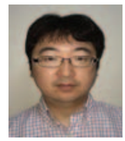
It's About Making Surfaces Invisible

Moth Eye, Antireflective Surfaces, and Soft Lithography

Geethamma V G, Kazuki Shigeta and John A Rogers

Antireflection is an essential requirement for certain opto-electronic devices. Antireflective surfaces can be generated by different methods. One method mimics the nanofeatures on the moth eye surface. This can be done by 'soft lithography' (SL), where nanofeatures are created on an elastomeric stamp. This stamp is then used for imprinting the pattern on other surfaces.

1  2 

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Introduction

In many cases, polished and bright, reflective, glossy surfaces yield a pleasing appearance. Examples include mirror, pearl, diamond, etc., (*Figure* 1). However, we often find difficulty in viewing objects through a transparent window pane or display panel due to the glare that arises from surface reflections of light. Similarly, the efficiency of solar cells is reduced due to the reflection of incident sunlight. In these and other cases, such as light emitting diodes, photodetectors, etc., antireflective surfaces become essential. Antireflective surfaces are also needed for televisions, computer monitors, clear view screens in automobiles, mobile phones, eyeglasses, etc., (*Figure* 2). In certain extreme conditions, an antireflective surface may even become invisible. This property is used in the development of stealth aircraft which is not detectable by the RADAR eyes of enemies.

Reflection and Antireflection

When light passes from one medium to another, a portion of the light is reflected from the surface between two media. The intensity of reflected light is known as the 'reflection coefficient'

Figure 1. Reflective and glossy surfaces.

Figure 2. Products where antireflection is important.

Keywords
Soft lithography, antireflection, nanopattern, moth eye, elastomer stamp, PDMS stamp, resolution, photolithography, nanostructure.

(reflectance). The extent of reflection depends on many factors like the ratio of refractive indices of the media, wavelength of light, angle of incidence, thickness of the surface coating, size and shape of surface structures, etc.

Refractive index (n) of a material is defined as the ratio of the speed of light in vacuum to the speed of light in the given material. Generally, silicon wafer is used as the substrate for fabricating electronic devices. Its refractive index is high (n_s~3.8), and hence light passes slowly through the material. When light enters it from air (n_0~1.0), most of the light is reflected due to its high refractive index and smooth polished surface.

Therefore, one requirement of antireflection is small refractive index of the material (*Figure* 3). The speed of light is high in such a material. Consequently, the incident light is transmitted

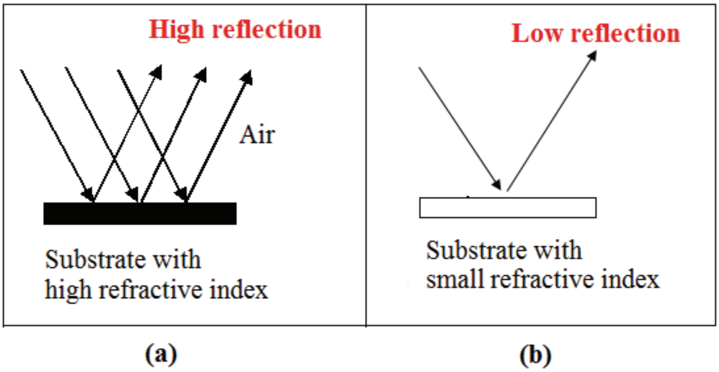

Figure 3. Reflectance depends on the ratio of refractive indices of air and substrate. **(a)** High refractive index leads to high reflection. **(b)** Small refractive index leads to low reflection.

or absorbed by the material rather than reflected. Two important methods to reduce reflectance are explained below.

Antireflective Coatings

One standard way to achieve antireflection is applying a thin coating of appropriate material like silicon nitride on the surface of substrate. But this method is expensive and ineffective across wide range of wavelengths.

As mentioned earlier, the refractive index of the coating (n_c) should be less than that of the substrate. Therefore, n_c is intermediate to that of air and substrate. When a coating is applied, the air-substrate interface is replaced by two interfaces – air-coating interface and coating-substrate interface. Hence light reflects twice. The reflection from each new interface and the combined reflection are less than that of air-glass interface.

