Advanced Materials for Electronic Applications by Polymerization of Cyclic Olefins Using Late Transition Metal Catalysts

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Introduction

Over the past few decades, there have been several reports in the literature regarding the addition polymerization of monocyclic olefins such as cyclobutene[1] and cyclopentene[2] or bicyclic olefins such as norbornene[3] using catalysts related to the original Ziegler-Natta inventions. In more recent years, interest in norbornene, and it's derivatives, has undergone a renaissance of sorts. Undoubtedly this is due two factors: the development of new, single-site catalysts that will polymerize these types of monomers with good activity and the realization that polymers containing significant quantities of these bicyclic monomers exhibit unique properties such as high glass transition temperatures and transparency. Indeed, early work at Mitsui Petrochemicals concentrated on polymerization of the multicyclic olefin, tetracyclododecene (TD), using EPDM-type, soluble vanadium catalysts[4] that eventually led to the commercialization of Apel™ amorphous polyolefins.[5] Later, the utility of metallocene catalysts for cyclic olefin polymerization was recognized by both Mitsui and Hoechst.[6] This led to the joint development of the Topas™ line of amorphous polyolefins.[7]

BFGoodrich has had over three decades of experience with cyclic olefins and polymers derived therefrom. Originally, this interest stemmed from the production of EPDM rubbers. Eventually, several businesses grew from BFGoodrich's polymerization expertise and cyclic monomer production capability. BFGoodrich is the largest supplier of dicyclopentadiene (DCPD) based reaction injection molding (RIM) polymers in the U.S. Since their introduction in 1990, Telene™ RIM Polymers has expanded from a research program to include a formulations business as well as a molded parts manufacturing operation. These polymers are based on the ring-opening metathesis polymerization (ROMP) of DCPD to form a thermoset material that exhibits an excellent combination of stiffness, impact strength, and heat deflection temperature. In 1996, BFGoodrich started production of high purity DCPD. Markets for Ultrene™ 97 and 99% DCPD include specialty resins, catalyst systems such as metallocenes, and processes requiring consistent, high purity DPCD.

BFGoodrich has brought its polymerization expertise to bear on the problem of addition polymerization of cyclic olefins. Inital efforts on copolymerization of cyclic olefins with α-olefins such as ethylene concentrated on traditional vanadium catalysts[8], then metallocenes.[9] As the incorporation of cyclic olefin increased so did the copolymer glass transition temperature. However, it was recognized that catalyst innovations needed to be made if truly high performance polymers were to be accessible since the rates of polymerization decreased as the content of cyclic olefin increased. In fact, at *MetCon '95* we stated that

> *Clearly a breakthrough in catalyst technology is required…before…the…ultrahigh glass transition homopolymer(s) of norbornenes can be exploited.*

Since then, BFGoodrich announced at *MetCon '97* that such a breakthrough has been achieved with single component catalysts based on Group VIII transition metals.[10] These catalysts are characterized by their ability to:

1. Produce ultrahigh glass transition temperature norbornene homopolymer (T_g = 380-390°C) that can be tailored by copolymerization with 5-alkylnorbornenes.
2. Produce polymers with molecular weights exceeding 2,000,000 down to oligomers by a novel chain transfer mechanism with α-olefins.
3. Polymerize and copolymerize norbornenes bearing functionality (carboxylic acid esters, ethers, anhydrides, etc.).

Polymers in Electronics

A complete electronic device typically performs five fundamental functions: generating, manipulating, transferring, storing, and displaying information.[11] To perform these functions, different components need to be integrated in making the final device. Materials used for the manufacture of these components run the gamut from silicon to ceramics to metals to polymers. Polymers are used in circuit boards, chip encapsulants, photoresists, conformal coatings, packaging, adhesives, and flexible circuits to name a few.[12] The ability of chemists to synthesize polymeric molecules with differing functionality offers the promise of engineering specific polymers for specific applications. This coupled with the ease of processing and fabrication makes polymers attractive materials for the electronics industry.

