Particuology 11 (2013) 20–24

Contents lists available at SciVerse ScienceDirect

Particuology

journal homepage: www.elsevier.com/locate/partic

Numerical simulation of nanoparticle pattern fabricated by electrostatic spray deposition

Wei Wei[a], Zhaolin Gu[a], Sheng Wang[b,*], Takeshi Fukuda[c], Kiwamu Kase[b], Jungmyoung Ju[b], Yutaka Yamagata[b], Yusuke Tajima[b]

[a] Xi'an Jiaotong University, 28, Xianning West Road, Xi'an, Shaanxi 710049, China
[b] RIKEN Institute, 2-1 Hirosawa, Wako City, Saitama 351-0198, Japan
[c] Saitama University, 255 Shimo-Okubo, Sakura-ku, Saitama 338-8570, Japan

ARTICLE INFO

Article history:
Received 6 December 2011
Received in revised form 27 March 2012
Accepted 30 May 2012

Keywords:
Nanoparticle pattern
Electrospray deposition
Deposition characteristics
Lagrangian model

ABSTRACT

Electrospray deposition (ESD) as a patterning method of nanoparticles deposited on a substrate has attracted much attention due to several advantages over other methods. However, obtaining an optimum ESD processing condition for nanoparticle pattern relies much on trial experiments because of the lack of reliable numerical simulation. In this study, the deposition characteristics of nanoparticle generated by electrospray were investigated by using a three-dimensional Lagrangian model. Three important process parameters, including solution dielectric constant, applied voltage and surface charge density on mask were considered by fixing the geometrical parameters of the ESD device. Simulation result showed that under the condition of without a mask, the spray diameter increases with increasing solvent dielectric constant, and higher applied voltage makes the spray area wider. Controllability of focusing by changing surface charge density on the mask was confirmed: higher surface charge density on the mask results in more focused deposition. Validity of the numerical simulation developed in this study was verified by comparison with experimental data.

1. Introduction

Patterning of nanoparticles over large areas is a prerequisite for making nanodevices. Several spray deposition methods have been proposed for patterning surfaces with nanoparticles. Compared to other deposition techniques, electrostatic spray deposition (ESD) has several advantages, e.g., high deposition efficiency, no ring-stain effect during deposition, high resolution and uniform patterning, controllability of the size of dried nanoparticles, etc. (Ju, 2009). ESD has been used in sample preparation in mass spectrometry (Fenn, Mann, Meng, Wong, & Whitehouse, 1989), organic film formation in solar cells (Ju, Yamagata, & Higuchi, 2009), making fuel cells, ink-jet printing (Park et al., 2007, 2010), etc.

Electrospray is an aerosolization method that involves both surface tension force and electrical force to feed a liquid through a capillary and to create an electric field gradient between the capillary tip and an electrode surface. When the surface tension force and electrical force in the liquid meniscus at the capillary outlet are in balance, the liquid assumes a conical shape, called Taylor cone, and emits a jet (Fernández de la Mora, 1996; Taylor, 1964). Viscous instabilities in the liquid cause the jet to break into highly charged droplets that undergo a series of fissions generating smaller droplets, until the droplets completely evaporate to become nanoparticles deposited on the substrate. The fine droplets are nearly monodisperse in size distribution (Nemes, Marginean, & Vertes, 2007), and their average diameter can be controlled by adjusting operation parameters (Gañán-Calvo, Dávila, & Barrero, 1997; Tang & Gomez, 1994).

To obtain an optimum deposition pattern using electrospray device, many parameters have to be carefully considered, and call for considerable efforts in experiments. Numerical simulation techniques have been developed to become an indispensable tool in both academia and industry. However, up to now only few numerical works have been published on modeling nanoparticles generated by ESD. Gañán-Calvo, Lasheras, Davila, and Barrero (1994) developed a numerical model to describe the transport of electrosprayed droplets. Wilhelm, Madler, and Pratsinis (2003) studied the electrospray transport, evaporation and deposition on a heated substrate with Lagrangian tracking of single droplet, and predicted the size of primary and satellite electrospray droplets. Jung, Oh, and Kim (2010) investigated the characteristics of spray evolution and deposition patterns as a result of multiple EHD

* Corresponding author. Tel.: +81 48 462 3872; fax: +81 48 467 9649.
E-mail addresses: guzhaoln@mail.xjtu.edu.cn (Z. Gu), swang@riken.jp (S. Wang).

