



**7<sup>th</sup> International Symposium on Directed Self-Assembly  
and Nanostructured Materials (DSA<sup>2024</sup>)**  
**October 17<sup>th</sup> and 18<sup>th</sup>, 2024 – Grenoble, France**



**Organizing committee:  
Dr. Christophe Travelet  
Prof. Redouane Borsali**

*Conference place: MaCI - Maison de la Création et de l'Innovation  
Université Grenoble Alpes  
339 avenue Centrale, 38400 Saint-Martin-d'Hères, France (tram stop: "Gabriel Fauré MUSE")*

**Sponsors:**



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# Foreword

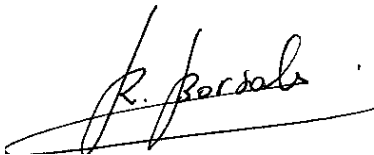
Dear Colleagues,

After the great success and impact of the previous editions of DSA – the last version was organized in 2022 in Daejeon (Korea) (chair: Prof. Sang Ouk Kim), we are very honored to organize the 7<sup>th</sup> edition of DSA, to be held on 17<sup>th</sup>-18<sup>th</sup> October, 2024 in Grenoble, France. This edition will gather well-established scientists from Asia, Europe and USA and consist of invited lectures, flash presentations and poster sessions.

The goal of this conference is to bring together scientists from universities and industries to exchange their views on the latest developments, uses and applications of **nanostructured materials and their directed self-assemblies and imminent applications** for the 21<sup>st</sup> century.

We cordially welcome all of you to the 7<sup>th</sup> International Symposium on Directed Self-Assembly and Nanostructured Materials (DSA<sup>2024</sup>).

Wish this conference be successful and bridge new collaborations.

A handwritten signature in black ink, appearing to read 'R. Borsali', with a long horizontal stroke underneath.

**Prof. Redouane Borsali**  
*Chair of the DSA<sup>2024</sup>*



## International Conference on Directed Self-Assembly and Nanostructured Materials (DSA<sup>2024</sup>)

October 17<sup>th</sup> and 18<sup>th</sup>, 2024  
Grenoble, France

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Université Grenoble Alpes  
339 avenue Centrale, 38400 Saint-Martin-d'Hères

| Thursday October 17 <sup>th</sup> , 2024 |   |
|--|---|
| 8:30 a.m.                                | Registration  |
| 9:00                                     | Welcoming words by<br><b>Redouane Borsali</b> , Grenoble Alpes University, UGA-CNRS-CERMAV – Grenoble, France   |
| 9:15                                     | <b>Sang Ouk Kim</b> , Korea Adv. Institute of Science & Technology (KAIST), Daejeon, Korea<br><i>"Block copolymer nanopatterning for semiconductor, IoT and beyond"</i> |
| 10:00                                    | <b>Caroline Ross</b> , Massachusetts Institute of Technology (MIT), Cambridge, MA, USA<br><i>"Directed self-assembly of multiblock copolymers in 2D and 3D"</i>         |
| 10:45                                    | <b>Flash Presentations</b>  |
| 11:00                                    | Coffee Break & POSTERS  |
| 11:30                                    | <b>Redouane Borsali</b> , Grenoble Alpes University, UGA -CNRS-CERMAV, France<br><i>"Self-assembly of sugar-based bloc copolymers"</i>                                  |
| 12:15                                    | Lunch On site   |
| 2:00 p.m.                                | <b>Makoto Ouchi</b> , Kyoto University, Kyoto, Japan<br><i>"Significant impacts of urea-based junction in PS-PMMA block copolymer on phase separation"</i>              |
| 2:45                                     | <b>Takuya Isono</b> , Hokkaido University, Sapporo, Japan<br><i>"Diverse PS-b-PMMA derivatives via post-polymerization modifications"</i>                               |
| 3:30                                     | Coffee Break & POSTERS  |
| 4:00                                     | <b>Makoto Muramatsu</b> , Tokyo Electron, Tokyo, Japan<br><i>"Multi-patterning holes by chemo-epitaxy process and the scalability"</i>                                  |
| 4:45                                     | <b>Hyeong Min Jin</b> , Chungnam National University, Daejeon, Korea<br><i>"Directed molecular self-assembly through photo-thermal processes"</i>                       |
| 5:30                                     | <b>Kenji Yoshimoto</b> , Kanazawa University, Kanazawa, Japan<br><i>"Potentials of multiblock copolymers for DSA applications"</i>                                      |
| 6:15                                     | Conclusion of DSA <sup>2024</sup> – Day 1   |
| 7:30                                     | Dinner at restaurant "L'Epicurien" - 1 place aux Herbes, 38000 Grenoble (downtown)  |



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# International Conference on Directed Self-Assembly and Nanostructured Materials (DSA<sup>2024</sup>)

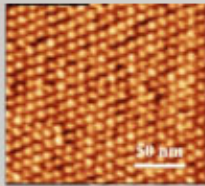
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| Friday October 18 <sup>th</sup> , 2024 |  |
|--|--|
| 8:30 a.m.                              | Registration   |
| 9:00                                   | <b>Jin Kon Kim</b> , Pohang University of Science and Technology, Pohang, Korea<br><i>"Tetragonally and rectangularly packed hierarchical cylinders from A<sub>1</sub>BA<sub>2</sub>C tetrablock terpolymer"</i> |
| 09:45                                  | <b>Teruaki Hayakawa</b> , Tokyo Institute of Technology, Tokyo, Japan<br><i>"Achieving ultra-small features with chemically modified block copolymers"</i>   |
| 10:30                                  | Coffee Break & POSTERS   |
| 11:00                                  | <b>Hai Deng</b> , Fudan University, Shanghai, China<br><i>"Kinetics and orientation study of fast-assembling fluoro BCPs"</i>  |
| 11:45                                  | <b>Itaru Osaka</b> , Hiroshima University, Hiroshima, Japan<br><i>"Design and synthesis of π-conjugated polymers for efficient organic photovoltaics"</i>  |
| 12:30                                  | Lunch On site  |
| 2:00 p.m.                              | <b>Su-Mi Hur</b> , Chonnam National University, Gwangju, Korea<br><i>"Exploring Directed self-assembly (DSA) in conjunction with EUVL for improved pattern quality via molecular simulations"</i>                |
| 2:45                                   | <b>Lander Verstraete</b> , IMEC, Institut de micro-électronique et composants, Leuven, Belgium<br><i>"Enabling chemically amplified resists towards tight pitch EUV patterning by DSA rectification"</i>         |
| 3:30                                   | Coffee Break & POSTERS   |
| 4:00                                   | <b>Jörg K. N. Lindner</b> , University of Paderborn, Paderborn, Germany<br><i>"Progress in the nanopatterning of silicon surfaces with block-copolymer lithography"</i>  |
| 4:45                                   | <b>Marc Zelsmann</b> , UGA, CNRS- LTM, Grenoble, France<br><i>"Self-assembly and dry etching of high-χ block copolymers in a microelectronics context"</i>   |
| 5:30                                   | <b>Michele Perego</b> , IMM-CNR, Agrate Brianza, Italy<br><i>"Doping of silicon at nanoscale by ultra-low energy ion implantation through block copolymer templates"</i>   |
| 6:15                                   | Conclusion of the DSA <sup>2024</sup>  |





