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Recent Advances in Nano Patterning and Nano Imprint Lithography for Biological Applications

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Abstract

Nano patterning and Nanoimprint lithography [NIL] has advanced to great heights in recent years. Customizing the surface at micro and nano scale is of great demand. It facilitates the handling and working at micro and nano scale level. Its applications towards medical field are growing day by day. Precise surface patterning with nanometer resolution has great potential in many medical and biological applications. It also provides a platform for fundamental studies of molecular and cell biology. This review article comprises of current trends and future scope of nano patterning and NIL. In this article we particularly focus on biological applications.

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*Keywords:*Nanoimprint, Imprinting, Patterning, lithography, AFM.

1. Introduction

Nano patterning is more of great need nowadays. It is the process of patterning the surface at nano scale. Optical lithography is the standard technique for pattern transfer inmicroelectronics and micro system technique. Now there are several alternatives for conventional lithography which has more advantages and applications. Prominent alternatives for conventional lithography are NIL, e-beam lithography (EBL), scanning probe techniques (dip-pen

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lithography, nano-shaving, nano-grafting), induced self-assembly and self-organizing imprinting, micro and nano-contact printing, electron projection lithography (EPL), atom lithography, masked ion beam lithography (MIBL), and focused ion beam lithography.[1-4]

NIL is a process of fabricating patterns of nanometre scales. NIL was successful because of its high resolution. It is a simple process with low cost and high throughput. Imprint lithography is a nano-patterning technique which has several advantages than conventional photolithography technique. This technique allows patterning features of size less than sub 100 nm. Imprinting techniques can be classified into thermoplastic nanoimprint lithography (T-NIL), UV-NIL, step and flash imprint lithography (SFIL), step and stamp imprint lithography (SSIL)and laser assisted direct imprinting.It facilitates various applications like bio molecule immobilisation at thenano-scale, scaffold for cell culture, high resolution cell replica imaging and forvarious other biomedical applications. In this article recent development, issues and applications of NIL related to biotechnology and biomedical field will be discussed. [1, 2, 5, 6]

Nomenclature

EBL	Electron Beam lithography
NIL	Nanoimprint Lithography
AFM	Atomic Force Microscope
EPL	Electron Projection Lithography
MIBL	Masked Ion Beam Lithography
SAM	Self Assembled Monomers
SFIL	Step and Flash Imprint lithography
SSIL	Step and Stamp Imprint Lithography
LADI	Laser Assisted Direct Imprinting
LISA	Lithographically Induced Self-Assembly

2. Various Patterning Technique

Several alternative techniques for the conventional optical lithography are being developed. Following are few methods.

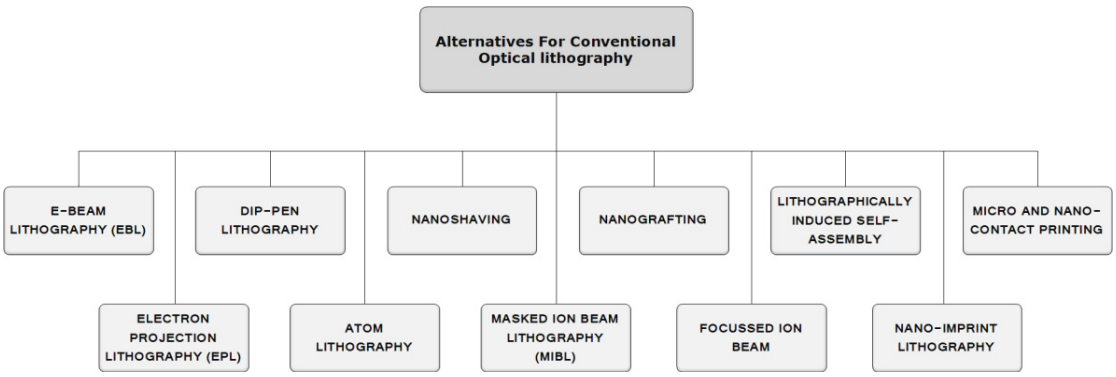


Fig. 1:Various alternatives for conventional optical lithography.