BFGoodrich has recognized the role that polymers play in the electronics industry and that cyclic olefin polymers have some inherent properties that the industry may find attractive: low dielectric constant, high transparency, and low moisture absorption to name a few. These properties and the ability to tailor the polymer T_g and functionality using BFGoodrich catalyst technology, as discussed above, allowed BFGoodrich to embark on the development and commercialization of three distinct polymer product families based on norbornene-type monomers designed for distinct segments of the electronic market. They include:

1. Appear™ Optical Polymers.
2. Avatrel™ Dielectric Polymers.
3. DUVCOR™ Photoresist Polymers.

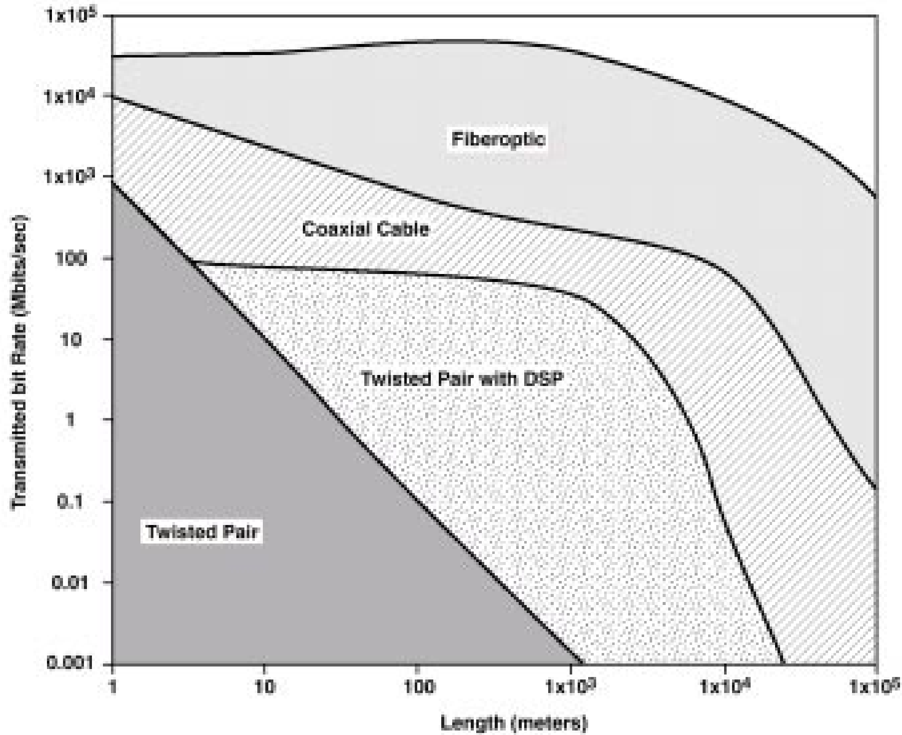
This manuscript will touch on each of these application areas, but will concentrate on the development of DUVCOR™ photoresist polymers.

Appear™ Optical Polymers

There are two fundamentally different ways to transmit data: wireless or "wired". Wireless transmission employs radio or microwaves and infrared waves. Wired transmission media include copper wire cables or traces on printed wiring boards (for electronic transmission) and fiber optic cable or waveguides (for photonic transmission). The efficient, speedy transmission of data has come under increasing pressure as the use of the Internet and video image transmission increases. According to Shannon's Law, capacity of data transmission (in bits/sec) is directly proportional to the bandwidth (or the

span in frequency used by the signal) of the transmission medium. As can be seen from Figure 1, the highest data transmission rate is offered by fiber optic (and by inference, waveguide) technology. How many of us have seen our level of frustration increase directly with the amount of time it takes to download an image from the World Wide Web to our PC's at home? Given the inherent fast transmission of data offered by photonics, this technology may be the choice of the future for all transmission irrespective of the distance involved.

