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A NOTE ON OPTICAL MATERIALS FOR PHOTOLITHOGRAPHY APPLICATIONS

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Abstract

Optical lithography or photolithography is well-established optical tool for patterning of substrates, layers or photonic crystals. Therefore, the materials involved in these processes play an important role, especially for the possibility of their further advancements and optimisation. In this review article, we discuss on the role and significance of photoresist materials from various perspectives like their performance in photonic applications and their dependence on various physical and chemical parameters. Further, several emerging now two-dimensional materials like graphene has also been discussed from photonic point of view. We aim to give a short overview of recent developments of such materials in this field.

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Streszczenie

Fotolitografia jest dobrze znanym procesem pozwalającym na tworzenie wzorów na podłożach, warstwach czy kryształach fotonicznych. W związku z tym materiały wykorzystywane w tym procesie pełnią istotną rolę, zwłaszcza ze względu na dalszy możliwy rozwój dziedziny oraz optymalizację procesu. W tym artykule przeglądowym omawiamy rolę i znaczenie fotorezystu z różnych perspektyw, np. jego wydajność w zastosowaniach fotonicznych czy zależność od różnych parametrów fizycznych i chemicznych. Ponadto, omawiamy wiele powstających obecnie dwuwymiarowych materiałów, jak grafen, z punktu widzenia fotoniki. Naszym celem jest przedstawienie krótkiego przeglądu ostatnich osiągnięć w dziedzinie tego typu materiałów wykorzystywanych w fotolitografii.

Contents

1

Introduction

For developing new optical components or devices, one has to rely on the range of available novel materials with tailored optical properties. There are a lot of scientific optical materials available that includes glass and semiconductor materials [1], polymer materials [2], tailored nanomaterials and metamaterials [3] and emerging synthetic biophotonic materials [4]. For nanopatterning of material surfaces, optical lithography is considered as one of the most reliable method so far. It is proved to be flexible, adaptable, and for more than three decades it has met the ever tightening semiconductor industry requirements. It is a photoengraving technique of transferring pattern into a reactive polymer film (resist) which will in turn replicate that pattern into an underlying thin film or substrate [5-10]. Advances in photolithographic technology is always associated with the development of photoresist materials based on the polymers best suited to the successive technologies. The chronological development of lithography and resist materials are shown in Figure 1.1. As can be seen from this figure, the wavelength used was initially visible emission g-line (436 nm) obtained from high pressure mercury lamp followed by the i-line (365 nm). The trend of moving towards shorter wavelengths persisted, the KrF excimer laser (248 nm) and ArF laser (193 nm) were later adopted and used till today [5]. It is also clear from the figure that significant improvement has been achieved by shortening an exposure wavelength.

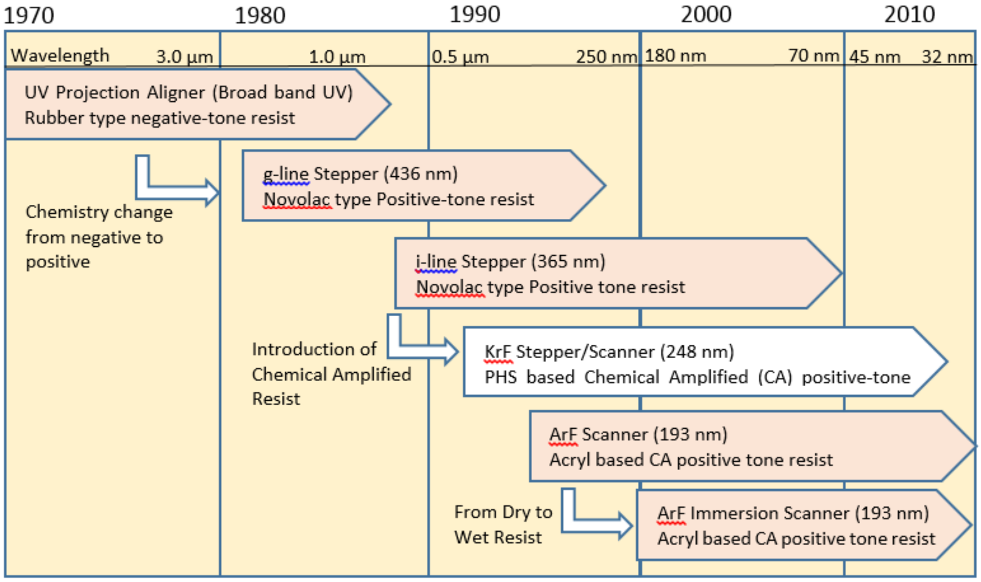

Figure 1.1: Trends of lithography and resist materials

On the other hand, two-dimensional (2D) materials has also attracted tremendous interest in the research community. Currently the best known material is graphene which has unique electrical, mechanical and optical properties, but the absence of bandgap restricts its use in many important applications. In this article, we have discussed about the role of photoresist materials in photolithography technique and various emerging 2D materials. Moreover, importance of parameters like diffraction, reflection and absorption has also been addressed. Generally, in photolithographic process a mask is produced which carries a typical information in the form of pattern that can be transferred by using some optical technique into a photoactive polymer or photoresist (or simply resist) [6]. Figure 1.2 shows the basic steps of photolithographic process in which the resist material is applied as a thin coating over some base and thereafter it is exposed in an image-wise fashion through a mask in such a manner that light strikes on the selected areas of the resist material. After that the exposed resist is developed by using suitable developer and the choice usually depends upon the chemical nature of the resist material. This process is carried out in order to produce a three-dimensional image in the resist material that is the reproduction of the opaque and transparent areas of the mask. The remaining areas of the resist that follows the exposing and developing processes are used to mask the underlying substrate for etching or other transfer steps. After the etching process, the resist is removed by stripping to produce an image which is lying in the substrate [6].