**DSA 2024**  
**CONFIRMED**  
**INVITED SPEAKERS**  
 Oct. 17-18, 2024  
 Grenoble, France



Sang Ouk Kim  
Korea



Caroline A. Ross  
USA



Redouane Borsali  
France



Takuya Isono  
Japan

Directed Self-Assembly and  
 Nanostructured Materials



Hyeong Min Jin  
Korea



Makoto Muramatsu  
Japan



Kenji Yoshimoto  
Japan



Jin Kon Kim  
Korea



Michele Perego  
Italy



Jörg K. N. Lindner  
Germany



Su-Mi Hur  
Korea



Makoto Ouchi  
Japan



Teruaki Hayakawa  
Japan



Itaru Osaka  
Japan



Lander Verstraete  
Belgium



Marc Zelmenn  
France



Hai Deng  
China



Shota Iino  
Japan



## International Conference on Directed Self-Assembly and Nanostructured Materials (DSA<sup>2024</sup>)

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| Flash presentations / posters |   |
|-------------------------------|---|
| France                        | <b>Dr. Hong Li</b> , Post-doc<br>UGA, CNRS-CERMAV, Grenoble, France, <a href="mailto:hong.li@cermav.cnrs.fr">hong.li@cermav.cnrs.fr</a><br><i>"Synthesis and self-assembly of sugar-based brush-like blockcopolymer systems"</i>  |
| France                        | <b>Gianluca Forcina</b> , PhD student<br>UGA, CNRS-LTM, Grenoble, France, <a href="mailto:gianluca.forcina@cea.fr">gianluca.forcina@cea.fr</a><br><i>"Nano-lithography with high-<math>\chi</math> block copolymers: inter-relation between self-organization and dewetting kinetics"</i>   |
| Japan                         | <b>Shinsuke Maekawa</b> , PhD student<br>Department of Materials Science and Engineering, School of Materials and Chemical Technology, Institute of Science, Tokyo, Japan, <a href="mailto:maekawa.s.ab@m.titech.ac.jp">maekawa.s.ab@m.titech.ac.jp</a><br><i>"High-<math>\chi</math> DSA using chemically tailored PS-<i>b</i>-PMMA derivatives for line and space patterns with sub-20 pitches"</i> |
| France                        | <b>Achmad Fajar Putranto</b> , PhD student<br>UGA, CNRS-LTM, Grenoble, France, <a href="mailto:achmad-fajar.putranto@univ-grenoble-alpes.fr">achmad-fajar.putranto@univ-grenoble-alpes.fr</a><br><i>"Controlled anisotropic wetting by plasma treatment for DSA of high-<math>\chi</math> block copolymers and optical applications"</i>  |





## Block copolymer nanopatterning for semiconductor, IoT and beyond

Sang Ouk Kim

Department of Materials Science & Engineering, KAIST Institute for Nanocentury,  
KAIST, 34141 Daejeon, Republic of Korea, [sangouk.kim@kaist.ac.kr](mailto:sangouk.kim@kaist.ac.kr)



### Abstract

BCP self-assembly can generate dense, periodic nanopatterns with sub-10-nm scale pattern precision, particularly interested in the semiconductor nanolithography application. We have contributed to this research field from the early days and established many interesting technologies, such as the original directed self-assembly (DSA) principle by nanoscale epitaxy [1,2], novel light induced DSA principles, and DSA for nonplanar geometry by exploiting graphene substrates. Noteworthy that most of previous research efforts for DSA has focused on how to induce regularly ordered patterns with minimal defects. Recently, we have reported an interesting new direction for the IoT security application of BCP self-assembly by utilizing the defective fingerprint like self-assembled nanopatterns in physically unclonable function (PUF) labels [3]. We are proposing a new prospect for the broad range of novel possible application areas of BCP nanopatterning towards IoT and beyond [4].



### Short biography

Prof. Sang Ouk Kim is a KAIST Chair Professor in the Department of Materials Science & Engineering at KAIST, South Korea and currently serving as the director for the National Creative Research Initiative Center for Multi-Dimensional Directed Nanoscale Assembly (NRF funding), and the KAIST Institute for Nanocentury. His main research interest is the directed nanoscale assembly of soft materials towards novel materials discovery, including block copolymers and low-dimensional materials for a broad range of advanced applications, including electronics, energy, environmental and biomedical fields. His scientific contribution has been widely recognized by prestigious honours, including the Highly Cited Researcher from Clarivate Analytics (2018), the KAIST Grand Prize for Academic Excellence (2015) and Presidential Young Scientist Award (2013). He is currently serving as an associate editor of *Energy Storage Materials* (Elsevier) as well as editorial advisors or board members for *Accounts of Materials Research* (ACS), *Small* (Wiley), *Molecular Systems Design & Engineering* (RSC) and so on. He has published more than 290 SCI Journal papers and 100 patents relevant to the nanomaterials science. Based on the Google Scholar statistics, Prof. Kim's H-index is 91 and the total citation number is more than 29000.

### References

- [1] S. O. Kim, H. H. Solak, M. P. Stoykovich, N. J. Ferrier, J. J. de Pablo & P. F. Nealey\*, *Nature* **2003**, 424, 411.
- [2] S.-J. Jeong, J. Y. Kim, B. H. Kim, H. S. Moon & S. O. Kim\*, *Materials Today* **2013**, 16, 468.
- [3] J. H. Kim, S. W. Jeon, J. H. In, S. H. Nam, H. M. Jin, K. H. Han, G. G. Yang, H. J. Choi, K. M. Kim, J. H. Shin, S. W. Son, S. J. Kwon\*, B. H. Kim\* & S. O. Kim\*, *Nature Electronics* **2022**, 5, 433.
- [4] G. G. Yang, H. J. Choi, S. Li, J. H. Kim, K. Kwon, H. M. Jin, B. H. Kim\* & S. O. Kim\*, *Nature Reviews Electrical Engineering* **2024**, 1, 124.

