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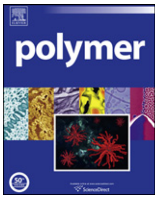

# Towards true 3-dimensional BCC colloidal crystals with controlled lattice orientation

Nina V. Dziomkina, Mark A. Hempenius, G. Julius Vancso*

*Materials Science and Technology of Polymers, MESA+ Institute for Nanotechnology, University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands*

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ABSTRACT

A fabrication method of colloidal crystals possessing the BCC crystal structure is described. BCC colloidal crystals with a thickness of up to seven colloidal layers were grown in the direction of the (100) crystal plane. Defect free colloidal crystals with a homogeneous surface coverage were obtained over a surface area of several square millimeters. Quality and thickness of grown colloidal crystals were controlled by a set of deposition parameters such as deposition voltage, deposition time, and concentration of colloidal particles in the colloidal suspension, colloid surface charge density and withdrawal speed of electrodes out of the suspension. Optimal deposition parameters leading to a controlled BCC colloidal crystal growth were established.

## 1. Introduction

Colloidal crystals have recently found use in a wide range of applications such as in optics [1], as chemical sensors [2] and in data storage [3]. In optics, colloidal crystals become particularly important as they can be used as a basis for photonic crystals. Photonic crystals [4] are 3-dimensional periodic structures that are able to block light propagation in one or more directions. The direction of light propagation in photonic crystals is highly dependent on the crystal structure. It was predicted that colloidal crystals with a diamond structure are able to block the light in all directions [5], therefore, opening many possibilities to guide light by defect structure control. Fabrication of colloidal crystals with the diamond structure by self-assembly of colloidal particles is still impossible due to a low colloidal packing fraction of 0.34. The structure that is usually obtained by self-assembly of colloidal particles on a flat substrate is a close-packed structure such as face-centered cubic (FCC) with a packing density of 0.74, stacked in the direction of the close-packed (111) plane [6,7]. The body-centered cubic (BCC) structure possesses a packing density of 0.68, only slightly lower than that of the FCC, but it is already a problem to fabricate such a structure in a controlled way. Realization of the controlled growth of a BCC colloidal crystal structure will allow one to make a step towards the non-close-packed diamond structure.

The method of template-directed colloidal crystallization has already been demonstrated to influence colloidal crystal orientation of close-packed crystals [8–10], the size of colloidal crystals [11,12] and to a certain degree the crystal structure [13,14]. Furthermore, the pattern of the surface predetermines the location of the colloidal crystal on the surface which is an important aspect for planar integration technology.

The application of an electric field accelerates the growth of the 3D colloidal crystals on the flat electrode surface [15]. Careful adjustment of colloidal concentration and electric field strength leads to the formation of various non-close-packed crystal structures [16]. These different crystal structures were observed using a confocal microscope directly in the colloidal suspension but not as solid crystals (a free-standing colloidal crystal). Capillary forces, acting between colloidal particles, simply destroy non-close-packed colloidal crystals when a sample is withdrawn from the colloidal suspension.

In this paper, the fabrication of free-standing colloidal crystals with a BCC crystal structure is discussed. The method of electrophoretic deposition of charged polymer colloidal particles onto patterned electrode substrates was applied [17]. This method combines the advantages of the methods mentioned earlier: application of the electric field gives the directionality to the colloidal crystal growth and defines the speed of the colloidal deposition, and the patterned electrode surface induces the colloidal crystal structure. The quality and thickness of grown BCC colloidal crystals in this case are highly dependent on the various deposition parameters such as deposition voltage, deposition time,

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* Corresponding author. Tel.: +31 534892974; fax: +31 534893823.
*E-mail address:* g.j.vancso@utwente.nl (G.J. Vancso).

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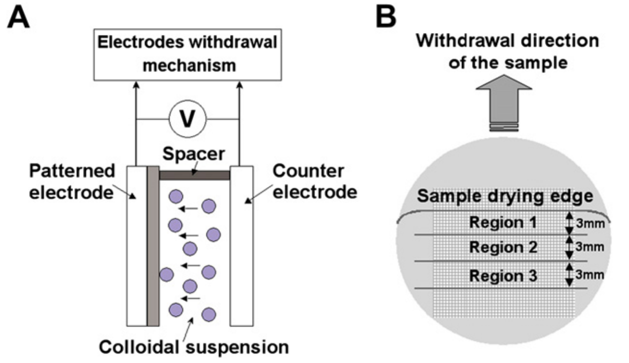

**Fig. 1.** A) Schematic illustration of the electrophoretic deposition set-up; B) Schematic representation of the patterned electrode showing the various regions used in SEM analysis.

concentration of colloidal particles in suspension, surface charge density of colloidal particles and withdrawal speed of the electrodes out of the colloidal suspension after the electrophoretic deposition. The influence of the deposition parameters on the BCC colloidal crystal growth is the main subject of this paper.

