Improving self-assembly quality of colloidal crystal guided by statistical design of experiments*

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A versatile and reliable approach is created to fabricate wafer-scale colloidal crystal that consists of a monolayer of hexagonally close-packed polystyrene (PS) spheres. Making wafer-scale colloidal crystal is usually challenging, and it lacks a general theoretical guidance for experimental approaches. To obtain the optimal conditions for self-assembly, a systematic statistical design and analysis method is utilized here, which applies the pick-the-winner rule. This new method combines spin-coating and thermal treatment, and introduces a mixture of glycol and ethanol as a dispersion system to assist self-assembly. By controlling the parameters of self-assembly, we improve the quality of colloidal crystal and reduce the effect of noise on the experiment. To our best knowledge, we are first to pave this path to harvest colloidal crystals. Importantly, a theoretical analysis using an energy landscape base on our process is also developed to provide insights into the PS spheres' self-assembly.

Keywords: self-assembly, colloidal crystal, polystyrene spheres, statistical design

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1. Introduction

Enormously widespread interest has been focused on colloidal crystal for its potential applications in solar cells,[1–3] nano-lithography,[4,5] and biosensors.[6,7] A lot of methods, such as Langmuir–Blodgett (LB) film technique,[8–11] floating-transfer method,[12,13] electric field assisted self-assembly,[14,15] and vertical deposition technique,[16,17] have been developed to create colloidal crystal. The LB film technique is usually used to deposit many successive single layers of molecules on a solid surface by dipping the surface into a liquid and then raising it out. Micheletto and co-workers used this technique to produce a two-dimensional ordered array of latex particles.[18] Their deposition covered an area of only about 1 cm^2, and only half of the area was covered by monolayers, in which hexagonally close-packed areas were much smaller domains. Moreover, floating-transfer method[19] is also commonly used, especially when the latex affects the performance of the solid sample. Lenzmann and his coworkers slowly and steadily deposited an ethanol dispersion of the spheres on a clean water surface using a syringe poised at an angle to the water surface, and then transferred the spheres onto a glass slide. Obviously, this method requires more artificial skills. The resulting colloidal crystal contains a lot of imperfections, and array sizes up to 0.5 cm^2 can be obtained. Additionally, electrical field assisted self-assembly method was developed to get monolayer spheres.[20] A liquid dispersion of colloidal spheres was confined between two parallel solid electrodes. The colloidal spheres that had been randomly deposited on the anode would move toward each other to form stable two-dimensional (2D) hexagonal arrays. This method is also only capable of building up colloidal arrays in small domains. To sum up, although these interface-mediated processes possess the inherent benefits of less restriction of substrates and nature of formation of monolayers, they are not applicable to some special substrates or devices.[21] Moreover, all of these methods seem infeasible for industrial-scale mass-fabrication due to their tedious fabrication processes and incompatibility with the wafer-scale batch micro-fabrication technology widely used in the semiconductor industry.

Spin-coating[22–25] is an alternative strategy to overcome the drawbacks mentioned above. However, there are few reports of using this method to prepare PS colloidal crystal. Fischer and co-workers[24] directly spread a droplet of latex spheres on glass and harvested 10 μm-long monolayers of latex spheres. The obtained colloidal crystal had imperfections including point defects, dislocations, and grain boundaries. Subsequently, Deckman's group[22] developed spin-coating to define a low-ordered polycrystalline material, namely, colloidal crystal, the area of which was still much smaller than an industrial wafer. Besides, the use of surfactants was an essential step, which in turn may reduce the capabilities of the produced nano-materials by the presence of surfactant impurities.

Here we present a new nano-fabrication technique, com-

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bining spin-coating and thermal treatment, which textures wafer-scale surface areas with a monolayer of hexagonally close-packed PS spheres. Through statistical design of experiments, a wafer-scale colloidal crystal can be harvested. We do not need salt or surfactant in solution or electrically charged particles for the self-assembly of PS spheres. Also, there is no confinement between any boundaries or surface pressure control during the self-assembly process. It is noteworthy that our procedure is compatible with today's semiconductor industry. To our best knowledge, it is the first time to utilize statistical design of experiments to improve the quality and scale of PS colloidal crystal. Importantly, a thorough theoretical analysis of the self-assembly of colloidal crystal is developed according our special process in energy landscape.

