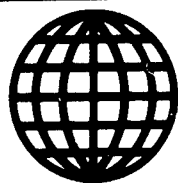


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POLYMERS FOR MICROELECTRONICS

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16 JANUARY 1990

SCIENCE & TECHNOLOGY

JAPAN

POLYMERS FOR MICROELECTRONICS

[Selected abstracts from PME '89 POLYMERS FOR MICROELECTRONICS held 29 Oct - 2 Nov 89 in Tokyo, sponsored by the Japan Society of Radiation Chemistry and cosponsored by the Japan Society of Polymer Science and the Chemical Society of Japan]

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Photopatternable Organic Dielectrics : Polybenzoxazole Versus Polyimides..... 129
R. Rubner, A. Hammerschmidt, R. Leuschner and H. Ahne (Siemens, FRG)

(Session B37) 14:00 - 14:20

Poly (4, 4'-Diphenyl Ether)
Pyromellitimide Modified with Oligoimidophenylene
A. I. Volozhin, E. T. Krut'ko and A. P. Solntsev
(Institute of Physico-organic Chemistry, Academy of Science of
Byelorussian SSR, Minsk, USSR)

(Session B38) 14:20 - 14:40

A Novel Positive Type Polyimide Based on Photoinduced Acidolysis 131
T. Omote, K. Koseki and T. Yamaoka (Chiba Univ., Japan)

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Chairperson : **T. Nishikubo** (Kanagawa Univ.)

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Preparation and Properties of Disilane Containing Photodegradable 133
Aromatic Polyamides and Polyimides from Bis (p-aminophenyl)
tetramethyldisilane
M. Padmanaban, M. Toriumi, M. Kakimoto and Y. Imai
(Tokyo Inst. Tech., Japan)

(Session B40) 15:20 - 15:40

Preparation and Properties of a Photosensitive Polyimide Having Low 135
Thermal Expansion and Stress
A. E. Nader, K. Imai, J. D. Craig, C. N. Lazaridis, D. O. Murray,
M. T. Pottiger and W. J. Lautenberger (Du Pont, USA)

(Session B41) 15:40 - 16:00

Photocrosslinking Reaction of Benzophenone Type Polyimide and 137
Its Derivatives
T. Yamashita, H. Higuchi, K. Horie and I. Mita
(Univ. Tokyo, Japan)

* : Invited Talk

Presentation Time :

Plenary Talk 40 minutes

(Presentation 30 min + Discussion 10 min)

Invited Talk (*) 30 minutes

(Presentation 24 min. + Discussion 6 min)

Contributed Talk 20 minutes

(Presentation 15 min + Discussion 5 min)

DYE-SENSITIZED ABLATION AND EXPANSION OF POLYMERIC MATERIALS BY LASER IRRADIATION

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INTRODUCTION

Laser irradiation to polymeric materials is a promising technique in micro processing, since it can lead to various kind of morphological change of the surface. It is generally considered that polymers can be ablated by photochemical and/or photothermal decomposition, and the mechanism depends on the wavelength of the laser pulse and the polymer material¹⁾. In this report, the mechanism of dye-sensitized ablation has been studied by using porphyrin derivatives as dopants. An advantage of dye-sensitization is capability to vary the laser-wavelength and the absorbance of the polymer film independently.

EXPERIMENTAL

Three types of polymer films were prepared as follows : poly(methyl methacrylate) doped with tetraphenylporphyrin (TPP/PMMA) ; poly(vinyl carbazole) with TPP (TPP/PVCz) ; gelatin with hematoporphyrin (HP/GL). Films were irradiated only once with either an excimer laser (XeF: 351nm, 15ns) or a Nd³⁺:YAG laser (second harmonic: 532nm, 10ns). Scanning electron micrographs were recorded with a Akashi WS-250 (Government Industrial Research Institute of Osaka). Depth profiles were measured by a Dektak 3030 (Yamada Lab., Kyoto University). Time-resolved luminescence spectra were also measured just upon laser irradiation by a streak camera system (Hamamatsu C2830/C3140).

RESULTS AND DISCUSSION

In the case of low fluence, an irreversible expansion of the irradiated surfaces was observed for all films examined (Fig. 1 (a)). Decreasing the absorption coefficient (α) increased a threshold of the expansion and also increased the maximum height of this morphological change. The height was $2\mu\text{m}$ for TPP/PMMA ($\alpha = 0.10\mu\text{m}^{-1}$), $0.7\mu\text{m}$ for TPP/PVCz ($\alpha = 0.075\mu\text{m}^{-1}$), and $4\mu\text{m}$ for HP/GL ($\alpha = 0.10\mu\text{m}^{-1}$). A further increase of the fluence changed the irradiation effect on the surface from expansion to ablation (Fig. 1(b)). The etch depth also depended on the irradiation fluence and the dye concentration in the polymer. Figure 2 shows relations between etch depth and laser fluence on TPP/PMMA. The ablated surfaces were quite rough and the trace suggesting thermal melting was observed by SEM.

Assuming that these morphological changes take place at a certain temperature for any dye concentration in each polymer film, the surface temperature at which expansion and ablation are initiated is represented by the following equation:

$$I_{th} = \Delta T \rho C (1/\alpha) \quad (1)$$

where I_{th} is the threshold fluence, ΔT is the temperature change, ρ is the density of polymer, and C is the specific heat²⁾. The experimental data can be analyzed by equation (1) independently of the excitation wavelength and the values of ΔT are obtained from each slope of the plots (Fig. 3). The threshold temperature for ablation is estimated as follows: 750 K for TPP/PMMA ; 800 K for TPP/PVCz ; 1100 K for HP/GL. The threshold

temperature for expansion is, however, around 450 K for all the examined films and lower than those for melting.

Dopant-induced ablation of PMMA films by 308 nm laser pulses have been reported by using pyrene and benzophenone as dopants³⁾. The morphological changes by the laser irradiation strongly depended on the dopant concentration and therefore the switching between photothermal and photochemical mechanisms determined by effective absorption have been considered. Hiraoka et al. studied the expansion and ablation of polyimide films doped with Rhodamine 6G by SEM observation and concluded that the etching is clearly photothermal¹⁾. On the contrary, the etched depth of Tinuvin-doped PMMA by the wavelengths of 308 or 351 nm has been reported to depend on the irradiation wavelength and a photochemical process only was taken into consideration⁴⁾.

In our experiment, the photon energy is quite low (3.53 eV or 2.33 eV) and not sufficient to cause any bond scission by a single photon excitation. The threshold of expansion and ablation can be explained by a simple photothermal mechanism. Moreover, as far as the porphyrin concentration is low, only the dopant fluorescence was observed just upon the ablation and no other emissions of decomposition products such as C₂ or CN radicals were detected. This spectroscopic result consist with the above explanation.

ACKNOWLEDGMENT

The present work is supported by a Grant-in-aid from the Japanese Ministry of Education, Science and Culture (63430003, 63612510).

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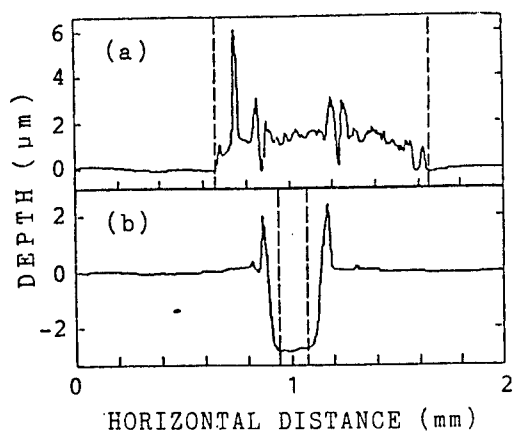


Fig. 1. Depth profiles of HP/GL after the 351 nm irradiation : 270mJ/cm² (a), 900mJ/cm² (b).

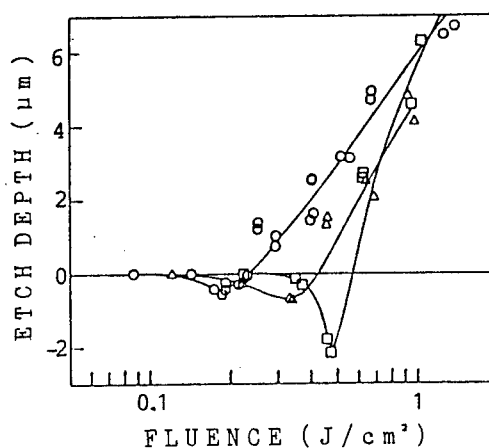


Fig. 2. Relation between etch depth and laser fluence of TPP/PMMA: $\alpha = 0.34 \mu\text{m}^{-1}$ ($\circ$) ; $\alpha = 0.26 \mu\text{m}^{-1}$ ($\triangle$) ; $\alpha = 0.10 \mu\text{m}^{-1}$ ($\square$).

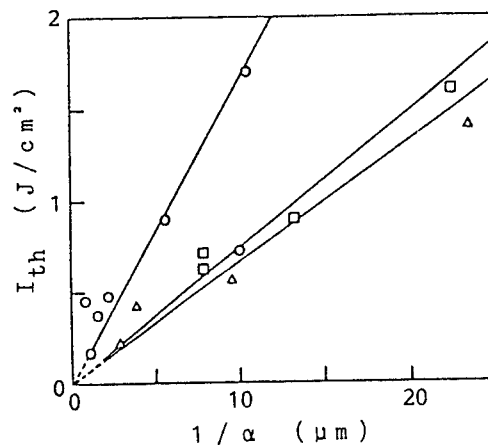


Fig. 3. Plots of threshold fluence (I_{th}) vs. $1/\alpha$: HP/GL ($\circ$) ; TPP/PVCz ($\square$) ; TPP/PMMA ($\triangle$).

LASER PHOTODECOMPOSITION OF POLYMER FILMS
CHANGES OF MOLECULAR WEIGHT OF PMMA
BY CO₂ LASER IRRADIATION

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1. The pulsed laser etching of polymer films is a very interesting and new area because it can be controlled by the laser power and duration. Especially, laser-initiated heterogeneous chemical reactions are viewed as a fundamental basis of microelectronics for the processing of semiconductor devices. The CO₂ laser irradiation on polymeric organic solids brings about the bond scission and the removal of the degraded fragments from the surface simultaneously. Especially, CO₂ laser is very interesting because we can excite vibrational band selectively. In order to clear out the mechanism of simultaneous energy injection of CO₂ to PMMA through non-stationary process, the temperature dependence of the degradation rate constant of PMMA was investigated. The comparison between the pulse irradiation and the isothermal heating was made(1).
2. PMMA samples of molecular weight of 4.7×10^4 , 2.2×10^5 and 1.0×10^6 were used. Films of 110-40 μ m thick was prepared from solvent cast. The light source of IR was CO₂ TEA laser (Lumonics, model 102-2). CO₂ laser irradiation was conducted at 985 cm⁻¹. The irradiation of a pulsed CO₂ laser was focused by KBr lens with a focal length f=40cm. The isothermal heating measurements were conducted at the temperature from 200°C to 350°C in electric furnace. The average molecular weight of the samples was measured by gel permeation chromatograph(GPC). TGA and DTA measurements were also conducted.
- 3.3-1. The Weight Loss by Laser Radiation; The weight loss per pulse measurements for various molecular weight PMMAs were pursued as a function of fluence as shown in Fig.1. When the fluence was low, the weight loss of the film did not show any changes. The weight loss started above fluence of about 1.2 J/cm², and increased linearly above 3 J/cm². The ejected gas from the material surface was produced simultaneously with the irradiation by CO₂ laser above 1.2 J/cm². When the fluence was further increased, there was observed a turbidity on the irradiated surface. This results indicate that melting of PMMA film is occurred by the rapid heating and cooling through energy transfer. The effect of molecular weight by CO₂ irradiation has been observed as shown in Fig.1. The weight loss for the high molecular weight PMMA was larger than that of low molecular weight in spite of the same fluence.
- 3-2. SEM Observation; Photographs of SEMs of the irradiated surfaces of PMMA have been taken. There was observed a number of craters and holes on the polymer surface as the fluences increased. The empty holes showed that the degraded molecules were carried away simultaneously by the excess energy of the photon pulse. The molten solid material was also recognized at the high fluence above 6 J/cm². It indicates that the CO₂ laser irradiation gives rise to the simultaneous temperature rise on polymer surface, which causes the degradation of PMMA.
- 3-3. Changes in Molecular Weight and Weight Loss; The change of the number average molecular weight per pulse has been conducted as a function of fluence, where M_{n0} and M_n are the initial number average molecular weight

of the unirradiated and irradiated sample, respectively. In order to reveal the differences in the thermal behavior of polymer between high and low molecular weight, isothermal heating measurements were made by changing isothermal temperature in an inert gas. The normalized residual weight of W/W_0 for PMMAs were obtained, where W_0 and W are the initial sample weight and the weight after heating time t . The normalized molecular weight vs the conversion ($=1-W/W_0$) of PMMAs was obtained for both systems of CO_2 irradiation and isothermal heating as shown in Fig.2. The normalized molecular weight (M_n/M_{n0}) for high molecular weight dropped rapidly as the conversion increased. These results suggest that the input energy on PMMA by CO_2 irradiation is high enough to occur bond scission and gives the weight loss. On the other hand, M_n/M_{n0} vs the conversion for low molecular weight PMMA in the case of isothermal heating lies on a 45° diagonal plot as the conversion increases. However, both of the change of M_n/M_{n0} and the conversion for low molecular weight by CO_2 irradiation are quite small in spite of the same irradiation condition as the case of high molecular weight PMMA. When molecules were depolymerized with random initiation by a constant zip length, it will give the steeper decrease of molecular weight fraction as the conversion fraction increases(2). However, if all molecules were unzipped completely once initiated, the decrease of M_n/M_{n0} is small. Then M_n/M_{n0} vs the conversion lies on the 45° diagonal line or the upside of the line. From the analysis of the rate constant of the decomposition by the isothermal heating, the activation energies of bond scission have been obtained as 48kJ/mol and 140kJ/mol for high molecular and low molecular weight PMMA, respectively. The presence of weak linkages is also recognized for high molecular weight PMMA from the measurements of DTA and TGA. The high molecular weight PMMA has the weak bond which was produced in the polymerization processes. The steeper decrease in the degradation for high molecular weight is reduced to the presence of this weak bond.