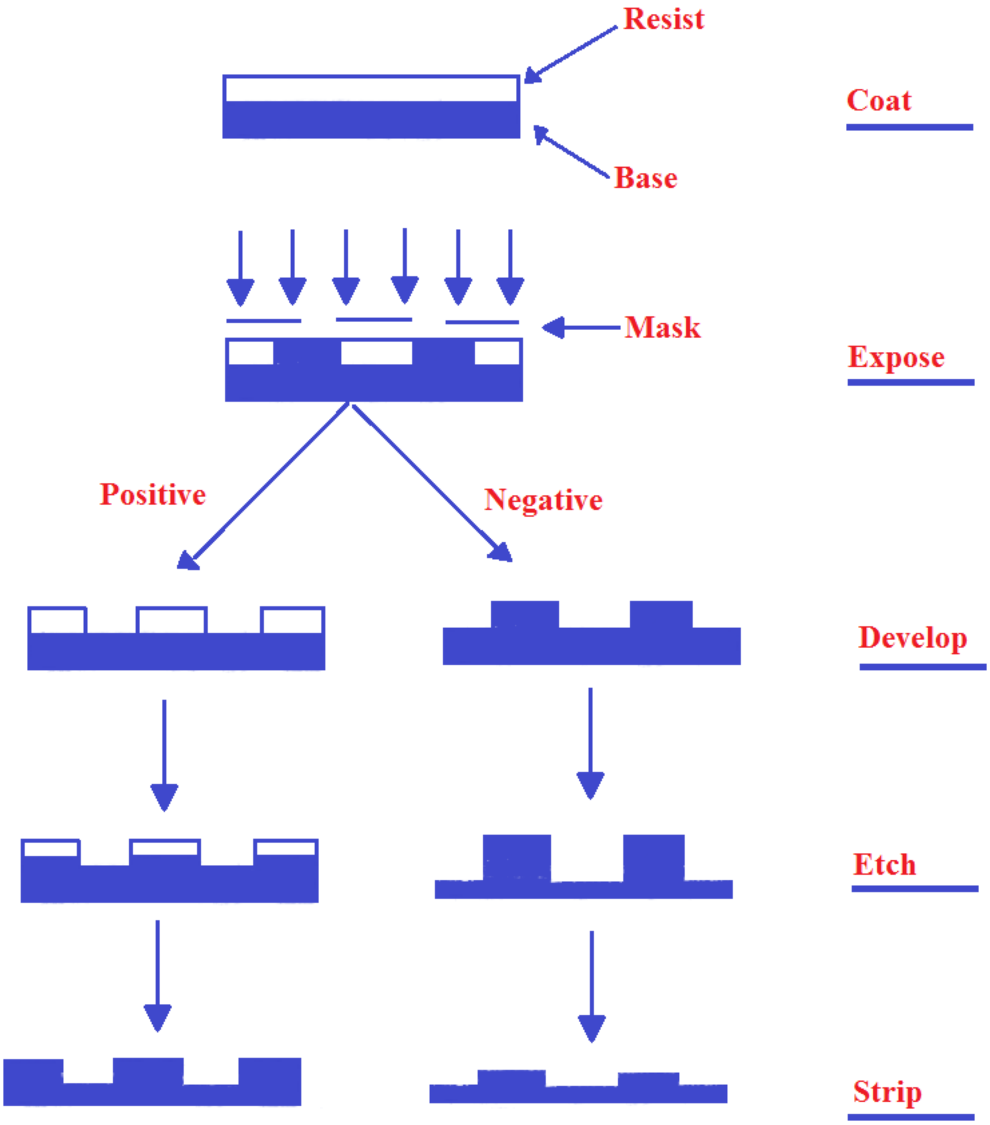

Figure 1.2: Schematic representation of photolithographic process [6].

2

Role of photoresist in photolithographic technique

Photoresist materials are considered as materials essentially required for the final device fabrication with today's technologies. As fragments of a final device are frequently of submicron diameter or less, therefore the processing of photoresists becomes sometimes the limiting factor. Achievable geometrical limits can be reduced by better controlling the photoresist processing and/or by the development of the new photoresist materials or techniques [10]. The following section is dedicated to the current state of the art of photoresist materials and the parameters on which they depend.

Materials that can be used for the synthesis of resist can be considered as appropriate, if it satisfies some criteria necessary for engraving of desired geometries in a chosen substrate. This engraving is done by some form of etching or erosion of the areas of substrate which is not covered by the resist. To obtain this, the photoresist must be impermeable to the etchant composition and it must have sufficient adherence to the substrate to maintain the geometrical boundaries of the desired pattern.

Commercially available photoresists are chemical solutions which consist of two main ingredients; one is the polymer which forms the etch-resistant coating and other one is the sensitizer or an activator. The role of sensitizer or activator is to accept the energy from the light source and to use this energy to change the solubility characteristics of the polymer. There are also some minor constituents that act as promoters or inhibitors and their role is to adjust certain physical properties of the polymer film. All these components are dissolved in the appropriate solvent or the mixture of solvents [10].

The process that can be used for any photoresist application depends upon the nature of the substrate material, the choice of photoresist and the size and tolerances of the desired geometry. Usually photoresist process starts with the preparation of the substrate and finishes with the removal of the photoresist coating after engraving the pattern onto the substrate. There are many parameters which affect the properties of photoresist materials, like environmental conditions, surface preparation, coating and drying etc. which are discussed briefly in the next section.

2.1. Environmental factor

During the processing of photoresist the main challenge is to control the processing environment. The main factors that need to be considered are temperature, humidity, vibration levels, lightening, chemical fumes and airborne particles [11]. Temperature and humidity are usually controlled for the entire processing room, whereas the other factors are controlled at either the room level or by using some special work stations, or sometimes by both. Temperature, humidity and chemical fumes can affect the chemical reactions which is used to process the photoresists. Factors like temperature and vibration will hamper the dimensional tolerances. Particulate contamination results in the defect of photoresist coatings by either scattering the exposing radiations or by causing discontinuities in the processed films. If the contamination is approaching the submicron level, it is advisable to have air filtration system which will reduce the ambient particles significantly below the size. Further, it is necessary to prevent the photoresist from the exposure of light and the lighting in the exposure area must be controlled to avoid the actinic wavelengths [12]. For better results, environmental conditions has to be properly controlled before using photoresist material.

2.2. Surface preparation

A surface of the substrate has to be prepared before the photoresist coating so that the adhesion between the two materials can be increased. The surface has to be free from particulate and chemical contamination. The chemical composition of surface layers of the substrate must be controlled and, in some situation, these surfaces are also precoated with thin layers of adhesion-promoting substances. There are many ways of cleaning the surface [13-14], for e.g. greases and oil can be cleaned by washing the surface with detergent-type solutions like by using standard vapour-degreasing techniques or by using acid and/or alkaline chemical oxidation. Contamination like dirt and oxides can be removed by scrubbing with a mild, non-scratching abrasive. At the end of all cleaning procedures, plenty of clean, purified water can be poured followed by drying the surface with a stream of oil free compressed air.

The chemical composition of the surface of the substrate can severely affect the adherence of photoresist and for this reason certain types of oxides, the valence state of the atoms and the presence of other surface compounds have to be controlled. To understand this situation, example of thermal SiO_2 (silicon dioxide) and Kodak photoresist has been discussed more closely [13]. For example, thermal SiO_2 has three types of surface structures. Type 1 surface consists of strongly absorbed molecular water whereas in type 2 one appreciable concentrations of silanol groups are present. Moreover, type 3 surface comprises of a predominantly siloxane structure. All these structures are shown in Figure 2.1.

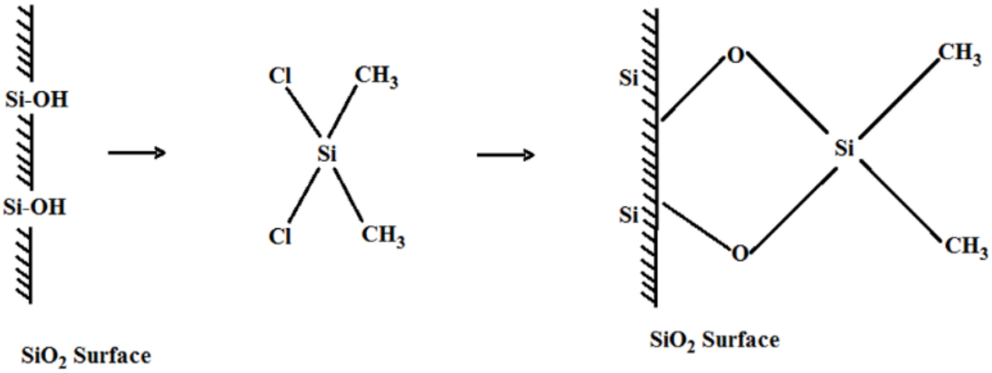

Figure 2.1: Reaction of dimethyldicholorosilane with SiO_2 surface silanol groups [10]

The adhesion of Kodak photoresists KPR-2 (Kodak photoresist), KTFR (Kodak thin film resist) and KMER (Kodak metal-etched resist) was checked with each of the surface structures and results summarized in Table 2.1.

Table 2.1: Effect of photoresist adherence on silicon dioxide surface structure [10]

	Adherence		
Type of Surface	KPR 2*	KTFR*	KMER*
Adsorbed H_2O	Poor	Poor	Good
Si-OH	Good	Poor	Good
Si-O-Si	Good	Good	Good

*KPR 2, KTFR and KMER are Kodak photoresists

Because of the variation in performance, one way is to either choose the best resist for the chosen substrate or else adjust the structure of the substrate surface to give the best performance with a chosen resist. The modification of the surface structure of the substrate can be done either during or after fabrication of the substrate layer. Recently, Liu et al. [10] proposed UV-ozone surface modification method to increase the adhesion between metal films and PMMA (polymethyl methacrylate) and found that the adhesion is significantly increased and it is mainly because of the surface wettability which generates polar oxygen-containing functional groups and the roughness of the surface in nanoscale. A specific post-fabrication surface treatment known as precoat has also been carried out. A precoat is a thin film of nonphotoresist material which is applied to the substrate before the use of photoresist. This layer acts as an adhesion base for the resist. The molecules that are used for precoats consist of sites capable of strong interactions with the substrate surface. It results in a new surface which is formed by close packing of those molecules on the substrate which interacts more strongly with the photoresist as compared to the original surface.