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Thus it is clear that further reduction in reflection can be achieved by adding subsequent layers of coating whose refractive indices decrease gradually upwards. Such a system is known as 'graded index' or 'gradient index film' (*Figure* 4a). Gradient means slope. Graded index film exhibits a smooth transition of refractive indices of different materials over a few wavelengths. Hence, the effective refractive index is a polarization dependent weighted av-

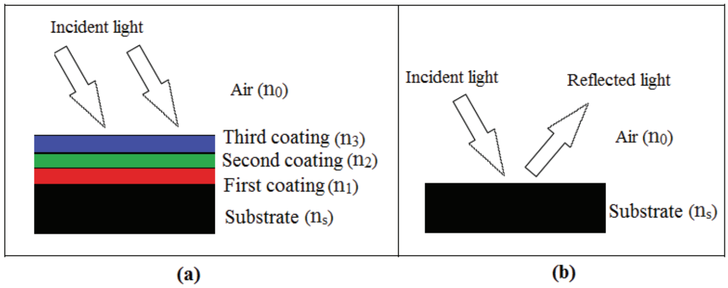

Figure 4. **(a)** Substrate coated with gradient index film possesses a gradual change in refractive index in the order $n_0 < n_3 < n_2 < n_1 < n_s$. This exhibits antireflection. **(b)** When no coating is given, the difference in refractive indices of air and substrate is drastic. Light is reflected.

erage of the indices of constituent materials. When light passes from air to the substrate, light is transmitted/absorbed due to the small refractive indices of the top layers of coating. This reduces reflectance of the system. But in the case of an uncoated substrate, there is a large difference between the refractive indices of substrate and air. So light is reflected (*Figure* 4b). Various parameters like the wavelength of light (λ) and effective thickness (d) of graded index coating can influence the reflectance. When $d << \lambda$, the interface is very sharp and the reflection occurs from this discontinuous boundary. Hence its reflectance is zero.

In nature, the lens of human eye is an example for graded index material. Here, the refractive index varies from about 1.406 in the central dense layers of the eye down to 1.386 in the outer layers. This enables human eye to have good resolution and low aberration.

Antireflective Surface Structures

Light trapping and thereby antireflection can be obtained by forming sub-wavelength, pyramidal surface structures on the substrate.

Refractive indices of all solids are much higher than that of air. As a result, light is reflected from most of the materials. Hence it is difficult to obtain suitable materials for preparing graded index coating in contact with air. However, light trapping and thereby antireflection can be obtained by forming sub-wavelength, pyramidal surface structures on the substrate. If the structure is smaller than the wavelength of incident light, it is called sub-wavelength structure. the shape of a pyramidal structure is such that the quan-

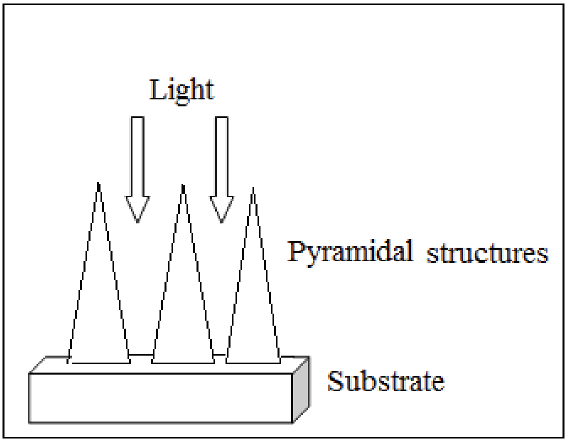

Figure 5. Pyramidal Structure: Refractive index gradually increases as light travels from air to the surface of substrate.

tity of material decreases gradually in the upward direction (*Figure* 5).

Such structures behave similar to a multilayer antireflection coating (*Figure* 6a), and the surface pattern acts as a gradient index film. This results in an effective medium where the refractive index gradually increases as light travels from air to the surface of the substrate. Such a grating is more durable than applying a coating as the former does not contain any external material. Moreover, antireflection is more effective in the case of pyramidal structures.

Also, reflection occurs when light beam falls on an object whose dimension is much larger than the incident wavelength. This means that if the surface carries sub-wavelength structures, reflection is small. It can trap light as in the case of corneal lens of moth eye surface. Under certain extreme conditions, such a surface may even become invisible. Antireflection of sub-wavelength nanostructures is also due to different phenomena like increased light transmission, destructive interference, scattering, etc.

