Colloid and Interface Science Communications 25 (2018) 16–21

Contents lists available at ScienceDirect

Colloid and Interface Science Communications

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

Large area deposition of ordered nanoparticle layers by electrospray

Bremnen Véliz[a,b], Sandra Bermejo[a,*], Jordi Vives[a], Luis Castañer[a]

[a] Polytechnic University of Catalonia, Dept. of Electronic Engineering, MNT Group, Barcelona, Spain
[b] Salesian Polytechnic University, Dept. of Electronic Engineering, GISCOR Group, Guayaquil, Ecuador

ARTICLE INFO

Keywords:
Nanoparticles
Electrospray
Taylor cone
Polystyrene
Multineedle

ABSTRACT

Mass production of ordered nanostructures with enhanced optical properties such as colloidal crystals for applications such as solar cells or organic light emitted diodes demands low-cost and large-scale manufacturing techniques. In order to enlarge the deposition area of colloidal crystals, this paper presents the results of two different approaches that use the electrospray technique. Areas as large as 25 cm^2 have been achieved by using an array of needles, whereas up to 7.5 cm^2 areas were achieved by using an additional focusing electrode placed on the same plane as the needle nozzle. COMSOL simulations have been used as a guide for the set up design. The ordered deposition of the nanoparticles has been assessed by reflectance measurements and SEM/FIB observations.

1. Introduction

Electrospray has been widely used in mass spectrometry [1] [2] to identify chemical elements and cancer diagnosis [3]. In addition, due to its simplicity there has been a growing use of this technique for the manipulation of different types of nanoparticles in microelectronics [4] and photonics applications [5] [6] [7], given that it does not require vacuum conditions, it is a low cost, and inherently scalable technique, requiring significantly short deposit times.

Within the energy storage field for supercapacitors, electrospray technique has been successfully used to reduce the fabrication complexity of 3-D porous graphene [8] and carbon nanotubes electrodes [9] resulting in improved specific capacitances. Therefore, increasing the deposit area is crucial to reduce the cost of large-scale production in this industry. The supercapacitor global market reached USD 0.76 billion in 2017 and it is estimated to grow USD 2.25 billion by 2023 [10].

On the other hand, colloidal nanostructures have a wide variety of application for photonic devices [11] such as solar cells and displays, where periodic nanostructures enhance the interaction with photons. For instance, porous photonic structures using nanoparticles electrospray have demonstrated to improve light absorption in organic solar cells [12]. 2-D and 3-D colloidal crystals on silicon wafers are proved to be used as template to fabricate light trapping structures [13] known as inverse opals. Silicon nanowire solar cells have been built using 2-D colloidal crystals as etching mask for a DRIE process [14]. However, the area where the deposit has an ordered structure is usually small to cover the required area for commercial devices which is in the range of 60cm^2.

While a huge variety of self-organized colloidal structures fabrication techniques exist, electrospray has a good tradeoff between quality, deposit time, deposit area and number of monolayers. For instance, a simple technique is drop casting [15] [16] [17], where the colloidal dispersion is dropped on a horizontal surface substrate followed by a few hours slow drying of the dispersion (water). However, the obtained areas are of a few square centimeters, 3D structures are not too good and it is also necessary to have precise temperature and humidity control. Other known techniques are: Vertical Deposition [18], Langmuir-Blodgett [19], Shear Induced, Spin coating [20] [21], Wedge-cell [22], Dip-Coating [23], Temperature assisted Dip-Coating [24], and a hybrid method of spin coating and peeling draining [25]. Recently, a new method called Micro-Propulsive Injection [26] has shown a large area polystyrene (PS) structure of 1.7 m^2 with a manufacturing time of 4 h. However, only a monolayer structure can be self-assembled with this method. Fig. 1 shows a radial plot of some common self-assembly techniques described in [27] altogether with the ones presented in this work.