2.3. Coating and drying

The main coating methods that can be used for coating a photoresist are dip coating, roller coating, spray coating or spin coating. Spin coating method is the most widely used technique as it can coat very small piece of substrate with desired thickness. In this method, the sample has to fix with a spindle, after that excessive amount of photoresist can be applied and then the piece is spun at a given speed. The spinning speed helps to spread the resist uniformly, throws of the excess and accelerates drying of the coating.

During coating of the substrate, the most important thing is to control the thickness of the film as it impacts the continuity of the film and the geometrical dimensions that has can be printed on the resist. A general thumb rule for finding the thickness of the resist is that the film thickness should be about one third the width of the smallest line to be reproduced [6, 16]. However, in practice the lower limit of film thickness is the minimum possible thickness that produces a continuous film. The chances of break in the film, or pinholes increases when the thickness of the film decreases [17]. The best idea is to optimize the thickness of the resist coating which can balance between the desired resolution and the tolerance of the pinholes.

In spin coating method, the thickness of the resulting film is controlled by adjusting the spin speed and the solid quantity of the resist solution. The coating thickness of the resist can be calculated from the following equation [17]:

$$t = {KP^2}/{\sqrt{W}} \tag{2.1}$$

where t is the thickness, P is the concentration of solids in the resist and W is the whirler speed. The constant K is a function of type of the resist used, the substrate to which the resist is applied, acceleration characteristics of whirler, and the units of P and W. The speed of the whirler can be adjusted mechanically. The concentration of the solids, P can be adjusted by diluting the resist into the resist solution by using proper solvents.

After the substrate is coated, the next step is to dry it. This step helps to improve the rate of interaction of the material with light and also it improves the image stability at the time of development. The samples can be dried at room temperature on a hot plate, baked in ovens or a combination of both. The time, temperature and method of drying is different for every individual case and it has to be optimized for every case. Drying conditions has to be carefully chosen because most of the resist materials thermally degrade which results in poor functional performance.

Researchers are continuously working on finding new materials for substrates, as every new substrate represents an adhesion problem to be addressed. The limitation in this area is to understand the adhesion mechanisms between photoresist and substrate material. Therefore in photoresist technology, as well as in other fields, considerable efforts are being carried out to put more efforts into the art of the adhesion.

3

Two dimensional material in optical lithography

Moore's Law describes the decrease of the feature size of silicon transistors to only few nanometers and because of that device operation will reach its limits. So, in order to improve the circuit performance in future, alternative materials and their usual fabrication technologies needs to be reviewed and developed. In the search of these new materials for circuits beyond the silicon era, researchers are focusing towards atomically thin materials like graphene [18], two-dimensional (2D) hexagonal boron nitride (h-BN) [19] or transitional metal dichalcogenides [TMDs] [20-22]. Each of these materials is unique in its own way and has specific physical properties that plays an important role in building high performance devices. For example, charge carrier mobility of graphene is very high [18], specifically electron mobility of graphene from kish graphite or highly ordered pyrolytic graphite (HOPG), synthesized from mechanical exfoliation can reach as high as 15,000 cm^2 V^{-1} s^{-1} at room temperature and it is almost ten times high as compared to silicon [18]. Similarly, some of the TMDs (such as MoS_2 and WSe_2) have attracted attention for their high on/off current ratio and low off-state current because of their intrinsic bandgap [20-22]. The latest property is complementary to graphene.

From synthesis point of view, fabrication of large area 2D materials including sublimation of SiC [23] and chemical vapour deposition [24-28] have been studied extensively and it has been found that mechanical exfoliation method can produce 2D flakes with better crystal quality and purity. Additionally, mechanical exfoliation is also a cost effective way. Further, some other characteristics of the exfoliated 2D material sheets are: its small size (typically in micron range), the random distribution and orientation of the sheets on the substrate as well as the irregular shape of the sheets. These characteristics impose challenges from device fabrication point of view, specifically in two respects: patterning of the 2D materials and alignment of the metal contacts to the patterned 2D sheets. Most of the researchers are trying to avoid the patterning of exfoliated 2D materials and fabricate electronic devices on as-exfoliated pristine 2D materials because it is hard to control the dimension of devices which in turn limits the practical application of such kind of devices. Moreover, electron beam lithography (EBL) is considered as one of the strongest patterning techniques for aligning of metal contacts to exfoliated 2D sheets for making electronic devices. But EBL has some drawbacks; for example, EBL is a serial process and it is taking a long time to expose the metal contact openings. In addition, electron beam irradiation can induce defects in the 2D sheets [29-31] which degrades the electrical properties of 2D materials [32-33]. Hence, researchers are opting for optical lithography over EBL for such situations. The main advantages of using optical lithography are low cost of the processes, speed of exposure and ease of patterning. This method is successful because of the successful implementation of mask design.

3.1. Graphene

In the recent years, graphene has attracted intensive interest and is considered as one of the competitive functional materials for electronics and optoelectronics because of its extremely high intrinsic carrier mobility, thin body and high transparency [18]. Additionally, recent progresses in graphene growth and transfer technology increases the feasibility of exploring and using graphene devices [28-34]. Many types of transfer technologies have been developed for transferring graphene from metal growth substrates to device-compatible substrates [31-33]. In addition, clean and crackless transfer of graphene has also been realized [32]. Further, devices based on graphene which is obtained from CVD (chemical vapour deposition) have been fabricated with high carrier mobility of up to 5000-10 000 $cm^2V^{-1}S^{-1}$ [30, 34-35]. All of them can be patterned by using E-beam lithography (EBL) which is certainly not a cost effective method and the method of fabricating graphene devices efficiently and cheaply has not been realized completely. It is well known that the bottleneck of micro/nano devices fabrication efficiency depends on the patterning technology and hence most of the graphene devices are compatible with photolithography, which is the most efficient patterning technology. Recently, more than hundred graphene devices are fabricated by using photolithography technique, but almost all the devices exhibit low carrier mobility between 1000-1400 $cm^2V^{-1}S^{-1}$ [16, 24, 27].

Photoresist are generally composed of polymers which are soluble in some known solvents. But after the exposure of UV, the solubility changes and then more aggressive solvents are required for post-exposure. However, it is easy to chemically remove almost all the resist from the surface of graphene, but some residues may remain which generally degrade the performance of the device and its thermal conductivity [36]. Though, there are some exceptions, for example, in Suk *et.al.* [37], biosensor fabrications was discussed and they observed higher sensitivity for devices with photosensitive residue. But in general, removal of the resist is important for the device optimization [38]. It can be done by using appropriate solvents, such as acetone, chlorobenzene or some commercially available photoresist strippers like Nano Removal PG (Microchem). Annealing in ultra-high vacuum or inert gas (Ar) atmosphere is also a common technique used to remove the residues. Proper care has to be taken while performing this so that it will not damage the device components.

It has been observed that, photoresists have caused more damage and contamination of graphene substrates as compared to electron beam resists. A comparison study carried out by Fan *et. al.* [39] between PMMA and a commonly used photoresist (AZ 6624) disclosed that the contamination and the disorder caused by PMMA could be completely reversed by annealing in an Ar atmosphere at 300 °C for 60 min, though recent studies shows at the same time that thermal annealing is not sufficient to eliminate all PMMA resist from graphene [39]. On the contrary, AZ 6624 resist, which was applied on the similar sample, could not be removed using the same annealing process. The Raman spectrum of AZ 6624 processed sample contains the traces of amorphous carbon which confirms that the resist was adsorbed on the surface of the graphene even after solvent and annealing treatments. Though the exact mechanism of adsorption was not investigated, and the number of components in commercial photoresist complicates the analysis. Since PMMA is usually supplied in a single solvent (chlorobenzene or anisole), on the other hand commercial photoresists can have number of components that may interact with graphene surface. So the fact that photoresist is difficult to remove completely should always be kept in mind while comparing the literature.

