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New Photosensitive High Temperature Polymers for Electronic Applications

Naoya Yoda[a]; H. Hiramoto[ab]
[a] Toray Industries (America), Inc., New York, New York [b] Film and Film Products Research Laboratories Toray Industries, Inc., Otsu, Japan

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New Photosensitive High Temperature Polymers for Electronic Applications

NAOYA YODA and H. HIRAMOTO

Toray Industries (America), Inc.
New York, New York 10017;
Film and Film Products Research Laboratories
Toray Industries, Inc.
Otsu, Japan

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ABSTRACT

A new photosensitive high temperature polymer stable up to 500°C with high photosensitivity and high resolution has been developed. The trend toward a high degree of integration in solid-state technology requires the use of new high temperature photosensitive insulating materials. Toray's Photoneece system provides such versatile polyimide pattern-generation techniques, containing a unique photosensitive polyimide precursor which can be spun or coated on the substrate. The resultant relief of photosensitive polyimide precursor, after exposure to UV light with a mask, development, and cure processing, is transformed into a cyclized aromatic polyimide. The new system has higher photosensitivity and resolution and eliminates three steps in the conventional pattern-making process for integrated circuits, resulting in a significant cost reduction. The characterization of pattern generation, the conversion to polyimide patterns, and the properties of both Photoneece and the patterns are discussed.

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INTRODUCTION

The innovative technology of advanced specialty materials, such as the high temperature polymers originally initiated by C. S. Marvel, brought about a new age of advanced industrial products. In the last few years, under the impetus of electronics, aerospace, and aircraft applications of advanced composite materials, high temperature polymers have been widely applied in matrix resins of graphite fiber, films, and molded parts in insulating materials. In microelectronics applications, the trend toward a higher degree of integration in solid-state technology is obvious, and there are increasing demands of new high temperature photosensitive polymers for micropattern generation technology.

In this paper a new type of photosensitive high temperature polymers for insulation multilayers in solid-state devices is prepared, and application for dielectrics for microelectronic applications is discussed.

Research on Photoneece, a high temperature photosensitive coating resin, was initiated by a Toray research project about 10 years ago and was commercialized in 1981. Toray had accumulated the following key technologies: (1) high temperature polymers for electronic chemicals, and (2) polyamide-type Torayleef photosensitive printing plates for graphic arts. This technology is the research result of the combination of these two key technologies established by Toray.

Reactions of photosensitive polymers as reported in patents and literature reveal the unique process of pattern generation systems, fabrication process, and characterization of polymers. In order to ensure an economical and reproducible method of preparation, the new photoreactive polyimide precursor was confirmed to utilize commercial methods of photoresist process and technology.

The first example of a photosensitive polyimide coating was reported by Kerwin and Goldrick at Bell Laboratories in 1971 [10]. The Bell formulation involves a cross-linking reaction of 3 parts of polyimide and 1 part of 2% potassium dichromate in sensitized DMSO solution as shown in Eq. (1). Since it has shelf life of only 4 to 8 h, it is not commercially appealing.

Rubner and co-workers at Siemens reported the formulation in 1979 as shown in Eq. (2) [11]. Monomers containing photosensitive groups were prepared and copolymerized with comonomers to form photosensitive polyimide precursors.

The photosensitive groups are attached to the carboxylic group of the polyimide precursor through an ester linkage. The cross-linking reaction, upon exposure to UV light, lowers the solubility of the polymer in the developing solvents. All photosensitive groups are eliminated at the curing stage. It has a low photosensitivity and a resolution limit of 5-10 μm.

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HOOC COOH
NHOC CONH O
n

Polymide Precursor (PIP)

Dichromate

⇨ Photosensitive Polymide Precursor

(1)

⇨ Photosensitive Polymide Precursor

Coating
Exposure to U V
Development

⇨ Curing at 250°C

OC CO N N O OC CO n

OC CO O O OC CO + R*OH ⇨

R*: $CH_2{=}C(CH_3)COOCH_2CH_2$

R*OOC COOR* HOOC COOH $\xrightarrow{SOCl_2}$ R*OOC COOR* ClOC COCl

(2)

NH_2–O–NH_2

⇨ OC CONH O NH R*OOC COOR*

Photosensitive Polymide Precursor

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TABLE 1. Photosensitive Polyimide Precursor (I)

PIP + C*

↓ Mixing

Photosensitive Polyimide Precursor

C* (photosensitive compounds)
Bisazide — Saiki et al. — 1
Diazide — F. J. Robrest et al. — 2
Bisdiazide — H. Ahne et al. — 3 — Positive Working

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Other examples of photosensitizations of polyimide precursors are summarized in Tables 1, 2, and 3.

In Table 1 the photosensitizations of polyimide precursors are carried out by adding photosensitive compounds to polyimide precursor solutions. Candidates for photosensitive compounds such as bisazide 1 by Saiki [1], diazide 2 by Robrest [2], and bisdiazide 3 by Ahne [3] have appeared in the patent literature. In the case of bisdiazide, a positive-type photoresist is obtained.

In Table 2 the copolymerization approach of monomers with the photosensitive group to obtain a photosensitive polyimide precursor is summarized. As monomers containing a photosensitive group, bisimide 4 copolymer reaction is described by Hiramoto of Toray [4] whereas diamine containing the cinnamic acid group 5 is reported by Shoji [5]. The bisimide is prepared by the reaction of pyromellitic imide with cinnamic acid chloride to form photosensitive polyimide precursor containing a photosensitive side chain. The diamine can be polymerized with pyromellitic anhydride to form polyimide precursors.

