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# A Feasible Routine for Large-Scale Nanopatterning via Nanosphere Lithography

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## 1. Introduction

Due to the unique electronic, optical, catalytic and biological properties, well ordered nanostructures have attracted enormous interest. They have potential applications in photonic crystal devices (Yablonovitch, 1987), large-density magnetic recording devices (Chou et al., 1994), novel electronic devices (Schmidt & Eberl, 2001), synthesis of DNA electrophoresis mediate (Volkmuth & Austin, 1992), nanocontainers (Chen et al., 2008), surface-plasmon resonance biosensors (Brolo et al., 2004), antireflective coatings for solar cells (Yae et al., 2005), and etc. Such broad applications of nanostructures were intimately associated with their unique properties, which are sensitively dependent on their size and/or shape. It is well-established that magnetic (Shi et al., 1996 ; Zhu et al., 2004), optical (Aizpurua et al., 2003; Larsson et al. 2007), electrocatalytic (Bralie et al., 2007 ; Narayanan & El-Sayed, 2004), optoelectronic (Chovin et al., 2004), data storage (Ma, 2008), thermodynamic (Volokitin et al., 1996; Wang et al., 1998) and electrical transport (Andres et al., 1996 ; Bezryadin et al., 1997) properties of the nanostructures are affected by the shape and the size, as well as the interfeature spacing.

In general, there are two approaches to realize ordered nanostructures with desired size, shape and arrangement. One is the "bottom up" approach on pre-patterned substrates (Zhong et al., 2007; Zhong et al., 2008). The other is the "top-down" approach (Ito & Okazaki, 2000). Both of these two approaches are always based on lithographic technology. In the first approach, lithographic techniques were employed to fabricate various patterned substrates, on which ordered nanostructures can then be realized by subsequent growth of desired materials. The main reason for this approach is to suppress defects in the nanostructures. In the second approach, ordered nanostructures can be directly fabricated by lithographic techniques. Several standard lithographic techniques are frequently exploited to fabricate desired surface nanostructures, including holographic lithography, electron-beam lithography (EBL) and ion-beam lithography (IBL) (Arshak et al., 2004 ; Ebbesen et al., 1998; Ito & Okazaki, 2000). Recently, a new extreme ultraviolet (EUV) lithography was developed, which is a potential candidate for achieving critical dimensions below 100 nm (Service, 2001). In addition, there are some other lithographic techniques applied in the fabrication of nanostructures (Haynes & Van Duyne, 2001). However, fabrication of nanostructures in a regular arrangement over large areas is still a major challenge in modern nanotechnologies. There is substantial interest in developing new technologies to facilitate pattern fabrication.

## 2. Nanosphere lithography (NSL)

Enormous efforts have been devoted to investigate alternative nanolithography approaches. One of promising methods is nanosphere lithography (NSL) (Fuhrmann et al., 2005; Haynes & Van Duyne, 2001; Hulteen & Van Duyne, 1995; Kosiorek et al., 2004; Sinitskii et al., 2007), which is a highly accessible, low cost, parallel fabrication process capable of producing nanostructured surfaces over large areas and with high resolution. In NSL, self-assembled nanospheres can be served directly as ordered nanostructures (Park et al., 1998) or a mask for the subsequent fabrication of nanostructures, which can be realized by deposition of desired materials, or by etching on desired substrates. A rich varieties of ordered nanostructures have been achieved by NSL, such as triangular structures (Winzer et al., 1996), metallic rings (Boneberg et al., 1997), nanopillars (Weeks et al., 2004), and multilayer with modified topography (Albrecht et al., 2005), nanodots (Chen et al., 2009; Weekes et al., 2007), 3D nanostructure (Zhang et al., 2007), discs (Hanarp et al., 2003) and nanoscale crescents (Gwinner et al., 2009; Retsch et al., 2009; Vogel et al., 2011). The shape, the size and the arrangement of ordered nanostructures can be readily controlled in combination of NSL and the subsequent deposition of desired materials (Haynes & Van Duyne, 2001; Zhang et al., 2007; Vogel et al., 2011).

### 2.1 Main features of NSL

To obtain desired nanostructures by NSL, one monolayer of self-assembled nanospheres is always obtained first and served as a mask for the subsequent fabrication of nanostructures. The material of the nanosphere can be nanoscale polystyrene (PS), SiO<sub>2</sub>, or polydimethylsiloxane (PDMS) (Choi et al., 2009), and etc. The shape of the resulting pattern is most often spherical. Using PDMS, the shape and the feature size of the pattern can be modulated by changing the stretching axis and ratio of the PDMS replica. The nonspherical shaped patterns, such as rectangular or elongated hexagonal shaped patterns, can then be obtained (Choi et al., 2009). An additional noteworthy feature of the PDMS is that different pattern can be produced from a single PDMS replica mold (Choi et al., 2009). In addition, binary nanospheres composed of two different-size colloidal particles can be self-assembled both in hexagonal lattices via a two-step process (Kim et al., 2009), forming binary colloid crystals (BCCs). Such BCCs may have potential applications in the fabrication of photonic crystal structures, theoretical models of phase transition, and templates of inverse structure (Kim et al., 2009). The arrangement of self-assembled nanospheres can be close-packed or non-close-packed (Vogel et al., 2011). In general, the self-assembled nanospheres are arranged in a hexagonal lattice. Using more sophisticated processes, squarely ordered array of nanospheres can also be realized, which is speculated to be metastable structures between more stable hexagonal structures (Sun et al., 2009).

