

# Photoresists for Microlithography

## 1. Role of Organic Chemistry in Microelectronics

*Debmalya Roy, P K Basu and S V Eswaran*



Debmalya Roy is working in interdisciplinary area in organic chemistry and trying to balance the academic and technological aspects of the subject. Apart from his fascination for Rabindranath Tagore and science, instrumental music and sports are his other interests.

Pradeep Kumar Basu has worked on bipolar IC's, MOSFET's, CCD's and MCT based IR devices. His primary hobby is reading various subjects, scientific or otherwise and listening to music both Indian and western: classical and modern.

S V Eswaran has worked on lac resin, heterocycles and nitrene-carbene conversion. Chemical education is his passion and his hobbies include reading, music, cricket and tennis.

Photoresist technology, which is used for micro-patterning exploits changes in properties of polymeric materials, such as their solubility or volatility, upon photo-irradiation. This process has greatly benefitted from the knowledge base of organic chemistry and photo-induced organic transformations. The role of chemistry in the development of photoresists is described in this article.

### Introduction

Integrated circuits (IC's), the subject of a recent Nobel Prize, are considered to be part of physics and electronics but the vital role played by chemistry in their production, is often less appreciated. Photoactive chemicals blended with polymers, solvents and certain other additives are referred to as photoresists (*Box 1*) and are the real workhorses of the burgeoning microelectronics industry. The construction of most modern electronic gadgets like computers, television, etc. is based on microlithography, which deals with patterning of electronic circuitry at micron or sub-micron level and enables one to make Very Large Scale Integrated Circuits (VLSI). This is a multibillion-dollar industry and the sales of these electronic chemicals, dominated by photoresists, was around 10.7 billion US dollars last year. These figures are bound to impress both students and industrialists alike.

This article aims at bringing out the key role played by chemistry in microlithography. In our opinion, the close connection between chemistry and microelectronics ought to be emphasized to the students better. Though the subject has grown enormously in the last three decades, yet most well established textbooks of chemistry/organic chemistry, except a very recent

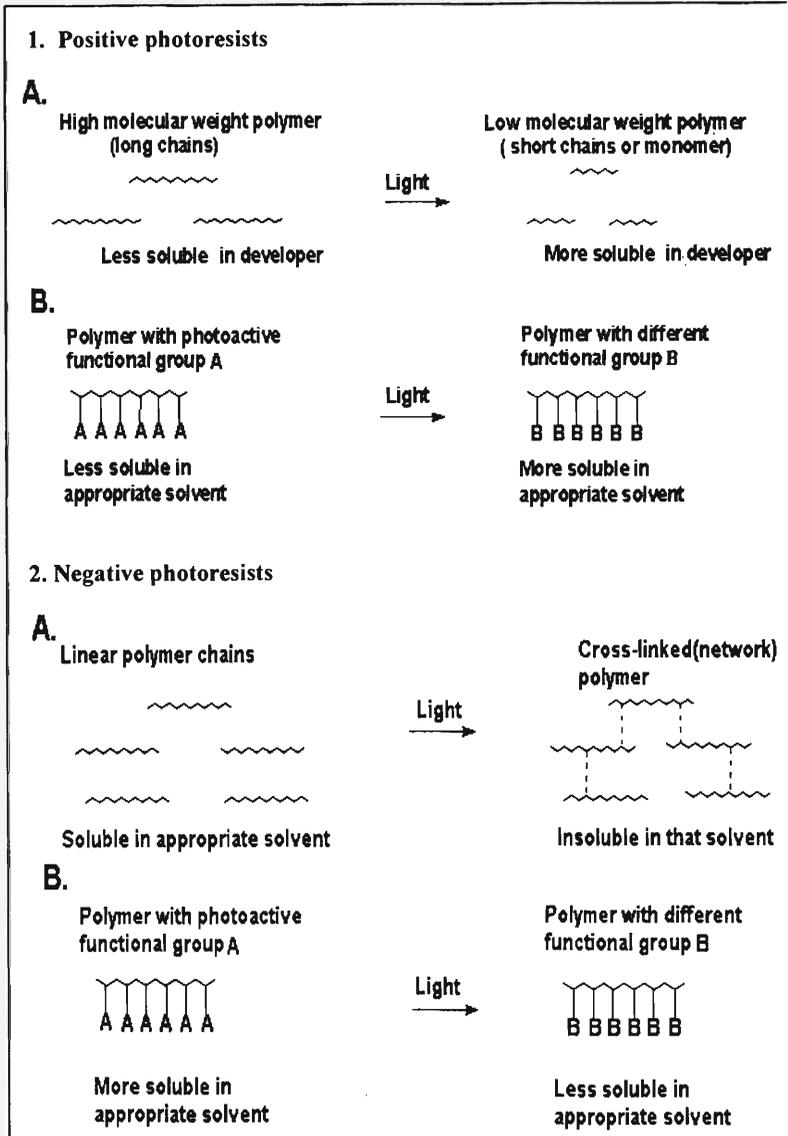
## Box 1.