Previous works from our group have shown the feasibility of this technique for the fabrication of colloidal photonic crystals with polystyrene and silica nanoparticles [28] [29] and with a deposit area of 1 cm^2. Electrospray set-up uses a flow controlled syringe and a high voltage bias between the syringe needle and the substrate in order to guide the nanoparticles (which are suspended in a colloidal dispersion) toward the substrate. Not only capillary force [30], but electrostatic force [31] cause the self-assembly ordering of the resulting structures, so the electrical field must always be present during the deposition as well as the drying up.

* Corresponding author at: Micro and Nanotechnologies Group, c/. Jordi Girona 1-3, Campus Nord, 08034 Barcelona, Spain.
E-mail address: sandra.bermejo@upc.edu (S. Bermejo).

https://doi.org/10.1016/j.colcom.2018.06.001
Received 28 February 2018; Received in revised form 5 June 2018; Accepted 13 June 2018

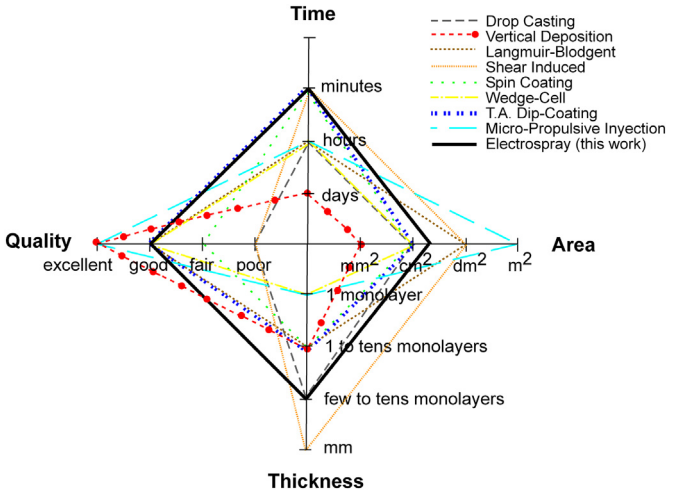

Fig. 1. Radial plot of common colloidal self-assembly methods. Four indicators are compared: Deposit time, area, thickness and quality.

The purpose of this work is to enlarge the deposit area while keeping the deposit time short and of high quality. As it can be seen in Fig. 1, the electrospray technique used in this work achieved a good quality deposit in minutes with areas of up to 25 cm^2. We have studied two modified electrospray methods; the first involves using a metallic guard ring polarized with a specific high voltage as simulations show that the resulting electric field widens the jet's dispersion, while the second method uses a four-needle matrix.

2. Experimental

The electrospray set-up was composed by a B.Braun infusion pump, a two channel Ultravolt high voltage DC source and a BD syringe containing 295 nm diameter polystyrene (PS) spherical nanoparticles in water dispersion (5% wt) supplied by Micro-particles GmbH. The nanoparticles dispersion had a pH = 7, which has been measured using a pH testing strip. The zeta-potential found in the literature [32] for polystyrene nanoparticles is around −36 mV. The metallic guard had an inner and outer diameter of 1.5 cm and 2.7 cm, respectively. In both set-ups, a stainless steel needle of 0.18 mm inner diameter and micro-tubes of 0.18 mm inner diameter were used to connect the needles, while an additional 1 mm inner diameter micro-tube was added to the four-needle setting in order to connect the syringe with a 5-way splitter implying a total distance traveled by the nanoparticle dispersion from the syringe to the needles approximately of 65 cm. For both set-ups, the positive terminal of the HV DC source was connected to the needles.

3. Results and discussion

Experiments lead to an increase in the area of about 7.5 cm^2 using one needle with a metallic guard, and 25 cm^2 using the four-needle matrix. In the first case the use of the guard ring with the appropriate voltage is responsible of the area increase whereas in the second case the increase of the number of sources covers a bigger area. Fig. 2 shows the images of both experimental arrangements. The substrate is a circular layer of aluminum previously deposited on a 4 in. silicon wafer.