2. Experimental section

2.1. Chemicals and materials

All the chemical reagents, such as styrene ($\geq$ 99.0 wt.%), sodium hydroxide ($\geq$ 96.0 wt.%), sodium dodecyl sulfate (CP grade), potassium peroxydisulfate ($\geq$ 99.5 wt.%), ethylene glycol ($\geq$ 99.0 wt.%), and ethanol ($\geq$ 99.5 wt.%) were used as received without further purification. They were purchased from Sinopharm Chemical Reagent Co., Ltd. (SCRC). The resistivity of the deionized water (DI water) was 18.25 MΩ·cm. Silicon wafers were cleaned according to the RCA procedure[26] and subsequently cleaned in Piranha solution (70% $H_2SO_4 + 30\%$ H_2O_2) for 12 h, followed by triple rinsing in DI water.

Spherical polystyrene particles were synthesized using emulsion polymerization of styrene in ethanol solution.[3] PS spheres with diameter of 460 nm were successfully synthesized and then cleaned using successive centrifugation and ultrasonic cleaning in an ethanol system three times. Prior to use, the purified polystyrene spheres were re-dispersed in different solvents, such as water, ethanol, miscible liquid of ethanol and glycol (using a 1:1 volume ratio mixture of ethylene glycol/ethanol). The final volume fraction of the PS latex was 20 vol.%, 40 vol.% and 60 vol.%, respectively.

2.2. Spin-coating of PS spheres latex

PS latex was spread over the substrate by spin-coating. The PS latex was spin-coated at 550 rpm on a commercial spin coater for 9 s and then the wafer was quickly accelerated to 3500 rpm for 30 s. For some samples, six-arm diffraction stars were formed in about 15 s. The substrates were transferred to an electric thermostatic drying oven for special times after spin-coating, exhibiting a variety of colors in the end.

2.3. Structure observation

Field emission scanning electron microscopy (SEM, JSM-6700F), operated at 5 kV, was employed to examine the morphology of our obtained colloidal crystals.

3. Results and discussion

A simple cartoon of the procedure to achieve monolayer hexagonally close-packed PS spheres, namely, monolayer colloidal crystal, is presented in Fig. 1. Briefly, a certain volume of PS latex is deposited on a silicon wafer and then spin-coating is carried out immediately. The PS latex is spread all over the surface of the substrate by shear force to form a thin film. The obtained thin film inevitably consists of multiple layers of spheres in some areas (Fig. 1(a)). To improve the crystalline quality of the colloidal monolayer, the silicon substrate is then quickly transferred to an electric thermostatic drying oven for thermal treatment. The thermal treatment introduces "stochastic forces" to assist crystallization of the colloidal monolayer (Fig. 1(a)), which seems to act in the role of noise acoustic vibration in the self-assembly of opal films to some extent.[27] In the view of statistical physics and thermal dynamics, self-assembly is a process of a phase transition. The direction of self-assembly is toward a state with minimum energy, and thus crystal formation.[28] The PS spheres can find the positions where they can form a state with minimum energy in the free energy landscape. Consequently, different phases may form under different thermodynamics conditions. With the thermal treatment, the kinetic energy of the PS spheres increases correspondingly. And hence, the PS spheres have a greater range of movement, promoting their capability to search for the state with the lowest energy. As the evaporation proceeds, an initial nucleus of 2D crystals forms. When the thickness of the concave layer of water is equal to the diameter of the PS sphere, a capillary force acts on the PS spheres near the nucleus, pushing them toward the nucleus zone (Fig. 1(b)).[29,30] Thereafter, the surrounding spheres transfer to the nucleus, driven by convective transport. Eventually, wafer-scale hexagonally close-packed spheres arrays, namely, colloidal crystal, are formed (Fig. 1(c)).

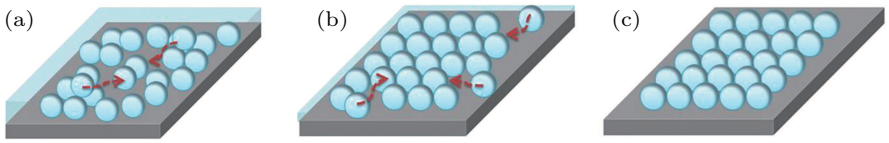


Fig. 1. (color online) Schematic of procedure to wafer-scale monolayer colloidal crystal: (a) break up the multiple layers of spheres into a monolayer by shear force and thermal treatment; (b) enable hexagonally close-packed PS spheres array by capillary-force; (c) colloidal crystal.