Figure 1. *Maximum data transmission for different media.*



At BFGoodrich, we believe that the intrinsically good optical, mechanical and moisture absorption properties of cyclic olefin polymers produced with our catalyst systems make them ideal candidates for photonic applications. In fact, BFGoodrich is working with our partners at 3M Company to develop waveguides (both core and cladding) and optical TAB (tape automated bonding) materials for on-board, high-speed data links. This collaboration is sponsored by the National Institute of Standards and Technology's Advanced Technology Program (ATP).[13]

Presently much of the video information from electronic devices is presented to the user via cathode ray tube (CRT) monitors. However, as devices become increasingly portable, large CRT's will no longer be suitable. Many devices have turned to liquid crystal displays (LCD's) as video ports. The performance of flat-panel displays in, for example, laptop computers is limited by many factors, including the nature of glass substrate materials. They are fragile, heavy, and do not offer optimal optical quality. Cyclic olefin polymers offer promise for overcoming these limitations. But before cyclic

olefin polymers can be incorporated into flat panel displays, several key performance criteria must be met.[14] The criteria are presented in Table 1 versus the performance of Appear™ Optical Polymers made using BFGoodrich catalyst technology.

Table 1. *Performance of BFGoodrich's Appear™ Optical Polymers vs. Flat Panel Display Requirements.*

Property	Target	Appear™ Optical Polymers
T_g	> 200°C	330°C
Refractive Index (n)	= 1.50 ± 0.1	1.50
Transmission	>90% (400 -700 nm)	92.2%
Retardation ($\Delta n_{xy}d$, λ = 550 nm)	< 20 nm	9.6 nm (88 μm film)
Specific Gravity	< 1.5 g/cm^3	1.0 g/cm^3
Mechanicals	Robust	Elongation = 20%

Another potential application for Appear™ Optical Polymers is optical data storage. This application would take advantage of the inherently low birefringence of the polymer; a critical property considering the product evolution toward higher data density and the use of shorter wavelength laser systems. In essence, Appear™ Optical Polymers would be suited for any application that requires high quality optical transmission, low birefringence, high use temperature, exceptional moisture resistance and moisture barrier properties.

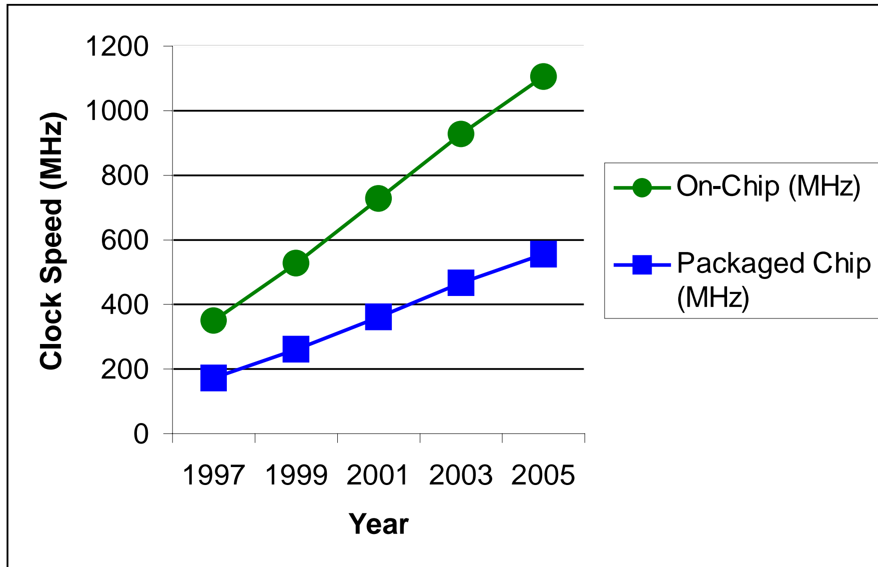
Avatrel™ Dielectric Polymers

In 1964, Gordon Moore, co-founder of Intel Corporation, predicted that the number of transistors on a chip would double every 16-18 months. Since then, the semiconductor industry has more or less kept up this feverish pace. In order to take advantage of the advances made in semiconductors, similar improvements need to be made in the other components that make up a complete electronic device. A key component in electronic devices is the package of the integrated circuit (IC or chip). According to Rymaszewski, Tummala, and Watari.[15]

