Dry etching of colloidal crystal films

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Two types of non-close-packed colloidal crystal films were prepared by etching the films made of polystyrene nanospheres using a hyperthermal neutral beam of oxygen gas. Etching without sintering above glass transition temperature of the polymer particles resulted in the non-close-packed structure of the nanospheres, in which polystyrene nanospheres in different lattice planes touched each other due to the reduction in the size of the nanospheres that occurred during the etching process. In contrast, a different non-close-packed structure with inter-connecting networks between etched nanospheres was generated by annealing of the colloidal crystal and a subsequent etching process. The photonic bandgap could be tuned during this dry etching of colloidal photonic crystals. This connected open structure could be used as a template for a silica inverse opal by chemical vapor deposition. An alternative dry etching process, reactive ion etching, mainly affected the morphology of particles near the top surface, and only a slight change in the stop band position of the colloidal crystal film was observed.

1. Introduction

A great deal of attention has been paid to the fabrications and applications of photonic crystals (PCs) that prohibit the propagation of a certain wavelength of light inside their periodic dielectric structures. Over the past few decades, there has been increasing interest in bottom-up approaches, such as colloidal self-assembly, for the preparation of photonic bandgap (PBG) materials due to their relatively cheap and facile nature, though the conventional micro-lithographic techniques have been developed as top-down approaches for more precise means to make periodic microstructures [1,2]. Recently, many efforts have been devoted to PBG tuning by modifying the lattice constants of colloidal crystals or by changing the refractive index contrast for precise control of the stop band position. In light of these considerations, bandgap tuning can be categorized into two types: passive and active control. For passive control, the lattice constant or the refractive index contrast is permanently modified to induce the change of PBG. Examples of this approach include the annealing of polymeric colloidal crystals at elevated temperatures [3] or the conversion of the spherical shape of building block particles into other morphologies such as ellipsoids [4–8]. Active tuning methods may attract a lot of interest due to the reversible nature of PBG changes, including solvent-based swelling of the PDMS matrix in composite colloidal crystals [9], changing the inter-particle distance between magnetically controllable building block particles [10], using a liquid crystal to infiltrate between building block particles to change the effective refractive index by an electric field [11], and changing the lattice constants of hydrogels or V2O5 opals via temperature control [12,13]. In addition to these approaches, the dry etching of PCs by plasma or reactive ions has been studied as a passive tuning mechanism for bandgap tuning and the modification of periodic structures [14–16]. Compared to other methods, the dry etching method has various advantages, since there are various control parameters such as power supplied to generate the plasma, plasma gas flow rate, composition of etching gas, and etching time [17,18]. Among the various dry etching processes, the reactive ion etching (RIE) process may cause charge damage due to the ionic nature of the etching gas, resulting in random rugged surfaces in the microstructure of dry-etched samples and the resultant non-isotropic morphology after etching. Thus, it is important to adopt a more powerful dry etching technique to obtain isotropic and uniform morphologies through the etching process. To this end, a hyperthermal neutral beam (HNB) with a high energy such as 1–10 eV can be used to obtain smooth and isotropic etched microstructures of samples using highly energetic charge-neutral etching gases inside the etching chamber.

In the present article, we applied HNB for etching the colloidal crystal film to form non-close-packed structures and studied the morphologies and optical properties before and after the etching.
In particular, non-close-packed colloidal crystals with or without inter-connecting networks between particles could be modulated by heat treatment before the etching process. In addition, the blue-shift of the reflectance spectrum of a dry-etched colloidal crystal film was observed due to the decrease of the refractive index contrast and the lattice distance. We also performed RIE for comparison with the morphology of the colloidal crystals etched by HNB. Finally, the connected open structures with inter-connecting networks were used as templates for the preparation of an inverted opal with high filling fraction of dielectric materials via chemical vapor deposition (CVD).

2. Materials and methods

2.1. Materials

For the synthesis of polystyrene (PS) nanospheres, styrene (monomer, 99%), potassium persulfate (initiator, 98%) and sodium hydrogen carbonate (buffer, 99%) were purchased from Kanto Chemicals. The comonomer, sodium styrene sulfonate was obtained from Aldrich. Silicon tetrachloride (Aldrich, 99%) was used as precursor material for silica CVD.

2.2. Synthesis of aqueous monodisperse PS colloids

PS nanospheres with narrow size distribution with 230 or 280 nm in diameter were synthesized by emulsifier-free emulsion polymerization using styrene as monomer, potassium persulfate as initiator and sodium hydrogen carbonate as buffer. Detailed reaction conditions can be found in elsewhere [19]. The diameters of PS nanospheres could be controlled by adjusting the amount of the comonomer, sodium styrene sulfonate. During polymerization, the reaction temperature was controlled at 70 °C and vigorous agitation was performed for through mixing of reactants at 300 rpm.