In the simplest NSL, a monolayer of close-packed nanospheres in a hexagonal lattice is first obtained on the substrate, which can be served as a mask for the subsequent deposition of desired materials. For generally vertical deposition, the three-fold interstices allow deposited material to reach the substrate, giving rise to an array of triangularly shaped nanoparticles with P<sub>6mm</sub> symmetry (Haynes & Van Duyne, 2001). The perpendicular bisector of the triangular nanoparticles,  $a$ , and the interparticle spacing,  $d_{ip}$ , are proportional to the nanosphere diameter,  $D$ , which can be simply calculated by,

$$a = \frac{3}{2}(\sqrt{3} - 1 - \frac{1}{\sqrt{3}})D, \quad d_{ip} = \frac{1}{\sqrt{3}}D$$

If double layer of nanospheres are employed as the mask, both  $a$  and  $d_{ip}$  will be changed (Haynes & Van Duyne, 2001). In addition, circular shaped interstice particles are frequently obtained in the case of small nanospheres mainly because some materials are not perpendicularly deposited in the interstices, and the general hot materials can diffuse in some region. More interestingly, for angle resolved deposition, some particularly-shaped nanostructures can be realized, such as nanochain structures (Haynes & Van Duyne, 2001) and nanocrescents (Vogel et al., 2011). If the monolayer of nanospheres is non-close-packed, more complex nanostructures can be obtained by changing the incidence angle of the material vapor beam and the azimuth angle of the vapor beam with respect to the normal direction of the nanospheres mask (Zhang et al., 2007).

The critical step of NSL is to form monolayer of ordered nanospheres on desired substrates. Several methods have been developed to form regularly arranged nanospheres on substrates, including transferal coating (Weekes et al., 2007), vertically dipping coating (Choi et al., 2009), spin coating (Hulteen & Van Duyne, 1995), drop coating (Hulteen et al., 1999), and thermoelectrically cooled angle coating (Micheletto et al., 1995). All of these formation methods are based on the ability of the nanospheres to freely diffuse to seek their lowest energy configuration. The diffusion processes and the interaction among nanospheres can be influenced by chemically modifying the nanosphere surface with a negatively charged functional group such as carboxylate or sulfate. Such a modification of the surface features of nanospheres can be easily realized for polystyrene (PS) spheres (Weekes et al., 2007). The self-assembled monolayer of nanosphere masks always include a variety of defects that arise as a result of nanosphere polydispersity, site randomness, point defects (vacancies), line defects (slip dislocations), and polycrystalline domains (Haynes & Van Duyne, 2001). These defects are always remained in the finally obtained nanostructures, which will degrade the properties of the ordered nanostructures. Therefore, it is important to try to get rid of those defects in the monolayer of self-assembled nanospheres.

## 2.2 NSL based on transferal coating

It was found that the transferal coating is much easier in operation to obtain ordered nanospheres in large areas than the other methods. The domain size of ordered PS spheres can be up to 1 cm<sup>2</sup> (Weekes et al., 2007). The key step of the transferal coating is to self-assemble highly ordered monolayer of PS spheres at the interface between water and air (or oil). In general, the suspensions (1-10 wt%) of PS spheres in de-ionized (DI) water are diluted in a 1:1 ratio in some spreading agent, such as ethanol or methanol. Drops of the diluted suspension of PS sphere are then introduced into water surface via a tilted glass from a pipet. On contact with the water, the PS spheres immediately form a monolayer and start to assemble. The inherent mechanism for the ordering of PS spheres at a liquid interface has been studied by several groups (Aubry & Singh, 2008; Boneva et al., 2009; Larsen & Grier, 1997; Nikolaidis et al., 2002; Pieranski, 1980; Trau et al., 1996; Yeh et al., 1997). A reasonable model has been provided to account for the ordering of PS spheres at the interface (Nikolaidis et al., 2002). It was suggested that the ordering arrangement of PS spheres resulted from the balance between an electrostatic repulsion and an additional capillary attraction among PS spheres. The former is originated from the negative charges on PS spheres (Weekes et al., 2007). The latter is due to the deformation of liquid meniscus

by electrostatic stresses at interface. Both of these two forces were associated with an electric dipolar field, which resulted from an asymmetric charge distribution on particles at the interface due to mismatch in dielectric constant of adjacent fluids. Such a creation of the attractive capillary force is crucial because spheres with diameters of less than  $5\ \mu\text{m}$  generally do not have sufficient weight to deform the liquid meniscus by means of gravity (Kralchevsky & Nagayama, 2000).

Considering the importance of the electrical field in self-assembling PS spheres at interface, it is natural to find ways to change the electric field to control the arrangement of PS spheres. One way is to apply an external electric field during the self-assembly of PS spheres at the interface (Aubry & Singh, 2008; Boneva et al., 2009; Nikolaides et al., 2002; Trau et al., 1996). This external electrical field will change the charge distribution on the surface of PS Spheres, leading to the change of the electric dipole field around PS spheres. It may also exert an additional electric force on the negatively charged PS spheres, which will affect the deformation of the surface. In a word, the external electric field will affect both the attraction force and the repulsion force mentioned above. It has been found that the inter-particle distance can be remarkably changed by the electric field (Nikolaides et al., 2002). As a result, the ordering of self-assembled PS spheres can be improved considerably, as shown in Fig. 1. In addition, the effect of an external electric field on the arrangement of PS spheres is more pronounced for smaller spheres.