1674-2001/$ – see front matter
http://dx.doi.org/10.1016/j.partic.2012.05.004

Nomenclature

ESD	electrostatic spray deposition
CCD	charge-coupled device
C_D	drag coefficient
d_i	diameter of ith droplet (m)
$\vec{E}_{ext}$	external electric field intensity (V/m)
$\vec{g}$	gravitational acceleration (m/s^2)
I	spray current (A)
K	conductivity of liquid droplet (Ω m)
q_i	droplet charge (C)
Q	flow rate (μL/min)
Re	Reynolds number
$\vec{r}_{ij}$	distance from the ith droplet to the jth droplet (m)
$\vec{v}_i$	droplet velocity (m/s)

Greek symbols

ρ	density (kg/m^3)
ε_0	permittivity of vacuum (F/m)
ε	dielectric constant
φ	applied voltage (V)
σ	surface tension coefficient (N/m)

Subscripts

i, j	droplet number
d	droplet phase
g	gas phase

spraying with a capillary-extractor–substrate configuration by changing the applied extractor–substrate voltage, the moving speed of nozzles, and the distance between nozzles. Kim et al. (2006) reported a concept of parallel focusing of nanoparticles via ion injection together with charged aerosols to create nanoarrays of nanoparticles on a surface. A self-assembly process of charged nanoparticles on a silicon substrate was demonstrated by Tang, Verrelli, and Tsoukalas (2009), who also discussed the dynamics of the focusing process and the spray time which affect the focusing effect by both experiment and Monte Carlo simulation.

However, all the above studies did not consider the effect of liquid property on the deposition pattern. To provide more detailed and reliable analysis for investigating the feasibility of using electrospray to aerosolize organic solutions to fabricate a photovoltaic device, this paper focuses on numerical methods using three-dimensional Lagrangian models to investigate the deposition characteristics. The effects of three important parameters, solution dielectric constant, applied voltage and surface charge density on the mask, on the deposition characteristics are studied by fixing the geometrical parameters of ESD device.

2. Numerical method

A numerical simulation method to track the trajectory of charged nanoparticles generated by electrostatic spray was developed to examine the spatial distribution of the spray and the deposition patterns on a substrate. A three-dimensional Lagrangian model based on the work of Gañán-Calvo et al. (1994) was used in this study under the assumption of spherical particles. Brownian motion of particles could be neglected, because the particle kinetic energy caused by the electric field is much greater than random thermal energy (Kim et al., 2006). The equation of motion based on Newton's second law for particle i can be written as follows:

$$\frac{\pi}{6} d_i^3 \rho_d \frac{d\vec{v}}{dt} = C_D \frac{\pi}{8} \rho_g d_i^2 |\vec{v}_i|^2 \vec{e} + q_i \vec{E}_{ext} + \frac{1}{4\pi\varepsilon_0} \sum_{i,j,i \neq j} \frac{q_i q_j}{|\vec{r}_{ij}|^3} \vec{r}_{ij} + \frac{\pi}{6} d_i^3 \rho_d \vec{g}. \tag{1}$$

The left-hand side of Eq. (1) accounts for the inertia of the particle i. The terms on the right-hand side account for the drag force by the surrounding gas, the electrical forces exerted by the external electric field, the electrical repulsion forces between the charged particles, and the gravitational force, respectively.

The drag coefficient of Newton's resistance law can be expressed as follows:

$$C_D = \frac{24}{Re}(1 + 0.15\, Re^{0.678}) \quad \text{for} \quad Re < 800, \tag{2}$$

where Re is the Reynolds number.

In electrohydrodynamics, the dynamic currents are small, and hence the effect of magnetic induction can be ignored. For simplicity, the effect of charged droplets self-induced electric field on external electric field is omitted (Hartman, Brunner, Camelot, Marijnissen, & Scarlett, 1999). So the electric field between capillary and substrate is given as

$$\vec{E} = -\nabla\varphi, \tag{3}$$

where φ is the applied voltage. The electrical potential distribution can be written as

$$\nabla^2\varphi = 0. \tag{4}$$

In the present study, particles with diameters of Gaussian distribution are assumed to be electrically charged even before entering the electric field. The average droplet diameter can be determined by $d_{ave} = (\rho_g \varepsilon_0 Q^3/\sigma K)^{1/6}$ (Gañán-Calvo, 2004).

When the charge of a droplet is above a critical point, i.e., the Rayleigh limit as expressed by Eq. (5) (Gomez & Tang, 1994), the droplet will become unstable and release its charge through a series of fissions. Therefore, the initial value of charge for each droplet must be smaller than the Rayleigh limit:

$$q_R = (8\pi^2 \varepsilon_0 \gamma d_i^3)^{1/2}. \tag{5}$$

The average charge per droplet was calculated using the spray current I and liquid flow rate Q by:

$$q_{ave} = \frac{\pi}{6} d_{ave}^3 \frac{I}{Q}, \tag{6}$$

where q_{ave} is the average charge per droplet, d_{ave} is the average droplet diameter and I can be determined by $I = f(\varepsilon)(\sigma QK/\varepsilon)^{1/2}$ (Fernández de la Mora & Loscertales, 1994). The charge on each droplet was calculated using the relationship between droplet size and droplet charge (Gañán-Calvo et al., 1994):

$$\frac{q_i}{q_{ave}} = \left(\frac{d_i}{d_{ave}}\right)^3. \tag{7}$$

Initially, all the particles are generated near the tip of the capillary and randomly distributed in the x and y directions with the initial speed of $(0, 0, w)$. Because of the same charge polarity, there is no interaction like collision or coagulation/agglomeration between particles. As the boundary condition to solve electric field, electric potentials on the capillary and substrate were set to φ_0 and 0, respectively. In this study, firstly, the external electric field was calculated by using Eqs. (3) and (4), and then Eq. (1) was solved using Runge–Kutta method to obtain the particle trajectory.