Directed Self Assembly: a Novel, High Speed Method of Nanocoating Ultra-thin Films and Monolayers of Particles

George A. Powch[*] and Ajaykumar R. Jain[**]

[*]Versatilis LLC, Shelburne, VT, USA, gpowch@versatls.com
[**] Versatilis LLC, Shelburne, VT, USA, ajay@versatls.com

ABSTRACT

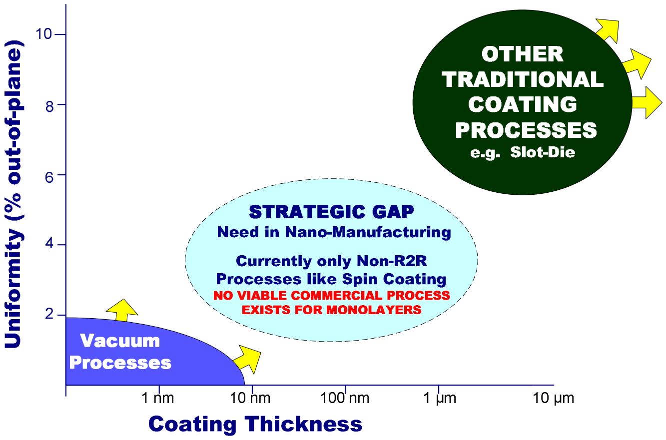
A novel, practical fluidic method is presented for coating ultra-thin, ultra-uniform layers and realizing self-assembled monolayers of particles well into nanoscale in atmosphere and room temperature at rates scalable to web processes at >4 m/min. A prototype machine is shown and a wide variety of deposited materials reviewed, including ultra-thin polymer films, and a variety of micro- and nano-particles.

Keywords: Nanocoating, Monolayers, Self-Assembled Monolayers, Ultra-thin Film Coating, Fluidic Self-Assembly, Directed Self-Assembly

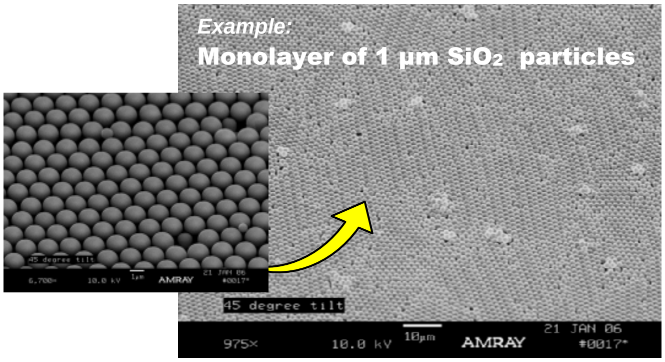
1 INTRODUCTION

Application of ultra-thin, micro- or nano-coatings << 1 µm thick (e.g. <20 nm), or particles <100 nm in a **monolayer**, at commercially viable scale (>4 meter/min) at room temperature without vacuum and with a high degree of control over uniformity and thickness is a significant manufacturing challenge. Applications in renewable energy markets are responsible for strong, emerging demand for such coatings, but there are few, if any viable technologies. Current processes like Slot Die, Extrusion, Spin and Spray Coating have difficulties in obtaining structured and organized deposition in a roll-to-roll (R2R) paradigm at room temperature and on varying, unstable or rough surfaced substrate materials.

The challenge can be characterized as depicted below, in terms of coating thickness vs. uniformity, with a "strategic gap" between vacuum processes and where traditional coating processes are effective for R2R processing:



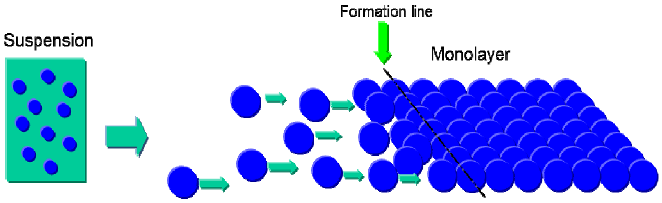
There is, for example, no known method for realizing densely packed monolayers of micro or nano-particles of organic or inorganic semiconducting particles, or even micro-die, at rapid rates. What is needed is a cost effective means to realize depositions such as the following at commercially viable rates:



