events. The synthesis of uniformly sized, spherical nanoparticles on

silicone oil is also demonstrated. Additional functional groups may be required to maintain their stability against coalescence, additional chemical groups may not be necessary with the use of ionic liquids incorporation. Thus a one-step synthesis procedure, utilizing ionic liquids for the fabrication of monodisperse particles by vapor deposition has also been demonstrated. The environmentally friendly fabrication of highly monodisperse, nanoparticles on the surface of ionic liquids was also studied. The formation of highly monodisperse nanoparticles is due to the effect of shared coarsening under high adsorption probability conditions. The particle stability arises from the inherent characteristic of the ionic liquid, which provides efficient particle encapsulation. The effect of two other ILs on the condensate microstructure was also studied. Furthermore since PMIM (I) is not toxic, the synthesized particles can have medical applications.

Chapter 8 Conclusions and Future Work

The significance and novelty of utilizing a liquid substrate for condensation of particles is investigated in this thesis. A variety of metals were thermally evaporated and deposited onto a selection of liquid substrates. Modeling was performed to obtain the condensate morphologies for a variety of physical parameters. The modeling results were compared to experimental results. The nucleation and growth mechanisms developed in this work highlight the influence of the structure of the liquid substrate. Therefore this study contributes to the understanding of nucleation and growth on a defect –free liquid surface. Furthermore, the findings were utilized to develop a method to synthesize monodisperse nanoparticles by physical vapor deposition. The major contributions and findings of this work are summarized below:

8.1 Demonstrated the influence of substrate structure on condensate morphology

Gold vapor onto both a liquid (silicone oil) and a solid substrate (amorphous carbon) resulted in formation of distinctly different morphologies, which was attributed to the substrate structure effect. The entropy driven response, to the perturbation of the liquid structure, leads to desorption of gold atoms, altering the nucleation/growth kinetics. Secondly, the non accommodating nature of the liquid substrate under weak binding forces delays or suppresses secondary nucleation. The condensate-condensate binding energy being stronger than the condensate-substrate binding energy, multilayer growth is observed in addition to saturation of particle density from the initial growth stages. Therefore these combined effects contribute to non-uniform condensate coverage on the liquid surface.

8.2 Modeling of nucleation and growth on liquid substrate using KMC simulation

The substrate structural properties are differentiated using two main parameters (1) molecular frequency and (2) adsorption probability in the simulated growth model. The proposed mechanism of a liquid substrate providing additional desorption events owing to its structure, is validated from this simulated growth model. The simulated morphologies under solid/liquid substrate conditions, specifically – high molecular frequency and low adsorption probability for a liquid, match with the experimental condensate morphology.

8.3 Emergence of monodispersity and effect of shared coarsening

The intriguing formation of monodisperse copper nanoparticles on a 2D liquid substrate enables us to experimentally study shared coarsening. The simultaneous coarsening of a smaller particle by several uniformly sized neighbor particles under 2D growth conditions is termed as shared coarsening. This phenomenon allows larger particles to grow at a uniform rate, resulting in large scale monodispersity. The particle spatial distribution is the critical factor for shared coarsening. The optimized surface diffusion length (short and intermediate) and substrate adsorption probability values assist in achieving particle monodispersity.

8.4 Condensate – substrate interaction is critical to growth morphology

The condensate – substrate binding energy and the mass of the condensate atom define the residence time of the adatoms for a given set of growth conditions. Heavy mass and weak binding forces of gold and silver atoms give rise to the observed low and non-uniform

condensate coverage. On the other hand, high binding energies of copper and aluminum atoms with intermediate and low mass gives rise to the formation of discrete particles on the surface of silicone oil. The influence of the condensate-substrate interaction is thus demonstrated with respect to a non-rigid liquid substrate.

