Innovation via Photosensitive Polyimide and Poly(benzoxazole) Precursors - a Review by Inventor

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In order to work out indispensable criteria for a promising process of innovation, a historical review is given for two paths of innovation, which the author was involved in as an chemist in electrical industry from the initial idea up to commercialization and application in the field of microelectronics and electronics. The examples concern the approach to thermally stable organic patterns via photosensitive precursors of polyimides (negative mode) and of poly(benzoxazoles) (positive mode). After direct photolithographic patterning the precursor layers can be thermally converted into polyimide and poly(benzoxazole), respectively. The photoresists have been commercialized by licensed chemical companies. They have been and still are mainly applied to memory and logic devices as protective and buffer coatings to reduce the stress caused by an encapsulating resin, and to thin film multichip modules as planarizing interlayer dielectrics.

Keywords: photoresist, polyimide, poly(benzoxazole), precursor, innovation

1. Introduction

Bernhard Plettner, former head of the Siemens Advisory Board, once stated [1]:

...The technological development in the past decades has been accelerated, the stepsize of technical progress became larger from decade to decade. Asking for the reason, there is a relatively simple and reasonable answer: This is the progress in materials science and the availability of new materials, which has been responsible for the progress of the last 50 years. ...

In very many cases innovation – a process which starts up with a new and useful idea from its conception and ends with its ultimate implementation as a useful and practical application – is based on new materials. In one of the most innovative fields, electrical engineering, megatrends are: shorter cycles of innovation and lifetime of products and systems, integration of more and more functions per less area available, increasing complexity of systems, global competition with costs, quality and time. To meet these trends, materials have to be selected cleverly, property profiles have to be tailored specifically, multifunctional materials with complex requirement profiles have to be provided, there is a need for computer aided molecular engineering, for compatibility of materials and processes, for better controlled materials (also regarding fine structure), for save processing with potential for automation, and for materials with better thermomechanical performance.

With this background the author got and took the chance to follow up the complete path of innovation as an industrial chemist in the field of electrical engineering and electronics. He will review now his experience of successful innovation.

2. Photosensitive Polyimide Precursors

Electronics is a field of rapid development. The invention of the silicon transistor and the implementation of the planar technology for producing thousands of transistors and other semiconductor components on a wafer simultaneously, and therefore very cheaply, were the basis for the progress in modern microelectronics. The need to obtain less expensive, but more complex and sophisticated systems, has led to a dramatic increase in the integration density of circuits and packaging. This continuous miniaturization required advanced materials and technologies.

Received August 27, 2004
In the early seventies organic photoresists were well established and steadily improved tools for fine patterning in electronics and especially microelectronics. These patterns served as masks for subsequent etching or vapor deposition processes. Finally the resist patterns had to be removed, as they would not resist to subsequent thermal treatment.

For dielectric and protection layers inorganic materials such as silicon dioxide, silicon nitride and boron-phosphorus-silicate-glass (BPSG) were used as highly temperature-resistant gate insulators, interlayer dielectrics, or passivation layers. However the layers were produced by thermally and costwise demanding processes, i.e. plasma-enhanced chemical vapor deposition or fluid coating (> 750°C). They had to be patterned via photoresists. Due to the brittleness of the layers the available thickness was limited. Such inorganic films with thicknesses of microns or less tended to reproduce the topography of the underlying substrate since they lack any planarizing properties. Poor step coverage and thinning of the coating over sharp surface relief ultimately led to poor linewidth resolution and to long-term reliability problems stemming from cracks and discontinuities in the conducting and insulating layers.

Especially in the packaging of new larger sized mega-bit DRAM memories, buffer coats in the form of organic films would have been preferable according to good adhesive power, sufficient elasticity and tensile strength. Due to increasing demands on such memories, testing conditions had become harsher, such as the pressure cooker test (boiling water at 122°C/2 bar for up to 500 hr) and cycling (more than 1000x between −65°C and +150°C).

