Advances in Colloid and Interface Science 228 (2016) 105–122

Contents lists available at ScienceDirect

Advances in Colloid and Interface Science

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

Historical perspective

Recent advancement on micro-/nano-spherical lens photolithography based on monolayer colloidal crystals

Ziming Zhang [a], Chong Geng [a], Zhibiao Hao [b], Tongbo Wei [c], Qingfeng Yan [a,*]

[a] Department of Chemistry, Tsinghua University, Beijing 100084, PR China
[b] Department of Electronic Engineering, Tsinghua University, Beijing 100084, PR China
[c] Institute of Semiconductors, Chinese Academy of Sciences, Beijing 100083, PR China

ARTICLE INFO

Available online 12 December 2015

Keywords:
Micro-/nano-spherical lens photolithography
Monolayer colloidal crystal
Highly ordered nanostructure

ABSTRACT

Highly ordered nanostructures have gained substantial interest in the research community due to their fascinating properties and wide applications. Micro-/nano-spherical lens photolithography (SLPL) has been recognized as an inexpensive, inherently parallel, and high-throughput approach to the creation of highly ordered nanostructures. SLPL based on monolayer colloidal crystals (MCCs) of self-assembled colloidal micro-/nano-spheres have recently made remarkable progress in overcoming the constraints of conventional photolithography in terms of cost, feature size, tunability, and pattern complexity. In this review, we highlight the current state-of-the-art in this field with an emphasis on the fabrication of a variety of highly ordered nanostructures based on this technique and their demonstrated applications in light emitting diodes, nano-patterning semiconductors, and localized surface plasmon resonance devices. Finally, we present a perspective on the future development of MCC-based SLPL technique, including a discussion on the improvement of the quality of MCCs and the compatibility of this technique with other semiconductor micromachining process for nanofabrication.

Contents

1. Introduction

In recent years, there has been an increasing demand for high-throughput and massively parallel fabrication strategies for the creation

* Corresponding author. Tel.: +86 10 62792830; fax: +86 10 62771149.
E-mail address: yanqf@mail.tsinghua.edu.cn (Q. Yan).

http://dx.doi.org/10.1016/j.cis.2015.11.012
0001-8686/

of large-area, highly ordered and periodic nanostructures, since these nanostructures have found a wide range of applications in many devices such as light emitting diodes (LEDs) [1], fuel cells [2], high dense data storage [3], photodetectors [4], surface plasmonics [5], photonic crystals [6,7], nanofiltration [8], artificial cells [9], metal–insulator–metal [10], and multi-functionalized DNA arrays [11]. The implementation of highly ordered nanostructure can be attained by a number of fabrication techniques including immersion lithography [12], electron-beam lithography [13,14], focused-ion-beam lithography [15,16], X-ray lithography [17,18], DUV lithography [19], UV interference lithography [20], nanoimprint lithography [21,22], near-field scanning optical microscope lithography [23], and other so-called top-down methods. Among these, immersion lithography with large numerical apertures provides a viable path for increasing the resolution but it is lack of high refractive index matching fluid. Electron-beam lithography reduces the diffraction limit and reaches feature size in the range of 20 nm but it is low-throughput due to its serial processing nature. Identical to this technology, ions can be used instead of electrons which is called focused-ion-beam lithography. X-ray lithography is a parallel process but it is high-cost. DUV lithography and UV interference lithography permit high-throughput, however they are high-cost and their resolution is limited by diffraction effect. The preparation of mold for nanoimprint lithography still relies on the expensive electron-beam lithography process in most cases, despite its high-throughput. The diffraction limit can be broken utilizing near-field scanning optical microscope lithography but it is limited by its high expenditure. All in all, these approaches are advantageous in that they achieve highly ordered and periodic nanostructures with uniform shape and size, nevertheless they are not suitable for many applications especially in fabrication of large-area nanostructures because of either high cost or low throughput. Thus, newer, cheaper and faster approaches arouse interest in fabrication of large-area, periodic and highly ordered nanostructures.

One of these promising methods is micro-/nano-spherical lens photolithography (SLPL). Even though research focusing on the single or multiple micro-spherical lenses go back several decades [24–27], the renewed interest is fueled by availability of monolayer colloidal crystals (MCCs), which was firstly proposed by Whitesides and coworks [28–32]. It demonstrated that the use of an array of transparent micro-/nano-spheres embedded in a transparent membrane could generate repetitive, micrometer-scale structures in photoresist (PR), beginning from masks with centimeter-scale patterns. The key element of this technique is an array of transparent colloidal micro-/nano-spheres with proper refractive index [33–36]. Each micro-/nano-sphere can fast receive incident illumination and accurately converge, and then produces a bright spot on its focal plane to exposure the PR [30,36]. Subsequently, it was noticed that both silica (SiO_2) and polystyrene (PS) have optical indices that are close to the optimum value at the wavelengths used by conventional UV light photolithography [37]. Therefore, MCCs of self-assembled SiO_2 or PS colloidal micro-/nano-spheres provided strong guarantee for optimizing the SLPL technique. So far, MCC-based SLPL has been recognized as an inexpensive, inherently parallel, and high-throughput approach to the creation of large-area and highly ordered nanostructures.

