Silver deposition on oil – cluster nucleation, growth and aggregation on a liquid surface

Thomas Michely a,c, Gao-Xiang Ye a,b, Volker Weidenhof a, Matthias Wuttig a,c,*

a Institut für Grenzflächenforschung und Vakuumphysik, Forschungszentrum Jülich, D-52425 Jülich, Germany
b Department of Physics, Hangzhou University, Hangzhou 310028, People’s Republic of China
c I. Physikalisches Institut, RWTH Aachen, D-52056 Aachen, Germany

Received 28 July 1998; accepted for publication 13 April 1999

Abstract

Experimental results for a new type of growth system are presented, namely for the vapor phase deposition of metal on a liquid surface. Large, ramified silver aggregates are formed after deposition of silver atoms on silicone oil surfaces. Initially, the deposited metal forms compact but thin disk-shaped clusters on the liquid surface. The essential physics during deposition can be described by nucleation theory similar to the one used for growth of a solid on a solid surface. The much slower cluster processes following the deposition are observed in real time. The disk-shaped clusters perform Brownian motion and adhere upon impact so that finally ramified cluster aggregates result. The processes dominating the growth of this system are a realization of cluster–cluster aggregation models, which lead to fractals with a characteristic Hausdorff dimension. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Brownian motion; Cluster aggregation; Silver; Solid–liquid interface

1. Introduction

In this paper a rather unconventional growth system is studied: the growth of silver from the vapor phase on a silicone oil surface. This system can serve as a prototype for the growth of a solid metal film on a liquid substrate. Compared with the more commonly studied growth of a solid film on a solid substrate, significant differences in the phenomenology are observed. These differences are predominantly related to the much enhanced diffusion of the deposit on the oil substrate. Large, flat, disk-shaped clusters of μm size are formed during deposition which are easily observable with an optical microscope. Following the cluster formation and growth, their aggregation due to Brownian motion and adhesion upon impact is observed in real time. Even cluster aggregates containing as many as $10^{10}$ atoms are found to perform random lateral and rotational walks on the oil surface. In contrast, for deposition on solid substrates, small clusters containing of the order of $10^3$ atoms may already be immobile at ambient temperatures [1,2].

Extending the comparison between growth of a solid film on a liquid and a solid surface, not only the differences but also the similarities are surprising: in both cases, the deposit material is found on the substrate. For low film thickness, islands are formed in both cases, and a saturation of their density with coverage is observed. The dependence...
of island number density on flux obeys a scaling law of identical form for both cases, albeit the value of the scaling exponent differs. Even the fractal shapes of cluster aggregates formed on the liquid resemble the fractal shapes of cluster or atom aggregates after deposition on a solid substrate [3–5], although there are differences in the fractal dimension.

In the following we shall extend our previous description of the growth experiments of silver on silicone oil [6], and present and discuss additional data related to the flux and film thickness dependence of the deposit morphology, cluster diffusion coefficient, substrate edge effect and fractal dimension of the cluster aggregates.

2. Experimental

In order to prepare flat liquid surfaces of well-defined thickness, silicone oil (Dow Corning 705 Diffusion Pump Fluid) with a vapor pressure below $10^{-8}$ Pa was spin-coated at 6000 rev min$^{-1}$ onto transparent plastic slides of size 10 mm $\times$ 10 mm. A stripe of about 1 mm width at the edges of the polycarbonate slides was roughened slightly by sandpaper prior to spin coating. This prevented the oil layer from dewetting the smooth plastic slides. The resulting oil films had a uniform thickness of $\approx 10 \mu$m, as measured by optical microscopy. The transparency of the plastic substrates, or more precisely the low reflectivity, was of crucial importance. It allowed the imaging of subsequently created silver aggregates with sufficient contrast by optical reflection microscopy.

Silver (99.999 % purity) was deposited by thermal evaporation in a vacuum of $2 \times 10^{-4}$ Pa at room temperature ($23 \pm 4^\circ$C). The deposition rate was varied from 0.01 nm s$^{-1}$ to 0.20 nm s$^{-1}$. The nominal film thickness deposited in the experiments presented here is in the range of 0.06–1.5 nm. The film thickness was determined by a quartz-crystal balance located near the substrate. The quartz-crystal balance was calibrated by atomic force microscopy and X-ray reflectometry for thick deposited films.

