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Growth dynamics of granular films produced by electrospray

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ABSTRACT

Particulate coatings produced by electrospray deposition (ESD) of ethyl cellulose particles are found to widen over time. We hypothesize that during the ESD process, the electrospray expands due to repulsion caused by accumulated electrostatic charge in the film. The radial profiles of film thickness, mass density (per unit area), and porosity (gas volume fraction) have been determined as a function of several factors which influence electrostatic charging, namely, collection time, relative humidity, and deposition flux. The mass density has been determined from the local film thickness attained upon thermal annealing, which is largest near the center of the spray. The local porosity is lowest at the film center (at between 0.5 and 0.6), whereas across the film, it is roughly uniform (between 0.6 and 0.7) for deposition in a dry ambient, and slightly higher and more variable for humid ambient deposition. The granular films are compact (with low fractality) as expected for ballistic deposition (large Peclet number).

1. Introduction

Electrospray deposition (ESD) is a suitable method for preparing micrometer-thin or thinner layers because it uses non-agglomerating micro- or nano-droplets of uniform sizes. In addition, the high electrical charge on the droplets facilitates their precipitation onto electrically conducting substrates [1]. Since ESD is up-scalable, films have been prepared by this method for a broad range of applications. (i) *Inorganics* (e.g., metals, ceramics, semiconductors, etc.) have been prepared by electrospraying either nanoparticle suspensions (sols) or solutions of thermally labile precursors of the coating material, which are subsequently pyrolyzed [1]. In addition to recent works [2–9], a 2007 review [1] cites ~90 articles dealing with ESD-coated inorganics for uses in fuel cells, solar cells, lithium battery electrodes, gas sensors, optoelectronic devices, and ferroelectric materials. (ii) *Synthetic polymers* have been wet-coated to form continuous films for uses in organic photovoltaic structures [10], organic light emitting diodes (OLED's) [11–13], superhydrophobic or controllable wetting surfaces [14,15], drug-eluting coatings of coronary stents [16,17], PEM fuel cell membranes [18], coatings for SAW resonators [19], and photoresist coatings over fragile thin films [20]. (iii) *Biopolymers* (proteins, DNA, polysaccharides) have been electrospray deposited to prepare protein and DNA-based arrays for biosensors and cell research [21–24] and starch films [25]. (Additional materials are cited in [1].)

In most studies, the functional properties of the films are tested *globally* (as a whole), while the morphological characterization of the film (typically by electron or force microscopies) is carried out *locally* on patches whose width is of order 10–100 μm. Usually, these patches are assumed to represent the entire film. However, in some electrospray studies [20,24], the film thickness has been shown to vary significantly from the center of the film to its edge. Non-uniform profiles of the mass flux arriving at the collection surface have also been predicted in numerical simulations of the ESD process, both for single electrosprays [26,27] and multiple-electrospray systems [28–30]. These observations suggest that uneven distribution of the local film properties (thickness, porosity, etc.) may be more common than is usually assumed. Therefore, it is important to investigate the factors which can influence such distributions.

The objective of this work is to study the growth dynamics of granular coatings produced by electrospray deposition over conducting substrates, in the case where the particles result from solute precipitation in the electrospray droplets. Ethyl cellulose (EC), a water-insoluble polysaccharide, has been chosen as the solute for this study because its coatings are highly stable under storage. Specifically, we have determined how the deposition dynamics and the evolution of the structure and dimensions of EC granular coatings are influenced by two factors: chamber relative humidity and

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collection mass flux. The latter factor is varied *via* the electrodes separation. These factors have specifically been chosen because they can influence the rate of charge accumulation on the coating. Indeed, we have observed a tendency for the coatings to not only grow thicker, but also wider. We reason that electrostatic charging builds up on these coatings, wherein the accumulated charges modify the electric field which is responsible for the particles' trajectories. Practitioners of ESD have long known that electrostatic charging must be prevented by depositing over conducting substrates [31]. However, no research articles (experimental or numerical) could be found that examine the effects on deposition due to electrostatic charging of the *coating* itself.

2. Materials and methods

2.1. Materials and solution preparation

All reagents were used as purchased, without further purification. Ethyl cellulose (EC, Sigma–Aldrich, 4 cP viscosity, 48% ethoxyl content, density $\rho_{EC} = 1.14$ g/ml) was dissolved at 50 g/L (5% w/v) in butanone (Sigma–Aldrich, ACS reagent grade) at room temperature. This suggests a number-average molecular weight around 13–15 thousand Dalton, according to the Mark-Houwink equation [32]. Two other polymer/solvent combinations are briefly mentioned in this report: 5% w/v poly(methyl methacrylate) (PMMA, Sigma–Aldrich, M_w 350,000) in butanone and 1% w/v ethyl cellulose (EC100, Sigma–Aldrich, 100 cP, 48% ethoxyl content) in dichloromethane (DCM, Sigma–Aldrich, reagent grade). To the EC100/DCM solution, we added rhodamine 6G (Rh6G, Sigma–Aldrich) at 1:100 Rh6G:polymer weight ratio to raise the electrical conductivity of the solution. The electrical conductivity of the solutions was measured in a homemade apparatus consisting of a power supply (0–30 V), a nano-ammeter, and a silica tube with known geometry which contained the solution. The measured values are 5.9×10^{-4} S/m for EC-butanone at 25.3 °C, 1.1×10^{-4} S/m for PMMA-butanone at 25 °C, and 2.4×10^{-4} S/m for EC100-DCM at 28.4 °C. Substrates were cut from p-type boron doped silicon wafers (Compart Technology Ltd., P/Boron, $\langle 100 \rangle$, 500 μm thickness) of various sizes and were used without further cleaning or removal of native SiO_2.