**What is a Photoresist?**

Photoresists are organic substances (polymeric or monomeric), which are sensitive to light.

**What are Positive and Negative Photoresists?**

Polymeric compositions or additives such as a solubility inhibitor, which undergo chemical transformations in presence of light and the exposed parts thus become soluble in the developer, are called positive photoresists. Generally in case of positive resists, an acidic group is generated on photolysis and the basic developer easily washes this out. On the other hand, in negative photoresists, the monomers usually polymerize or undergo crosslinking, on exposure to light and the exposed parts become insoluble in the developer, usually an organic solvent. Schematically it is shown here.



one [1], fail to even mention it. This situation needs to be remedied. In India in particular, it has become urgent as almost all the chemicals required for microlithography are presently imported. The recent sanctions imposed by USA have jeopardized

**Keywords**

Photoactive compounds, novolak resins, CA resists, sub-micron lithography.

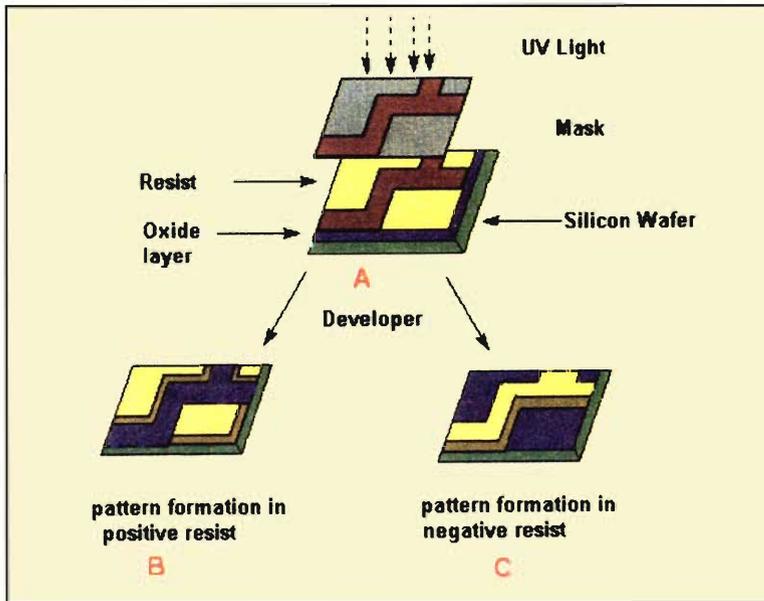
Niepce not only  
invented  
photography, he  
also invented  
photolithography.

dized the basic needs of research and development, particularly the defence R&D requirements. Students of chemistry must be made aware of the spectacular advances in the field. This will help them gain pride from the fact that their subject is fundamental to an area that catches so much public attention and is ever in the news.

### Historical Perspective

Although the present form of microlithography is only three decades old, lithography itself has a long history. It could be said that it arose almost when Nicephore Niepce took the first photograph in Chalon, France in 1826. Niepce thus not only invented photography, he also invented photolithography. The film was first coated with photosensitive compound – chromated gelatin (which was called *resist*; a term first coined by E A Bequerel of France in 1840 as it resisted or protected the substrate from light) and exposed to light [2]. The exposed film was then developed with warm water. After drying, it was etched by ferric chloride solution and the image was produced. This is the basis of the lithography technique and soon photolithography became the most popular branch of the printing industry.