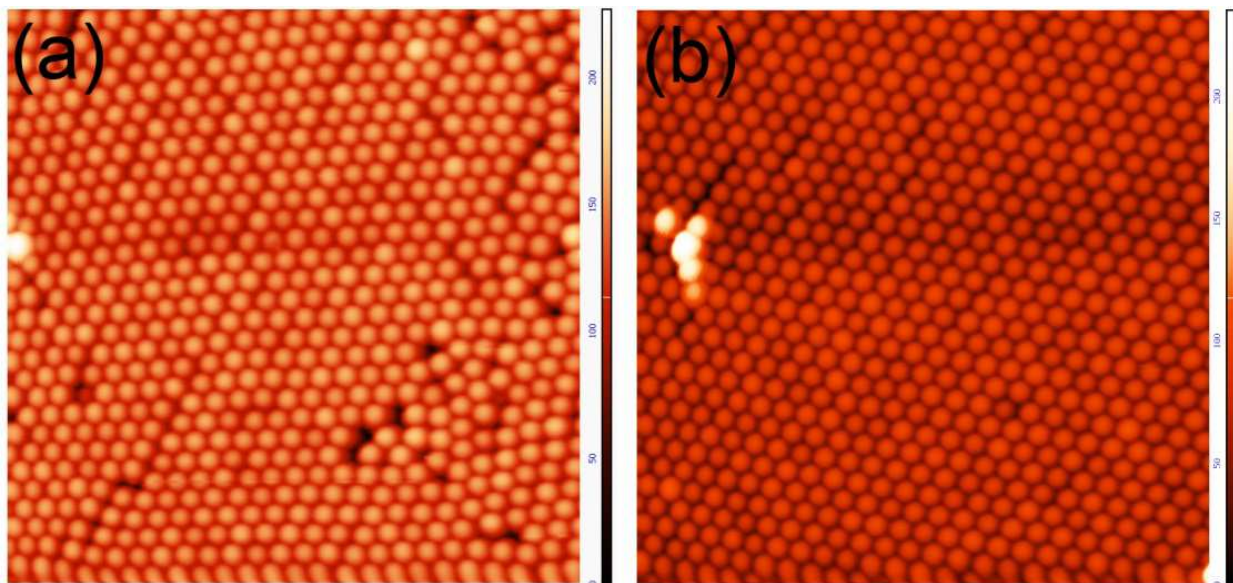


Fig. 1. Self-assembled monolayer of PS spheres ( $5 \times 5\ \mu\text{m}^2$ ) with an external electric field of, (a)  $0\ \text{V/m}$ , (b)  $5 \times 10^4\ \text{V/m}$ . The diameter of PS sphere is  $200\ \text{nm}$ . The electric field is upward and perpendicular to the interface of water and air. The external electric field can efficiently reduce defects in the regular arrangement of PS spheres, remarkably improving the ordering of the self-assembled monolayer of PS spheres.

Another way to modify the balance between the attraction force and the repulsion force among PS spheres is to change the surface chemistry of PS spheres or the electrostatic environment of the water-air interface (Sirotkin et al., 2010). By adding some electrolyte, e.g. acid ( $\text{H}_2\text{SO}_4$ ) and  $\text{NaCl}$ , into the water, effective surface charge density of PS spheres and /or effect of electric screen of PS spheres can be changed, which give rise to the change of

the interaction among PS spheres. It has been found that the ordering of self-assembled PS spheres at interface can be considerably improved by adding suitable acid ( $\text{H}_2\text{SO}_4$ ) in water (Sirotkin et al., 2010), as shown in Fig. 2. Given that the charges on PS spheres are related to the diameter of PS spheres, the suitable amount of acid or other electrolyte is dependent on the size of PS spheres. In addition, the temperature of the water to some degree also affect the self-assembly of the PS spheres at the interface. It was found that ordering of PS was improved on the water of  $\sim 4$  °C. Such an improvement may be related to the increase of water surface tension and the suppression of the Brownian motion of the PS spheres and dust clusters in the water.