> *Packaged electronics is the embodiment of all electronic equipment - calculators, personal computers, mainframe computers, telephones, television, and so forth...Active components are interconnected, supplied with power, and housed in packaging. Success in a very competitive marketplace hinges on superior performance and price.*

Despite the pivotal role that packaging plays in electronics, performance has not kept pace with semiconductors improvements. In the future this disparity is expected to grow. A comparison of bare chip speed versus single chip packaging speed over the next decade is presented Figure 2.[16]

Figure 2. *Comparison of bare chip speed vs. single chip packaging speed.*



Obviously, the bare chip speed has outpaced the packaged chip speed. As pointed out by Doane and Franzon.[17]

> *...chip interconnections play a more dominant and limiting role in determining overall system speed and performance. Packaging of the chips has become a more significant factor in performance. Systems level performance improvements are now being limited more by the packaging and the interconnection technologies, and less by the chip technology itself.*

In order to leverage the great strides made in semiconductors, focus must now turn to improvements in packaging. The four main functions of electronic packaging are: signal distribution, power distribution, heat dissipation, and protection.[18] As Shaw states:

> *Simply put, the package enables the chip to communicate to the outside world by connecting small bonding elements on the chip (pads or small solder balls) to a printed circuit board network.*[19]

Given the role of packaging, it is apparent how inefficient packaging materials of construction, packaging design and fabrication could limit the performance of semiconductors.

Materials for packaging range from metals, to ceramics, to organic polymers. Polymers in Level 1 packaging range from interlayer dielectrics, to passivation layers, to die attach adhesives, to chip encapsulants (both molding and adhesive) and underfill

materials to name a few application areas. Most chips are packaged as single chips today. However to the extent that applications requiring advanced high-density chips are more in demand, multichip packages (or modules, MCMs) are becoming preferred since they:

> *decrease the wiring distance between chips by packaging the chips as close together as possible to reduce the propagation delay and increase the packaging interconnect wiring.*[20]

Several MCM's designs have been developed: MCM-C (ceramic substrate), MCM-L (laminate substrate), MCM-Si (silicon substrate), and MCM-D (deposited dielectric substrate). For MCM's, according to Feger and Feger[21], polymers are becoming the dielectric materials of choice because:

1. The low dielectric constant of polymers allow higher packaging densities, faster transmission speeds, and lower power consumption.
2. Polymers are easy to process.
3. Polymeric properties can be tailored by changing their chemical compositions.

This is especially true for MCM-D/L (deposited dielectric over laminate) technology. These thin film multi-layered structures have the capability of closing the gap between the feature geometries of ICs (about 1 micron) and printed wiring boards (about 50-100 microns). This technology promises the ultimate in packaging, providing the highest density and speed in electronic devices.

BFGoodrich, along with our colleagues at Georgia Institute of Technology's Packaging Research Center, have been developing cyclic olefin-based Avatrel™ Dielectric Polymers that exhibit many of the key performance criteria required for this demanding application. They include:

- *Excellent, isotropic electrical properties.* Dielectric constants of 2.4 to 2.6 have been demonstrated. Low dielectric constant is crucial as interconnect density increases. As space between conducting lines shrinks, inductance and cross-talk become problematic, but can be mitigated with lower dielectric constant materials. Polyimides, which are used extensively in the industry, exhibit anisotropic electrical properties; in-plane dielectric constant can be as high as 4 while out of plane dielectric constant is generally above 3.

- *Very low moisture absorption.* Typically, Avatrel™ Dieletric Polymers absorb less than 0.1 weight percent water, while polyimides typically range from 2 to 3 wt%. Water uptake increases the dielectric constant of the medium and can facilitate conductor corrosion.

- *Good thermo-mechanical properties.* Glass transition temperatures range from 300 to 340°C. Thermal stability is good up to 400°C. Elongation to break is typically 20%. On wafer stress is 18 MPa, less than half that found for typical polyimides.

