Directed block copolymer self-assembly implemented via surface-embedded electrets

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Block copolymer (BCP) nanolithography is widely recognized as a promising complementary approach to circumvent the feature size limits of conventional photolithography. The directed self-assembly of BCP thin film to form ordered nanostructures with controlled orientation and localized pattern has been the key challenge for practical nanolithography applications. Here we show that BCP nanopatterns can be directed on localized surface electrets defined by electron-beam irradiation to realize diverse features in a simple, effective and non-destructive manner. Charged electrets can generate a built-in electric field in BCP thin film and induce the formation of perpendicularly oriented microdomain of BCP film. The electret-directed orientation control of BCP film can be either integrated with mask-based patterning technique or realized by electron-beam direct-writing method to fabricate microscale arbitrary lateral patterns down to single BCP cylinder nanopattern. The electret-directed BCP self-assembly could provide an alternative means for BCP-based nanolithography, with high resolution.
Block copolymer (BCP) self-assembly can spontaneously generate periodic arrays of microdomains with versatile morphology and nanoscale feature size in the range of ca. 10–100 nm (ref. 1). The well-defined nanostructures of BCP have been utilized as templates to control spatial order of other functional materials for a variety of applications2,3 such as microelectronic devices4,5, photovoltaic devices6, magnetic storage devices7, microreactors8 and porous filtration membranes9. In particular, BCP-based nanolithography10,11, which utilizes the self-assembled BCP thin film to pattern the substrates, has been widely recognized as a viable alternative or complementary approach to conventional photolithography12,13. It is promised to address the conflict between the continuous demanding to shrink the feature size of electronic devices and the technology and cost limits of photolithography. Owing to the favourable advantages such as high throughput, low cost and most notably, compatibility with current nanolithography streamline, BCP-based nanolithography has been targeted as one of the most important next-generation lithography techniques in the International Technology Roadmap for Semiconductors12.

For a typical BCP-based nanolithography, orientation of domains normal to the substrates is essential to facilitate robust pattern transfer13,14. The most common way to control the orientation of BCP microdomains is to fabricate a neutral surface through surface energy modification to balance its interfacial energy with both BCP components15,16. Taking advantage of the dielectric constant difference of each block, orientation control of the BCP self-assembly can also be achieved by applying an external electric field, although it is generally limited to BCP films with micrometre-scale thickness17,18. In addition, surface topology modulation19,20, solvent annealing21,22 and other methods23,24 have also been proposed to control BCP microdomain orientation. Besides the perpendicular orientation, controlled BCP self-assembly with lateral order and localized nanostructures25–28 is also necessary in practical lithography processes to realize pattern registration and addressable device-oriented patterns with low defects29,30. Directed self-assembly, which integrates the BCP self-assembly with the traditional lithography processes, has been developed to achieve oriented and localized ordering of BCP films31,32 utilizing chemical epitaxy and graphoepitaxy methods33–36. In addition, electrohydrodynamic jet printing was utilized to fabricate complex and hierarchical patterns of BCP films37,38. While these methods have improved the ordering of BCP films and advanced the process of registration and addressing, they are generally subject to complex lithographic steps, limited substrates and/or physical destruction of the substrates. It would be rewarding to develop a simple, effective and non-destructive method to realize device-oriented features with versatile patterns and high nanopatterning resolution.

Herein, we introduce a novel method to achieve simultaneously orientation control and localization of BCP self-assembly implemented by surface-embedded electrets, which is fabricated by electron-beam (e-beam) irradiation. Electrets are materials that retain trapped charges or polarization, forming a quasi-permanent, macroscopic electric field around the perimeter39–41. Similar to external electric filed, which can align the BCP blocks, the electric field around the electrets is also found to be able to control the orientation of BCP film. The surface electrets-mediated BCP self-assembly provides a facile approach to BCP nanopatterning, and can yield customized nanopatterns with arbitrary geometry and high fidelity by employing an e-beam direct-writing technique. More attractively, by tuning the parameters of e-beam irradiation carefully, we can realize the formation of individual cylinder nanopattern with extremely high accuracy, which represents the utmost resolution of BCP-based nanolithography and is critical for the formation of contact and via holes in integrated circuit.