3.2. Other 2D materials

Nevertheless, graphene (Figure 3.1A) has metallic nature and because of that it is not very suitable for light generating functions and hence the properties of other 2D materials has to be explored. Apart from graphene, hexagonal boron nitride (hBN) [40], as can be seen from Figure 3.1B, is also a layered material with honeycomb lattice structure. It has a large bandgap of around 6.0 eV which makes it an outstanding dielectric material which helps in enhancing the electronic and optoelectronic performance of many devices. Recently, single-layer transition metal dichalcogenides (TMDCs), like molybdenum disulphide (Figure 3.1C) and tungsten diselenide is a point of attraction because of its energy range which lies in between 1.5-2.5 eV and beyond. It is very much useful for fabricating devices because of its finite and direct bandgap in the monolayer form [41]. Further, it also gives exciting opportunities for the research of novel optical phenomena. In the year 2014 there has been an arrival of new member in 2D family named black phosphorous (Figure 3.1D) [42-43]. It is a layered material with a moderate bandgap of 0.3 eV in its thin film form and it is comfortably tunable to around 2.0 eV in a single layer form. It bridges the gap between zero bandgap graphene and wide bandgap of transition metal dichalogenides. The development of these materials is mainly hampered by the lack of cost effective fabrication methods that produce high quality material in sufficiently large quantity. Although photonics with new 2D materials is still largely unexplored, the potential of these materials can be forecasted to be very high [44].

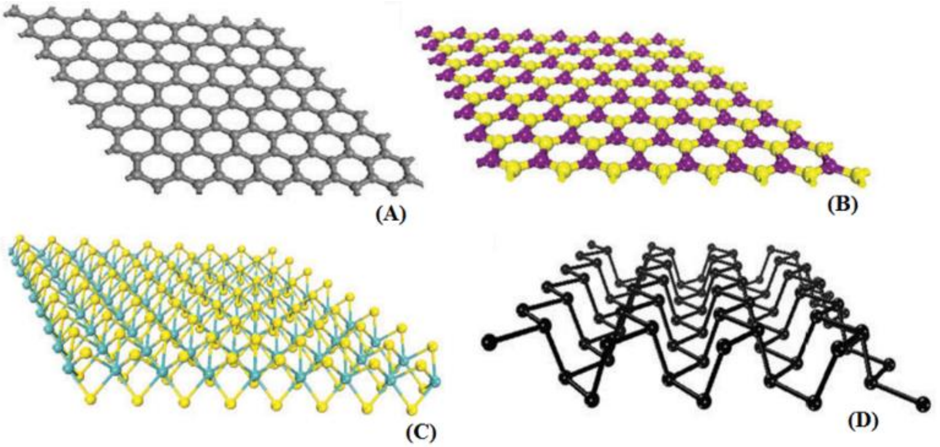

Figure 3.1: Lattice structure of various 2D materials (A) Monolayer Graphene (B) Monolayer hexagonal boron nitride (C) MoS_2 monolayer (TMDC) (D) Single layer black phosphorous [44]

Apart from the above 2D materials, metamaterials are also a major attraction now a days. In essence, metamaterials are all about new functionalities that can be obtained by using conventional materials just by rearranging them on a small scale. Metamaterials consist of periodic subwavelength metal/dielectric structures that are resonantly coupled to the electric or magnetic or both components of the incident electromagnetic fields. They exhibit effective electric (represented by electric permittivity ε) and/or magnetic (given by magnetic permeability μ) response which is not found in nature [45].

Further, metals like Al, Cr, Au etc. can be conveniently used in silicon-based processes, hence metallic mixers can be fabricated with conventional photolithography. Generally, silicon oxide layer or even silicon wafer substrate can act as a sacrificial layer. Deposition of metallic layer on sacrificial layer can be done by using evaporation, sputtering or by electroplating. Thin metallic films up-to 10 μm can be done by using evaporation and sputtering technique because of slow growth rate whereas thicker layer can be obtained by using electroplating. A metallic layer can be patterned by a lift-off process or by chemical etching.

4

Diffraction, absorption and reflection in photolithography process

For photolithography, diffraction of light is an important parameter as it sets the limit of the maximum resolution or the minimum size of the individual elements which can be achieved. Diffraction is a phenomenon in which apparent deviation of light ray propagation which takes place as it passes through an obstacle such as an edge of opaque obstacle/object. From qualitative point of view in geometrical optics, if an opaque object is placed between a point light source and a screen, the edge of the object will cast a sharp shadow on the screen. Light will not reach the screen at points within the geometrical shadow, whereas outside the shadow the screen will be uniformly illuminated. In actuality, the shadow which is cast by the edge is diffused and it consists of alternate bright and dark bands that extend into the geometrical shadow and this bending of light around the sharp corner is called diffraction of light. Clearly, diffraction causes the image of a perfectly defined edge to become blurred or diffused at the resist surface.

The theoretical resolution capacity of shadow photolithography with a mask that comprises of equal lines and spaces of width b is given as [6]:

$$2b_{min} = 3\sqrt{\lambda\left(s + \frac{d}{2}\right)} \tag{4.1}$$

where 2b is the grating period (1/2b is the fundamental spatial frequency υ), s is the gap width between the mask and the photoresist surface, λ is the wavelength of the radiation used and d is the thickness of the photoresist. In case of hard contact printing, the gap width, s is equal to 0 and the maximum resolution for 400 nm wavelength and one micron thick photoresist will be slightly less than 1µm [46]. In order to obtain higher resolutions, shorter wavelength light and lens systems with larger numerical apertures should be used. Generally, the minimum feature size that can be achieved is nearly the same or slightly smaller than the wavelength of light used at the time for exposure, when a relatively large numerical aperture (typically > 0.5) is used. But when the lens system with high numerical aperture is used, the depth of the focus becomes very short and because of that the exposure process becomes sensitive to slight variations in the thickness and absolute position of the resist layer [6, 47].

Photoresist, by its very nature, must absorb some portion of the exposing radiation in order to undergo a photochemical reaction. The optical effects that occur in the photoresist and substrate during exposure are important factors that influence the verticality of the photoresist walls. Light is absorbed along its way through the photoresist, so the exposure dose absorbed at the top of the resist is higher than at the bottom. This results in inverted v-shape photoresist line cross-section in case of positive resist (where parts with higher dose are more resilient) and v-shape line cross-section in case of negative resist as can be seen in Figure 4.1 (a-b) (where parts with higher dose are less resilient and can be removed more easily).

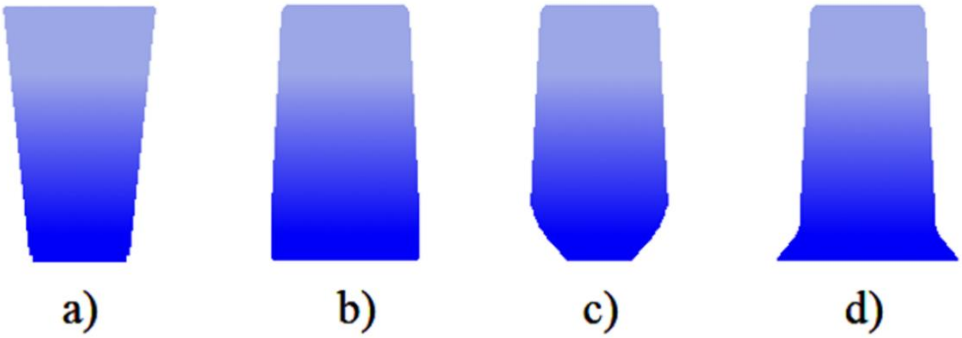

Figure 4.1: Various shapes of developed photoresist: a) inverted v-shape, b) almost rectangular v-shape c) undercut d) footing; the shapes correspond to the results presented in [5, 48]

For example, in simple case of a non-reflecting substrate, the light travels only downward through the resist film of thickness D. The fraction of light reached to the bottom (E_{bottom}) with respect to (E_{top}) is given by:

$$E_{bottom}/E_{top} = T_D = e^{-\alpha D} \tag{4.2}$$

where, α is the resist absorption coefficient, which is assumed to be constant through the resist film.