8.5 New Approach for Monodispersed Metallic Nanoparticles from Physical Vapor

Gold vapor deposited onto PMIM(I) ionic liquid results in the formation of highly uniform gold nanoparticles. The knowledge of shared coarsening is tested for the formation of monodispersed particles under high adsorption probability conditions. Particle stability is achieved using the environmentally friendly ionic liquid without the use of additional stabilizing agents. Therefore this facile fabrication method of uniform particles with minimal chemical contamination is a significant technological contribution of this work.

8.6 Recommendations for Future Work

8.6.1 In-situ ellipsometric studies of vapor deposition on liquid substrates

To gain deeper understanding of the science behind condensation onto liquid substrates, in-situ ellipsometric studies could be carried out. This methodology can aid in overcoming the current limitation in characterizing the growth of the condensate. A simple illustration of the set-up is shown in Figure 8.1. A vacuum chamber can be built with suitable optical ports for the in-situ set up. The chamber window allows for polarized light to enter and the reflected beam is detected and thus analyzed. The measurements made can determine the time required for nucleation, growth rates of a solid/liquid substrate. This will enable us to quantify the overall kinetics of particle formation on solid and liquid substrates. Similar studies have been set up to observe the growth of thin films from sputtering

techniques^{198,199}.

Figure 8.1: Schematic of vacuum chamber with optical ports to observe condensate growth.

8.6.2 Metallic Vapor deposition onto Organic Liquids

An improvised nanoparticle fabrication technique can be developed if organic liquid substrates are incorporated. These organic liquids could be dispersions containing stabilizing agents, such as thiolated ligands or citrate molecules^{200,201} to enable a self-capping mechanism of the particles. Upon achieving a certain size, the particles would sink into the liquid (given their increased mass), and thus become stabilized by the capping agents. Continuous deposition can result in new particles, improving the particle yield (Figure 8.2).

Figure 8.2: Formation of stable nanoparticles with physical vapor deposition onto a liquid solution with stabilizing agents

Another application which can be developed by using organic liquids for vapor deposition (Figure 8.3) is illustrated. A suitable polymer based solution is dissolved in a volatile liquid and cast on a desired solid substrate. Metal vapor deposited on the surface of the solution can result in the formation of nanoparticles. The volatile nature of the liquid can lead to high deposition rate. After deposition, with complete evaporation of the organic liquid, the particles are embedded in the polymer thin film. Thus with the use of this method metallic nanoparticles embedded in polymeric film can be cast on any substrate. These type of hybrid materials have a number of potential applications such as biosensors²⁰², gas separation membranes²⁰³, optical devices²⁰⁴ etc.

Figure 8.3: Schematic showing the fabrication of metallic nanoparticles embedded polymeric films by deposition onto a polymer solution.

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APPENDIX I

A1 Morphology obtained on Liquid Substrate:

After metal vapor deposition onto the liquid substrate, vapor dissolution technique was employed for ease in TEM characterization of the condensate morphology. In order to ensure no disturbance was caused to the condensate morphology from this technique, few images were captured with the presence of the liquid substrate. Figure A1.1 shows the condensate morphology (unclear due to the presence of the oil) of gold condensate on silicone oil and copper particles obtained on silicone oil. The liquid substrate is highly sensitive to the electron beam and thus it causes the sample to burn away as seen on Figure A1.1d. The gold deposition was carried out under the same deposition rate for all the images captured (a –c) ($2.26 \times 10^{20} \text{ atoms}/(\text{s} \cdot \text{m}^2)$) for a deposition time of 20 s.

The copper vapor deposition rate was $9.31 \times 10^{17} \text{ atoms}/(\text{s} \cdot \text{m}^2)$ for all the samples shown (d – f). Figure A1.1d shows the morphology captured after 20 s, whereas Figures A1.1d & e, were captured after 25 s of copper vapor deposition. Therefore, these images confirm that the dissolution technique doesn't alter the overall morphology even after the liquid is removed. It only enables to view the condensate structure clearly.