2.2. Electrospray deposition apparatus

The electrospray chamber is drawn to scale in Fig. 1a. It has 4 equal glass walls and a methacrylate top plate, and sits on an aluminum bottom plate. Two thin strips of foam are arranged along the base of two parallel glass walls (not shown in Fig. 1a), forming two slits under the other two chamber walls (see Fig. 1a). Through these slits, collection substrates are easily introduced in and out of the chamber. The distance between the needle and the plate H (see Fig. 1a) can be adjusted by moving the needle and back plate subassembly as a whole. The electrospray current collected on the bottom plate with a homemade nano-ammeter is acquired at 10 Hz into a computer. Nitrogen (Carburos Metálicos, Premier grade) continuously enters at the chamber top at 1 slpm, exiting through the mentioned slits. Water vapor can be added to this gas to change the relative humidity (RH) in the chamber, which is monitored using a Vaisala HM34 meter probe inserted through the bottom plate. The electrosprayed solution is infused with a Harvard Apparatus HD-2000 syringe pump at 2 μL/min into the electrospray capillary tube ("needle"), a square-cut polyimide-coated fused-silica tubing (OD = 200 μm, ID = 100 μm, length ∼80 mm). Concentric with this needle is a glass tube (Fig. 1b), which supplies a gentle (0.015 slpm) co-flow of solvent vapor laden nitrogen ("sheath gas") around the needle to prevent polymer precipitation at the liquid meniscus caused by solvent evaporation (following [33]). In addition, a circular back plate electrode ("back plate") is positioned 17 mm behind the needle in order to configure a more directional electric field in the spray region. The edges of this plate are polymer-coated to prevent electrical discharges. It has several small perforations to allow for nitrogen flow; however, gas also flows in the space between the back plate and the chamber walls. The nitrogen flow pattern in the chamber did not cause non-circular depositions at $H = 20$ mm, whereas at $H = 40$ mm, the deposits were slightly non-circular (although this effect may not be due to the airflow pattern). The high voltage is generated with power supply (HVPS) Matsusada AMS-10B2-LC. It is fed through a safety resistor to the solution via a metal connector and to the back plate (Fig. 1a).

2.3. Electrospray film deposition

In a typical experiment, the *Taylor cone* meniscus characteristic of the *cone-jet* electrospray mode was stabilized at the needle end

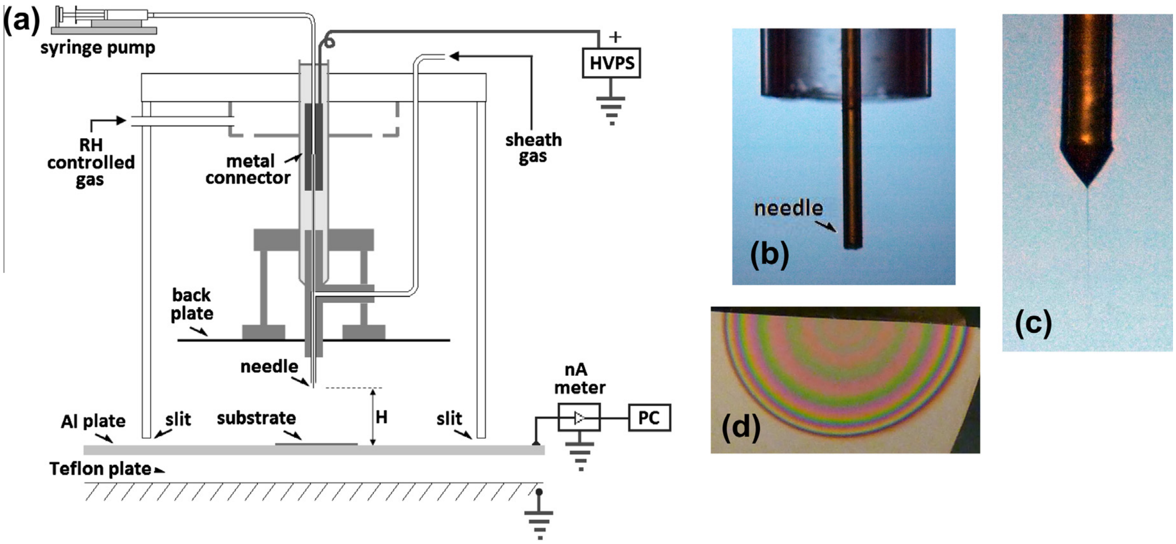

Fig. 1. (a) Electrospray deposition chamber (approximately to scale, with $H = 20$ mm as shown) and surrounding equipment, (b) close up of the silica tube ("needle") and sheath gas tube, (c) Taylor cone-jet meniscus at the end of the needle, and (d) annealed film with Newton rings.