2.3. Fabrication of colloidal crystal film

Colloidal crystal films of PS nanospheres were prepared on glass substrate or silicon wafer by a modified vertical deposition method, dip-coating process [20]. Before colloidal crystallization of PS nanospheres, thin glasses or silicon wafers were cleaned with acetone and 2-propanol for washing out organic contaminants. Then, O₂ plasma was applied to increase the hydrophilicity on the surface of the substrates by using plasma cleaner/sterilizer (HARRICK). During dip-coating process, the lift-up speeds of the substrate were controlled with stage controller to adjust the film thickness. The dip-coating speed was controlled in the range of 0.1–1 μm/s to obtain the colloidal crystal films with thickness ranging from 1.5 μm to 9 μm. The annealing of the PS colloidal crystal film was performed by heating inside convection oven at different temperatures before dry etching process. For HNB samples, we performed the annealing of colloidal crystal films at 100 °C prior to the etching process. The HNB-etched samples without annealing process were also prepared to compare the resultant morphologies of the colloidal crystal samples (Refer to the Types I and II morphologies in Fig. 1a and b). For RIE samples, the annealing process was not adopted before the etching step.

2.4. Dry etching of colloidal crystal film

HNB etching of colloidal crystal was performed by using our patented apparatus[17]. The schematic figure of HNB apparatus is shown in Fig. S1a in the Supporting Material. The etching gas, oxygen was fed into the plasma chamber in the apparatus, and the energy to generate oxygen plasma was supplied from high frequency power source to the antenna in the chamber, which is connected with vacuum line for the reduction of the internal pressure up to 200–300 mTorr. The resultant charged oxygen plasma was fed into the heavy metal plates with many cylindrical holes for wall neutralization to generate neutral beam during the inelastic

![Fig. 1. (a) Scheme for the etching of colloidal crystal without sintering. (b) Scheme for the etching of colloidal crystal after annealing of polystyrene nanospheres. Necks between building block particles can be generated.](image-url)
collision of charged plasma ions of oxygen with the plates. During the neutralization, charged species was collided with the metal plates with the aids of bias which is connected with the plates, followed by the absorption of electron into the plates. The generated neutral beam with hyperthermal energy of ca. 10 eV was applied to the loaded sample. The chamber was also operated at low pressure of 10⁻³ mTorr. Fig. S1b shows the schematic figure of plasma ions impinging with three heavy metal plates having many holes, which allow the movement of neutral beam into the etching chamber. The reflected neutral species from the first metal plate can be directed to the plates again during the collision with internal wall of the plasma chamber made of aluminum [21]. The plasma reactor was operated with 800 W of RF power. The structure of colloidal crystals, both annealed or un-sintered films were controlled by adjusting the etching time or input voltage of plasma reactor from 1 to 5 min and −10 to −30 V, respectively.

We also tested RIE with oxygen as etching gas. The collision of oxygen atoms, molecules, or ions with high energy to polymer particles generates carbon monoxide, carbon dioxide, and water vapor, resulting in the size reduction of PS nanospheres. Reactive ions of oxygen gas were fed into the sample under the conditions of 50 sccm of gas flow rate and 60 W of operating power.

2.5. Fabrication of silica inverse opals by chemical vapor deposition

The deposition of silica was achieved in a batch reactor under atmospheric pressure and at room temperature. Silicon tetrachloride (SiCl₄) was used as the silica precursor. The colloidal crystal film was exposed alternately to water vapor for 30 min and subsequently to vapor for 10 min. The concentration of SiCl₄ was varied from 0.01 vol.% to 0.05 vol.% in moisture-free argon gas and water vapor in 60% relative humidity. SiCl₄ vapor reacted on the moistened particle surface of the colloidal crystal, producing silica through of the sol–gel synthetic route. After the coating of silica, the organic PS nanospheres were calcinated by burning out at 500 °C for 5 h to obtain inverse opals with filling fraction larger than 26%.

2.6. Characterization

Field emission scanning electron microscope (FE-SEM, Philips, XL30SFE) was used to observe the dry-etched samples of colloidal crystals. The reflectance spectra were measured by reflectance measurement system composed of Xenon lamp (Hamamatsu, C2577) and monochrometer. Transmission spectra were measured by using UV/VIS/NIR spectrometer (Perkin Elmer, Lambda 900).

