

# Lithography Techniques For Advanced Materials

S. Madhava Reddy, K. Sudhakar Reddy, J Pavan Kumar

**Abstract:** The objective of the paper is to provide an overview of advances and developments with lithography. The need for high resolution and cost effective surface patterning techniques to develop advanced functional materials with characteristic surface properties resulted in tremendous amount of research in the last few years. Lithography is the influence on production costs of integrated circuits. Advanced lithography techniques with fundamentally diverse principles have been proposed and conventional ideas have been modified to push the limits of micro- and nano-patterning on metallic, ceramic, polymeric and biological surfaces.

**Index Terms:** Lithography; nano-patterning; micro manufacturing; material design.

## 1. INTRODUCTION

The development of high performance integrated circuits and micro scale chips sparked the need for micro and nano-patterning techniques such as lithography that can generate feature sizes ranging from tens of millimeters to few nanometers. Micro and nanolithography are the key technologies in manufacturing of integrated circuits. Masked lithography techniques such as photolithography, soft lithography, and nano-imprint lithography and mask-less lithography techniques such as electron beam lithography, focused ion beam lithography, and scanning probe lithography have been developed and been in extensive use to create patterns with different architectures and depth on the material surface. These techniques have been extremely useful and were applied successfully to produce micro-electromechanical systems (MEMS), nano-electromechanical systems (NEMS), advanced ICs, micro and nano-fluidics, bio- and gas-sensors, bio-electronics and to develop advanced functional materials with bio-inspired, electronic and optical properties [1, 2]. However the thirst for high resolution surface architectures, throughput and economically feasible lithographic processes resulted in tremendous amount of research with modifications in the conventional lithographic processes and also led to the discovery of new patterning techniques. An exhaustive review of all the lithographic techniques developed in the last few decades is a tedious task and is out of the scope of the present work. Here in, we present a concise review of very recent developments made in lithographic techniques particularly focusing the method viz., beam pen lithography, nanomotor lithography, coaxial lithography, atomic layer deposition lithography, photon upconversion lithography, oxygen-inhibition lithography, membrane projection lithography, meniscus mask lithography, and marker pen lithography.

## 2. LITHOGRAPHY TECHNIQUES

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### 2.1 Beam Pen Lithography

Beam pen lithography is a low cost and high throughput soft lithographic technique that doesn't need sophisticated clean rooms for nano patterning and finds its application in photochemical and biological studies. It combines the principles of polymer-pen lithography and near-field scanning optical microscopy to create large scale patterning with feature sizes above and below the diffraction limit of light. Huo, F. et al., [3] demonstrated this technique (Figure 1) by fabricating transparent pyramid shaped polymer (polydimethylsiloxane) arrays with edges several tens of micrometres in length and tip diameters of around 100 nm. Using thermal evaporation, a layer of gold is coated on the polymer pyramids and the array is then brought into contact with adhesive surface of poly (methyl methacrylate). The adhesive coated surface removes the opaque gold layer from the apex of each tip and creates apertures exposing the transparent polymer. Light exposed above the polymer array passes through the apertures of tips and single dot feature per tip can be created on a photo resist coated surface placed below. By controlling the contact force of the polymer arrays on the adhesive surface, the diameters of the apertures and thus the feature sizes can be varied.

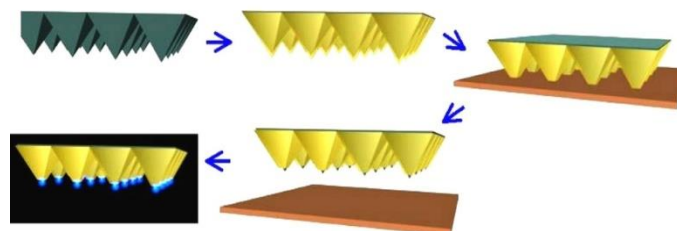
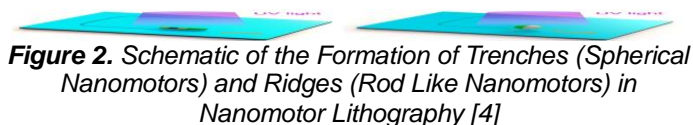


Figure 1. Schematic of Process Flow in Beam Pen Lithography [3]