## Directed self-assembly of multiblock copolymers in 2D and 3D

Caroline A. Ross

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Massachusetts Institute of Technology, Cambridge MA 02139, USA, [caross@mit.edu](mailto:caross@mit.edu)*



### Abstract

The microphase separation of thin films of block copolymers can be directed by topographical or chemical substrate features, leading to well-ordered patterns with long range order and/or non-bulk morphologies that offer compelling opportunities in nanofabrication and nanolithography. The utility of directed self assembly (DSA) can be enhanced by expanding the range of possible microdomain geometries available via complex polymer architectures, and by developing methods to control self-assembly in the out-of-plane direction to make three dimensional structures. We will first show how 3D structures can be built up via sequential layering, including a method to reversibly lock and unlock the microdomain morphology of underlying layers using metal infiltration. We will describe the formation of 3D structures such as crosspoint and T-shaped junctions with both in-plane and out-of-plane oriented segments and show how the structures are guided by topographical trenches including trenches with a trapezoidal cross section. We then turn to multiblock polymers that form hierarchical structures with two independently tunable periods, such as Janus bottlebrush triblock terpolymers that yield a substructure (meshes, cylinders or lamellae of one block in a matrix of a second block) within a superstructure (layers of a third block). DSA of these structures yields templated patterns within and perpendicular to the plane. Combinations of novel polymers, templating approaches, and processing techniques yield an extensive array of rectilinear and 3D pattern geometries that can expand current nanofabrication capabilities.



### Short biography

Ross is the Ford Professor in the Department of Materials Science and Engineering at MIT. In addition to studying the directed self-assembly of block copolymers, she works on magnetic and multiferroic properties of complex oxides such as iron garnets, spinels and perovskites. She joined MIT in 1997 after spending six years at Komag, Inc. in CA working on magnetic data storage. She has a PhD from Cambridge University followed by a Postdoctoral Fellowship at Harvard University. Her group site is <https://caross.mit.edu/>.

## Self-assembly of carbohydrate block copolymers: from glyconanoparticles to thin films to photonic crystals

Redouane Borsali

University Grenoble Alpes, CNRS, CERMAV, Grenoble, France, [redouane.borsali@univ-grenoble-alpes.fr](mailto:redouane.borsali@univ-grenoble-alpes.fr)



### Abstract

To date, numerous studies have been focused on the self-assembly of petroleum-based BCPs for potential applications in multidisciplinary fields, such as nanoparticles for drug delivery, or nano-organized films for biosensors, or nanolithography, etc. Such materials are derived from fossil resources that are being rapidly depleted and have negative environmental impacts. In contrast, carbohydrates are abundant, renewable and constitute a sustainable source of materials. This is currently attracting much interest in various sectors and their industrial applications at the nanoscale level will have to expand quickly in response to the transition to a bio-based economy. The self-assembly of carbohydrate BCP systems<sup>[1-4]</sup> at the nanoscale level via the bottom-up approach, has allowed the conception of nanostructured thin films and nanoparticles (micelles, vesicles,...) whose external shell is made from carbohydrates. We will present recent results on the self-assemblies of carbohydrate-based block copolymer leading to nanoparticles presenting different shapes (spherical, cubic, ...), highly nanostructured thin films for nanobioelectronic applications and more recently brush-like glycopolymers exhibiting photonic crystals behavior leading to colored materials.<sup>[5]</sup>



### Short biography

Redouane Borsali is a CNRS research Professor at Grenoble Alpes University (CNRS-CERMAV). He is actually the Director of the PolyNat Carnot Institute (Grenoble), France and the co-director with of IRP-CNRS-UGA-NTU “green material institute” (Taipei), Taiwan. He was elected a Member of the European Academy of Sciences (EurASc) in 2022, awarded the SPSJ international award (Society Polymer Sciences, Japan) in 2021 and the Scientific Grand Prize France Taiwan–Awards Academy of Science (France) in 2018. Before his actual position, he served as the Executive Director for International Relations Grenoble Alpes Univ, Director of CERMAV–CNRS (Grenoble) and Group Leader (LCPO), Bordeaux University. R. Borsali was a visiting Professor at Stanford University and visiting scientist at IBM, Almaden, CA, USA. He spent his Post-doc at Max-Planck-Institute for Polymer Research, Mainz, Germany. He earned his Master and PhD in polymer sciences at Louis Pasteur University at Strasbourg, France. He has more 350 publications, 4 books and 5 patents. Prof. R. Borsali’s expertise is focused during the last decade on the Self-assemblies of Carbohydrate-based block copolymers (BCP) systems with controlled architectures, leading to:

- Nanostructured Thin films: smart surfaces, nanolithography, photovoltaic, memory transistors, HR-biosensors, Directed Self-Assembly (DSA)
- Nanoparticles (micelles) & Polymersomes
- Photonic crystals – colored biomaterial



### References

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Carbohydrate-Based Block Copolymer Thin Films: Ultrafast Nano-Organization with 7 nm Resolution Using Microwave Adv. Mater., 1701645, doi: [10.1002/adma.201701645](https://doi.org/10.1002/adma.201701645), 2017, 1-6
2. Y.C. Chiu, H.S. Sun, Wen-Ya Lee, R. Borsali & W.C. Chen  
Oligosaccharide Carbohydrate Dielectrics High-Performance Non-Volatile Transistor Memory Devices, Adv. Mater., 27(40), Doi: [10.1002/Adma.201502088](https://doi.org/10.1002/Adma.201502088), 2015, 6257-6264
3. J.D. Cushen, I. Otsuka, C.M. Bates, S. Halila, S. Fort, J.A. Easley, E. Rausch, A. Thio, R. Borsali, C.G. Willson & C.J. Ellison,  
Oligosaccharide/Silicon-Containing Block Copolymers - 5 Nm Features for Lithographic Applications », ACS NANO, 6(4), 2012, 3424-3433
4. Hong Li, Muhammad Mumtaz, Takuya Isono, Toshifumi Satoh, Wen-Chang Chen, Redouane Borsali, Self-assembly of carbohydrate-based block copolymer systems: glyconanoparticles and highly nanostructured thin films, Polymer Journal 2022, 54, 455-464, DOI: [doi.org/10.1038/s41428-021-00604-w](https://doi.org/10.1038/s41428-021-00604-w).
5. H. Li, M. Mumtaz, W.-C. Chen and R. Borsali (to be submitted)

## Significant impacts of urea-based junction in PS-PMMA block copolymer on phase separation

Makoto Ouchi

Kyoto University, Japan, [ouchi.makoto.2v@kyoto-u.ac.jp](mailto:ouchi.makoto.2v@kyoto-u.ac.jp)

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|---|--|---|
|  <p>DSA 2024</p> | <p><b>Abstract</b><br/>We have designed a series of PS-PMMA block copolymers carrying urea-based junctions having different structures/sequence to promote the phase-separation. Interestingly, the junction structure was very crucial to the phase-separation behaviors and the incorporation of cyclohexyl spacer was found effective for the promotion. Eventually, we achieved the long-range ordered phase separation of lower molecular weight PS-PMMA (<math>M_n &lt; 12000</math>).</p> |  |
|---|--|---|

### Short biography

Makoto Ouchi is a Professor at Kyoto University (2017-present).

