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Self-assembly of ordered silica nanostructures by electrospray

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ABSTRACT

In this paper we introduce the electrospray technique as a suitable method to create SiO_2 3D ordered nanostructures. We describe the experimental procedure and deposition parameters required. We have found that the use of a high electric field is mandatory to, first, induce the Taylor cone and then, to get 3D order while the nanospheres assemble in the substrate in the drying phase.

1. Introduction

Nanofabrication of structures and devices enable a completely new range of applications from optics to sensing or electronics. In recent years two approaches have been investigated: (a) top-down, such as electron beam, laser 3D and, AFM lithography among the most important, and (b) bottom-up approaches, also referred to as self-assembly, among them vertical deposition, Langmuir–Blodgett, shear-induced, spin-coating and wedge-cell [1]. All these techniques are mainly useful to create three dimensional ordered structures, or colloidal crystals, useful for photonic crystals or other nanophotonic devices. However, they fall short to provide these ordered layers in sufficiently large size and thickness unless long fabrication time is used or the samples are pre-processed [2].

Order of the particles in the self-assembled layer is fundamental to exhibit useful optical properties size is generally restricted to few millimeters, far from the centimeter range required in many applications and the thickness of ordered layers is usually restricted to few monolayers. It is frequently found that the layers show cracks [3] thereby jeopardizing the optical properties and device operation.

Despite the challenges and due to the nature of self-assembly process, it looks as the best candidate to produce thick, large area and defect free devices. Recent reviews [2,4–6] have compared the capabilities and achievements of existing technologies, most of them based on capillary forces [7,8], electrophoretic forces [9], ink-jet printing [10] and dip coating [11,12]. In the specific case of mono and multi-layers of nanoparticles, there are plenty of examples on possible optical and electrical applications [13–16].

In this paper, the electrospray technique is investigated to produce thick 3D ordered colloidal crystal of SiO_2 nanoparticles. Recently, this technique has shown, for the first time, how thick 3D ordered colloidal crystal made of polystyrene nanospheres can be fabricated with centimeter size [17]. Encouraged by these results and, in a effort to widen the breadth of the electrospray technique to other applications where tens of monolayers with good optical quality and centimeter range size are required, we describe in sections below the results of electrospraying SiO_2 nanoparticles. SiO_2 withstand greater temperatures than polystyrene and hence facilites the compatibility with other fabrication processes requiring higher temperature steps such as electrode evaporation or resist curing.

We describe in this work the experimental technique and deposition parameters such as flow rate, solution concentration, electrical potential, and distance between electrodes and how they relate to the quality of the 3D ordering of the layers. SEM (scanning electron microscope) micrographs and FIB (Focused Ion Beam) trenches were used to assess the uniformity and periodicity of the layers underneath the surface.

2. Experimental

The experimental setup consists on a Ultravolt high voltage power supply from 15 kV to −15 kV(Ultravolt, Ronkonkoma, NY, USA), an infusion pump from B. Braun SA (Melsungen, Germany) to transport the nanofluid at a controlled rate and a 130

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μm-diameter needle from Zephyrtronics (Palomares, CA, USA). The substrate of the target sample is negatively biased whereas the needle is positively biased in a way that promotes the formation of a Taylor cone at the tip of the needle. The deposition area is placed inside a glow box and the chamber is purged with nitrogen to dry out the samples and keep the process clean from unwanted particles and reproducible. Fig. 1 shows the needles position and a couple of Taylor cones.

In this work, both, glass and silicon substrates were used. In order to make possible an electric bias, the substrates were coated with aluminum or ITO (Indium Tin oxide) [18] which is a conducting and transparent material which was patterned to create localized electrodes. The nanofluid used in this work is an off-the-shelf dissolution of 230–250 and 290 nm SiO_2 nanoparticles in distilled water from Corpuscular Inc., (Cold Spring, NY, USA).

We first checked the required conditions to produce the Taylor cone [19] that in our case were basically a distance from needle to sample in the range of 10–15 cm and the applied voltage ranging from 8000 to 15000 V which was the limit of our equipment.

We have done a large number of tests, mainly changing the distance from needle to substrate, changing the voltage within the range aforementioned and the conductivity of the dissolution from few μS to some mS The conductivity was modified by adding 1.5% formic acid. Our best layers were fabricated using the off-the-shelf solution with no conductivity modification, applying +9000 V to the needle and −1000 V to the substrate, and a pumping rate of 2.2 ml/h. Those conditions were similar to the ones we used to deposit polystyrene nanospheres [17].

