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COMMUNICATION

Large-scale patterning by the roll-based evaporation-induced self-assembly

Won Kyu Park,†[ab] TaeYoung Kim,†[a] Hyeongkeun Kim,[a] Yena Kim,[a] Tran Thanh Tung,[c] Zhiqun Lin,[d] A-Rang Jang,[e] Hyeon Suk Shin,[e] Jong Hun Han,[f] Dae Ho Yoon*[b] and Woo Seok Yang*[a]

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The large-scale fabrication of highly regular polymer stripes was achieved either on rigid or flexible substrates *via* the roll-based evaporation-induced self-assembly (EISA) method. A control of stripe size was rendered by an adjustment of the jig speed and the polymer concentration. Large-scale graphene stripes on a flexible substrate were also crafted by capitalizing on an optimized condition of the roll-based EISA technique.

Evaporation-induced self-assembly (EISA) is unique in offering a non-lithographic route to creating well-ordered two-dimensional (2D) patterns with a large variety of complex architectures. The basic principle of EISA is analogous to the coffee ring phenomenon in which a drop of colloidal solution leaves behind a ring-like deposit at the perimeter upon solvent evaporation.[1–4] In the evaporation process, nonvolatile solutes in the droplet are carried to the pinned edge (*i.e.*, contact line) and deposit near the contact line.[1–7] As the contact line undergoes a repeated stick–slip motion, regular patterns are generated with features depending on the motion of the contact line.[5–32] Therefore, the key parameter of the EISA method to achieve well-ordered 2D patterns is controlling the contact line effectively. Recently, Lin *et al.* reported an improvement over the conventional EISA, that is, controlled evaporative self-assembly in a confined geometry.[8–26] With a spherical lens on the substrate, the contact line is well controlled to yield highly regular patterns of diverse materials, including colloidal nanoparticles, conjugated polymers, and carbon nanostructures.[8–26]

While the controlled EISA technique provides a simple and cost-effective route to generating well-organized patterns, it is limited with regard to its scalability and coverage over a large area. In most cases, a stationary jig (*e.g.*, a spherical or cylindrical lens) has been utilized to guide the self-assembly of materials such that the resulting patterns were found in a relatively limited area.[8–30] In addition, the obtained patterns are not likely to show evenly spaced pattern intervals or pattern widths, but rather show a gradient nature.[8–30] Unlike earlier work based on EISA,[5–7] we designed a continuous roll-based system by a judicious movement through the speed control of a cylindrical roll-type jig, thereby producing large-area surface patterns *via* a self-assembly process. In addition, we quantified the size of diverse patterns formed by the control of the speed of the jig and the concentration of nonvolatile solutes. Based on this technique, we also demonstrated the fabrication of large-scale graphene patterns on arbitrary substrates.

Results and discussion

Fig. 1a schematically illustrates the procedure for the fabrication of large-area polymer patterns *via* the roll-based EISA method. While