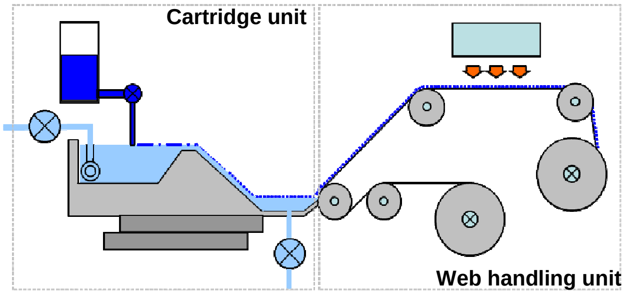
A novel, practical method is presented for depositing ultra-thin nanoscale layers of polymer thin films and assembling dense, tightly packed **monolayers of micro- or nano-particles at commercially viable scale.** The technique can realize monolayers of particles down to 5 nm or up to 100 µm with <0.1% out-of-plane, or ultra-thin polymer films < 20 nm with variation in uniformity <5% in a R2R process at 4 m/min. A prototype model has been shown, with up to a 30 cm web; however, there is no intrinsic reason why it cannot be scaled to meter wide widths.

2 OPERATING PRINCIPLE

The technique involves an automated variation on the well-known Langmuir Blodgett technique; the material (or particulates) to be deposited are put into a suspension, then dispensed in a precise, controlled manner onto the surface of a carrier liquid of suitable density on which they "float," forming a bi-layer. The top layer is then made to self-assemble by inducing the bottom carrier liquid to flow, a function of dispensing and flow rates, surface tension and surfactants:



The exact mechanism is realized as follows, consisting of a "cartridge" unit with a ramp between two ponds at different heights containing the carrier fluid which is pumped at a controlled rate to form a closed, recirculating loop, and a web handling unit which passes a moving substrate close to a lip along the edge of the lower pond:



The flow of the carrier fluid causes a controllable lateral pressure on the top layer which assembles what is floating into a tight configuration on the surface of the ramp, dictated by the physics of the particles and fluids involved. The assembled layer is then smoothly transferred onto a passing substrate over a colloidal bridge formed along the lip of that lower pond. The coating thickness can be tightly controlled, with high uniformity of deposition.

Unlike slot die coating or other systems, the material to be deposited is **not** diluted to control thickness, which would then require precise evaporation (drying) of the dilutant to control thickness and uniformity, with a huge footprint in high cost drying ovens. Rather, **only incidental traces** of the carrier fluid, or of the solvents used to prepare the initial suspensions that had not already evaporated (or settled out into the carrier fluid) need be evaporated, which is typically easily handled with IR lamps, as illustrated above.

A prototype, lab scale tool with a 100 mm. web (and delivery cartridge) has been built and demonstrated, and appears as follows. It can move at 0-5 cm/sec, controllable ± 0.1 mm/sec, and uses gravity to supply carrier fluid pressure by simply mounting a reservoir of the carrier fluid (e.g. water) on the elevated platform shown. Lateral surface pressure can be made to vary 0-72 mN/m ± 2 mN/m:


Prototype Lab Scale Coating Tool

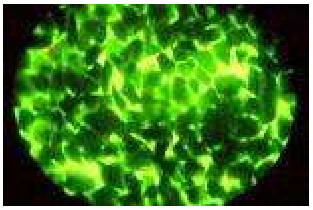
3 RESULTS

A wide variety of materials, liquid and particulate, in various sizes and shapes have been deposited using this technique for various applications as illustrated below; there are some 40 recipes for coating different materials:

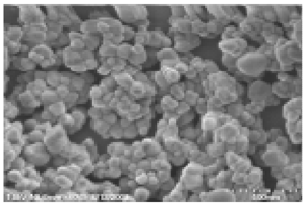
Particle	Shape	Size
SiO2	Spheres	20 nm – 1.5 μm
PMMA	"	250 nm – 950 nm
Wax	"	100–300 μm
Reflectospheres	"	1– 100 μm
Quantum Dots	"	2 –10 nm
Fluorescent	Spheroids	Blue 1.5 μm
"	"	Green 1.5 μm
Thermo–chromic	"	Blue – white 2 μm
"	"	Pink – white 2 μm
BSA Protein	Spheroids	20 nm
TiO2	Irregular	100 nm
Diamonds	"	250 nm
Silicon	irregular	5–10 μm, 30 μm
Gold	Spherical	5 nm
Graphite–Platinum	"	30 – 100 nm
CNT	Bundles	≈ 1 μm
CNT–Platinum	"	≈ 1 μm
Carbon	Chunks	> 1 μm
Carbon–Platinum	"	> 1 μm