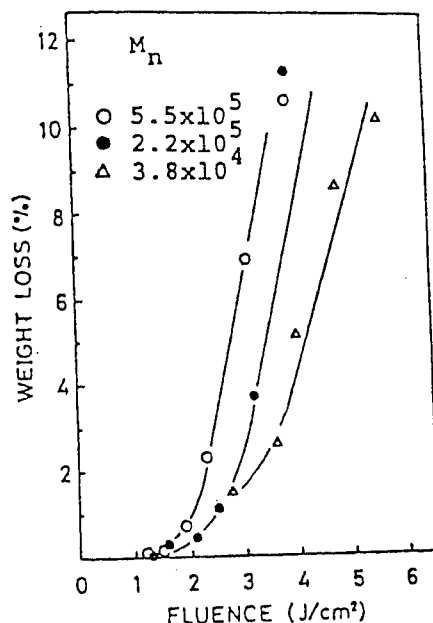


Fig. 1. Weight Loss vs Fluence for various molecular weight

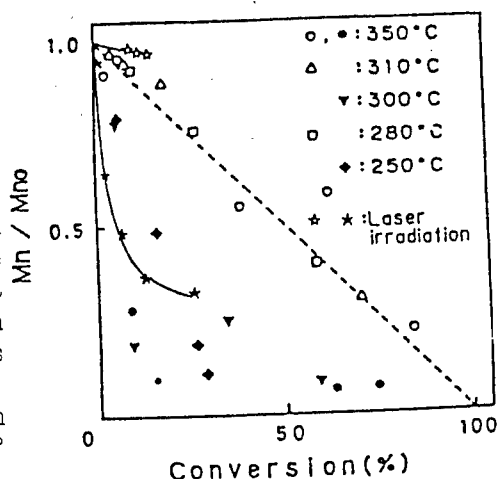


Fig. 2 M_n/M_{n0} vs. conversion with heating at different temperature in nitrogen, open symbol; $M_n=4.7 \times 10^4$ closed symbol; $M_n=1.0 \times 10^6$

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FLUORESCENCE CHARACTERIZATION OF CAST AND SPIN-COATED
FILMS OF DOPED POLY(METHYL METHACRYLATE) BY TOTAL
INTERNAL REFLECTION SPECTROSCOPY

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Structures and properties of film surfaces are generally considered to be different from those of bulk. However, photophysical, photochemical, and photoconductive studies on polymer films have carried out without this viewpoint.

When light traveling in a material with higher refractive index is incident upon an interface at an angle greater than the critical angle, although the light undergoes into total reflection, the excitation light penetrates into the material with the lower refractive index as an evanescent wave. This can be used to excite fluorescent molecules which are located in the vicinity of the interface. The fluorescence spectra and their rise as well as decay curves from these molecules were detected and compared with those from the bulk (Fig. 1). This total internal reflection (TIR) fluorescence spectroscopy has been applied here to poly(methyl methacrylate) (PMMA) films doped with pyrene. The change of micropolarity around pyrene molecule and the difference in the aggregate state of pyrene between the interface and the bulk have been investigated.

Sapphire was used as an internal reflection element ($n_1=1.81$ at 310 nm) and the same as before.¹ Polymer films were cast on sapphire plates from chlorobenzene solution containing PMMA and a known amount of pyrene at room temperature. The refractive index of PMMA (n_2) is 1.53 at 310 nm, so the critical angle (θ_c) given by $\sin\theta_c = n_2/n_1$ was calculated to be 57.7° .

Fluorescence spectra of PMMA films doped with pyrene are shown in Fig. 2. These spectra are normalized at the third vibronic band (0-2) of the monomer fluorescence. The fluorescence intensity ratio of the first to the third vibronic bands of pyrene monomer (I_1/I_3), which is known to be a probe of micropolarity of the surrounding environments,² was larger under the TIR condition than under the normal one for both samples. The difference in I_1/I_3 is not attributed to the reabsorption and the overlap of the excimer fluorescence. For polystyrene film doped with pyrene, no such difference was observed between both optical conditions.

Figure 2 shows also that the intensity ratio of the monomer to the excimer fluorescence under the TIR condition is larger than that under the normal one. For the wide concentration range where the excimer fluorescence is observed, the same phenomenon was observed. Avis and Porter reported that an increase in the pyrene concentration leads to both an increase in the excimer fluorescence intensity and a decrease in a $1/e$ lifetime of both the monomer and excimer nonexponential fluorescence decays.³ The decrease in the $1/e$ lifetime of both fluorescence was attributed to a formation of dimer which is responsible for quenching of the fluorescence. The monomer fluorescence decay curves were measured by monitoring at 374 nm under the both optical conditions. The $1/e$ lifetime of the monomer fluorescence decay was shorter under the TIR condition than

under the normal one for all samples with different concentrations (Fig. 3). Similar experiments were performed for the air/polymer interface of these films, and also we have investigated the fluorescence behavior of spin-coated films.

Conclusions are summarized in the followings.

- 1) The micropolarity around pyrene molecules in the vicinity of the sapphire/polymer interface is higher than that of the bulk.
- 2) Near the sapphire/polymer interface, the concentration of excimer forming pair is low and the concentration of the non-fluorescent pair is responsible for the quenching is high as compared with the bulk. This means that an aggregate state of pyrene is different between the interface and the bulk.
- 3) The aggregate state of pyrene near the air/polymer interface is similar to that for the sapphire/polymer one.
- 4) The similar results were obtained for spin-coated films.

These results are considered to be important and basic information for the field of microlithography.

Acknowledgment

The present work was partly supported by the Grant-in-Aid from the Japanese Ministry of Education, Science, and Culture (63612510).

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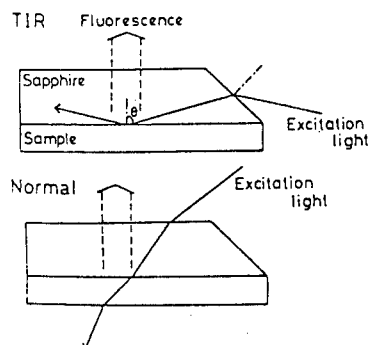


Fig. 1 Optical sets.

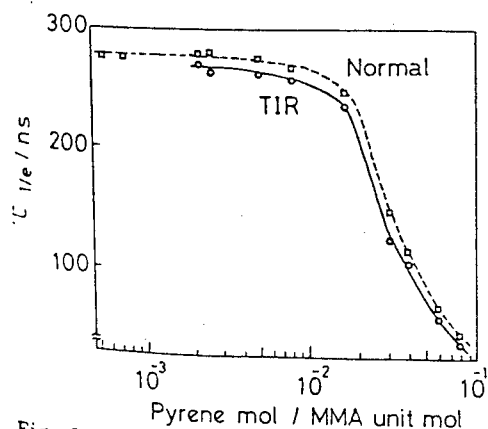


Fig. 3 Dependence of the $1/e$ lifetime of the monomer fluorescence on the concentration of doped pyrene.

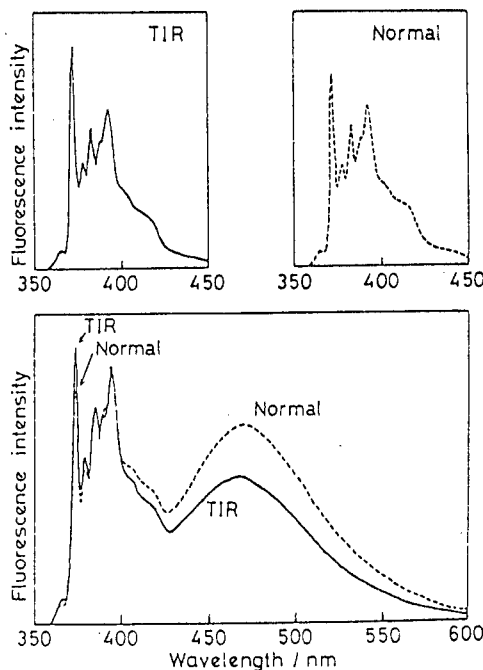


Fig. 2 Fluorescence spectra of pyrene in PMMA films. (1) 7.29×10^{-4} and (2) 5.55×10^{-2} mol/MMA basic unit mol.

RECENT PROGRESS IN EXCIMER LASER LITHOGRAPHY

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Excimer laser exposure has been first tried in 1980 using PMMA and a KrF excimer laser. Since then, excimer laser lithography has been situated as the next generation lithography tool behind g/i-line optical lithography, and many studies have been made. At present, both excimer laser steppers and resist materials are commercially available, and have reached the level of trial manufacturing of lower submicron VLSI devices beyond 16 Mbit DRAMs. Furthermore, experiments on ArF excimer laser lithography are being tried. This paper reviews the recent progress in excimer laser lithography, based on previous papers and experimental results obtained in our laboratory.

Today's commercially available excimer laser steppers are equipped with a chromatic quartz lens of more than 0.35 NA and with a spectral narrowing KrF excimer laser, because of the difficulty in manufacturing an achromatic lens system. In this case, the elimination of speckle noise, realization of TTL alignment and stabilization of the spectral bandwidth of the excimer laser are major issues to be solved. The speckle noise is due to an increase in coherence of the light beam, and is successfully solved by changing the optical path length during exposure, which can be performed by the swing of a mirror or a phase plate. The realization of TTL alignment is very difficult, due to the large difference in the focal length between the exposure and alignment wavelengths. Several means for solving have already been proposed in previous papers, but the off-axis alignment scheme is still currently adopted.

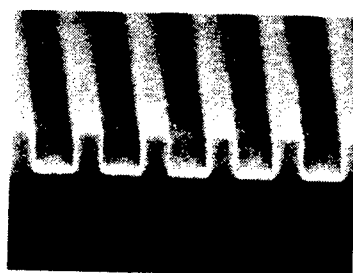
An excimer laser system has many inherent problems, such as reliability, maintainability, operation cost and dimensions of the system, which mainly originate from the difficulty of spectral narrowing. A spectral bandwidth of less than 5 pm and a wavelength drift of less than 1 pm can be achieved by using an etalon or grating. It can be generally said that the grating method has more excellent performance and durability than the etalon method. Thus, reliability and maintainability are now being improved.

By using an excimer laser stepper and a 0.5 μm thick novolac type positive photoresist, a 0.4 μm lines and spaces pattern can be obtained with about 1 μm focus latitude. An actual device pattern of the 64 Mbit DRAM level can also somehow be fabricated. However, development of the resist material is another issue, where much effort should be concentrated. That is, a resist material, which simultaneously satisfies resolution, sensitivity and dry etching resistance, has not yet been completed. To obtain a higher resolution with a steep resist profile, the resist material must have a suitable

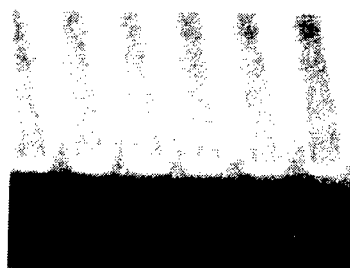
bleaching effect and an enhancing effect between the exposed and unexposed areas as well as high optical transmittance, as observed in novolac type positive g-line resists. In these situations, a chemical amplification resist is expected. Figure 1 shows an example of a resist pattern. A $0.35\text{ }\mu\text{m}$ lines and spaces pattern with a steep profile can be obtained, where the exposure dose is 54 mJ/cm^2 , and the resist thickness is $0.5\text{ }\mu\text{m}$.

Since it is impossible to use a resist of more than $1\text{ }\mu\text{m}$ in thickness, multi-layer resist systems, such as a tri-level resist system, must be used to fabricate the present actual devices, when considering device topography. However, the process sequence of the tri-level resist system is very complicated, and its cost performance is not so good. Thus, the development of the resist process technology is also important. Various single layer resist process techniques, which combined alkali treatment, post exposure bake and ammonia gas treatment, are being studied in our laboratory to improve the resist profile of the novolac type positive photoresist.

The present status and recent progress in excimer laser lithography, placing emphasis on the exposure system, excimer laser source, resist material and resist process, have been described. There are still many technical subjects should be solved in excimer laser lithography to be applicable to a volume production line. However, excimer laser lithography will no doubt remain the dominant technology for future lower submicron VLSI devices.



$0.4\text{ }\mu\text{m}$ lines and spaces



$0.35\text{ }\mu\text{m}$ lines and spaces

Figure 1 Resist pattern obtained by a chemical amplification resist.

