

# Mimicking Nanometer Atomic Processes on a Micrometer Scale via **Electrophoretic Deposition**

Partho Sarkar,\*,<sup>†</sup> Debnath De,\*,<sup>‡</sup> Kimihiro Yamashita,\*,<sup>§</sup> Patrick S. Nicholson,\*\*,<sup>‡</sup> and Takao Umegaki<sup>\*,¶</sup>

Advanced Materials Group, Alberta Research Council, Edmonton, Alberta, Canada T6N 1E4

Department of Materials Science and Engineering, McMaster University, Hamilton, Ontario, Canada L8S 4L7

Institute for Medical and Dental Engineering, Tokyo Medical and Dental University, Tokyo 101-0062, Japan

Department of Industrial Chemistry, Tokyo Metropolitan University, Hachioji, Tokyo 192-03, Japan

The process of submonolayer formation during the electrophoretic deposition (EPD) of colloidal films of micrometersized (diameter  $\approx 0.5 \,\mu\text{m}$ ) silica particles on a silicon wafer has been observed as a function of deposition time. The process of nucleation and growth of the silica monolayer is compared with that of atomic film growth (10000 times smaller scale) via molecular-beam epitaxy (MBE), and for the first time, a striking similarity between the two growth processes is observed. Likewise in the atomic growth process via MBE, the entire nucleation, growth, and aggregation process during EPD of silica particles can be broadly classified into two regions. At low surface coverage when silica particles are deposited outside of clusters, diffuse randomly, and stick to a cluster on touching them, the mechanism of growth in this region follows diffusion-limited aggregation (DLA) and the fractal dimension of the two-dimensional clusters is found to be close to 1.65. Later on, as the clusters grow in size, deposition of particles inside the clusters become important and clusters become more and more compact, resulting in a dense, close-packed, and homogeneous monolayer. This region is termed a consolidation region, and a change in fractal dimension from 1.65 toward 2 with increasing surface coverage has been observed.

### I. Introduction

THE order-disorder transitions of monodispersed microspheres from "fluids" to "crystals" in colloidal suspensions can serve as a direct analogue of the structural phase transitions of atoms in crystalline materials.<sup>1</sup> Unlike atoms in crystalline materials, spheres in colloidal dispersion can be tracked and imaged by digital video microscopy. The phase transition of colloidal spheres from regular, ordered crystalline arrays to chaotic-fluid disorder can be controlled by manipulating their concentration and chemical environment in the colloidal suspension.<sup>2</sup> The mechanism of colloidal film growth of micrometer-sized particles is poorly understood, and insight could result from comparison with atomicscale, thin-film growth via molecular-beam epitaxy (MBE). In the latter, controlled numbers of atoms are deposited from the gas phase onto a well-characterized, crystalline substrate under controlled growth conditions.<sup>3</sup> The deposition of atoms onto the substrate disturbs the system equilibrium which is restored by aggregation of the atoms into clusters.<sup>4</sup>

Colloidal film processing from a stable suspension of nanometer- to micrometer-sized particles involves manipulation of the particles by externally imposed fields, e.g., electrophoretic deposition (EPD) by an electrical field, slip-casting by capillary forces, centrifugal-casting by centrifugal forces, pressure-casting by fluid pressure differences, and sedimentation by the gravitational field. Demand for minimal defect-, close-packed-, dense-, and homogeneous-microstructure-film is developing in the advanced microelectronic, optical, magnetic, and high-performance structural device fields. The morphology and growth of a colloidal film is influenced by the properties of two-dimensional arrays of particles or clusters that evolve during submonolayer formation on the substrate.5

This paper describes visualization of the process of submonolayer formation during the film growth of micrometer-sized colloidal particles by EPD. The mechanism of colloidal film growth process is investigated and compared with atomic-scale, thin-film growth by MBE.

#### **II. Experimental Procedure**

A colloidal suspension of monodispersed silica spheres (PCI, Inc., diameter  $\approx 0.5 \ \mu\text{m}$ ) in ethanol (0.05 g of silica/100 mL of ethanol) was stabilized by tetramethylammonium hydroxide (TMAH) (pH  $\approx$ 9.5). The SiO<sub>2</sub> sphere zeta potential was -75 mV(Coulter DELSA 440 Analyzer). EPD was conducted at room temperature (25°C) (constant current = 0.25 mA). The cathode (substrate) was an optically polished silicon wafer (depositing area: 126 mm<sup>2</sup>). The anode was platinum and was separated from the cathode by 20 mm. Silica particles were electrophoretically deposited on the substrate for different times. The substrate was then taken out of suspension and dried. Figures 1(a) through (d) show the SEM images of the substrate as a function of deposition time (or surface coverage). Capillary-force-driven fusion of domains at the periphery of the deposited layer during drying is neglected.<sup>6,7</sup> Figures 1(a) through (d) resemble the *in situ* particleclustering images during EPD of latex particles as reported by Böhmer.<sup>6</sup> The present authors also visualized similar particleclustering images (Figs. 1(a) through (d)) in situ via an optical microscope during the EPD of silica particles. SEM images were digitized and a prefixed basis area encompassing a cluster of particles chosen to calculate the fractional surface coverage (area covered by the particles/the basis area) by the particles. The fractal dimensions of the ramified clusters (Figs. 1(a) through (d)) were

C. Randall-contributing editor

Manuscript No. 189007. Received June 4, 1999; approved November 30, 1999. \*Member, American Ceramic Society. \*\*Fellow, American Ceramic Society.