After deposition, the samples were removed from the evaporation chamber. The silver/oil surface was characterized under ambient conditions with an optical microscope (Zeiss Axioscope) mounted on a vibration-isolation table. The first images were taken between 30 min and 1 h after deposition. Subsequently, the evolution of the film structure with time was followed up to one week. From the apparent silver coverage of the total oil area compared with the deposited film thickness, we conclude that the silver forms flat platelets with thicknesses of between three and seven atomic layers. By moving the focal plane of the microscope objective through the oil film, it is found that the silver clusters are located at the oil surface or, more precisely, not further than 0.2 $\mu$m away from the top surface.

3. Results

To identify the processes that govern film formation, deposition experiments were performed over a wide range of deposition rates (Fig. 1). The left column (Fig. 1a1, b1, c1 and d1) depicts the topographs obtained by optical reflection microscopy 0.5–1.0 h after deposition of 0.15 nm silver. From top to bottom, the deposition rate decreases by a factor of 20 from 0.20 nm s$^{-1}$ to 0.01 nm s$^{-1}$. Two observations are obvious: (1) the shape of the silver islands changes with decreasing deposition rate from ramified to compact and almost circular clusters; and (2) the minimal lateral dimension of the clusters, i.e., their diameter or branch thickness, increases with decreasing deposition rate. The right column (Fig. 1a2, b2, c2 and d2) presents the topographs of the same experiments as in the first column but taken much later; i.e., 2.5–168 h after deposition. It is found that the silver clusters are located at the oil surface or, more precisely, not further than 0.2 $\mu$m away from the top surface.
Fig. 1. Images of silver islands formed by deposition of silver on silicone oil. Four samples prepared with different deposition rates, $f$, and imaged after different times, $t$, after deposition are shown. Film thickness, $h=0.15\text{ nm}$; image size $52\text{ nm} \times 44\text{ nm}$. (a1) $f=0.20\text{ nm s}^{-1}$, $t=0.5\text{ h}$; (a2) $f=0.20\text{ nm s}^{-1}$, $t=18\text{ h}$; (b1) $f=0.07\text{ nm s}^{-1}$, $t=0.5\text{ h}$; (b2) $f=0.07\text{ nm s}^{-1}$, $t=2.5\text{ h}$; (c1) $f=0.03\text{ nm s}^{-1}$, $t=1.0\text{ h}$; (c2) $f=0.03\text{ nm s}^{-1}$, $t=30\text{ h}$; (d1) $f=0.01\text{ nm s}^{-1}$, $t=1.0\text{ h}$; (d2) $f=0.01\text{ nm s}^{-1}$, $t=168\text{ h}$. 
Following their motion continuously from the first topograph taken 0.5–1.0 h after deposition to the late stage (right column of Fig. 1), three kinds of motion of the silver clusters are observed. The first is a ‘hydrodynamic’ drift motion of the entire assembly of silver islands in the field of view, which occasionally dominates the apparent motion of the clusters. We attribute this motion to slight temperature gradients in the film that might be partially caused by the illuminating light.

Second, superimposed on the drift motion is a random-walk motion of the entire issue has a more vague and speculative character. The dependence of the diffusion coefficient on assembly of silver islands in the field of view, which occasionally dominates the apparent motion of the clusters. We attribute this motion to slight temperature gradients in the film that might be partially caused by the illuminating light.

The third and final motion is that the clusters which the islands of each have similar size. This analysis reveals that \( \langle \Delta r^2 \rangle \) increases linearly with time \( \Delta t \) and that the silver-island pair with the larger total area has the smaller mean-square displacement. It is therefore reasonable to define a diffusion coefficient \( D \) of the silver-island pair’s random walk by \( \langle \Delta r^2 \rangle = 4D\Delta t \). The diffusion coefficient \( D \) is dependent on cluster size. Fig. 2 presents the results of an analysis of the diffusion coefficient determined for a number of silver-island pairs, varying in size over approximately one order of magnitude. The data scatter considerably, but support the general notion of a decreasing diffusion coefficient; i.e., a decreasing mobility with increasing silver-island size. An additional remark to this issue has a more vague and speculative character.