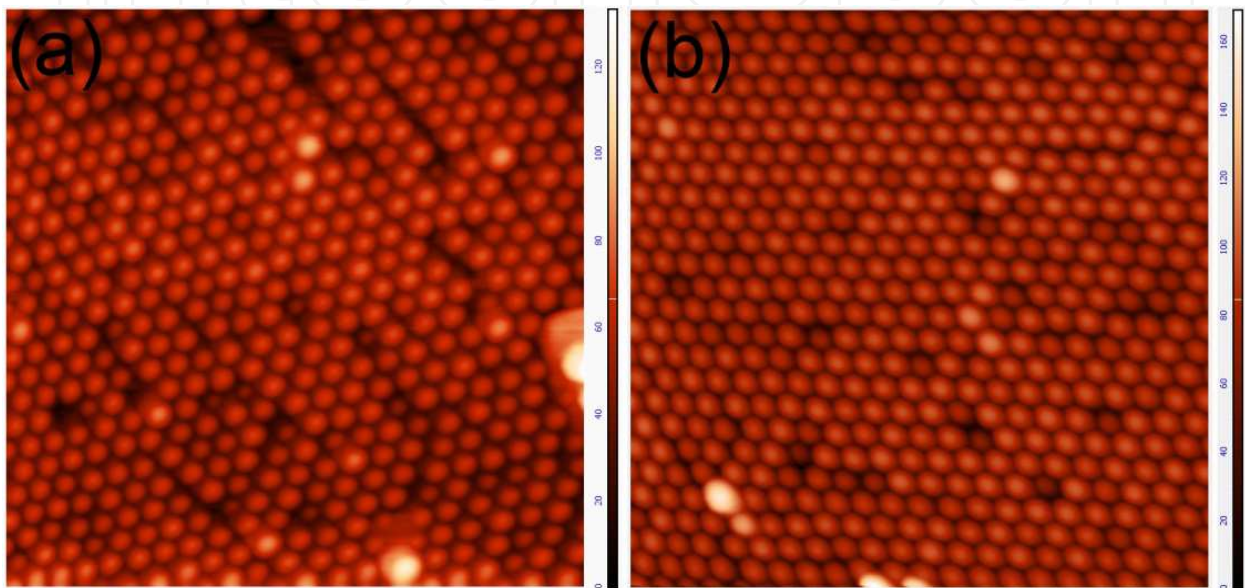


Fig. 2. Self-assembled monolayer of PS spheres ( $5 \times 5 \mu\text{m}^2$ ) at the interface of air and the solution of de-ionized water and  $\text{H}_2\text{SO}_4$  with PH value of, (a)  $\sim 7$ , (b)  $\sim 5.3$ . The diameter of PS sphere is 240 nm. The  $\text{H}_2\text{SO}_4$  can provide some additional ions around PS spheres, which can effectively change the interaction among PS spheres. Under certain PH value of the solution, considerable improvement of ordering of PS spheres can be made.

The self-assembled monolayer of PS spheres can be finally transferred to varieties of smooth substrates underneath the water by draining off the water. This process can be affected by some charges on the substrates. In addition, some cracks may appear once the monolayer was disturbed by movements of the water during draining. The PS spheres nearby the cracks slightly displaced from the ideal sites of a hexagonal lattice. In this case, the long-range ordering of the subsequent structure is degraded. The monolayer of ordered PS spheres on substrates can then serve as a mask for the subsequent fabrication of ordered nanostructures by deposition of varieties of materials or by etching.

### 2.3 Periodic pit-pattern obtained by NSL and chemical etching

Periodic pit-pattern can be obtained in combination of NSL and selective chemical etching (Chen et al., 2009). The processes mainly involves three steps: (i) self-assembling monolayer of PS spheres on hydrogenated Si surface; (ii) forming a novel net-like Au-Oxide mask via Au catalyzed oxidation; (iii) resulting in periodic pits by selective chemical etching of Si in KOH solution.

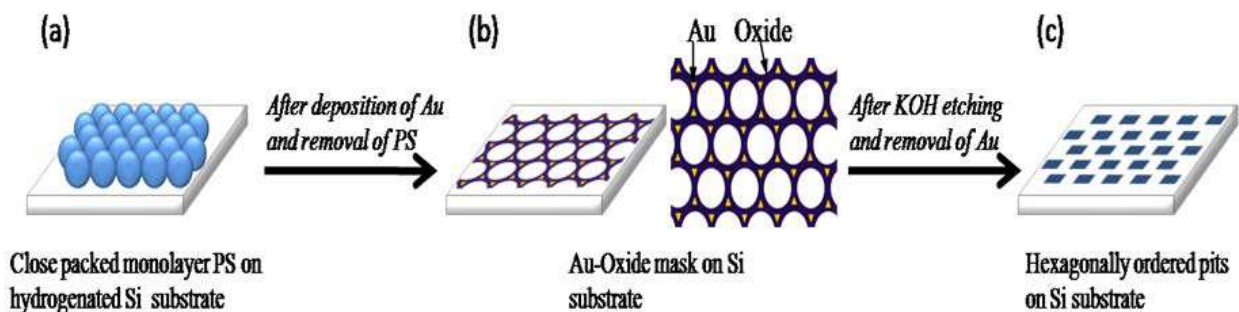


Fig. 3. Schematic illustration for the fabrication of ordered pit-pattern using nanosphere lithography.

The experimental processes are schematically illustrated in Figure 3. It starts with self-assembling monolayer of PS spheres onto hydrogenated Si (001) substrates. The PS spheres with different diameters of 100nm, 200nm, 500nm, 600nm or 1.6  $\mu\text{m}$  were used. All PS sphere suspensions were purchased from Duke Scientific Corporation. The Si (001) substrates were chemically cleaned and hydrogenated by a subsequent HF dip. The close-packed monolayer of PS spheres was self-assembled on the surface of DI water as mentioned above, which was then transferred onto Si (001) substrates immersed in DI water by draining away the DI water. Fig. 4 shows a large-area highly ordered PS spheres on a hydrogenated Si substrate.

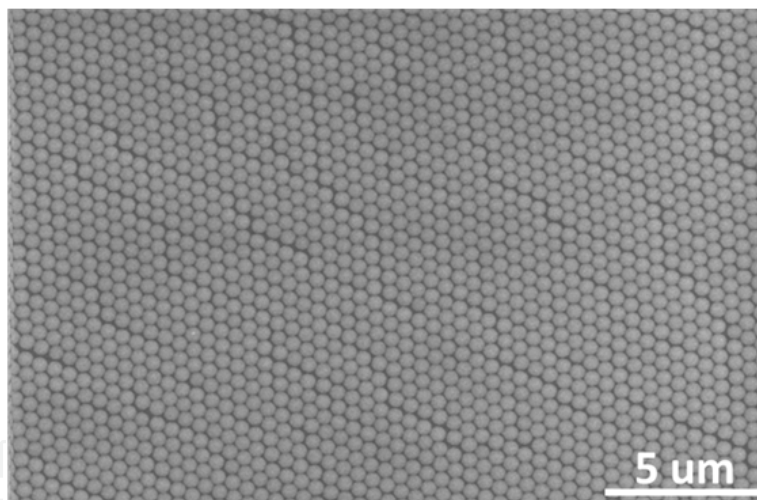


Fig. 4. Representative SEM image of self-assembled monolayer of PS spheres with a diameter of 500 nm on a hydrogenated Si (001) substrate.

