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Published in:
Science Bulletin

Link to article, DOI:
10.1016/j.scib.2019.06.001

Publication date:
2019

Document Version
Publisher's PDF, also known as Version of record

Link back to DTU Orbit

Citation (APA):
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1. Introduction

Nanotechnology has a revolutionary impact in the twenty-first century. Nanofabrication technologies are instruments and methods that enable the fabrication of surfaces such as freely suspended nanotubes or nanowires. As developing custom instruments is required to advance this emerging technology, we discuss the evolution of ice lithography instruments and highlight major instrumentation advances. Finally, we present the perspectives of 3D printing of functional materials using organic ices. We believe that we barely scratched the surface of this new and exciting research area, and we hope that this review will stimulate cutting-edge and interdisciplinary research that exploits the undiscovered potentials of ice lithography for 3D photonics, electronics, and nanodevices for biology and medicine.
energetic electrons, leading to the formation of a solid deposit. Because of its working principle, the FEBID process speed is slower than that of EBL. Nevertheless, a dramatic development in FEBID is the creation of a free-standing truncated icosahedron with the characteristic edge dimension down to 200 nm [12], which is unachievable by EBL.

Invented in 2005, ice lithography (IL) is a versatile technique, and it has shown great potential in fabrication of 3D nanostructures. In this review, current status and future perspectives of IL are presented. Furthermore, it also covers different ice resists and IL instrument design. Special emphasis is placed on advantages of IL for 3D nanofabrication.

It is important to point out that IL is a nanolithography tool, and for many applications, EBL and FEBID are more suited than IL. For instance, FEBID is a more powerful method for building extremely small 3D nanostructures. For 2D patterning on larger samples, EBL resists can be applied uniformly by spin coating, and EBL provides faster patterning speed than IL. In EBL, an additional conductive layer such as an Al thin-film can be applied on the top of thick resist layer to relieve undesired charging effects, and Al can be removed before resist development. However, this strategy is not applicable to IL, since a metal film covering on water ice will affect the further patterning process.

2. Ice lithography method and performance

The Nanopore group at Harvard University first proposed ice lithography [13]. The basic principle of ice lithography is simple. Provided by a gas injection system (GIS) inside an electron microscope, a precursor gas condenses on a cold surface is exposed by a focused electron beam. This brief description shows similarity to FEBID. A closer look at the process flow of IL in Fig. 1, however, reveals that IL is an electron-solid-surface interaction while FEBID is an electron-gas-surface interaction. During IL, vaporized material firstly condenses onto the precooled sample (130 K) and forms a uniform amorphous ice thin-film. Then the e-beam exposes the ice layer to generate nanoscale patterns. This is a subtractive patterning process for water ice, where ice within exposure areas vanishes (Fig. 1b and c). The mechanism is yet unclear, but probably due to electron-stimulated reactions at solid water [14,15]. Final pattern transfer is realized through metallization. All above IL processes are accomplished in one instrument except the last lift-off step or "melt-off" step. For alkane ice, cross-linking occurs during cooling process for water ice, where ice within exposure areas vanishes (Fig. 1b and c). The mechanism is yet unclear, but probably due to electron-stimulated reactions at solid water [14,15]. Final pattern transfer is realized through metallization. All above IL processes are accomplished in one instrument except the last lift-off step or “melt-off” step. For alkane ice, cross-linking occurs during cooling process for water ice, where ice within exposure areas vanishes (Fig. 1f and g). The...
3. Toward 3D nanofabrication

3.1. Fabrication on non-flat surfaces

Interest for fabrication on non-flat surfaces is growing in different fields such as micro- and nano-optics, MEMS, and biophotonics. For example, in optics, an aplanatic lens with aberration correction consists of at least two elements, while optical metasurfaces can manipulate light at the subwavelength scale and exhibit aberration correction function using a single element. However, the fabrication of an aplanatic metasurface is challenging, because one necessary step is to pattern nanostructures on a curved surface [26]. Another example is the realization of miniature optical instruments such as endoscopes and fiber-imaging systems, which also relies on advanced 3D nanofabrication techniques [27].