Apart from the motion of the silver clusters, we can also determine the reduction in island density by in situ observation of the samples. For two

---

**Fig. 2.** Diffusion coefficient, \( D \), as a function of cluster size, \( S_0 \), for a deposition rate \( f = 0.20 \text{ nm s}^{-1} \) and thickness \( h = 0.15 \text{ nm} \). The two insets (30 µm x 22 µm) give examples of the two cluster groups from which the diffusion coefficients are determined.

**Fig. 3.** Time dependence of the angular displacement \( \langle \theta \rangle \) for a given time interval again decreases with increasing silver-island area.
different deposition rates and the standard deposited thickness of 0.15 nm, Fig. 4 presents the time evolution of the cluster density. As already apparent qualitatively in Fig. 1, the cluster density decreases with time. The solid lines represent a fit to the data by an exponential decay law of the form $N = N_0 \exp(-t/\tau)$, with time constants $\tau$ of $5 \times 10^3$ s for the deposition rate of 0.07 nm s$^{-1}$ (open circles) and of $1.2 \times 10^4$ s for the deposition rate of 0.03 nm s$^{-1}$ (full squares). By video microscopy, it is seen that the mobile objects adhere to each other if two of them touch or impact in their random-walk motion. Only rarely do two of those islands separate again after such an impact. On the time scale of hours, two adhering silver islands did not change shape — i.e., the resulting shape of two silver clusters could be envisioned as the mere addition of the two initial silver clusters. Specifically, two compact silver islands were not observed to coalesce into one new compact silver island.

Prior to a full discussion, which follows in the next section, we shall introduce a hypothesis about the formation of the ramified silver islands based on the data presented above. We assume that at the end of deposition — for all deposition rates used here — compact, disk-shaped silver clusters are present in a certain flux-dependent density. These silver clusters result from nucleation and growth of silver atoms and smaller intermediate silver clusters. After deposition, due to the random walk and adhesion upon impact, the clusters aggregate to larger cluster aggregates which are themselves mobile and aggregate further. Long after deposition, finally large ramified cluster aggregates result, whose number density remains almost constant. Owing to their size, these large aggregates are practically immobile on the experimentally accessible time scale. Support for this hypothesis is most evident for the case of low deposition rates (e.g., Fig. 1c and d). Yet, we assume that it holds also for the case of high deposition rates (Fig. 1a and b), when already at the first observation ramified cluster aggregates are observed. In this case, due to the smaller average silver-cluster size at the end of deposition, the mobility of the silver clusters is much higher and the aggregation process has already proceeded far when the first images are taken 0.5 h after deposition.

For the ramified cluster aggregates, we performed also an analysis of the Hausdorff dimension by the box-counting method [7]. As an example, Fig. 5 presents the results obtained for Fig. 1a2. The number $S$ of square boxes needed to cover the ramified aggregates as a function of

![Fig. 4. Time dependence of the cluster density of two samples determined for the conditions of Fig. 1a2. The number $N$ of square boxes to cover the ramified aggregates as a function of the inverse of the edge length, $L$ (in pixels), indicates scaling behavior over more than one order of magnitude.](image1)

![Fig. 5. Fractal dimension of the ramified cluster aggregates as determined for the conditions of Fig. 1a2. The number $S$ of square boxes to cover the ramified aggregates as a function of the inverse of the edge length, $L$ (in pixels), indicates scaling behavior over more than one order of magnitude.](image2)
inverse of the edge length $L$ of the boxes exhibits clear scaling behavior, with $S(L) \sim 1/L^{D_H}$. The Hausdorff dimension $D(H)$ of the cluster aggregates in the example of Fig. 5 is $1.38 \pm 0.01$. While we generally observe such a scaling behavior, the values for $D(H)$ range between 1.3 and 1.5. The scatter is partially due to differences in the morphology as a function of deposition conditions, in particular the deposition rate. In addition, difficulties and ambiguities in digitizing the photographs of the cluster aggregates contribute to the scatter in the data.