NOVEL KrF EXCIMER LASER RESIST, SLEX

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KrF excimer laser lithography is the most promising technique for microfabrication in a sub-half micron region. This technology demands new resist systems which are based on design different from diazonaphthoquinone photoresists. Our approach is that the photoactive organic polyhalides are used as the pendant groups of phenolic resin (single component system, SLEX-1) or photoactive compounds (two component system, SLEX-2).

In the initial study SLEX-1 was synthesized and was lithographically evaluated. SLEX-1 is a trichloroacetate of hydroxystyrene/methyl methacrylate copolymer (copolymerization ratio; 1:1) as depicted in Fig.1. It has an absorption coefficient of $1.2 \mu\text{m}^{-1}$ at 248.5 nm, and gives negative tone images upon deep UV irradiation followed by development in an organic solvent mixture. The sensitivity to KrF excimer laser is 150 mJ/cm^2 . SLEX-1 has a resolution of sub-half micron as shown in Fig.2. In this single component system the increase of the content of hydroxystyrene is not preferable because the absorption at 248.5 nm of the resist significantly increases, which results in large undercutting resist profile and lowering the resolution.

Next approach was separation of the photoactive group from the base polymer in SLEX-1 for the purpose of modifying it to an alkaline developable resist. Various organic polyhalides such as chloroacetamides and poly(chloromethyl) aromatics were examined, and it was found that a mixture of highly transparent PHS and tris(trichloromethyl)-s-triazine shown in Fig.3 gave a high sensitivity and a desired resist pattern profile. This two component resist, SLEX-2, has an absorption coefficient of $0.87 \mu\text{m}^{-1}$ at 248.5 nm and a sensitivity of 60 mJ/cm^2 . SLEX-2 was exposed on a KrF excimer laser stepper to result in $0.5 \mu\text{m}$ line/space patterns in a $0.9 \mu\text{m}$ thick-film as shown in Fig.4.

In this resist system, post exposure baking (PEB) is necessary to insolubilize the exposed area in TMAH solution. The molecular weight of SLEX-2 increases with an increase in the exposure dose to set to gel. In contrast, when the monofunctional photoactive compound, 2,4-dichlorobenzotrichloride is used instead of trifunctional one, tris(trichloromethyl)-s-triazine, the molecular weight of the resist does not increase. A radical trapping experiment shows that the concentration of the radical species in the resist film rapidly increases at the early stage of exposure and then gradually decreases at the latter stage (dose is over 400 mJ/cm^2 , Xe-Hg lamp was used), which suggests that the insolubilization in TMAH solution is based on not a radical polymerization but also an ionic condensation reaction, and that the latter reaction consumes the radical generator, polyhalide. From IR spectral analysis it is confirmed that a phenyl ester of an aromatic carboxylic acid is produced upon deep UV exposure. Accordingly, it is considered that insolubilization of SLEX-2 is caused by the formation of

s-triazinecarboxylate of PHS as shown in Fig.5. This ester crosslinkage results from coupling of the dichloromethyl radical on the triazine skeleton and the phenoxyl radical followed by hydrolysis of the resulting moisture sensitive α,α -dichloro ether intermediate.

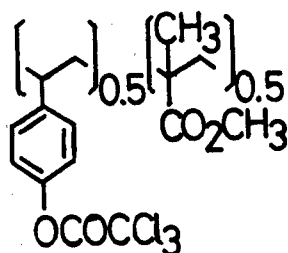


Fig.1 Structure of SLEX-1

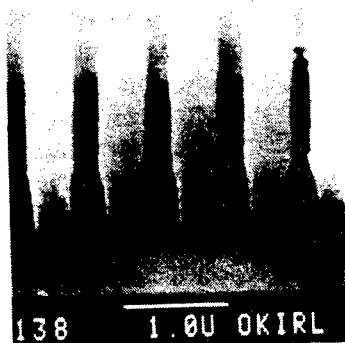


Fig.2 SEM photograph of 0.38 μm line and space patterns delineated in 1.0 μm -thick SLEX-1

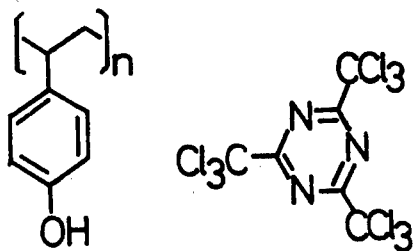


Fig.3 Composition of SLEX-2

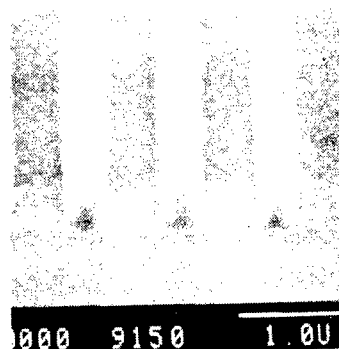


Fig.4 SEM photograph of 0.5 μm line and space patterns delineated in 0.9 μm -thick SLEX-2

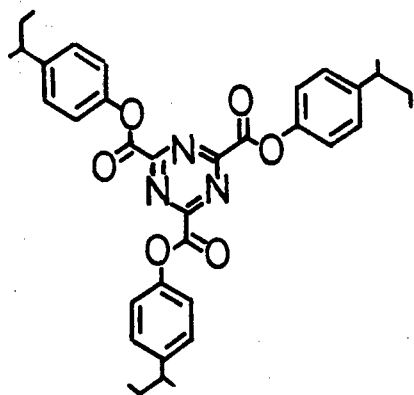


Fig.5 Photoreaction product of SLEX-2

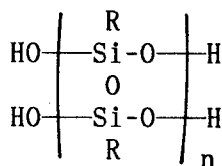
NEW TWO-COMPONENT-TYPE SILICONE RESISTS BASED ON ALKALI-SOLUBLE SILSESQUIOXANE OLIGOMER

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The continuing drive toward pattern size minimization in LSI has created a strong demand for high lithographic resolution. A two-layer resist system using silicone resists is a promising solution to obtain a higher resolution than is possible with a single layer system. Recently, we have synthesized a new alkali-soluble silicone resin, acetylated phenylsilsesquioxane oligomer (APSQ) [1,2], and prepared various kinds of alkali-developable silicone resists using APSQ as a matrix resin.

APSQ was synthesized along with Friedel Crafts acetylation. A solution of phenylsilsesquioxane oligomer in acetylchloride (AcCl) was reacted with a solution of anhydrous AlCl_3 in AcCl below 20 °C. After stirring for 90 min, the solution was poured into ice water to obtain APSQ.

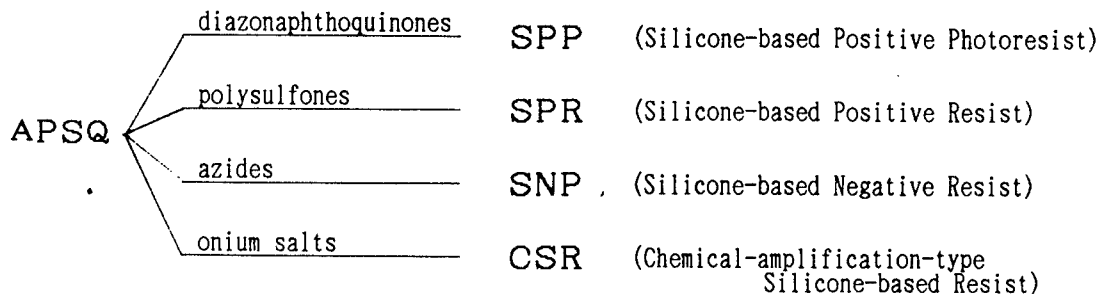
IR and NMR studies indicated the molecular structure of APSQ is as follows:



$\text{R} = \text{C}_6\text{H}_5, \text{C}_6\text{H}_4\text{COCH}_3, \text{OH}$
 $\text{Mw} = \text{ca } 1300$

A typical molar ratio of C_6H_5 , $\text{C}_6\text{H}_4\text{COCH}_3$, and OH groups was 0.55 : 0.07 : 0.38. An important issue is the simultaneous formation of silanol groups during the acetylation, because the solubility of APSQ in alkaline aqueous solutions directly relates to the presense of silanol groups. ^{29}Si NMR indicated that Si-phenyl and Si-O bonds were partly scissored during the acetlation. We think that silanol groups are produced through the chlorination of Si-Phenyl and Si-O bonds under AcCl/ AlCl_3 and following hydroxylation in water.

APSQ was used for various two-component-type resists as a matrix resin like novolac.



An APSQ-diazonaphtoquinone resist named SPP [1,3] can be described as a quasi-AZ-type resist. SPP resolved $0.4\ \mu\text{m}$ for UV lithography (g-line stepper, NA=0.6). Besides, SPP was useful for negative tone imaging using high energy sources. Resist sensitivities of SPP to EB, X-ray and deep UV were, $5\ \mu\text{C}/\text{cm}^2$, ca $160\ \text{mJ}/\text{cm}^2$ and $10\ \text{mJ}/\text{cm}^2$, respectively. [4]

An APSQ-polysulfone resist named SPR is sensitive to electron beams (EB) [5] and X-rays. Polymethylpentene sulfone was used as a dissolution inhibitor in SPR. Resist sensitivity of SPR to EB (20kV) was $5\ \mu\text{C}/\text{cm}^2$.

An APSQ-azide resist named SNP is sensitive to deep UV, EB, and X-ray. $0.36\text{-}\mu\text{m}$ line-and-space pattern was successfully fabricated by excimer laser lithography. [6] EB lithography also presented the high-resolutional pattern for a negative resist due to a little swelling.

An APSQ-(onium salt) resist named CSR is classified as a chemical-amplification-type resist. Strong acids produced from onium salts by exposures catalyze the condensation of silanol groups in APSQ. Post exposure baking (PEB) at $100 - 120\ ^\circ\text{C}$ accelerates this condensation and enables negative tone imaging. Fig. 1 shows $0.3\ \mu\text{m}$ line-and-space pattern of the CSR/MP2400 two-layer resist delineated by EB lithography.

We confirmed the wide availability of APSQ as a matrix resin for alkali-developable silicone-based resists, which had a high potential for sub-halfmicron lithography.

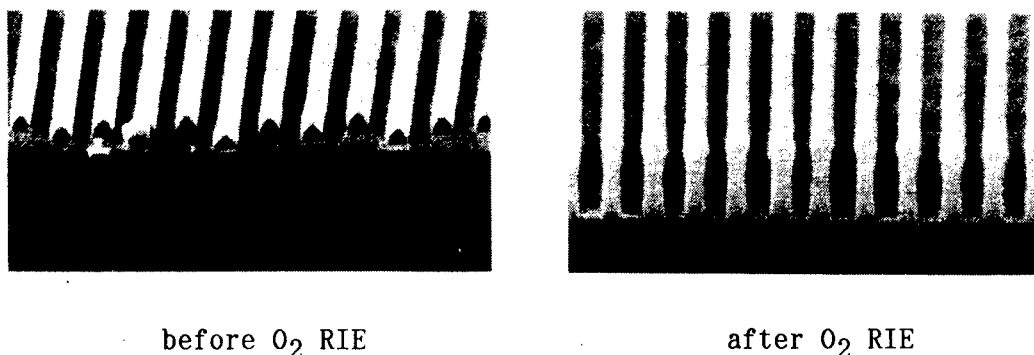


Fig. 1 SEM micrographs of CSR/MP2400 two-layer resist pattern fabricated by electron beam lithography. Keys: CSR; $0.47\ \mu\text{m}$, hard-baked MP2400; $1.0\ \mu\text{m}$, onium salt; diphenyliodonium trifluoromethyl sulfonate, EB acceleration voltage; 20kV, dose; $5.6\ \mu\text{C}/\text{cm}^2$. PEB; $120\ ^\circ\text{C}$, 5 min.

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A NOVEL SILICON-CONTAINING RESIST FOR HALF-MICRON PHOTOLITHOGRAPHY

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With the increasing density of VLSI circuits, resist materials are required to have half-micron resolution capability and higher resistance to dry etching. A conventional one-layer resist system cannot satisfy all VLSI fabrication requirements.¹⁾ Bi-layer resist systems have various advantages over the one-layer resist system such as better resolution and minimization of optical interference effects caused by reflection from topographic features. Si-containing resists are promising candidates for top imaging layers in bi-layer resist systems.²⁻⁵⁾ However, no photoresist is available commercially for the UV region with high resolution and silicon content over 10wt%.

We report here on the properties of a newly developed Si resist and its application to a bi-layer resist system.⁶⁻⁸⁾

1) Design and synthesis

To obtain high resistance to oxygen plasma and solubility in alkaline solution, we synthesised a novel Si-containing novolak resin which was derived from phenol with a siloxane group(-Si-O-) and formaldehyde by condensation reaction. The molecular structure of the polymer is shown in Fig.1.

2) Resolution

A positive working resist was developed using the Si-containing resin and a naphthoquinone diazide compound, which has sensitivity to near-UV and KrF excimer laser.

0.5 μ m L/S patterns were fabricated with good rectangular profile using a g-line stepper (NA=0.45). The exposure energy was 250mJ/cm². 0.3 μ m L/S patterns were fabricated using an excimer laser stepper (NA=0.42) with a sensitivity of about 140mJ/cm². However, the resist pattern profile was tapered because of the strong absorption of KrF excimer light by the Si-containing resist as shown in Fig.2.

3) Resistance to oxygen plasma

This resist has a high resistance to oxygen plasma, with an etching rate ratio of 61:1 (photoresist/Si resist). 0.5 μ m L/S patterns were precisely transferred to the bottom layer by O₂ RIE with vertical side walls.