The guard ring produced a dispersion of droplets resulting in an enlargement of the useful area. This happens due to the proximity of the ring to the needle, generating a strong potential gradient that achieves a bending jet with stable Taylor cone [33] [34], which in turn causes the droplets to be dispersed, but the pattern of dispersion was random as it left the center of the area as can see in Fig. 2.a. The short distance of both biased metals also caused an electrostatic buzzing, reason why this procedure was carefully carried out so as not to produce an electric discharge.

On the other hand, the four-needle approximation achieved four stable cone-jets in each needle for electrospray. The experimental stable conditions of the depositions are shown in Table.1, which includes the voltage of each channel from the HV source, the flow rate of the pumping machine, the distance between the needle(s) and the sample, deposition time (containing the time interval comprising all stable Taylor Cone's formation until the desired region is fully covered) and average drying time, which increases directly with the liquid quantity. The flow rate had to be increased up to 4 ml/h to feed four needles requiring a voltage of up to 13,500 V to control the higher flow bump. A picture of one of the four stable Taylor cones is shown Fig. 2.c.

Recently extensive research has been conducted [35] on the electrospray of DI water and depending on the value of the dimensionless α and β parameters, diverse regimes have been identified: straight jet, transition and whipping jet.

$$\alpha = \frac{\rho K Q}{\gamma \varepsilon_o \varepsilon'} \quad (1)$$

$$\beta = \frac{\sqrt{\varepsilon_O} V_a}{\sqrt{\gamma D}} \quad (2)$$

where ρ is density (Kg/m^3), K is electrical conductivity ($\Omega^{-1}\,m^{-1}$), Q is flow rate (m^3/s), γ is surface tension (Nm^{-1}), ε' is relative dielectric constant, V_a is applied voltage (V) and D is the inner diameter needle (m). In this work the experimental values were estimated for deionized water and corresponding to $\alpha = 0.65$ and $\beta = 11.2$ ($\rho = 1000 Kg/m^3, K = 1.2x10^{-4}\Omega^{-1}m^{-1}, Q = 2.78x10^{-10}m^3/s$, $\gamma = 0.072 Nm^{-1}, \varepsilon' = 80.2, V_a = 13500V$) which would correspond to a Taylor cone jet mode of a straight-jet regime, but really close to micro-jet mode [35].

At the beginning and at the end of the experiment, small variations of the jets caused a no symmetric distribution of deposit by each needle. Surely, the water evaporation, the individual long capillary path and/or a micro-obstruction, caused that variation.

Despite the precise electrospray regime, this work concentrates in the deposition order and sample size of nanoparticle layers produced by this method concluding that the addition of bias ring and split of needles achieve larger areas of deposits.

We have also observed [28], differences when isopropanol is added to the dispersion to modify the parameters α and β, namely the forming of a cone-jet and pulverization. However, total 3D ordered nanoparticles are not achieved this way; instead the resulting structure is a disordered thin layer of nanoparticles. Although isopropanol has been used as solvent in electrospray ionization mass spectrometry to produce ion clusters [36], it has not been proved useful for our purpose.

COMSOL simulations— were performed for the two configurations in order to analyze the electric field lines, taking into consideration only the electrostatic behavior in vacuum. The distance from the needles to the substrate was set to 6 cm. Fig. 3a and Fig. 3b show the electric field lines for one needle with a metallic guard ring setting. The needle was biased at 6 kV, the guard ring at -3 kV and the sample substrate was grounded. A non-uniform distribution of electric field lines is expanded over the substrate, which will produce the desired nanoparticle dispersion. Alternative guard ring polarizations were analyzed, but led to unsatisfactory results, as the electric field lines diverged outside of the desired path.

Fig. 3c and Fig. 3d show the electric field pattern for the four-needle approach. The needles were biased at 6 kV and the substrate at -3 kV. The increase of the number of needles obviously increases the electric field lines density. Additionally, there is a higher electric field density in the sample's center. This distribution agrees perfectly with the density of nanoparticles observed in Fig. 1b, where the largest volume of deposited nanoparticles is in the center and decreases gradually towards the outside.

Scanning Electron Microscope (SEM) and Focused Ion Beam (FIB)