However, large surface structures (with dimensions of a few micrometers) can also reduce reflection (*Figure* 6b). When the surface structure is larger than the wavelength of light, rays are reflected many times on the patterned surface before reflecting to

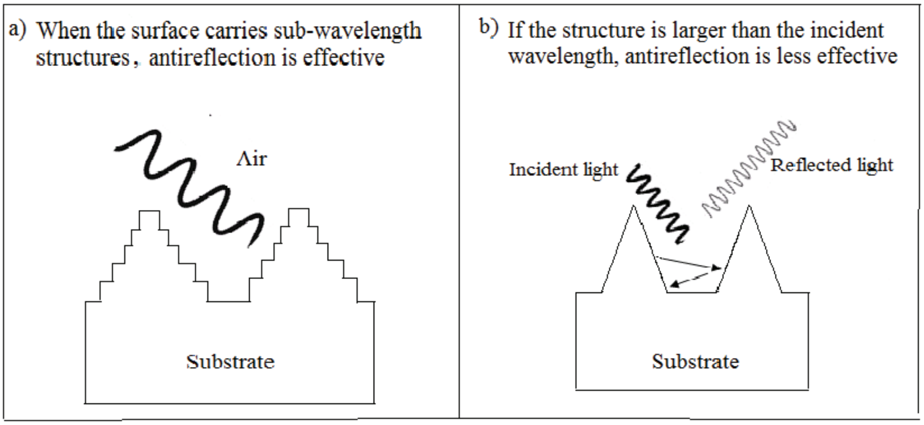

Figure 6. **(a)** Effective antireflection of a surface carrying graded index sub-wavelength pyramidal structures. **(b)** Less effective antireflection due to features larger than the incident wavelength.

the surroundings. This increases the possibility of absorption and refraction of light. Due to refraction, the path length of light is longer than that with a smooth surface. For example, rough surface of walls are not at all reflective due to large structures present on its surface.

Inspiration From the Moth Eye

Moth eye surface is not smooth, but it has periodic, hexagonal and conical features about 200 nm in height and spacing. The effective refractive index, as a result, gradually increases as light passes from air to the cornea of the moth eye.

Moth is an insect similar to butterfly. There are about 16000 species of moths. Moth is a nocturnal insect and it possesses powerful eyesight in darkness. This is because of the peculiar characteristics of its eyes (*Figure* 7). Moth eye surface is not smooth, but it has periodic, hexagonal and conical features about 200 nm in height and spacing. The effective refractive index, as a result, gradually increases as light passes from air to the cornea of the moth eye. It is graded from 1 at the top to about 3.4 at the surface of the eye, which indicates negligible reflection. Also, these structural features are smaller than the wavelength of visible light. All these peculiarities help moth eyes absorb more light than that is reflected. The light waves destructively interfere with one another keeping the eyes dark. This helps the moth in two ways. High light absorption of the eye surface enables the moth to fully utilize even the dimmest light available and so it has good

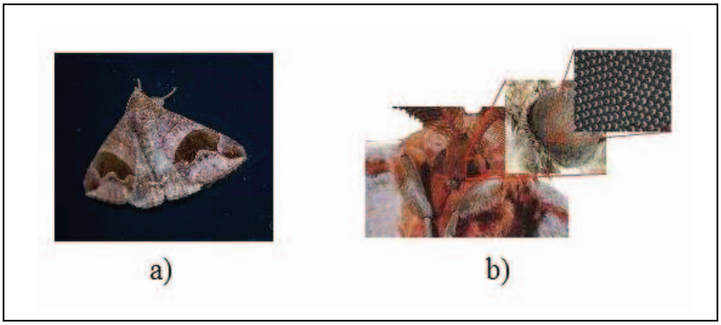

Figure 7. (a) Moth (Photo courtesy: Pixabay.com). (b) Moth eye surface at different magnifications. Hexagonal features on the moth eye surface can be seen (Photo courtesy: University of Delaware, published in PhysOrg.com).

eyesight in darkness. Secondly, as there is no reflection, eyes do not glimmer in the dark and it can escape from the predators by camouflage.

Preparation of Nanopatterns by Lithography

Antireflective surfaces can be created by forming nanopatterns analogous to moth eye pattern. Nanofabrication is the preparation of functional structures with minimum dimensions of approximately 100 nm. It is essential in bio-mimicking technology as well as in the miniaturization/integration of electronic devices. In the latter, as the component becomes smaller, the chip can accommodate larger number of components. This in turn results in better performance, faster operation, low power consumption, low cost, etc.