2.1. E-Beam Lithography (EBL)

Electron-beam lithography (EBL) is the process of using focused beam of electrons to pattern the surface covered with an electron sensitive film called a resist. The electron beam alters the resist solubility. Thus by using this property the areas which are either exposed or non-exposed can be selectively removed by the process called etching.[1] This method is used for developing several biochips and biological handling devices at micro and nano scales.[7-11]

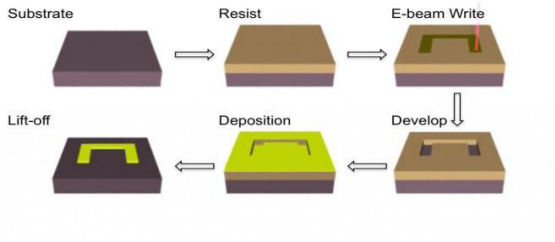


Fig. 2: EBL Process. [12]

2.2. Electron Projection Lithography (EPL)

Electron projection lithography (EPL) is a process in which broad beam of electrons are patterned by a physical mask. The patterned beam is then reduced down and projected onto the sample. By this method, the resolution is increased and process time is reduced. Though the hurdles involved in this method is designing of the mask. The opaque areas of mask have to absorb the electrons without the production of significant heat and should conduct them within microseconds. Scattering with angular limitation projection electron-beam lithography (SCALPEL) method is used for semiconductor manufacturing with feature sizes beyond the capabilities of optical lithography. [13, 14]

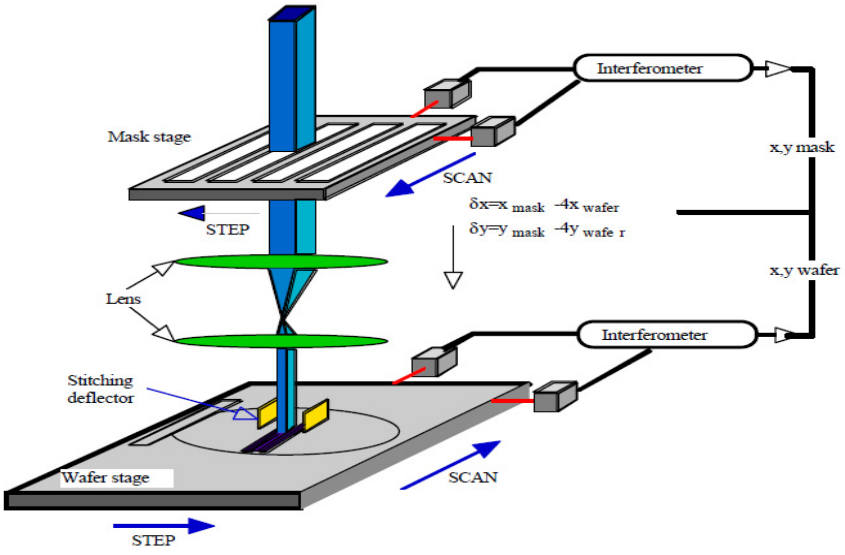


Fig. 3: SCALPEL Process. [13]

2.3. Dip-Pen Lithography

It is a scanning probe technique in which nano pattern is obtained with the help of AFM tip. In this process inking (nanomaterial) is applied on the tip of the AFM tip and is operated in the contact mode to deliver it to the substrate surface. In this technique AFM is mostly used in contact mode, but even tapping mode is also used. The efficiency of the process depends on the properties of nanomaterial (ink) and substrate and also the geometry of the AFM tip. Substrate morphology, scanning time and tip-substrate contact time are few factors to be considered for better results. Positive aspects of this method are that it has high throughput and better resolution. It also enables direct deposition of the materials to the target.[1, 15-18]