<sup>&</sup>lt;sup>†</sup>Advanced Materials Group, Alberta Research Council.

<sup>&</sup>lt;sup>\*</sup>Department of Materials Science and Engineering, McMaster University. <sup>\*</sup>Institute for Medical and Dental Engineering, Tokyo Medical and Dental University. <sup>¶</sup>Department of Industrial Chemistry, Tokyo Metropolitan University.



Fig. 1. SEM microstructures of submonolayer of colloidal silica particles (diameter  $\approx 0.5 \ \mu$ m) as a function of deposition time: (a) at low deposition time (10 s), (b) at 120 s, (c) at 960 s, and (d) at complete monolayer coverage of surface by a dense, homogeneous and close-packed film.

calculated by the box-counting method, following the fast algorithm of Liebovitch and Toth<sup>8</sup> (software, FD3, written by John Sarraille and Peter DiFalco<sup>9</sup>).

## III. Results and Discussion

A plot of cluster fractal dimensions versus fractional surface area coverage during submonolayer formation is shown in Fig. 2. At low surface coverage (Fig. 1(a)), particles arrive on the substrate surface, deposit, and diffuse randomly; i.e., the deposition and diffusion processes simultaneously take place. When one



Fig. 2. Fractal dimension of clusters in Figs. 1(a) through (d) as a function of surface coverage during submonolayer formation of silica particles.

particle meets another, they form a critical nucleus with less mobility, i.e., an island or cluster. Deposition inside a cluster is initially neglected since mostly single particles exist on the electrode surface. An island grows when a particle meets a cluster and attaches to its edge (due to the total interaction energy barrier (the result of ionic and van der Waals forces) (Fig. 1(b))). A particle arriving on top of an existing island will diffuse until it falls off the edge of island (or it stays on the upper terrace due to the total interaction energy barrier). Particles on the cluster surface have a surface mobility that allows clusters to attain minimum energy and the equilibrium configuration of close-packed structures. The surface mobility of particles is due to (1) Brownian motion and/or (2) electro-osmotic<sup>7</sup> flow. Solomentsev et al.<sup>7</sup> reported that electro-osmosis around a charged, nonconducting particle, near or on a flat conducting surface, creates a fluid flow adjacent to the particle. The fluid is drawn laterally (at 90° to electrical field) toward the particle near the electrode due to electro-osmosis and is pushed outward from the particle further away from the electrode (above the particle). This lateral convective fluid flow results in either particle-particle or cluster-cluster aggregation over length scales comparable to their respective sizes. Solomentsev *et al.*<sup>7</sup> also demonstrated that this long-range electroosmotic flow causes surface mobility and reorientation of the particles in a given cluster, resulting in a close-packed (equilibrium) structure.

Figure 1(a) shows that, at short times and low surface coverage, the size of isolated islands is small and their number density increases more rapidly than single particles. When the number density of islands and single particles becomes comparable, the rate of increase of the number density of islands slows (Fig. 1(b)). When the size of the islands is  $\cong$  the distance between them, a rapid decrease of number density of single particles is observed as well as an unchanged number density of islands (Fig. 1(c)). No further islands form in this regime.

As time progresses, the islands grow and become consolidated by deposition of particles inside them. As a result, the individual islands grow into close-packed structures with minimum configurational energy and distinct domain boundaries. When the consolidated islands touch each other, their growth stops. Finally, the close-packed islands, forming a monolayer where the distinct domain boundaries of the islands are preserved, cover the entire surface (Fig. 1(d)). Cluster formation on top of this monolayer now becomes relevant.

The mechanism of nucleation, growth, and aggregation during submonolayer formation of micrometer-sized particles can be classified into two regions as per the classical DDA (deposition, diffusion, and aggregation) model of atomic thin-film growth during MBE. At low surface coverage (region A in Fig. 2 where deposition and diffusion of particles take place simultaneously), the mechanism of growth is similar to the diffusion-limited aggregation (DLA) of atomic, thin-film growth where atoms deposit outside clusters, diffuse randomly, and stick to a cluster on touching. Figure 2 shows that the fractal dimension of the two-dimensional ramified clusters in this region is  $\approx 1.65$ . In the classical DLA mechanism, only single atoms diffuse and this is the only source of aggregation. The fractal dimension of twodimensional clusters in the classical DLA mechanism is  $\approx 1.7$ .<sup>10</sup> Meakin<sup>11</sup> reported that, when the clusters also diffuse, the fractal dimension (x) is 1.45 < x < 1.5. In the present experiments, single particles and clusters diffuse, and long-range, electro-osmotic flow<sup>8</sup> plus diffusion results in particle aggregation. The fractal dimension ( $x \approx 1.65$ ) in this DLA region is 1.45 < x < 1.7. Subsequently, as clusters grow, deposition of particles inside them becomes important and the latter become more consolidated and form a close-packed structure (region B in Fig. 2). This region constitutes the consolidation process of clusters (like the consolidation of atom clusters in the atomic thin-film growth process) and Fig. 2 shows a change of fractal dimension (1.65 toward 2) with increasing surface coverage.