In Table 3 the photosensitizations of polyimide precursors by reacting photosensitive compounds with polyimide precursors are sum-

TABLE 2. Photosensitive Polyimide Precursor (II)

M + M*

↓ Polymerization

Photosensitive Polyimide Precursor

M* (Monomers containing photosensitive radicals R*)	
Bisimide	H. Hiramoto et al.
C_6H_5-CH=CHCON(OC)₂C_6H_2(CO)₂NCOCH=CH-C_6H_5	4
Diamine	F. Shoji et al.
H_2N, NH_2 - C_6H_3 - $COOCH_2CH_2OC(=O)CH=CH$-C_6H_5	5

marized. The reaction of glycidyl cinnamate 6 with a polyimide precursor is reported by Shoji [6]. Other examples of photosensitive compounds reacting with polyimide precursor are isocyanate compound 7 by Takemoto [7], cinnamic acid chloride 8 by Hiramoto [8], and amine compound containing phenylazide 9 by Kataoka [9].

In recent years there has been a trend toward a higher degree of integration in solid-state technology and a higher reliability of material, together with a larger size of substrates required in the electronic industry centering around semiconductors. There are increasing demands of new insulation materials using a practical photoprocessing system with heat-resistant photosensitive polymers.

Since a high degree of integration can generally be achieved through micropattern generation technology, the application of photolithography technology is indispensable. As larger structural dimensions are required and the areas of integrated circuits become larger, the defects of density per area should be minimized, otherwise the yields of the integrated circuit ratio decrease drastically.

This implies that photoprocessing steps must be more reliable, and thermal and chemical stability as well as the lowest possible level of impurity are required to meet the additional requirements.

In the Research Laboratories at Toray, the authors have extensively

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TABLE 3. Photosensitive Polyimide Precursor (III)

PIP + R*X → (Reaction) → Photosensitive Polyimide Precursor

R*X (compounds containing photosensitive radicals R*)			
R*-CH_2CH—CH_2 (epoxy, —O—)	F. Shoji et al.	C$_6$H$_5$—CH=CHCOOCH$_2$CH—CH$_2$ (epoxy, —O—)	6
R*—NCO	K. Takemoto et al.	C$_6$H$_5$—CH=CHCONCO	7
R*—COCl	H. Hiramoto et al.	C$_6$H$_5$—CH=CHCOCl	8
R*—NR_2	F. Kataoka et al.	N_3—C$_6$H$_4$—COOCH$_2$CH$_2$N(CH$_3$)$_2$	9

engaged in the research and development of high temperature polymer synthesis and new applications for the electronics industry during the last decades. One of the versatile approaches for high value added products by polymer reactions of direct polymerization of fully aromatic heterocycles is the introduction of a photosensitive group into the pendant side chain of aromatic polymer chains.

The concept of molecular design for heat-resistant photosensitive polymers can be defined as having three important key elements for necessary and sufficient conditions:

(1) The polymer precursor should be soluble in solvents and processable for microcoating on the substrate.

(2) A sharp contrast of segregation of polymer solubility, either an increase or a decrease, between the photosensitive cross-linking part and the noncross-linked part in common solvents.

(3) Items (1) and (2) should provide sufficiently high resolution and high photosensitivity for the complete removal of volatile photoreactive parts by curing process.

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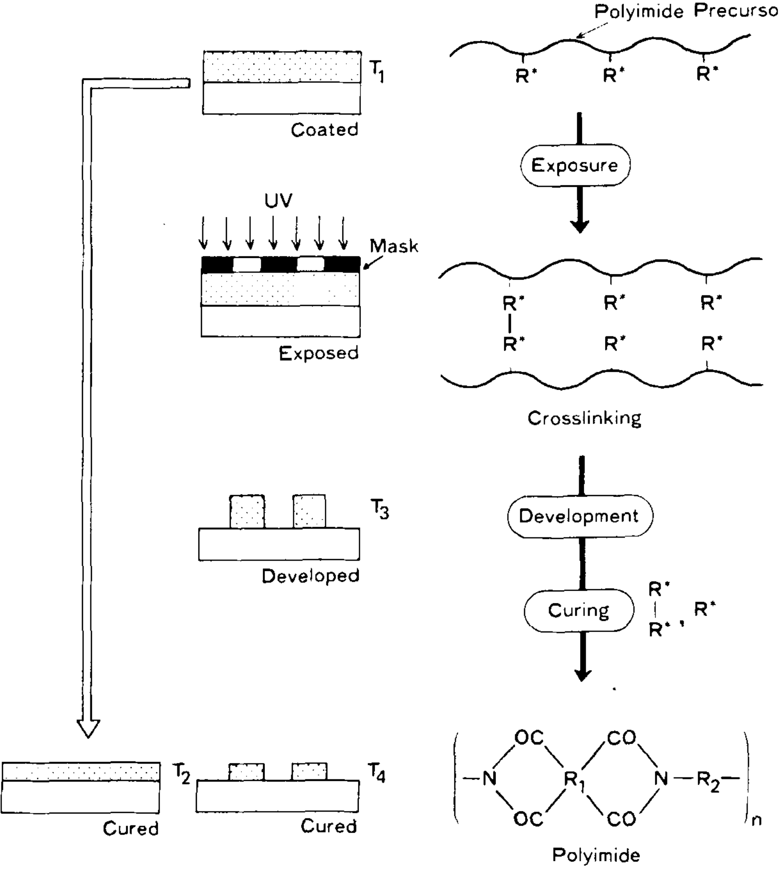

FIG. 1. Photoneece Toray photosensitive polyimide coatings.

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For higher reliability, purity of material, stability, and safety factors in the total system are all important.