Up to now, the processes occurring after the end of deposition, when a distribution of disk-shaped clusters has been generated, have been analyzed. Now we focus on the additional information we can obtain about the nucleation and growth of clusters during deposition. We shall show that this is possible, although this stage of morphology evolution is not directly accessible to observation in our experiments. According to the hypotheses introduced above, at the end of deposition only compact clusters are present. As the diffusion coefficient is relatively small for the large objects formed by the low deposition rate of $0.03 \text{ nm s}^{-1}$, in this case the silver-cluster density observed 1.0 h after deposition still closely resembles the cluster density at the end of deposition. In Fig. 6 topographs obtained after deposition of (a) 0.09 nm, (b) 0.18 nm, (c) 0.30 nm and (d) 0.45 nm are presented. It is seen from the topographs (a)-(c) that the cluster number density saturates even though the nominal thickness of the deposited film increases. The increase in material deposited leads, however, to a growth in the average size (area, diameter) of the clusters. This implies also that the disk thickness stays relatively constant, although the deposited nominal film thickness more than triples. For the nominal deposited film thickness of 0.45 nm, percolation is observed and a continuous film is formed. Once percolation occurs the morphology changes dramatically from a cluster morphology to a hole morphology. Also, the typical film-structure size, where now holes play the role previously taken by clusters, decreases considerably upon percolation. A quantitative representation of the cluster density as a function of the nominal deposited film thickness reveals that the cluster density is already saturated at about 0.06 nm and stays almost constant until percolation. In conclusion, there is a broad maximum in island density and the island density at the 'standard' nominal film thickness of 0.15 nm can be assumed to be saturated. Above it was shown that the clusters present at the end of deposition aggregate to cluster aggregates without coalescing. Hence, the average branch thickness of the ramified aggregates present long after deposition must correspond to the average cluster diameter at the end of deposition.
Thus, by measuring the average branch thickness $d$ of aggregates, we obtain information about the cluster diameter at the end of deposition. This number is directly related to the island number density at the end of deposition. We performed an analysis of the cluster diameter for a deposited nominal film thickness of 0.15 nm. Fig. 7 is a log-log plot of the branch thickness — averaged over a suitable number of locations — versus deposition rate $f$. Apparently, the average branch thickness scales with the deposition rate according to $d \sim f^{0.69 \pm 0.05}$. We assume a fixed cluster thickness for the deposition rates analyzed. Then, the average branch thickness $d$ is related to the saturated island number density, $N_s \sim 1/d^2$. Therefore, the island number density shows a pronounced dependence on flux, such that $N_s \sim f^{1.38 \pm 0.1}$.

Finally, we present an interesting experimental effect which indicates that the resulting morphologies depend critically on the properties of the liquid layer supporting the silver clusters. While the oil film has a relatively uniform thickness in the large central part of the sample, at the edge of the sample the oil film thickness goes smoothly down to zero. This happens in a bounding stripe of about 1 mm width surrounding the homogeneously thick oil film, henceforth called the edge stripe.

Fig. 7. Log-log plot of the average branch width $d$ of the ramified islands versus the deposition rate $f$ for a deposited nominal film thickness of 0.15 nm. The straight line is a fit to the experimental data.

Fig. 8 represents a typical sequence of morphologies obtained in the edge stripe with increasing distance from the edge of the oil film. It is apparent that, with increasing separation from the oil film edge, the silver-structure size increases and the silver-cluster density decreases. Although at pre-
sent we cannot offer a quantitative explanation for this effect, it is likely that the increase in cluster size or branch thickness is related to an increase in oil film thickness. The basis of this correlation could be a thickness-dependent mobility of the oil molecules. Assuming with decreasing oil thickness a more and more limited motion implies that less kinetic energy can be transferred from the oil molecules to the silver clusters. A reduced silver-cluster mobility and increased island density would result, which is in accordance with our observation.