### 2.2 Nanomotor Lithography

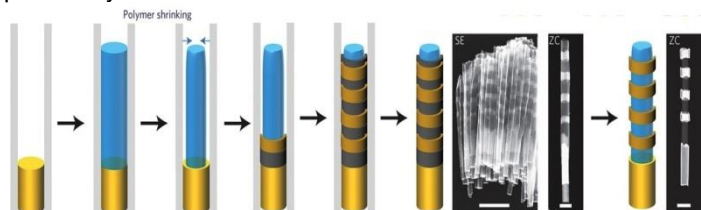
Nanomotor lithography provides an affordable and simpler alternative to the current nanofabrication methods to produce complex surface patterns. Jinxing Li et al., [4] successfully demonstrated this interesting technique inspired by natural nano machines. This method translates the movements of chemically powered, self propelled and magnetically controlled nanomotors or nanorobots into nano scale structural features by the use of light focusing and light blocking characteristics of the nano motors (Figure 2). The scientific team synthesized spherical nanomotors made of silica, and rod-shape nanomotors made of metal. When UV light is radiated onto the photo resist, the moving spherical nanorobot focuses the light like a near-field lens, to build a trench pattern, while the rod-shape nanorobot blocks the light to create a ridge pattern.



**Figure 2.** Schematic of the Formation of Trenches (Spherical Nanomotors) and Ridges (Rod Like Nanomotors) in Nanomotor Lithography [4]

### 2.3 Coaxial Lithography

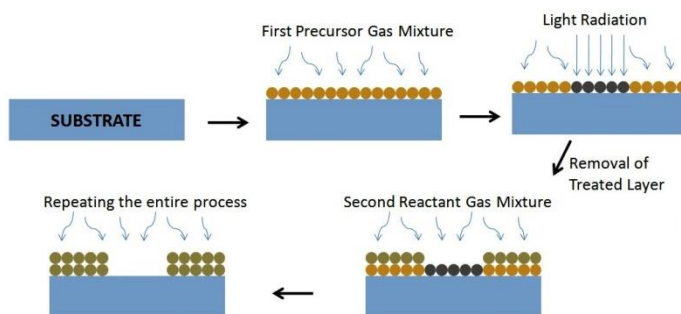
The intrinsic constraints of conventional synthetic and lithographic techniques limit the types of nanowire material structures that can be produced. To overcome this Tuncay Ozel et al., [5] developed a high-throughput coaxial lithography process to prepare coaxial nanowires composed of combinations of metals, metal oxides, metal chalcogenides and conjugated polymers with sub 10 nm control over structural parameters. The technique bridges templated electrochemical synthesis and ordinary lithographic process to create coaxial nano wires. In this technique, gold was electrochemically deposited into the nanopores of an aluminium oxide template, followed by deposition and shrinking of polymer in vacuum. A multi-segmented shell around the polymer was then obtained by depositing sacrificial nickel layer and gold at regular intervals. Subsequent dissolution of alumina template and etching of nickel layer produced coaxial nanowires with a polymer core and segmented gold outer shell. The schematic of the process along with the scanning transmission electron microscopy (STEM) images of the produced structures are shown in Figure 3. The team also demonstrated the synthesis of a core/shell semiconducting nano wire with an embedded plasmonic nano ring that cannot be prepared by any previously known method.



**Figure 3.** Schematic of Coaxial Lithography Process to Produce Coaxial Nanowires and STEM images of the nanowires [5]

### 2.4 Atomic Layer Deposition Lithography

This new technique has been patented recently and was developed to control process defects with minimum structure damage in a lithographic process. Banquiu Wu et al., [6] demonstrated this method by combining the aspects of atomic layer deposition and lithographic processes. Initially, a monolayer of material is deposited on a substrate from a first precursor gas mixture. Selective areas are treated with light radiation and are removed. Then second reactant gas mixture is pulsed onto the first monolayer selectively to form a second monolayer. By continuously repeating the process of selective radiation treatment of the deposited monolayers, and subsequent atomic layer deposition produces structures with minimal defects and structure damage caused by ordinary lithographic and etching processes. The schematic of the process is shown in Figure 4.



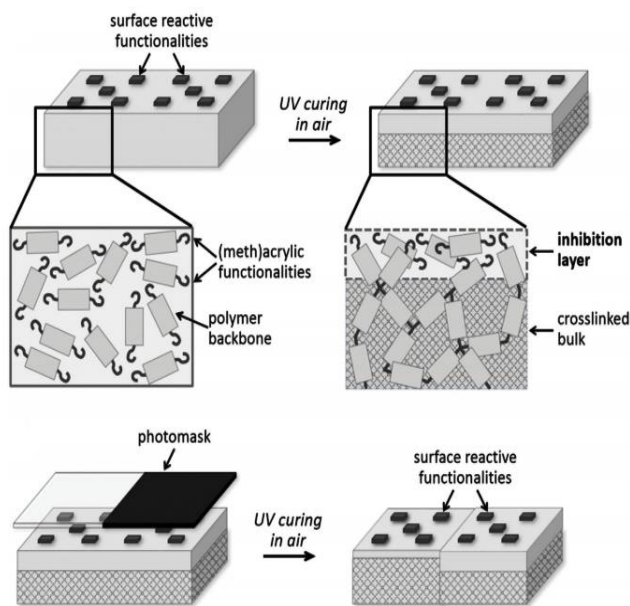
**Figure 4.** Schematic of Process Flow in Atomic Layer Deposition Lithography. Redrawn Based on [6]