Moreover, reflection from the substrate interferes with the incident light. It can create standing waves that can lead to swing curves, i.e. sinusoidal dependence of the "dose to clear" of the resist thickness. It also affects the shape of the resist profile leading to resist undercut or footing [Figure 4.1(c-d)] [5]. Hence, controlling the magnitude and, more importantly, phase of reflection from the substrate can significantly change the resolution and performance of the patterning. To this end, usage of substrate (e.g. photonic crystal) which optical properties can be toggled externally with use of incident polarization [49], temperature [50], electric voltage [51] or magnetic field [52] etc. may allow to obtain the desired shape of the photoresist profile.

5

Wet chemical etching of quartz

Quartz is considered as one of the interesting materials for various optical applications [53-55]. It has many properties which are complimentary to silicon but the major hurdle which limits the use of quartz is the limited suitable processing methods for producing structures with desired shapes. Some of the physical properties of quartz are summarized in Table 5.1 [56].

Table 5.1: Physical Property of Quartz

Property	Value ∥ Z	Value ⊥ Z	Temperature dependency (T)
Thermal Conductivity (cal/(cm/s/°C))	29×10^{-3}	16×10^{-3}	Decreases with T
Dielectric Constant	4.6	4.5	Decreases with T
Thermal expansion coefficient (1/°C)	7.1×10^{-6}	13.2×10^{-6}	Increases with T
Electrical resistivity [Ω-cm]	0.1×10^{13} (ionic)	20×10^{13} (electronic)	Decreases with T
Young's modulus	9.7×10^{10}	7.6×10^{10}	Decreases with T
Density [kg/m^3]	2.66×10^3	-	-
Curie Temperature [°C]	573	-	-

Etching is a process of material being removed from the surface of other materials. There exist two types of etching; wet chemical etching and dry chemical etching. The etching process in which liquid chemicals or etchants are used to take off the substrate material is called as wet etching. Wet etching is completely a chemical process which requires simple instruments. Whereas, in dry etching plasmas or etchant gases are used to take off the substrate. Wet chemical etching of quartz is a standard processing method, but its high degree of anisotropy and trigonal symmetry hinders its study and use. Figure 5.1 shows the schematic diagram of etching process.

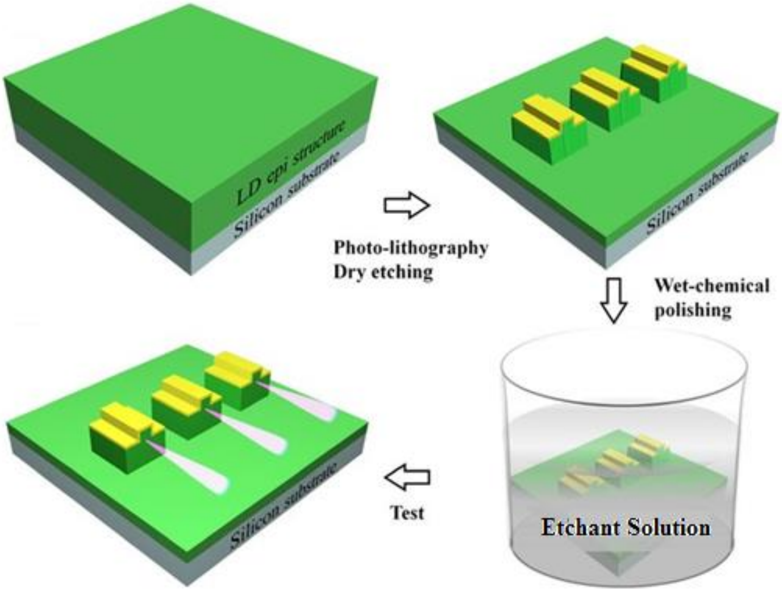

Figure 5.1: Schematic diagram of etching process [57]

Wet etching is carried out by using aqueous hydrofluoric acid [HF] and ammonium fluoride [NH_4F] act as a buffer. The etched profiles changes a lot with process conditions, mostly with etchant temperature and concentration. The etch rate is much higher along the Z-axis as compared to the other directions [58]. The most detailed etch diagram was given by Ueda et al. [53] in which they summarized the etch rate of 21 substrates, all cut with different crystallographic orientations. The etchant used in the study was ammonium bifluoride [NH_4HF_2] and buffer (HF: NH_4F) in the ratio of 2:3 at 82 °C [59]. Rangesten et al. [60] on the other hand performed the same etching experiment at 55 °C and they observed that etchant solution produces smooth surfaces and they possess an anisotropic behaviour.

Hydrofluoric acid [HF] is the only etchant which can be used to etch amorphous SiO_2, quartz or glass with a significantly high etch rate. Moreover, almost all common photoresist are quite stable against HF as it comparatively a weak acid and the value of degree of dissociation is 3.14. The main challenge during HF etching is the poor adhesion that causes an underetching below the resist mask which leads to isotropic etching (Figure 5.2). To overcome this problem, adhesion of resist and substrate has to be carefully checked. For instance there are some steps which can be performed at the time of pre-treatment of substrate and resist processing which enhances the adhesion between substrate and resist. For example, at first the contamination on the substrate especially organic impurities should be cleaned properly with a two-stage cleaning process. Further, in case of clean substrates, the substrate should be baked for few minutes at 120-140 °C which helps in desorption of water. For better adhesion the resist and to avoid the re-absorption of water, coating should be done immediately after cooling the substrate from baking to room temperature. Moreover, incomplete etching of the substrate with HF before resist coating also results in a very poor and non-reproducible resist adhesion but it can be restored with a bake temperature greater than 700 °C. One more solution for improving adhesion is to bake the substrate at 120-130 °C for 5 to 10 minutes after development. After baking, the substrate should not be cooled abruptly and it should be carefully handled to prevent it from crakes [56].

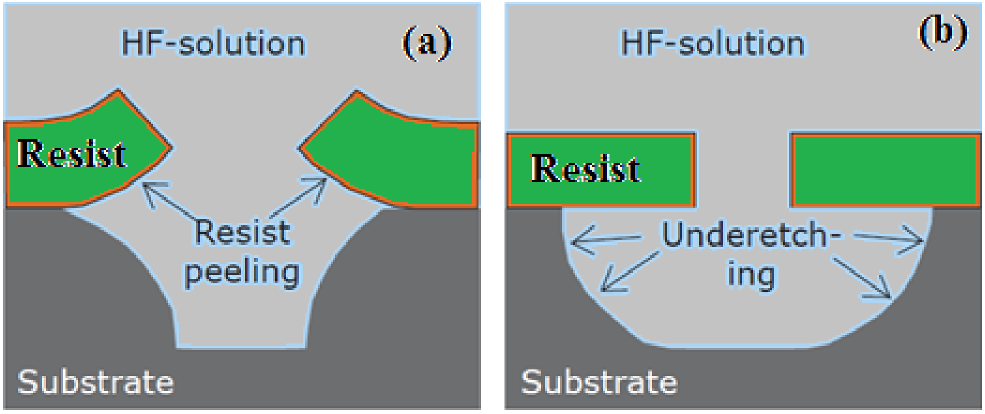

Figure 5.2: (a) Resist adhesion is poor (b) Prediction of underetching leads to isotropical etching

5.1. Structure of quartz crystal and its influence on etching

Quartz has various crystalline phases, out of which the most stable phase is α-quartz. The typical symmetry of the quartz crystal is threefold around the optical axis i.e. Z axis. Perpendicular to the Z axis are the three electrical X axes, each X axis has a twofold symmetry as can be seen from Figure 5.3. The natural crystallographic planes of quartz are *s*, *R*, *m* and *r*. The *R* and *r* planes are rombohedral planes, *m*-planes are the hexagonal prism planes, the trigonal trapezoid is denoted as *x* and trigonal bipyramidal planes as *s*. All the planes have Si atoms with one double bond at their clean surface and hence they are stable [61].