4) Resist profile simulation

The two-dimensional development process simulation program "SAMPLE" was improved to carry out more precise profile simulation. We propose a modified "string model" which takes into account the shape of the resist profile during development. 0.5 μ m L/S pattern profiles were simulated well with our modified model.⁹⁾

The newly developed Si-containing resist can be used to fabricate 0.5 μ m L/S patterns precisely with conventional optical lithography. It is promising for the fabrication of submicron patterns on substrates with topographic features in the generation following the 16MDRAM chip.

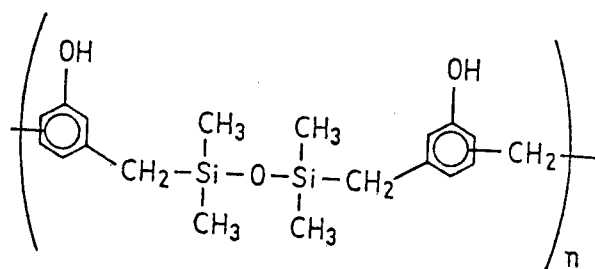


Figure 1. Molecular structure of the polymer.

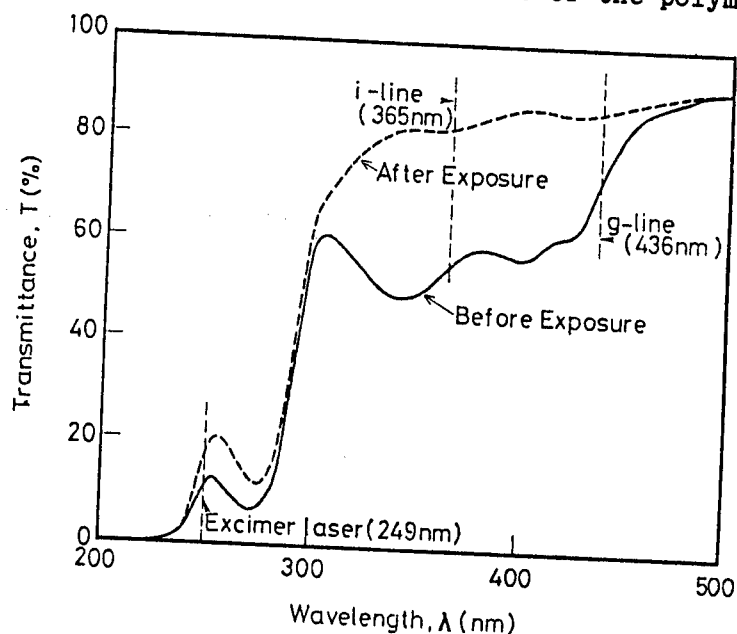


Figure 2. UV spectra of 0.5 μ m thick Si-resist.

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RESIST PROCESSES APPLIED TO DEVICE FABRICATION USING X-RAY AND E-BEAM LITHOGRAPHY

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X-ray and e-beam lithography is expected to play a major role in the production of future LSI's having a minimum dimension below the resolution limit of optical lithography. Through great technological improvements in exposure systems, mask fabrication, pattern data preparation, resist materials and their processing, e-beam and X-ray lithography has been applied to the device fabrication process.

In our laboratories, direct write e-beam technology has been successfully applied to the test fabrication of DRAMs[1] and several advanced MOS devices[2]. The feasibility of X-ray lithography has been confirmed through the fabrication of small geometry NMOS devices using a conventional X-ray source[3,4]. Recently, we succeeded in fabricating deep-submicrometer NMOS devices using a synchrotron radiation (SR) source[5]. This paper introduces the lithography process in fabricating these devices and discusses the performance, emphasizing resist processes and their characteristics.

NTT has developed a variety of e-beam resists. Negative CMS[6] and positive ϕ -MAC[7] are typical examples, having good dry etch durability like AZ-type photoresists. These were successfully applied to the megabit level DRAM process with a 0.5 μm minimum width[1]. Linewidth control was fairly good. Deviations were as small as 0.06 μm in 3σ .

The major requirements for resists are high resolution, high sensitivity and good dry etch durability. In general, tradeoffs arise between these requirements with any resists. CMS has high sensitivity but is inadequate for future deep-submicrometer technologies because of its resolution capability. ϕ -MAC exhibits high resolution but is relatively low in sensitivity. To overcome these dilemmas, multilayer resist systems have been proposed where each requirement is met in each layer.

Considerable efforts have been concentrated to develop practical multilayer resist technology. A low temperature O_2RIE method was devised to achieve highly accurate pattern transfer into the bottom layer without undercutting[8]. A new silicone resin, SIR, was developed as a spin-on intermediate layer for process simplification[9]. FBM-G, positive e-beam resist, has high sensitivity at the expense of poor dry etch durability. By combining FBM-G with the above multilayer resist technologies[10], a high-sensitive trilayer resist technology was developed. This technology was satisfactorily applied not only to the e-beam direct write process but also to X-ray and SR pattern replication processes.

A silicone-based resist enables a relatively simple bilayer system. Our efforts have been focusing on the development of silicone-based resists with higher performance. SNR[11] is an example of this research. Recently, we have developed a Silicone-based Positive Photoresist, SPP[12]. The characteristic features of SPP are: 1) alkali-developable nature, which ensures high compatibility with currently used LSI processes, and 2) high resistance to O_2RIE , which is suitable for bilayer applications. At first, SPP was developed as a positive UV resist, as the name implies. Later, an

image reversal process was found in SPP, which performs high resolution and high sensitivity to e-beam and X-ray lithography.

The SPP image reversal process has been applied to the fabrication of NMOS devices using SR lithography at all exposure levels involving isolation, poly-Si gate and Al metallization levels[5], except contact hole levels by the FBM-G trilayer resist system. Patterning was quite satisfactory. Figure 1 shows the exposure latitude for linewidth control of the SPP bilayer system as a function of nominal width of the isolated line, together with a typical curve for i-line stepper (NA=0.42) for comparison. Here the exposure latitude is defined as the dose variation range generating a $\pm 10\%$ linewidth variation from the nominal width. This shows that the exposure latitude of SR lithography using SPP is very large enabling highly accurate patterning. Figure 2 shows an SEM micrograph of a finished 51 stage ring oscillator. A delay time of 22.5 ps/gate was obtained.

One of the advantages of SR lithography is in the possible use of simple single layer resists. However, higher performance resists with little tradeoff as mentioned above are necessary. A chemical amplification resist seems to be a promising candidate. But it should be noted that the wide process latitude is important for a single layer resist system in practical SR lithography.

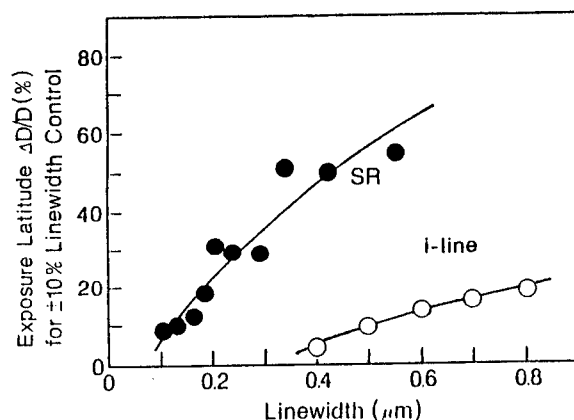


Fig.1 Exposure latitude for line width controll

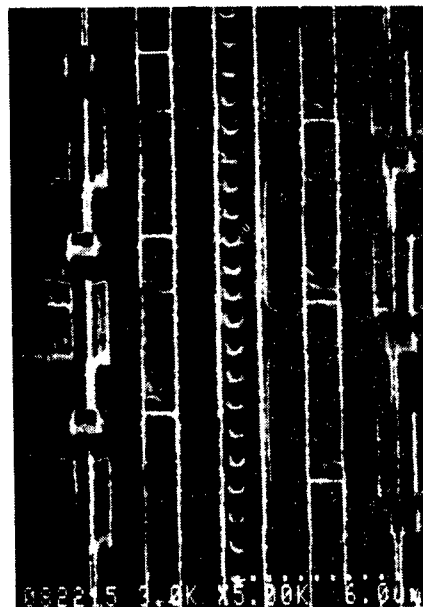


Fig.2 SEM micrograph of 0.2 μm gate-length ring oscillator. Minimum dimensions of Al line and contact hole are 0.3 μm .

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A HIGH SENSITIVITY POSITIVE ELECTRON BEAM
RESIST EBR-9 HS31

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Although EBR-9^{1,2,3)} is the primary positive EB resist of choice in Japan, its usage in the United States is rather limited. Conventional EBR-9 has two shortcomings. The first is its lower sensitivity compared to PBS. The second is its limited plasma etch resistance. We attempted to overcome these shortcomings, with the development of two new polymers. The first, named EBR-9 DR60⁴⁾, shows good dry etch resistance, but the sensitivity is lower than that of the original EBR-9. The second, named EBR-9 HS30⁵⁾, shows higher sensitivity, with the same dry etch resistance as EBR-9.

EBR-9 HS30 has been used for maskmaking in several Japanese electronic companies. It was found that this resist gave its best resolution performance when developed in straight MIBK⁶⁾. However, the unexposed thickness loss is excessive and the contrast is lower than desired.

We have now further improved the performance of HS30. The basic goals for the new resist were as follows: (1) better contrast, (2) lower unexposed film thickness loss, and (3) the ability to use straight MIBK as the developer. The first point is required for higher resolution, the second point for better etch resistance, and the third for the following reasons. (1) We evaluated hundreds of solvent systems for the development of EBR-9 and HS30, and found that single solvent systems gave better resist performance than mixture systems. (2) Immersion development is still widely used in Japan, and single solvent systems are preferred because there will be no compositional change after repeated use. (3) MIBK is readily available and much less expensive than MIAK, which is the main component of PBS developer.

The molecular structure of the base polymer has been optimized to obtain improved resolution and also for the usage of straight MIBK as the developer. These two requirements were achieved in the development of EBR-9 HS31.

The basic performances of HS31 were obtained by experimental EB exposure system (Elionix ERE-301). Sensitivity and film thickness loss vs prebake time, sensitivity curves at various development temperatures and time, and sensitivity vs film thickness were measured.

To demonstrate the ultimate resolution of this resist, 0.1 μm l/s of chrome were fabricated by wet etching, using 0.4 μm of HS31 resist, 600A pure chrome layer and a 0.08nA (0.07 μm diameter) electron beam.

It is well known that the sensitivity of positive⁶⁾ EB resists are greatly affected by the cooling process after prebake⁶⁾. The coated blanks of HS31 were prebaked at 190°C on a hot plate and cooled on cooling plates which have temperatures 30-120°C. It was found that the development time is decreased to one half when 30°C cooling plate was used

compared with 130°C cooling plate.

EBR-9 HS31 was evaluated on a MEBES III and the results were compared to PBS. At a $1.0 \mu\text{C}/\text{cm}^2$ dose, EBR-9 HS31 is less affected by the humidity in the development chamber. Practically no change in sensitivity was observed after prebake and exposure. Other performance characteristics are equivalent to these of PBS. At $1.5 \mu\text{C}/\text{cm}^2$ dosage (0.1 μm address), we have found excellent resolution down to 0.3 μm .

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THE MECHANISM OF REACTION IN DEVELOPMENT-FREE VAPOR PHOTOLITHOGRAPHY

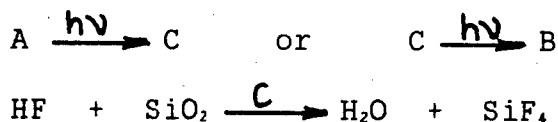
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An unusual phenomenon of etching under exposed but not developed photoresist was disclosed decade ago. A silicon wafer with SiO_2 surface is coated with cinnamate type photoresist, then masked and exposed to UV light. An etching gas (hydrofluoric acid vapor) is passed over the wafer in a chamber at above 100°C for a definite time. The SiO_2 under the photoresist film in the exposed area is etched and removed completely while the SiO_2 in the unexposed area remains. Thus a clear positive pattern is formed. Based on this phenomenon a dry photoetching process (Fig.1), which we called development-free vapor photolithography, was developed and successfully used in manufacturing microelectronic devices^[1-2]. The advantages of this technique over the conventional wet process include higher resolution (0.7μ), omitting three steps, overcoming problems induced in the development step, etc.. The subsequent research conducted by us and other people broadened the scope of this technique^[2-5]. However, the understanding of the mechanism of the etching reaction is still fragmentary. In this paper we propose a new mechanism to explain this phenomenon. The main points are following:

- (1) In this reaction the etching gas first diffuses to the interface between SiO_2 and photoresist film where etching reaction occurs, and then the products of reaction diffuse out through the film;
- (2) The reaction of hydrofluoric acid vapor with SiO_2 at above 100°C differs from the reaction of aqueous hydrofluoric acid with SiO_2 . The former reaction is accelerated by some compounds, which can be regarded as catalyst;
- (3) The rate of etching reaction is a function of catalyst concentration, therefore, the differential catalyst concentration may cause the differential etching rate;
- (4) Since light (or other radiation) can irradiate a surface selectively, the photochemical reaction is the best way to create a great differential concentration.