In addition there were special requirements for applications in multilayer interconnections: very pure, finely patterned and economically priced dielectrics with good adhesive qualities, good planarization, and low dielectric constants (<3.5) were needed in order to achieve high switching speeds with thin film multichip modules (MCM-D), a promising mounting and connection system. To planarize the conductor pattern a film thickness of several microns was necessary.

However, the spectrum of suitable organic materials was limited due to the requirements of an extremely high short-term resistance to temperatures up to 450°C, which occurred during the process of manufacturing integrated circuits. Amongst organic materials, the high demands on thermal and mechanical properties had, until then, been best met by polyimides. Thus polyimides rapidly became of general interest in the field of electronics.

As polyimides are insoluble, there was one approach to apply a soluble polyimide precursor, poly(amic acid), to substrates via spin coating followed by a tempering step, in order to obtain polyimide. Such layers can be patterned photolithographically by using a photoresist. In this case, the photopatterned resist layer acts as a mask for the lower polyimide layer (indirect patterning). Apart from the large number of processing steps involved (Figure 1), there is a problem, in that undercutting of the polyimide layer to be patterned could arise because of its solubility in the wet developer. This proved to be unfavorable, not only with respect to the reproducibility of the whole process, but also especially regarding the resolution capability. Never-the-less this indirect patterning still is being used to some extent.

![Figure 1. Indirect patterning of polyimides](image)

Along with the general guideline for materials research and development in industry – it is not sufficient, to have a technology available, which works. One must be better and/or cheaper and/or faster than the competitors on the market - the
author’s vision was to provide polyimide precursors, that possess photoresist properties.


Three years after that the author got the basic idea, sitting at his desk in the Erlangen Research Center of Siemens late in the evening. The worldwide first entirely organic photoresist to create polyimide patterns was born. First of all, a very general principle was realized and patented, allowing to implement organic photoreactive precursors of many highly thermal resistant polymers, i.e. polyimides, polybenzoxazinodiones, polyquinazolinodiones, Poly(isoindoloquinazolodiones) [3]. At all of these photoreactive precursors chain segments are linked by bridges carrying amide groups, adjacent to which photoreactive groups are bound in an ester-like fashion. The chemical principle and the processing steps involved are illustrated in Figure 2 exemplary for polyimide precursors.

The solution of the polyimide precursor together with photoinitiators is deposited on the substrate by spin coating, spraying, etc., and is then dried. The resulting film is exposed through a mask. The photocrosslinking that takes place via the photoreactive groups R* gives rise to a large solubility difference between the exposed and unexposed regions of the layer to be patterned, thus allowing the following developing step to be carried out safely and reproducibly. By extracting the still soluble regions in the shadow of the mask with an organic solvent, high-resolution patterns can be obtained, which are finally converted into the polyimide by tempering. At the same time, the crosslinks depolymerize to give the alcohol that had originally been integrated into the soluble polyimide precursor as a photoreactive ester group. The resulting polyimide patterns are appropriately pure for applications in microelectronics. Figure 2 also reveals, that compared with indirect patterning these polyimide precursors with photoresist properties provide less costs and higher yields due to less, time-saving and safer processing steps.

The author and his team focussed on optimizing these polyimide precursors. For practical purposes, it was important to manufacture the base polymer with the highest possible purity and as inexpensively as possible. The original method developed for the synthesis of the soluble polyimide precursors used aromatic dianhydrides, which were reacted with the photoreactive alcohol [4]. The resulting tetracarboxylic diester was then converted to the corresponding acid chloride and subsequently polycondensated with aromatic diamines. This synthesis was highly reproducible and could easily be scaled up. So in parallel the technology for manufacturing polyimide patterns for practical applications could be optimized, using clean room environment.

With regard to high speed of photocrosslinking hydroxyethylmethacrylate proved to be the best choice as photoreactive alcohol component of the polyamic acid ester. In combination with optimizing photoinitiators, solvents and developers the best and most tolerant processing conditions for reproducibly getting well resolved polyimide patterns up to high thickness were worked out.