The first advantage of IL is to process samples with non-flat and irregular surfaces. Different from spin coating of EBL resists, ice resists are able to coat all accessible freezing surfaces of the sample during ice deposition [17]. This is nicely illustrated by patterning on AFM probes. First, a well-controlled water vapor condenses on a pyramidal tip of an AFM probe. Second, water ice then is removed by patterning a rectangle area centered on the tip by the focused e-beam, which reveals the underlying tip. Third, with in-situ metal deposition, Au with Ti adhesive layer covers the entire probe including the exposed tip. Finally, after immersing the sample in isopropanol and melting water ice at room temperature, the pyramidal surface is clean and residual-free, and only a Ti/Au cap remains on the AFM apex (Fig. 3a inset).

The second advantage of IL is the ability to pattern on a tiny and fragile nanostructure, exemplified in the case of suspended single-walled carbon nanotubes (SWCNT). It is very interesting and also extremely challenging. Here, the suspended carbon nanotubes were grown over a trench in a very thin and fragile free-standing silicon nitride membrane [17] (Fig. 3b inset). Spin and spray coating of EBL resists can not apply a uniform layer of resist onto such suspended nanotubes, and the surface tension during resist drying

The critical dose in IL is less dependent on resist thickness. Moreover, the critical dose for nonane ice is two orders of magnitude smaller than water ice. Hence, it is much faster to process organic ices and allows larger patterns.

Table 1

<table>
<thead>
<tr>
<th>Method</th>
<th>Resist/Precursor</th>
<th>Tone</th>
<th>Electron energy (keV)</th>
<th>Contrast $\gamma$</th>
<th>Sensitivity ($D_{50}$, mC/cm²)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>IL</td>
<td>$H_2O$</td>
<td>Positive</td>
<td>5, 20</td>
<td>1.84, 2.24</td>
<td>200, 450</td>
<td>[20]</td>
</tr>
<tr>
<td>IL</td>
<td>$C_7H_8O$</td>
<td>Negative</td>
<td>5, 20</td>
<td>0.91, 1.03</td>
<td>3, 15</td>
<td>[22]</td>
</tr>
<tr>
<td>IL</td>
<td>$C_8H_{18}$</td>
<td>Negative</td>
<td>80</td>
<td>1.62</td>
<td>40</td>
<td>[19]</td>
</tr>
<tr>
<td>IL</td>
<td>$C_9H_{20}$</td>
<td>Negative</td>
<td>5, 20</td>
<td>1.8, 4.3</td>
<td>2, 10</td>
<td>[21]</td>
</tr>
<tr>
<td>IL</td>
<td>$C_{11}H_{24}$</td>
<td>Negative</td>
<td>80</td>
<td>1.43</td>
<td>20</td>
<td>[19]</td>
</tr>
<tr>
<td>IL</td>
<td>$C_{14}H_{30}$</td>
<td>Negative</td>
<td>80</td>
<td>0.18</td>
<td>20</td>
<td>[19]</td>
</tr>
<tr>
<td>EBL</td>
<td>PMMA</td>
<td>Positive</td>
<td>50</td>
<td>5.4</td>
<td>0.42</td>
<td>[23]</td>
</tr>
<tr>
<td>EBL</td>
<td>HSQ</td>
<td>Negative</td>
<td>70</td>
<td>5</td>
<td>0.15</td>
<td>[24]</td>
</tr>
<tr>
<td>FEBID</td>
<td>$MeCpPtMe_3$</td>
<td>Negative</td>
<td>20</td>
<td>–</td>
<td>250*</td>
<td>[25]</td>
</tr>
</tbody>
</table>
will destroy the nanostructure. However, water ice resist can condense on cold carbon nanotubes. After e-beam removal of the ice, Ti is deposited onto the surface of the nanotube as a seed layer for Al₂O₃ growth by atomic layer deposition (ALD). The IL patterning combined with ALD processing can precisely control the locations and sizes of the Al₂O₃ particles.

For the third advantage, we are able to observe nanostructures under the ice resist through SEM imaging, benefiting from the very low sensitivity of water ice. It is not possible with a sensitive EBL resist, as SEM imaging would expose the resist. This advantage is illustrated in Fig. 3c by patterning on a single nanowire, whereupon we can align nanoparticles neatly [20]. The diameter of the nanowire is 160 nm, and the alignment accuracy is less than 50 nm.