The process diagram of the Toray Photoneece photosensitive polyimide coating system is shown in Fig. 1. The three major processes are (1) exposure, (2) development, and (3) curing, in which the polymer side chain has the function of a push-pull mechanism. As shown in Eq. (3), polyamic acid was used as a polyimide precursor and R* indicates a polymer side-chain containing a photosensitive group which essentially has the function of pattern generation in the polymer system.

Toray's technology consists of polyimide precursors containing amines with photosensitive groups, and photosensitizers. As amines with photosensitive groups, allyl amines, vinyl pyridine, and amino

$$\left(\text{–OC–}C_6H_2(\text{–COOH})_2(\text{HOOC})\text{–CONH–}C_6H_4\text{–O–}C_6H_4\text{–NH–} \right)_n$$

Polyimide Precursor (PIP)

$$\xrightarrow{R'-NR_2} \left(\text{–OC–}C_6H_2(\text{HOOC}\cdots R'-NR_2)(\text{COOH}\cdots R_2N-R')\text{–CONH–}C_6H_4\text{–O–}C_6H_4\text{–NH–} \right)_n \quad (3)$$

Photosensitive Polyimide Precursor

acrylates are employed. As photosensitizers, the following compounds were found to be effective: 4,4'-bis(diethylamino) benzophenones, benzoyl ether, anthraquinones, and Michler's ketones. The reaction mechanism of cross-linking is based on a free radical reaction to form insoluble polymer. Toray's photosensitive polyimide precursor is formed by the reaction described in Eq. (3). The Photoneece solution has the following properties: Solid concentration, 17%; viscosity, 1000 cps at 25°C solvent; mixed solvents of NMP and methyl cellosolve.

A variety of fully aromatic polyamides containing a carboxyl group form amine salt quantitatively with amines, which form stable polymer solutions. When vinyl pyridine, allyl amines, or amino methacrylate is used in the presence of a photosensitizer, a specific formulation affords optimum condition of high resolution and high photosensitivity in the particular polymer system.

FABRICATION PROCESS

In electronic applications, photosensitive polyimide coatings can generate patterned polyimide films by a process similar to photoresists. Most of them are negative working polyimide coatings whose exposed area becomes insoluble in a developer. There are polyimide coating resins without photosensitive properties, such as Semiconfine by Toray, Pyralin by DuPont, and PIQ by Hitachi. They can only generate patterned polyimide films by an ordinary photolithographic procedure as shown in Fig. 2, in which polyimide decomposes with hydrazine hydrate. The polyimide precursor is coated on a substrate. After prebake, a photoresist is coated on the polyimide film. In the usual method, it is exposed, developed postbaked, and then polyimide is etched by using a photoresist pattern as the etching mask. After removal of the photoresist, the polyimide is cured to obtain the final

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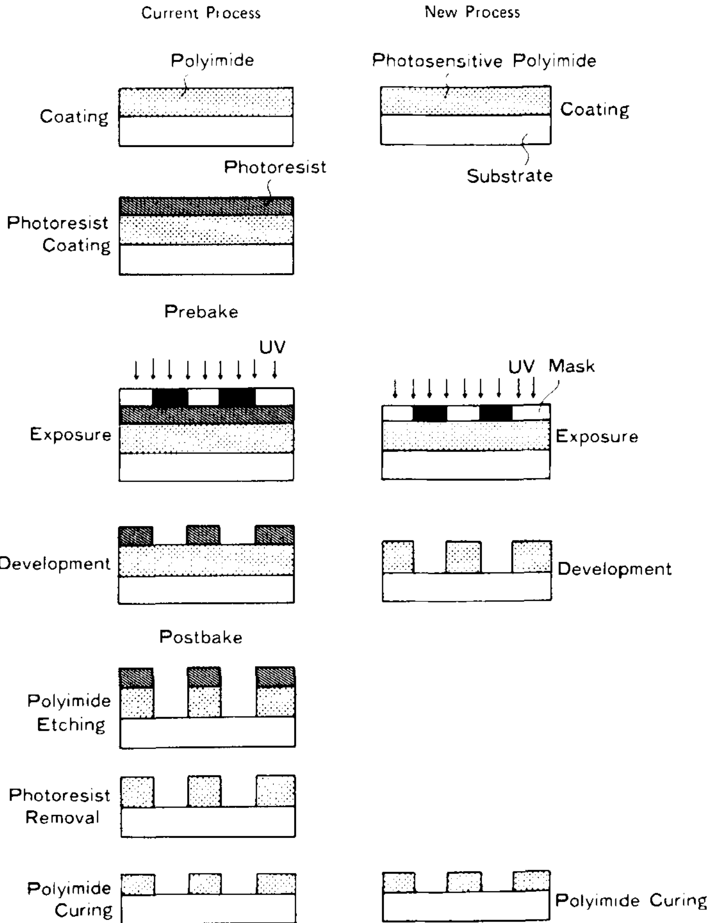

FIG. 2. Polyimide pattern generation process.

product. This process is complicated, and when a photosensitive polyimide is employed, the pattern generation process is simplified by three steps, and rationalization is achieved in the pattern generation process as shown in Fig. 2.

The typical process cycle of pattern formation of a Photoneece solution is described in Table 4 [13].

(1) A photosensitive high temperature polymer solution containing polyimide precursors is coated by spin coating on a substrate for a period of 30 s at 1500 rpm, and then for 2 s at 3000 rpm to take off the thick edge of the film at a higher rotational speed.