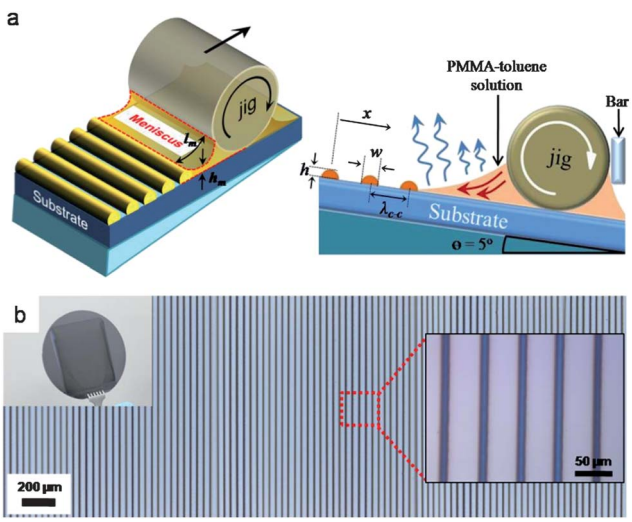

Fig. 1 (a) Schematic illustration of the EISA method using the cylindrical roll-type jig. l_m and h_m represent the meniscus length and the distance between the meniscus and the substrate, respectively. w, λ_{c-c}, h and x represent the width of the pattern, the distance between neighboring stripes, the height of the pattern and the distance from the initial pattern, respectively. (b) The representative microscope image of PMMA patterns formed on a 4 inch Si substrate. The inset on the top left is a photograph of large-scale PMMA patterns formed on the 4 inch Si substrate.

[a]*Electronic Materials and Device Research Center, Korea Electronics Technology Institute, Seongnam 463-816, Republic of Korea. E-mail: wsyang@keti.re.kr*
[b]*School of Advanced Materials Science and Engineering, Sungkyunkwan University, Suwon 440-746, Republic of Korea*
[c]*Smart Plastics Group, European University of Brittany, LIMATB-UBS, Lorient, France*
[d]*School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, GA 30332, USA*
[e]*Interdisciplinary School of Green Energy, Low Dimensional Carbon Materials Center and KIER-UNIST Advanced Center for Energy, Ulsan National Institute of Science and Technology (UNIST), Ulsan 689-805, Korea*
[f]*School of Applied Chemical Engineering, Chonnam National University, Gwangju 500-575, Korea*
† These authors equally contributed to this work.

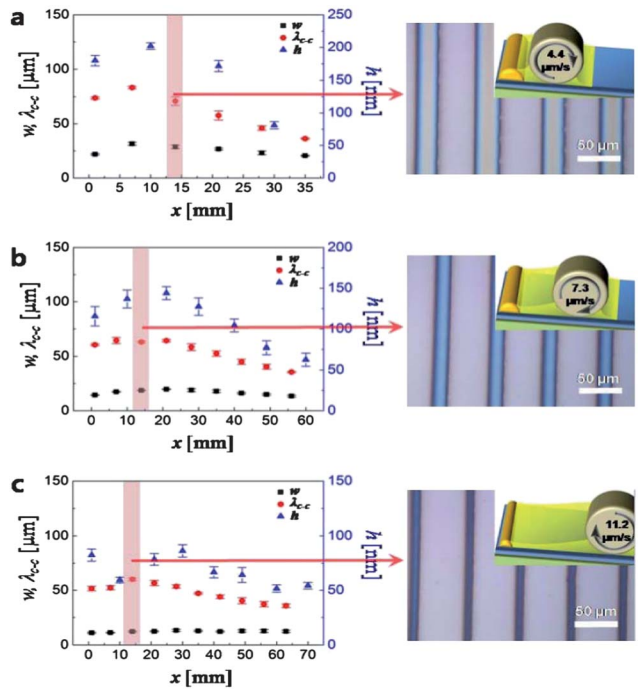

Fig. 2 The variation of PMMA pattern width (w), the distance between neighboring stripes (λ_{c-c}) and the height (h) as a function of the distance (x) from the initial pattern. The roll moving speed was (a) 4.4, (b) 7.3, and (c) 11.2 μm s^{-1}. The microscope images of the PMMA patterns at the same location (~14 mm from the initial pattern) are also displayed. The inset illustrates the pattern formation with respect to the roll moving speed.