To be suitable for attractive applications in microelectronics the polyimide patterns had to
withstand harsh test conditions and should provide good long-term properties. Consequently it was necessary to make sure, that the curing conditions were sufficient to get fully imidized patterns. The imidization process of polyamic acid methacrylate ester was followed by differential scanning calorimetry (DSC) and infrared spectroscopy (IR) [5]. According to Figure 3 the main imidization process starts at about 160°C, it continues at 340°C, and is completed at 450°C (100% polyimide). As established by mass spectroscopy (MS) in combination with gas chromatography, more than 95% of the volatile product is hydroxyethylmethacrylate, which results from depolymerization of the crosslinks. Due to the volatilization of the photoreactive groups the initial film thickness is reduced by ca. 50%.

![Fig. 3 Differential scanning calorimetry of polyamic acid methacrylate ester and temperature-dependant degree of imidization, determined by IR-spectroscopy](image)

At this state of development, it turned out, that in the field of semiconductor devices there was a big need for extremely thick photolithographically patterned polyimide layers on 16K up to 256K generations of memory chips in order to protect the devices against α-particles being emitted by radioactive trace elements (U;Th) present in the package consisting of ceramics or filled resins. These α-particles caused random errors in the function of the memory chips.

As a consequence the author and his team reproducibly manufactured the photoreactive polyimide precursor with an ion content of less than 1 ppm and a U,Th content of a few ppb in a semi-technical scale in the research laboratory. The mounting factory line steadily was supplied with the precursor and with photosensitive ready-to-use solutions. For the latter a storage stability of about 3 months at 23°C and 6 months at −15°C could be achieved. The resulting memory devices, whose cell areas were protected by thick polyimide patterns, can be seen in Figure 4. A SEM view on the edge of such a 35 μm thick protection layer is given in Figure 5.

![Fig. 4 Memory devices on a silicon wafer, the cell arrays are protected by thick polyimide patterns (dark areas)](image)

![Fig. 5 SEM of edges of a 35 μm thick polyimide protection layer on a memory device](image)

Later in order to further reduce costs a new synthetic path devoid of chlorine was developed [6]. In this case the intermediate tetracarboxylic acid diester, resulting from adding the photoreactive alcohol to an aromatic dianhydride,
is directly polycondensated with the diamine in the presence of dicyclohexylcarbodiimide to yield the polyamic acid methacrylate ester (Figure 6)

![Chemical structure](image)

**Fig. 6** Chlorine-free synthesis of polyamic acid ester with dicyclohexylcarbodiimide

In parallel to all these activities chemical companies like Asahi Chemical, Tokyo, Japan (tradename Pimele®) and DuPont, Wilmington, Delaware, USA (tradename Pyralin PD®) were licensed to manufacture and sell such resists based on the ester-type photosensitive polyimide precursors. They further optimized the technical performance specifically for various applications, i.e., general purpose, low stress or i-line exposure. These resists differ in photosensitization and in backbone structures [7,8]. They contain additives to enhance the photospeed, resolution capability and adhesion properties. These include photoinitiators, sensitizers, mono- or polyfunctionalized methacrylate or acrylate monomers and integrated adhesion promoters. Most formulations are sufficiently sensitive (150-400 mJ/cm²) for the use in production lines. With regard to purity, the author was deeply impressed, when he visited the factory line of Asahi Chemical for producing the precursor powder in a technical scale under clean room conditions. (!) He was looking back, sitting at his desk in the evening ...

**Figure 7** presents an advanced state of photolithography using ester-type photoreactive polyimide precursors.

As the mega chip generations became larger in size, stress problems could arise from the extremely thick polyimide patterns needed for α-protection. Therefore very pure packaging resins with an acceptable low level of alpha-radiation were developed by the suppliers. Hence a thin patterned polyimide layer of some microns became sufficient to protect Mbit DRAMS and logic devices (ASICS) in the assembly process during the separation of the chips by sawing and to work as an adhesive layer and a “buffer coat” towards the packaging resins. Figure 8 shows a wafer with an assembly of ca. 2304 Mbit DRAMS and a wafer with ca. 90 logic devices (ASICS) with polyimide patterns as a buffercoat, made from the ester-like photoreactive precursors. The devices withstand more demanding test conditions, such as the pressure cooker test (boiling water at 122°C/2 bar for a minimum of 500 hr) and cycling (2000x between −65°C and +150°C), resulting in improved long term properties. In view of the large quantity this was, and still is, the most important application for such polyimide patterns.