Lithography is very important among the several nanopatterning methods. In Greek *litho* means 'stone' and *graphein* means to 'write'. Lithography was invented by Alois Senefelder in 1796 as an inexpensive method to reproduce artwork. The image was carved on a stone; it was inked and then pressed on a paper to get the replica.

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But in the field of micro and nanofabrication, lithography means the transfer of surface pattern on a mask to a thin film of photosensitive material (photoresist) coated on a circuit board or semiconductor wafer. Optical or X-ray lithography is used in computer chip manufacturing. Here, a master is made by chemical methods (explained in the later section), and then light is passed through it to produce the structures. This is essential for modern devices such as integrated circuits, information storage devices, video screens, micro electromechanical systems, microfluidic devices, biochips, and sensors. A classification of various lithographic techniques is given in *Figure* 8.

Effectiveness of Lithography

The performance of a lithographic method is assessed based on three parameters – resolution, registration, and throughput. Resolution is the minimum distance between distinguishable features which can be viewed with high fidelity. It is also the ability to distinguish (to resolve) closely spaced structures. This property is an important criterion to rate different microscopes. Registration is the ability to align or overlay the successive patterns on previously created pattern on the same wafer. Throughput is the amount of material/items/data passing through a system/process in a specific time. It is a measure of the productivity of a system. In lithography, throughput is the number of wafers that can be exposed per hour for a specific mask. Low cost and high throughput are required for mass production.

The lithographic processes are divided into serial and parallel methods based on their characteristics. This is comparable with the advantages of a printing press (parallel) over writing by hand (serial). In the parallel method, whole area of the mask can be patterned onto the photoresist in a single step. A comparison of these methods is given in *Table* 1.

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Soft Lithography

Rigid inorganic materials like silicon, quartz, and metals are used in conventional lithography whereas soft lithography (SL) utilizes soft and flexible rubber (elastomer) stamp for imprinting,

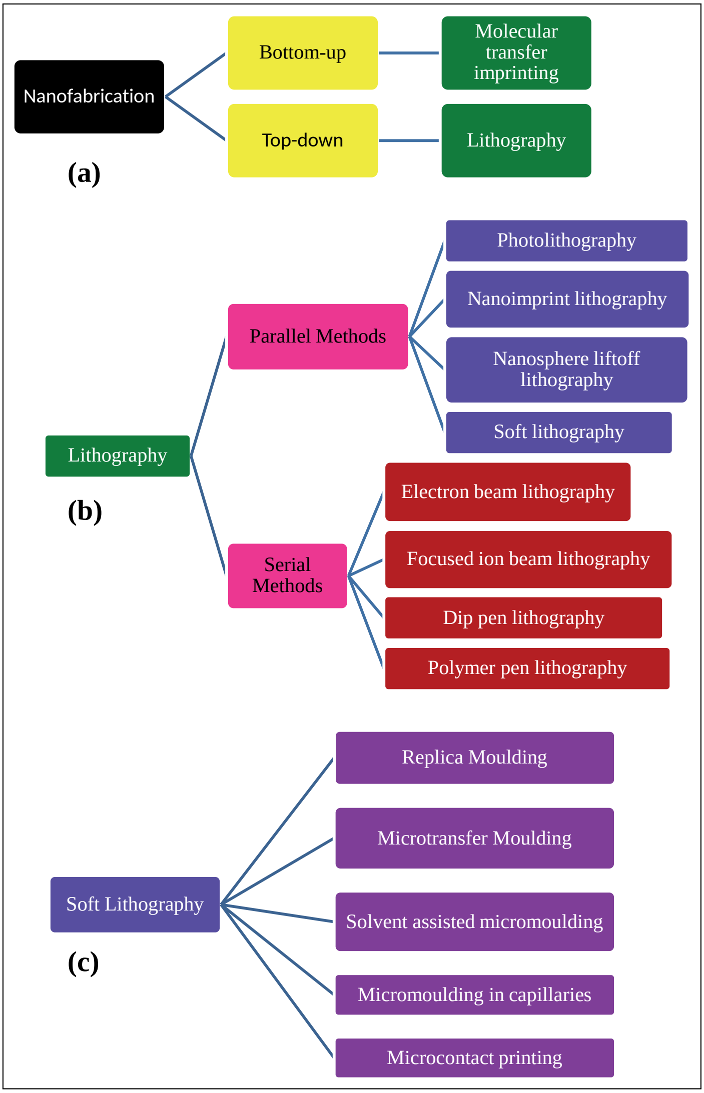

Figure 8. Different methods of nanofabrication.

i.e., transferring the pattern to the substrate. The stamp is made up of poly(dimethyl siloxane) or PDMS. The Young's modulus of silicon is 130 GPa whereas that of PDMS is about 2 MPa.