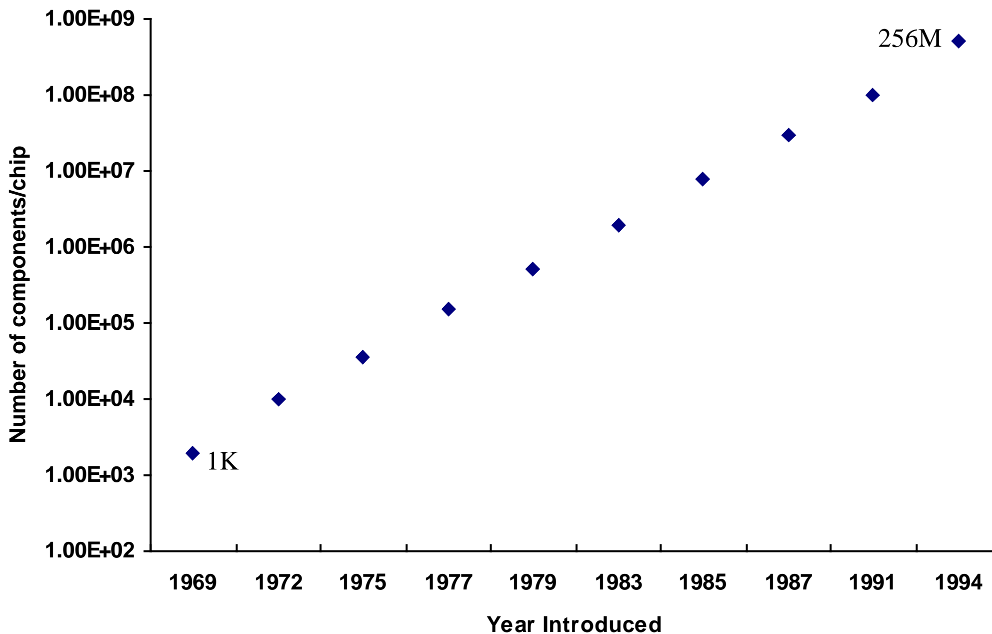
- *Good adhesion to metals.* Avatrel™ Dielectric Polymers exhibits good adhesion (passes the cross-hatched tape test, ASTM D-3359-95a and IPC 650-TM) to metals

such as Cu, Au, Al, Cr, Ti, and Si, as well as SiO_2. Polyimides on the other hand require tie layers and adhesion promoters.

DUVCOR™ Photoresist Polymers

The electronics revolution is due in part to the dramatic increase in information processing capability provided by the invention of the integrated circuit (IC or chip) in 1960. Information processing capability is directly linked to the number of components (transistors, capacitors, and resistors) that can be manufactured on the silicon substrate. Figure 3 tracks this increase over time for the dynamic random access memory chip.[22]

Figure 3. *Number of components per dynamic random access memory (DRAM) chip as a function of time.*



Enabling technologies for chip manufacture are, for example, thin film deposition, etching, and lithography. Lithography enables the chip designer to transfer the electronic circuitry "blueprint" that is written on a photomask onto the silicon wafer.

There are two types of photoresists: negative and positive photoresists. The negative resist reacts upon exposure to light to form an insoluble form of the photoresist. Addition of developer then dissolves the unexposed regions of the resist. A positive resist reacts when irradiated to produce a soluble form of the resist that is then washed away by the developer.