TABLE 4. Typical Process Cycle of Photoneece (T_1 = 5.5 μm, T_4 = 3.1 μm)

Process	Condition
Spin coating	30 s at 1500 rpm and 2 s at 3000 rpm
Prebaking	60 min at 80°C in N_2 convection oven
Exposure	250 mJ/cm^2 (365 nm) using contact mask aligner with high-pressure mercury lamp
Developing	Ultrasonic development: Developer DV-140; Temperature 25°C; Time 90 s
Rinse	Ultrasonic rinse and then immersion rinse in isopropylalcohol, each for 15 s at 25°C. Drying: Nitrogen blow immediately after rinse
Postbake	30 min at 135°C, 30 min at 200°C, 30 min at 300°C, and 30 min at 400°C

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(2) Prebaking is for 60 min at 80°C in an N_2 convection oven.
(3) Exposure is at 50-250 mJ/cm^2 at 365 nm with a contact mask aligner.
(4) Development: Ultrasonic development
Developer DMAC/alcohols, DV-140
Eltrosonic rinse, and immersion and rinse in isopropanol
For thick film, ultrasonic development is important
(5) Postbake heat treatments at
(1) 135°C/30 min
(2) 200°C/30 min
(3) 300°C/30 min
(4) 400°C/20 min

PROPERTIES AND CHARACTERIZATION

The photosensitivity characteristics of Photoneece are shown in Fig. 3. The horizontal axis shows the exposure energy expressed in mJ/cm^2, and the perpendicular axis indicates residual yield in percentage. Figure 3 shows the T_4/T_2 ratio on the Y_1 axis, which corresponds to the residual yield of development. The lower figure indicates the T_4/T_1 ratio on the Y_2 axis, which means the residual yield of both

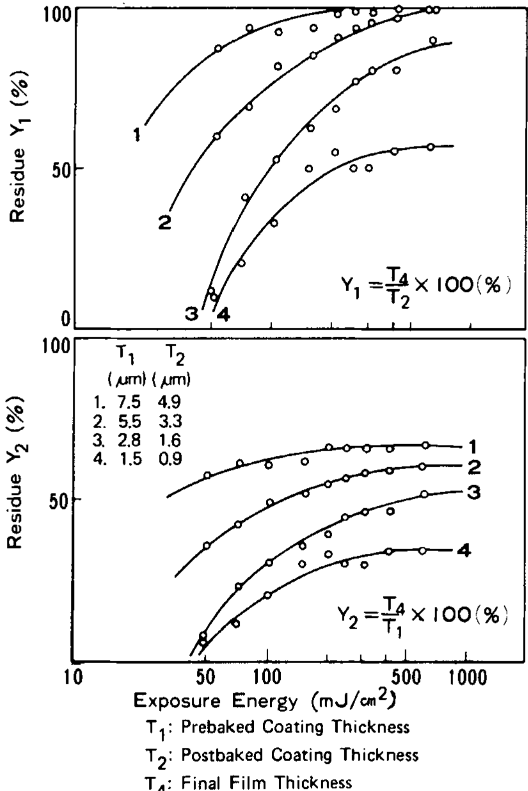

FIG. 3. Characteristic curves of Photoneece.

development and heat-treatment. That is, it represents the ratio of final film thickness (T_4) versus the initial thickness of the spin-coated film (T_1). Curves 1, 2, 3, and 4 in Fig. 3 refer to T_1 7.5 μm, 5.5 μm, 2.8 μm, and 1.5 μm, respectively. It is concluded from the curves shown in Fig. 3 that the required exposure energy varies according to the thickness of coated film, and 50-300 mJ/cm is required for exposure energy. This means that the photosensitivity of Photoneece is 1/5 to 1/6 of the positive resist photosensitivity used in the semiconductor process. Although it is within commercial level photosensitivity, further improvement is necessary. It is also shown in this figure that the residual yield decreases with decreasing film thickness. This is considered to be due to "the oxygen effect." Due to the diffusion of oxygen from the film surface, free radical is destroyed by the oxygen effect and decreases photosensitivity.

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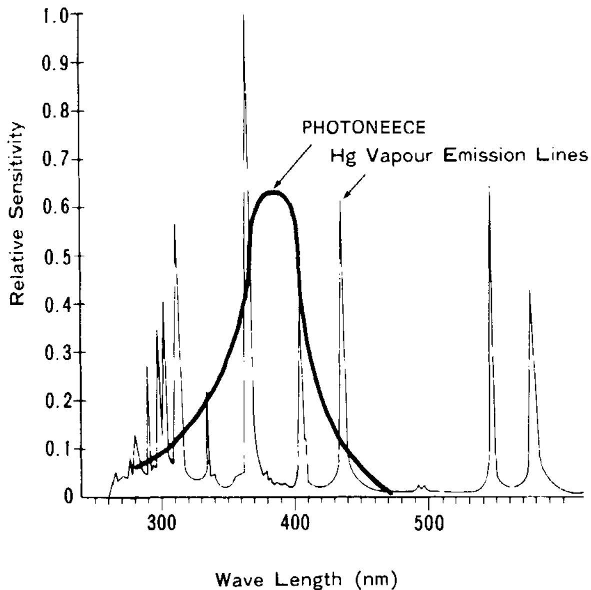

FIG. 4. Sensitivity spectrum of Photoneece.

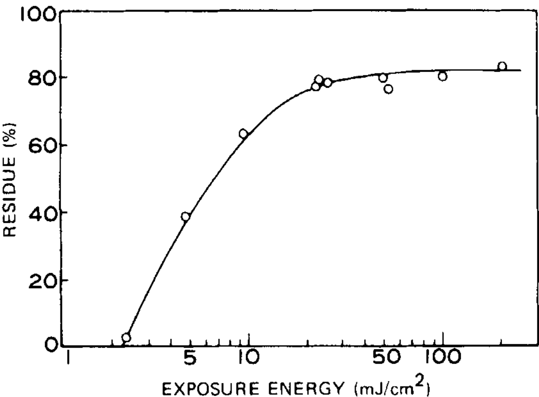

FIG. 5. Characteristic curve of Photoneece, new type.