## 2. Results and discussion

Colloidal crystals were fabricated using an electrophoretic deposition set-up as shown in Fig. 1. This figure also shows a schematic representation of the patterned electrode and the various regions used for SEM analysis. Effective surface coverage as an equivalent value of the average number of colloidal layers was calculated from SEM images over three regions. Homogeneous surface coverage was observed in regions 2 and 3. Surface coverages reported here were obtained from region 2.

Deposition results at different applied voltages are presented in Fig. 2. Colloidal particles with a surface charge density of 16.2 μC/cm$^2$ and a colloid concentration of 0.5 vol% were deposited on a patterned electrode surface for 1 min and finally withdrawn from the colloidal suspension with a speed of 0.04 mm/s. An increase in the applied voltage leads to an increase in the surface coverage. A significant growth of colloidal crystals was detected above a certain voltage, called the threshold voltage. The value of the threshold voltage was determined as 3.0 V. Therefore, for colloidal crystal growth, values of applied voltages above the threshold voltage were used.

As it is clearly seen in the SEM images, thick colloidal crystals with polycrystalline domains were obtained with packing features that do not correspond to the electrode pattern. The polycrystalline structure of the colloidal crystals can be a result of high concentration and/or the relatively low withdrawal speed of electrodes out of the colloidal suspension. In the first case, colloidal particles do not have enough time to rearrange to accommodate packing in accordance to the electrode pattern because they are too many. In the second case, colloidal particles under the influence of the high capillary force get rearranged and become tightly packed. Therefore, by adjusting colloidal concentration and withdrawal speed of electrodes, ordering of colloidal particles into a BCC structure can be induced.

The results of the deposition of colloidal particles at different concentrations such as 0.175, 0.2 and 0.5 vol% are presented in

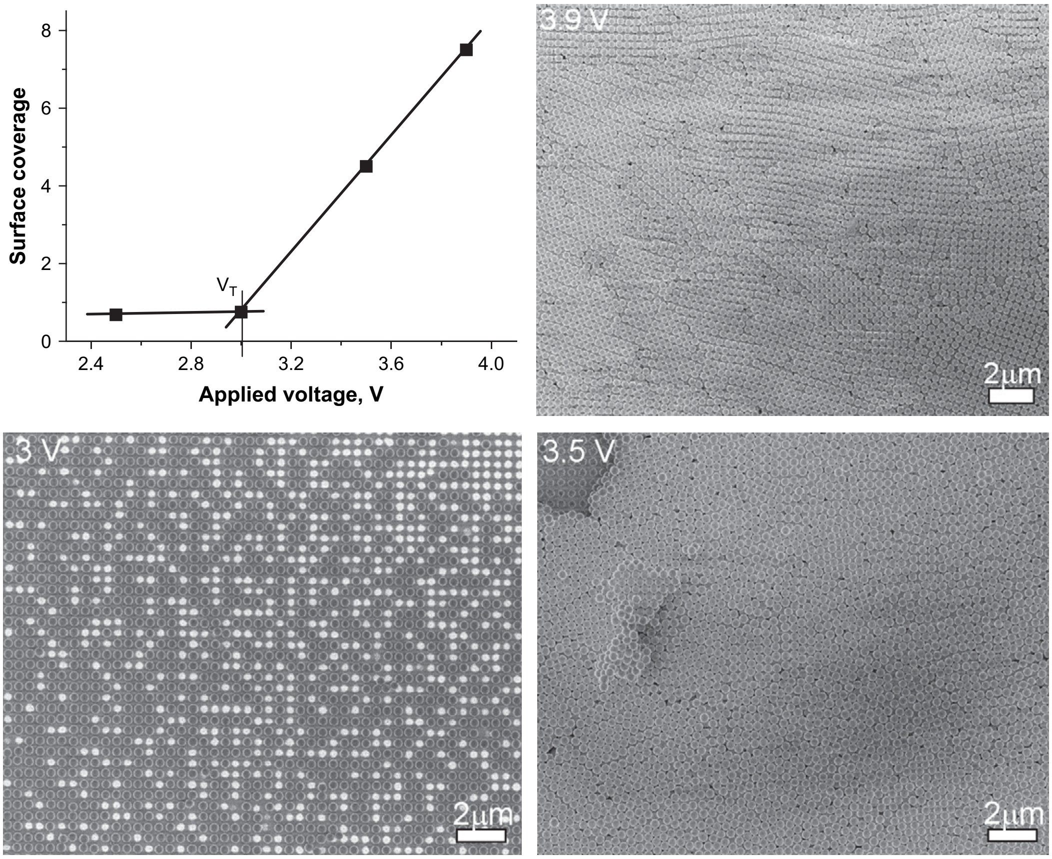

**Fig. 2.** Surface coverage of colloidal particles versus deposition voltage. The threshold voltage was determined to be 3.0 V. SEM images show a top view of the grown colloidal crystals.