### Reference

[1] Yoshimura, T.; Morishita, T.; Agata, Y.; Nagashima, K.; Wylie, K.; Nabae, Y.; Hayakawa, T.; Ouchi, M. *Macromolecules* **2022**, *55*, 2148-2159.

# Diverse PS-*b*-PMMA derivatives via post-polymerization modifications

Takuya Isono

Faculty of Engineering, Hokkaido University, Japan, [isono.t@eng.hokudai.ac.jp](mailto:isono.t@eng.hokudai.ac.jp)

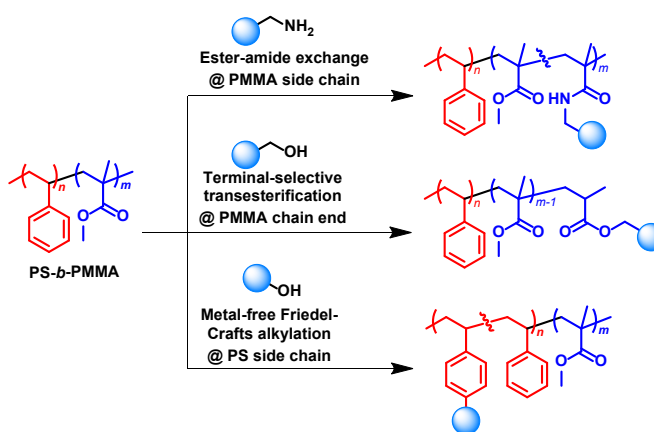


## Abstract

In this presentation, we aim to demonstrate that chemically inert PS-*b*-PMMA, a standard material for DSA applications, can serve as a versatile starting material for post-polymerization modification (PPM). By employing PPM on either the PS or PMMA block, we have successfully introduced functional groups on the PS benzene ring, PMMA side chain, and PMMA chain end. These strategies have enabled the realization of microphase-separated structures with small domain-spacings from low-molecular-weight PS-*b*-PMMA.

Post-polymerization modification (PPM) approach serves as an effective tool for generating a diverse range of polymers from a single starting material, which would facilitate the discovery of novel materials with desired functions. However, a crucial prerequisite for successful functionalization is the presence of reactive functional groups, such as hydroxyl group, olefins, and epoxide, in the starting materials. Meanwhile, polystyrene-*block*-poly(methyl methacrylate) (PS-*b*-PMMA), a standard material for directed self-assembly (DSA) applications, is now commercially available with high quality. We envisaged that if PS-*b*-PMMA can be directly used as the starting material for PPM, diverse PS-*b*-PMMA derivatives can be easily created, which could potentially overcome many issues in terms of DSA application.

In this presentation, we aim to demonstrate that chemically inert PS-*b*-PMMA can indeed serve as a versatile starting material for PPM. For example, ester-amide exchange reaction on PS-*b*-PMMA successfully installed polar functional groups on the PMMA block. On the other hand, Friedel-Crafts alkylation using tertiary alcohol enabled the direct functionalization of the polystyrene benzene ring. By applying terminal selective transesterification, we have successfully introduced a wide range of functional groups, including polymeric substituents, on the PMMA chain end. These strategies have enabled the realization of microphase-separated structures with small domain-spacings from low-molecular-weight PS-*b*-PMMA.



### Short biography

Takuya Isono is an Associate Professor at the Faculty of Engineering at Hokkaido University in Japan. He earned his Ph.D. degree in polymer chemistry from the Graduate School of Chemical Sciences and Engineering at Hokkaido University in 2014. During his Ph.D. studies from 2012 to 2014, he was a JSPS research fellow (DC1). After completing his Ph.D., he began his research career as an Assistant Professor at the Faculty of Engineering at Hokkaido University in 2014. Since April 2021, he has held his current position at Hokkaido University. His expertise is in precise polymer synthesis, and his research interests are currently centered on organocatalytic polymerization, bio-based polymers, block copolymers, and topological polymers. He has received scientific awards for his research, including the Inoue Research Award for Young Scientists from the Inoue Foundation for Science in 2016, the Polymer Research Encouraging Award from the Society of Polymer Science, Japan in 2020, the Research Encourage Award from the Chemical Society of Japan in 2021, and Nanomaterials 2021 Young Investigator Award from the MDPI in 2022.

### References

Isono, T. et al. *Macromolecules* **2018**, *51*, 8064–8072; *Macromolecules* **2018**, *51*, 8870–8877; *Polym. Chem.* **2019**, *10*, 3390–3398; *Polym. Chem.* **2023**, *14*, 2675–2684.

## Multi-patterning holes by chemo-epitaxy process and the scalability

Makoto Muramatsu<sup>1</sup>, Takanori Nishi<sup>1</sup>, Kiyohito Ito<sup>2</sup>, Yoshihito Takahashi<sup>2</sup>, Yasunori Hatamura<sup>2</sup>, Takahiro Kitano<sup>3</sup>, Tomohiro Iwaki<sup>4</sup>

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DSA 2024

### Abstract

The application of DSA (Directed Self-Assembly) to semiconductor processes is expected to realize the repair of fine patterns made by existing lithography and the improvement of pattern density. Multi-patterning technologies such as SADP (Self-Aligned Double Patterning) and SAQP (Self-Aligned Quadruple Patterning) are also mature technologies for improving pattern density, but there are many issues such as the number of processes and the improvement of pitch walking. The use of EUV (extreme ultra-violet), which has been widely used in recent years, can form fine patterns with a single exposure, which contributes to reducing the number of masks. However, since the pattern is formed with a smaller number of photons than conventional exposure, defects are likely to be generated stochastically, and further improvement is required to ensure sufficient process margin. In particular, in high-density hole patterns required for the capacitor layer of DRAM (Dynamic Random Access Memory), suppressing the occurrence of missing and kissing defects is contradictory to reducing the exposure dose. Therefore, it is expected that a technology combining DSA and optical lithography can achieve both cost and pattern performance. In this presentation, we will report on the hole pattern multiplication process using DSA, the pattern performance, and future scalability.



### Short biography

1995 Bachelor of Science, Osaka Prefecture University, Osaka

1995-1997 Tokyo Electron Kyushu, Ltd.