The deposition process started by filling the reservoir with the dissolution, switch ON the nitrogen flow inside the glow box at a pressure of 1.5 bar, switching ON the power supply and switching ON the pump. The deposition process was started then and lasted few minutes. We characterized the relationship between the deposition time and the layer thickness that typically was 7 μm thick in 10 min. After the deposition phase was finished, we first switched OFF the pump and then we let the nitrogen flow and the power supply ON for a few more minutes in the drying phase.

The main difference in the SiO_2 nanospheres compared to the polystyrene nanospheres deposition process concerned the drying phase where we used a different nitrogen flow inside the glow box. Our observations indicated that there are three main conditions in the drying phase that have an effect on the quality of the layers. First, the nitrogen flow is to be adjusted to slow down the drying process, otherwise we observed more cracks appearing. Second, we observed that to get 3D nanoparticles ordering, the electric field has to remain switched ON during the drying process as well. This appears to be indispensable. Third, the deposition has to have a certain degree of liquid when the nanospheres get to the substrate, as we have found that if it is too wet we observed coffee stain effect, whereas if it was too dry order was not achieved. It is difficult to quantify what the wetness level should be but after a few experimental trials the right conditions can be found.

We first observed the effect of letting a drop of nanofluid with the silica nanoparticles in suspension to dry in nitrogen atmosphere Fig. 2 shows a picture of the result after the liquid has completely evaporated. As can be seen no significant order is found and particles assemble in clusters of different orientations and voids are clearly seen.

After this observation, we performed a series of experiments using the electrospray technique and we found a combination of conditions that in our case lead to 3D ordered layers in centimeter square size with tens of microns thickness and in few minutes. The following conditions are required: conductive liquid in the range of 350-μS of conductivity, stable liquid flow rate in the range of 0.6–2.2 ml/h, stable Taylor cone formation in the range of 8000–15,000 V, nitrogen flow in the glow box with some overpressure (1.5 bar) and check for some degree of wetness in

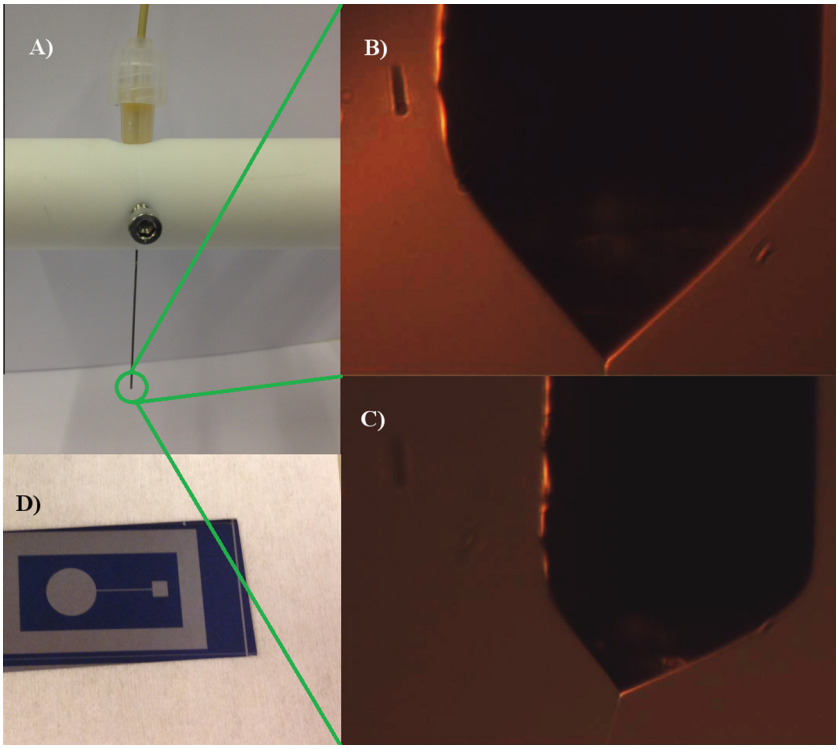

Fig. 1. The electrospray setup. (A) View of the experimental setup exhibiting the needle. (B) Enlarged images of the tip of the needle showing the Taylor cone. (C) Another view of the Taylor cone slightly twisted during deposition. The jet is 4 μm in diameter approximately in both cases. (D) Example of patterned aluminium on top of a silicon substrate used as the bottom electrode.