The ordered PS spheres in a hexagonal lattice on Si substrate then serves as a mask for thermal evaporation of Au. After deposition of about 1 nm Au onto the PS spheres covered substrates, six Au particles around each PS spheres on Si surface were obtained. Because Au is directly deposited onto the Si surface without  $\text{SiO}_2$ , Si adjacent to Au particles then electrochemically oxidizes, or anodizes upon exposure to air (Robinson et al., 2007). As a result, an Au-oxide mask was naturally formed, as illustrated in Fig. 3(b). To avoid oxidation of the Si surface underlying PS spheres, the samples were immediately rinsed in tetrahydrofuran to remove PS spheres and then etched in 20% KOH solution at room temperature. Since Au-oxide mask protects the underlying Si from KOH etching, well ordered and uniformed 2D pit-pattern was then formed.

The periodicity and the size of the pits were determined by the diameter of PS spheres. The period of the patterned pits is in fact equal to the diameter of PS spheres. This indicates that the period of ordered pits can be readily changed by using PS with corresponding diameter, as demonstrated in Fig 5. In addition, the lateral size of inverted-pyramid-like pits was essentially decreased linearly with the diameter of PS, as shown in Fig.6. This is mainly because the area underlying the PS spheres for etching is nearly proportional to the projection of PS spheres on Si substrates. Moreover, according to the fitting line in Fig. 6, the lateral size of pits will decrease to be zero when the diameter of spheres equals to  $\sim 40$  nm. This result can be explained by the fact that the Au-catalyzed  $\text{SiO}_2$  partially fill up the region underlying the PS. It means that the minimum period of patterned pits can be down to 40 nm by present method. On the other hand, any dispersion of the diameter of PS will degrade the ordering of the pits near this limit. Thus, before approaching the limit of the nanosphere lithography, more uniformed PS is required so that homogenous and ordered small pits can be obtained.

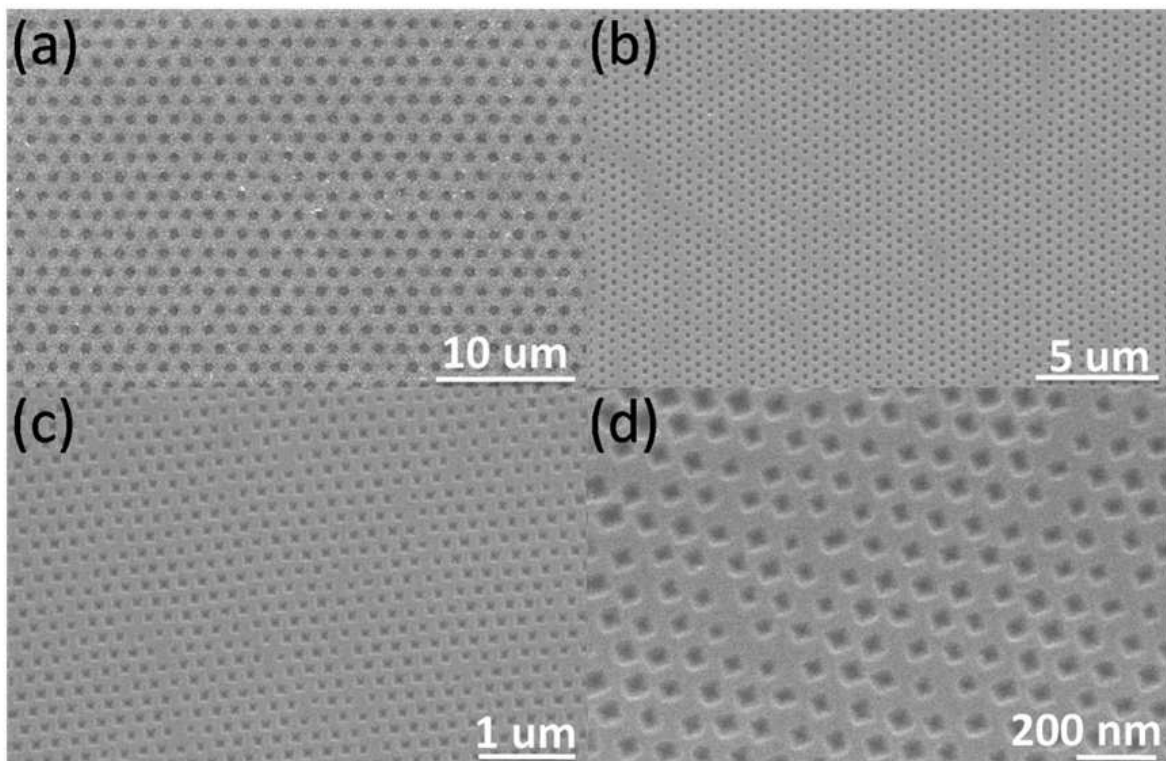


Fig. 5. Representative SEM images of pit-patterns with a periodicity of: (a) 1.6  $\mu\text{m}$  (after 1 minute etching), (b) 500 nm (after 3 minutes etching), (c) 200 nm (after 3 minutes etching), (d) 100 nm (after 1 minute etching) .