1997-2001 Tokyo Electron America, Inc.

2001-present Tokyo Electron Kyushu, Ltd.

### References

[1] Muramatsu, M., Nishi, T., Ito, K., Takahashi, Y., Hatamura, Y., Kitano, T., " Hexagonal arrays of contact holes with chemo-epitaxial DSA," Proc. SPIE 12054, 1205402 (2022).

[2] Muramatsu, M., Nishi, T., Ito, K., Takahashi, Y., Hatamura, Y., Kitano, T., Iwaki, T., " Pattern fidelity improvement of DSA hole patterns," Proc. SPIE 12497, 124970J (2023).

[3] Muramatsu, M., Nishi, T., Ido, Y., Kitano, T., "Defect mitigation of chemo-epitaxy DSA patterns," Proc. SPIE 11326, 113260Y (2020).

[4] Muramatsu, M., Nishi, T., Ido, Y., Kitano, T., " Self-aligned double pattern process using DSA pattern," Proc. SPIE 11612, 116120N (2021).



[5] Muramatsu, M., Nishi, T., Ito, K., Takahashi, Y., Hatamura, Y., Kitano, T., " Hexagonal arrays of contact holes with chemo-epitaxial DSA," Proc. SPIE 12054, 1205402 (2022).

[6] Muramatsu, M., Nishi, T., Ito, K., Takahashi, Y., Hatamura, Y., Kitano, T., Iwaki, T., " Pattern fidelity improvement of DSA hole patterns," Proc. SPIE 12497, 124970J (2023).

## Directed molecular self-assembly through photo-thermal processes

Hyeong Min Jin\*

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|  | <p><b>Abstract</b></p> <p>In this study, the effective directed molecular self-assembly processes are presented by introducing the photo-thermal process from diverse light sources. First, how lateral laser writing on graphene substrates enables directional molecular self-assembly will be discussed. The use of a line-shaped laser beam induces the alignment of block copolymers and supramolecular dendrimer patterns by creating a quasi-static order-disorder boundary. Notably, graphene serves as a flexible, conformal layer that efficiently absorbs light, enabling effective photothermal conversion with a low-energy laser. Secondly, rapid assembly process for block copolymers using a high-intensity flash light, which leverages the photo-thermal effect will be discussed. This method allows for rapid heating and quenching, facilitating the self-assembly of high-<math>\chi</math> block copolymers without causing thermal degradation or dewetting. Moreover, the process is compatible with graphoepitaxial patterns, achieving directed self-assembly of block copolymers within milliseconds.</p> |  |
|---|--|---|

### Short biography

Prof. Hyeong Min Jin is currently assistant professor at Chungnam National University in the Department of Organic Materials Engineering. He got his Ph.D. in Materials Science and Engineering at KAIST in 2017 (Advisor: Prof. Sang Ouk Kim), and subsequently worked as a postdoctoral research fellow at the University of Chicago (Adviser: Prof. Paul F. Nealey) in 2018. Between 2019 and 2022, he worked as a beamline scientist for small angle neutron scattering (SANS) at the Korea Atomic Energy Research Institute (KAERI). His research now primarily explores the directed block copolymer and supramolecular self-assembly for nanopatterning applications, and the structural analysis of porous materials through X-ray and neutron scattering techniques.

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# Potentials of Multiblock Copolymers for DSA Applications

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The current directed self-assembly (DSA) process utilizes diblock copolymers composed of polystyrene (PS) and polymethylmethacrylate (PMMA) as standard materials. However, domain pitch of the self-assembled PS-*b*-PMMA,  $L_0$ , are limited due to its weak segregation. In this study, we investigate if we can go further below the lower limit of  $L_0$  by the use of multiblock copolymer (PS-*b*-PMMA)<sub>*n*</sub>. As a proof of concept, we conduct simulations of (PS-*b*-PMMA)<sub>*n*</sub>, using so-called the theoretically informed coarse-grained model of symmetric AB diblock copolymers (A: PS, B: PMMA). Figure 1 illustrates the self-assembled morphology of diblock, tetrablock, and hexablock copolymers obtained from our 2D bulk system. It is clearly seen that the lamellae become smaller and tighter by linking more AB diblocks. Such reduction of  $L_0$  stems from some unique conformations of multiblock copolymer chains, whose details will be presented at the conference.

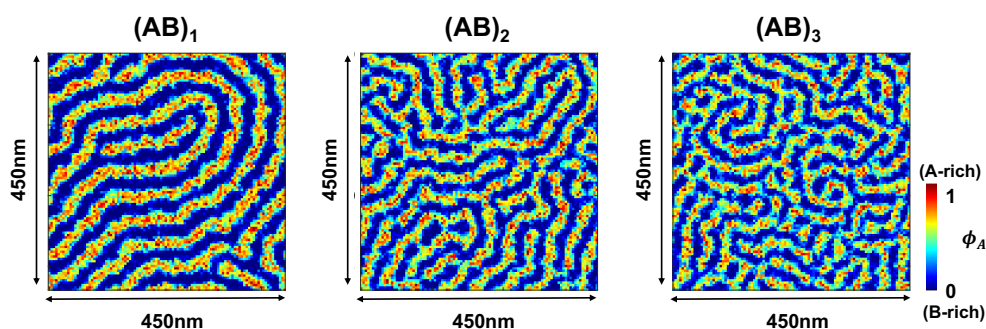


Figure 1. Self-assembled morphology of (AB)<sub>*n*</sub> multiblock copolymer in the two-dimensional bulk system. The color indicates the normalized bead density of A,  $\phi_A$ , with red denoting A-rich region and blue representing B-rich region.

Kenji Yoshimoto is an Associate Professor at Advanced Manufacturing Institute, Kanazawa University (Japan, 2024-). He earned Ph.D. in Chemical Engineering from the University of Wisconsin - Madison (USA) in 2005. Following his postdoctoral training at the Scripps Research Institute (USA, 2006-2007), he began an industry career at Advanced Micro Devices (USA, 2008-2009), and subsequently joined GlobalFoundries (USA, 2009-2012). Transitioning to academia, he served as Program-Specific Associate Professor at Kyoto University (Japan, 2012-2019). In 2019, he moved to Toray Industries, Inc. (Japan), and he lead a computational team until 2023. During this period, he was also affiliated with the Research Association of High-Throughput Design and Development for Advanced Functional Materials (Japan, 2020-2022). Throughout his career, he has conducted extensive research in the simulations of various polymer materials across academia and industry. His current interests include the phase-separation materials and processes, such as the directed self-assembly for next-generation lithography and the non-solvent induced phase separation process for polymer separation membranes.