3. Results and discussion

Fig. 1 contains the schematic diagrams of colloidal crystal films during dry etching process. Fig. 1a and b represents different etched structures of colloidal crystal films, respectively, depending on the sintering prior to etching steps. As shown in Fig. 1a (Type I), PS nanospheres in the same crystalline lattice plane will be separated each other during the etching, resulting in non-close-packed colloidal crystals. For this case, the PS nanospheres in different crystalline lattice planes will contact each other during the reduction of particle size. On the contrary, the close contact between particles in different planes can be avoided by annealing of colloidal crystal films prior to etching process at sufficiently high sintering temperature, as shown in Fig. 1b. Heat treatment of PS nanospheres in colloidal crystals at temperature above T_g (glass transition temperature) induces strong bonding between PS nanospheres, causing the deformation of spherical particles into hexagonal shape. These strong bonding between PS nanospheres will be maintained after etching and size reduction of the particles, generating thin cylindrical networks between neighboring particles in colloidal crystal films, as depicted schematically in Fig. 1b (Type II). Since the collision energy of etching gas into PS nanospheres decreases from top surface to interior region of colloidal crystal, the size reduction of PS nanospheres is most significant for the nanospheres on top layers of opal film, generating the gradient of particle size after dry etching process, as depicted in the schematic cross-section of etched structures shown in both cases.

First, we performed HNB etching without the annealing of PS colloidal crystals as shown in Fig. 1a (Type I). The degree of size reduction of PS nanospheres was controlled by changing the bias voltage of oxygen plasma before surface reflection neutralization keeping the same etching time. Fig. 2a contains the surface scanning electron microscope (SEM) image of PS colloidal crystals of 230 nm in diameter before etching, which represents (1 1 1) surface in fcc lattice. After etching the PS opal with oxygen HNB for 5 min with bias voltage of −10 V, we could obtain ordered non-close-packed structure of PS nanospheres as shown in the SEM image in Fig. 2b. As can be seen in the inset picture of Fig. 2b, the size reduction of PS nanospheres in top surface is more significant than those of the particles in the second layer. However, the size reduction of PS nanospheres during HNB etching is not limited to the particles in the top few layers. As shown in SEM image of the cleaved part of the sample in Fig. S2, the sizes of PS particles in second, third, and the forth layer are also decreased during HNB etching process although the size reduction is not significant unlike the nanospheres in the first layer. The volume reduction rate of particles on the top surface was calculated as 12.3%/min from the inset picture of Fig. 2b, assuming that the particle morphology was maintained as sphere after HNB etching process. Meanwhile, when we increase the bias voltage as −30 V, the collision energy of oxygen HNB with polymeric opal was so high that the PS building block particles were sintered together, causing fusion of the particles in opal structure as shown in Fig. 2c.

Fig. 3 contains the reflectance spectrum of PS colloidal crystal and etched samples displayed in Fig. 2. The stop band position of colloidal crystal can be represented as the wavelength at the maximum reflectance, λ_max, at fixed incident angle of light. This can be analyzed by the following simple Bragg diffraction Eq. (1), and λ_max can be represented as a function of incident angle of light, θ, effective refractive index of colloidal crystal film, n_eff, and lattice spacing d, which is proportional to diameter of constituting PS nanospheres, D.

\[
\lambda_{\text{max}} = 2d n_{\text{eff}} \sin \theta \\
n_{\text{eff}}^2 = \frac{f_{\text{ps}} n_{\text{ps}}^2 + f_{\text{air}} n_{\text{air}}^2}{f_{\text{ps}} + f_{\text{air}}} \\
d = \sqrt[3]{\frac{2}{3} \theta} \ D 
\]

Thus, by HNB etching colloidal crystal, Both n_eff and d can be reduced, which influence directly the stop band position λ_max, obtaining bandgap tuning of colloidal crystal by passive way. The wavelength at maximum reflectance λ_max shifts from 575 nm to 540 nm for original PS opal and dry-etched sample by bias voltage of −10 V for 5 min of etching process. This is due to the combined effect of decreased lattice constant d during the size reduction of PS nanospheres, which affects both d and n_eff in Bragg diffraction Eq. (1). However, λ_max increases to 550 nm again, which means red shift of reflectance takes place, when the bias voltage increases to −30 V. This can be attributed that the sintering of colloidal crystal films causes inter-particle fusion, resulting in increasing the
effective refractive index, \( n_{\text{eff}} \). Also important to note is that the reflectance intensity at \( \lambda_{\text{max}} \) decreased significantly due to the decrease of refractive index contrast during HNB treatment for the bias voltage of \(-10\, \text{V}\) and \(-30\, \text{V}\) and partially due to more etching of surface layers.