The photosensitivity spectrum of Photoneece, which has maximum photosensitivity at 390 nm, is shown in Fig. 4 with emission lines of a high pressure mercury lamp. Photoneece is photosensitive to the emission lines at 365 and 405 nm but not sensitive to the emission line

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at 436 nm. Photoneece has a resolution of 3-5 μm in the case of a final film thickness of 1-2 μm. The resolution of Photoneece varies with the film thickness, and it decreases with increasing film thickness.

In Fig. 5 a characteristic curve of the new Photoneece high photosensitive type is shown. It has an improved exposure energy range of as low as 8-10 mJ/cm^2 at 50% residual yield as shown in Fig. 4.

The liquid properties of Photoneece are shown in Table 5 [13]. The solid content is 17%, which can be increased to 20%. Viscosity is 1000 cP at 20° C, and it is dissolved in a solvent mixture of NMP and methyl cellosolve. Metal ions and chlorine content are both controlled within minimum allowance for the commercial requirements of semiconductor applications of random access memory devices: (1) Uranium causes soft errors and should be minimized. (2) alkali metals deteriorate the semiconductor characteristics, and (3) chlorine ion causes corrosion of aluminum circuits.

As for film properties, tensile strength, thermal and electrical properties are summarized in Table 6 [13]. As shown in Table 6, physical film properties are maintained at the same level as the polyimide prior to the introduction of the photosensitive group. It is confirmed by IR and DTA analyses that the photosensitive group introduced for this application is eliminated in the heat-treatment process. The photosensitive group does not affect the physical properties of the final film.

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TABLE 5. Liquid Properties of Photoneece UR-3100

Items	Units	Typical values
Solids	%	17
Viscosity	CPS/25° C	1000
Metallic ion content		
Na	ppm	0.4
Ca	ppm	0.3
Cu	ppm	Less than 0.1
Fe	ppm	0.1
U	ppb	Less than 0.3
Chlorine ion content	ppm	Less than 1
Solvent	-	Mixed solution of N-methyl-2-pyrrolidone and Methyl Cellosolve

TABLE 6. Film Properties of Photoneece UR-3100

Properties	Items	Units	Typical values
Physical	Tensile strength	kg/mm^2	14.2
	Elongation	%	11
Thermal	Melting point	°C	None
	Flammability	-	Self-extinguishing
Electrical	Dielectric constant (1 kHz, 25°C)	-	3.2
	Dissipation factor (1 kHz, 25°C)	-	0.0018
	Volume resistivity	Ω·cm	1.3×10^{16}
	Surface resistivity	Ω	10^{16}
	Dielectric strength	kV/mm	307

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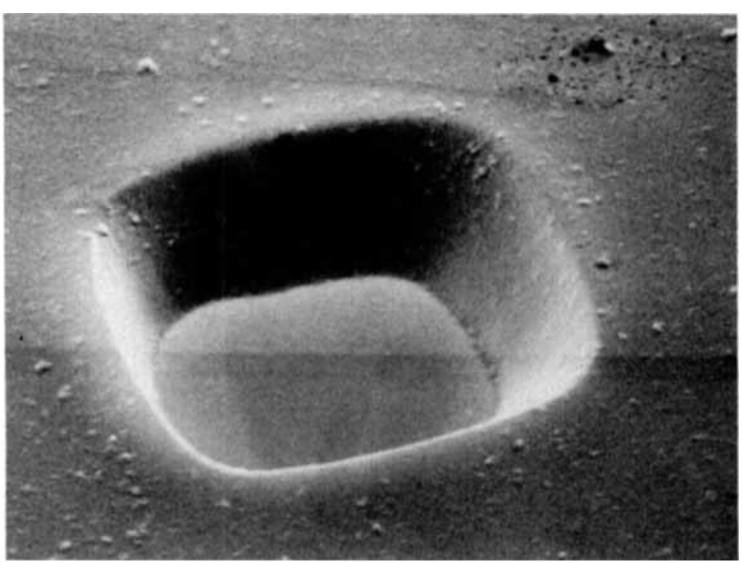

FIG. 6. Electron microscopic pattern of a clean through-hole of 10 μm diameter.

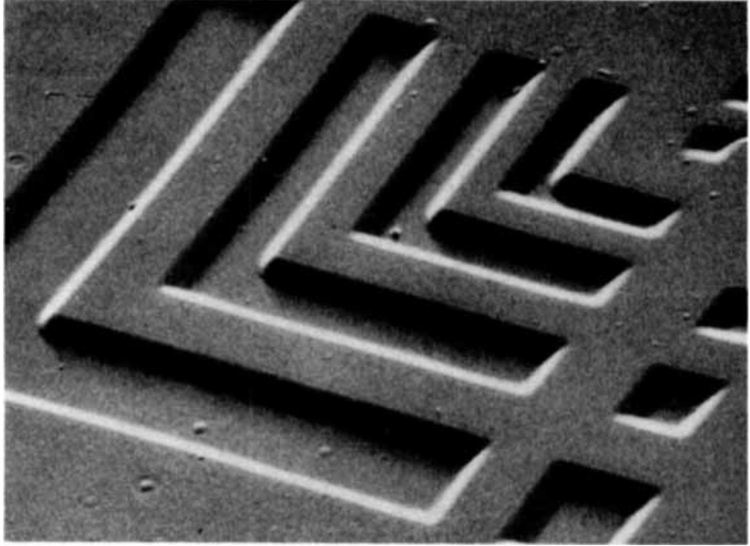

FIG. 7. Electron microscopic patterns of 15, 10, 8, and 6 μm diameter.

