Materials and Failures in MEMS and NEMS

Edited by Atul Tiwari and Baldev Raj
Materials and Failures in MEMS and NEMS
Materials Degradation and Failure Series

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Manufacturing, diagnosis and treatment of biospecies, agriculture, energy and infrastructure, governance, security, etc., need sensors and devices based on well-grounded concepts, engineering and technology. Miniaturization demands new materials, designs and fabrication technologies. The decrease in the size and volume of devices has necessitated the incorporation of a high level of fabrication technologies. There is a priority need to address failures in micro- and nanodevices.

The invention of Microelectromechanical Systems (MEMS) and Nanoelectromechanical Systems (NEMS) fabrication technologies has revolutionized the science and engineering industry. It is estimated that market prospects for MEMS and NEMS will increase rapidly to reach $200 billion in 2025. The key to the success of MEMS and NEMS will be the development of technologies that can integrate multiple devices with electronics on a single chip. Among the technologies available so far, the fabrication of MEMS and/or NEMS has been predominately achieved by etching the polysilicon material. Novel materials and technologies are being explored to overcome the challenges in fabrication or manufacturing processes. In order to meet the ever-increasing demands of MEMS and NEMS, enormous amounts of research, applications and innovations have been explored and exploited. Most of the relevant information originating from such efforts is being treated as confidential or privileged, which seeds extensive barriers to the research, development and aspirational demands of these technologies.

This book includes chapters written by eminent experts in the area of MEMS and NEMS. The opening chapter of this book reviews various C-MEMS fabrication technologies involving patterning of polymeric precursors of carbon such as epoxy photoresists and sol-gel polymers, followed by pyrolysis to generate glassy or semicrystalline carbon. Another chapter discusses the origins of fault in such devices, related mathematical models and utilization of filters in fault diagnosis. Also, the authors have illustrated the structure of a multiple-model adaptive estimator and its application in fault diagnosis simulation. Another chapter provides an overview of the design of MEMS heat exchangers such as heat sinks, heat pipes and two-fluid heat exchangers. The formation of porous silicon devices by electrochemical etching of silicon and the control over the porosity and pore size are discussed in a separate chapter. The use of such porous silicon devices as biosensors is thoroughly investigated by these contributors. Further, a chapter provides an overview on MEMS and NEMS switches using Si-to-Si contact. An interesting chapter discusses the design challenges during fabrication and failure analysis of cMUT devices. Investigators have compared the device fabrication by surface micromachining and wafer bonding techniques. Moreover, failure analysis of cMUT using various materials characterization techniques and their importance for successful device fabrication are also investigated.
A successive chapter investigates an effective approach to solve inverse problems in MEMS and NEMS. This chapter describes inverse problems in micro- and nanomechanical resonators and also the stiction test of MEMS and NEMS. Further, there is a chapter in the book dedicated to the control of ohmic RF-MEMS switches operating under different actuation modes, such as single pulse, tailored pulse, and tailored-pulse optimization methods, based on Taguchi’s technique of resistive damping; and the hybrid actuation mode, which is a combination of the tailored pulse, the resistive damping, and Taguchi’s optimization technique. Additional challenges involved in design methodologies, and available simulation packages to model and simulate MEMS devices are explored in a separate chapter. To develop MEMS devices and to understand the inception of fabrication defects, researchers have explored fabrication techniques such as surface micromachining and bonding silicon to glass. The use of different characterization techniques, such as visual, electrical and mechanical, for inspecting the defects in these devices has also been demonstrated. An independent chapter systematically investigates the buckling behavior of a typical micron-scale constantan-wire/polymer-substrate structure under electrical loading. Another crucial chapter discusses many important aspects of microcantilever sensors such as operation principles, fabrication of silicon and polymer microcantilevers, mechanical and electrical characterization, readout principles, applications of microcantilever sensors for vapor-phase chemical or gas detection, biosensing and agriculture applications; and nanogenerators for energy harvesting. A chapter in the book elaborates the inherent challenges encountered in CMOS–MEMS along with the possibility of integration at board and chip levels. This chapter also lists various circuit architectures being used in capacitance detection along with a detailed comparison on their merits and demerits. The final chapter proposes a mathematical model to determine strategies for preventive replacement and inspection for MEMS that are subject to multiple dependent competing failure processes as a result of degradation and/or shock loads.