Some examples include:

Nanodiamonds (250 nm)

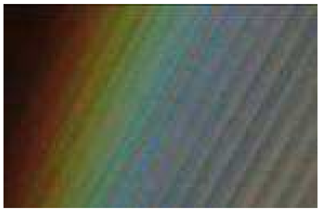


TiO2 Fines 300-500 nm



10 nm CNTs / 50-100 nm Pt

Reflected Light SiO_2 Monolayer Film 5-10 μm



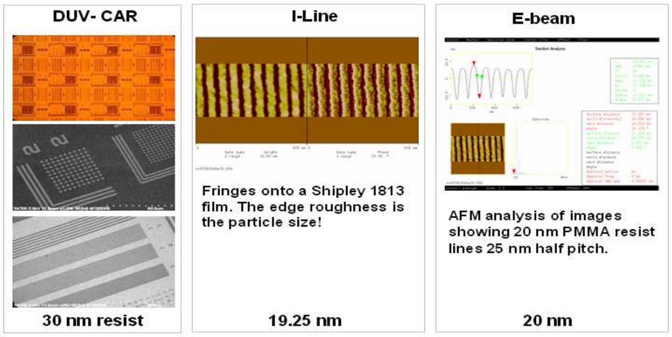
Potential applications have ranged in "Printed" Electronics, to include flexible TF Solar and Solid State Lighting which require deposition of expensive material (OLED chemistry, Semiconducting Inks, etc.) in ultra-thin, ultra-uniform layers, as well as new forms of transparent conductors such as **silver nanorod** meshes, **graphene** flakes and other …

3.1 Polymer Thin Films

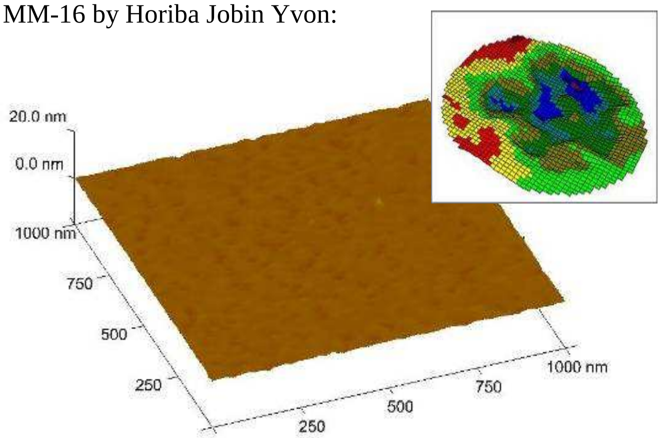
The process is well suited to ultra-thin polymer films: after injection onto a moving flat fluid layer, the polymer solution thins down in different ways depending on the physical-chemical characteristics of the solvents and liquids; e.g. after spreading, the solvent fades down from the gas-liquid interface through evaporation and immersion. The natural properties of the gas-liquid interface: flatness, mobility and tension, together with natural forces such as gravity hydrodynamically drive the material at the interface toward and onto a film formation line. The pressure applied onto the film's long axis is kept constant while the film is transferred from the liquid surface toward a solid substrate.

The pressure inside a 1 nm monolayer is about 300 atmospheres, a compression level where no lateral forces on the solid surface are likely to rupture the thin film. In fact, thinness as small as 1 nm with PMMA has been achieved, with no pin holes and defects. Detected defects are primarily from environmental particles and not from surface or resist particles.

We have shown a broad range of typical photoresists at 20 nm down to 1 nm, suggesting applications for EUV photolithography. For example, common photoresists and polymers for I-line, DUV and E-beam lithography have been shown, to include SP1813, UV1400, AZ9260, NED, ZEP, and PMMA:

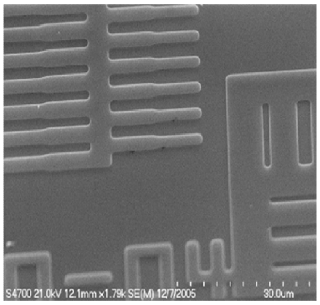


Shown below is an AFM example of 70 nm of UV1400 coated onto a 200 mm wafer with full thickness variation in the order of 1 nm and 0.2 nm Roughness as measured with MM-16 by Horiba Jobin Yvon:



PVDF, PVPH and Polyimide have also been tested for various applications.