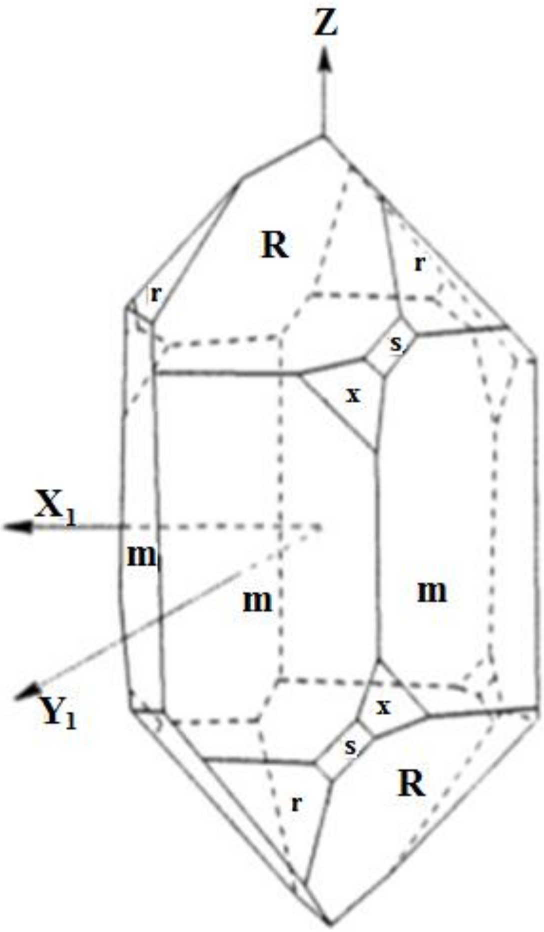

Figure 5.3: Right hand α-quartz and its projection on the XY plane [56]

The Wulf-Herring-Jacodine diagram can be used to predict the etch results provided that a two-dimensional etch diagram exist for that specific mixture of etchant and the chosen temperature and etch condition. These diagrams also reflect the possible planes and their etch rate. Unfortunately, general etch diagrams for arbitrary concentrations and temperatures are not available.

5.2. Mechanism of wet chemical etching of Quartz

Wet chemical etching of quartz and amorphous SiO_2 is mainly done by HF-based (hydrofluoric acid) etch solutions. It has been observed that chemical etch mechanism is same for amorphous and crystalline SiO_2, but the particular active substance is different. The general principle states that the etch mechanism is based on the chemical bond between Si and O atoms at the surface. It has been proved experimentally that the presence of HF and HF^{-}_{2} is required for the Si atom to detach from a SiO_2 surface. Moreover, the etch rate of amorphous SiO_2 depends mainly on the concentration of HF_2^-, hence the dominating etch reaction is [62]

$$SiO_2 + 3HF_2^- + H^+ \longrightarrow SiF_6^{2-} + 2H^+ + 3H_2O \tag{5.1}$$

and in the presence of buffer NH_4F

$$2NH_4^+ + SiF_6^{2-} \leftrightharpoons (NH_4)_2SiF_6^- \tag{5.2}$$

Whereas, when etching of crystalline α-quartz is carried out then HF is the active substance and the etch reaction for quartz would be

$$SiO_2 + 6HF \longrightarrow SiF_6^{2-} + 2H^+ + 2H_2O \tag{5.3}$$

5.3. Experimental details of wet chemical etching

Quartz wafer obtained from supplier is 200 µm thick, polished and coated with Cr/Au from both sides. The etching pattern was observed on the mask layer by photolithographic technique in which the positive photoresist Shipley 1813 was used. The Au and Cr layer were etched by using KI (potassium iodide) solution and chromium etch solution respectively. For etching of quartz a mixture of HF: NH_4F in the ratio of 2:3 was used. The etchant mixture was kept at a constant temperature of 55 °C in a Teflon beaker with a cooled lid, in a water bath with continuous stirring. In order to identify the etch rates, triangular openings and rectangular openings of different sizes are produced. The openings were aligned along X and Y axes respectively. The etch timing was carefully chosen so that the largest opening displayed all crystal planes of interest [63].

It has been observed from the studies that the relative etch rate of the crystal planes is: $m < r < s < r_2 < r_4$. For absolute etch rates and orientations SEM micrographs are taken for the substrate. From the experiments they also found that the slowest etching planes reflects concave structure [Figure 5.4]. It can be seen from the figure that four X groove with four different initial widths are obtained. Further, it is also evident that slightly faster etching planes gradually disappear with time [60].

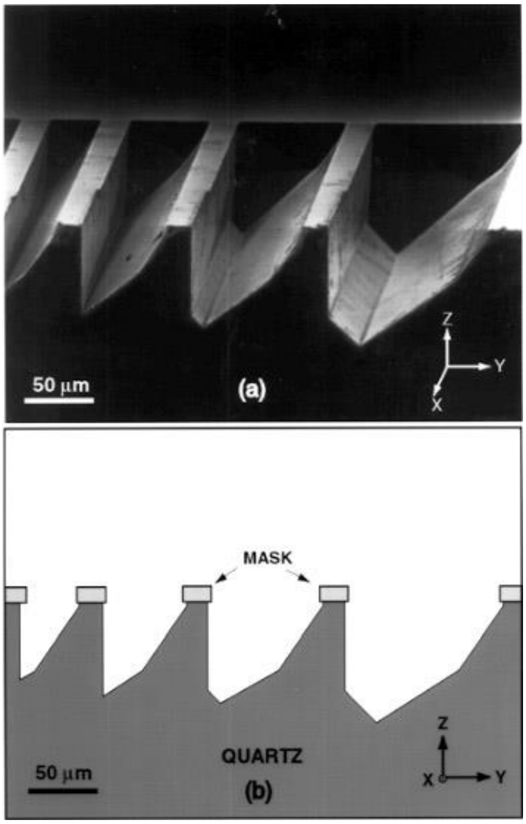

Figure 5.4: SEM micrograph (a) confirming four X grooves with four different widths (b) Simulation of mask opening [60]

6

Conclusions

In conclusion, photolithography is a photonic technique or process in which a light sensitive polymer or photoresist is exposed and developed to form a three-dimensional relief images on the substrate. It is one of the powerful methods for patterning large areas with high throughput. With suitable selection of materials, there is a possibility to achieve more with this technique. For that goal scientist are working hard to introduce new materials into the devices that can act as a photoresist layer placed on a substrate. Every new substrate provides some solution to address the adhesion problem. One solution is to modify the substrate which results in increasing its adhesion. Another approach is to use electron-beam resist in which the low-energy electrons scan the resist coated substrate and draws the desired pattern on it. One more solution is to eliminate the photoresist etchant mask completely and directly exposing the material with high energy sources such as lasers or electron beams. All these advanced techniques are still in their relative infancy and need a lot of further research in order to use them in a standard manner and to allow them to play a significant role in producing advanced photonic and optoelectronic devices.

Further, post treatment methods like etching is one of the important process which has to carefully perform. Wet chemical etching is very much substrate specific and from the studies, it can be concluded that reaction controlled symmetrical etch process can be done in quartz substrate. The etching process highly depends upon the geometry of quartz as the orientation of the crystallographic coordinate system decides the side wall profiles and the profiles have different slopes. These slopes varies with the different etchant and temperature. Generally, the anisotropy and etch rate increases with increase in the concentration of HF.