We are confident that this book will constitute a large knowledge bank for students, research scholars and engineers who are involved in the research, development and deployment of advanced MEMS and NEMS for a wide variety of applications. To the best of the editors’ knowledge, such a book that addresses the developments and failures in these advanced devices has not yet been available to readers. Comprehensive expertise is mapped out and discussed in this book to advance the knowledge bank of readers in order to enable precise control over dimensional stability, quality, reliability, productivity and life cycle management of MEMS and NEMS.

The editors look forward to constructive suggestions and feedback for improving the next edition of this book on this important, relatively young subject of increasing importance and relevance.

Wishing you a purposeful and wonderful reading experience.

Atul Tiwari, PhD
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Carbon as a MEMS Material

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Abstract
Carbon has become a popular material in microelectromechanical (MEMS) applications because of its versatile electrochemical and mechanical properties, as well as the numerous precursor materials and facile fabrication methods available. This review details various C-MEMS fabrication technologies, most of which involve the patterning of polymeric precursors of carbon such as epoxy photoresists and sol–gel polymers followed by their pyrolysis to create glassy or semicrystalline carbon pattern replicas. The structure and properties of glassy carbon, as well as the pyrolysis process and concurrent shrinkage, are also discussed in detail, as these directly affect the applicability of the carbon structures and devices. The integration of carbon structures in MEMS devices by means of surface modification and the incorporation of additives and fillers such as carbon nanotubes and carbon nanofibers to enhance the functional properties are also discussed.

Keywords: Carbon, C-MEMS, pyrolysis, volumetric shrinkage, MEMS integration, lithography

1.1 Introduction
Carbon is one of the most versatile materials in the periodic table. Due to its ability to form $sp$, $sp^2$, and $sp^3$ hybridized covalent bonds with various elements including itself, carbon-based compounds and materials are amongst the most adaptable materials available to us. The ability of carbon to form bonds with itself is manifested in the form of many allotropes of carbon including fullerenes, nanotubes, graphite, graphene, and diamond. Even within these allotropes, despite being all made of carbon, the properties such as electrical conductivity, hardness, and strength vary widely with allotrope due to different microstructures in terms of crystallite size, long-range order, anisotropy, etc. [1]. Amorphous or glassy carbon, in particular, has a wide window of electrochemical stability as well as high thermal conductivity and excellent biocompatibility, warranting its use in various electrochemical and biological applications [2]. Diamond-like carbon or DLC, another form of carbon, has superior tribological properties and wear...
resistance, and anisotropic carbon materials such as nanotubes and nanofibers can be leveraged for their unique and anisotropic electromechanical properties as well [2–4].

When this versatility in functional properties is combined with appropriate micro/nanofabrication techniques, carbon structures become highly viable as elements in micro and nano electromechanical systems (MEMS/NEMS). In order to create micro- and nanosized electromechanical structures such as actuators and microsensors from carbon, appropriate robust and facile micro/nanofabrication techniques have to be adopted. The methods to pattern carbon and its precursors into MEMS structures are divided, like other microfabrication techniques, into top-down and bottom-up techniques. Top-down techniques are subtractive processes such as reactive ion etching (RIE) and lithographic patterning with photons, electrons, or ions. Bottom-up or additive processes include sputtering, evaporation, and chemical vapor deposition (CVD) [5]. While top-down techniques create deterministic patterns with good shape and size control, bottom-up techniques result in increased functionality and have greater capability for three-dimensional (3D) patterns. Self-assembled structures that are formed with very little external guidance or direction also fall in the latter category of bottom-up techniques. Apart from strictly top-down and bottom-up techniques, many fabrication techniques include a combination of these two. For example, hierarchical structures can be achieved by top-down patterning of large-scale structures and bottom-up patterning of smaller, 3D features. Soft lithographic techniques such as micromolding and nanoimprinting are often considered a third classification of microfabrication techniques and have also been used successfully in the patterning of C-MEMS (Carbon MEMS) structures [6].

One process that facilitates the fabrication of amorphous or glassy carbon microstructures involves the pyrolysis of carbon-containing precursor molecules (usually polymers) that have been prefabricated into requisite micro/nanostructures (Figure 1.1). Pyrolysis or carbonization is the method of heating carbon-containing precursors to temperatures upward of 600 °C in an inert atmosphere such as nitrogen.