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# Tetragonally and rectangularly packed hierarchical cylinders from A<sub>1</sub>BA<sub>2</sub>C tetrablock terpolymer

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DSA 2024

## Abstract

Hierarchical cylindrical nanostructures with different diameters (or shapes) have received much attention because of potential applications to next-generation lithography or advanced optical devices. Here, we observed, via small-angle X-ray scattering and transmission electron microscopy, tetragonally and rectangularly packed hierarchical cylindrical nanostructures by tailoring the volume fraction of polystyrene mid-block in polystyrene-*block*-polyisoprene-*block*-polystyrene-*block*-poly(2-vinylpyridine) tetrablock terpolymer (S<sub>1</sub>IS<sub>2</sub>V). P2VP becomes the main cylinder, while PI forms satellite cylinders surrounding the main P2VP cylinder. When the length of PS<sub>2</sub> block is relatively short, tetragonal arrangement of cylinders is observed. But, a rectangular arrangement of cylinders is formed for larger PS<sub>2</sub> block. The experimentally observed hierarchical cylindrical nanostructures are in good agreement with the prediction by the self-consistent field theory [1].



## Short biography

Dr. Jin Kon Kim is currently Professor of Chemical Engineering at the Pohang University of Science and Technology (POSTECH) in Korea. He received his PhD in Chemical Engineering from Polytechnic University (Now, NYU Tandon School of Engineering), New York, in 1990. After working at LG Chemical Co. for 2 and half years, he joined the Department of Chemical Engineering in 1993. He is Namgo Chaired Professor in POSTECH since 2018. He is a director of National Creativity Research Initiative Program of Block Copolymer Self-Assembly supported by Korean Research Foundation since 2004, and the director of National Institute of Nanomaterials Technology (NINBT) during 2020-2023. His research interests include block copolymer (BCP) self-assembly, new functional materials based on BCP, and nanorehology.

He has published more than 320 peer reviewed journal articles, 3 book chapters and 50 patents. He served as an Editorial Advisory Board of *Macromolecules*, *ACS Macro Letters*, *Polymer*, *NPG Asia Materials*, and *Progress in Polymer Processing*. He is a Fellow of American Physical Society (2009) and Royal Society of Chemistry (2023). He has also served as an external board member of LG Chem, LG Hausys and Toray Advanced Materials in Korea.

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## ACHIEVING ULTRA-SMALL FEATURES WITH CHEMICALLY MODIFIED BLOCK COPOLYMERS

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DSA 2024

Block copolymer (BCP) lithography has the potential to produce features smaller than 10 nm; however, realizing practical BCPs for this application remains a significant challenge. In this study, we present the development of a chemically engineered block copolymer that is both reliable and suitable for practical use, achieving sub-10-nm line patterns through directed self-assembly. We synthesized polystyrene-*block*-[poly(glycidyl methacrylate)-*random*-poly(methyl methacrylate)] (PS-*b*-(PGMA-*r*-PMMA) or PS-*b*-PGM), a derivative of PS-*b*-PMMA with 10–33 mol% of PGMA, which is then post-functionalized with thiols. Incorporating 2,2,2-trifluoroethanethiol enhances the Flory–Huggins interaction parameter ( $\chi$ ) of the resulting polymers (PS-*b*-PG<sub>F</sub>Ms) by 3.5 to 4.6 times compared to PS-*b*-PMMA, leading to precisely defined higher-order structures with domain spacings of less than 20 nm. This approach achieves the smallest perpendicular lamellar domain size of 12.3 nm reported to date. Additionally, the directed self-assembly method consistently and reproducibly aligns thin-film lamellar domains vertically, forming line patterns with a half-pitch size of 7.6 nm.



Short biography: Teruaki Hayakawa is a professor in the Department of Materials Science and Engineering at Tokyo Institute of Technology, where he has taught since 2017. He earned his Ph.D. from Yamagata University in 2000 under Prof. Mitsuru Ueda, with early research on  $\pi$ -conjugated polymers and self-organizing materials. Prof. Hayakawa has served as Associate Dean and is involved in various professional organizations, including as Associate Editor for Materials Today Chemistry and a vice president for the Society of Photopolymer Science and Technology. His research has earned him several awards, including the Photopolymer Science and Technology Award (2016, 2020), the SPSJ Wiley Award, and the SPSJ Hitachi Chemical Award.

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## Kinetics and orientation study of fast-assembling fluoro BCPs

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### Abstract

Comparing to EUVL, DSA materials face challenge of high defectivity. Industrial players such as IMEC have suggested that a fast-annealing process could reduce defectivity, finding that the annealing process could be completed within 5 minutes at 250°C, resulting in the disappearance of defects. However, high annealing temperature could cause liability issue by damaging the underneath layer. In this study, series of block copolymers (BCPs) with fluorinated blocks and PS/PMMA-typed blocks were synthesized via reversible addition-fragmentation chain-transfer (RAFT) polymerization and anionic polymerization. The strong interblock interaction resulted in high  $\chi$  values  $> 0.4$  and domain spaces  $< 9$  nm. Self-assembly kinetics were investigated using small-angle X-ray scattering (SAXS) and scanning electron microscopy (SEM). The resulting BCPs were classified into ultra-fast assembly BCPs and functionalized BCPs with slower assembly kinetics. Functionalized BCPs with bulky groups required annealing at temperatures exceeding 160°C for over an hour, whereas fast-assembling BCPs completed self-assembly at temperatures below 80°C within 3 minutes. This rapid assembly was facilitated by the high mobility and low friction of the fluorine-containing blocks, suggesting that assembly speed is independent of the  $\chi$  value. By varying the thin-film thickness (from less than 20 nm to over 65 nm), the orientation of hexagonal microdomains could be altered from parallel (monolayer) to perpendicular to the bare Si substrate. Similarly, the orientation of lamellar microdomains could be changed from parallel layers to perpendicular alignments through chemical modification of the Si substrate.