4. Discussion

In this section, the mobility of the silver clusters on the oil surface will be discussed and a two-stage model of cluster aggregate formation will be introduced. The model accounts for the experiments described above and relates the two stages to nucleation theory [8–10] and cluster–cluster aggregation models [11–13], respectively. In addition, a number of aspects are pointed out for which there is currently no detailed understanding. Finally, possible future experiments and investigations for growth on liquid surfaces are suggested.

During the entire process of cluster aggregate formation, it is assumed that silver atoms, clusters of various sizes and aggregates of clusters all migrate on the oil surface by a random walk. This motion is due to statistical fluctuations in their momentum by collisions with liquid molecules. Their mean-square displacement, \( \langle \Delta x^2 \rangle \), is given by \( \langle \Delta x^2 \rangle = 4kTt^{-1} \Delta t \) for a two-dimensional motion according to the theory of Brownian motion [14,15], where \( k \) is the Boltzmann constant, \( T \) is the temperature, \( \Delta t \) is time and \( F \) is the friction coefficient. The friction coefficient \( F \) is a function of the size and shape of the aggregates, and is expected to increase with the number of particles in the object. It is related to the diffusion coefficient \( D \) by \( D = kTF^{-1} \).

The experimental evidence for these assumptions has been presented in the last section: (1) the formation of \( \mu \)-sized clusters (Fig. 1) itself presupposes the mobility of silver atoms and small silver clusters; (2) the motion of the observable silver clusters after deposition was shown to be a random walk with a mean-square displacement linearly increasing with time; and (3) the diffusion coefficient measured was found to be size-dependent — i.e., it decreases with the contact area \( S_0 \) of the clusters to the oil surface.

It is interesting to compare the experimentally found size dependence of the friction coefficient \( F \) to some well-established cases. For Brownian motion of spherical particles containing \( n \) atoms in a liquid, according to Stoke's law, a friction coefficient \( F \sim n^{1/3} \) is expected [15]. For Brownian motion of platelets on a surface with friction proportional to the contact area, one expects \( F \sim n \). According to Fig. 2 and with \( D \sim F^{1} \) we obtain for the measured range of cluster areas between \( 10^{-8} \) cm\(^2\) and \( 2 \times 10^{-17} \) cm\(^2\) an average friction exponent of about 0.6, which is within our expectations. As pointed out in the Results section, the friction exponent appears to be shape-dependent with a smaller value of about 0.3 for compact branched clusters. Since the data in Fig. 2 scatter considerably, no safe conclusion with regard to this issue may be drawn here. In order to determine the friction exponent reliably, it will be necessary to obtain diffusion coefficients for equal-shaped clusters over a size range of more than an order of magnitude. Also, the overall drift motion should be minimized. Besides the lateral random walk, also random rotation of branched clusters was observed (Fig. 3). The observed change in friction exponent for lateral random walk might be related to the fact that as soon as the clusters become branched, the fraction of the average kinetic energy of the cluster present in the rotation increases at the expense of the one present in lateral motion.