Summarizing the research results, two major approaches were given for creating differential rate between exposed and unexposed areas. (1) Photoinduced differential Tg of polymer film approach: When catalyst is evaporable, a higher

T_g area of film will contain more catalyst than that in the lower T_g area after heating. Photocrosslinking at low temperature can greatly raise the T_g of film in the exposed area. Photodecomposition is the reversal. (2) Photo-latent catalyst approach: If a film contains a latent catalyst which can turn into catalyst on irradiation, or the reverse case, the irradiation may create high differential catalyst concentration between the exposed and unexposed areas (Scheme 1) .



Scheme 1

Though this mechanism stated above is still an assumption, it can explain the known facts and provides leads for further research.

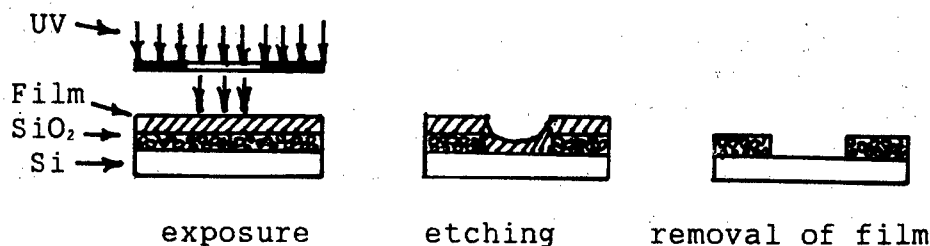


Fig.1. Development-free vapor photolithography process

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DESIGN CONCEPT FOR THERMALLY RESISTANT POSITIVE PHOTORESIST

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As the density of VLSI circuits increases, higher heat resistance as well as higher resolution capability is required for positive photoresist. We have been trying to improve positive photoresist performance through modifications of novolak resins[1-3]. In this paper, we investigate the influence of various factors of novolak resins such as molecular weight, isomeric structure of cresol, methylene bond position and molecular weight distribution on the heat resistance of positive photoresist. We also study the effect of the content of quinonediazide compounds in photoresist compositions.

There were four methods to improve heat resistance; (1) to raise molecular weight (2)to increase the ratio of paracresol to metacresol (3)to increase the content of quinonediazide compounds in photoresist (4)to optimize molecular weight distribution of novolak resins. On the other hand, it was not preferable to use high-ortho novolak resins that have high contents of ortho-ortho bonding. These results are explained in terms of the polymer structure and the image formation process. On the basis of the experimental results, we propose a design concept for thermally resistant positive photoresist.

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1,3-DIOXIN-4-ONES AS NEW SENSITIZERS FOR EXCIMER LASER LITHOGRAPHY

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KrF excimer laser (248 nm) lithography is a hopeful method for fabricating 64 Mbit DRAMs.¹⁾ Few photoresists are effective for use with a KrF excimer laser, because of their usual high absorption at 248 nm. The authors researched the photoreaction of 1,3-dioxin-4-ones and applied these compounds to photoresists for KrF excimer laser lithography. 1,3-dioxin-4-ones are known to undergo a cyclo-reversion to acylketenes, which react with dipolar dienophiles to produce heterocyclic compounds, under irradiation at 254 nm.²⁾

1,3-dioxin-4-ones were synthesized according to pertinent literature.³⁾⁴⁾⁵⁾ The photoreaction was carried out using a low pressure mercury lamp. The photoreaction products of 1,3-dioxin-4-ones and m-cresol monomer were determined by ¹³C-NMR and the mass spectrum. Photoresist solutions were prepared from 1,3-dioxin-4-ones, p-vinylphenol polymer and 1-acetoxy-2-ethoxyethane, and coated on silicon wafers and quartz wafers. The UV spectrum and IR spectrum were measured before and after UV irradiation (254 nm). The resist film was exposed using a KrF excimer laser stepper (NA=0.37), baked at 120 °C, and developed using a tetramethylammonium hydroxide solution (1.19 %).

Ketoacid ester and a carbonyl compound were found after UV irradiation of 1,3-dioxin-4-ones and m-cresol. (Fig. 1) The UV transmittance value at 248 nm for a 1.0 micron thick resist film was changed from 11 % to 32 % by UV irradiation. (Fig. 2) The IR spectrum change before and after UV irradiation are shown in Fig. 3. The 1738 cm⁻¹ peak, which was assigned to the conjugated ketone of 1,3-dioxin-4-one, disappeared and a 1720 cm⁻¹ peak appeared. These results suggest that the same reaction occurred in the solution and in the resist film. The SEM photograph of the resist pattern is shown in Fig. 4. 0.35 micron line and space resist patterns were resolved.

1,3-dioxin-4-ones decomposed and reacted with phenol to form phenol ester under irradiation at 254 nm. The resist, which was prepared from a 1,3-dioxin-4-one derivative and polyvinylphenol, had good resolution for KrF excimer laser exposure.

ACKNOWLEDGMENTS

The authors would like to thank T. Sato for accomplishing the exposures with the KrF excimer laser reduction step and repeat system. The authors express their appreciation to Dr. M. Nakase for his many helpful suggestions. They are also indebted to F. Umibe for proofreading and correcting the original English manuscript.

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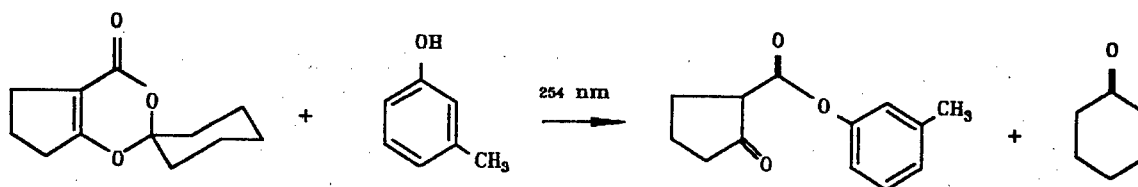


Fig. 1 Photoreaction for 1,3-dioxin-4-one derivative and m-cresol

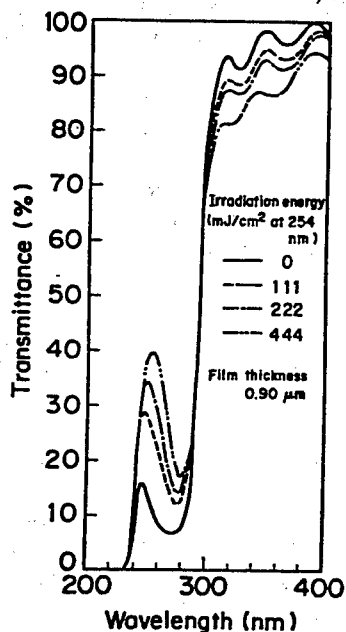


Fig. 2 UV spectrum change in resist, before and after UV irradiation

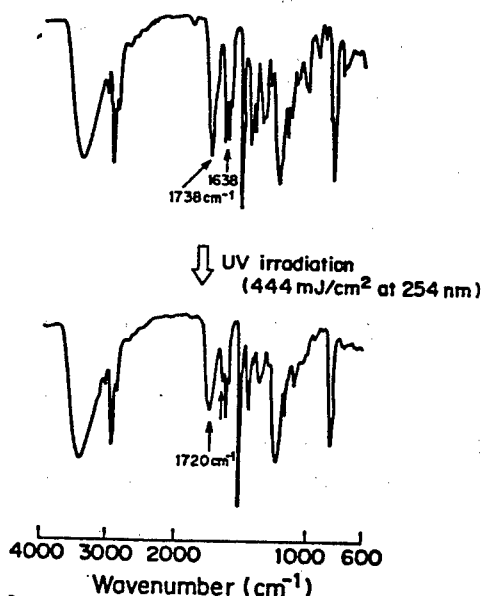


Fig. 3 IR spectrum change in resist, before and after UV irradiation

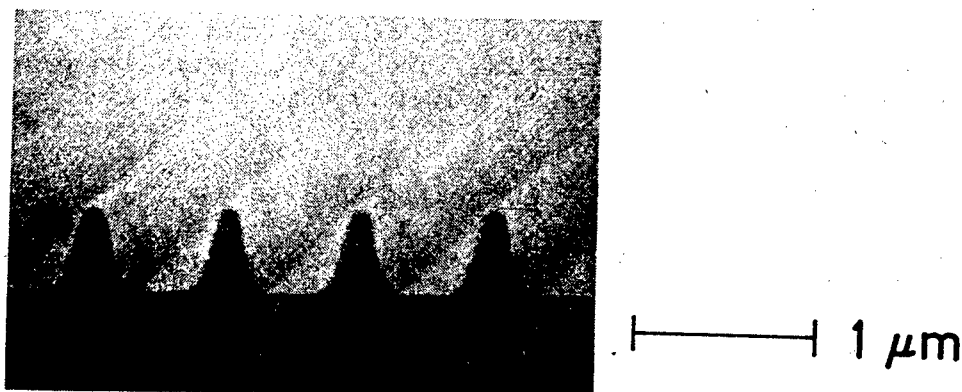


Fig. 4 SEM photograph of 0.35 micron line and space resist patterns

CHEMICAL AMPLIFICATION POSITIVE RESIST SYSTEMS USING NOVEL SULFONATES AS ACID GENERATORS

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Positive resist systems composed of Novolak resin and an appropriate diazonaphthoquinone are widely used in the integrated circuit industry today. In these systems the sensitizer molecule acts as a dissolution inhibitor for aqueous base development of the Novolak resin. An electron beam resist NPR[1] has been introduced utilizing a polymeric dissolution inhibitor. Recently 3-component systems composed of Novolak resin, an acid-labile dissolution inhibitor and a radiation sensitive acid generator have been reported. These systems which lead to high sensitivity due to "chemical amplification"[2] have been applied to deep-UV[3], and X-ray lithography[4]. Onium salts, halogen compounds and nitrobenzyl sulfonates[5] have been utilized as acid generators in chemical amplification systems. We have found that some sulfonates(sulfonic acid esters of phenol derivatives) also act as acid generators for chemical amplification system.

Resist formulations were prepared by dissolving Novolak resin along with acid generators (sulfonates or onium salt) and acid sensitive inhibitors in suitable solvents. As acid sensitive inhibitors, polyvinylphenol protected to a certain degree with tetrahydropyranyl group (THP-M) and Bisphenol-A protected with tetrahydropyranyl group (THP-BA), tert-butoxycarbonyl group (tBOC-BA), and trimethylsilyl group (TMS-BA) have been used. Resist films spin-coated from above formulations were exposed to the 250nm irradiation from a Xe-Hg lamp through an interference filter to generate acid. A post exposure bake was carried out at 80 or 100°C. The resist film was developed in an aqueous base developer.

With onium salts as acid generators in the above resist formulations, an overexposure with a dose of two or three times the dose necessary for positive image formation led to negative behavior. (Fig. 1) On the other hand, the resist using tri(methanesulfonyloxy)benzene as an acid generator gave no negative tone behavior even at an exposure dose of one order higher than that for positive image formation. (Fig. 1)

We have synthesized several kinds of sulfonates and evaluated these compounds as acid generators in chemical amplification resist systems. The exposure characteristic curves for various sulfonic esters with pyrogallol are shown in Fig. 2. The composition of the resist is Novolak/tBOC-BA/sulfonate=100/13.3/1.65 (mol%). The order of the sensitivity of sulfonate-containing resist systems is methanesulfonate> ethanesulfonate> propanesulfonate> butanesulfonate> benzenesulfonate> toluenesulfonate> naphthalenesulfonate. It is interesting to note that smaller sulfonic acid is effective for deprotection reaction of

tBOC-BA.

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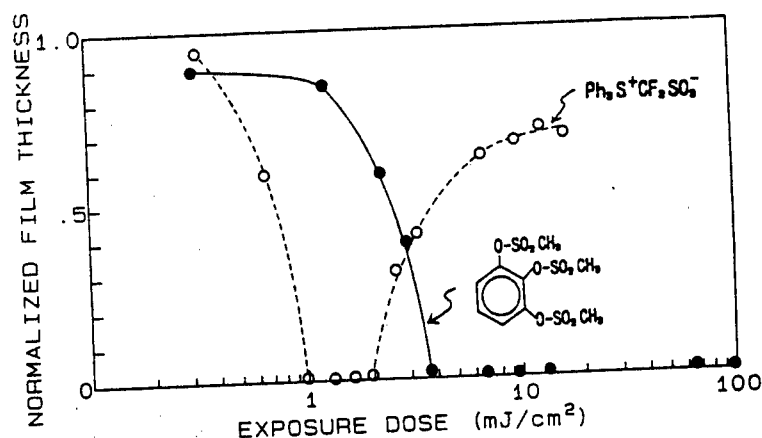


Fig. 1 Exposure characteristic curves for chemical amplification resist systems. Acid generator/tBOC-BA/Novolak.

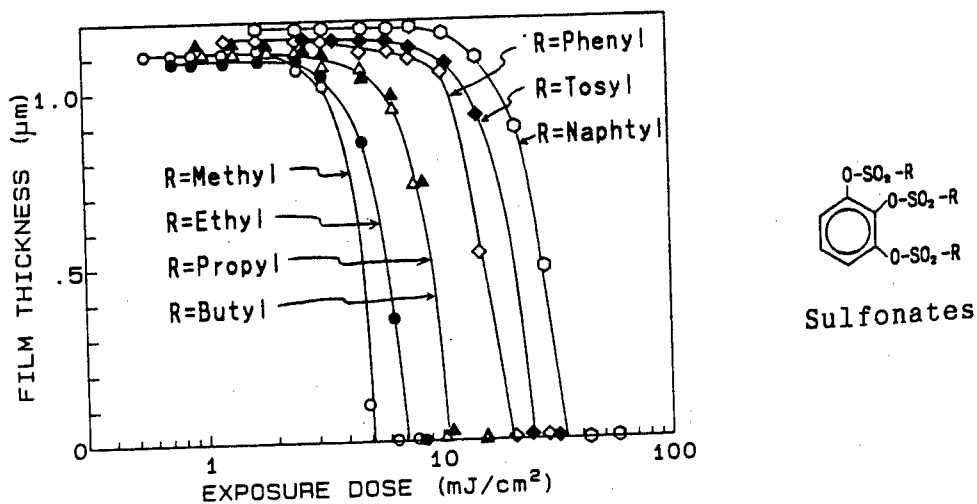


Fig. 2 Exposure characteristic curves for chemical amplification resist systems. Sulfonates(acid generator)/tBOC-BA/Novolak.