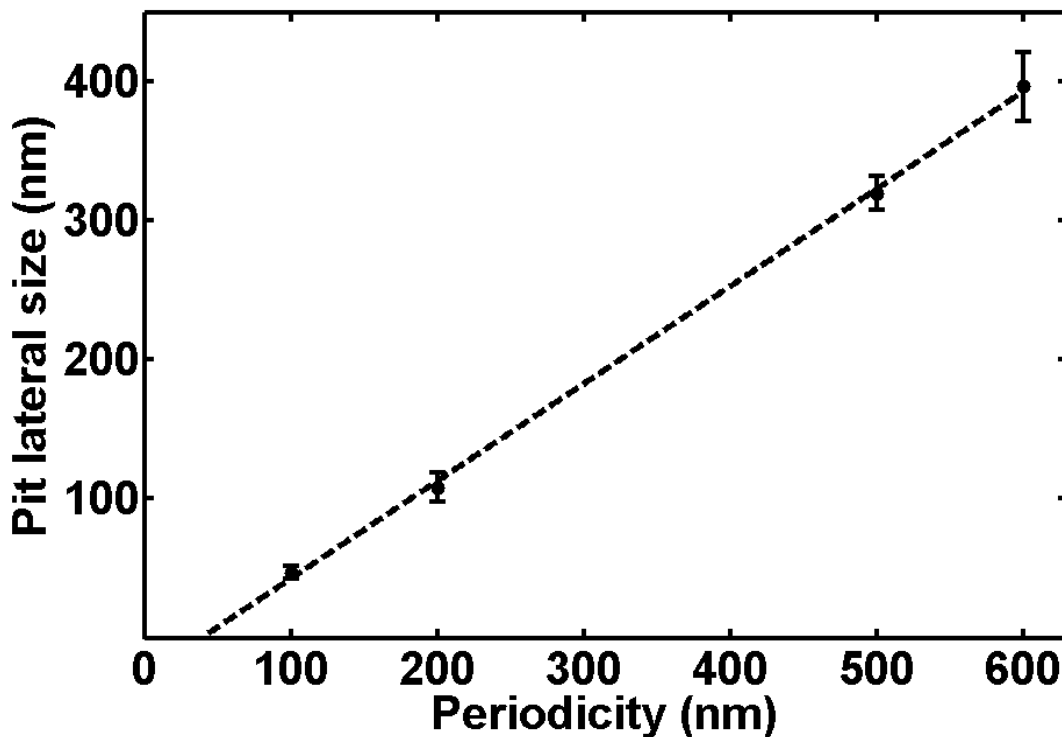


Fig. 6. Mean lateral size vs periodicities of pits. The broken curve is a fitting line.

Moreover, the shape of pits can be tuned by controlling KOH etching time. Depending on the etching time, three types of pits can be obtained. At the beginning of etching, shallow pits with rounded open-mouth (type I pits) can be obtained, as shown in Fig. 7 (a). For an intermediate etching time, inverted truncated-pyramid-like pits with  $\{111\}$  facets and flat (001) bottom (type II pits) are obtained, as shown in Fig. 7 (b). After sufficiently long etching time, inverted pyramid-like pits with  $\{111\}$  facets (type III pits) are obtained, as shown in Fig. 7 (c) and (d). Such a shape evolution with etching time is related to the anisotropic etching rate of Si by KOH solution (up to 100:1 for the etching of Si along  $\langle 100 \rangle$  and  $\langle 111 \rangle$  direction at room temperature). As a result,  $\{111\}$  facets will finally appear in the pits. The depth of type III pits approximates to be  $w / 2 \times \tan(54.7^\circ)$ , where  $w$  is the lateral size of pits with sidewalls of  $\{111\}$  facets having slope angle of  $54.7^\circ$ . In addition, the etching time corresponding to each type of pits depends on the periodicity of the patterned pits. As described above, a larger periodicity of patterned pits is accompanied with a larger area region for etching, which gives rise to a larger pits. It takes time to form the sidewalls of pits completely with  $\{111\}$  facets from their appearance. The larger pits will have larger area sidewalls, as results in longer etching time corresponding to different types of pits. Therefore, the pits with a periodicity of  $1.6 \mu\text{m}$  in Fig. 5 (a) are of type I. The pits with a periodicity of 500 nm in Fig. 5 (b) are actually of type II. The pits with a periodicity of 200 nm and 100 nm in Fig. 5 (c) and (d) are of type III. It has been found that some materials growth on Si substrates was orientation-dependent (Zhang et al., 2008). Such patterned Si substrates with the coexistence of spatially ordered (001) surface and  $\{111\}$  facets may provide potential templates to form ordered unique nanostructures of orientation dependence.

Well ordered GeSi nano-islands were obtained by deposition of Ge on such pit-patterned Si (001) substrates using molecular beam epitaxy (Chen et al., 2009), as shown in Fig. 8(c). Such preferential formation of GeSi nano-islands within each pit is energetically favorable under the assistance of growth kinetics (Zhong et al, 2007; Zhong et al., 2008). In comparison, GeSi nano-islands on a flat substrate under identical growth conditions are random, as shown in Fig 8(d). With decreasing the periodicity of the pit-pattern by using small PS spheres, higher density of smaller GeSi nano-islands in a hexagonal lattice are expected, which can facilitate the investigation of size-dependent quantum confinement effect of nano-islands.