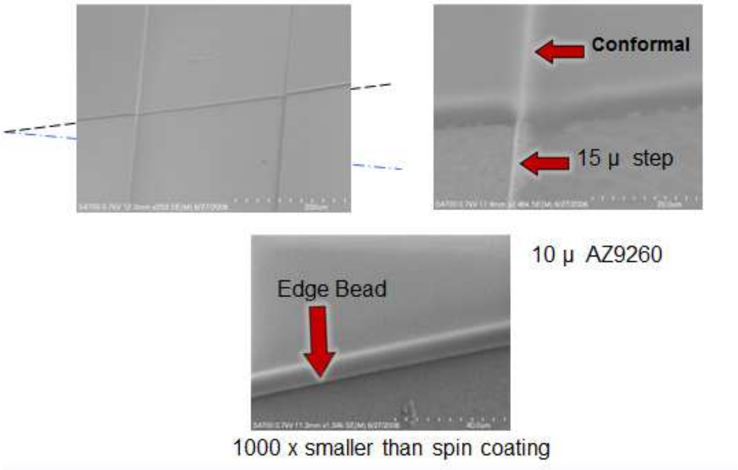
Ultra-thin coatings are further highly conformal; shown below is a patterned substrate with a conformal resist coating, compared to same with an Acetone Drop to show the presence of polymer over the topography:



Patterned Substrate with Conformal PR Coating

Acetone Drop to show Polymer Presence

Further below are magnified details of a 10 µm coating of AZ9260 showing conformability across a 15 µm step, as well as the significantly smaller edge bead realized with this technique, when compared to traditional spin coating:



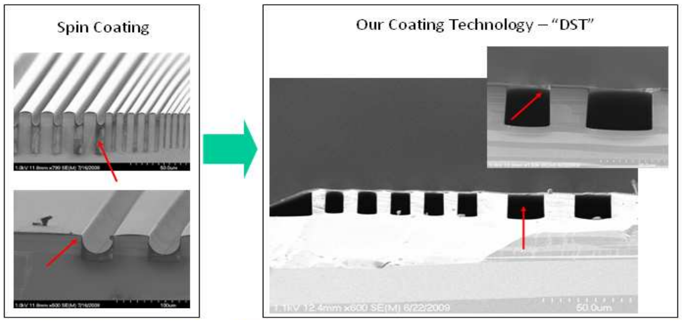
While this coating process can be shown to produce coatings significantly better than state-of-art spin and spray coating, it is **not** positioned per se to compete against such well established processes for wafers, but is focused instead on **new** web (R2R) based, and novel applications that lever its unique capabilities, particularly for particle monolayers.

Note also that the process can be enclosed (a prototype tool with such enclosures has been built) and an ambient gas such as N_2 introduced to create a differential vapor pressure above the assembling layer. This provides another degree of control for certain applications where such capability is critical, or where the evaporation rate of the solvents used for preparing the initial suspension need be controlled.

Following are brief descriptions of some unique capabilities of this process, and some related applications enabled by such a tool capability.

3.2 Dynamic Static Tensioning (DST) Mode

There is a unique mode intrinsic to this process with many typical polymer materials, where layers of a certain thickness (typically >500 nm) under certain rates of deposition and carrier flow, can be made to act the opposite of conformal and be suspended across the topography as literally a membrane, causing the surface to planarize:

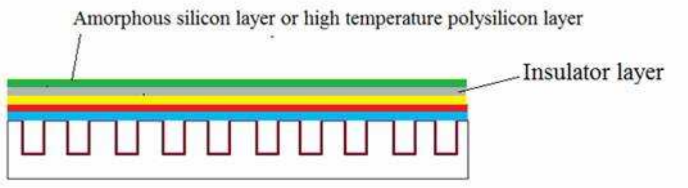


Spun Coatings Tend to Conform

While a ~1 µm PR Film can be "Suspended" Across the Topography, Planarizing Top Surface