Results

Fabrication of nanopatterns. The overall fabricating process of electrets-induced polystyrene-b-poly(methyl methacrylate) (PS-b-PMMA) self-assembly is shown in Fig. 1a. Briefly, a SiO2/Si wafer was first irradiated by e-beam, with proper dose and then spin-coated with BCP film. After thermal annealing, the BCP film underwent microphase separation and self-assembled into stable cylindrical or lamellar nanostructures, depending on the molecular weight ratio of the blocks. Figure 1b shows the plain view scanning electron microscopy (SEM) image of a cylinder-forming BCP thin film on the SiO2/Si wafer, of which the central region has been irradiated by the e-beam. The as-obtained hexagonal arrays (Fig. 1b and Supplementary Fig. 1) in the irradiated region prove that microdomains of PS-b-PMMA orient normal to the substrate surface. Similar results are found in the lamellar BCP film. Fingerprint arrays are formed in the irradiated area, with the lamella microdomains oriented normal to the substrate (Fig. 1c and Supplementary Fig. 2). In contrast, in the area where SiO2/Si wafers have not been treated by e-beam irradiation, parallel orientations are observed (Supplementary Fig. 3). To probe the internal perpendicular orientation of the entire thin films, we
performed grazing-incidence small-angle X-ray scattering (GISAXS) experiment. In the two-dimensional GISAXS pattern of cylinder PS-b-PMAA film self-assembled on the irradiated SiO₂/Si of ∼1 cm² (Supplementary Fig. 4a), the symmetric scattering peaks are confined in the Qx direction and the first-order scattering peaks at Qx = 0.196 nm⁻¹ reflect the perpendicularly oriented microdomains of the entire film with a period (domain space) L = 32.1 nm (2π/Qx). Similarly, perpendicular orientation of lamellae is supported by the GISAXS pattern in Supplementary Fig. 4b (Qx = 0.119 nm⁻¹ and L = 52.8 nm). In addition, the e-beam-induced BCP self-assembly is found widely feasible; all the tested PS-b-PMAAs of different molecular weights and block ratios show vertically oriented patterns (Supplementary Fig. 5). The above results indicate that with the aid of e-beam irradiation, we can readily achieve perpendicularly oriented microdomain of PS-b-PMAA films.

The e-beam irradiation is considered critical to induce BCP orientation. To ascertain this point, we studied the influence of e-beam parameters on the self-assembly of BCP film. Here we use the area ratio of perpendicularly oriented cylinder microdomains (C⊥) in the whole irradiated region, that is, coverage of C⊥, to represent the degree of orientation. As shown in Fig. 2, the coverage of C⊥ increases gradually with e-beam dose (dose = beam current × irradiation time/area) and then stabilizes to ∼100% at an optimized e-beam dose (∼200 mC cm⁻²). A threshold e-beam dose is required to achieve 100% coverage of C⊥, which is affected by the e-beam parameters, such as beam current and accelerating voltage (Supplementary Fig. 6). The dependence of the BCP orientation on the e-beam parameters indicates that the BCP self-assembly by this method hinges largely on the surface charges induced by e-beam irradiation.

Mechanism study. The orientation dependence of PS-b-PMAA self-assembly on irradiation dosage provides an important cue to understand the mechanism. In this work, native layer of SiO₂ exists on Si wafer after standard cleaning procedure (thickness: 2.3 nm). It has been well documented that SiO₂ is an electret material that can trap charges.41,42 We preformed Kelvin probe force microscope (KPFM) to trace the charges of the SiO₂ surface, as it can measure relative surface potential and is an effective technique to uncover the charge trapping of substrates.43 Figure 3a shows a schematic diagram of KPFM measurement and a typical KPFM mapping image of a SiO₂/Si wafer, of which the central region has been irradiated by e-beam. According to the KPFM image, the contact potential difference (CPD, between the substrate and the tip) in the irradiated region increases significantly compared with the pristine region. The positive CPD reflects that positive charges are trapped in the SiO₂ layer after e-beam irradiation, forming a surface-embedded electret. The CPD increment (ΔCPD) increases gradually with the e-beam dose and finally stabilizes to 300–350 mV (Fig. 3b). The evolution tendency of ΔCPD is similar to that of nanopattern coverage (Fig. 2), indicating that orientation of BCP film is closely correlated to the charge state of the surface.

