Colloids and Surfaces A: Physicochem. Eng. Aspects 385 (2011) 188–194

Contents lists available at ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

journal homepage: www.elsevier.com/locate/colsurfa

Fabrication of colloidal crystals on hydrophilic/hydrophobic surface by spin-coating

Young Gun Ko[a], Dong Hun Shin[b], Gil Sun Lee[c], Ung Su Choi[a,*]

[a] Energy Mechanics Center, Korea Institute of Science and Technology, Hwarangno 14-gil 5, Seongbuk-gu, Seoul 136-791, Republic of Korea
[b] 3M Innovation Center, 2-5 Seokwu-dong, Whaseong-si, Kyunggi-do 445-170, Republic of Korea
[c] Research Institute of Clean Chemical Engineering Systems, Korea University, Anam-dong, Seongbuk-gu, Seoul 136-701, Republic of Korea

ARTICLE INFO

Article history:
Received 3 March 2011
Received in revised form 3 June 2011
Accepted 9 June 2011
Available online 17 June 2011

Keywords:
Colloidal crystals
PS nano-spheres
Spin-coating
Surface wettability
TiO_2 inverse opal

ABSTRACT

Herein, we demonstrate the structure of the PS colloidal crystals which were fabricated on the hydrophilic/hydrophobic Si wafers by a spin-coating technique. Monodisperse PS colloids are spin-coated onto self-assembled monolayers of 3-(aminopropyl)triethoxysilane and propyltrimethoxysilane coated Si wafers. PS spheres organized as ordered close-packed face-centered cubic structure with (1 1 1) planes on the hydrophilic surface while they gathered without the crystal structure on the hydrophobic surface. This paper also reports a simple and rapid method to fabricate the close-packed structure of hollow TiO_2 spheres. The colloidal crystal of TiO_2 hollow spheres was prepared using the PS sphere template on the hydrophobic surface. The mechanism for the growing multilayers of self-assembled PS particles from a suspension onto a hydrophilic and hydrophobic Si wafer substrates using the spin-coating method at various rotating speeds is also discussed in this paper.

1. Introduction

The ordered arrays of colloidal particles, three-dimensional (3D) periodic structures from monodisperse colloids [1], have been extensively explored due to their wide range of potential applications as photonic band gap materials [2], optical devices [3], data storage [4], chemical and bio-sensor [5], and ordered porous materials [6]. Colloidal self-assembly method is inexpensive, offers relative ease of processing and requires short processing time, compared to the stepwise manner of microfabrication techniques [7]. A great deal of effort has been expended in the study of the colloidal crystals using various methods, such as electrophoretic deposition [8], gravitational sedimentation of colloidal particles [9], vertical deposition by evaporation [10] or by lifting the substrate [11], ice crystallization [12], deposition on a horizontal substrate [13], centrifugation (spin-coating) [14], colloidal assembly at an air-water interface [15], fluidic cell method [16], and colloidal assembly on a liquid metal surface [17].

From an industrial point of view, the scaling-up from a laboratory-scale production to an industrial-scale mass fabrication is the key point. Many methods for the fabrication of the colloidal crystals seem infeasible due to their tedious fabrication process and incompatibility to the wafer-scale batch microfabrication widely used by the semiconductor industry. Jiang and McFarland demonstrated the formation of high-quality, large-area, 3D ordered nanocomposites, colloidal crystals, and macroporous polymers on the Si wafer with controllable thickness by a simple and fast spin-coating process [18]. The spin-coating technique is a simple, convenient, cheap, one-side, material saving, rapid and highly reproducible method to produce homogeneous films on a rigid flat or slightly curved substrate [19]. Meyethofer described the dependence of the thickness of spin coated layer on the processing and materials like angular, velocity, viscosity and solvent evaporation rate [20]. Other researches also have described only the film thickness not the crack in the colloidal crystals [21]. The crack in the colloidal crystal is a very important parameter for the application to the industrial field.

To fabricate the photonic crystal with hollowed TiO_2 spheres, hollow TiO_2 spheres should be synthesized first. This process needs many processing steps and causes much loss of TiO_2. The easy and economic process fabricating the photonic crystal with hollowed TiO_2 spheres was focused in this study. Herein, we demonstrate the fabrication of the colloidal crystals on the hydrophilic and hydrophobic silicon (Si) wafers using the spin-coating technique to confirm the effect of wettability on the formation of the colloidal crystal. The surface wettability of the Si wafers is controlled by the formation of the self-assembled monolayer of 3-(aminopropyl)triethoxysilane (APTS) for the hydrophilic property and propyltrimethoxysilane (PTS) for the hydrophobic property on the Si wafers. The fabricated colloidal crystal on the hydrophilic

* Corresponding author. Tel.: +82 2 958 5657; fax: +82 2 958 5659.
E-mail address: uschoi@kist.re.kr (U.S. Choi).

0927-7757/$ – see front matter © 2011 Published by Elsevier B.V.
doi:10.1016/j.colsurfa.2011.06.011

Si wafer was more close-packed than on the hydrophobic Si wafer. We also fabricate the macroporous TiO_2 replica (inverse opal) with the fabricated polystyrene (PS) colloidal crystals. The interesting result in this study is that the structure of ordered close-packed hollow TiO_2 spheres was fabricated with the template of arrayed PS spheres which formed on the hydrophobic Si wafer.