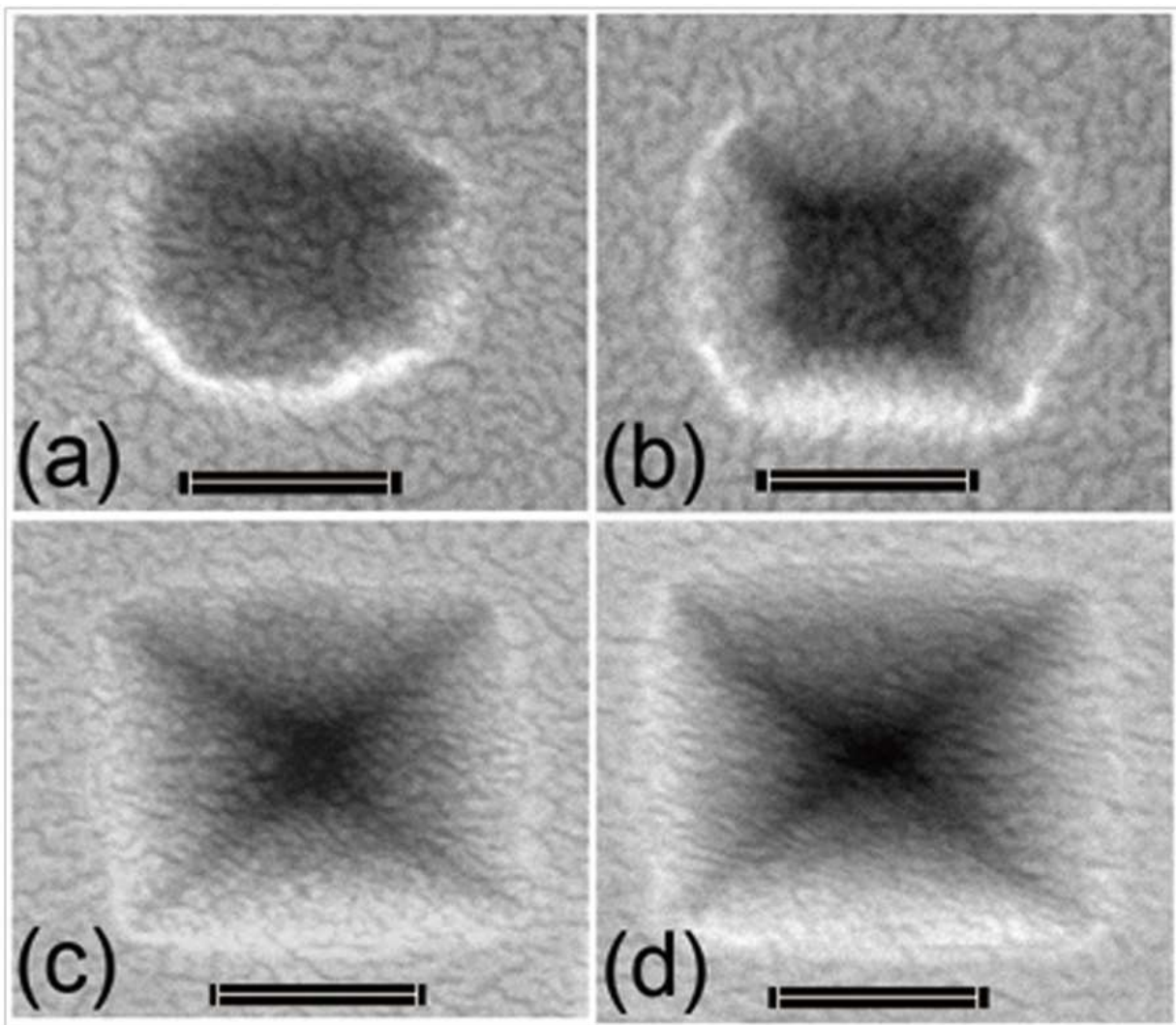


Fig. 7. SEM image of a pit (the diameter of PS spheres used is 600 nm) obtained after etching of (a) 2 minutes, (b) 3 minutes, (c) 5 minutes, (d) 7 minutes. The scale bar is 200 nm.