### 2.5 Photon Upconversion Lithography

This is a modified photolithographic technique developed mainly to pattern biomaterials using near-infrared light. Patterning of biomaterials using light prevents contact contamination of biological systems and provides high spatial and temporal resolution. Most photolithographic processes employ UV light or near infrared light. However, UV light cannot penetrate deep into the tissue of a biomaterial and lacks spatial resolution, while patterning using near infrared light based on two-photon absorption is time consuming. Taking this into account, Zhijun Chen et al., [7] demonstrated a new photolithographic technique that uses near infrared light via lanthanide doped upconverting nanoparticle (UNCP) assisted photochemistry. Proteins were adsorbed onto the UNCP-decorated surface cografed with Ru complex and polyethylene glycol, via electrostatic interactions. In the exposed areas via a photomask, UNCPs convert near infrared light into blue light that cleave the Ru complexes and induced local release of proteins, thus fabricating the protein patterns.

### 2.6 Oxygen Inhibition Lithography

Oxygen inhibition lithography (Figure 5) developed by Vitale, A et al., [8] is a modified photolithographic technique that makes use of oxygen inhibition which is often treated as a problem in photo-polymerization and photo-curing, during ultra-violet curing in air to obtain multi-ssurfaces. When the multifunctional (meth)acrylic monomcale and multi-material patterns on material ers are UV irradiated, the bulk of the sample is transformed into a cross linked network but the surface remains liquid due to oxygen inhibition. The inhibition layer of monomer is irradiated using UV in air using a photo mask, to create polymeric patterns on top of the polymeric substrate. Finally UV exposure on the substrate is done under nitrogen to completely cure the selected regions, followed by development of the uncured resin. The research team believe that the patterned layers will have excellent adhesion and that the method is robust, cost efficient and reproducible.



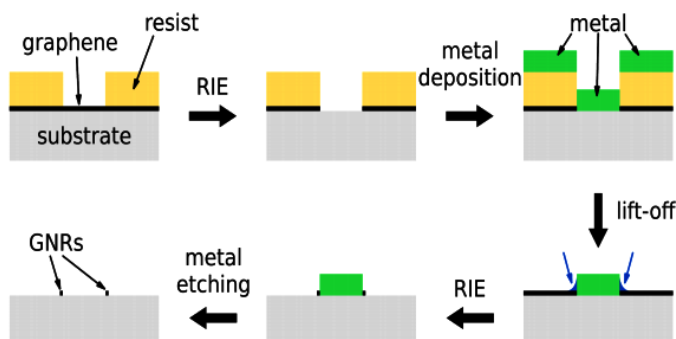
**Figure 5.** Schematic of Oxygen Inhibition Lithography Method to Produce Polymeric Structures [8]

### 2.7 Membrane Projection Lithography

Recently patented membrane projection lithography process includes planar lithography followed with a sequence of processing steps to create micro-scale 3D structures with out of plane components. This technique developed by D. Bruce Burckel et al., [9] starts with a standard planar lithographic process to pattern the membrane. The holes in the membrane are used to allow for local dissolution of substrate by generating cavities underneath the membrane by the use of suitable etching medium. After the cavities underneath the membrane are obtained, directional evaporations are used to position the membrane on the walls of the cavities. The decorated cavity is obtained after a final lift off. The matrix material can be monocrystalline or polycrystalline silicon, gallium arsenide, germanium, dielectric materials such as silica and silicon dioxide or non-conducting materials based on the desired characteristics. Sacrificial backfill materials may include silicon, silicon dioxide, polyimide, or photoresist. Membrane materials may include photoresists, silicon, silicon dioxide, silicon nitride, metals, and nitrides or other compounds of metals.