The era of bichromated gelatin ended with the invention of the transistor in Bell Labs in late 1947. To improve the efficiency of those early day semiconductors, lithographic technique was used to fabricate transistors on a single crystal of silicon. But bichromated gelatin had serious drawbacks. A milestone was achieved when Kodak researchers entered the field and Martin Hopher and Hans Wagner discovered the first ever industrial photoresist called Kodak thin film resist (KTFR). It was composed of cyclized rubber (poly *cis*-isoprene) and a bis-azide (2,6-bis (4-azidobenzal)-4-methylcyclohexanone). Using this resist the dimensions of the semiconductor device reached up to 2 micrometers. This discovery led to a boom in the mass fabrication of solid-state devices and gave birth to industrial microlithography.



*Figure 1. Behaviour of positive and negative photoresists in a developer solution – In positive photoresists the exposed parts become more soluble (B in Figure 1), while the exposed parts become more insoluble in negative photoresists (C in Figure 1).*

## The Conventional Lithographic Technique

In the lithographic process the substrate (usually a silicon wafer) is first coated with some oxide layer and a radiation sensitive polymer film (resist) is deposited on it (A of *Figure 1*). The substrate is then exposed to light through a mask. The transparent part of the mask allows light/radiation to pass through and the other opaque part blocks it. Photochemical reactions change the chemical and physical properties of the exposed regions of the film. By utilizing these changes of properties a pattern is developed, based on the difference in the solubilities of the exposed and unexposed regions. The schematic diagram of the lithographic process is given here (*Figure 1*).

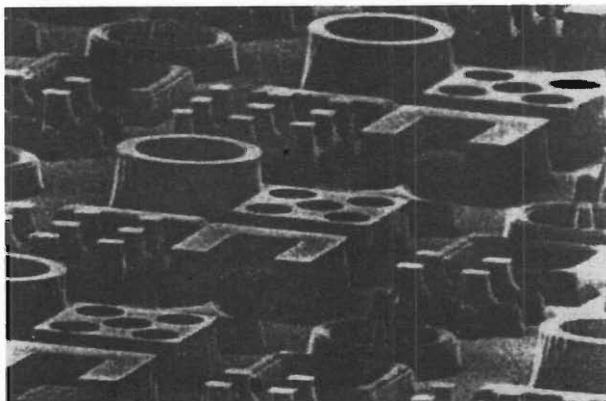
A typical pattern of 1 micron resolution based on the microlithographic technique using positive photoresist is shown in *Figure 2*.

## The Reign of DNQ-Novolak Photoresist

The negative tones of KTFR had high sensitivity and were easy to handle but gradually gave way to the positive photoresists (*Figure 3*), which dominate the market today. This move away



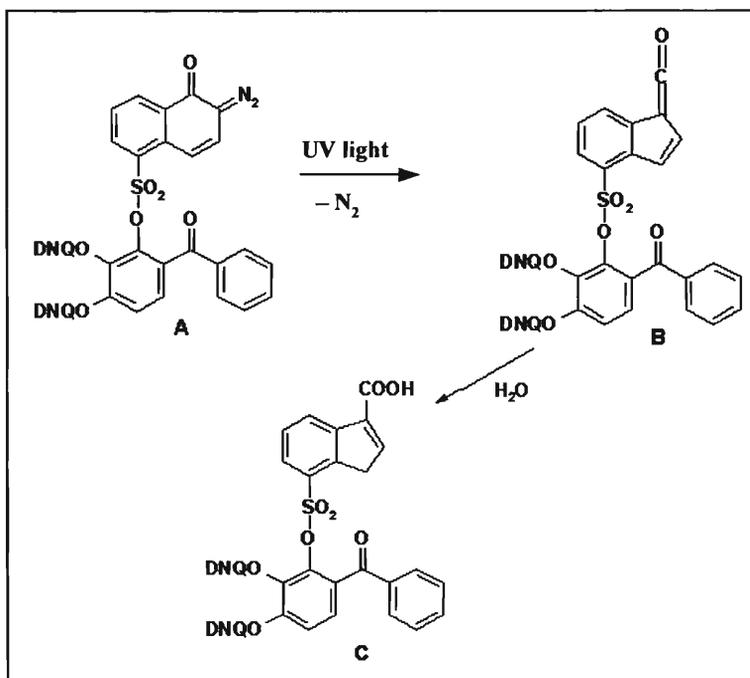
Figure 2. A typical pattern obtained by photo-micro-lithography.