In addition to KPFM measurement, SEM and X-ray photoelectron spectroscopy (XPS) can also reflect the charging behaviour of the SiO₂ layer. The SEM image of electret irradiated by e-beam shows higher contrast difference compared with the non-irradiated region (Supplementary Fig. 7a). The voltage contrast image is attributed to the charging of the electret. XPS was performed to examine the surface constitution and chemical states of the SiO₂/Si wafers before and after irradiation (Supplementary Fig. 7b). Binding energies of Si–Si and Si–O bonds increase gradually with the e-beam irradiation, and 0.3 eV increment of the Si–Si binding energy is found in the SiO₂/Si substrate after irradiation (3.9 mC cm⁻²). The small positive shift of binding energy indicates the accumulation of positive charges (holes). The positive charges result from the net outcome of electron injection and secondary electron emission during irradiation. As the secondary electron emitting from the wafer occurs mainly on the surface and cannot be counteracted by the electron injection, accumulated holes are formed on the SiO₂ layer, thereby charging the SiO₂ electret.42

Earlier reports have revealed that external electric field can align the blocks of PS-b-PMAA along the field and control its orientation due to the dielectric permittivity difference of blocks.38,45 The e-beam irradiation introduces positive charges into the surface-embedded electret and generates a static electric field E at the SiO₂/Si surface (inset in Fig. 1a). For a planar electret, whose lateral dimension is much larger than its thickness D and the film thickness L, one has

$$E = \frac{\Phi}{L + D_{AB}/\varepsilon_s}$$

(1)

where ϕ is the surface potential at the electret (determined by the charges trapped in the electret), ε_s is the dielectric constant of diblock copolymer A–B (Supplementary Discussion) and ε_s is the dielectric constant of the electret substrate. Therefore, the electric field strength is 1.5–9.5 V μm⁻¹ through BCP films with thicknesses of 30–200 nm (Supplementary Discussion). These values are comparable with typical external fields (1.0–40 V μm⁻¹, Supplementary Table 1) used previously in the electric field alignment of the BCP films. As the electric field is strong enough to compensate the energetic penalty from the orientation change, it would induce PS-b-PMAA films to orient normal to the electret substrate.

It is noted that the surface energy of substrate could also be changed after e-beam irradiation. To clarify whether electric field or the surface-wetting property underlies the orientation control, a series of control experiments was conducted. A thin self-assembled monolayer of phenyltrichlorosilane was grafted onto the e-beam-irradiated SiO₂/Si wafer, which would alter the surface energy but should not shield the electric field. As a result, on the irradiated region, PS-b-PMAA microdomains can still form perpendicularly oriented similar to the uncoated samples, whereas parallel orientation is obtained in the non-irradiated area (Supplementary Fig. 8). Thus, the electric field is considered the driving force for BCP alignment; if the orientation control were caused by the surface energy change during e-beam irradiation,
the self-assembled monolayer modification should have removed
the surface energy difference at the irradiated/non-irradiated
regions and the morphology of BCP film should be the same.
Furthermore, we removed the charges in the SiO2/Si electrets
deliberately by thermal annealing (>500 °C; electrets are
relatively stable at ~250 °C) or by piranha solution cleaning
before PS-b-PMMA self-assembly. Parallel polarization is
obtained on the SiO2/Si without the electric field alignment
(Supplementary Fig. 9). Third, we have extended the present
method to achieve perpendicular orientation of BCP film
on other electret substrates. Uniform vertical cylindrical
PS-b-PMMA films are attained on various e-beam-irradiated
electrets, including SiO2/Si, PI and Si3N4/SiO2/Si (nitride–oxide–
silicon (NOS); Supplementary Fig. 10). Intriguingly, wettability
experiment shows that charged SiO2/Si is preferential to PMMA
block, charged PI is relatively preferential to PS block and charged
NOS is non-preferential for both blocks (see Supplementary
Table 2 and Supplementary Discussion for more discussion).
Perpendicular orientation of PS-b-PMMA film is successfully
achieved regardless of the preferential wetting properties (SiO2/Si,
PI). These results further prove that the electric field from
the charged surface electret is the critical driving force for the
perpendicular orientation of PS-b-PMMA films.