the substrate was tilted ~5°, a cylindrical roll-type jig was placed on the substrate to form a curve-on-flat geometry. The roll on the tilt was supported by a bar connected to a servo motor. The PMMA toluene solution was injected into the space between the cylindrical jig and the substrate. As the roll moved down the substrate with a programmed speed, the polymer pattern started to form at the solution edge (*i.e.*, contact line) and continuously evolved on the substrate at a constant speed. In the EISA process, a repetitive stick–slip motion of the contact line occurs at the droplet perimeter. In the general case where the stationary jig is used, the resulting patterns are found in a limited area near the location of the jig.[8–30] In contrast, our roll-based EISA method described here allows the jig roll to translate on the substrate, the stick-and-slip motion of the contact line persists over large areas, resulting in the large-scale PMMA patterns. Fig. 1b shows a representative optical microscope image of large-scale, striped PMMA patterns formed on a 4 inch Si wafer by the roll-based EISA method (the moving speed of the roll: 11.2 μm s^{-1}, the concentration of PMMA solution: 2.0 mg mL^{-1}). The striped PMMA patterns with 55 mm length were generated all the way over the entire Si wafer.

In the magnified optical image (Fig. 1b, inset), the PMMA stripes were formed perpendicular to the roll moving direction and were well separated from neighboring stripes.

The resulting pattern feature is likely to depend on the meniscus shape of the evaporating solution, which is in turn affected by the roll moving speed. Therefore, the optimization of the roll moving speed is important to control the dimension of the resulting polymer patterns. Fig. 2 shows the changes in the pattern size as a function of roll moving speed. As the roll moving speed was increased from 4.4 to 11.2 μm s^{-1}, the surface pattern coverage was varied accordingly with the distance between the initial and final patterns increasing from 35 to 70 mm. Considering that an equivalent amount of polymer solution was injected, the variation in surface coverage with respect to the roll moving speed is likely due to the different moving distance of the roll for the equivalent time allowed for solvent evaporation. The dimension of the resulting surface patterns also varies with the roll moving speed in a manner that the pattern width (w), interval (λ_{c-c}), and height (h) become smaller with increasing roll moving speed. This is closely related to the meniscus shape of the evaporating polymer solution, which also varies with the roll moving speed. When the PMMA solution was injected in a confined space and the roll starts to move, the meniscus was stretched from the pinned contact line

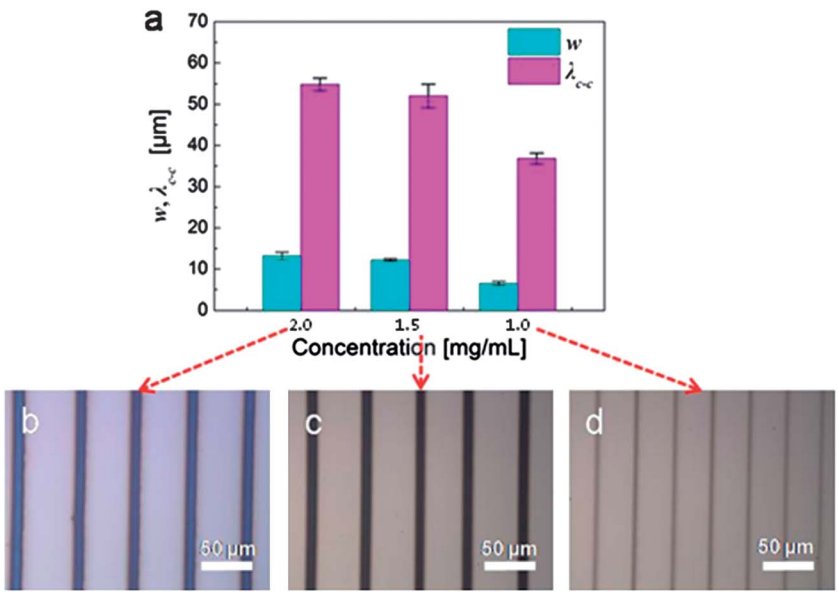

Fig. 3 (a) The variation in PMMA pattern width (w) and the distance between neighboring stripes (λ_{c-c}) as a function of PMMA concentration. The microscope images show the resulting patterns formed at PMMA concentrations of (b) 2.0, (c) 1.5, and (d) 1.0 mg mL^{-1}.