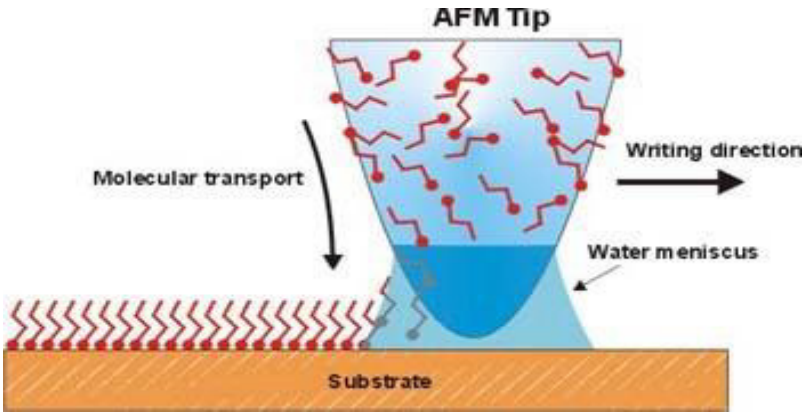


Fig. 4: Schematic representation of Dip Pen Lithography Process. [15]

2.4. Nano-shaving

Nano shaving as the name implies it is shaving of material at nano scale. It is also a lithographic technique based on scanning probe. In this method using AFM tip the resist material is mechanically removed, which in turn creates nanometer scale patterns on surfaces. The resolution of this process depends on the mode in which the AFM is operated and immediate removal of the displaced adsorbate. This method has showed very good results for the fabrication of multi component biomolecule nano structures.[1, 18-21]

2.5. Nano-grafting

Nano-grafting is the extension of nano-shaving. Nano-grafting is mostly used over the surfaces modified with SAM. In this method the preformed SAM is removed by the process of nano-shaving and those regions are replaced by a surfactant molecule which has more affinity to the surface than the molecule being removed. Hence new SAM is formed in the patterned area by the latter molecules. The positive aspects of this method are that it allows precise and accurate patterning of the surfaces. Points to be considered while performing nano-grafting are the properties of SAM. SAM should be easy enough to be removed by the AFM tip and the second surfactant should form new SAM.[1, 18, 22, 23]

2.6. Lithographically Induced Self-Assembly (LISA)

Lithographically induced self-assembly (LISA) is the process of developing formations and patterns which are induced externally. In this method, the homo-polymer (polymethylmethacrylate-PMMA) is flat and in melt state initially on a plate. Once when it is induced by a mask plate, the periodically assembled pillar patterns are formed by melt rising against the gravitational force during heat-cool cycle. Height of the pattern is equal to the height of the

spacer. Different micro pillar patterns are formed with same mask for different spacer height. Spacer height is the gap between the plate and mask. Electrostatic force is the driving force for LISA. [24]

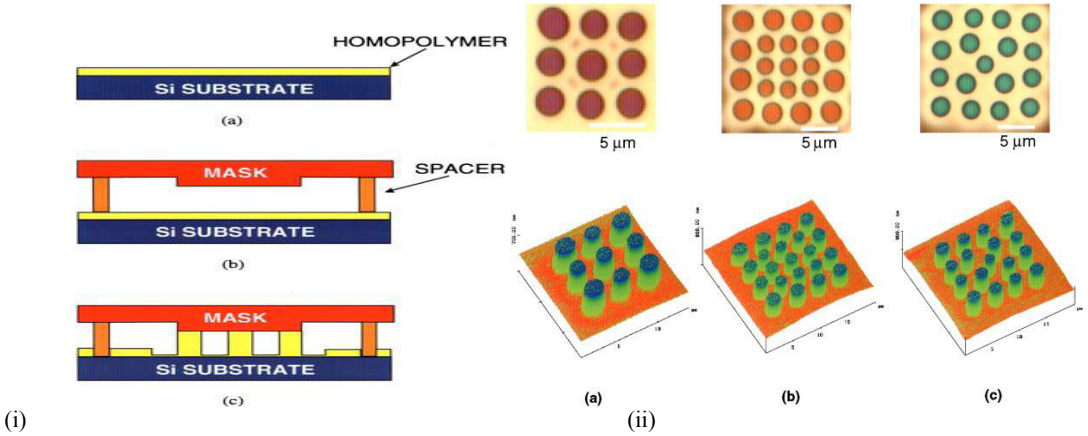


Fig. 5:(i)Process of LISA (a) A thin layer of homopolymer spin coated on a flat silicon wafer (b) A mask with protruding patterns placed a distance above the film, but separated by a gap (c) During a heat-cool cycle, the film self-assembled into patterns,
(ii) Optical and AFM images of the induced self-assembled patterns formed under protruding square patterns with sides of (a) 10, (b) 14, and (c) 14µm. The separation between the masks and the substrates in (a), (b), and (c) are 430, 280, and 360 nm, respectively. [24]