ORGANIC THIN FILMS FOR ELECTROLUMINESCENCE DISPLAYS

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Electroluminescence (EL) in organic thin films has attracted much interest, because of promising applications for large-area display devices. Recently, we have reported that bright EL emission can be obtained in multilayer-type thin film EL cells which consist of an emitter dye layer and carrier transport layers(1-3).

In this report, we will show that a variety of organic fluorescent dyes can be used as an emitter material in the multilayer EL cells, if we properly design the cell structures based on the electronic properties of the emitter materials.

Because the electronic properties of emitter materials are markedly different, an appropriate cell structure must be selected according to semiconductive natures of emitter materials for getting high performance EL cells. Figure 1 shows three typical cell structures. Indium-tin-oxide (ITO) and MgAg alloy are used for an anode and a cathode, respectively, and vacuum-deposited organic thin films are employed for hole and electron transporting layers. When the emitter materials possess the electron transporting tendency (electrons are easily injected from an electrode to an emitter layer and move rapidly), the cell structure SH-A which has a hole transporting layer is used. In contrast, when the emitter material has the hole transporting tendency, the cell structure SH-B should be used. If the emitter material has the bipolar carrier transporting tendency, the cell structure DH in which a bipolar emitter is sandwiched with hole and electron transporting layers is preferable.

Many fluorescent materials, such as luminescent dyes and pigments, optical brightening agents, organic scintillators, laser dyes, and fluorescent tracer reagents, may be used for the emitter

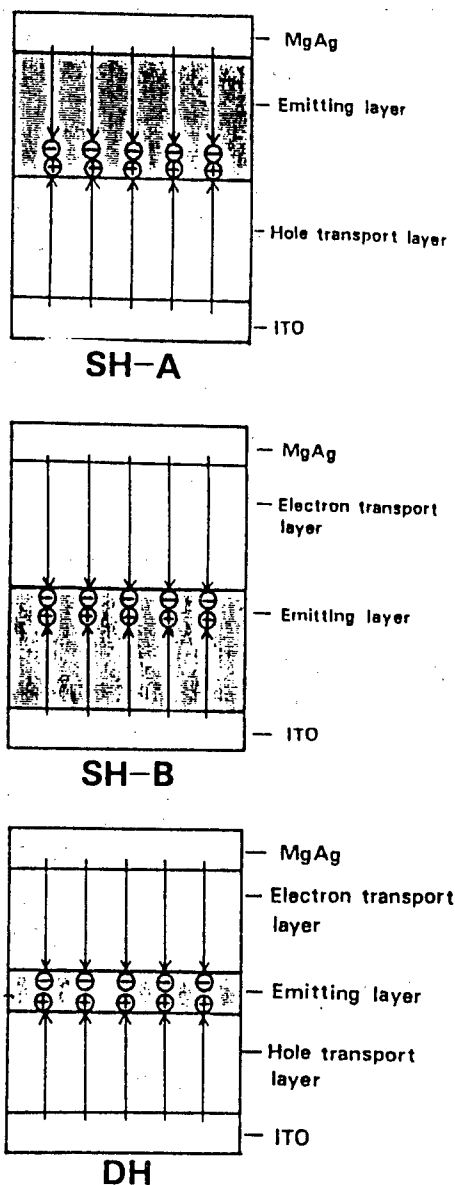


Fig. 1. Three types of EL cell structures.

materials. The guiding items for the selection of emitter materials are as follows; 1) the materials possess high quantum efficiency of photoluminescence in solid states, 2) pin-hole free thin films are easily prepared with the vacuum-vapor deposition, 3) efficient injections of holes and electrons into emitter layers are possible, and 4) the formation of the charge-transfer complex at the interfaces between two organic layers is avoided.

We succeeded in fabricating high performance EL cells with a wide variety of emission colors using more than ten fluorescent materials (4,5). Figure 2 shows some examples of EL spectra of those cells. The peak wavelengths of EL emission were 460(blue), 520(green), and 630 nm(red). The luminance of each cell exceeded 100 cd/m^2 at the current of 100 mA/cm^2 . The applied dc voltage was less than 10 V.

High₂ luminance exceeding 1000 cd/m^2 , low dc drive voltage of less than 10 V, high luminance efficiency, wide selection of emission colors, and very simple cell structures in our EL devices promise future application for full-color flat-panel displays, although durability of the devices has not been fully investigated yet.

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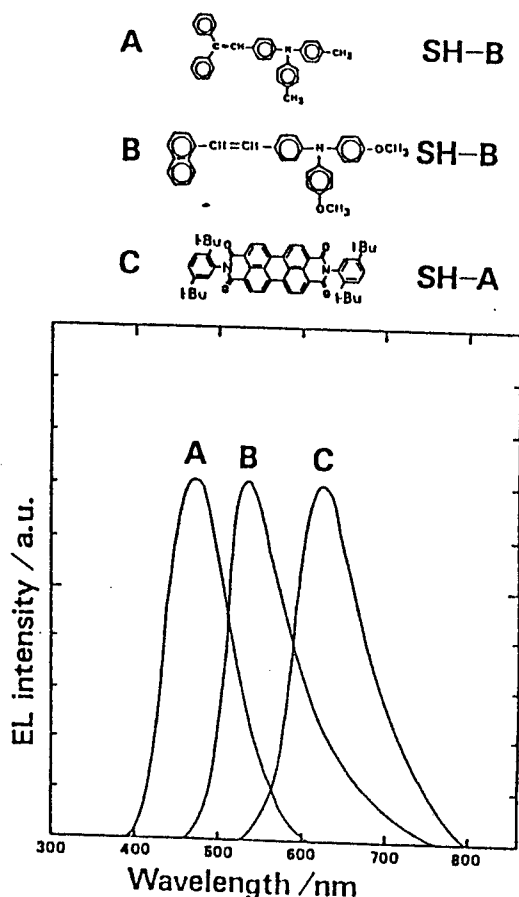


Fig. 2. Emission spectra of three EL cells.

PLANARITY OF HIGH SOLID TYPE POLYIMIDES

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Polyimides are widely used as an interlayer insulator of micro-electronic devices because of its good step coverage¹⁾. The increase in circuit density in recent years, planalization technology by the insulation layer becomes a main concern to perform a high density devices²⁾. In order to achieve the improved step coverage by polyimide layer, several types of polyamic acids with different solid content and molecular weights were synthesized, and their properties, such as step coverage, thermal resistance and mechanical strength were evaluated. It was found that solid content was an important factor in determining the degree of step coverage, therefore, the capability to controll the solid content and viscosity of polyamic acid without sacrificing other properties such as thermal resistance and mechanical strength becomes a key technology.

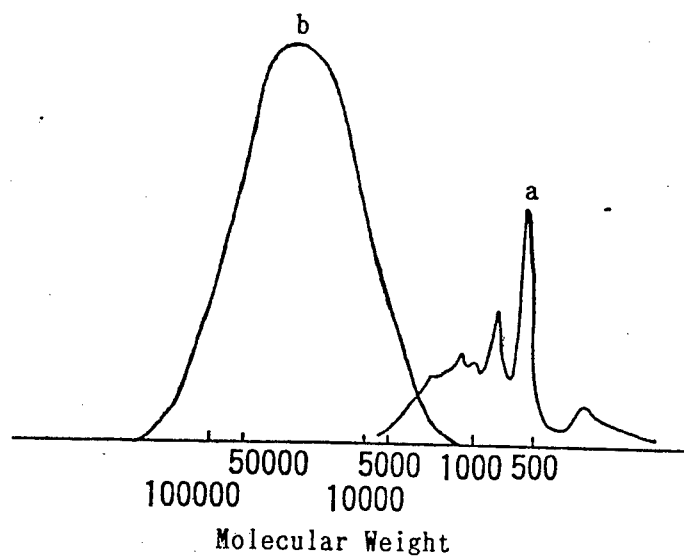
By employing a improved synthesizing technique³⁾, polyamic acids with high solid content and low viscosity(i.e. low molecular weight polyamic acids), were prepared and evaluated, and were found to give excellent step coverage and possess high heat resistance.

Figure 1 shows and compares the molecular weight distribution of that low molecular weight/high solid type polyamic acid and conventional polyamic acid. Note that the low molecular weight/high solid type has an oligomeric molecular weight distribution.

Figure 2 shows the relation between solid content and viscosity for the two types of polyamic acid. Low molecular weight type has a low viscosity in spite of high solid content.

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(Calculated with Std. polystyrene)

Figure 1 Molecular weight distributions of Polyamic acids.
 a) Low molecular weight type
 b) Conventional type

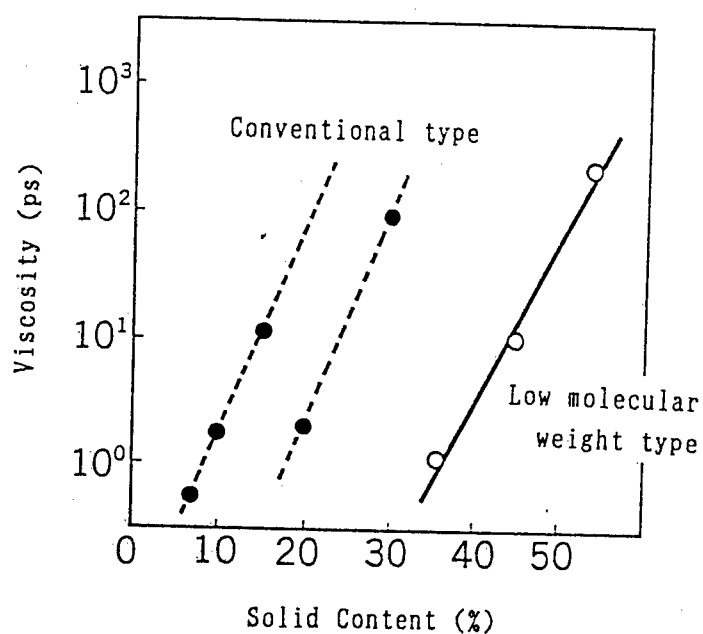


Figure 2 Relation between Solid Content and Viscosity of Polyamic acids.

PLANARIZATION OF TOPOGRAPHIC SUBSTRATES BY NEW POLYSILPHENYLENESILOXANE RESIN FOR FABRICATING ADVANCED MICROELECTRONIC DEVICES

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Multilevel interconnection has become a key component in advanced microelectronic devices with submicron wiring patterns. It cuts down the chip size, reduces the wiring length, and increases freedom of design. A planarized interlevel dielectric layer is needed to fabricate multilevel interconnections. However, planarizing substrate topography caused by wiring patterns has become more and more difficult as patterns become finer. The aspect ratio of substrate topography has increased since the thickness of wiring metal cannot be reduced due to the migration properties. So far, CVD of inorganic materials such as SiO_2 and PSG have been used as interlevel dielectrics, but they reproduce the topography of the substrate and form voids in narrow space patterns.

Silicones have been widely studied as interlevel dielectrics because they make the fabrication process quite simple. They can be easily spun on wafers, conventional carbon-based resists can be used as the mask for subsequent dry etching, and they adhere to inorganic materials such as SiO_2 , PSG, and wiring metals. Moreover, the dielectric constants of silicones are generally lower than those of inorganic materials. This is another significant advantage of silicone resins because interlevel dielectrics with low dielectric constant reduce the propagation delay.

However, all current silicone resins are easily oxidized when exposed to oxygen, which is inevitable in the CVD of SiO_2 or PSG and when removing organic resists. This oxidation causes cracks in silicone layers, and they make further processing impossible.

To develop an interlevel dielectric polymer with an excellent planarizing property that does not crack even when exposed to oxygen at high temperatures, we synthesized a new polysilphenylenesiloxane (SPS) resin and examined its properties.

SPS was synthesized by hydrolysis of chlorosilanes or methoxysilanes followed by dehydrated condensation polymerization. The backbone of the synthesized resin consists of both silphenylene and siloxane bonds and side chains are methyl substituents (Fig.1).

From the thermogravimetric analyses carried out in an oxygen flow of 100 cm^3/min , and infrared spectra measured after heat treatments at various temperatures in oxidative atmosphere, no oxidation of organic elements such as methyl and phenylene substituents in SPS was measured below 450°C . This means that SPS is less easily oxidized than other silicone resins which oxidize below 400°C .

The dielectric constant measured by an LCZ meter was quite low (3.0), and we confirmed that the SPS reduced the propagation delay.

