Controllable Growth of (001) Surface-Oriented Colloidal Crystals by Edge Meniscus Effect

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Abstract. Colloidal crystal films have been fabricated on silicon substrates using a flow-controlled vertical deposition (FCVD) method. Scanning electron microscopy shows that large areas of the colloidal crystal films can exhibit regular square arrangement or related 1xn superstructure induced by the surface relaxation of colloidal spheres. They are shown to be the (100) facing crystals of face centred cubic (FCC) structure. Their formation is related to meniscus bending at the edge of the wafer, which can be controlled by varying the width of the substrate or the wetting properties of the backing substrate. This (100) surface-oriented colloidal crystal could be used as a template to fabricate square arrangements of nanopore and nanodot arrays.

1. Introduction
Nanostructured surfaces with long range periodicity are of growing importance because of their interesting physical properties such as optical responses. They are useful as templates for fabricating of highly oriented colloidal crystals, biologically active substrates, they are also useful avenue to production of high density optical devices [1], chemical and bio-sensors [2], and high-density magnetic and optical data storage [3-4]. Colloidal nanoparticles, because of the ease with which their sizes can be controlled, are favourite building blocks for low cost fabrication of such nanostructured surfaces. Monodispersed colloidal nanoparticles can easily self-assemble to form 2D or 3D lattice structure on other substrates when suitably dried of its solvent [5]. However, such self-assembly alone usually only produces close-packing ordering. In applications where the arrangement of the nanoparticles in the exposing surface is important, such as photonic crystals [6], this can be restrictive and has prompted research into methods that can produce other forms of regularly arranged nanoparticles.

To date, a popular approach is colloidal epitaxy, i.e. directed colloidal crystal growth on patterned substrates, such as on surfaces with imprinted relief [7], square pyramidal pits [8] or V-shaped grooves [9]. In addition, applications of an external electrical, magnetic, or optical field have also been examined as a promising strategy to control the growth direction [10]. Stretching of substrate in lift-
up lithography is another alternative to produce non-close-packing ordering on surfaces [11]. Those methods are usually too complicated and expensive for large-scale applications. Relative large-scale, template-free growth of colloidal crystal domains with square surface patterns has been reported [12] using a spin coating method. However, the effects of the experimental factors such as the dispersion media, particle size and liquid concentration are not fully understood.

Here, we demonstrate template-free formation of mm$^2$-scale colloidal crystals with their (100) planes parallel to the surface. More importantly, they are shown to be related to the curved meniscus due to the edge effect of the substrate. Our result opens a new avenue of meniscus engineering for low cost and large-scale fabrication of nanostructured surfaces of a non-close-packing order. Additionally, we also report the use of this colloidal temperate to fabricate metal dots which can be used in plasmonics and information storage.

2. Experimental Section

The crystals in our experiment were fabricated using 290 nm polystyrene spheres purchased from the Institute of Physics and Chemistry, Chinese Academy of Sciences. Colloidal suspensions with volume fractions of 1.0% in deionised water were prepared. The method used to grow the crystals was FCVD as described elsewhere [13]. The dropping speed of the suspension level was set at 0.002ml/min and the temperature of the container was maintained at 20±2°C. Strips of silicon wafers used as supporting surfaces were treated in a mixture of H$_2$SO$_4$/H$_2$O$_2$ (98%H$_2$SO$_4$:30%H$_2$O$_2$=3:2, v/v) for 8 hours, then ultrasonicated in acetone, ethanol and deionised water respectively. This was repeated three times to make the surfaces hydrophilic. The treated silicon wafers were immersed, with a tilt angle of 10°, in the colloidal suspension. Scanning electron microscopy (SEM) (JEOL JSM6301f), Atomic Force Microscopy (AFM) (Nanoscope IIIa) operating in the tapping mode and reflection optical microscopy (NEOPHOT32) were used to characterize the morphology of the samples. For SEM inspection, the samples were coated with a thin gold film to stop charging effect as customary.

**Figure 1.** (Color online)
(a) An SEM top view of square arrangement of 290 nm colloidal spheres (the inset shows the corresponding Fourier transform).
(b) An SEM top view of square arrangement of 290 nm colloidal spheres with 1x6 periodicity (the inset shows the corresponding Fourier transforms).
(c) An SEM top-view of square arrangement of colloidal spheres near the edge of a cleaved colloidal film.
(d) An AFM image of square arrangement of 290 nm colloidal spheres.
(e) An AFM image of square arrangement of 290 nm colloidal spheres with 1x5 periodicity.