2.7. Micro and Nano-Contact Printing

Micro and nano-contact printing is the process by which the patterning of the surfaces is extended to the scale of micro and nano dimensions respectively. The process consists of two steps. Initial step is the preparation and fabrication of stamps. Second step is the printing process using the stamps which was prepared from previous step.

Currently practiced different µCP and nCPways are planar method, roller method and curved method. In this process PDMS is chosen because of its properties like elastomeric (deforms elastically and not plastically). Moreover it presents a chemically inert surface with low surface energy, which is more suitable for biological applications. SAMs is also used in these processes depending upon the applications. Another important factor on obtaining high resolution prints relates with the ink utilized. Biomolecules are most preferred nano-contact printing inks which results in high-resolution features. [25]

2.8. Atom Lithography

Noble gases have energy levels that lie far (10–20 eV) above the ground state. When an atom in one of these energy levels hits a surface with resist then all this energy can be deposited in a very small area and so drastically change the surface and one can etch the pattern into the surface. Neon, argon and helium beams have been used to form patterns on resists. Masks used can be of either physical or light. The light masks de-excite the metastable atoms to the true ground state before they reach the sample surface. This method has several novel features like focusing light masks, direct deposition and material or isotopic selective light masks when compared with optical or charged beam lithography. [27-32]

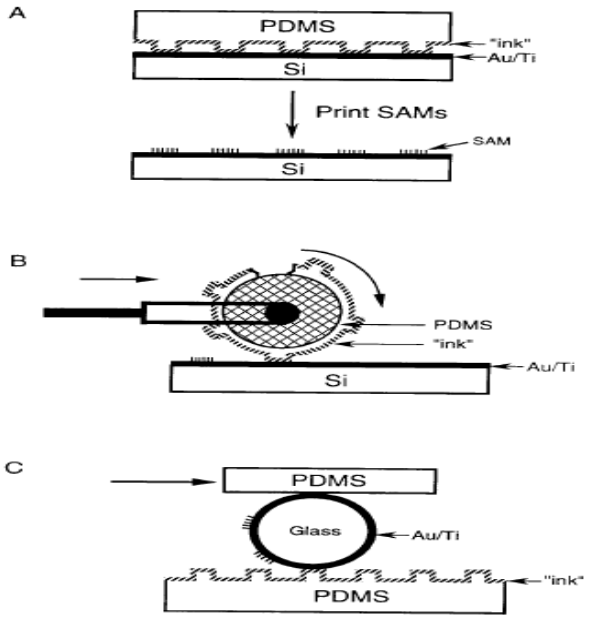


Fig. 6:Different Methods of Micro-contact and Nano-contact printing (a) Planar method (b) Roller method (c) Curved method. [25]

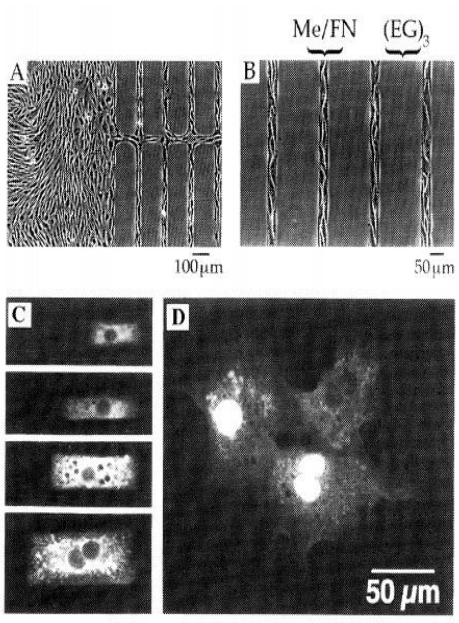


Fig. 7: Optical micrographs of cells grown on surfaces patterned with adsorbed protein. (a,b)Bovine endothelial cells plated on patterned fibronectin. (Me-CH3-terrninated SAM, FN:fibronectin. (EG)r : HO(CH:CHzO).3-terminated SAM) (c) Primary rat hepatocytes plated on patterned laminin. (d)Hepatoclites plated on unpatterned laminin. [25]