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A clear 10 μm^2 through-hole is shown in an electron microscope picture (Fig. 6). The bottom of the hole core spans to the size of the mask measurement of 10 μm. The side section shrinkage has a 60° angle slant due to postbake contraction. The slant is especially importnat in applications as insulating film for microelectronics.

The electron microscopic picture in Fig. 7 shows an example of a Photoneece pattern corresponding to a mask with 15, 10, 8, and 6 μm lines and space. Even the 6-μm pattern is clearly resolved.

An example of a thick film pattern with an undercut for lift-off application is shown in Fig. 8.

An example of a thin film of 1 μm thickness with a 2-μm through-hole at the mask point is shown in Fig. 9.

In Fig. 10 the cross-section of Photoneece with a 3-μm pattern is shown.

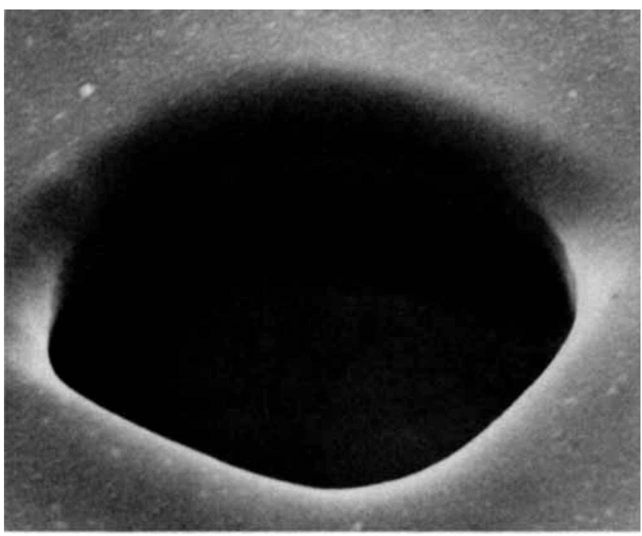

FIG. 8. Electron microscopic photograph of a thick film pattern with an undercut.

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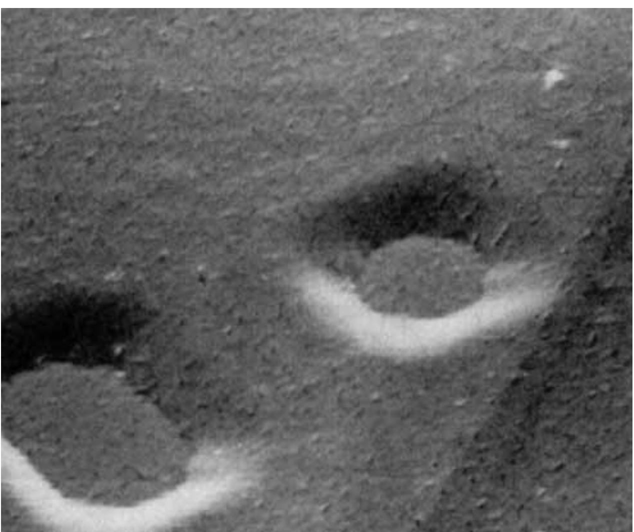

FIG. 9. Electron microscopic photograph of 1-μm thick film with a 2-μm through-hole.

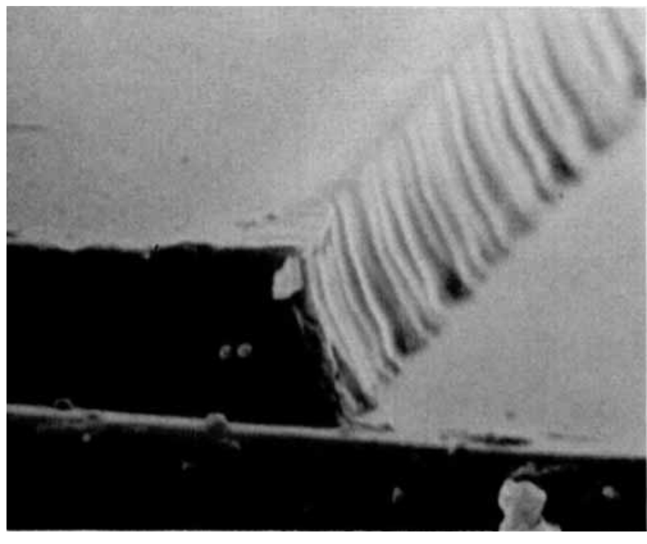

FIG. 10. Cross-section of Photoneece with a 3-μm pattern.

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ELECTRONIC APPLICATION AND FABRICATION PROCESS

In electronics devices manufacturing, the trend toward a higher degree of integration, a larger substrate size, and a high device reliability requires new insulating materials.

The insulating materials have to have such characteristics as thermal stability, patternability by photolithography, tough film formation, high dielectric properties, high purity, and the capapility of solution coating as described in Fig. 11. Polyimide-type coatings are one of the best candidates for such insulating materials. The polyimide-type coatings can provide required patterns by the photoetching process. The photoetching process is complicated and lacks reproducibility and reliability.

The complicated process of pattern generation is a bottle-neck with ordinary polyimides for electronics applications. A new type of photosensitive high temperature polymer coating varnishes is required to solve this problem and to increase productivity in such electronic industries as semiconductors.