### 2.8 Meniscus Mask Lithography

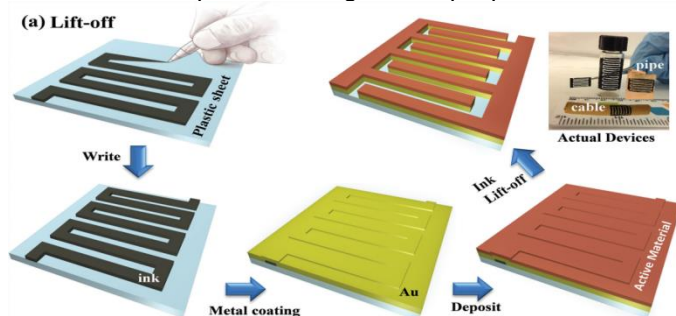
Meniscus mask lithography is a simple planar top-down method developed by Abramova et al., [10, 11] to produce sub 10 nanometer narrow graphene, nanoribbons, metallic and semiconductor nanowires of a variety of materials like silicon, silicon dioxide, chromium, tungsten, aluminum, gold, titanium and titanium dioxide. This highly reproducible technique does not require highly sophisticated and high resolution lithography tools. The tendency of water to adhere to surfaces was taken advantage to use it as a mask to make patterns. Wherever a raised pattern joins the target material, the water molecules join together and form a curved meniscus due to surface tension. The process thus involves masking by water adsorbed at the edge of the pattern written on top of the target material. Figure 6 represents the schematic of the process to produce graphene nanoribbons. They were able to obtain nano wires of widths from 6 to 16 nm.



**Figure 6.** Schematic of Meniscus mask Lithography to Produce Graphene Nanoribbons [11]

### 2.9 Marker Pen Lithography

Qiu Jiang et al., [12] proposed and experimentally demonstrated a simple and a low cost lithographic method to fabricate flexible and curvilinear micro super-capacitors. The technique (Figure 7) involves hand-written sacrificial ink patterns using commercial marker pens on substrates. The team took advantage of the solubility contrast of the written ink patterns between aqueous and organic media, to deposit electro active materials using aqueous electrolytic baths. The method is then followed by lift-off of the ink in acetone or alcohol. The authors argue that multi-stack patterning of materials is also possible using this simple pen method.



**Figure 7.** Schematic of Marker Pen Lithography Process [12]

## 3. APPLICATIONS OF NEXT GENERATION PATTERNING TECHNIQUES

Beam pen lithography is a technique to create arrays of patterns with wide range of feature sizes based on the contact force of the polymeric tips. A variety of materials can be patterned using this method. Nanomotor lithography is a simple method that uses the movements and light transmission properties of self or externally propelled nano motors. The feature sizes that can be obtained depend on the size of the nanomotors and the method will find its use in patterning wide range of material surfaces. Coaxial lithographic technique is developed to create conducting or semi conducting nanowires with co axial layers of materials. Metallic, metal oxide, metal chalcogenides and polymeric materials can be patterned using this technique. Sub 10 nm resolution in both axial and radial directions of nanowires can be achieved in this technique. Atomic layer deposition lithography combines the principles of atomic layer deposition process and lithographic method to selectively deposit and etch the monolayers of materials. The substrate materials may include any non conductive, dielectric materials, metal nitrides and alloys. Photon upconversion technique uses near infra red light via UNCP assisted photochemistry and is particularly suitable for biological materials and proteins. Oxygen inhibition

lithography uses oxygen inhibition layers of monomers and UV irradiation to create polymeric patterns. This method is strictly limited to polymeric materials. Membrane projection lithography is a method developed to be able to produce 3D structures using a sequence of steps. The matrix material that can be used in this technique may be semi-conducting, dielectric and non-conducting materials based on the desired characteristics. Membrane materials may include photo resists, silicon, silicon dioxide, silicon nitride, metals, and nitrides or other compounds of metals. Meniscus mask lithography is a simple and highly reproducible planar top-down method that takes the advantage of the tendency of water to adhere to surfaces, to produce sub-10 nanometer narrow graphene nanoribbons, metallic and semiconductor nanowires of a variety of materials like silicon, silicon dioxide, chromium, tungsten, aluminium, gold, titanium and titanium dioxide. Marker pen lithography is a simple and a low cost lithographic method to fabricate flexible and curvilinear micro super-capacitors on polymeric sheets and the feature sizes depend on the diameter of the tip of the marker pen.

#### 4. CONCLUSION

The advances in lithographic processes discussed above were the result of the need for low cost, high throughput and high resolution techniques that can produce complex patterns on the material surface with relative ease. These advanced techniques provide a fruitful contribution to the pace of MEMS/ NEMS industry and in the development of advanced surfaces with functional properties such as optical, electronic, superhydrophobic, superhydrophilic, wear and adhesion.

#### 5. ACKNOWLEDGMENT

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