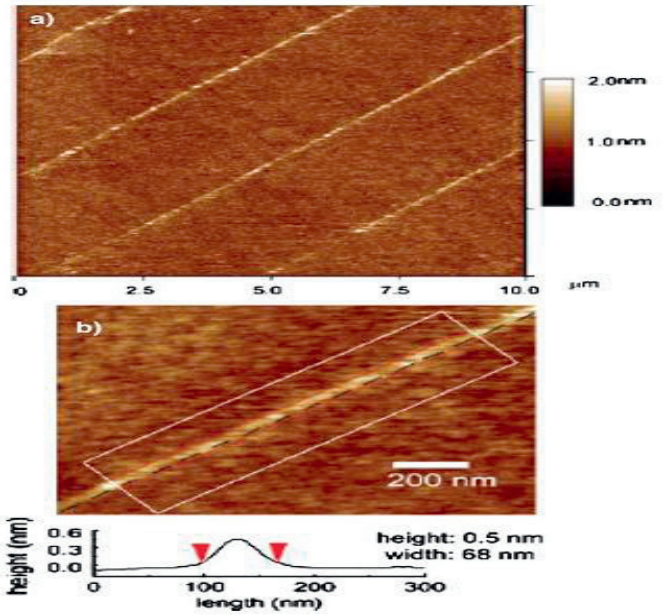


Fig. 8: AFM tapping mode images of nano-contact printed titinmultimer protein lines on a silicon surface a) at large scale and b) athigh-resolution with height profile[1, 26]

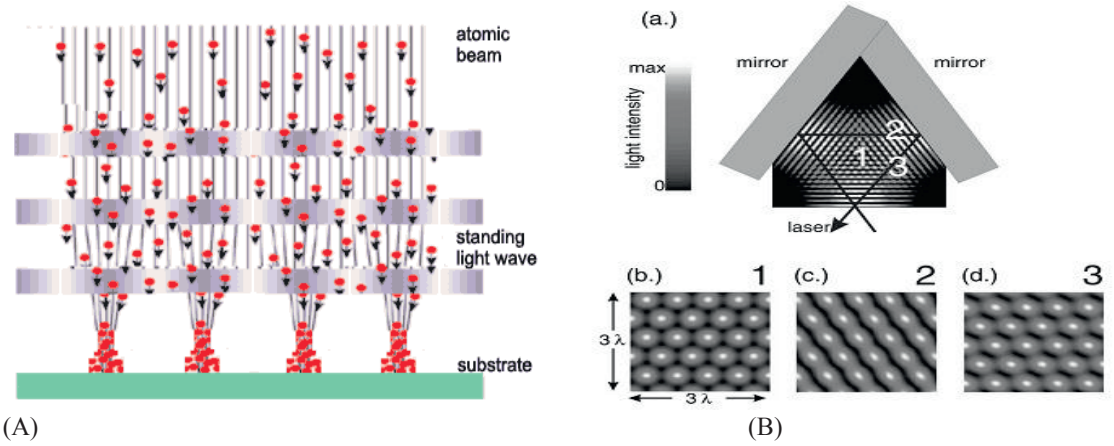


Fig. 9: (A)Atom lithography process [32], (B) Schematic drawing of the optical setup for the two-dimensional standing wave. The calculated intensity distribution is shown with a much exaggerated wavelength, to make the interference patterns visible.[27]