Figure A1.1: TEM images showing (a – c) gold condensate morphologies and (d – f) copper condensate morphologies obtained under the same deposition conditions, observed before and after liquid removal *via* the vapor dissolution technique.

A2 Characterization of Silicone Oil:

The structure of silicone oil was probed using FTIR characterization. The various vibration modes of the functional groups were identified as shown in the transmittance vs wavenumber plot of the Far – IR spectrum (Figure A2.1). The vibration frequency of the aromatic groups and the $\text{Si}(\text{CH}_3)$ group is identified to be 620 cm^{-1} and 570 cm^{-1} respectively. The Si-O-Si rocking frequency has been identified to be at 440 cm^{-1} ²⁰⁵. The other low frequency peaks could be assigned to the weak modes of vibration of the hydrocarbon functional groups or the hydrogen bonding. The measurements were carried out at room temperature conditions while the silicone oil remained in its liquid phase itself.

Figure A2.1: FTIR – Far IR spectrum of Silicone oil is shown. The three critical functional groups of aromatic compounds, $\text{Si}(\text{CH}_3)$ group and Si-O-Si groups (rocking vibrations) have been identified and labeled accordingly.

A3 XPS Characterization of Copper/Al Films:

The copper film deposited onto the surface of silicone oil and carbon substrates were characterized using X-ray Photoelectron Spectroscopy (XPS) for elemental analysis. The copper and copper oxide binding energy peaks along with the identification of other elements are shown.

It is to be noted that, the copper condensate is identified to have undergone oxidation. The survey spectrum shows strong copper peaks centered at 928.2 eV and 948.2 eV corresponding to $\text{Cu } 2p_{3/2}$ and $\text{Cu } 2p_{1/2}$ with a 20 eV gap as reported in literature²⁰⁶. These binding energies indicate the presence of both Cu metal as well as Cu_2O . The oxygen O1s peaks and the photoelectron peak for carbon (C1s) have also been identified.

However the peaks are slightly shifted towards lower binding energies for both the substrates, indicating a similarity in the condensate elemental analysis. The intensity of the peaks however is significantly lower for liquid substrate due to sample preparation techniques.

Figure A3.1: The various elements identified from the XPS characterization of copper condensate formed on both silicone oil and solid (glass) substrates are shown. The peaks identified correspond to the oxidation of copper.

A4 Effect of low/high adsorption probabilities on PSD:

A4.1 Low Adsorption Probability (dilute system):

A surface offering a low value of adsorption probability (0.1) was investigated for the formation of particles with narrow size distribution. The diffusion energy value of 0.24 eV was used and maintained to be the same across all the sticking coefficients and diffusion length values. A low SC means that, a lesser number of atoms are available on the surface to perform diffusive motion. This decreases the collision probability for the adatoms. To achieve the critical size of nucleation a longer time would be required, as the adatoms would have to scan comparatively larger surface areas. Due to this the primary nucleation time itself can be expected to be delayed. Thus a low density of particles with relatively smaller sizes is formed, due to the low adatom concentration. Consequently, the incubation time for secondary nucleation can also be expected to be prolonged. Also as the primary nuclei would have larger influencing zones, the interparticle distances did also be larger. The morphologies obtained after an intermediate time stage and their corresponding PSDs are as shown first, for varying diffusion lengths. The images were captured at time step t5 considering the lower concentration of adatoms on the substrate, requiring longer growth times.

FigureA4.1: Simulated morphologies at t_5 for $AP = 0.1$, for varying diffusion lengths of $l = 4, 8, 16$ (a, b, c). Their corresponding PSDs are also as shown (d, e, f). The length scale of the simulated images is in units of A^0 .