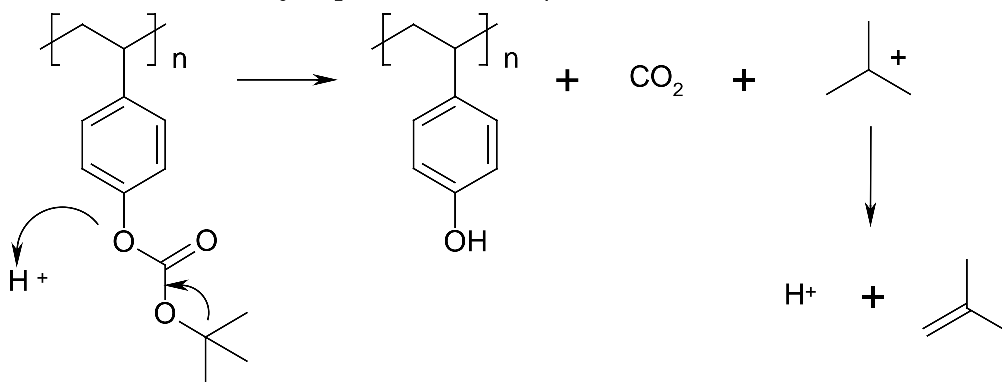
A typical lithographic positive photoresist process is outlined in Figure 4. Step 1: A photoresist is spin-coated onto a silicon wafer. Step 2: The photoresist is exposed by shining light through the photomask. Step 3: The photoresist is developed by dissolving away the unreacted photoresist. Step 4: The exposed oxide is etched away. Step 5: The remaining photoresist is stripped to give a patterned silicon wafer. While there are

several types of lithography (e. g., X-ray and electron-beam), the electronics industry has invested much of it's capital in optical lithography.

The ability to pack more components on a chip is related to the feature size of the components themselves. While the 1K DRAM chip relied on feature sizes of around 10 μm, the 256M chip has been manufactured using feature sizes of 0.35 μm, almost a two order of magnitude decrease. The industry has responded to the call for smaller feature sizes by moving to shorter and shorter wavelength UV light, from 436 nm (G-line), to 365 nm (I-line), and more recently to 248 nm light. This is because resolution (R) is directly proportional to the wavelength (λ) of the incident irradiation.[23] For G- and I-line irradiation, positive-tone novolac-diazanaphthoquinone photoresists are the industry standard.

Advances in photoresist technology has made the move to 248 nm wavelengths possible. The use of novolac-diazanaphthoquinone resists at this wavelength is limited by the system's strong UV absorbance. Poly(hydroxystyrene) (or PHS) was found to be a suitable polymer backbone around which the 248 nm photoresists could be built. PHS is marginally transparent at 248 nm. Without sufficient transparency, light cannot penetrate to the bottom of the resist film resulting in only a partially developed resist.

As wavelengths get shorter, the sources become dimmer. Efficient use of photons becomes paramount. A major advance in resist technology was the introduction of chemical amplification, pioneered by IBM, in which a single photon can cause a cascade of chemical transformations. A chemically amplified resist system typically contains a photosensitive acid generator (or PAG) such as triarylsulfonium hexafluorophosphate and a polymer containing an acid sensitive moiety. This moiety undergoes an acid (released by photolysis of the PAG) catalyzed deprotection forming a functionality that renders the formally solvent soluble polymer aqueous base soluble. Commercially, derivatives of poly(hydroxystyrene) are protected from unexposed dissolution through a judicious choice of an acid-reactive group such as a *t*-butylcarbonate.