### 3.2. Nanoscale additive manufacturing

Additive manufacturing (AM), also known as 3D printing or rapid prototyping, refers to a class of manufacturing processes, which enables unprecedented engineering and production possibilities. In AM, a part is built by adding layers of material on top of one another, and AM objects are fabricated from metals, ceramics and opaque plastics. Examples of AM methods are inkjet printing [28], stereolithography [29], two-photon polymerization [30], and FEBID. For EBL, patterning related to premade nanostructures is usually obtained through overlay process. Such a stacking layer strategy can also be regarded as an AM processing, where the fabrication of each layer needs a series of procedures including spin-coating, lithography, developing, deposition and lift-off. Here, additional markers should be fabricated previously around the exposure area for registration and alignment between layers. However, none of these technologies is able to deliver AM on the nanoscale with competitive throughput, and achieve a balance among resolution, alignment, stability, and adaptability.

Ice lithography with water ice enables marker-less fabrication, which results in much fewer processing steps required for fabricating 3D nanostructures [20]. Fig. 4 shows fabrication of a pyramidal nanostructure by repeating ice deposition, e-beam exposure and metallization three times. Here, 10 processing steps and one load-unload operation on the instrument are required. In comparison, the EBL procedure for fabricating such a structure includes 19 processing steps and 8 load-unload operations. IL can also implement similar architecture with organic ice (Fig. 4k) through the cycle of deposition and exposure [18]. Moreover, applying the strategy of greyscale lithography, IL with water ice successfully fabricates partially suspended nanostructures like a mushroom (Fig. 4l) or a bridge (Fig. 4m). This flexible approach combined with layer-stacking strategy brings new and exciting opportunities in 3D nanofabrication.

![Fig. 4.](Image)

Fig. 4. (Color online) 3D layered and suspended nanostructures produced by IL. In-situ SEM images after different processing steps including ice deposition (a, d, and g), e-beam exposure (b, e, and h) and metallization (c, f, and i). A pyramidal nanostructure obtained using water ice (j) or organic ice (k), with corresponding line scan by AFM. Similar to greyscale lithography, IL can also realize 3D mushroom-like (l) and bridge-like (m) nanostructures. Figure reproduced with permission: (a-j, l, and m) Ref. [20], Copyright 2018 ACS; (k) Ref. [18], Copyright 2017 ACS.
4. IL instrument and its evolution

Cutting-edge instrument research and development is the fundament of ice lithography research. Depending on the type of ice resists, an IL instrument consists of 5 or 6 subsystems (Fig. 5a). Subsystems 1 and 2 are off-the-shelf equipments, while the others are highly specialized.

1. The electron beam is provided by a scanning electron microscope (SEM).
2. An EBL module is needed for e-beam patterning.
3. A specially designed cryostage for sample cooling, and a cold trap to shield the sample from vacuum contaminants is required. A heater is fitted into the cryostage for the sublimation of organic ice.
4. Water or organic vapor is injected into the SEM chamber through a custom gas injection system, which also controls the deposition rate and final thickness of ice thin-films.
5. A load-lock allows fast sample transfer and exchange, while maintaining vacuum and cryogenic conditions in the process chamber.
6. For processing water ice, an additional integrated metallization system is necessary. In this metallization system, another cryostage is included to suppress the sublimation of water ice during thermal evaporation or magnetron sputtering of materials.

In 2005, the first report on nanopatterning ice with e-beam was carried out using a cryosystem designed for biological applications [13]. However, this instrument was ill-suited for IL. Five years later, in 2010, the same research group demonstrated the successful IL process for device fabrication, and the first dedicated IL instrument was reported [31].