2. Experimental

2.1. Synthesis of monodispersed polystyrene colloidal particles

Styrene (bp 145–146 °C, 99%, Aldrich Chemical Co.) was distilled at reduced vacuum to remove traces of the inhibitor 4-*tert*-butylcatechol (bp 285–286 °C). Thermal self-initiation during transit and storage is prevented by the addition of a small quantity of inhibitor (10–15 ppm) by the manufacturer. The risk of thermal self-initiation is minimized during the removal of the initiator by distilling at reduced pressure, and the use of a dark environment reduces the risk of light-initiated polymerization.

Colloidal polystyrene (PS) spheres were synthesized by an emulsion polymerization using a free radical initiator (potassium persulfate, $K_2S_2O_8$, 99%, Aldrich). 20 g of styrene (99%, Aldrich), 200 g of deionized water, 0.2 g of potassium persulate (99%, Aldrich), and 0.14 g of sodium dodecyl sulfate (SDS, 99%, Aldrich) were added into the reaction flask, and then the polymerization was carried out in aqueous solution at 70 °C for 7 h under a nitrogen atmosphere. The reaction mixture was agitated using a twin-paddled overhead stirrer at 350 rpm. In this condition, monodisperse 255 nm diameter polystyrene colloidal particles were synthesized. The used deionized water (DI water, 18.2 MΩ cm^{-1}) was obtained from a Milli-Q water system.

2.2. Preparation of hydrophilic/hydrophobic patterned Si wafer

A square-hole (depth: 10 μm, width and length: 4 cm × 4 cm) pattern was fabricated on a silicon (Si) wafer (P-doped (1 0 0), LG

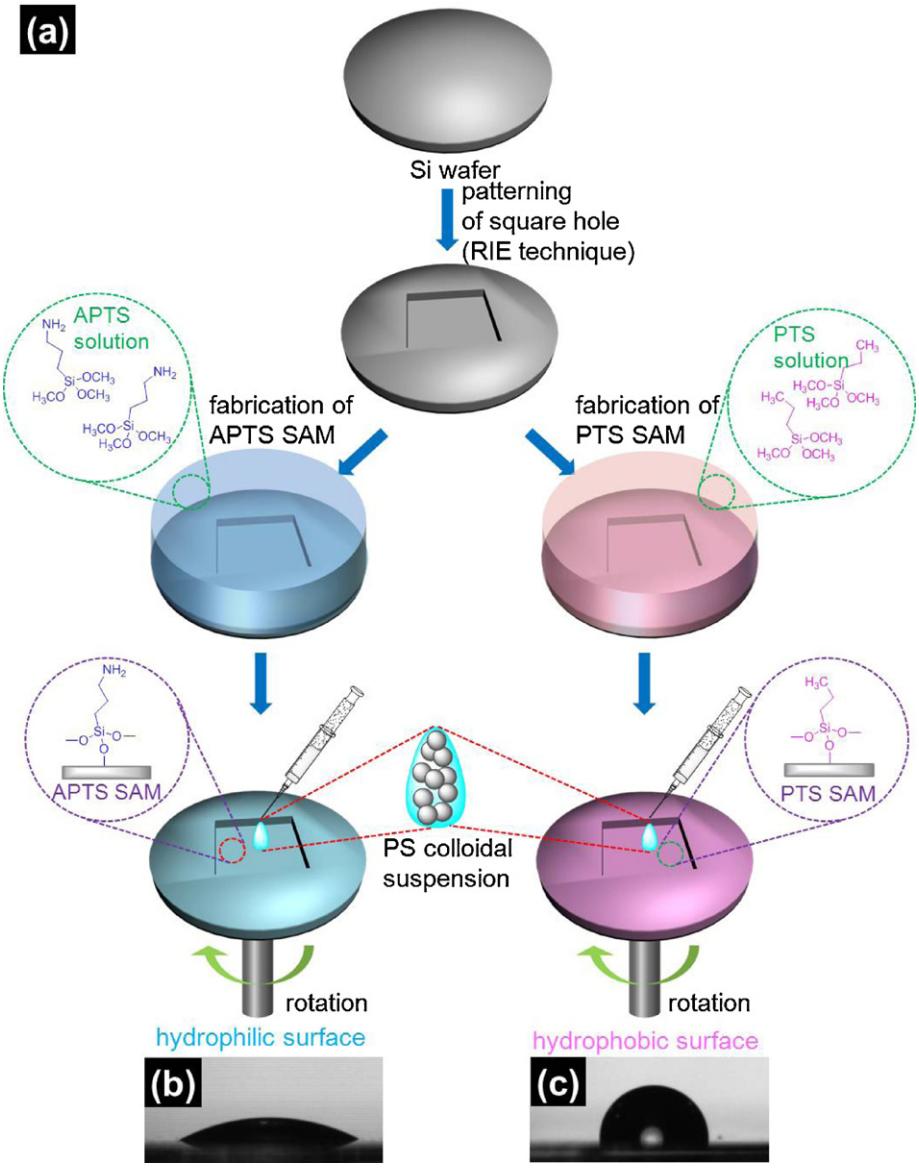

Fig. 1. (a) Schematic of fabrication of colloidal crystals on hydrophobic/hydrophilic patterned Si wafers, and photographs of the DI water drop on (b) the hydrophilic Si wafer and (c) the hydrophobic Si wafer. (RIE: reactive ion etching, SAM: self-assembled monolayer, APTS: 3-(aminopropyl)triethoxysilane, PTS: propyltrimethoxysilane, PS: polystyrene.)