![Diagram](image.png)

**Figure 1.1** Fabrication of Carbon MEMS structures using top-down, bottom-up and soft lithographic techniques.
or argon to remove noncarbonaceous components in a material by volatilizing them into gaseous and hence removable compounds. This method, apart from allowing the creation of any required shape as long as appropriate formable precursors are used, also allows tweaking the properties of the final carbon micro/nanostructures by the rational use of various precursors with different functional groups. Appropriate precursors are those carbon-containing polymers that result in a high enough yield of carbonaceous residue and at the same time do not reflow when subjected to high temperatures during pyrolysis [2]. Thus, the methods to create glassy carbon MEMS structures can be decoupled into various methods to create microstructures in appropriate precursors and the pyrolysis processes (Figure 1.1).

This review is structured as follows. Due to the fact that majority of C-MEMS/NEMS processes involve polymer-derived amorphous or semicrystalline carbon, its properties are reviewed and contrasted with other MEMS materials. The process of pyrolysis for the carbonization is discussed in detail along with methods to address the issue of shrinkage. Then, lithographic techniques and their capabilities and modifications for C-MEMS/NEMS fabrication are discussed. This is followed by a description of bottom-up techniques, in particular self-assembly techniques for C-MEMS/NEMS. Soft lithographic techniques are also briefly covered. Finally, additives and surface modification techniques to improve and expand the applicability of carbon are examined.

### 1.2 Structure and Properties of Glassy Carbon

Glassy carbon is typically a hard solid prepared by treating polymeric precursors such as copolymer resins at elevated temperatures (600–3000 °C) having increasing amount of graphitic content with increasing temperature. The high temperature removes almost all of the noncarbon elements present in the polymers leaving behind a carbonaceous residue. A fully graphitic material does not develop in usual pyrolysis due to the difficulty in breaking the C–C bonds in the parent polymeric chains as well as other factors such as ratio of sp² to sp³ carbon atoms and amount of hydrogen present in the precursor. The structure is generally understood as entangled ribbons of graphitic planes containing small isolated crystals of graphite. When characterized by Raman spectroscopy, two first-order bands around 1360 cm⁻¹ (D band) and 1580 cm⁻¹ (G band) are usually observed, which indicate the defect-induced, double-resonance scattering and symmetry in-plane stretching of graphite, respectively. Weak second-order bands related to the 3D ordering of graphite may also be observed between 2700 and 2900 cm⁻¹. It is important to note that the D band mainly arises due to the finite graphite crystallite size and associated defects [7]. As glassy carbon contains smaller crystallites of graphite, its density is less than that of graphite and can be applied in applications requiring lightweight yet chemically inert or thermally stable materials.

While the different preparation methods result in a range of physical properties of glassy carbon, it does have many advantages as a MEMS material. Glassy carbon, for instance, has a lower Young’s modulus compared to silicon (10–40 GPa compared to 40–190 GPa for silicon) and a lower surface energy. Thus, carbon can be used in MEMS actuators or other devices where high stiffness is detrimental. The lower surface energy of carbon also solves the problem of stiction in contacting or proximal MEMS elements.
where capillary forces cause sticking between close surfaces. Carbon resulting from pyrolysis is also rather inert and impervious in many corrosive chemical environments. It is also possible to tailor the porosity and functionalize the surface of glassy carbon using various carbon chemistry routes as illustrated in Section 1.4.

Glassy carbon is also a model material or gold standard for electrochemists to compare the electrochemical properties of electrodes of other materials as it exhibits excellent electrochemical properties. The electrochemical and physical properties of photoresist material pyrolyzed at temperatures between 600 °C and 1100 °C have been studied in detail, and it has been found that resistance of the material is lower and the electrochemical performance of the carbon material is often found to be better. The pyrolyzed positive photoresist (e.g., AZ 4330) films have low capacitance as well as background current [8].