Consider the system having the shorter diffusion length of adatoms at $l=4$. This indicates that the mean distance covered by the adatoms is shorter and thus gives rise to higher density of smaller particles with correspondingly shorter inter particle distances. The diffusion length of the particle is also dependent on this value and thus the particle mobility is also slower. Thus their probability of growth by direct capture of adatoms from the surface via diffusion than from the vapor directly is lower. On the other hand, a low number density of bigger particle sizes can be seen with the increase in diffusion length. The inter-particle distance conventionally known to be a function of the atomic diffusion length is also large. As the adatoms are capable of covering larger distances in a given time frame, they have larger influencing zones, higher chances to attain the critical size. After the nucleation stage the particles themselves also possess higher mobility and thus result in higher clustering/coalescence events with growth. This reduces particle number

density and also increases mean particle sizes. The broad particle size distribution shown in the corresponding higher diffusion length histogram confirms that, at low adsorption probability values, shorter diffusion length is most favorable to obtain narrow PSD.

Nevertheless a substrate displaying a low AP has an additional advantage. Given the relatively slow growth of the particles, even at later stages the particle size and distribution remain to be narrow. Late growth stage morphology along with their PSDs is shown for varying diffusion lengths. It can be observed even with growth time, the particle size deviation is not very high and for $l = 4$, a narrower PSD is seen at the later stage. The standard deviation in particle sizes increase from 0.64 to 0.78 to 1.07 for the diffusion lengths of 4, 8 and 16 respectively as shown in figure (late stage). The dilute system can thus be considered to be in agreement with the conventional LSW theory. The concentration fields around the particles being low, a uniform growth rate is seen.

Shared coarsening may not be occurring at this stage given the low particle density. However it can be expected to occur at a much later stage or with an increase in deposition rate, which would make available a larger number of neighboring secondary nuclei under these conditions. The standard deviation vs time plot for the AP = 0.1 with respect to $l = 4, 8$ is shown in figure. Constantly low deviation in particle sizes can be seen even with increase in time, which is one of the main advantages of using low AP substrates.

Figure A4.2: Late stage growth morphologies obtained for diffusion length (l) of (a) 4 (b) 8 and (c) 16 at substrate adsorption probability of 0.1. The blue particles show growth only by direct capture of vapor atoms/surface adatoms and the red particles indicate growth via coalescence and/ or coarsening events as well.

Although low adsorption probability substrates give rise to narrow size deviations; on a practical note particle yield is considerably low. In addition, it is difficult experimentally to achieve this monodispersity under 2D vapor condensation conditions. Firstly, when condensate-condensate binding energy is higher, the gradient in binding energy between substrate and particle causes a majority of incoming vapor atoms to directly attach/grow onto existing particles. This could not only result in uneven multilayer growth but also hinders the overall number of particles formed on the surface, altering secondary nucleation kinetics. To overcome these limitations, several additional measures might have to be incorporated on a practical scale. For example, by introducing capping agents for particles or by adopting additional filtering techniques or by controlling the deposition mode to be continuous or intermittent a higher monodispersity can be achieved. Hence if

supplementary processing steps are included under these conditions, an improvement in particle yield and efficiency can be achieved.

A4.2 High Adsorption Probability:

On the other hand, consider a substrate displaying a high adsorption probability of 0.8. This permits an abundant number of atoms to be available on the surface. Thus, the collisional frequency of the adatoms is very high, resulting in the formation of a high number density of particles. The early onset of secondary nuclei adds to increasing the particle density at a much faster rate. This could cause them to undergo easier coalescence and/or coarsening events. Thus, the particle size deviations are large for such systems. Meanwhile the spatial arrangement at a very early time scale (close to nucleation time) could display shared coarsening conditions. A high density of uniformly sized particles could be achieved, although the effect could be short lived. Figure A4.4 shows the growth morphology and their PSD for varying diffusion length scales and here again smaller diffusion lengths give rise to best size uniformity. However, when the adatom mobility is high, i.e., when diffusion length is high, particle size distribution becomes broad and thus does not favor formation of uniform particles.