from the negative photoresist can be attributed to the loss of resolution due to swelling of negative resist film during development with organic solvents, which moreover also caused environmental pollution.

Positive DNQ-NOVOLAK photoresists soon became the real workhorses of the semiconductor fabrication industry. Modified forms of this resist are still used currently. The main credit of developing this resist of such great technological interest

Figure 3. Mechanism of action of positive photoresist proposed by Sues: 'A' is diazonaphthoquinone-5-sulphonic acid esterified with 2,3,4-trihydroxybenzophenone, 'B' is ketene intermediate possibly via ketocarbene or oxyrene pathway, 'C' is indene-1-carboxylic acid and 'D' is abbreviation of diazonaphthoquinone.



should go to the German organic chemist, Oskar Sues of Kalle Company in Wiesbaden. These consist of a photoactive compound (PAC) viz. 2,1-Diazonaphthaquinone-5-sulfonic acid esterified with 2,3,4 trihydroxybenzophenone in a polymer matrix like novolak resins, which are polymers of cresols or other phenolic compounds with formaldehyde (*Novo* means new and *lak* means lacquer or resin).

Upon irradiation with UV light, the substituted diazonaphthaquinone undergoes the Wolff rearrangement and forms a ketene (possible via a ketocarbene or oxirene intermediate) [3]. The ketene then reacts with water to form the 1-indene carboxylic acid rendering the exposed part of the resist soluble in the alkaline developer. In the unexposed regions, however, the diazonaphthaquinone remains unchanged. If we develop the film with base then the resist in the exposed part gets washed out due to solubility of indene carboxylic acid. The unexposed part, however, remains insoluble and patterns are thus obtained on development.

The mechanism of action of negative photoresists (*Figure 4*) is mainly based on insertion/crosslinking reaction of reactive nitrene intermediate obtained from the bisazide photoactive component with cyclized rubber (a polymer of isoprene). This renders the exposed regions more insoluble by increasing the molecular weight. Hence on development a negative image is obtained. This contrasts with positive photoresists where the exposed parts are rendered more soluble.

### The Era of the Chemically Amplified Resists

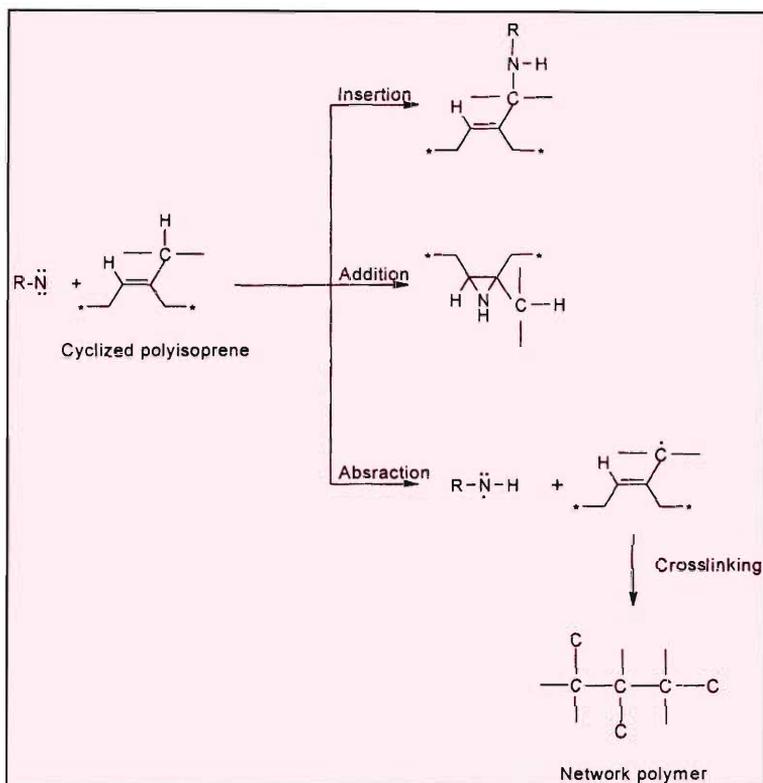
Although by optimizing the polymer matrix (Novolak), higher resolutions are achievable, newer photoresists are being considered, as DNQ-Novolak resist cannot be used at lower wavelength mainly because of two reasons:

1) The substituted DNQ absorbs UV light very intensely as we go down to lower wavelength of radiation, resulting in a loss of pattern.

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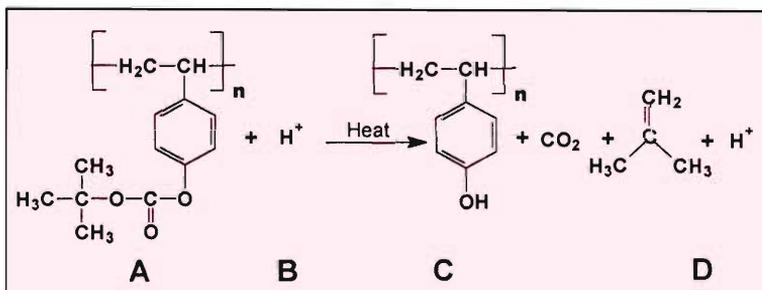
**Figure 4. Mechanism of action of a negative photoresist.**



**Figure 5. The mechanism of action of chemically amplified photoresist: The non-polar *t*-Boc derivative of polystyrene (A) is hydrolysed by acid (B), generated from the PAG by photochemical reaction and A gets converted to the polar polyhydroxy styrene (C). During this reaction acid (D) is generated and hence the acid concentration is, amplified many times, ensuring the completion of the hydrolysis reaction, which makes the exposed part of photoresist more soluble in base.**

2) The quantum yield of the DNQ-Novolak resists is very low.

The third generation of photoresists for deep UV (DUV) was developed by C G Willson of Texas University. Here the main components are a photoinactive polymer with an acid labile pendant ester group and photoacid generators (PAG). When light falls on the resist, PAG generates an acid, which hydrolyses the ester group of the polymer film and makes the exposed part of the resist soluble in the alkaline developer [5] (Figure 5).



These resists are called chemically amplified (CA) resists, since the concentration of acid increases by the photochemical reaction. The amplification of acid by chemical reaction during the post exposure baking shoots up the quantum yield even above one. In CA resists the main resist film is photo-inactive, so there is no question of strong absorption of light beam and it is possible to design high transmittance acid labile polymers in deep UV regions. The large polarity change brought about by acid catalyzed reactions in the exposed and unexposed parts give high contrast in CA resist. After C G Willson's discovery of the first CA resist, there are now hundreds of CA resists and different photoacid generators (PAG), as well.

But CA resists also suffer some drawbacks [6]. The major difficulty with CA resists is the unwanted acid diffusion into the unexposed parts. The acid generated by photochemical reaction and the  $H^+$  ions developed during post exposure bake (by thermal reaction) do not diffuse vertically alone and so are not bound into the exposed parts only. Acid diffusion into the unexposed parts has been overcome by using base along with the polymer film itself. The base however itself consumes the acid generated by the thermal reaction in the exposed part and this reduces the resolution. To avoid this the base itself should be photoactive so that the basicity is lost in the exposed part by photochemical reaction and in the unexposed parts the basicity remains intact.