Apart from glassy carbon, other carbon-based materials such as DLC, carbon nanotubes (CNTs), and carbon nanofibers (CNFs) have also been applied to great benefit in MEMS devices. However, these materials often lack the capability to form the entire MEMS device by themselves due to fabrication and manipulation constraints. For instance, while DLC is particularly useful as a coating material to improve the wear resistance, reduce friction, and stiction in contacting microcomponents in MEMS devices, the residual stresses that are created in most of the high-energy techniques involved in DLC fabrication often lead to delamination of thicker DLC films precluding their use as structural elements [3]. CNTs and CNFs have unique and anisotropic thermal and electrochemical properties and have been used as structural elements such as cantilevers and microsensors. However, the manipulation and assembly of fabricated CNTs and CNFs on MEMS devices are nontrivial due the possibility of physical damage or morphological changes occurring. Cook and Carter [9] have recently reviewed the effect of different MEMS processes on arc-discharge produced and catalytically grown multiwall CNTs (MWCNTs) and found that while CVD deposition of other materials is compatible with MWCNTs, plasma etching processes tend to cause significant damage. Dau et al. [10] have been able to manually maneuver CVD-grown CNT films onto a substrate and pattern it using e-beam lithography into a mechanical sensor. It is also possible to directly synthesize patterned CNT structures for MEMS applications by methods such as CVD on patterned catalyst substrates [11–14], direct or post-synthetic patterning [15–18], templated deposition [19], etc. The incorporation of CNTs and CNFs into C-MEMS devices can be as fillers or (surface) additives to enhance useful properties or as structural elements integrated with the rest of the device. Both these uses are discussed in Section 1.4.

1.3 Fabrication of C-MEMS Structures

1.3.1 Mechanism and Features of the Pyrolysis Process

As most C-MEMS processes involve the use of pyrolysis, also known as carbonization, for the conversion of precursors to carbon, a good understanding of this process is a prerequisite for understanding C-MEMS fabrication. Pyrolysis, from the Greek for fire (pyro) and separation (lysis), is the thermochemical decomposition of a material and in
the context of carbonization refers to the breakdown of carbon-containing precursors at elevated temperatures in an inert or reducing environment. As early as the 1970s, carbon-containing polymers such as phenol formaldehyde, polyacrylonitrile (PAN), and polyimide have been pyrolyzed to amorphous carbon and their electrical properties studied. Jenkins and Kawamura [20] were amongst the first to study the process of pyrolyzing polymers into glassy carbon, where the polymers do not go through a plastic or reflow phase. They have classified the pyrolysis mechanism into four typical stages:

i. Around 300 °C – pre-carbonization stage – polymer turns black.
ii. 300–500 °C – carbonization stage – elements such as nitrogen and oxygen are removed from the material.
iv. 1200 °C and above – annealing stage.

As mentioned earlier, the graphitization of the carbon also occurs when pyrolyzing at elevated temperatures with percentage graphitization increasing with increasing temperatures. At pyrolysis temperatures between 2500 °C and 3300 °C, it is assumed that all non-graphitic regions are annealed out resulting in a near-complete graphitization of the material. Hence, this regime is referred to as graphitization regime.

In the case of lithography-based C-MEMS structures, both positive and negative polymeric photoresists can be used as carbon precursors and have the potential to be carbonized after patterning (Table 1.1). Hsia et al. [27] have researched the formation of carbon from SPR-220 (positive photoresist), by heating in Ar atmosphere to 900 °C followed by a second annealing step in a H2/Ar (reducing) mixture. It was found that this results in a porous carbon with a high surface area, which has been applied as a supercapacitor electrode material for energy storage applications. Negative photoresists, such as SU-8, on the other hand, have a tendency to burn due to the dissolved oxygen present within them [39]. Thicker films of negative photoresist-derived carbon structures can also delaminate from silicon substrate and require ameliorative measures such as slow heating during pyrolysis to minimize thermal stresses and/or an intermediate layer to improve adhesion.

One of the most salient features of the pyrolysis process is the volumetric shrinkage that accompanies it. While this shrinkage can be advantageous in reducing the dimensions of realizable structures [36], it can cause defects such as buckling in constrained structures. In bulk or block structures, where the entire part is unconstrained and shrinks isotropically, the buckling is minimal, however, in the case of devices involving C-MEMS structures integrated with other materials or on a substrate, this is an issue. In self-assembled structures such as xerogels and aerogels, the random orientation and open structure allow their shrinkage and expansion during processing steps such as pyrolysis [40]. Much research has gone into optimizing the pyrolysis process to reduce the defects such as buckling, cracking, and delamination that occur as a result of thermal and shrinkage-related stresses.