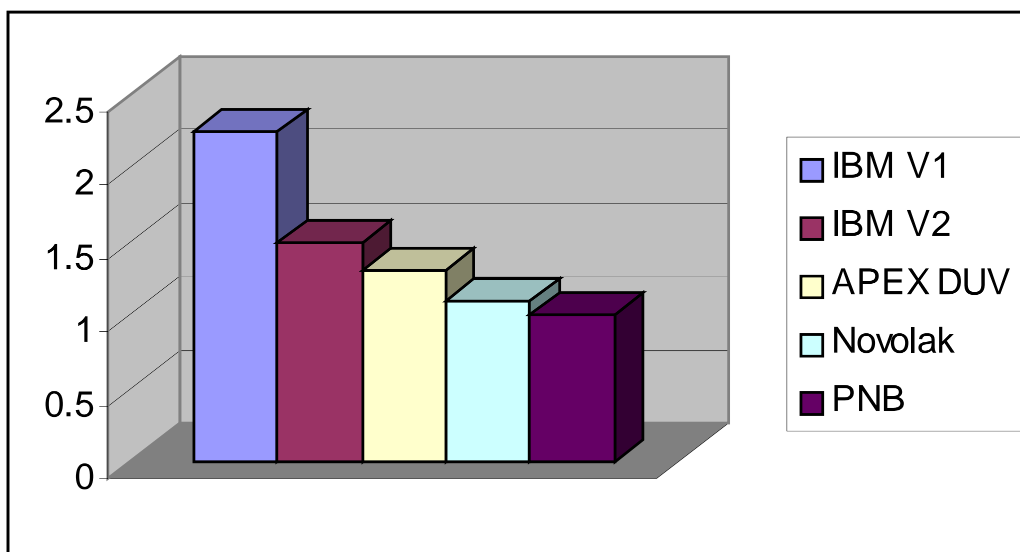
The solubility switch reaction regenerates acid making the reaction catalytic in acid. Therefore, a photon that generates acid reacts with many reactive groups to make an aqueous base soluble polymer. Thus, a catalytic polymer solubility switch takes place upon irradiation. In this manner the effect of the light that does reach the resist is chemically enhanced or amplified.[24]

As the industry strives for the 1G DRAM chip, 0.18 μm feature sizes are called for in the *National Technology Roadmap for Semiconductors*. By 2006, feature sizes of 0.1 μm will be required to keep pace with the increase in

DRAM chip capability.[25] After 248 nm, the next conveniently available wavelength is 193 nm; the wavelength of light emitted by a krypton-fluoride excimer laser. While the chemical amplification concept should work at 193 nm, just as it does for 248 nm photolithography, a major innovation in polymeric backbone photoresists design needs to be made before 193 nm lithography becomes a commercial reality. Poly(hydroxystyrene), the 248 nm polymer backbone, is opaque at such short wavelengths. Of the several polymers that do have appreciable transparency at 193 nm, acrylates, maleic anhydride copolymers, and cyclic olefin addition polymers have been considered as candidate photoresists.[26]

However, simply being transparent at the wavelength of interest is only the first hurdle in choosing a candidate polymer backbone. A commercial photoresist must not only undergo the appropriate solubility switch upon irradiation, but the insoluble polymer that remains after aqueous base development must "resist" decomposition under plasma etching conditions, i. e., conditions in which the exposed portions of the silicon wafer are etched away. Otherwise 3-D features, and therefore components, could not be built into the wafer. Thus etch rate is a very important parameter that must be measured for candidate photoresist polymers; the lower the etch rate, the better. In Figure 5, the etch rate of five polymers are presented. All of these experimental polymers have higher etch rates than standard novolac resists (normalized to 1) except one: addition polymerized poly(norbornene).

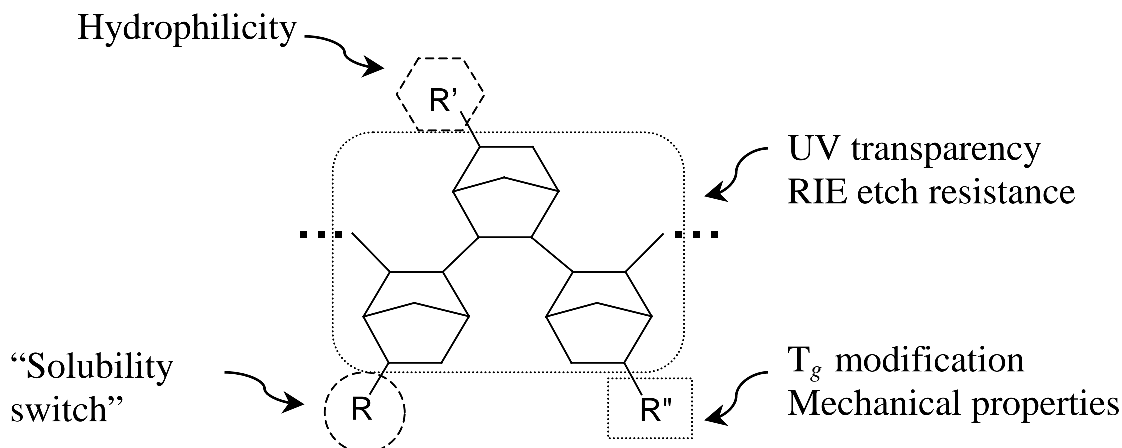
Figure 5. *Comparison of RIE etch rate.*