2.9. Ion Beam Lithography (IBL)

Ion beam lithography (IBL) is the process of using ion beams for patterning the surfaces. IBL is similar to EBL, but in the former heavy charged particle ions are used. IBL is useful for transferring high-fidelity patterns on three-dimensional surfaces. In this method shot noise tend to be more. It has two extended versions called masked ion beam lithography (MIBL) and focused ion beam lithography (FIBL). In MIBL, ions are masked in prior application to the surfaces for patterning. FBL uses high energy focused ion beams for patterning. FIB offers high resolution as there will be absence of proximity effects. [33-35]

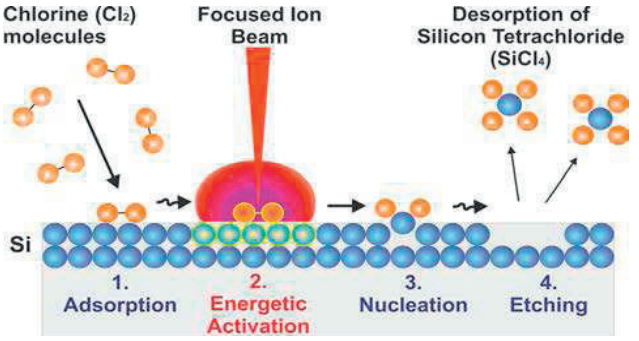


Fig.10:Illustration of the FIB-induced etching process[33]

2.10. Nano-Imprint Lithography

Nano-imprint lithography methods are broadly classified and described in the following sections.

3. Nanoimprint Lithography methods

Different nano-imprint methods which are practiced currently are reported in this section.

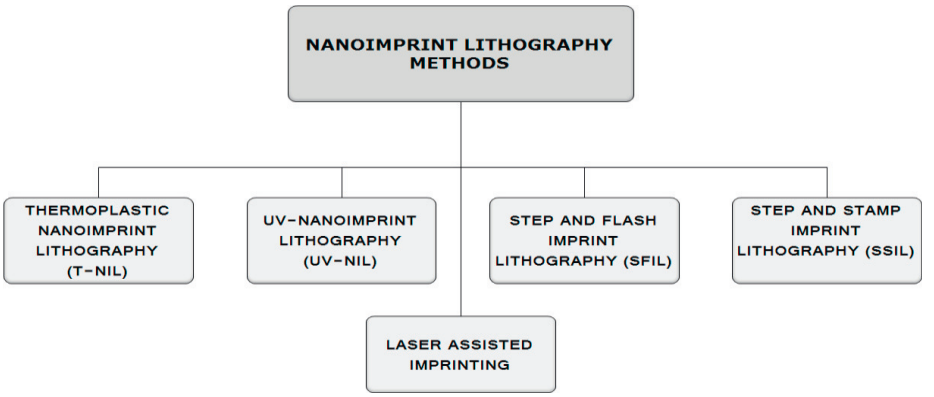
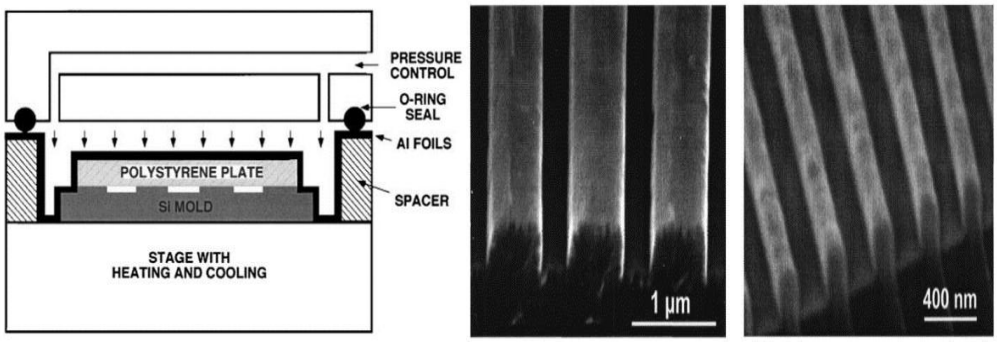


Fig. 11: Different methods of NIL

3.1. Thermoplastic Nanoimprint Lithography (T-NIL)

Thermoplastic Nanoimprint lithography (T-NIL) is very old technique which is even now practiced because of its simple process, low costand high throughput. In this process a thermo cure resist is spin coated on the substrate. The property of thermo cure resist is that once it is heated above the glass transition, the polymer is of liquid state. After cooling it becomes hardened by crosslinking. Using this property of the resist, the mold of specific feature is pressed on to the resist upon heating above the glass transition temperature. After cooling, the pattern gets transferred to the resist from the mold and mold is separated from the resist. Features in the mold can be transferred to the substrate by using chemically reactive plasma to selectively remove the deposited material.