To address the issue of shrinkage and related stresses, creating an optimal pyrolysis protocol by modifying heating and cooling rates, temperature of pyrolysis and the atmosphere of carbonization is one of the solutions, and modifying the carbon precursor material with filler material, etc., and creating patterns with lower possibility of buckling
are other techniques. Tang et al. [41] have utilized a three-step linear pyrolysis method as well as a mechanical interlocking step, the latter to achieve better bonding and prevent delamination. Naka et al. [42] have approached the problem of high-temperature pyrolysis by employing a resistive heating process as the last step of the pyrolysis of a polymeric microstructure on silicon structure. This resistive self-heating is achieved by means of a microheater designed into the microstructure of photosensitive polyimide (Figure 1.2). After initial pyrolysis step, a current is applied to the microheater to complete the carbonization by resistive heating. Since the polymeric structure carbonizes itself by self-heating, the thermal damage of other materials in the MEMS device is prevented.

Wang et al. [21] have illustrated a dual use of the pyrolysis process by using a two-step pyrolysis technique with forming gas [H\textsubscript{2} (5%)/N\textsubscript{2} mixture] at 900 °C as a second step to cause the local CVD of CNFs from gases emanating from the polymer during pyrolysis. A gold layer coated on the substrate on which modified SU-8 photoresist was patterned was converted into gold nanoballs at the base of carbon posts. It is also possible to exploit the shrinkage during pyrolysis to create unique shapes as has been shown by deVolder et al. [2] who have created canopy shapes connecting carbon pillars by intentionally fabricating an SU-8 topping layer that shrinks and pulls the pillars together as shown in Figure 1.2.

While shrinkage is one of the aspects of pyrolysis, the pyrolysis conditions also affect the functional properties of the MEMS structures. For example, faster heating rates increase the porosity of the pyrolyzed carbon. Teixidor et al. [43] have evaluated the effect of pyrolysis conditions on the battery characteristics of a pillar array of epoxy resin and found that pyrolysis at higher temperatures and slower ramping up schedules reduce the irreversible capacity of the carbon electrodes illustrated in Figure 1.3.

1.3.2 Lithographic Processes for the Fabrication of C-MEMS Structures

Lithographic processes are amongst the most pervasive techniques used for C-MEMS devices. So much so that the term “C-MEMS fabrication” is used synonymously with photolithographic patterning followed by pyrolysis. This is in part due to the carbonizable nature of the negative photoresist SU-8 as well as most other photoresist materials.
Carbon as a MEMS Material

Table 1.1). SU-8 also falls in the class of chemically amplified photoresist meaning that the cross-linking of the exposed region of the material occurs by means of a self-catalyzed reaction allowing thicker films to be cross-linked completely. This combined with its high transparency, and high contrast allows higher aspect ratio structures in SU-8. Positive photoresists are more challenging to pattern as high-aspect-ratio structures due to the difficulty in using high-thickness films. Multi-exposure and molding are some of the methods used to create high-aspect-ratio structures in positive photoresist.

Lithographic processes result in regular and ordered micropatterns as mentioned before, and Lyons [23] was amongst the first to pyrolyze a patterned photoresist material – novolac resin – in order to understand its electrical properties as a function of the temperature of pyrolysis. He observed the decrease in resistivity of the film upon carbonization. Many researchers since then have used various forms of lithographic processing to pattern C-MEMS structure including conventional UV photolithography [26, 41, 44–47], two-mask lithography [48], five-beam interference lithography [22], and more recently e-beam lithography [30, 49].

The conventional UV photolithography process has been used most extensively, and a detailed explanation of the process steps is warranted. Also, as mentioned earlier, SU-8
Table 1.1. Representative list of carbon precursors.