Let us see the requirements of a material for a good stamp. The PDMS stamp is a multipurpose object. It is used as the stamp for printing, soft mold for imprinting, and as conformable phase masks in near-field optical lithography. Generally, fabrication

	Serial	**Parallel**
Advantages	High resolution, selective placement of specific chemicals at different portions of the pattern.	High throughput, large area printing.
Disadvantages	Limited throughput, small area printing, slow process.	Duplicates only the patterns produced by serial methods.

Table 1. Comparison of serial and parallel lithography.

of devices require large area nanopattern with good resolution. Large area pattern is obtained using a flexible stamp made up of compliant polymer with low modulus. Contradictory to this, good pattern resolution is obtained using a rigid stamp made up of polymer with high Young's modulus. Hence, in order to meet both the requirements, a rigiflex stamp with intermediate modulus is used. Also, the material should possess low surface energy to facilitate its easy removal from the master. If the material is to be cured using UV radiation it should be transparent to it. In brief, the material should possess flexibility, rigidity, low surface energy, and transparency to make a stamp. Polymers are used as flexible and rigiflex stamps.

Soft lithography utilizes the concept of self-assembly. George Whiteside's research group at Harvard University did pioneering work in this field. Initially, there were five variations of soft lithography, viz., micro contact printing (μCP), replica molding (REM), micromolding in capillaries (MIMIC), microtransfer molding (μTM), and solvent assisted micromolding (SAMIM). Later, modifications of these methods have been developed by other research groups. Examples are proximity field nanopatterning (PnP), nanotransfer printing (nTP), decal transfer lithography (DTL), etc.

In order to achieve both – large area pattern and good pattern resolution – a rigiflex stamp with intermediate Young's modulus is used.

Advantages of Soft Lithography

The rubber stamp carries the negative pattern. Also SL is not suitable for making multilayered structures in electronic devices. These are the disadvantages of SL. But it has many advantages over conventional lithography.

At first, in SL, the rubber stamp makes a conformal contact with the rigid substrate accommodating the surface imperfections, if any. As a result, only a small area of non-contact is created. This is contradictory to optical lithography, where it is difficult to obtain close contact between the rigid mask and the rigid substrate on a nanoscale because any dust or imperfection on the surface results in large wedge spacing.

The other important advantages are the ability to create 3D nanostructures and to imprint the pattern on non-planar surfaces. Printing 3D nanostructures is achieved using solid ink and multilayer imprinting. Hence SL is used in the production of unconventional devices in plastic electronics, biotechnology, photonics, data storage, medical science, drug delivery, microfluidics, etc.

Generally, antireflective surfaces in optoelectronic devices are made up of molding or photolithographic techniques. These methods are highly expensive and laborious. But SL is inexpensive and easier. SL is compared over photo lithography in *Table* 2.

Making Surfaces Invisible

Preparation of antireflective surfaces involves two major phases; both involve soft lithography. First phase is the fabrication of a suitable elastomer stamp. Second, transfer of the nanopattern onto the substrates of devices using the elastomer stamp. Main stages involved in the preparation of antireflective surfaces are given in *Figure* 9.