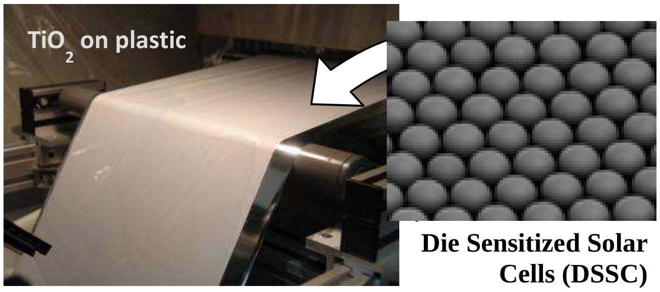
The effect is well demonstrated and suggests the process can be an effective planarizing technique for uneven substrates such as the metal foils being used for printed electronics, TF solar, and the like.

A novel application has been suggested for a releasable membrane or bond/debond method in flex electronics, where such a coating (e.g. a Polyimide or inorganic sol gel) deposited over a perforated carrier substrate can be quickly released post processing with the perforations providing easy access for etchants to quick release the membrane:



3.3 Particle Monolayers

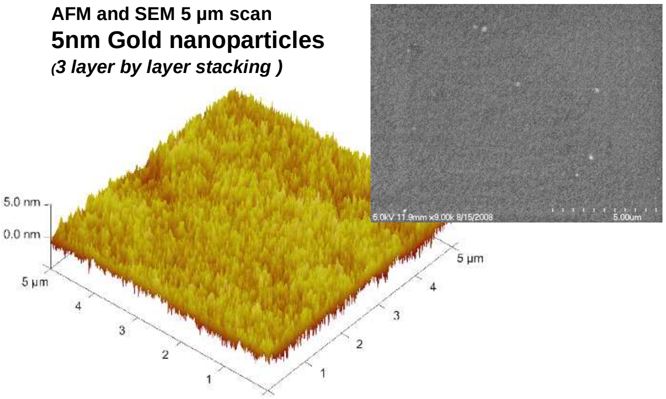
The process is particularly well suited for monolayers, where no other known process is as fast or effective. A variety of applications have been explored, including the following as representative examples:



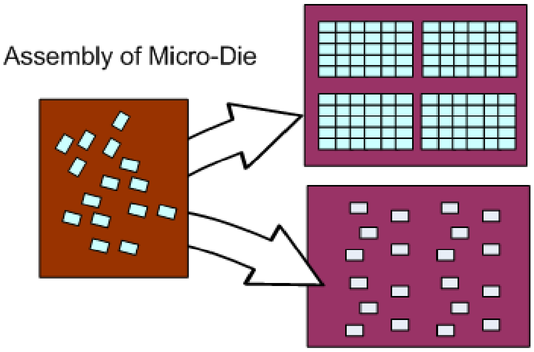
Die Sensitized Solar Cells (DSSC)

Uniform, ordered layers of deagglomerated, **nano-porous** (for increased die absorption) 500 nm TiO_2 particles were deposited on an aluminized plastic film roll in a 30 cm web based tool at speeds to 1.2 m/min. Porosity was controlled by the applied lateral pressure, varying 0 – 72.5 mN/m. A variety of materials are further being tried for several thin film battery concepts.

A multi-pass, 3 layer by layer stack of 5 nm Gold particles was demonstrated for texturing of Poly-Si wafers as AR or reflective coatings, or texturing for SSL apps, and as a method for realizing photonic crystals or for LBL assembly:



Finally, the process is a ready, fluidic means of rapidly assembling not only particles, but other structures such as micro-die, silicon slivers, and the like … a number of applications are being explored:



4 SUMMARY

A novel, fluidics based method for depositing ultra-thin, nanoscale layers of polymer thin films and assembling dense, tightly packed monolayers of micro- or nano-particles has been shown. Prototype lab scale machines have been built and materials, ranging from nanoparticles of gold, silicon, SiO_2 and BSA Proteins, to QDs to a broad variety of photoresists, have been deposited on substrates from standard silicon wafers to continuous 6-10 in. rolls of metal foils, mylar, PET, PEN, and others. The technology is scalable to >30 cm widths at >4 m/min production rates and suitable for a wide variety of applications in "Printed" Electronics and the emerging energy devices market such as TF solar, OLEDs, and thin film batteries.