### Short biography

1984-1988 Sun Yat-sen University, Bachelor in Organic Synthesis

1990-1992 Kyoto University, Master's in Polymer Chemistry

1992-1995 Tokyo Institute of Technology, Ph.D. in Polymer Chemistry

1996-1996 University of Akron, USA, Postdoctoral Fellow in Polymer Science

1997-1998 University of California, Berkeley, Chemistry Department, Postdoctoral Fellow

1998-2000 Rohm and Haas Company, USA, Senior Researcher

2001-2014 Intel Corporation, USA, Photoresist and Litho Material Manager

2014-2015 TOK America, Fellow

2015-Present Fudan University, Professor

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# Design and synthesis of $\pi$ -conjugated polymers for efficient organic photovoltaics

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## Abstract

Bulk-heterojunction organic photovoltaic cells (OPVs) based on  $\pi$ -conjugated polymers as the p-type semiconductor (electron donor) have been intensively investigated in the last few decades since they can enable lightweight, flexible, semi-transparent, low-cost, and low-energy fabrication in contrast to the conventional silicon photovoltaic cells. While polymer-based OPVs with fullerene derivatives as the n-type semiconductor (electron acceptor) afford power conversion efficiencies of more than 10%, those with non-fullerenes show even higher efficiencies over 18%. A key to improving the power conversion efficiency is to control the polymer order as well as the morphology (phase separation) of the blends that determines the charge separation and charge transport processes. Therefore, careful molecular design of  $\pi$ -conjugated polymers to manage the backbone coplanarity and intermolecular interactions is imperative. We have been studying a number of  $\pi$ -conjugated polymers by incorporating various heteroaromatics into the polymer backbone. In this presentation, I will show the design and synthesis of new  $\pi$ -conjugated polymers and discuss how the molecular structure affects the polymer order in the thin film and thereby OPV performances.



## Short biography

Professor Itaru Osaka received his doctoral degree from University of Tsukuba in 2002. After a 4-year research stint at Fujifilm, he worked as a postdoctoral researcher in Carnegie Mellon University in 2006–2009. He then started his professional carrier at Hiroshima University as an Assistant Professor in 2009, and moved to RIKEN as a Senior Research Scientist in 2013. He was appointed as a Professor at Hiroshima University in 2016. His research interests include design and synthesis of  $\pi$ -conjugated materials, in particular, polymers for organic electronics such as field-effect transistors and solar cells.

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**Exploring Directed self-assembly (DSA) in conjunction with EUVL  
for improved pattern quality via molecular simulations**

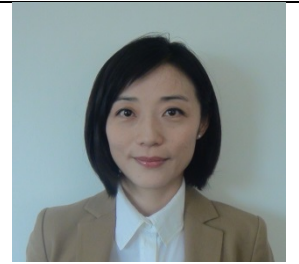
**Su-Mi Hur**

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**Abstract**

Extreme ultraviolet (EUV) lithography, while pivotal for sub-10 nm patterning, encounters significant challenges in controlling pattern quality, particularly in reducing line edge roughness (LER) and defects for high-volume manufacturing. In this context, combining Directed self-assembly (DSA) with EUV lithography, using EUV patterns as 1:1 guiding substrates for DSA, emerges as a promising solution. This study employs coarse-grained molecular simulations to assess DSA's effectiveness in correcting defective line-space or vertically interconnected area (VIA) patterns produced via EUV lithography. We explored various line-space patterns, including variations in LER, pitches, line-space ratios, and bridge defects, as well as hexagonally packed cylindrical patterns characterized by roughness, missing holes, misplacement, and size variations. Our results confirm that DSA significantly reduces LER and effectively eliminates various defect types in EUV patterns, which are major contributors to performance degradation. Additionally, we identified the limits of guiding pattern defects that DSA using linear block copolymers cannot rectify. To address these limitations, we investigated alternative block copolymer architectures to expand the range of structures accessible through DSA.



**Short biography**

Su-Mi Hur obtained her PhD from the Chemical Engineering department at the University of California, Santa Barbara. She continued her research career as a postdoctoral associate at the University of Chicago and Argonne National Laboratory. In 2015, she joined Polymer science and engineering department at Chonnam national university, Korea. Her research expertise lies in applying statistical mechanical theory and field-/particle-based coarse-grained simulations to investigate structural, thermodynamic, and dynamic phenomena in polymer-based soft materials. Her interests also lie in designing macromolecular systems and processes assisted with computational techniques including machine learning.

# ENABLING CHEMICALLY AMPLIFIED RESISTS TOWARDS TIGHT PITCH EUV PATTERNING BY DSA RECTIFICATION

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The use of extreme ultraviolet (EUV) lithography tools at an exposure wavelength of 13.4 nm enables the semiconductor industry to reduce the complexity and cost for the most critical device layers, and ensures continued dimensional scaling. However, heading into the era of EUV lithography, dealing with stochastic variability has become a new reality. As critical dimensions decrease, the significance of stochastics are increasing, while the patterning requirements are getting stricter. This conflict is most apparent for chemically amplified resists, which are suffering from low EUV absorption cross-section, molecular dispersity, and limited etch resistance. In view of this, there is significant interest in alternative resist platforms or auxiliary patterning techniques such as directed self-assembly (DSA). DSA has the capability to rectify EUV resist patterns for dense line/space and hexagonal hole structures [1-3]. Given its resilience to small resist variations, DSA can mitigate the stochastic issue and push EUV patterning close to the resolution limit. In this talk, we will firstly discuss rectification of pitch 24 nm line/space CAR patterns. It is shown how to minimize line edge roughness and line bridge defects of the DSA patterns by tuning the materials in combination with the stack choice and pattern transfer etch processes. Secondly, the use of DSA for rectification of pitch 30 nm hexagonal hole arrays will be presented. A significant challenge lies in controlling the positional offset of the block copolymer (BCP) cylinders (also referred to as the pattern placement error). Strategies to control the pattern placement error will be discussed.



**Lander Verstraete** obtained his master's degree in chemistry from the University of Leuven in 2015. Afterwards, he pursued a PhD in the group of Professor S. De Feyter on the topic of 2D self-assembly of small molecules at the liquid-solid interface. He obtained his PhD degree from the chemistry department at the University of Leuven in 2019. Since then, he joined imec to work on directed self-assembly of block copolymers for logic and memory patterning applications.

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## Progress in the nanopatterning of silicon surfaces with block-copolymer lithography

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### Abstract

The progress in the fabrication of regular surface patterns and nanomaterials with periodicities in the sub-10 and sub-20 nm range is exemplified using two different block-copolymers, PS-*b*-PDMS and PS-*b*-PMMA.

According to the bulk phase diagram in [1], block-copolymers (BCPs) with a large enough combined Flory-Huggins-parameter  $\chi N > 10$  can form ordered domains upon microphase separation. Since this happens even for small degrees of polymerization  $N$ , BCP lithography is a convenient way to create sub-20 or even sub-10 nm structures suitable for applications in microelectronics [2]. For this, one of the polymer species of a BCP thin film is selectively removed and the remaining pattern is used as a nanomask through which material can e.g. be deposited on the substrate. However, the bulk phase diagram is not applicable to thin films because of interfacial energy and strain effects, making predictions difficult. Thus, in order to achieve small ordered lithography structures on a substrate, it is necessary to study the microphase separation of each BCP in detail depending on the processing parameters. In addition, when using the BCP films for lithography applications, dewetting effects of the deposited material on both the mask and the substrate may become dominant in pattern formation.