Preparation of Master

The SiO_2 suspension is coated on a silicon wafer. The positive relief created on the silicon wafer by the subsequent photolithographic process is known as the 'master'. It is silanized to avoid sticking of PDMS to the wafer. The master is prepared as shown in *Figure* 10a. The master is durable and can be used several times. In order to increase its lifetime, the master can be repli-

No.	**Soft lithography**	**Photo lithography**
1	Relatively fast, convenient and inexpensive	Expensive
2	Utilizes an elastomeric stamp patterned with relief features	Rigid photomask is used
3	Materials that can be patterned are photo resist, salts, conducting materials, ceramics etc. biological materials (proteins, cells), polymer beads, sol-gel,	Only photo resist can be patterned non-UV sensitive materials like SAMs,
4	Surface irregularities cause small defects	Surface irregularities cause large wedge errors
5	Resolution is a few nm	Resolution is less than 10 nm
6	Can be carried out in normal lab	Clean room facility is required
7	Since the basis is self assembly, certain types of defects are avoided	
8	Process is additive and so the wastage of materials is low	
9	Pattern structure can be varied by mechanical deformation of the PDMS stamp	
10	Non-planar surfaces can be patterned	
11	3D pattern can be generated	
12	Large area patterning is possible	

Table 2. Comparison of soft lithography and photo lithography.

cated in hard polymer, such as epoxy/polyurethane.

Preparation of Stamps

Fabrication of a suitable elastomer stamp is a key factor which determines the success of subsequent stages. Prepare the mixture (base and curing agent) for casting and remove the bubbles. The mix is poured over the master (*Figure* 10b), and is kept at room temperature overnight for curing. The rubber conforms to the features of the master replicating it with high fidelity. Then the stamp is peeled off the master. The ridges on the master appear

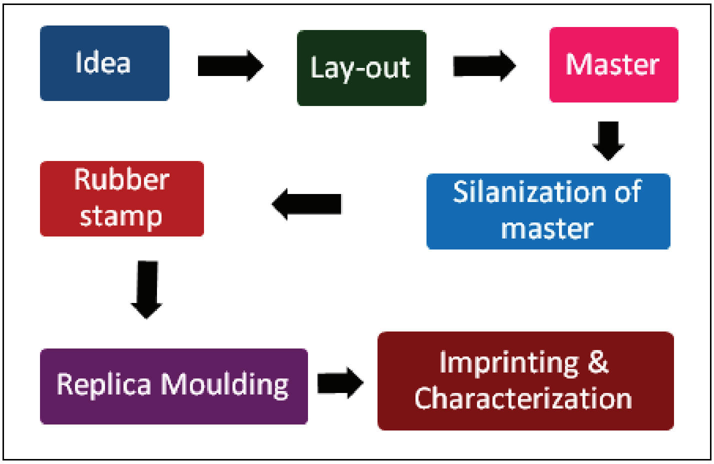

Figure 9. Stages involved in the preparation of antireflective surfaces.

as recesses on the replica, and so it is a negative relief.

Preparation of Antireflective Surfaces

In replica moulding (REM), the flexible PDMS stamp produced is used instead of a rigid mold. The stamp itself acts as the master to duplicate 3D topology in a single step. The pattern on the stamp can be replicated by forming structures on a curable polymer (*Figure* 10c). The relief structures on the replica are complementary to those on the stamp but similar to that of the original master.

The pattern on the stamp can be imprinted on various substrates. This can be done by nanotransfer molding. The curable liquid polymer is placed on the patterned surface of elastomer stamp and it is placed in contact with the substrate. The liquid polymer is allowed to crosslink. When the stamp is removed, a patterned structure is left on the substrate surface. Scanning electron micrographs (SEM) of these imprints are taken to check the fidelity of the nanopattern. The extent of antireflective property of the pattern can be assessed by various testing methods.