We examined the planarity of SPS on Si substrates with 1- μ m high aluminium wirings. The weight-average molecular weight of the SPS we used in this experiment was in the range from 10,000 to 30,000. Polydispersivity was from 1.7 to 3.0. SPS of this molecular weight has a melting temperature of about 200°C. This is a good temperature for planarization of topographic substrates. The SPS first melts and flows into narrow spaces when it is heated. Then, it hardens by crosslinking reaction. We took SEM photographs of the cleaved silicon wafers, which were spin-coated with SPS. They were heat treated for one hour at 400°C in air. No cracks are observed, and the planarization of 1- μ m high topography is almost perfect (Fig.2).

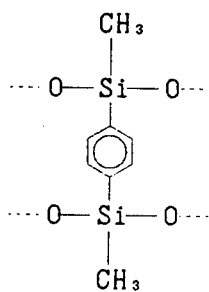


Figure 1 Molecular Structure of SPS

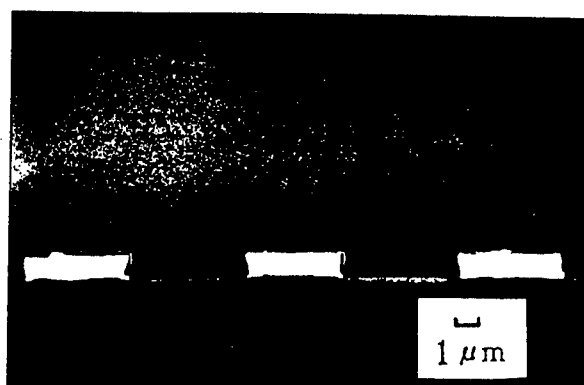


Figure 2 Planarized profile of topographic substrate by SPS

REGULAR SEQUENCE CONTROLLED COPOLYPYROMELLITIMIDE

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It has been known that wholly aromatic polyimides are extensively used in electric and electrical device applications due to their excellent mechanical and electrical properties and thermal stability.[1]

The conventional polyimide films such as "APICAL" or "KAPTON" have higher thermal expansion coefficients compared with metals and ceramics, so they don't have sufficient dimensional stability for fine pattern applications.

There are many previous studies[2] in regard to polyimides having very low thermal expansion coefficients. They reported that some aromatic polyimides in which rigid segments are introduced have very low thermal expansion coefficients.

Generally in order to achieve a low thermal expansion coefficient, some of aromatic diamines such as p-phenylenediamines (p-PDA) are used for a rigid segment. However the polyimide films ever made by using rigid segments of those diamines didn't have satisfactory mechanical properties.

Recently, we have demonstrated that a very regularly sequence controlled copolypyromellitimide was prepared by developing a novel method of copolymerization and that a film made from its polymer had a low thermal expansion coefficient, good mechanical and thermal properties.[3]

In this study, we report characterization of film made from the sequence controlled copolypyromellitimide in detail.

The chemical structure of this sequence controlled copolypyromellitimide (1) is shown in figure 1.

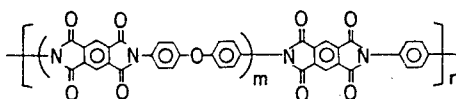


Figure 1. 1

Firstly, we've investigated an effect of mole fraction of p-PDA as co-monomer. Figures 2 and 3 show the results of the thermal expansion coefficients and the elongation at break versus mole fraction of p-PDA, respectively.

○: Regularly sequence-controlled copolypyromellitimide film.
●: Random copolypyromellitimide film.

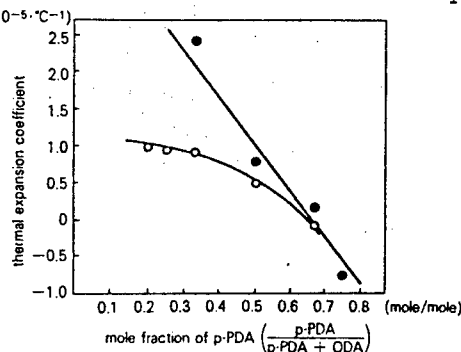


Figure 2. Relationship between Thermal Expansion Coefficient and Mole Fraction of p-Phenylenediamine (p-PDA).

* To whom correspondence should be addressed

○: Regularly sequence-controlled copolypyromellitimide film.
 ●: Random copolypyromellitimide film.

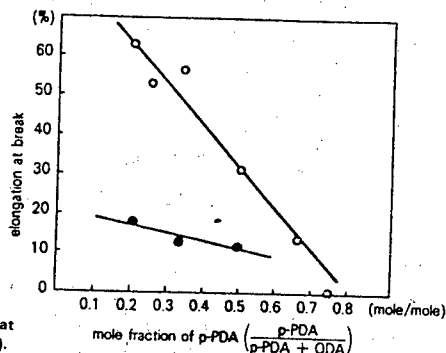


Figure 3. Relationship between Mechanical Properties (Elongation at Break) and Mole Fraction of p-Phenylenediamine (p-PDA).

Secondary, we've investigated inter-molecular conformation by Wide-angle x-ray diffraction patterns (WAXS) and density of films. (refer to figure 4)

X-ray diffraction study of the polymers were performed by the film method using nickel-filtered Cu-K α radiation. The intensity of sequence controlled copolymer is larger than that of random copolymer. Also the density of regular sequence controlled copolymer is larger than that of random copolymer.

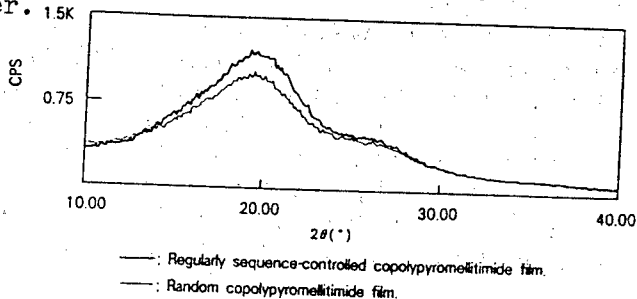


Figure 4. X-ray Diffraction Patterns of Copolypyromellitimide Films.
 p-PDA/ODA = 1/3 (mole./mole.)

These results suggest that the control of intra-molecular regularized structures by our method results in inter-molecular regularized structures. Consequently, we presume that these phenomena lead to particular characteristics such as a low thermal expansion coefficient and a good flexibility.

Lastly, we've evaluated various properties of films of regular sequence controlled copolyimide. Typical mechanical properties of this film were tensile strength of 323MPa, elongation at break of 90%, and tensile modulus of 4.26GPa. The thermal expansion coefficient is $1.6 \times 10^{-5} \text{ } ^\circ\text{C}^{-1}$ in the range 100-200 $^\circ\text{C}$. It is much smaller than that of ordinary polyimide film and is equivalent to that of copper foil which has $1.7 \times 10^{-5} \text{ } ^\circ\text{C}^{-1}$ in the range 100-200 $^\circ\text{C}$. The other mechanical and electrical properties of film will be discussed in our presentation.

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REQUIRED CHANGES IN POLYIMIDES FOR MICROELECTRONICS

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1. INTRODUCTION

The development of semiconductor devices using a polymer insulating layer began at Hitachi almost twenty years ago. The particular success of ICs using the polyimide PIQ has contributed significantly to their current advanced status. This success is based on the advantages of the polyimides including PIQ, such as good processability, planarizability, thermal stability, excellent mechanical strength, and low dielectric constant. Consequently, many kinds of electronic parts, such as bubble memories, GTO thyristors, multilevel interconnections of facsimile heads, protecting layers of VLSIs, multi-chip modules, etc. have been developed.

In the earliest stage of the development, the following subjects were studied: purification of polymers to avoid contamination, thermal stability to withstand heating in the fabrication process, etchability for patterning, and adhesiveness between the polymer and other materials. With increased applications, concerns have spread to desires for a lower dielectric constant, a low thermal expansion coefficient (TEC), higher planarizability, and higher adhesiveness to obtain even better quality and reliability. In the present paper, with the changes in applications from the insulating layers of ICs to multi-chip modules and the like, changes in polymer materials requirements for use in microelectronics are discussed.

2. LOW THERMAL EXPANSION POLYIMIDES

For the protection layer of large scale semiconductor chips, the thick insulating layer of multi-chip modules, and the like, the most significant problem is thermal stress due to the difference in TECs between the polymer and substrates. However, almost all polymers had been believed to have large TECs, so a polymer having a low TEC was considered as nonfeasible. However, low TEC polyimides were reported in 1984 (1). The chemical structure of these low TEC polyimides is a linear one. The low TEC of the film, in which the linear molecules are arranged at random, appears because the linear polymer molecules having a negative TEC in the molecular chain direction restrict the thermal expansion due to expansion of intermolecular spaces between them.

In application to interlayer dielectrics of VLSIs, multilayered dielectrics of the low TEC polyimide and inorganic layer gave excellent reliability in moisture exposure and temperature cycling tests (2). Usefulness of the low TEC polyimides in a variety of fields has been ascertained.

3. HIGHLY PLANAR POLYIMIDES

In most polyimide applications, the material has been used as the planar insulating layer of multilevel interconnections. However, at this time it is no longer enough to planarize the high aspect ratio conducting lines in much denser wired LSIs and multi-chip modules. To planarize such very uneven surfaces, a more planarizable coating is indispensable.

In order to planarize uneven surfaces, a hot-melt type coating is ideal. However, for high temperature polymers with rigid molecular chains, this is not possible and use of high solid content varnishes with higher fluidity seems to be the best way. This makes low molecular weight varnishes necessary. However, to obtain a final, high molecular weight strong film, polymerization should occur during curing. It has been reported that a solution of esterified dianhydride and diamine gave a high solid content varnish which could be converted to a high molecular weight polyimide film by heating because dianhydride was formed (3). But, since monomers suitable to this method are limited, a more practical approach is desired.

4. LOW DIELECTRIC CONSTANT POLYIMIDES

In applications which need a higher signal propagation speed, such as multilayer modules, not only reduced path length, but also low dielectric constant are required. Since the dominant factor of the dielectric constant of a polymer is electronic polarization, reduction of the imide ring density or introduction of fluorine atoms are very effective for lowering the dielectric constant. Therefore, various kinds of fluorine containing polyimides from large molecular weight monomers have been developed. However, their properties are not suited for multi-chip modules, because of low glass transition temperatures, high TECs, etc. Polyimides having linear molecules with fluorine-containing side groups have been synthesized and confirmed to have both low dielectric constant and low TEC (4). Hereafter, new polymers which satisfy all the demands need to be developed.

5. ADHESIVENESS BETWEEN POLYIMIDE AND THE OTHER MATERIALS

Since electronic parts are made by lamination of various thin films, many studies concerning the reliabilities of their interfaces have been done. However, few studies from the viewpoint of interfacial chemical reaction have been done because of difficulty in analyzing. The weakest interface is that of metal on polyimide. Deposition of Cr or Ti between copper on polyimides was reported to increase greatly the adhesion strength (5,6), due to a chemical reaction, such as complex formation, or ionic bonding at the interface. Satsu et al. (7) reported that N_2 plasma treatment enhanced adhesive strength of Cu or Ti on the polyimides. And Momose et al. (8) found that CF_4 plasma treatment caused a chemical reaction and enhanced adhesiveness of Al on polyimides. Hereafter, more investigations are necessary before adhesiveness of various interfaces can be controlled at will.

Lastly, although not touched on in this paper, patterning of polyimides requires development of a new process or a new material which makes finer and denser wiring easier.

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POLYIMIDE OF HIGH PURIFICATION FOR MICROELECTRONICS.

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A high efficiency of polyimide application as an interlayer dielectric in integral circuits with multilayer metallization in multilayer printed circuit boards and as protective coatings for microcircuits has been shown recently.

A very high technological effect of the polyimide application in microelectronics is connected with the development of special types of especially pure polyimide resins which in comparison to other polymers possess outstanding dielectrical properties, higher thermal and radiation resistance, mechanical strength and high processibility. In the present paper a method of synthesis and properties of polyimides on basis of pyromellitic dianhydride (PMDA) and diaminodiphenylether of diphenylpropane are described.

For synthesis of prepolymer — polyamide acid on base of the above mentioned monomers — dimethylformamide of high purity was used. Purifying of commercial PMDA was carried out by sublimation. The required degree of purity was achieved by recrystallization of the product from ethyl alcohol of high purity.

The results of analysis are given as for the content of microimpurities in the initial components before and after the purification as well as in the polyimide synthesized on their base.

It has been shown that the use of PMDA and DADD permits to achieve their high purification by simple, ecologically harmless methods and to produce polyimide films and coating of high quality and purity for microelectronics.

The application of such polyimide in integral circuits of electronic systems essentially increases functional features of these systems and significantly increases their operating reliability.

THE PROPERTIES AND MOLECULAR STRUCTURE OF
AROMATIC POLYIMIDES.
THE SOLVED AND NEW PROBLEMS.

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The fundamental relations between thermomechanical properties and molecular structure in the class of aromatic polyimides (PI) are considered. At the beginning the general classification of PI macromolecules and their models are discussed. PI are divided into four groups which differ from each other in the presence and position of chemical "inner hinges" making the changing of chains conformations possible. The corresponding molecular models differ in number, mobility and size of rings, number and position of inner hinges, size and shape of rigid segments of chains. The abrupt change of thermomechanical properties at passage from one group to other shows the necessity of the classification.