Here, we report on the progress in nanopatterning of Si surfaces using two different BCPs, PS-*b*-PDMS and PS-*b*-PMMA, the former microphase-separated by solvent vapor annealing (SVA), the latter by thermal treatment in vacuum.

In case of the PS-*b*-PDMS used, due to the high  $\chi$  and a block chain length ratio of  $N_B/N_A \approx 0.25$ , a bcc arrangement of sub-10 nm PDMS spheres in a PS matrix is expected in the bulk-state. For the very thin films necessary for lithography applications we observe by top-view SEM and AFM that depending on the solvents used in SVA either lamellar/cylindrical structures or hexagonal arrangements of cylinders/spheres are formed. Cross-sectional TEM reveals the real shape of domains in the third dimension. The morphology of features and their arrangements are shown to be highly sensitive to slight changes in layer thicknesses and annealing conditions.

In case of the PS-*b*-PMMA, standard procedures [3] are used to fabricate sub-20 nm lamellar PS masks on SiO<sub>2</sub>/Si surfaces. The dewetting of ultra thin electron beam evaporated Au films upon thermal annealing is studied on PS lithography masks as well as on planar PS films and is shown to create interesting morphologies for plasmonic applications.





### Short biography

Jörg K.N. Lindner is a professor for Experimental Physics at Paderborn University, Germany, heading a research team specializing in self-organization based techniques for the large-area fabrication of regular surface nanostructures, using different thin film deposition, plasma and ion beam techniques. Together with his team he develops and employs novel ultra-high resolution transmission electron microscopy techniques for the characterization of nanostructures.

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## Self-assembly and dry etching of high- $\chi$ block copolymers in a microelectronics context

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### Abstract

With the advent of highly incompatible (high- $\chi$ ) block copolymer (BCP) systems, needed for sub-10 nm resolution, interface manipulations by substrate processing and use of top-coats have become critical to obtain well-ordered and usable nanostructures. At LTM, we developed dedicated functional top-coats associated with a 9 nm resolution silicon-containing lamellar BCP, in order to control the mechanical stability of the BCP thin film, choose the local orientation of the lamellas or allow the stacking of several layers of BCPs [1]. Furthermore, combined with anisotropically-treated photo-lithography substrates (plasma-treated spin-on-carbon (SOC) trenches), we recently demonstrated the directed self-assembly of vertical lamellas [2]. Moreover, thanks to the expertise of the laboratory in plasma etching, state-of-the-art transfer results in various substrates could be achieved [3]. Finally, on a more fundamental aspect, the mechanisms driving the interactions between the self-assembly of the BCP and the wetting of the polymer thin film are being explored. This subject is little studied in the literature, even though a fundamental understanding of these mechanisms is crucial both for the control of the (thermo)dynamic stability of the films or to produce more advanced nano-architectures based for example on local modifications of wetting [4].



Marc Zelsmann

### Short biography

After a PhD at the CEA-IRIG in Grenoble on SOI photonic crystals, Marc Zelsmann worked in Ireland, at the Tyndall National Institute, on the development of nanoimprint lithography applied to optics. Since 2006, he has been a CNRS research fellow at the University of Grenoble Alpes at the Laboratoire des Technologies de la Microélectronique (LTM, located inside the CEA-LETI-Minatec facilities). He works on alternative lithographies for microelectronics. He is responsible for the contribution of LTM to several European and French projects and is the coordinator of a French project dedicated to the study of the interrelation between the self-assembly and the stability of block copolymer thin films. He has published more than 80 scientific articles and 13 patents.

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# Doping of silicon at nanoscale by ultra low energy ion implantation through block copolymer templates

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## Abstract

The integration of BCP thin films in conventional lithographic processes has been widely explored in the literature [1] because of the low cost of the self-assembly process if compared to conventional photolithography [2] and the high throughput if compared to serial lithographic processes, such as electron beam lithography (EBL). After selective removal of one of the two blocks, the self assembled polymer thin film can be transferred to the substrate using either subtractive or additive processes. In particular, the nanostructured polymeric masks have been used for lift-off processes to deposit metals, oxides, or other materials.[3,4] Alternatively, they have been employed as sacrificial layers to pattern the underlying substrates by reactive ion etching.[5] Additionally, sequential infiltration synthesis has been explored to convert the organic template into an inorganic one, enhancing etch selectivity and pattern transfer fidelity.[6,7] Surprisingly, the possibility to use those nanostructured polymeric films as a soft mask to promote local modification of the substrate by conventional ion implantation has not been investigated in detail.[8,9] In this work, we explore the possibility to combine ultra-low energy ion implantation and block copolymer lithography to modulate the concentration of dopant impurities in the near-surface layer of a Si wafer. P ions were implanted at 3keV and high dose ( $5 \times 10^{14}$  atoms/cm<sup>2</sup>) into a high resistive Si substrate promoting local amorphization of the top Si layer. Solid phase epitaxial regrowth (SPER) of the implanted region was exploited to activate the P atoms by with a simple thermal treatment at 650°C, preventing P diffusion and preserving spatial localization of the dopant impurities.[10] Activation of dopants was demonstrated by room temperature sheet resistance and hall measurements in van der Pauw configuration. Low temperature measurements highlighted peculiar properties of the heavily doped Si layer in terms of resistivity and magnetoresistance, showing clear evidence of weak antilocalization phenomena and Kondo effect.[11,12] Performing the same process through nanostructured polymeric thin films obtained by block-copolymer self-assembly used as masks excellent control of lateral distribution of P ions was demonstrated. Local electrical characterization by scanning capacitance and conductive force microscopy confirmed the localization and activation of the dopants. The experimental results highlight the possibility to locally modify the potential landscape and conductivity of a semiconductor substrate by a periodic modulation of dopants. Deterministic control on the localization of dopants at nanoscale could be exploited to promote engineering of the semiconductor band structure, synthesis of artificial crystals, or formation of quantum dot arrays in a semiconductor host matrix.



## Short biography

Michele Perego received the Degree in Physics from Università degli Studi dell'Insubria in 1999. In February 2004 he obtained the PhD in Physics, Astrophysics and Applied Physics from the University of Milano. In the period 2004-2007 he has been Post-Doctoral Fellow at the MDM Laboratory. He has been employed as a Research Scientist from 2007 to 2019 at IMM-Unit of Agrate Brianza. In 2019 he became Senior Research Scientist. Since 2020 he has been appointed Research Director at CNR-IMM. He is interested in the development of novel strategies to control matter at the nanoscale, integrating self-assembling materials into conventional top-down processes.

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