3. Result and discussion

Figure 1a shows a typical SEM image of colloidal crystals with simple square arrangement and the inset at the top right corner is its Fourier transformed image. Obviously the non-close-packing nature of the surface colloidal spheres can be observed. Figure1d is its corresponding AFM image. We can get the average spacing between centres of two neighbouring spheres which is 332±26 nm and the angle between the unit cell vectors is about 87°. The distorted pattern shows that it is not really a regular square arrangement. In figure 1b, a square domain with a 1x6 periodicity is also observed and this is just a typical example of many such 1xn domains observed where n can vary from 2 to 7. The
angle between the unit cell vectors is about 88°, which also varies from place to place. The inset at the top right corner is the corresponding Fourier transform image, confirming the square ordering of the spheres. According to the AFM analysis for a 1×5 structure (figure 1e), the average spacing between centres of two neighbouring spheres in the top layer is 295±16 nm and that in the trench is 312 nm, which are very close to the nominal size of the starting nanosphere dispersed in liquid.

Figure 1c is a SEM top-view image of the colloidal films near its broken edge. Obviously, spheres in the bottom layer have also formed a regular square array and the upper spheres rest on the interstitial hollow sites formed by four neighboring spheres in a square arrangement. The side-view reveals a hexagonal stacking pattern down to the bottom layer. We therefore confirm that the square arrangement is consistent with the (100) face of the FCC colloidal crystal. From surface defects such as point vacancy (fig. 1b), we could find that the surface nanoparticles also sit on the hollow sites of the subsurface layer and the colloidal spheres in sub-layer also have a regular square arrangement. Therefore we can speculate that the 1×n structure forms owing to the surface reconstruction of a regular square structure. However, until now, the parameters influencing the number n are not completely clear and further systematic work is required to understand their formation in details [15].

The colloidal films with either the simple square arrangement or the 1×n structure are all multilayer stacking of nanospheres. The number of deposited colloid layers was measured, using STM on cleaved Si strip samples, from left to right along the direction parallel to the suspension level. The results for samples with different silicon strip widths are summarized in figure 2. This reveals that, on average, the number of layers decreases, with the Si stripe width, down to the limit of one monolayer.

In addition, we can see clearly those square domains are mostly found near the edge of the wafers. As the wafer width reduces, the square domains at the edge usually merge to produce a large patch of square domains in the middle. For example, for the wafer with a 1.4 mm width (fig. 2a), the square domains dominate the substrate with the hexagonal arrangement decorating the step edges, i.e. the hexagonally arranged surface is now a transitory phenomenon. As for the substrate with 2.8 mm width (fig. 2c), the square domains reduce to linear regions and acquire an intermediate thickness for n to n+1 hexagonal layers. To correlate the shape of the meniscus, which is an mm-scale phenomenon, with the formation of the square domains, we have exploited the different optical effect of the square and hexagonal domains [14]. The greenish patch can be associated with the Van Hover-like high density of photonic states in the (001) projections of FCC structure of 290 nm spheres. The yellow patch is associated with the high density of photonic states of the FCC crystal in its (111) projection. Film thicknesses variation only causes a slight variation within the color bands. The shape and location of the green patch representing square domain is a strong function of the curvature variation of the contact lines, later achieved by varying the wetting properties of the backing materials [15].
domains decorated with the yellow lines corresponding to hexagonal arrangement is formed at the edge of the wafer. As for the silicon substrates whose meniscus has a concave downward bow (fig. 2c), the green region with small areas now appears at the interior. This suggests that the square domains opt to locate at regions where the meniscus is heavily curved and the contact line pinned [15].

Figure 3.
(a) A SEM image of square pore arrays.
(b) A SEM image of square Ni dot arrays.

The ordered square colloidal crystal, prepared by this method, can be used as templates in diversified areas. Figure 3a shows a typical square pore array by selectively dissolving the colloidal crystal with its (100) plane parallel to the substrate [16]. Such a pore array can be used as a template to prepare an array of metallic squares. To achieve that, the porous template was first treated with reactive ion etching to remove the remaining thin layer at the bottom of the pores. Ni was then deposited by vacuum evaporation through the ordered pores. After ultrasonically washed in toluene, the polymeric template was removed, leaving an array of Ni squares on the substrate. Figure 3b shows the SEM image of the Ni squares; obviously the surface coverage of the array is quite high. The bright features around some Ni nanodisks are polymer residuals not completely removed. Such metal square arrays are important for applications such as information storage, where the readout signal can be maximized.

4. Conclusions
We have demonstrated the growth of (100)-orientated FCC colloidal crystal films on template-free silicon substrate by FCVD method. The largest square domains could exceed mm² magnitude. The shape of the meniscus on the substrate is found to be critical in controlling square domain size and location. We have used this colloidal template to fabricate ordered metal dot arrays. The square domains may exhibit different properties that are valuable for many practical applications.

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