Features and merits. As the directed self-assembly of PS-b-
PMMA film is implemented with surface-embedded electrets, this
method exhibits several pronounced advantages. First, this
method is feasible, requiring virtually no chemical pretreatments,
and is applicable to many electret materials. As discussed above,
other electret substrates besides SiO2 are suitable for this method.
In addition, this method is applicable to SiO2 layer with a wide
thickness range (Supplementary Fig. 11).

In the conventional approaches to control the BCP orientation
by surface energy modification, the BCP thickness is generally
limited to below ~3 L0 in PS-b-PMMA. For thicker films, driving
force from neutral interfaces declines and the vertical micro-
domains would not penetrate through the entire film. External
electric field-based alignment method is applicable for
film thickness of micrometres, but it is difficult to be applied
to BCP with nanometre scale, as BCP film with sufficient thickness
is required for electrode separation. In contrast, the built-in
electric field originated from the surface electret eliminates the
limitation of external electric field to apply to film thickness down
to tens of nanometres. As shown in Supplementary Fig. 12, the
PS-b-PMMA films of different film thicknesses up to 161 nm can
orient normal to surface of the electret and the degree of long-
range lateral order slightly increases with the film thickness.
We can further fabricate PS(53k)-b-PMMA(54k) film with thickness
of 208 nm (~3.9 L0), with vertical orientation penetrating the
entire film thickness (Supplementary Fig. 13a). Moreover, in the
GISAXS pattern (Supplementary Fig. 13b), the pronounced first-
order peak at Qy = 0.12 nm−1 and the high-order peaks with
relative Qy ratios of 1:2:3:4 also evidence that the lamella BCP
microdomains orient normal to the substrate throughout the
entire film.

The electrets-mediated BCP orientation can yield nanopatterns
in millimetre scale (mm scale) and produce customized patterns.
By increasing e-beam diameter and beam current, the process of
e-beam irradiation can be significantly accelerated. For example,
when e-beam of 20 μm in diameter (see Mode 3 in the Method)
is employed, the irradiation speed increases from 0.4 to
2.5 × 103 μm2 s−1 and it takes ~30 min to irradiate a region of
3.0 × 2.2 mm2. As shown in Supplementary Fig. 14, perpendicu-
larly oriented cylinder morphology is realized in several square
millimetres with high uniformity. The orientation quality of the
mm-scale BCP film is comparable to those fabricated by surface
energy modification, surface topology modulation and external
electric alignment. In addition, the electret implantation
can be guided by customized masks to realize patterned BCP
orientation in mm scale (see Supplementary Fig. 15 for the
process and pattern images).