<table>
<thead>
<tr>
<th>Material</th>
<th>Chemical composition and properties</th>
<th>Patterning method</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>SU-8</td>
<td>Epoxy resin, negative photoresist</td>
<td>Photolithography, interference lithography, electrospinning</td>
<td>[2, 21, 22] etc.</td>
</tr>
<tr>
<td>Novolac resin</td>
<td>Phenol formaldehyde polymer</td>
<td>Photolithographic patterning</td>
<td>[23]</td>
</tr>
<tr>
<td>EPON SU2.5</td>
<td>Bisphenol-A type novolac epoxy</td>
<td>Photolithographic patterning</td>
<td>[24, 25]</td>
</tr>
<tr>
<td>AZ 9260, AZ 4330, etc.</td>
<td>Polymeric resins containing di-azo compounds, positive photoresists</td>
<td>Photolithographic patterning</td>
<td>[26]</td>
</tr>
<tr>
<td>SPR 220</td>
<td>Cresol novolac resin and ethyl lactate</td>
<td>Photolithographic patterning</td>
<td>[27]</td>
</tr>
<tr>
<td>SC-100</td>
<td>Conventional cyclic polyisoprene photoresist</td>
<td>Photolithographic patterning and buckling-instability-induced patterning</td>
<td>[28]</td>
</tr>
<tr>
<td>KMPR 1050</td>
<td>Epoxy, negative photoresist</td>
<td>Photolithographic patterning</td>
<td>[29]</td>
</tr>
<tr>
<td>PMMA</td>
<td>Poly methyl methacrylate, e-beam resist</td>
<td>Electron-beam lithography and simultaneous carbonization</td>
<td>[30–32]</td>
</tr>
<tr>
<td>Resorcinol diglycidil ether and derivatives</td>
<td>Epoxy resin</td>
<td>Two photon lithography, 3D microtransfer molding</td>
<td>[33]</td>
</tr>
<tr>
<td>Copolymers of furfuryl alcohol–phenol</td>
<td>Phenolic resin</td>
<td>Micromolding in capillaries, microtransfer molding</td>
<td></td>
</tr>
<tr>
<td>Resorcinol formaldehyde</td>
<td></td>
<td>Sol–gel, microtransfer molding</td>
<td>[34–36]</td>
</tr>
<tr>
<td>Polymer Cirlex</td>
<td>Polymide</td>
<td>Lithographic patterning</td>
<td>[37]</td>
</tr>
<tr>
<td>Parylene</td>
<td>Poly-(p-xylylene)</td>
<td>CVD</td>
<td>[38]</td>
</tr>
</tbody>
</table>
is the most popular material for C-MEMS fabrication, and the process is explained for this material. A photoresist is a material that is sensitive to photons, and the transformation that occurs in such a material when exposed to light makes it either more or less prone to attack by a developer. Materials that become more prone to attack by developer are called positive photoresists, and those that become more resistant to attack by developer are called negative photoresists. The process of lithography involves the exposure of selective regions of a photoresist and masking other regions either using a physical mask or by other means. The process of lithography for SU-8 typically involves the following steps: (1) coating of SU-8 of desired thickness by spin coating or other methods, (2) soft baking in which most of the solvent present in SU-8 is evaporated, (3) exposure step in which light from a UV source of wavelength between 300 and 400 nm is incident on the SU-8 surface through appropriate mask, (4) post baking or post exposure bake (PEB) in which the chemical amplification is enhanced by thermal means to create high-aspect-ratio structures, and finally, (5) development step in which the unexposed regions are removed. These steps are illustrated in Figure 1.5.

Conventional lithography is mainly a planar or two-dimensional technique with little control on the height of the patterns fabricated. So, techniques such as five-beam interference lithography as well as combination of e-beam and FIB have been developed to allow 3D patterning that is often required in MEMS structures. Three-dimensional structures such as fractals can improve competing properties such as surface area and transport resistance in a material and within the context of MEMS, engender better electrodes. Yamada and Chung [24] have developed a novel method for the 3D patterning carbon material by including a vaporizable thermoplastic spacer below a carbon precursor epoxy film. Fractal geometries have been synthesized by many techniques including sol–gel synthesis, CVD deposition on carbon posts, doped photore sist method, and 3D carbon microstructures from grayscale lithography of SU-8 [40].
Five-beam interference lithography was used by Jin et al. [22] to create a woodpile structure with silica shell support (to reduce shrinkage) by the carbonization of patterned SU-8 photoresist. Long et al. [50] have tailored the diffraction-induced light distribution of a photolithographic process to fabricate suspended C-MEMS structures. This has been achieved by modeling the light distribution to predict conditions and parameters such as mask pattern dimensions, gap distance between photomask and photoresist, and exposure time for the formation of suspended structures. Interdigitated array electrodes have also been reported by Heo et al. [48] as having an increased current amplification factor due to efficient recycling of redox species between carbon nanoelectrodes having 1:1 aspect ratio. Here, a two-mask process was used to fabricate the electrodes.