Another major problem the CA resists suffer from is due to airborne contamination. The resist film takes up the airborne contamination of bases from paints of windows, walls and adhesives that use additives like hexamethyldisilazane, *N*-methylpyrrolidone (NMP), which neutralizes the photogenerated acid in the surface portion of the exposed regions. So the surface skin gets neutralized and remains insoluble during development with base. One way to reduce this problem is the thorough purification of the enclosing atmosphere by using activated charcoal filters and protective overcoating. Sulfonic acid esters, disulfones, etc. are mixed with resist film for dual purposes. On



In projection lithography, ultra violet light is focused from a source through a mask to generate a pattern that is reduced several times over by an imaging system

the one hand they work as additives to promote the adhesion of the resist film with the substrate and on the other also react with airborne contamination and deactivate them.

### **Microlithography – The Road Ahead**

It is a well-known fact that device performance and speed are largely influenced by the feature size of the device. During the last couple of years, work to develop a viable sub-100 nm next-generation lithography has become very highly competitive. With both economical and technological aspects getting equal importance.

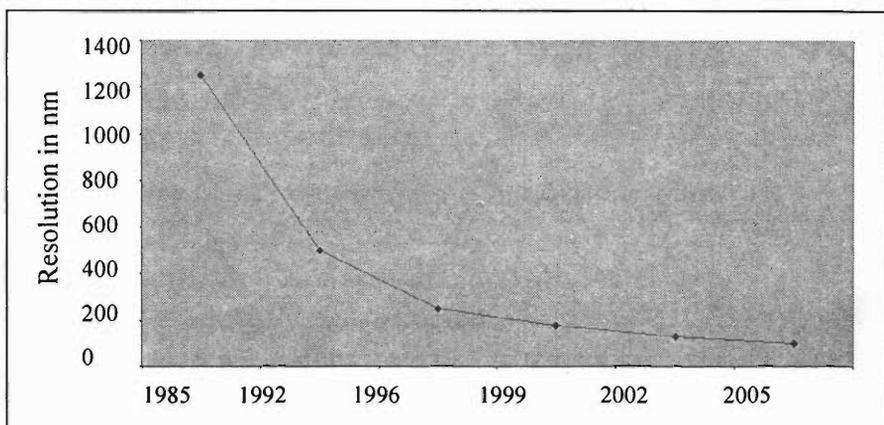
In projection lithography, light (UV) is focused from a source through a mask to generate a pattern that is reduced several times over by an imaging system (comprising a definite orientation of concave and convex lenses) and projected onto a silicon wafer. The wafer is covered with a photoresist designed to protect the desired areas of the wafer from etching, ion implantation, metallization, or other processes. Illumination sources for lithography initially consisted of discharge lamps. As feature sizes shrank to 250 nm and below, the industry switched over to excimer laser illumination, first at 248 nm (krypton fluoride; KrF laser), then at 193 nm (argon fluoride; ArF laser) and later at 157 nm ( $F_2$  laser).

The consensus-based technology road maps are introduced to chalk out the development of fabrication technology and synergy between the various aspects of microlithography. The semiconductor feature sizes and proposed year of implementation are shown in the following road map (*Figure 6*).

The 248 nm lithography is widely deployed in fabrication facilities around the world although 193 nm steppers have been available for several years, the technology still requires improvements. Currently the spotlight of development is on 157 nm lithography with fluorine ( $F_2$ ) lasers.

So the competition for the hot seat of sub-100 nm micro-litho-





graphy is wide open. Both technological and economical considerations are decisive for choosing the 'trade off' process. There also might be a radical change from the current attentions to some newer direction for microlithography in the near future.

In Part 2 of this article, we shall discuss the role of polymer microstructure on the photoresist performance.

### Acknowledgments

We are grateful to the Director, Solid State Physics Laboratory, Delhi, for the sanction of a project, a fellowship and for permission to publish the paper in *Resonance*.

### Suggested Reading

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**Figure 6.** The proposed roadmap of the past, present and future dimension feature sizes.

#### Address for Correspondence

Debmalya Roy, P K Basu  
Solid State Physics Laboratory,  
Lucknow Road  
Delhi 110054, India.

S V Eswaran  
Principal, Deshbandhu  
College, University of Delhi  
Kalkaji  
New Delhi 110019, India.