There are several important applications of dielectrics for microelectronics applications. Examples of applications are:

(1) Protection coating of integrated circuit.
(2) Multilayer circuit insulation of integrated circuit.
(3) Protective layer of diode and transister.

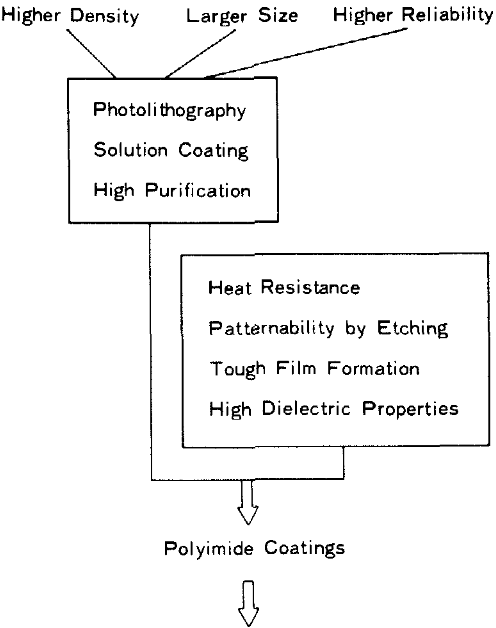

FIG. 11. Polyimide coatings for electronics.

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(4) Alignment layer of liquid crystal device.
(5) Insulation layer of thermal head of facsimile.
(6) Insulation layer of thin film magnetic recording head.
(7) Interlayer insulation film of assembly package of large-scale integrated circuits.
(8) Soft-error protection coating of very large-scale integrated circuit.
(9) Lift-off process.
(10) Ion-Implantation mask.

Figure 12 shows the cross section of a 64-kbit, Random Access Memory, which is the highest integration of a memory device at present. Integrated circuits are sealed in ceramic packages. The ceramic package contains a trace of natural uranium, and a small amount of α-particle emission is observed. The effect of the α-particle is negligible up to 4 kbits RAM. However, for higher micro-systems of memory cells of higher integration of elements to 16 and 64 kbits, the electronic charge formed by irradiation of the α-particle causes the memory to reverse. To solve this problem, a high purity

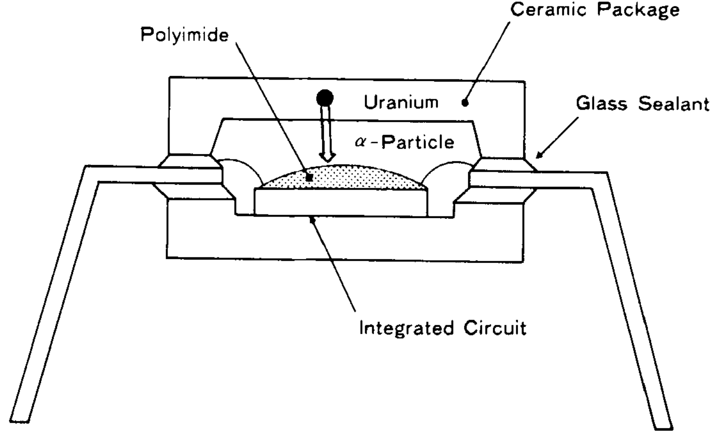

FIG. 12. α-Particle protection coating.

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polyimide film coating of 50 to 100 μm thickness can be applied to the integrated circuit.

In Fig. 13, two methods of multilevel interconnecting systems are shown. One is the conventional method using inorganic interdielectrics such as CVD SiO2 and the other is the planar metalization method using a polymer insulating material such as polyimides. In the conventional method the rough surface of the substrate enters the insulation films and circuit layers and causes steps in the 2nd level metallizations.

Planar metallization with polyimide avoids step formation as shown in Fig. 12. The step part causes the cut-off circuit to decrease reliability drastically. Therefore, a two level circuit is the limit in the conventional method, and it is impossible to obtain the multilevel interconnecting systems of more than three layers. In the polymer solution coating method, a planar level is formed at each level and no step structure is obtained. In principle, multilevel structures are possible, and this method will be applied to large-scale integrated circuits in the future.

In Figure 14 the cross section of a thin film magnetic recording head is shown. In this application a polyimide insulation layer is effective in giving a planar structure on the conductor coil between magnetic layers. In Fig. 15 a liquid crystal device is shown. The liquid crystal layer is located between two polyimide aligning layers. Polyimide is used in this application because a uniform film is formed on large-scale substrates by coating and because there is high temperature resistance at the curing temperatures of epoxies and a high diffraction index.

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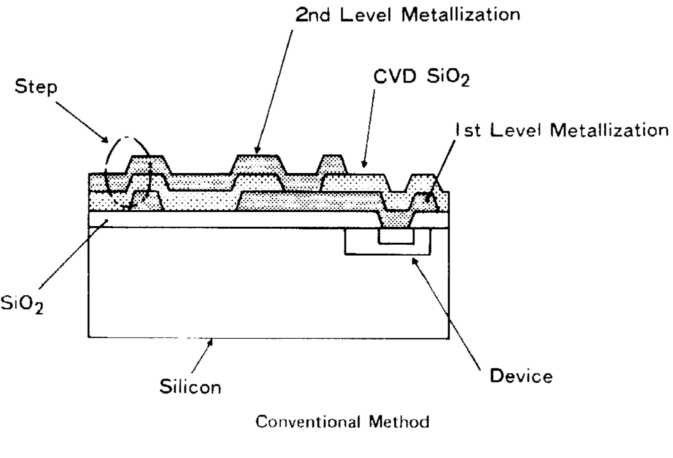

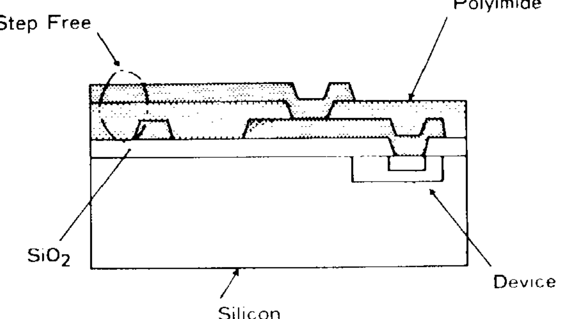

FIG. 13. Dielectrics in multilevel interconnect systems.