Finally, the electret charging can be realized by the technique of
e-beam direct writing (EBD) for patterns with precise size and
customized geometry. EBD technique has been extensively
applied in fabricating patterned templates as a mask-free method.
By exploiting EBD to manipulate the e-beam moving path, we
can fabricate e-beam-irradiated region with arbitrary geometries
and sizes. The fine and arbitrary features of EBD endow this
method with splendid abilities to produce versatile user-defined
layouts for localized and self-registered BCP nanopatterns. We
elucidate this combined technique with a pattern of Tai Chi
diagram. The Tai Chi-patterned electret was first fabricated by
EBD, which was demonstrated by the KPFM image (Fig. 4a).
After BCP self-assembly on the customized electret pattern, Tai
Chi patterns can be easily built with perpendicularly oriented
lamella microdomains in high fidelity (Fig. 4b,c and
Figure 3 | Surface potential analysis of electrets. (a) Schematic diagram of KPFM measurement and a representative surface potential distribution of a
SiO2/Si surface with central region irradiated by e-beam. (b) Evolution of corresponding incremental CPD (ΔCPD) with e-beam dose.
highly focused e-beam. Patterns of isolated hole or several holes can be formed with an irradiated circle region by careful e-beam manipulation (Fig. 5). Highly focused e-beam can precisely control the spatial distribution of the electret, at surface of which local electric field is strong enough to control the orientation of PS-b-PMMA for nucleation in a minimum volume51. As shown in Fig. 5b, individual cylinders can be realized on the SiO$_2$ surface electret obtained from superfine e-beam irradiation. The control over individual microdomain of BCP self-assembly, as the resolution limit of the BCP nanopattern, is of paramount importance for application as contact holes in integrated circuit12. Moreover, the high-resolution nanopattern implemented on the localized electrets is free from small guiding templates or physical destruction of the substrate, and thus remarkably facilitates the process of subsequent high-resolution nanopattern transfer to other substrates35. Increasing the irradiated size or e-beam dosage, several cylinders are achieved in a controllable manner (Fig. 5c–e). An array composed of ordered vertical cylinder can also be successfully fabricated on an irradiated linear region (Supplementary Fig. 17a). When applying a lamella-forming polymer to such linear electret, vertical lamellae orient normal to the domain boundary (Supplementary Fig. 17b) for minimizing the free energy52. We can envision that the approach of surface electret-directed BCP self-assembly holds feasibility and opportunity to form accurate registering patterns provided with ultra-high-resolution e-beam53.

**Discussion**

We have experimentally demonstrated the mechanism and appealing merits of the electret-mediated BCP self-assembly. The charged electret introduces an electric field that aligns the BCP film. In the electric field $E$ over the electret, diblock copolymer A–B consisting of blocks with different dielectric constants ($\varepsilon_A$ and $\varepsilon_B$) is aligned by the driving force47,54:

$$f_e \propto \frac{(\Delta \varepsilon)^2}{\varepsilon_{AB}} E^2$$  \hspace{1cm} (2)

where $\Delta \varepsilon = |\varepsilon_A - \varepsilon_B|$ is the dielectric constant contrast of blocks A and B, and $\varepsilon_{AB}$ is the dielectric constant of A–B. The microdomains would be aligned parallel to the electric field (that is, perpendicular to the substrate) as long as the electrostatic energy ($F_e$), which favours the perpendicular orientation of BCP, overcomes the energy penalty from the BCP orientation transformation ($F_P$), mainly the elastic free energy and interfacial energy. Under a critical condition, the change of free energy ($\Delta F_e$ and $\Delta F_P$) of BCP film from parallel to
perpendicular orientation equals 0, that is,

$$\Delta F = \Delta F_e + \Delta F_p = 0$$  \hspace{1cm} (3)$$

The critical surface potential ($\varphi_c$) can be derived from equation (3), which is the threshold of surface potential to compensate the surface energy penalty and provides a theoretical assessment of possibility to align the BCP via the charged electret. Key parameters influencing $\varphi_c$ include dielectric constants ($\varepsilon_a$ and $\varepsilon_b$), BCP film thickness $L$ and interfacial energy mismatch $\delta$. On the basis of the lamellar diblock copolymer A–B (in a strong-segregation regime) and a planar electret model, the dependence of $\varphi_c$ on these parameters is theoretically calculated and plotted in Supplementary Fig. 18 (see Supplementary Discussion for details). According to the theoretical estimation, the influence of dielectric constant contrast $\Delta\varepsilon$ (electrically relative) is significant, whereas the effect of interfacial energy is minor. The interfacial energy influences the BCP self-assembly by changing the threshold of the surface potential. The dependence of the electret-directed self-assembly on the film thickness is also insignificant.