Inspired and guided by the design and challenges of the original IL system, another two instruments have been constructed at Technical University of Denmark (DTU) [21] and Zhejiang University (ZJU) [20], respectively. The DTU design (Fig. 5b) is very accessible and modular. Only the load-lock is permanently installed on the SEM, while the other parts can be quickly removed, enabling flexible switching between an IL instrument and an SEM imaging system. Without a metallization system, the DTU IL instrument focuses on nanofabrication using organic ice resists. In contrast, the IL instrument in China (Fig. 5c) includes two metallization chambers. The small chamber is equipped with a “single-pot” evaporator, while the big ultrahigh vacuum (UHV) chamber with several metal sources allow high quality epitaxial thin-film deposition. Therefore, this instrument can also be used for in-situ characterization of thin-films growth at low temperature. To our best knowledge, the ZJU instrument is the most advanced instrument today. The research field is growing, and at least four other instruments around the world are under construction and development.

5. Opportunities and future perspectives

This review has shown that ice lithography appears highly promising for simplifying and streamlining fabrication and advancing 3D nanofabrication. We believe that there are many more unexplored opportunities in nanoscale additive manufacturing of functional materials. Using organic ices, the deposited

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Fig. 5. (Color online) (a) IL instrument consisting of 5 (for organic ice) or 6 subsystems (for water ice). (b) IL instrument at Technical University of Denmark. (c) IL instrument at Zhejiang University.
material is a cross-linked product of the original organic ice. The resulting product shares common features with polymers of the original organic molecules. E.g. if alkane ices are used, the e-beam cross-linked product is chemically similar to cross-linked polythene. We hypothesize that polymer analogues with sufficient mechanical and dielectric properties can be additively fabricated by condensation of monomers and e-beam irradiation.

Apart from carbon and oxygen containing organic chemicals, organometallic compound that contains most elements of the periodic table is a very interesting class of organic chemicals. FEBID using organometallic precursors showed that pure gold (Au) [32] and superconducting tungsten (W) nanowires [33] can be formed. Using liquid phase precursors, FEBID can also deposit silver (Ag) and copper (Cu) structures [34], respectively. We hypothesize that metal can be additively made by freezing organometallic compounds, cross-linking by e-beam and post processing. This will pave the way for nanoscale 3D printing of nanophotonic and electronic devices.

Since organic semiconductor chemistry is also a branch of organic chemistry, we hypothesize that it is possible to condense and cross-link organic semiconductors. If IL is able to 3D print organic dielectrics, electric conductors, and semiconductors, it is likely that we could 3D print and do rapid prototyping of nanoelectronic devices. Hence, we propose the concept of icetronics.

Regarding to lithography perspectives, although this approach has many advantages, such as sub-10 nm resolution, easily doing lift-off and patterning on non-planar and fragile substrates, an essential issue is still not very clear: why and how ice lithography works. Both the underlying physics of electron-matter interactions and the science behind transforming ice into what it becomes after exposure need to be investigated in detail. Particularly, what else ice is effective as a positive-tone resist in IL, remains an open question. To investigate the principle of IL and approach its ultimate resolution will undoubtedly have major impact on 3D manufacturing.

For instrumentation perspectives, the current cryostage in IL instrument is cooled by liquid nitrogen, and its lowest temperature is around 130 K. More efficiently cooling is beneficial for exploring the ice resist with low freezing point, such as frozen CO2, which has been applied to the dry lithography of organic semiconductors [35]. Moreover, none of the current IL instruments allows injection of two or more precursors and fast and automatic switching among them. In the future, a new prototype instrument equipped with more in-situ characterization techniques including a nanomanipulator for electrical measurement and nanoprofilometer for thickness measurement of ice thin-films, will provide more thorough understanding and more striking applications of IL. Finally, IL is a scalable technology, thanks to the development of multi-e-beam technologies with over 600,000 parallel e-beams [36]. High throughput production of 3D nanodevices is possible by combining IL and multi-e-beam technology.

Conflict of interest

The authors declare that they have no conflict of interest.

Acknowledgments

This work was supported by the National Key Research and Development Program of China (2017YFA0205700) and the National Natural Science Foundation of China (61425023). D.Z. acknowledges support from the European Union’s Horizon 2020 research and innovation program under the Marie Sklodowska-Curie grant agreement No. 713683.

Author contributions

D.Z., A.H. and M.Q. discussed and prepared the review; all authors discussed and contributed to the final manuscript.

References


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