In 1984, Hiramoto et al. [9] reported an alternative route to negative working photosensitive polyimide precursors. They photosensitized a poly(amic acid) solution by adding photoreactive tertiary amines containing an acryloyl group, and a sensitizer. This leads to a
salt-like interaction between the amino groups and the carboxylic groups of the poly(amic acid). Photoresists based on this chemical principle have been optimized at Toray and commercialized under the tradename Phontenece®. Again specific formulations for various applications were made available.

In the scope of this publication it does not seem to be feasible and helpful to compare the performance of various formulations of ester-type and salt-like-type polyimide precursors. Both types have their merits and are well established in the market.

3. Photosensitive Poly(benzoxazole) Precursors

When using organic dielectrics for multilayer interconnections (Figure 9), positive tone photopatternable materials would be preferable for producing the necessary via hole patterns. In this case the areas to be irradiated are much smaller. Thus a dust particle would not be harmful as long as it is not located directly above a contact, which is much less probable. Furtheron the side walls of the via holes should have a positive slope, so that they can be conformally covered by conductor layers. On a strongly reflecting uneven substrate negative tone resists would result in via holes with sharp edges or even negative slopes, while positive tone resists should lead to the desired pattern, as Figure 10 illustrates.

This in mind the author and his team followed another path of innovation. The idea was to couple poly(o-hydroxy-amide) – a poly(benzoxazole) precursor – with diazonaphthoquinone, thus inhibiting the solubility of the precursor in aqueous basic developers [10]. As shown in Figure 11 upon irradiation an indene-2,3-carboxylic acid is being formed and the inhibition is neutralized, resulting in solubility in the basic developers. The positive mode patterns can be thermally converted into poly(benzoxazoles).

![Fig. 9 Organic dielectrics for multilayer interconnections](image)

![Fig. 10 Reliable opening of via holes with positive tone photo-patternable dielectrics](image)

![Fig. 11 Poly((benzoxazole) patterns made from photoreactive precursors](image)

A reproducible synthesis for the chain length optimized precursor was worked out, reacting the aromatic dicarboxylic acid with bis(o-aminophenol) using a condensing agent. As in the case of the polyimide precursors the most suitable solvent and developer and the best tempering conditions for the final conversion to poly(benzoxazole) were chosen.
Figure 12 shows the smooth edges of a via hole on a rough ceramic substrate, and Figure 13 demonstrates poly(benzoxazole) test patterns.

![Image of poly(benzoxazole) test patterns]

**Fig. 12 Poly(benzoxazole), patterned in a positive mode: contact hole on a rough ceramic substrate (Al₂O₃)**

Propertywise very attractive are a thermal decomposition temperature of 530 °C (5% weightloss), a low dielectric constant of 2.8 (1 kHz, 50% rel.hum.,23°C), a tensile strength of 110 MPa, a Young's modulus of 2.7 GPa, an elongation of 9%, a TEC of 50 ppm/°C.

The path of innovation reached its target with the successful commercialization of the positive tone photo-patternable poly(benzoxazole) precursors by the licensee Sumitomo Bakelite, Tokyo, Japan.

4. Conclusion

The author described two paths of innovation which he was involved in – the way to negative mode photosensitive polyimide precursors and to positive mode photosensitive poly(benzoxazole) precursors from the initial idea up to commercialisation and application, mainly as buffer coating and protective patterns for Mbit memory and logic devices and as organic dielectric patterns for multilayer interconnections in microelectronics and electronics, respectively. Both developments were driven by the needs of the market. This is in accordance with a general trend towards innovaton driven by “market pull” and less towards technology driven innovations (“technology push”).

The author wants to thank his coworkers, especially Helmut Ahne, and his colleagues in the Siemens business units and equally those at the licensees for the very good and the trustworthy cooperation.

References