Though this has several applications, but it cannot be used for the applications dealing with live cells. The process can damage the cells because of heating. This technique drawbacks are as follows cannot be performed at room temperature and it requires high imprint pressures which cause accuracy lack in alignment.[2]



(i) (ii)

Fig. 12: (i) Configuration of nanoimprint lithography system with tissue-culture polystyrene plates on top of the Si mold,(ii) Nanoimprinted structure in thick tissue-culture polystyrene: (a) gratings with 0.5 μm half-pitch and 440 nm height and (b) gratings with 120 nm half-pitch and 290 nm height. [36]

3.2. UV-Nanoimprint Lithography (UV-NIL)

The process of UV-NIL is almost same as like T-NIL, but the resin used is UV curable. The property of the UV curable resin is that initially it is at liquid state which is then hardened and cross-linked by exposing it to UV radiation. In this process, the mold is pressed on to the resin and then it is cured by UV radiation. Later mold is separated from the resin leaving back the features on to the resin which is then cleaned to remove any residuals.Positive aspects of this method are that it can be performed at room temperature and with low imprint pressure, so the alignment accuracy is better. Below Fig. 13 shows the bioimprint technique to obtain the cancer cell replica for cancer research investigations.[5, 20, 37]

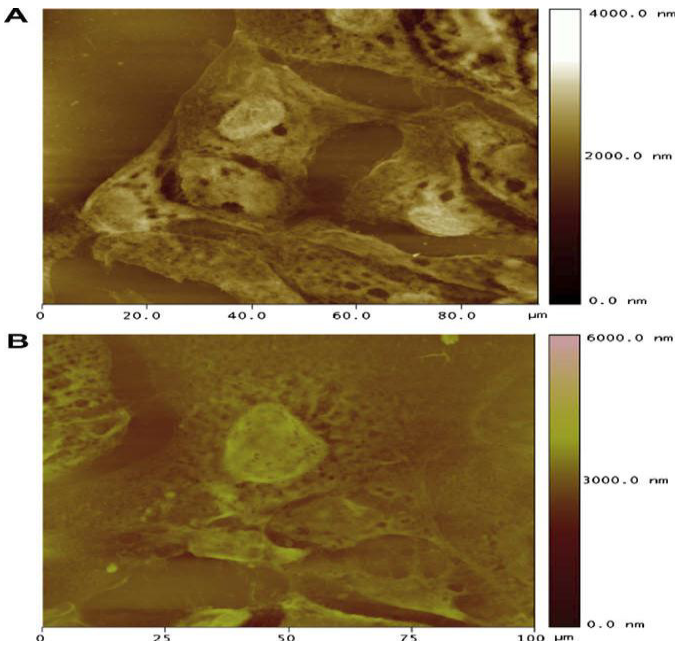


Fig. 13: AFM imprint images of Ishikawa endometrial Cancer cells.[38]

3.3. Step and Flash Imprint Lithography (SFIL)

SFIL uses a low viscosity, photo-curable, organosilicon liquid. Template used in this is transparent, rigid so that it allows layer-to-layer alignment. High throughput, low cost, no projection optics and operation at room temperature is the main advantages of the SFIL.Repeated use per wafer decreases stamp lifetime. In Fig. 14(a) the process is clearly explained. If the process is not carried out carefully, then it can produce defects in a propagating manner as shown in Fig. 14 (b).[39, 40]

