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Fabrication of large-area, close-packed, monolayer colloidal crystals via a hybrid method of spin coating and peeling–draining

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ABSTRACT

Large-area, close-packed, monolayer colloidal crystals can be used as templates in the preparation of micro/nano films. This work proposes a hybrid method of spin coating and peeling–draining for the production of large-area, close-packed, monolayer colloidal crystals. First, large-area monolayer polystyrene (PS) colloidal crystals were obtained through spin coating. Then, the colloidal crystal film was peeled from surface of the intermediate spin-coated silicon wafer and transferred to another substrate using a customized experimental device. Oxygen plasma treatment was utilized to modify the wettability of the silicon wafer, increase the uniformity of spin coating, and reduce the adhesion work of peeling. The key process parameters, such as the duration of oxygen plasma treatment, spin speed, peeling speed, and drop rate of water surface, of the proposed method were thoroughly analyzed and optimized. Three-inch, wafer-scale, large-area, close-packed monolayer colloidal crystals were obtained using the proposed method, which combines the advantages of spin coating and gas-liquid interface self-assembly and offers a stable and controllable approach to the fabrication of monolayer PS colloidal crystals.

1. Introduction

Large-area, close-packed, monolayer colloidal crystals exhibit considerable potential applications in photonic crystals [1,2], high-density magnetic storage [3], chemical and biological sensors [4–6], nanolithography [7–10], solar cell films [11], and superhydrophobic surfaces [12–14]. Therefore, the preparation of high-quality, large-area, close-packed, monolayer colloidal crystals is crucial to many applications.

Scientists have recently proposed different methods for the preparation of monolayer colloid crystals [15,16]. By adjusting spin speed and acceleration, Chen et al. [17] obtained large-area polystyrene (PS) colloid crystal films on a 3-in. silicon wafer. The quality of the film, however, has yet to be improved. Cheng et al. [18] obtained high-quality monolayer colloid crystals by spin coating, but the as-obtained film had an area of only 1 cm^2. Zhang et al. [19] fabricated large two-dimensional arrays of colloidal particles at the air–water interface by using a needle-tip flow method. Nevertheless, this method has comparatively low efficiency. Cui's group [20] has proposed a micro-propulsive injection method for the rapid self-assembly of large-area colloidal crystals. This method, however, requires specialized equipment and precise control. Yu et al. [21] obtained a film of monolayer colloid crystals on a glass substrate by gas-liquid interface self-assembly. Similar to that obtained by Cheng et al., the film only had an area of 1 cm^2. M. Bardosova et al. [22] used the Langmuir–Blodgett method to synthesize colloidal photonic crystals from silica spheres. Although the Langmuir–Blodgett method is a popular method for transferring particles floating on a water surface onto a solid substrate, this method is susceptible to the effects of environmental factors, such as temperature, humidity and pressure [23,24].

In the present study, a hybrid method of spin coating and peeling–draining is proposed for the preparation of large-area, close-packed, monolayer colloidal crystals. As shown in Fig. 1, the wettability of wafers is first changed through treatment with oxygen plasma technology. Second, large-area, non-close-packed, monolayer PS colloidal crystals are obtained through one-step spin coating. Third, PS particles are transferred from the spin-coated intermediate silicon wafer to the water surface by peeling. Finally, PS colloidal crystals are transferred from the water surface to the final silicon substrate and the large-area, close-packed, monolayer colloidal crystals with high quality are obtained by draining. The PS particles, which are floating when originally transferred to the Si substrate, settle down on the Si substrate after the evaporation of liquid at room temperature. The proposed method produces large-area, close-packed, monolayer colloidal crystals with high quality and efficiency. In addition, this method is less susceptible to the effects of environmental factors.

2. Experiment

2.1. Preparation of PS microsphere suspension

A total of 400 μL original PS microsphere suspension (909 nm, SD = 0.025 μm, Microparticles GmbH, Germany) was injected into two

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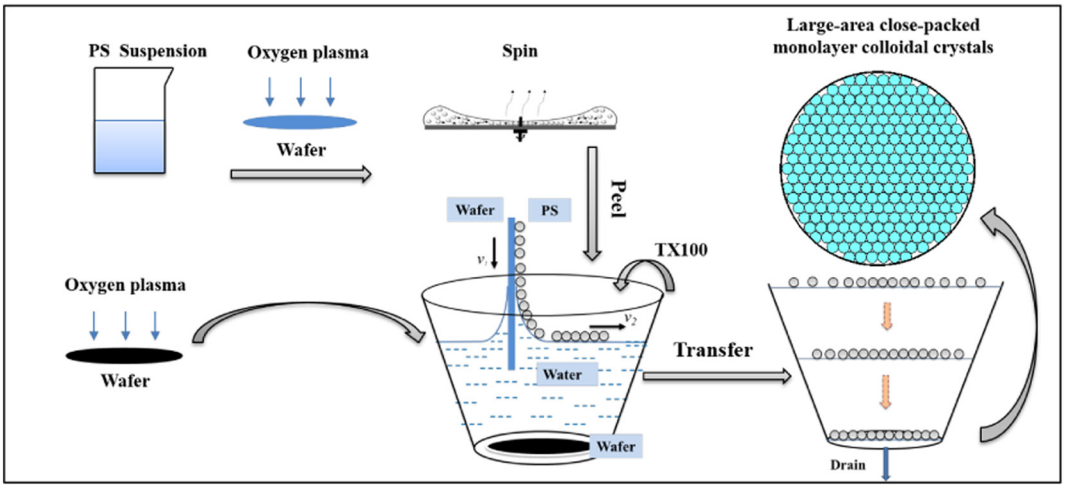