Another interesting non-close-packed structure can be also generated in the sintered PS colloidal crystals as described schematically in Fig. 1b (Type II). As can be seen from the top view of SEM image in Fig. 4a, the shapes of PS nanospheres in sintered opal possess hexagonal due to the close contact between particles during heat treatment at \(100\, \text{°C}\) for 12 h. Fig. 4b and c contains the SEM images obtained experimentally by etching the sintered PS colloidal crystal for 1 and 3 min, respectively. Only slight etching effect and necked nanospheres were observed for the 1-min etched sample as shown in Fig. 4b. The arrow shown in the inset SEM image of Fig. 4b clearly indicates the inter-connecting network between PS nanospheres. The inter-connecting networks between PS nanospheres were removed due to increased etching time for 3 min as displayed in Fig. 4c. However, besides PS nanospheres on top surface, the inter-connected structures with 12 thin cylindrical networks per each particle were maintained as can be seen from the inset cross-sectional image in Fig. 4c. (See low-magnification SEM image in Fig. S3) Previously, wet etching technique of sintered silica colloidal crystals with hydrofluoric (HF) acid has been already reported by Fenollosa and his colleagues to fabricate non-close-packed opals with inter-connecting networks between building block particles [22,23]. Compared to this result, the non-close-packed structure of colloidal crystals can be successfully generated by dry etching techniques.

To compare the etching effect of PS colloidal crystals, we tried to use \( \text{O}_2 \) RIE instead of \( \text{O}_2 \) HNB etching by using colloidal crystal film with 280 nm PS nanospheres. Fig. 5a and b contains the dry-etched sample of PS opal with \( \text{O}_2 \) RIE for 1 min, representing the size reduction of particles during etching is mainly effective for the PS nanospheres on the top surface. As displayed in the top view of SEM image of Fig. 5a, the structure of RIE-etched PS colloidal crystal looks similar for the samples treated with \( \text{O}_2 \) HNB. The volume reduction rate of the particles on the top surface during RIE was calculated as 31.8% min according to the SEM image in Fig. 5a. However, as can be seen from the PS nanospheres inside the cleaved part of colloidal crystal film in Fig. 5b, the size of PS nanospheres inside the opal seems to be almost maintained, implying that the degree of RIE etching is quite weak for most PS nanospheres except the nanospheres on the top surface. The spherical morphology of particles was not maintained for prolonged etching time like 3 min, as shown in Fig. 5c. This is due to the ionic nature of etching gas during RIE process generating non-isotropic etching and beam damage to the polymeric surface, and the masking effect of the particles in the overlayer of colloidal crystal film.

Since the etching effect was not uniform for the entire cross-section of colloidal crystal films, the position of stop band was not significantly changed as shown in the transmission spectrum of the samples in Fig. 6. Only slight envelops in the transmission spectrum were generated near 560 nm for the samples etched for 2 and 3 min, implying the RIE etching effect is only valid for the particles near top surface of colloidal crystal causing only slight decrease of effective refractive index of opal films.

Meanwhile, the inverse opal structure with high filling fraction of dielectric materials has great importance due to their potential applications for the tuning of PBG width by controlling the lattice
parameters of inverted structures [24]. This structure has been made by backfilling the ordinary inverse opal by CVD process reported by Zhao and his colleagues [25]. This can also be fabricated by colloidal templating method using non-close-packed colloidal crystals shown in Fig. 4c as template. High temperature calcination yielded silica inverse opal with high volume fraction shown in the SEM image in Fig. 7a. As can be confirmed clearly from more magnified SEM image displayed in Fig. 7b, the exposed macropores do not contact closely each other, which means the original shape of colloidal crystal template is non-close-packed opal.

4. Summary and conclusions

Dry etching of colloidal crystal films was performed to PS opals by hyperthermal neutral beam with oxygen gas. The nano-structure of dry-etched sample was controlled by sintering prior to etching process or control variables such as bias voltage inside plasma chamber and etching time. The optical stop band of colloidal photonic crystal was controlled by changing these control variables. Inverse opal with high filling fraction was fabricated from the dry-etched opals as templates by room temperature chemical
vapor deposition method. Reactive ion etching was also tested for the nano-scale shaping of PS colloidal crystals, albeit the effect was mainly valid for the size reduction of particles near the top surface of the sample.

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**Appendix A. Supplementary data**


**References**