On the other side of development, atomically thin materials such as graphene and transition metal dichalcogenides are of great interest because of their interesting properties like extremely high field confinement, tunability and long lifetime. These materials also offer variety of choices including metals, semimetals and semiconductors with small or large optical gaps which opens a window for new and different application and it is certainly beyond the capacity of conventional bulk materials. To fully use these materials there is apparent need to gain fundamental understandings like their intrinsic and extrinsic optical behaviours. Though issues like low light absorption and short light-matter interaction length of two dimensional materials needs to be focussed on. New areas of research wherein correlation between conventional photonic elements including cavities, waveguides or plasmonic nanostructures can also be studied for these materials. Conclusively, it is a need for an hour to develop controllable and stable chemical doping for graphene and other two-dimensional materials to exploit them fully for their application in lithography and related fields.

Bibliography

1. B.J. Zeng, J.Z. Huang, R.W. Ni, N.N. Yu, W. Wei, Y.Z. Hu, Z. Li and X.S. Miao. Metallic resist for phase-change lithography. *Scientific Reports,* 4: 5300-1-7, 2014.
2. H. Eom, J-H Kim, J. Hur, T-S Kim, S-K Sung, J-H Choi, E. Lee, J-H Jeong and I. Park. Nanostructured polymer substrate for flexible and mechanically robust metal electrodes by nanoimprint lithography. *ACS Appl. Mater. Interfaces*, 7 (45): 25171-25179, 2015.
3. I. Bergmair. B. Dastmalchi, M. Bergmair, A. Saeed, W. Hilber, G. Hesser, C. Helgert, E. Pshenay-Severin, T. Pertsch, E.B. Kley, U. Hubner, N.H. Shen, R. Penciu, M. Kafesaki, C.M. Soukoulis, K. Hingerl, M. Muehlberger and R. Schoeftner. Single and multilayer metamaterials fabricated by nanoimprint lithography, *Nanotechnology,* 22 (32): 325301-325306, 2011.
4. K.S. Lee, C. Andraud, K. Tamada, K. Sokolov, K.T. Kotz and G. Zheng, Feature issue introduction: biophotonic materials and applications, *Biomed Opt Express* 7 (5): 2078-2081, 2016.
5. C. Mack. *Fundamental principles of optical lithography: the science of microfabrication*. John Wiley & Sons Ltd, 2007.
6. G. Cao and Y Wang. *Nanostructures and Nanomaterials; Synthesis, Properties and Applications*. Imperial College Press: London, 2004.
7. K. Suziki, S. Matsui and Y. Ochiai. *Sub-Half-Micron Lithography for ULSIs*. Cambridge University Press: Cambridge, 2000.
8. D. Brambley, B. Martin and P.D. Prewett. Microlithography: An overview, *Adv. Mater. Opt. Electron* 4 (2): 55-74, 1994.
9. M. Gentili, C. Giovannella and S. Selci. *Nanolithography: A Borderland between STM, EB, IB and X-Ray Lithographies*. Kluwer, Dordrecht: Netherlands, 1993.
10. R.O. Lussow. Photoresist materials and applications. *J. Vac. Sci. Technol.* 6 (1):18-24, 1969.
11. A. Sarangan. *Nanofabrication: Principles to Laboratory Practice*. CRC Press, 2016.
12. W.V. Pink, *Western Electric Engr*. 11: 27, 1967.

13. Photosensitive Resists for Industry, Industrial Data Book, Eastman Kodak Co., Rochester N.Y. 1962.
14. K. Nakamura, Photopolymers; Photoresist materials, Processes and Applications, CRC Press, 2014.
15. J. Liu, L. He, L. Wang, Y. Man, L. Huang, Z. Xu, D. Ge, J. Li, C. Liu and L. Wang. Significant enhancement of the adhesion between metal films and polymer substrates by UV-ozone surface modification in nanoscale, *ACS Appl. Mater. Interfaces* 8 (44): 30576-30582, 2016.
16. D. Roy, P.K. Basu and S.V. Eswaran. Photoresist for microlithography. *Resonance* 7(7): 44-53, 2002.
17. R.F. Kelly. *Proc. Kodak Seminar on Microminiaturization*. June 1965, 38.
18. K.S. Novoselov, A.K. Geim, S. Morozov, D. Jiang, Y. Zhang, S.A. Dubonos, I. Grigorieva and A. Firsov. Electric field effect in atomically thin carbon films *Science* 306 (5696): 666-669, 2004.
19. L. Song, L. Ci, H. Lu, P.B. Sorokin, C. Jin, J. Ni, A.G. Kvashnin, D.G. Kvashnin, J. Lou, B.I. Yakobson and P.M. Ajayan. Large scale growth and characterization of atomic hexagonal boron nitride layers *Nano Lett.* 10(8): 3209-3215, 2010.
20. B. Radisavljevic, A. Radenovic, J. Brivio, V. Giacometti and A. Kis. Single-layer MoS_2 transistors *Nat. Nanotechnol.* 6 (3): 147-150, 2011.
21. Q.H. Wang, K. Kalantar-Zadeh, A. Kis, J.N. Coleman and M.S. Strano. Electronics and optoelectronics of two-dimensional transition metal dichalcogenides. *Nat. Nanotechnol.* 7 (11): 699-712, 2012.
22. H. Fang, S. Chuang, T.C. Chang, K. Takei, T. Takahashi and A. Javey. High-performance single layered WSe_2 p-FETs with chemically doped contacts. *Nano Lett.* 12 (7): 3788-3792, 2012.
23. V.Y. Aristov, G. Urbanik, K. Kummer, D.V. Vyalikh, O.V. Molodtsova, A.B. Preobrajenski, A.A. Zakharov, C. Hess, T. Hänke, B. Büchner, I. Vobornik, J. Fujii, G. Panaccione, Y.A. Ossipyan and M. Knupfer. Graphene synthesis on cubic SiC/Si wafers perspectives for mass production of graphene-based electronic devices. *Nano Lett.* 10(3): 992-995, 2010.
24. Y. Lee, S. Bae, H. Jang, S. Jang, S.-E. Zhu, S.H. Sim, Y.I. Song, B.H.Hong and J.-H. Ahn. Wafer scale synthesis and transfer of graphene films. *Nano Lett.* 10(2): 490-493, 2010.
25. J.K. Huang, J. Pu, C.L. Hsu, M.H. Chiu, Z.Y. Juang, Y.H. Chang, W.H. Chang, Y. Iwasa, T. Takenobu and L.J. Li. Large-area synthesis of highly crystalline WSe2 mono layers and device applications. *ACS Nano* 8 (1): 923-930, 2014.
26. Y.C. Lin, W. Zhang, J.K. Huang, K.K. Liu, Y.H. Lee, C.T. Liang, C.W. Chu and L.J. Li. Wafer scale MoS_2 thin layers prepared by MoO_3 sulfurization. *Nanoscale* 4(20): 6637-6641, 2012.