In order to discuss stage I of cluster aggregate formation, we name a cluster stable if it more probably grows than shrinks [16]. Note that, in our case of cluster-size-dependent mobility, the stability of a cluster implies (1) that the rate of material dissociation from the cluster is smaller than the rate of material incorporation and (2) that the probability of the mobile cluster to be ‘eaten’ by an even larger cluster is negligible. At the beginning of stage I, due to deposition, the concentration of silver atoms increases with time. These atoms migrate rapidly over the liquid surface forming small silver clusters upon encounter. Subsequently, larger, slower and stable silver clus-
The stable clusters efficiently pre-empt their surroundings of adatoms and small clusters. Hence, after a short nucleation phase, no more stable clusters are formed. As the diffusion of large clusters is slow, the encounter of two stable clusters is a rare event. The number density of stable clusters therefore remains almost constant during their subsequent growth; i.e., it saturates. These stable clusters communicate via their diffusion fields and grow for similar times from nucleation until the end of deposition. Therefore, at this time, a relatively narrow size distribution of clusters is expected. The growing clusters remain compact during growth since silver surface self-diffusion is efficient at room temperature [17,18]. The scenario presented here corresponds largely to classical nucleation theory in epitaxy [8] with the additional assumption of cluster-size-dependent mobility as in the deposition, diffusion and aggregation (DDA) model [9,10]. The experiments strongly support this scenario. Both classical nucleation theory as well as the DDA model predict saturation of the cluster density for a certain deposited amount. This is in line with our observation for the deposition rate of 0.03 nm s$^{-1}$ (Fig. 6). Both models predict scaling of the saturated cluster density $N_x$ with the deposition rate $f$ according to $N_x \sim f^\gamma$, at least as long as the friction coefficient scales to some power with the cluster size. Experimentally, such scaling behavior is observed and the determined exponent is $\gamma = 1.38 \pm 0.10$ (Fig. 7). The value of the exponent might appear unexpectedly large. Classical nucleation theory, which excludes the mobility of stable nuclei, predicts a scaling exponent of $1/3$ if the dimer is a stable nucleus. However, the dependence of island density on deposition rate becomes much stronger with increasing size $i$ of the smallest stable cluster, i.e., atoms contained in the smallest stable nuclei. Theory predicts $\chi = i/(1+i)$, which approaches 1 for large sizes $i$. In the DDA model — which additionally includes the mobility of clusters — it was shown that, at least for the case of $i=2$, the scaling exponent $\chi$ exceeds the value obtained without cluster mobility considerably: 0.42 compared with 0.33. In conclusion, the large value of $\gamma = 1.38$ is consistent with a large size of the stable nuclei and cluster mobility. Finally, we note that neither standard nucleation theory [8] nor the DDA model [9,10] fits the experimental situation completely. Nucleation theory does not include mobility of stable clusters of any size, while in the DDA model the clusters present at the end of growth are ramified rather than compact, since surface self-diffusion is not included in the model.

Stage II starts at the end of deposition and is accompanied by a switch in time scales. While stage I is completed after a few seconds, those changes in island density, size and shape, which are characteristic for stage II, are observed on a time scale of hours or even days. On this time scale, the Brownian motion of the compact clusters formed during deposition is no longer negligible and mean-square displacements of the order of $\mu$m occur. The large clusters migrate and if two clusters touch they adhere to each other, but do not coalesce. All this is seen directly during the observation of the samples after deposition (see, for example, Fig. 1).

Occasionally we had the impression that adjacent clusters were attracted towards each other. As the surface tension of the silicone oil (3.6 $\times$ 10$^{-2}$ J m$^{-2}$ [19]) is smaller than the one of silver (1.1 J m$^{-2}$ [20]), the reduced Laplace pressure in the space between the clusters must be assumed to lead to an attractive interaction for short distances [21]. Such an attractive interaction between the clusters would explain why the clusters were not seen to separate again after impact. However, it would also cause slight deviations from random walk for nearby clusters. It is not evident why the large clusters, once they adhere to each other, do not coalesce. We have postulated, on the contrary, that in stage I small unstable clusters are incorporated into large stable clusters, which maintain their compact shape. We can envision two possible scenarios which fulfil the apparently contradicting requirements.

1. Silver atoms and small unstable clusters (smaller than the oil molecules) move relatively free through the oil molecules. Once the silver clusters are large compared with the oil molecules, they are slow and oil molecules can adsorb at the cluster surface. A silver atom or a small silver cluster is able to penetrate the layer of oil
molecules of a large silver cluster and thus becomes incorporated into the cluster. Supply of such small clusters to a growing large one allows the latter to maintain a compact shape during growth. However, two large clusters that impact during their random walk will not be able to penetrate their respective layers of oil molecules and are thereby not able to merge.  

2. Coalescence occurs also for two large clusters, but it is slow compared with our observation time scale of \( \approx 1 \text{ h} \). Indeed, in Figs. 1 and 6 there are clusters observable which are not circular but appear to have the shape of an 8, i.e., appear as if they were just in the process of coalescing. In contrast, for small unstable clusters impacting on stable ones, coalescence is fast and thereby the stable clusters growing during deposition remain compact. This assumption is based on the fact that the efficiency of transport processes is strongly dependent on the related length scale. While at present it is not possible to decide which of the scenarios applies, the discussion suggests that there is no evident contradiction between incorporation of small clusters into large ones and adhesion without coalescence upon the impact of large clusters.