3.1. The dispersion system's effect on self-assembly of PS spheres

The choice of solvent as the dispersion system is a critical issue. To improve the quality of the colloidal crystal, high temperature, which may be accompanied with strong capillary force, is usually helpful. But overly high temperature should be avoided. As is commonly known, the solvent evaporates more quickly at higher temperature. And hence, the higher the temperature is, the less time is left for the self-assembly of PS spheres. Enough time is needed to accomplish the process of self-assembly. A kind of solvent that can both endure high temperature and wet substrate can be used as the dispersion system. Herein, we investigated three different dispersion systems for self-assembly, and the results are shown in Fig. 2(a). PS spheres arrays formed with ethanol as the dispersion system are almost random arrays and have a lot of small vacancies even multiple layers of spheres. This can be understood from the self-assembly time of different dispersion systems. Although ethanol can wet the wafer, it dries before the spin-coating process is over. Our experimental time span is too short for the PS spheres to assemble well. By using water as the dispersion media, the quality of the colloidal crystal is greatly improved (Fig. 2(b)), which is ascribed to the wetting time lasting longer than the ethanol's. However, the time is still not enough for the self-assembly process because the liquid dried up in just minutes at room temperature (25 °C) after the spin-coating, which led to some line defects and small vacancies, as shown in Fig. 2(b). There is no chance to improve the quality of the colloidal crystal further until the self-assembly time can last long enough. To obtain good wettability and enough self-assembly time, a mixture of ethanol and glycol was introduced as the dispersion system for PS spheres. We found that it dried in fifteen minutes when placed in 45 °C environment. Moreover, the mixture of ethanol and glycol can wet the spheres better than water. And hence, it can impose stronger capillary force on the PS spheres, which is crucial to close-packing the PS spheres. Colloidal crystal obtained from the mixed solvent of ethanol and glycol as dispersion media is packed more closely than in other cases (Fig. 2(c)). The mixed solvent of ethanol and glycol is selected as the dispersion media for self-assembly of PS spheres.

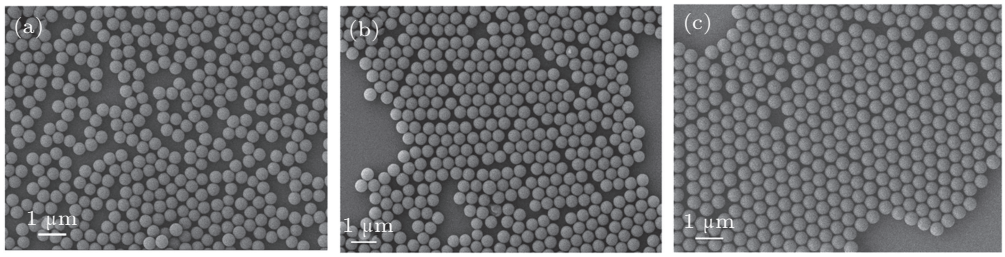


Fig. 2. Different dispersion media for PS spheres self-assembly: (a) ethanol, (b) water, (c) a mixture of ethanol and glycol. Other self-assembly conditions are the same for all samples: self-assembly temperature of 25 °C (room temperature), latex concentration of $\varphi = 20$ vol.%, final spin-coating speed of 3500 rpm, and spin-coating time of 30 s.

3.2. Temperature effect on self-assembly of PS spheres

Point defects can still be found in Fig. 2(c) because the quality of the colloidal crystal is sensitive to the self-assembly environment — temperature, etc. In our previous experiments, we tried all kinds of latex concentrations, but the obtained colloidal crystal was either not wafer-scale or there were multiple layers of spheres in micro-regions. To overcome these drawbacks, we introduced thermal treatment and investigated temperature effects on self-assembly. Typical results are shown in Fig. 3. Except the self-assembly temperature, all other conditions, such as latex volume fraction (20%), spin coating time (30 s), and spin coating speed (3500 rpm) were the same.