In this study, the surface electrets were charged via e-beam irradiation to produce BCP nanopatterns with sizes ranging from nanoscale to mm scale. In fact, electrets can also be charged via corona discharge or a metal-coated polydimethylsiloxane stamp, to yield inch-scale built-in electric field, which is promising to make the electrets-aided patterning practically scalable. It is noteworthy that though this BCP self-assembly method applying corona discharge or a metal-coated polydimethylsiloxane stamp, not only can the electrets-aided self-assembly be achieved, but also the resolution limit of BCP nanopattern and provides promising prospect in achieving accurate registering.

**Methods**

**Cleaning of substrates.** Silicon wafers were cleaned in piranha solution at boiling water bath for 30 min and then rinsed with super-pure water. Polyamide film was immersed in phenylteichlorosilane/toluene mixture (1 vol%) for 0.5 h and was then washed in toluene to remove the unreacted silane.

**E-beam irradiation and post treatment.** Three e-beam irradiation modes were used in this work for different experimental purposes. E-beam irradiation and post treatment took place in a commercial e-beam system (IBA Irradiation, Co., Ltd). E-beam dose was user-defined. The point-to-point spacing was 4.6 nm. Diameter of the e-beam was ~5 nm.

**Formation of PS-b-PMMA film.** Cylinder-forming PS-b-PMMA (46k-b-21k, 68k-b-33.5k, and 12k-b-12.5k g mol$^{-1}$) and lamellar PMMA (53k-b-5k and 23k-b-22k g mol$^{-1}$) diblock copolymers were purchased from Polymer Source. The BCPs were dissolved in toluene and spin-coated onto the substrates irradiated by Mode 1. Without otherwise stated, the film thickness of PS-b-PMMA (46k-b-21k) and PS-b-PMMA (53k-b-5k) was 37 and 56 nm, respectively, which was determined by a spectroscopic ellipsometer (SE 850 DUV, SENTECH Technologies). The BCP films were annealed at 250 °C for 2 h in Ar flow for microphase separation.

**KPFM measurement.** The KPFM measurement was performed on Multimode 8 (Bruker Corp.). The samples were prepared with the Helios 600i system, and a marker was added near the irradiated zone to locate the irradiated zone quickly under the charge-coupled device of KPFM system. We used Si probe with 1.5 N m$^{-1}$ force constant and 250 kHz resonance frequency. Scan velocity was 0.6 Hz, and the number of scan lines was 512. All KPFM images were analysed using Nanoscope Analysis software.

**Characterization.** The surface morphology of the BCP films was observed by Helios 600i SEM system with an accelerating voltage of 5 kV. To increase the contrast of SEM image, all the annealed samples were treated with Ar plasma (power, 50 W; flow rate, 20 s.c.c.m.) to remove the PMMA domains selectively. GISAXS experiments were conducted on beamline 16B of the Shanghai Synchrotron Radiation Facility. The synchrotron X-ray energy was 10 keV and sample-to-detector distance was 1,820 mm. The incident angle of X-ray beam was 0.185°. A vacuum guide tube in which the scattered beam passed through was used to minimize air scattering. The two-dimensional GISAXS patterns were recorded on a Mar 165 charge-coupled device detector (2,048 × 2,048 pixels, 80 μm per pixel). The surface elemental information was analysed by the X-ray photoelectron spectroscopy on the Thermo Scientific ESCALab 250Xi using 200 W Al Kα radiation. The irradiated SiO$_2$/Si wafers for GISAXS and XPS measurement were prepared by Mode 3.

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Author contributions
D.W. and M.-L.W. conceived the idea; M.-L.W. conducted the experiments; all the authors participated in discussing the results; M.-L.W. and D.W. drafted the manuscript.

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