Poly methyl methacrylate (PMMA), one of the more popular e-beam resists, does not yield high carbonaceous residue [51]. Thus, e-beam lithography has not been used as extensively as UV lithography for C-MEMS applications. Madou and co-workers [52] have modified the process of e-beam lithography for use in SU-8 by coating a thin layer of conductive metal on the nonconductive SU-8 surface. This on pyrolysis gave complex C-MEMS structures such as suspended bridges and networks. Recently, Huigao et al. [30] and Gautsch et al. [31, 32] have found that the overexposure by e-beam can also carbonize a PMMA resist while simultaneously patterning it giving rise to carbon nanostructures by direct e-beam exposure without development. One of the structures fabricated by this method is shown in Figure 1.6. This patterning and simultaneous carbonization occur due to e-beam-induced collapse of the PMMA macromolecular chains. However, further carbonization and graphitization required a protected annealing step at 600 °C in Ar. The authors have also favorably compared this method to the

![Figure 1.5 Steps involved in the photolithographic patterning of negative photoresist SU-8](image-url)
electron beam-induced deposition or EBID method of creating carbon nanostructures. Malladi et al. [52] have also used the method of e-beam writing to controllably fabricate carbon nanowires that connect carbon pillars (Figure 1.7).

**1.3.3 Soft Lithographic Techniques**

The materials that can be patterned by lithographic techniques, *i.e.*, sensitive to photons, electrons, or ions, are arguably few, and not all photoresists can be converted to carbon. Furthermore, modified lithographic techniques for 3D patterning are far from
simple. Soft lithographic techniques such as molding and imprinting can extend the capability of conventional lithographic techniques in terms of 3D capability and various materials. Schueller et al. [53] have replicated MEMS elements such as accelerometers, interdigitated capacitors, and electrostatically actuated optical deflectors using poly (furfuryl alcohol) in an elastomeric mold (Figure 1.8).

Sharma et al. [36] have used micromolding and exploited the isotropic volume shrinkage of resorcinol–formaldehyde during drying to repeatedly miniaturize micropatterns. They have been able to achieve down to 379 nm periodicity (Figure 1.9) in C-MEMS
patterns which is limited by the wettability of the PDMS (polydimethylsiloxane) intermediate molding material with hydrogel patterns. More recently, Daicho et al. [33] have not only developed two new photopolymers based on resorcinol di-glycidyl ether that carbonize during pyrolysis, but they have also illustrated microtransfer molding of 3D patterns (Figure 1.10) fabricated by two-photon lithography using PDMS as a transfer mold. Penmatsa et al. [54] have used nanoimprint lithography to pattern an AR-UL-01 photoresist and pyrolyzed it to create carbon micropatterns. Nanoimprint lithography is able to achieve down to 50 nm resolution of features and is relatively inexpensive compared to e-beam or other nanopatterning techniques. However, they have found significant vertical shrinkage which could be an issue for patterning high-aspect-ratio structures.

1.3.4 Self-Assembly and Bottom-Up Processes for the Fabrication of C-MEMS Structures

Lithographic top-down processing involves the directed or guided patterning of the material into useful structures. In contrast, self-assembly and additive bottom-up processes involve the arrangement of the material without active guidance. Electrospinning of fibrous mats which can then be used as sensor platforms is an example of a self-assembly method for MEMS fabrication. CVD (for the fabrication of CNTs or DLC, etc.) is an example of a bottom-up technique. Both self-assembly and other bottom-up processes are characterized by reduced control of the MEMS/NEMS feature shape and dimensions due to the absence of any external guidance. However, these techniques have a strong advantage in creating smaller feature sizes with inexpensive equipment. Furthermore, they have better 3D patterning capability thus able to create high-surface-area structures for surface-active applications such as bio/chemical sensing.

Recent research has rediscovered the advantageous aspects of fractal and other 3D geometries in battery applications due to the higher active surface area. Fractal
structures, in particular, reduce the internal resistance of the carbon electrode while maximizing surface area in battery applications [40]. Self-assembly-based fabrication which relies on the intrinsic chemical and physical properties of the material to create ordered structures is better suited to creating such structures. Electrospraying and electrospinning, sol–gel processes, and instability-based self-organization of polymers are some of the examples of self-assembly methods to create fractal and hierarchical structures. Sharma et al. [35] in an example of a self-assembly based fabrication, have been able to create carbon xerogel particles and folded fractal-like patterns by the sol–gel polycondensation of resorcinol and formaldehyde followed by pyrolysis.

Figure 1.11. Electrospinning based method to create carbon nanowires connected carbon posts. (Reproduced with Permission from Ref. [50], Copyright 2011 Elsevier B.V.)