(Fig. 2a). If the roll moving speed is increased, the meniscus is further stretched to have a long and shallow shape with a low contact angle (as depicted in the illustration, Fig. 2b and c). Thus, the time to reach the critical contact angle for the contact line to slip to another position is much faster and the time allowed for the PMMA pattern evolution is relatively short.

Therefore, the faster roll speed leads to the decrease in the pattern dimension. In addition, the roll moving speed is critical to the formation of evenly spaced surface patterns with the constant pattern width over large areas. In case the roll moving speeds of 4.4 and 7.3 μm s^{-1} were applied, a gradual decreasing trend in the pattern dimension along the roll moving direction was observed. This is likely due to the imbalance between the roll moving speed and pattern evolution rate, which results in a gradient in pattern dimensions. However, at the roll moving speed of 11.2 μm s^{-1}, the pattern dimension is almost the same extending over a large area, which suggests that a uniformity of surface pattern can be achieved when optimized conditions are used.

The pattern dimension was also affected by PMMA concentration in solution. To explore the effect of PMMA concentration in the solution, the striped patterns were formed by using PMMA solutions with various concentrations (c = 1.0, 1.5 and 2.0 mg mL^{-1}), while the roll moving speed was fixed at 11.2 μm s^{-1}. As shown in Fig. 3, the pattern width and interval at the same distance from the initial pattern increase with increasing PMMA concentration. This phenomenon can be reasonably explained as follows. When PMMA concentration was increased, more PMMA molecules were carried and deposited at the capillary edge, leading to a wider pattern width. In addition, as the relatively large amount of PMMA molecules was carried to the capillary edge, the sticking time of the contact line becomes longer, resulting in an increased distance of the contact line to the next new position and a wider pattern interval.[9]

On the basis of the above results, we applied the roll-based EISA method on a flexible substrate (90 × 90 mm PET film) and investigated whether this process can be applied to pattern a graphene film. Fig. 4a illustrates the fabrication procedure of graphene stripes *via* the roll-based EISA method on a graphene/PET substrate. A single-layer graphene film has been grown on a copper foil by the CVD method and transferred to a PET film.[33] The PMMA stripes were formed on the graphene/PET film under the previously optimized condition (the roll moving speed: 11.2 μm s^{-1}, the concentration of PMMA solution: 2.0 mg mL^{-1}). Subsequently, the PMMA-patterned graphene/PET film was treated with O_2 plasma at 25 W for 30 s to etch the graphene exposed between the PMMA stripes and the PMMA stripes used to protect the graphene patterns were then removed by acetone. As seen in the microscope image (Fig. 4b, inset), the resulting graphene patterns on the PET film have dimensions similar to those of PMMA patterns. To further investigate the electrical properties of graphene patterns, gold electrodes were deposited by thermal evaporation at both ends of graphene stripes with a distance of 5 mm between the electrodes. Fig. 4b shows a measured I–V curve of the patterned graphene/PET film, which exhibits a typical linear ohmic behavior with a resistance of 860 kΩ.