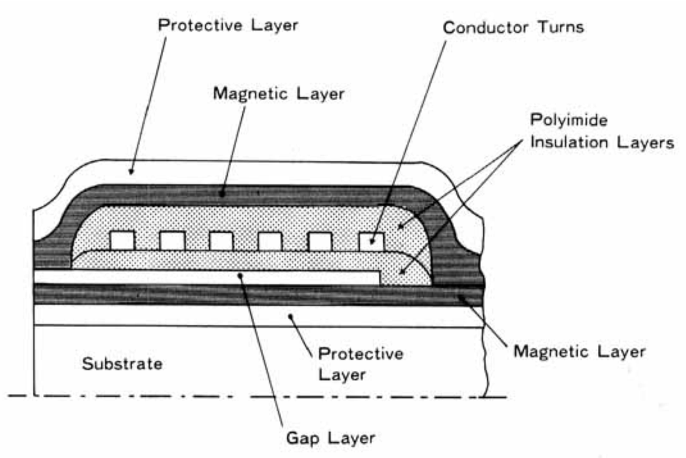

FIG. 14. Thin film magnetic recording head.

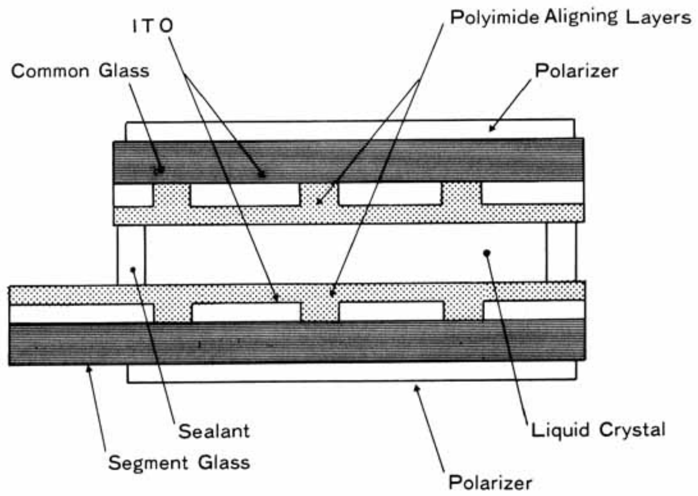

FIG. 15. Liquid crystal device.

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CONCLUSION

A new photosensitive high temperature polymer stable up to 500°C has been developed as a photoreactive polyimide coating solution. It can be processed into polyimide patterns by the conventional photoresist patterning process. Photoneece was developed by Toray, based on a long-term R&D effort in the technology of cyclopolycondensation reactions and the application of high temperature polymers and photosensitive polymers in graphic arts.

The unique characteristics of Photoneece are summarized as follows. (1) It has high photosensitivity and high resolution. The photosensitivity measured at an UV wavelength of 365 nm, 50% residual, is

		Exposure energy
Photoneece	UR-3100	50-250 mJ/cm^2
	New Type	8-10 mJ/cm^2

This is the first technology to achieve a high level of photosensitivity with polyimide. The proprietary technology of Toray's formulations is by a combination of specific photosensitive compounds with specific photosensitizers. The wavelength of the UV absorption band is in the range of 390 nm. A resolution of postcured film of 1-2 μm thickness through hole diameters of 3-5 μm is obtained.

(2) It has a low concentration of impurities. It has an extremely low level of alkali metal ions, chloride ions and heavy metal ions, in-

cluding uranium, which prevents the properties of semiconductor devices from deteriorating. The low level of uranium is effective for soft-error protection coating. The low level of halogen ion content is also effective in preventing metal corrosion of the aluminum circuit.

(3) Photoneece has a long shelf life. It is stable up to 6 months at 10°C in dark refrigeration without gelation.

(4) It has an excellent cost-performance relationship. The simple pattern generation process utilizes three steps: coating with photoresist, etching, and stripping the photoresist.

(5) There is a versatile technology of polyimide precursor formulation for other fully aromatic heterocycles.

(6) The cured film of a fine polyimide pattern essentially maintains the superior properties inherent in the aromatic polyimide without such deteriorating film properties as heat resistance, electrical insulation, and mechanical toughness.

A wide variety of new applications are being explored including protective coating and multilayer insulation for diodes, transisters, IC, LSI, VLSI, and microelectronic circuits in computers and facsimiles. The area of heat-resistant removal of photoresist for the dry etching process may be important.

In future advanced design specialty polymer systems, besides the high temperature polymers with high photosensitivity properties we have described, such functions as lower gas permeability, high temperature plus low moisture regain, and high temperature resistant membrane with enzymatic functions will be important targets. The authors are convinced that there are good opportunities and a bright future for the development of these new advanced composite polymer systems.

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In 1962-1963 the author (N.Y.) was engaged in postdoctoral research work in Tucson, Arizona, and enjoyed not only the research atmosphere of Dr Marvel's group but also the beautiful Arizona sunshine.

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