In this article, we review the state-of-the-art of MCC-based SLPL nanofabrication strategies, with an emphasis on their principles and their demonstrated applications in various areas. In Section 2, we highlight the advancement of fabrication of large-area and high-quality MCCs, which is the basis of SLPL. The principles of a variety of SLPL techniques based on MCCs are demonstrated in Section 3. Applications of highly ordered nanostructures derived from SLPL in the areas such as LEDs, nano-patterning semiconductors, and localized surface plasmon resonance devices are shown in Section 4. Finally, a perspective on the future development of MCC-based SLPL is presented in Section 5, including a discussion on the improvement of the quality of MCCs and the compatibility of this technique with other semiconductor micromachining process for nanofabrication.

2. Fabrication of large-area and high-quality MCCs

Monolayer colloidal crystal is the basis of SLPL technique. It is a two-dimensional (2D) periodic ordered structure and consists of self-assembled colloidal micro-/nano-spheres. Since Denkov et al. [38,39] firstly reported the mechanism of 2D crystallization of colloidal micro-/nano-spheres, much interest has been focused on the fabrication of MCCs. During the self-assembly, the van der Waals forces, steric repulsions, and Coulombic repulsions play a balancing role [40–42]. Based on such an understanding, a variety of strategies for the self-assembly of MCCs have been developed, including drop-coating [38, 39,43], dip-coating [44,45], spin-coating [46,47], Langmuir–Blodgett [48,49], electrophoretic deposition [50,51], self-assembly at the gas/liquid interface [52,53], and so forth, which can refer to some recent reviews [54–61]. For the successful implementation of SLPL, large-area and high-quality MCCs are always in demand.

Among the above strategies, spin-coating is the simplest approach to fabricate large-area MCCs on a flat substrate. However, the experimental parameters such as the spinning speed and the time to reach the required speed have a significant impact on the self-assembly process, which leads to difficulty in achieving highly ordered MCCs [62–64]. In order to overcome this problem, Jiang et al. [65] developed an improved spin-coating strategy that allowed for the fabrication of wafer-scale non-close-packed (NCP) SiO_2 MCC. The SiO_2 colloidal nano-spheres-monomer mixture covered the entire wafer area by spin-coating. After polymerizing monomers, polymer embedded NCP SiO_2 MCC with full wafer coverage was obtained. The polymer matrix could be removed by oxygen plasma etching, leaving behind a SiO_2 MCC with uniform interparticle distance, as shown in Fig. 1a and b. Langmuir–Blodgett method is a controllable self-assembly technique and commercially available. A picture of a typical Langmuir–Blodgett trough is shown in Fig. 1c [66]. This method can be used to compress monolayer of amphiphilic materials on the surface of a given subphase for depositing single monolayer on a solid substrate. However, the technique involves several key parameters including surface pressure of the subphase, the subphase temperature, the dipping rate of the solid substrate, surface concentration of the materials and the purity and cleanliness of the whole system. Self-assembly at the air/water interface has been proved another facile and efficient approach towards large-area MCCs. Colloidal micro-/nano-spheres at the air/water interface are able to exclusively form a single layer without variation in the layer thickness, which can hardly be achieved in other evaporation-induced self-assembly strategies [49,50]. Large-area MCCs with several tens of cm^2 in area could be obtained in a few minutes. One more advantage of this method is that the MCCs can be transferred to any kind of substrates regardless of surface wettability and smoothness. In principle, the area of MCC fabricated by this strategy only depends on the dimension of the glass vessel. However, systematic study revealed that the behavior of interfacial self-assembly of MCCs would be influenced by several factors, such as the particle concentration, hardness of the micro-/nano-spheres, zeta potential of the micro-/nano-spheres in the suspension, surface tension of the water phase, solubility parameter of spreading solvents, addition of a salt in the suspension [67], and hydrophilic treatment of the substrates [68]. Further, for the fabrication of large-area MCCs with improved quality, it is essential to avoid possible sedimentation of colloidal micro-nano-spheres into the liquid phase via delicate control of the addition of the colloidal suspension onto the solvent surface. Generally, the colloidal micro-/nano-spheres with hydrophobic surface are required when self-assembly at the air/water interface. For example, SiO_2 colloidal micro-/nano-spheres prepared by the conventional Stöber process are hydrophilic, and hence have to be made hydrophobic before using to generate a MCC through the air/water interface self-assembly. Recently, Moon et al. [67] presented an improved method for self-assembly at the gas–liquid interface, in which the hydrophilic colloidal nano-spheres can also be assembled into large-area MCCs on water surface. By utilizing