Along with a photochemically activated solubility switch, UV transparency and ion etch resistance, a viable photoresist polymer must exhibit some degree of hydrophilicity. This will help in the adhesive and film forming properties of the polymer as well as the dissolution rate of the exposed resist in developer. Other considerations include glass transition temperature and mechanical properties. A balance of all of these properties is achieved by designing a polymer which has the appropriate chemical

functionality, either in the polymer backbone or as a pendant group, as shown in Figure 6. Functional tolerance of the BFGoodrich proprietary catalyst technology enables the production of cyclic olefin polymers for the demanding photoresist application.

Figure 6. *Design of a 193 nm photoresist polymer.*



Scanning electron microscopy (SEM) images of formulations based on DUVCOR™ Photoresist Polymers are presented in Figure 7. Note that well-resolved lines and spaces are produced with 0.18 and 0.16 μm feature sizes.

Conclusions

Taking advantage of a breakthrough in catalyst technology, BFGoodrich can polymerize functional cyclic olefins to provide transparent polymers with good thermo-mechanical properties, high T_g, low dielectric constant and low moisture absorption. These polymers can be tailored to afford materials that have application in the electronics market.

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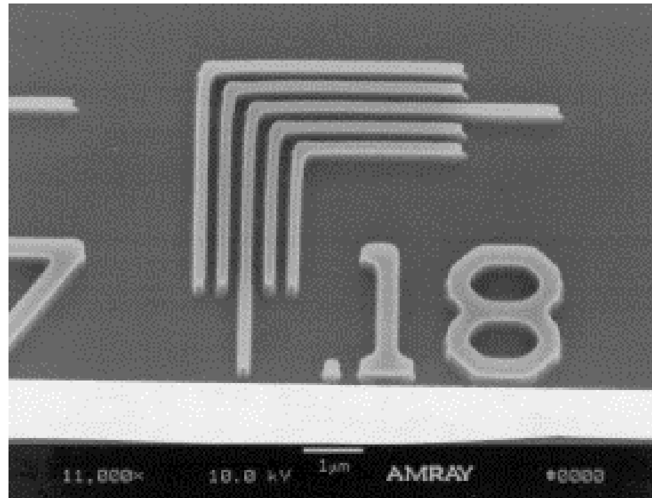
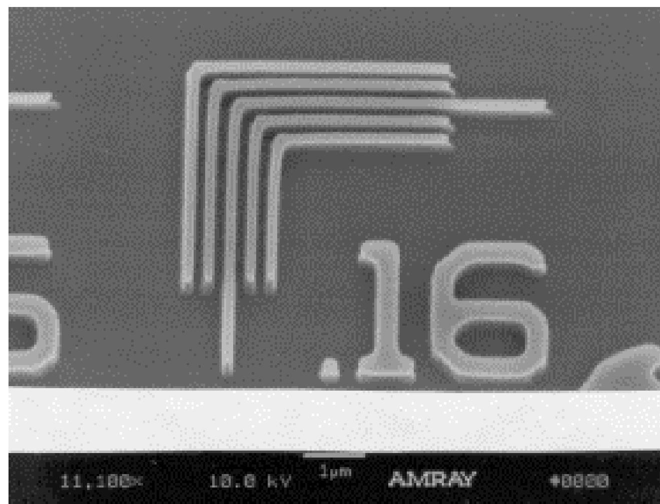
Figure 7. *Scanning electron micrographs of formulations containing DUVCOR™ Photoresist Polymers.*





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