It is clear that multiple layers of spheres even mountains of spheres are formed at 25 °C. This phenomenon can be explained as follows: when the latex is spread from center to edge during the spin-coating process, multiple layers of spheres are inevitable in some areas unless the latex concentration is extremely low (such $\varphi = 3$ vol.%). In Fig. 3(a), the spheres are packed in a loose way in some areas, which is caused by the weak capillary attraction. With the self-assembly temperature increasing (such as at 45 °C), multiple layers of spheres and loose-packed spheres disappear. Unfortunately, multiple layers of spheres appear at higher temperatures, such as 65 °C and 85 °C (Figs. 3(c) and 3(b)). At favorable high temperatures, the liquid evaporates more quickly and the capillary attraction becomes stronger, leading to close-packed spheres (see insets of Figs. 3(c) and 3(b)). On the other hand, over-high temperature decreases the self-assembly time significantly, leaving little chance for monolayer close-packed PS spheres to form. In addition, larger vacancy areas form at higher temperature (85 °C), as shown in Fig. 3(d). Through a lot of experiments, we found that for 45 °C environment, the time is enough to let PS spheres assemble in high order, so it is the best temperature for the self-assembly of PS spheres. It is mentioned here that although there are still some point defects and line defects in some small domains (Fig. 3(b)), we believe that the defects caused by the initial crystallization are inevitable. Fortunately, a few defects are tolerable in most of the modern semiconductor industry.

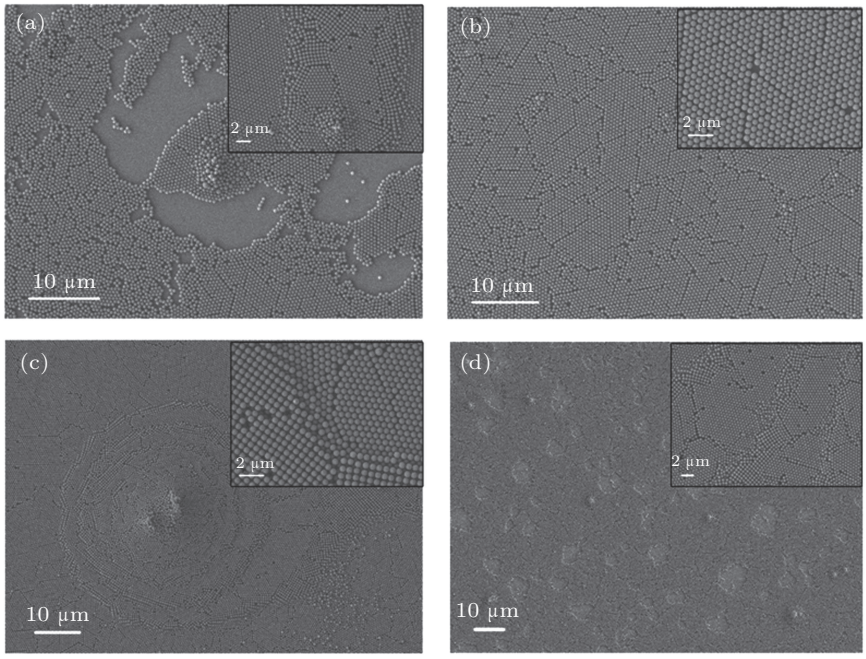


Fig. 3. Typical top-view SEM images of colloidal crystal obtained by thermal treatment: (a) 25 °C, (b) 45 °C, (c) 60 °C, (d) 80 °C. Other conditions such as the latex concentration of $\varphi = 20$ vol.%, final spin-coating speed of 3500 rpm, and spin-coating time of 30 s are the same.

3.3. Concentration of PS latex effect on self-assembly of PS spheres

As described by the spin-coating theory of Middleman,[31] the final film thickness is in the form

$$H \approx A/\omega\sqrt{t}, \tag{1}$$

where A is a constant determined by the viscosity and density of the solution, ω and t are the final speed and time span of spin. Formula (1) reveals that the final film thickness is inversely proportional to the final spin speed and the square root of the final spin time. So the higher rotation speed and longer rotation time are, the larger PS latex volume fraction is needed to obtain the same thickness latex film. Based on the above analysis, we set proper spin-coating parameters, namely, 3500 rpm for 30 s, to achieve the thin latex film.