The scenario we assume for stage II corresponds largely to cluster-cluster aggregation models \([11,12]\). In these models, Brownian motion of the clusters is assumed. It is shown that the resulting morphology does not depend critically on the friction exponent \([12]\). In the models initially a statistical distribution of equal-sized clusters is assumed. Experimentally, at the end of deposition the clusters are not distributed statistically but are correlated in position via their overlapping diffusion fields which suppress short neighbor distances. Also, the clusters are not equal in size, but have a certain size distribution which is nevertheless relatively sharp (compare Figs. 1 and 6). Long after deposition, when aggregation is essentially finished, the cluster–cluster aggregation models yield fractal dimensions \( D(H) \) of 1.32–1.50. The experimentally obtained fractal dimensions from the silver aggregates a long time after deposition fall in the range between 1.3 and 1.5. They are thus consistent with the results of the cluster–cluster aggregation models, supporting our claim that the experimental system presented here is a realization of such models. The experimental results certainly disagree with the values of around 5/3 obtained from the model of diffusion-limited aggregation \([23–25]\) and experimentally found also for fractals formed on solid surfaces by atoms \([3–5]\) or clusters \([26,27]\). The lower fractal dimension obtained on the liquid substrate is consistent with the less branched appearance of the silver aggregates on oil. The different fractal dimensions of the two classes of system are most likely due to the fact that motion of atom or cluster aggregates is absent on solid substrates under conditions where fractals are formed, while Brownian motion is present on the liquid surface even for cluster aggregates. Additional information related to stage II of aggregate formation is contained in the decay of the cluster density with time. The data we analyzed appear to follow an exponential decay law. While at present we are not able to present an analytical model of this behavior, it might be a general feature of cluster–cluster aggregation processes. This could be tested by Monte Carlo simulations for cluster–cluster aggregation.

A number of questions and unsolved problems remain. In the entire paper we did not discuss the actual interaction of the silver atoms and silver clusters with the oil molecules on the atomic level. It is this interaction which must lead to the presence of silver at the surface of the oil film, a fact which is by no means self-evident. Our experiments do not give information on this issue. Certainly it would be very desirable to grow and observe the silver clusters under well-defined conditions. This would include good vacuum conditions, a constant temperature and the absence of spatial temperature gradients. Such conditions would allow the study of temperature effects on nucleation and growth of clusters, in growth experiments typically the most important parameter. In the experiments presented, temperature was not under full control. In addition, temperature gradients might have contributed to the overall drift motion of the

\[^{1}\text{In a previous realization of a cluster–cluster aggregation model \([22]\), the agreement between model and experiment for } D(H) \text{ had been less satisfactory.}\]
clusters. In situ observation and video taping of the cluster formation and aggregation would give a much broader data basis for quantitative analysis. It would also allow us to study precisely the transition from cluster formation to cluster aggregation; i.e., from stage I to stage II. Finally, it would also be highly interesting to study the observed phenomena as a function of liquid film thickness and film viscosity. These two parameters probably have a strong effect on the friction of the silver clusters and aggregates on the surface.

Acknowledgements

We thank Josef Larscheid, Inés Friedrich, Marc Henke, Bernd Schirmer, Han-Willem Woltgens and Sun-Joung You for useful discussions and technical assistance. G.-X. Ye gratefully acknowledges the hospitality of the Institut für Grenzflächenforschung und Vakuumphysik and the support by the Pao Yu-kong and Pao Zhao-long Scholarship of China. The financial support from the Chinese Natural Science Foundation (Grant No. 19504003) and the Zhejiang Provincial Natural Science Foundation of China (Grant No. 1997-RC9603) is gratefully acknowledged. Th. Michely acknowledges support by a Heisenberg fellowship of the Deutsche Forschungsgemeinschaft and M. Wuttig acknowledges support by the same institution.

References