Figure A4.3: Intermediate stage growth morphologies obtained for diffusion length (λ) of (a) 4 (b) 8 and (c) 16, at substrate adsorption probability of 0.8 and their corresponding PSDs are as shown (d, e, f).

Figure A4.4: Evolution of particle size and distribution with time for varying adsorption probability values (a) 0.1 (b) 0.5 and (c) 0.8 at a given intermediate diffusion length of $l=8$.

APPENDIX II

List of Author Publications

Journal Publications:

1. P.Anantha, ChengTing & C.C. Wong, (2014) “Modeling of Nucleation and Growth during Vapor Condensation on Liquid Substrates”, Journal of Materials Science 49 (3), 1025 - 1033
2. P.Anantha, ChengTing & C.C. Wong, (2014), “Condensation of Gold Vapour on Silicone Oil – effect of the Liquid Substrate”, Philosophical Magazine, 94 (17) 1967 – 1981
3. P.Anantha, Xiu Wang & C.C. Wong, (Nov. 2011), “One-Step Synthesis of Stable Gold Nanoparticles on Eco Friendly Ionic Liquid”, MRS Fall Proceedings
4. P.Anantha, Xu Chen & C.C. Wong, (April 2011), “Ordered Ring Structures of CdSe Nanoparticles by Water Droplet Self Assembly”, NNL Vol. 3 , No.2, pp. 254-257
5. P. Anantha, Cheng Ting, YY Tay, C.C. Wong, R.V. Ramanujan (July 2014), “Emergence of monodispersity in particle growth on a surface”. *[Manuscript under preparation]*
6. P. Anantha, C.C. Wong, R.V. Ramanujan (July 2014), “Condensate – substrate effect during physical vapor deposition on liquid surfaces”. *[Manuscript under preparation]*

Other publications:

7. P. Anantha & C. S Tan (Jan. 2014), “Homogeneous Chip to Wafer Bonding of InP-Al₂O₃-Si using UV/O₃ Activation”, ECS, Journal of Solid State Science and Technology, 2014 volume 3, issue 4,P43-P47

8. J. Fan, P. Anantha, C. Y. Liu, M. Bergkvist, H. Wang & C. S. Tan, (June 2013), "Thermal Characteristics of InP-Al₂O₃/Si Low Temperature Heterogeneous Direct Bonding for Photonic Device Integration", ECS, Journal of Solid State Science and Technology, 2 (9) N169-N174 (2013)
9. MV Deepthi, M.Sharma, R.R.N Sailaja, P Anantha, et.al.,(2010), "Mechanical & Thermal Characteristics of High Density Polyethylene - Fly Ash Cenospheres Composites", Materials & Design, Volume 31, Issue 4, pg. 2051- 2060

International Conferences:

1. Oral Presentation: P.Anantha, Xiu Wang & C.C. Wong, (Nov. 2011),"One-Step Synthesis of Stable Metallic Nanoparticles on Eco Friendly Ionic Liquids" MRS Fall, Boston, MA, USA
2. Oral Presentation: P.Anantha, Xiu Wang & C.C. Wong (June 2011),"Synthesis of Gold Nanoparticles by Vacuum Evaporation Onto Ionic Liquids" at *ICMAT*, Singapore
3. Oral Presentation: P.Anantha, Xu Chen & C.C. Wong, (April 2010),"Ordered Ring Structures of CdSe Nanoparticles by Water Droplet Self Assembly" at *Thin Films*, Harbin, China
4. Oral Presentation: P.Anantha, F.Y.Ling & C.C. Wong (2009),"Porous Polymer Films by Breath Figure Arrays" at *ICMAT*, Singapore
5. Oral Presentation: P Anantha, G Shubham & C. S Tan, (Dec. 2013), "UV/O₃ Assisted InP/Al₂O₃/Si Low Temperature Die to Wafer Bonding". WaferBod'13, Stockholm, Sweden