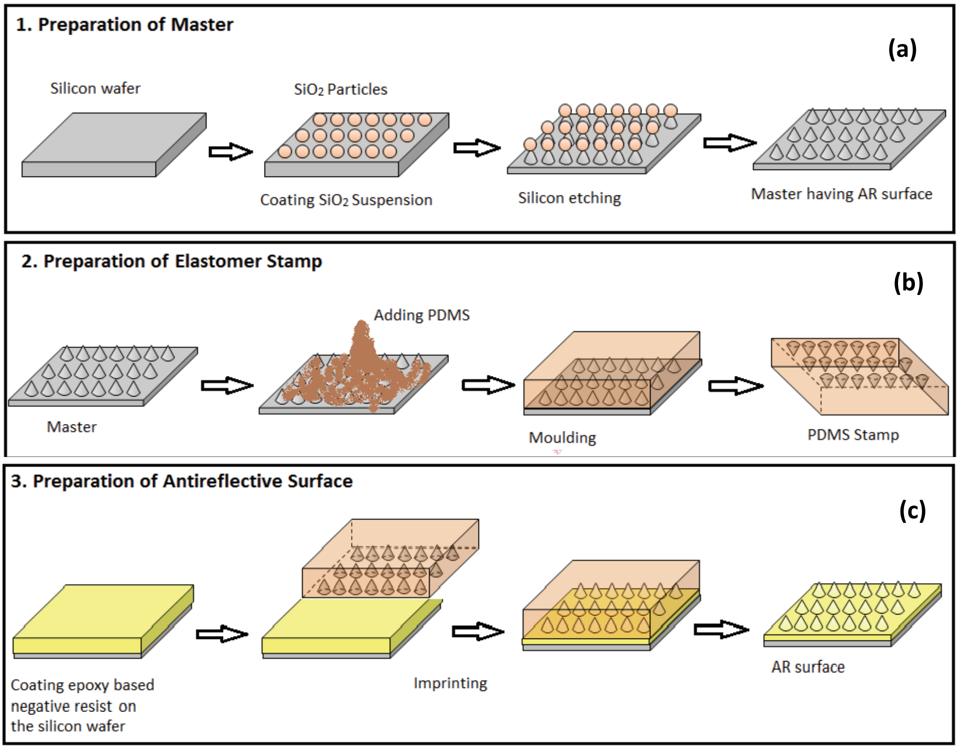

Figure 10. **(a)** Preparation of master **(b)** Preparation of elastomer stamp **(c)** Preparation of antireflective surface.

Challenges in Mimicking Nature

In the actual preparation of antireflective surfaces, the nanostructure is not exactly the same as the real moth eye, but larger than that instead. The feature height is 400–600 nm and spacing is 150 nm, in contrast to 200 nm height and spacing in real moth eye. The difference in dimensions ensures better antireflection. Nanofeatures with higher aspect ratio than moth eye pattern ensures smooth transition of refractive index from the substrate to air.

Our studies indicate that one of the options is to make a stamp with perfluoro polyether (PFPE). The stamp made up of PFPE can replicate nanofeatures efficiently.

Conventional PDMS stamp cannot replicate nanofeatures having high aspect ratio with fidelity, and hence large area patterning is difficult. It is essential to fabricate a stamp which performs better than a traditional two-layer stamp. Our studies indicate that one of the options is to make a stamp with perfluoro polyether (PFPE).

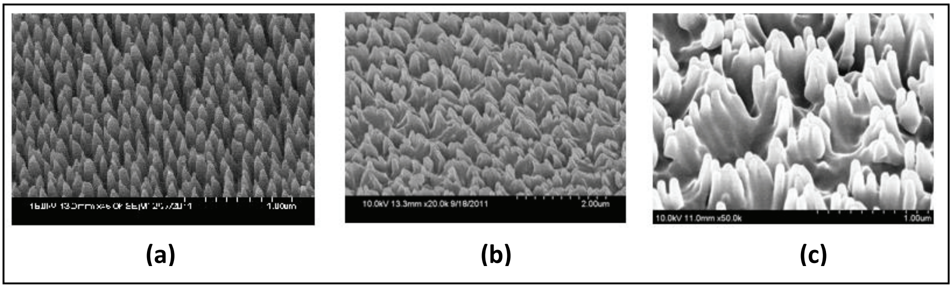

Figure 11. SEM of **(a)** Master, **(b)** Imprinted pattern using PDMS stamp **(c)** Imprinted pattern using PFPE stamp.

SEMs of the master and the imprinted pattern using PDMS stamp are shown in *Figures* 11a and 11b respectively. It can be seen that the stamp made up of PDMS is unable to replicate the pattern successfully. This gives rise to a pattern with low fidelity. But the stamp made up of PFPE can replicate nanofeatures in a better way (*Figure* 11c).

The characteristic eye surface of a moth is essential for its survival. Nature has perfected the moth eye surface over millions of years. So naturally, there are challenges when we mimic the nanopattern on moth eye surface to achieve antireflective surfaces. At present, the antireflective surfaces in solar cells and other optoelectronic devices are made through molding – quite expensive and tedious method. But soft lithography is comparatively easier and cheap. If we can resolve the challenges in replicating the nanopatterns on moth eye surface successfully, it will reduce the cost of the products mentioned earlier, and no doubt, this will enhance the quality of our life.

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Suggested Reading

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