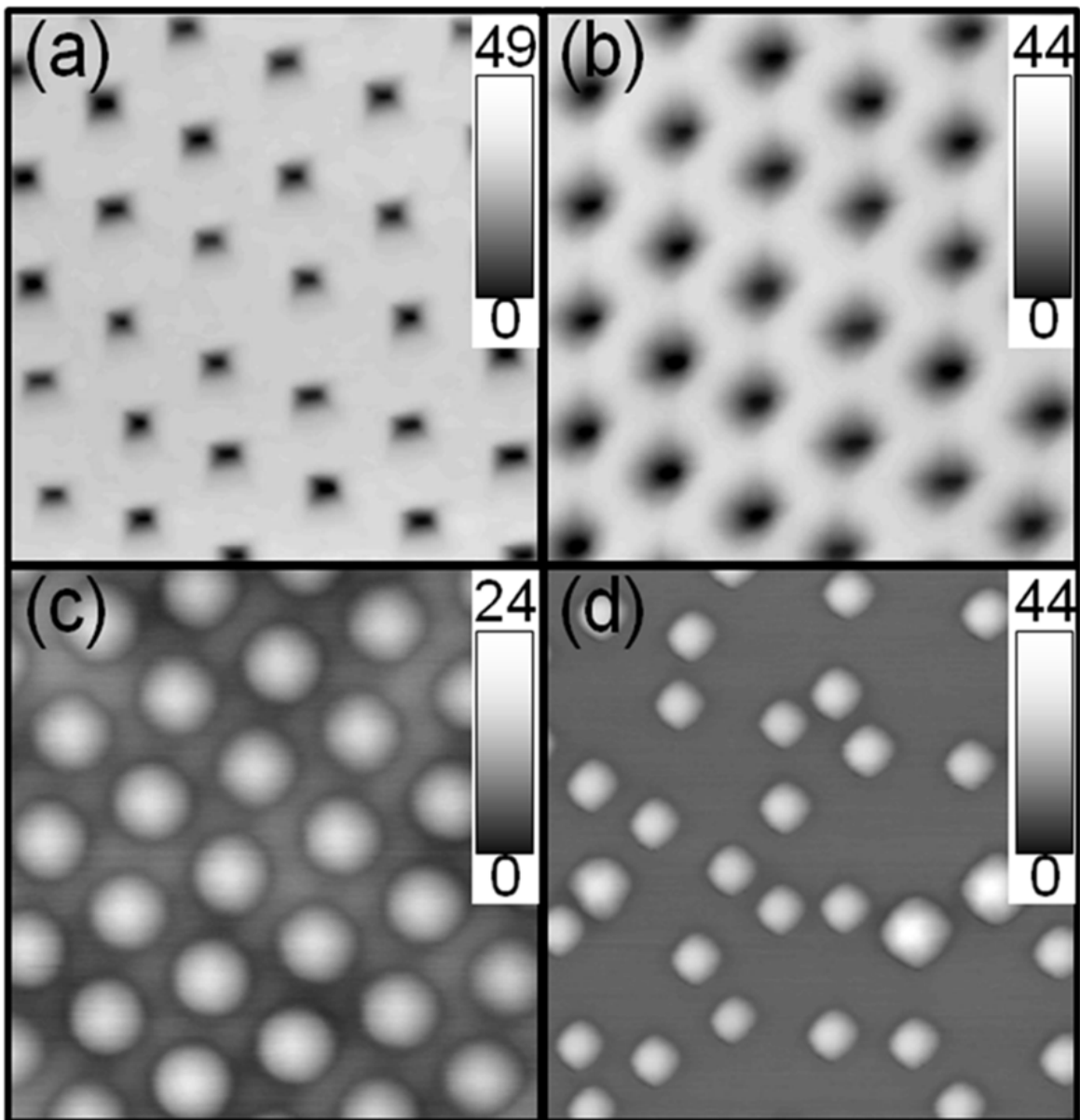


Fig. 8. AFM images ( $1 \times 1 \text{ } \mu\text{m}^2$ ) of (a) pit-pattern with a periodicity of 200 nm, (b) pit-pattern after Si buffer layer growth, (c) ordered GeSi nano-islands after deposition of 10 monolayers Ge by molecular beam epitaxy on a pit-patterned Si (001) substrate, (d) Randomly distributed GeSi nano-islands grown under the same conditions on a flat Si (001) substrate. The unit of height bar is nm.

### 3. Conclusions

A scalable approach to fabricate periodic nanopatterning in a large-scale area with controllable periodicity using nanospheres, so called NSL, has been developed. The NSL generally started with self-assembling monolayer of PS spheres on the substrates, which can be obtained by various methods. One potential routine to obtain ordered monolayer of PS spheres is via self-assembling PS spheres at the interface between water and air. Such a regular arrangement of monolayer PS spheres in a hexagonal lattice resulted from the balance between an electrostatic repulsion among adjacent spheres and a capillary attraction due to the deformation of liquid meniscus by electrostatic stresses. An external electrical field perpendicular to the water surface, which affected the interaction between PS spheres, could efficiently improve the ordering of PS spheres, particularly of small PS spheres. The interplay among PS spheres can also be affected by changing the surface chemistry of PS spheres or the electrostatic environment of the water-air interface, which can be readily realized by mixing some electrolytes, such as solution of H<sub>2</sub>SO<sub>4</sub> or NaCl. In addition, it was found that the ordering of PS spheres was improved on the water of ~ 4 °C mainly due to the increase of water surface tension and the suppression of the Brownian motion of the PS spheres and dust clusters in the water. This ordered monolayer PS spheres could be transferred onto the substrate placed previously inside water by draining off the water. This method facilitates large-area highly ordered monolayer of PS spheres on substrates, which can act as a mask or a template for subsequent lithography to obtain ordered nano-wires or nano-pits, or for subsequent growth of desired nanostructures. Two-dimensionally ordered nanopattern with a periodicity equal to the diameter of PS spheres in the range of several micrometers to less than 100 nm could be readily obtained. The geometrical profiles of the nanopattern could be modulated by controlling the etching conditions. NSL has been exploited in fabricating ordered nano-wires and nano-dots. This technique was characterized by its low-cost, high throughput, and easy manipulation for producing large-scale periodic patterns. More interestingly, NSL can be applied to obtain nanostructures of various materials on many kinds of substrates, which will facilitate the production of varieties of ordered nanostructures.

### 4. Acknowledgements

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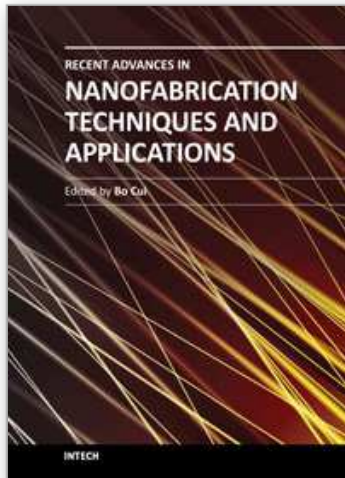
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Nanotechnology has experienced a rapid growth in the past decade, largely owing to the rapid advances in nanofabrication techniques employed to fabricate nano-devices. Nanofabrication can be divided into two categories: "bottom up" approach using chemical synthesis or self assembly, and "top down" approach using nanolithography, thin film deposition and etching techniques. Both topics are covered, though with a focus on the second category. This book contains twenty nine chapters and aims to provide the fundamentals and recent advances of nanofabrication techniques, as well as its device applications. Most chapters focus on in-depth studies of a particular research field, and are thus targeted for researchers, though some chapters focus on the basics of lithographic techniques accessible for upper year undergraduate students. Divided into five parts, this book covers electron beam, focused ion beam, nanoimprint, deep and extreme UV, X-ray, scanning probe, interference, two-photon, and nanosphere lithography.

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