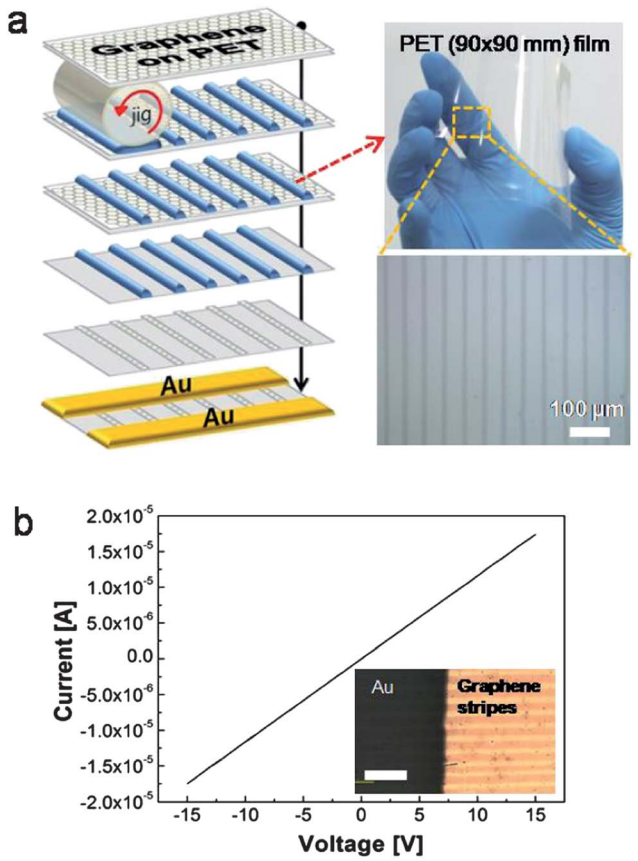

Fig. 4 (a) Schematic illustration of the fabrication of graphene patterns by the evaporation-induced self-assembly (EISA) method: the CVD-grown graphene was transferred to a PET substrate; PMMA formed an ordered array on the graphene surface by the EISA method; the exposed graphene between PMMA stripes was etched by O_2 plasma treatment, and PMMA on the graphene patterns was removed by solvent washing, resulting in the striped graphene patterns. (b) I–V characteristics of the graphene patterns. Inset: the laser scanning microscope image of patterned graphene.

Conclusions

In summary, we demonstrated the large-scale fabrication of highly regular polymer stripes either on rigid or flexible substrates *via* the roll-based EISA method. This method uses a self-assembly-guiding jig roll that can move on the substrates and thus continuously generate surface patterns with a large surface coverage. By optimizing self-assembling conditions such as the roll-moving speed and concentration of polymer solution, a regularly ordered array of polymer patterns was formed over large areas. Based on our roll-based EISA techniques, we also demonstrated the large-scale fabrication of graphene stripes on a flexible substrate. This process may pave the way for a scalable and compatible methodology for the large-scale and roll-to-roll production of a wide range of surface patterns.

Experimental sections

Preparation of PMMA toluene solution

Poly(methyl methacrylate) (PMMA; number-average molecular weight, M_n = 309 kg mol^{-1}; polydispersity index, PDI = 1.57) was chosen as the nonvolatile solute to prepare the large-scaled PMMA stripe patterns. The PMMA toluene solution (2.0 mg mL^{-1}) was prepared by dissolving PMMA in toluene and purified with a 0.2 μm hydrophobic membrane filter.

Procedure for PMMA self-assembly on substrates

To produce polymer stripes on substrates such as silicon and PET, a cylindrical roll-type jig with 60 mm length and 24 mm diameter made of glass was placed above the substrate that was tilted about 5 degrees. Silicon and PET substrates were treated with a nano-strip and acetone solution to make their surface hydrophilic, since polymer patterns were reported to form on hydrophilic surfaces.[29] The jig roll on the tilted substrate was supported by a bar connected to a servo motor and set to move down the substrate by adjusting the motor speed. A drop of PMMA toluene solution was injected into a confined space between the substrate and the roll and then the roll was moved down the substrate with a programmed speed. This roll-based EISA process typically completed in less than 150 minutes, after which the upper jig roll was separated from the substrate. We note that the PET substrate could be slightly damaged by the long exposure of the toluene solution, resulting in a non-uniform formation of patterns. Uniform pattern formation was obtained with the optimization of the solvent evaporation rate by adjusting the roll moving speed. The resulting PMMA patterns formed on the substrate were examined by an optical microscope.

Fabrication of graphene patterns on a PET film

To fabricate graphene stripes, the graphene sheet grown by the CVD method was transferred to a PET film.[33] The PMMA stripes were then formed on a graphene/PET film by the roll-based EISA. Subsequently, the uncovered graphene between PMMA stripes was etched by O_2 plasma and PMMA stripes were removed by acetone.

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