Fig. 1. Fabrication of large-area, close-packed, monolayer colloidal crystals through spin-coating and peeling–draining.

centrifuge tubes. The supernatant was removed after centrifugation at 510 rpm for 5 min (Legend Micro21, Thermo Fisher Scientific Inc.). Then, a mixture containing ethanol (concentration ≥ 99.7%, Tianji Chemical Reagent Co., Ltd.), deionized water (resistivity ≥18 MΩ·cm), and the surfactant TX100 (0.01% *w*/*v*) at the volume ratio of 1:1:0.04 was injected into the centrifuge tubes containing the PS microsphere colloids. The two centrifuge tubes containing the colloidal solution were agitated on oscillators (XH-D, Jiangsu Kangjian Medical Apparatus Co., Ltd.). The contents of the tubes were then poured into a small beaker, which was then placed in an ultrasonic generator for 3 min (SA0150, Xi'an Kehao Biological Engineering Co., Ltd.). Eventually, 2.5% (*w*/*v*) of PS microsphere suspension was obtained.

2.2. Preparation of monolayer PS colloidal crystals by spin coating

To make the silicon wafer sufficiently hydrophilic, the silicon wafer was placed in a plasma cleaner (YZD 08-5C, Beijing Huiguang Venture Technology Co., Ltd.) for 5 s of oxygen plasma treatment (power = 80 W). A total of 350 μL of 2.5% (*w*/*v*) PS microsphere suspension was added dropwise to the center of the wafer. The colloidal solution was allowed to spread over the entire wafer within 1 min. Then, the silicon wafer was placed on a spin coater (SC100-SE, Best Tools LLC, USA) for spinning at 800 rpm at an acceleration of 200 rpm/s and rotation time of 60 s. Monolayer PS colloidal crystals were acquired after spinning. However, the PS colloidal crystals did not form a close-packed monolayer. Therefore, the next stage of its assembly process was performed.

2.3. Experimental device for peeling and draining

The experimental device, which was designed to allow stable and controllable peeling and draining (Fig. 2), comprised a microstepper motor, a screw, a sliding platform, a clip and tapered groove, and a drain valve. The microstepper motor drove the screw to move the sliding platform up and down by positive and negative rotation. The rate of movement was adjusted to within 0.5–10 mm/s. The upper and lower diameters of the tapered groove were 200 and 130 mm, and the height of the groove was 125 mm. The tapered groove in the experimental apparatus helps form a continuously close-packed PS microsphere film due to the contraction effect. During slow drainage, the level of the liquid surface decreased gradually. A Teflon film was attached to the inner wall of the tapered groove to reduce the adhesion of water to the inner wall.

2.4. Preparation of large-area, close-packed, PS colloidal crystals by peeling and draining

A new silicon wafer was treated with oxygen plasma for 5 s (power = 80 W) to enhance its hydrophilicity and was immediately placed horizontally at the bottom of the tapered groove as shown in Fig. 2. The tapered groove was filled with deionized water. The spin-coated wafer was clamped on the device shown in Fig. 2 and descended vertically at 1 mm/s. A monolayer film was peeled off from the wafer surface at the meniscus of the solid–liquid–gas interface. The surfactant TX100 [concentration of 0.01% (*w*/*v*)] was added dropwise on the water surface to push away the film after peeling was completed to ensure that the PS colloidal crystal film spread out uniformly. Meanwhile, the wafer was pulled out at a rate of 3 mm/s. After the liquid surface stabilized, the water in the tapered groove was drained by adjusting the flow rate of the drain valve to control the drop rate of water level. Draining was continued until the film nearly settled on the silicon wafer at the bottom of the tapered groove. Eventually, large-area, close-packed, monolayer colloidal crystals formed on the silicon surface through evaporation at room temperature.

2.5. Observation and characterization

The large-area, close-packed, monolayer colloidal crystals were observed through three-dimensional digital microscopy (KH-7700, HIROX Company Ltd.) and scanning electron microscopy (SEM, VEGA3

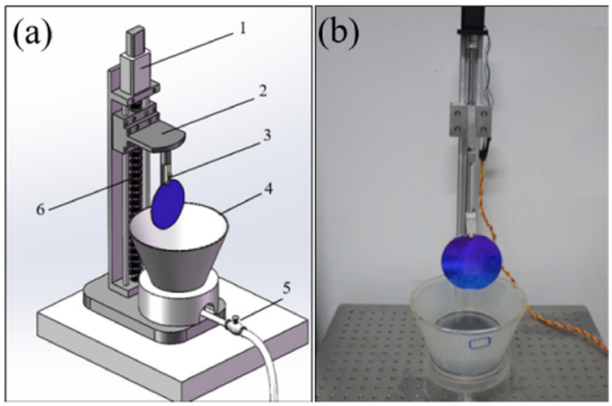

Fig. 2. Experimental device for peeling and draining. (a) 3D design schematic: 1 — microstepper motor, 2 — sliding platform, 3 — clip, 4 — tapered groove, 5 — drain valve, 6 — screw. (b) Photograph of the actual apparatus.