Following the classical DDA model of atomic thin-film growth, the time scale of the two competing processes, i.e., deposition and diffusion (or nucleation and growth) of particles, depends on the flux of deposition (F) and the surface diffusion coefficient (D) for particles. As F increases, the deposited particles must diffuse over a shorter distance before meeting others; i.e., the time scale for diffusion of a particle is proportional to 1/D. In the formation of a submonolayer of micrometer-size particles, diffusion is enhanced by long-range electro-osmotic flow and results in particle aggregation. At a fixed surface coverage, an identical surface morphology is expected as long as the ratio D'/F (D' is the enhanced diffusion coefficient) remains constant during the film growth process, since deposition and enhanced diffusion processes are in competition in the early stages of submonolayer formation by micrometer-size particles. The flux of the particles (F) remains

virtually constant with time (since EPD is conducted at constant current) and the change of particle concentration in the large volume of suspension is negligible. D' for particles is also assumed to be approximately constant with time at room temperature if the particle flux is constant. Thus, Figs. 1(a) through (d) show the variation of island size and number, as a function of surface coverage, for  $D'/F \cong$  constant.

Thus, the mechanism of nucleation, growth, and aggregation during the submonolayer formation of micrometer-size particles mimics the classical DDA model of the atomic, thin-film growth process as per MBE. The results provide insight into the growth kinetics and the microstructural manipulation of films of micrometer-size particles as practiced in the semiconductor, ceramic, polymer, and other coating industries.

## **IV.** Summary

Submonolayer formation as a function of deposition time has been observed during the colloidal film growth of silica particles (diameter  $\approx 0.5 \ \mu m$ ) on a silicon wafer substrate by electrophoretic deposition. A close-packed, homogeneous, dense monolayer of silica particles evolves at the end of submonolayer formation. Analysis of the fractal dimensions of the particle clusters versus fractional surface-area coverage by particles reveals that the film growth of silica particles mimics the classical DDA model of the atom-by-atom, thin-film growth process via MBE.

#### References

<sup>1</sup>C. A. Murray and D. G. Grier, "Video Microscopy of Monodisperse Colloidal Systems," *Annu. Rev. Phys. Chem.*, **47**, 421–62 (1996).

<sup>2</sup>A. E. Larsen and D. G. Grier, "Like-Charge Attraction in Metastable Colloidal Crystallites," *Nature (London)*, **385** [16] 230–33 (1997).

<sup>3</sup>Z. Jhang and M. G. Lagally, "Atomistic Processes in the Early Stages of Thin-film Growth," *Science*, **276** [18] 377–83 (1997).

<sup>4</sup>H. Roder, E. Hahn, H. Brune, J. Bucher, and K. Kern, "Building One- and Two-Dimensional Nanostructures by Diffusion-Controlled Aggregation at Surfaces," *Nature (London)*, **366**, 141 (1993).

<sup>5</sup>H. H. Wickman and J. N. Korley, "Colloidal Crystal Self-Organization and Dynamics at the Air/Water Interface," *Nature (London)*, **393** [4] 445–47 (1998).

<sup>6</sup>M. Böhmer, "In Situ Observation of Two-Dimensional Clustering during Electrophoretic Deposition," *Langmuir*, **12** [24[rsqb] 5747–50 (1996).

<sup>7</sup>Y. Solomentsev, M. Bohmer, and J. L. Anderson, "Particle Clustering and Pattern Formation during Electrophoretic Deposition: A Hydrodynamic Model," *Langmuir*, 13, 6058–68 (1997).

<sup>8</sup>L. S. Liebovitch and T. Toth, "A Fast Algorithm to Determine Fractal Dimension by Box-Counting," *Phys. Lett. A*, **141**, 386–90 (1989).

<sup>9</sup>J. J. Sarraille and P. DiFalco, A Program for Calculating Fractal Dimensions, FD3, version 0.3 (ftp://ishi.csustan.edu/pub/; email: john@ishi.csustan.edu), Department of Computer Science, California State University, Stanislaus, Turlock, CA 95382.

<sup>10</sup>A. L. Barabasi and H. E. Stanley, *Fractal Concepts in Surface Growth*; Ch. 17. Cambridge University Press, New York, 1995.

<sup>11</sup>P. Meakin, "Formation of Fractal Clusters and Networks by Irreversible Diffusion Limited Aggregation," *Phys. Rev. Lett.*, **51**, 1119 (1983).