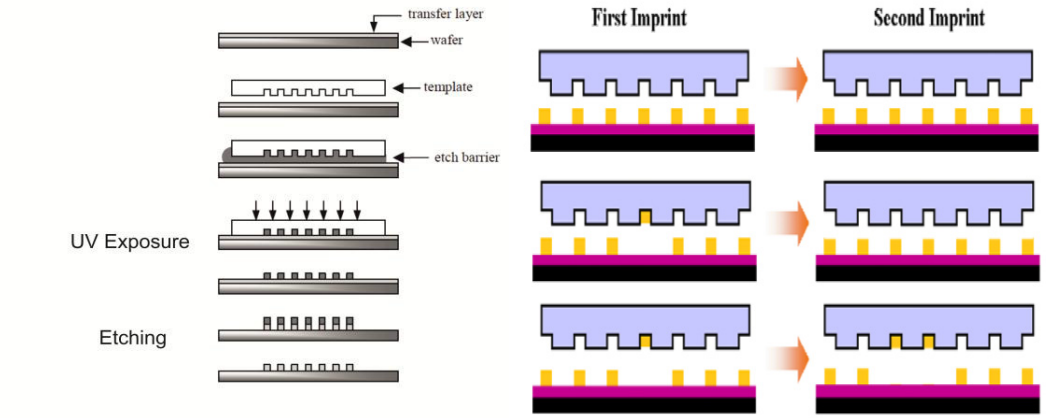


Fig. 14:(A)Step and Flash Imprinting Process,
(B)Hypotheses for defect generation and propagation in SFIL Process. [39]

3.4. Step and Stamp Imprint Lithography (SSIL)

In this technique, a stamp is pressed on to the polymer for creating the imprints. Stamp is lifted and pressed next to create more imprints. And the process is repeated to produce more of same imprints.Alignment of stamp to already existing features on the substrate makes it possible to use SSIL together with UV lithography for mix and match.[41]

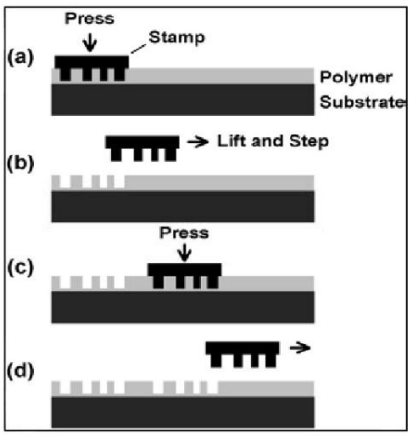


Fig. 15: Step and Stamp Imprinting Process.[41]

3.5. Laser Assisted Direct Imprinting

In this method, imprints are made directly with the use of lasers. The quartz moulds were diced to fit within the excimer laser beam area, ensuring that all the silicon beneath the mould melts during (Laser Assisted Direct Imprinting) LADI. Then the pressure between the mould and silicon wafer were applied by sandwiching them between two large press plates. Mould is placed above the silicon wafer. Mould is placed above the silicon wafer. Mould is made of fused quartz and hence transparent to the laser beam. Based on the reflectivity of the silicon, the process monitored. When silicon melts, it changes from a semiconductor to a metal, hence its surface reflectivity to visible light increases.[4, 42, 43]

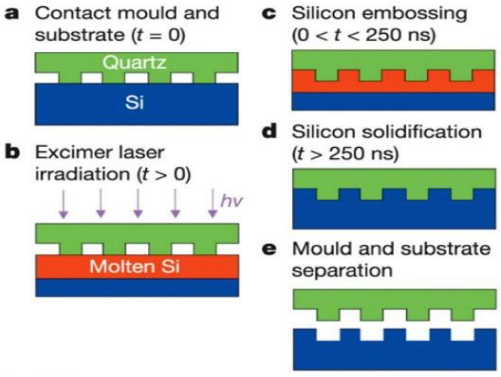


Fig. 16:LADI Process.[42]

4. Conclusions

Nanopatterning and Nanoimprintinghas more scope in coming years. It has several applications in various fields. Accurate and precise operation is one of the major advantages of this technology. This facilitates the miniaturization process. Merits of these technologies are cost effective, efficient, reliable system and low power consumption. Towards biomedical and biotechnology areas, though several research is going on, yet it needs to be explored more.

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