27. Y.-H. Lee, X.-Q. Zhang,W. Zhang, M.-T. Chang, C.-T. Lin, K.-D. Chang, Y.-C. Yu, J.T.-W. Wang, C.-S. Chang, L.-J. Li and T.-W. Lin. Synthesis of large-area MoS2 atomic layers with chemical vapor deposition. *Adv. Mater.* 24 (17): 2320-2325, 2012.
28. A. Tarasov, P.M. Campbell, M.Y. Tsai, Z.R. Hesabi, J. Feirer, S. Graham,W.J. Ready and E.M. Vogel. Highly uniform trilayer molybdenum disulfide for wafer-scale device fabrication. *Adv. Funct. Mater*. 24 (40): 6389-6400, 2014.
29. D. Teweldebrhan and A.A. Balandin. Modification of graphene properties due to electron-beam irradiation. *Appl. Phys. Lett*. 94 (1): 013101-03, 2009.
30. R. Zan, Q.M. Ramasse, R. Jalil, T. Georgiou, U. Bangert and K.S. Novoselov. Control of radiation damage in MoS_2 by graphene encapsulation. *ACS Nano* 7 (11): 10167-10174, 2013.
31. A. Garcia, A.M. Raya, M.M. Mariscal, R. Esparza, M. Herrera, S.I. Molina, G. Scavello, P.L. Galindo, M. Jose-Yacaman and A. Ponce. Analysis of electron beam damage of exfoliated MoS_2 sheets and quantitative HAADF-STEM imaging. *Ultramicroscopy* 146: 33-38, 2014.
32. I. Childres, L.A. Jauregui, M. Foxe, J. Tian, R. Jalilian, I. Jovanovic and Y.P. Chen. Effect of electron-beam irradiation on graphene field effect devices. *Appl. Phys. Lett.* 97 (17): 173109-01-03, 2010.
33. C. Durand, X. Zhang, J. Fowlkes, S. Najmaei, J. Lou and A.-P. Li. Defect-mediated transport and electronic irradiation effect in individual domains of CVD-grown monolayer MoS_2. *J. Vac. Sci. Technol. B* 33 (2): 02B110-1-7, 2015.
34. M.M. Benameur, B. Radisavljevic, J.S. Heron, S. Sahoo, H. Berger and A. Kis, Visibility of dichalcogenide nanolayers, *Nanotechnology* 22 (12):125706-1-5, 2012.
35. R. Zhang, T. Chen, A. Bunting and R. Cheung. Optical lithography technique for the fabrication of devices from mechanically exfoliated two-dimensional materials. *Microelectronic Engineering* 154: 62-68, 2016.
36. M.T. Pettes, I. Jo, Z. Yao and L. Shi. Influence of polymeric residue on the thermal conductivity of suspended bilayer graphene. *Nano Letters* 11(3):1195-1200, 2011.
37. J.W. Suk, W.H. Lee, J. Lee, H. Chou, R.D. Piner, Y. Hao, D. Akinwande and R.S. Ruoff. Enhancement of electrical properties of graphene grown by chemical vapour deposition via controlling the effects of polymer residue. *Nano Letters* 13(4): 1462-1467, 2013.
38. K. Shoorideh and C.O. Chui, On the origin of enhanced sensitivity in nanoscale FET based biosensors. *Proc. Natl. Acad. Sci. USA* 111(14) 5111-5116, 2014.
39. J. Fan, J. Michalik, L. Casado, S. Roddaro, M. Ibarra and J. De Teresa. Investigation of the influence on graphene by using electron-beam and photo-lithography. *Solid State Commun.* 151 (21): 1574-1578, 2011.

40. K. Zhang, Y. Feng, F. Wang, Z. Yang and J. Wang. Two-dimensional hexagonal boron nitride (2D-hBN): synthesis, properties and applications. *J. Mater. Chem. C.* 5 (46):11992-12022, 2017.
41. M. Chhowalla, H.S. Shin, G. Eda, L.J. Li, K.P. Loh and H. Zhang. The chemistry of two-dimensional layered transition metal dichalcogenide nanosheets. *Nat. Chem* 5 (4): 263-275, 2013.
42. H.O. Churchill and P. Jarillo-Herrero. Two-dimensional crystals: Phosphorus joins the family. *Nat. Nanotechnol* 9(5):330-331, 2014.
43. H. Liu, Y. Du, Y. Deng and P.D. Ye. Semiconducting black phosphorus: synthesis, transport properties and electronic applications. *Chem. Soc. Rev.* 44(9): 2732-2743, 2015.
44. H. Zhao, Q. Guo, F. Xia and H. Wang. Two dimensional material for nanophotonics application. *Nanophotonics* 4(1): 128-142, 2015.
45. C.M. Soukoulis and M. Wegener. Past achievements and future challenges in the development of three dimensional photonic metamaterials. *Nat. Photonics* 5(9): 523-530, 2011.
46. M. Chen, H. Rokni, W. Lu and X. Liang. Scaling behaviour of nanoprinting lithography for producing nanostructures of molybdenum disulphide. *Microsyst. Nanoeng*. 3:17053-1-8, 2017.
47. S. Okazaki. Resolution limits of optical lithography. *J. Vac. Sci. Techol. B* 9(6) 2829-2833, 1991.
48. J. L. Lenhart, D. Fischer, S. Sambasivan, E. K. Lin, W.-L. Wu, D. J. Guerrero, Y. Wang and R. Puligadda. Understanding deviations in lithographic patterns near interfaces: Characterization of bottom anti-reflective coatings (BARC) and the BARC–resist interface. *Appl. Surf. Sci.* 253(9): 4166–4175, 2007.
49. A. Roszkiewicz and W. Nasalski, Transmission and reflection properties of two-dimensional finite metal crystals, Eur. Phys. J. D 71 (182):1-12, 2017.
50. D. Shrekenhamer, J. A. Miragliotta, M. Brinkley, K. Fan, F. Peng, J. A. Montoya, S. Gauza, S.-T. Wu and W. J. Padilla. Electronic and Thermally Tunable Infrared Metamaterial Absorbers. *Proc. of SPIE* 9918 99180U-1 (2016).
51. V. Caligiuri, L. De Sio, L. Petti, R. Capasso, M. Rippa, M. G. Maglione, N. Tabiryan and C. Umeton. Electro-/all-optical light extraction in gold photonic quasi-crystals layered with photosensitive liquid crystals. *Adv. Optical Mater.* 2 (10): 950-955, 2014.
52. Yu. V. Bludov, M. I. Vasilevskiy and N. M. R. Peres. Magnetic field assisted transmission of THz waves through a graphene layer combined with a periodically perforated metallic film. *Phys. Rev. B* 97(4): 045433-1-20, 2018.

53. T. Ueda, F. Kohsaka, D. Yamazaki and T. Iino. Quartz crystal micromechanical devices. Proc. 3rd Int. Conf. on Solid-State Sensors and Actuators, Transducers ’85 (Tokyo, 1985) pp 113–6.
54. E. Eernisse, R.W. Ward and R.B. Wiggins. A survey of quartz bulk resonator sensor technologies. *IEEE Trans. Ultrason. Ferroelectr.* Frequency Control UFFC-35 (1988) 323–30.
55. J.S. Danel and G. Delapierre. Quartz: a material for microdevices. *J. Micromech. Microeng.* 1(4):187–98, 1991.
56. M. J. Madou. *Fundamentals of Microfabrication: The Science of Miniaturization Second Edition*, (2002), CRC Press.
57. J. He, M. Feng, Y. Zhong, J. Wang, R. Zhou, H. Gao, Y. Zhou, Q. Sun, J. Liu, Y. Huang, S. Zhang, H. Wang, M. Ikeda and H. Yang. On-wafer fabrication of cavity mirrors for InGaN-based laser diode grown on Si. *Sci. Rep.* 8:(7922) 1-8, 2018.
58. Y. Xing, J. Zhang, M. A. Gosalvez, H. Zhang, Y. Li and S. Zhou. The Maximum Positive Curvature Recognition Method to Determine Etch Profiles in Wet Etching of Quartz on AT and BT Cuts. *J. Microelectromec S.* 27(4): 730–738, 2018.
59. K. Hjort, G. Thornell, R. Spohr and J. –A. Schweitz (n.d.). Heavy ion induced etch anisotropy in single crystalline quartz. Proceedings of Ninth International Workshop on Micro Electromechanical Systems, 267-271, 1996.
60. P. Rangsten, C. Hedlund, I. Katardjiev and Y. Backlund. Etch rates of crystallographic planes in Z-cut quartz-experiments and simulation. *J. Micromech. Microeng.* 8 (1): 1-6, 1998.
61. S. Azimi, J. Song, Z.Y. Dang, H.D. Liang and M.B.H. Breese. Three dimensional silicon micromachining. *J. Micromech. Microeng.* 22(11): 113001-8, 2012.
62. C. Hedlund, U. Lindberg, U. Bucht and J. Söderkvist. Anisotropic etching of *Z*-cut quartz. *J. Micromech. Microeng.* 3 (2): 65–73, 1993.
63. H. Zhang, Y. Xing, J. Zhang and Y. Li. The microscopic activation energy etching mechanism in anisotropic wet etching of quartz. IEEE Micro Electro Mechanical Systems (MEMS), (2018) 471-474.