Only about three fifths of the area is covered by PS spheres when the PS latex is 20 vol.% (Fig. 4(a)). The areas covered by PS spheres become larger along with a rising concentration of PS latex. Wafer-scale monolayer close-packed spheres form when the PS latex concentration is increased to 40 vol.% (Fig. 4(b)). However, multiple layers of spheres emerge seriously when the concentration of PS latex is 60 vol.% (Fig. 4(c)). An interesting feature is evident: the covered area is not a simple linear function of the PS latex concentration. Eventually, we found that the optimal concentration of PS spheres is 40 vol.%.

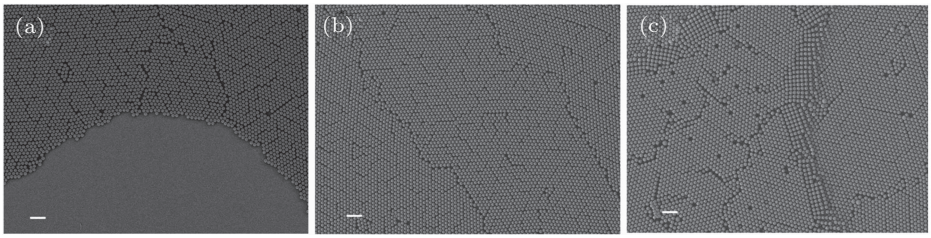


Fig. 4. Different PS latex concentrations for spin-coating: (a) 20 vol.%; (b) 40 vol.%; (c) 60 vol.%. Other conditions are the same: the self-assembly temperature, the final spin-coating speed, and time are 45 °C, 3500 rpm, and 30 s, respectively. Scale bar is 2 μm.

3.4. Colloidal crystal obtained at the optimized conditions

We used the optimum conditions, namely, 40 vol.% PS sphere volume fraction and 45 °C self-assembly temperature, to achieve wafer-scale (i.e., four inch, etc.) monolayer-close-packed PS sphere arrays. To identify the features of monolayer, hexagonal close-packing, we randomly selected some areas to scan the morphology using SEM, and the results are shown in Fig. 5. The spheres characterized with hexagonally close-packed properties can be seen in Fig. 5(b) and the monolayer is clearly revealed from Fig. 5(c). The spin-coating technique described here has a number of advantages over the previous means of self-assembly. For example, it is rapid and also highly manufacturable. A wafer-scale colloidal crystal can be routinely made within half an hour, while early methods take

days or even weeks to produce a centimeter-size crystal.[32]

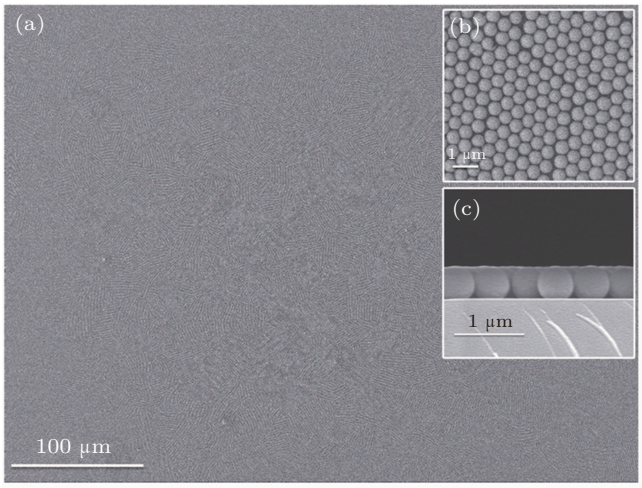


Fig. 5. SEM images of the colloidal crystal fabricated under optimum condition: (a) low magnification, top-view; (b) high magnification, top-view; (c) high magnification, side-view.

4. Conclusion

We have demonstrated the formation of high-quality, wafer-scale, 2D colloidal crystal using our new method, namely, a systematic statistical design and analysis method. The method we proposed has greatly improved both the scale and the quality of the resultant colloidal crystal. The obtained colloidal crystal can also be applied to self-assembly of PS spheres of other diameters. It is not only less time-consuming but also easier to control. Moreover, a thorough theory analysis of the self-assembly of PS spheres is provided according our special process in energy landscape. Moreover, this approach is highly compatible with contemporary micro- or nano-fabrication which may accomplish the eventual mass production of low-cost practical devices.

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