Then the main temperature transitions and yielding of PI are discussed. The glass temperatures T_g of PI are between 150 and 600 °C. Their values obey the known Gordon-Taylor and Zurkov-Endreus equations connecting T_g with molecular composition of the polymer. It shows that the glass-liquid transition in PI is regulated by free volume amount and molar concentration of the strongest intermolecular bounds, that is, the same molecular factors as in others polymers. The melting temperatures T_m of PI are between 350 and 1000 °C. It was found that qualitative analysis of T_m relating to molecular structure is possible with the help of mentioned models which take into account the ring-chain nature of PI macromolecules. It shows that the process of melting of PI and other ring-chain polymers has to be treated as consisting of several elementary stages in contrast with carbon-chain polymers where it is sufficient to consider only the chain backbone melting.

The specific effects at PI softening and melting caused by high temperatures of the transitions as well as the simple method for calculation of PI degree of crystallinity are also discussed.

It is shown that the equations of the disclination theory of glassy polymers plasticity allow to discover the qualitative relations between yield stress, shear modulus, temperature and the justice for PI and others polymers in glassy state.

The new fundamental problems arise during the searches of ways to improve the properties of PI films such as strength, thermostability and elongation at rupture. Some problems arising at experiments with chemical imidisation, stabilizer addition and orientation at stretching are discussed.

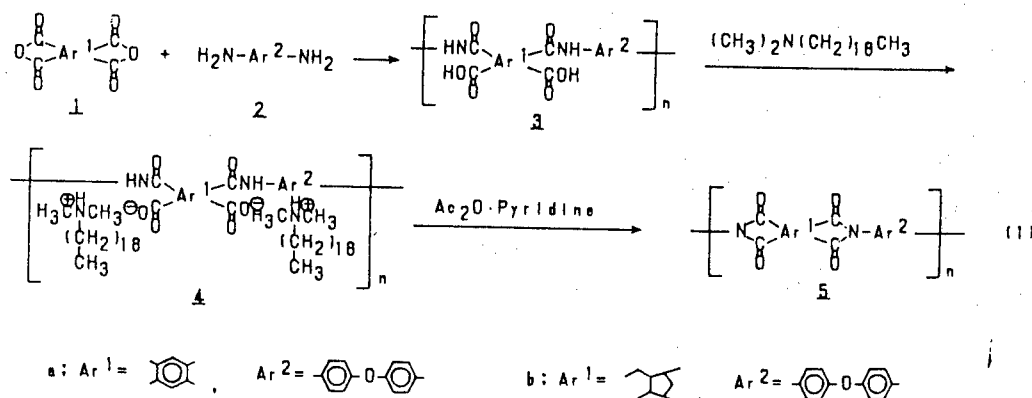
PREPARATION AND MICROELECTRONIC APPLICATIONS OF LANGMUIR-BLODGETT FILMS OF POLYIMIDES AND RELATED POLYMERS

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Langmuir-Blodgett (LB) technique is one of the most elegant method for the preparation of ultra thin films possessing well ordered structure in molecular level. Therefore, this technique may be accepted as the most promising fabrication method for "molecular devices".

We have developed LB films of condensation polymers, which offer mechanically improved and thermally stable LB films. One of the examples is LB films of polyimides well known as high temperature polymers.[1-3] Since polyimides are neither soluble in organic solvents nor amphiphilic, "precursor method" has been developed for the preparation of polyimide LB films. As shown in Eq. 1, this process consists of three steps; 1) preparation of monolayer films of precursor polyamic acid long-chain alkylamine salts **4** at air/water interface, 2) deposition of the monolayer films on to an appropriate substrate, 3) treatment of the precursor LB films with a mixture of acetic anhydride and pyridine to form LB films of polyimides **5**.



Defects in LB films are generally important problems to be discussed. The defects of polyimide LB films were evaluated by electrochemical method.[4] The LB films were prepared on a glassy carbon electrode surface, and redox behavior of potassium ferrocyanide was studied using the electrodes. The LB film of polyimide **5a** had lower level of defects compared with that of cadmium arachidate, the most popular compound for LB films. Furthermore, it was found that the number of the defects could be minimized by selection of the chemical structure of polyimides. Thus, no defects were detected in ten layers of LB film of aliphatic polyimide **5b** using above method.

Design of electron transfer system is one of the examples of LB film applications, because such systems require well ordered structure of each functional groups. Tetraphenylporphyrin (TPP) is a typical artificial synthetic model of chlorophyll, which is an important part of active center of the photosynthesis in plants. A photodiode was prepared by

combination of an electron donor (D), a sensitizer (S), and an electron acceptor (A). Each functional components were constructed by polyimide LB films possessing ferrocene, TPP, and usual aromatic polyimide, respectively. The photochemical properties of the electrode were investigated by using the electrochemical cells, where the electrode, a gold plate, and a saturated calomel electrode (SCE) were used as the working, counter, and reference electrode, respectively. The photocurrent-time curves under the stepped illumination of monochromatic light of 430 nm at 0 V vs. SCE are shown in Fig. 1. The photocurrent was observed with a long lifetime only when the light was irradiated. This magnitude was about 5-10 times larger compared with the reported values of the similar photodiode LB systems.[5] Such high efficiency of the light-electricity conversion should be brought about from the absence of the long alkyl chain between each layers.

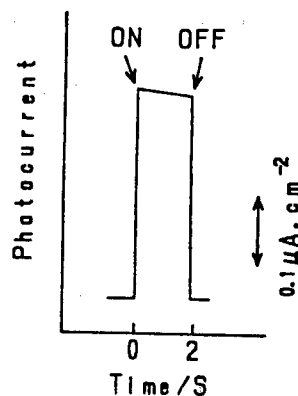
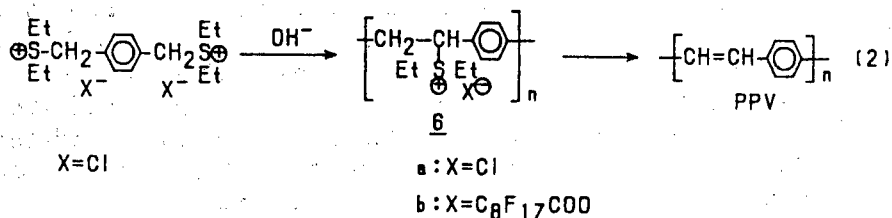


Fig. 1. Photocurrent-Time Curve

The same concept of "precursor method" was applied to the preparation of poly(p-phenylene vinylene) (PPV) LB film as shown in eq. 2.[6] First, the precursor LB film of polysulfonium perfluoroalkylcarboxylate was prepared, and then the LB film was heated at 250 °C, giving PPV LB film. The conductivity values of sulfur trioxide doped films were 0.5 S/cm and 4×10^{-6} S/cm for in-plane and normal direction, respectively.



The characteristics of these LB films are as follows; 1) since they have no long alkyl chain, monolayer thickness of the LB films is only around 0.5 nm, 2) they are chemically and thermally stable, 3) functional groups can be easily introduced into the main chain structures.

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ELECTRICAL PROPERTIES OF POLYIMIDE LANGMUIR-BLODGETT
FILMS DEPOSITED ON NOBLE METAL ELECTRODES

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There has been much interest in the Langmuir-Blodgett (LB) technique as a means of producing high-quality organic ultrathin films. If the ultrathin films are pinhole free, they can be used as an electrical insulating layer in electronic devices. In the present paper, thermally stable multilayer films of polyimide (PI) were prepared on base-(noble metal) electrodes by using the conventional LB technique. Here, the monolayer thickness of the multilayer PI LB films was about 0.4 nm. Then, we have examined the electrical properties of ultrathin PI LB films by using tunnel junctions with structures of Au/PI/Au and Au/PI/Pb-Bi. Here, the Pb-Bi is a top-superconducting electrode.

For Au/PI/Au junctions, most of the junctions were electrically shorted due to the existence of metallic wires passing through the PI layers, when the number of deposited PI layers was less than 30. On the contrary, most of the junctions were not electrically shorted, when the number of deposited layers was greater than about 30. It was concluded from this result that we can get ultrathin PI LB films which are good electrical insulators when the thickness of deposited PI layers is greater than about 12 nm.

We have also investigated the electrical conduction mechanism through PI LB films sandwiched between Au-electrodes. It was found from the investigation that the electrical conduction was ruled by the Simmons' tunneling theory, where the magnitude of a current flowing across Au/PI/Au junctions did not depend on the temperature in the range between 20 K and 300 K, and effects of the polarity of biasing voltage were not seen in the I-V characteristics of the junctions (Fig.1). It was also found that PI LB films did not electrically breakdown at the electric field up to about 10^7 V/cm.

For Au/PI/Pb-Bi junctions, typical I-V characteristics of tunnel junctions were obtained at a temperature of 4.2 K, when the number of deposited PI LB layers was 27 (Fig.2). In Fig.2, a gap voltage (Δ/e) of about 1.2 mV of the Pb-Bi alloy is seen. The gap voltage depends on the temperature of the junction and it approaches zero as the temperature approaches the critical temperature T_c (= 7.3 K) of the Pb-Bi

alloy. From a theoretical analysis based on the BCS theory, it was found that our experimental results agree well with the theoretical curve predicted by the BCS theory. This result indicates that the PI LB layer was a good tunnel barrier when the number of deposited PI layers was 27.

In conclusion, PI LB films can be used as an electrical tunnel barrier in electron devices.

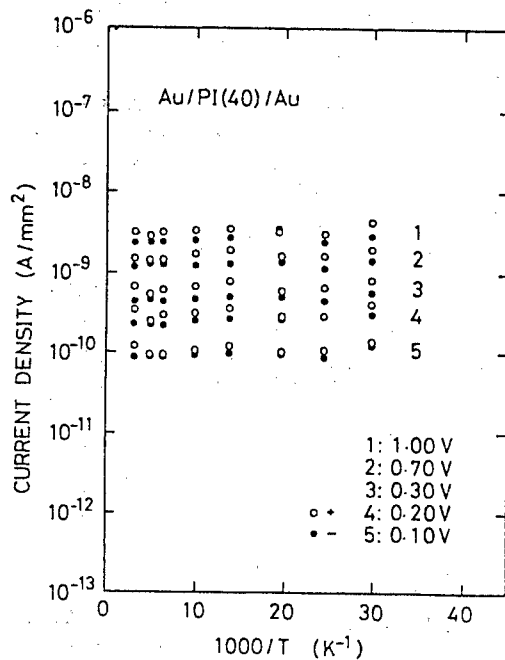


Fig.1

A typical example of the $I-1/T$ characteristics for Au/PI/Au junctions with 40 deposited layers at various biasing voltages.

Open circles represent the data for positive biasing, and full circles the data for negative biasing. The biasing voltages are 1: 0.1 V, 2: 0.2 V, 3: 0.3 V, 4: 0.7 V and 5: 1.0 V.

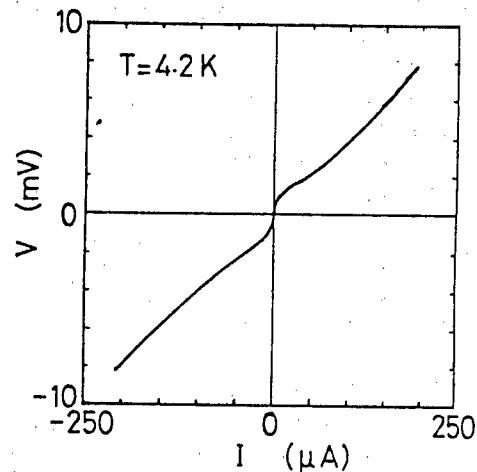


Fig.2

A typical I-V characteristic for the Au/PI/Pb-Bi junction with 27 deposited layers at a temperature of 4.2 K.

NEGATIVE RESISTANCE AND ELECTRON EMISSION IN METAL/LANGMUIR-BLODGETT FILM/METAL STRUCTURES

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Langmuir-Blodgett (LB) films have been expected to provide the homogeneous and thin insulating layer in metal/insulator/metal (MIM) sandwich structures. However, the conduction in metal/LB film/metal (M-LB-M) sandwich structures has been dominated by metallic pathways through the LB films originating in structural defects in the LB films. Recently, high quality LB films free from defects have been prepared even on the noble metals, and the high impedance M-LB-M devices have been fabricated on a noble metal base electrode whose surface was hardly oxidized[1]. In these devices, the reproducible memory switching phenomena have been shown under atmospheric pressure[2].

On the other hand, the tunnel emission of electrons into vacuum has been expected in MIM devices with very thin insulators[3]. We present the results of the voltage-controlled negative resistance (VCNR) and the electron emission in the M-LB-M devices under vacuum.

The M-LB-M devices used were composed of a gold bottom electrode, a polyimide LB film insulator, and an aluminum top electrode. The polyimide LB film was prepared by thermal imidation of the polyamic acid-hexadecylamin salt LB film. Top and bottom electrodes were fabricated by vacuum evaporation. The M-LB-M junction area was about 1mm^2 . All measurements were carried out under vacuum of a pressure less than 3×10^{-6} torr.

The M-LB-M devices were initially in very high impedance state. The impedance of the M-LB-M devices irreversibly decreased under vacuum by application of a positive voltage to either gold or aluminum electrode, and another impedance state was induced. This phenomenon has been called a forming which was distinctly different from dielectric breakdown.

Figures show a current-voltage characteristic (a) and an emission current-voltage characteristic (b) in the formed M-LB-M device which incorporated 24 polyimide monolayers 9.6nm thick and an aluminum top electrode 15nm thick. The VCNR appeared in the formed M-LB-M device by application of a positive voltage to either gold or aluminum electrode as shown in Fig.(a). Electron emission was observed in the formed M-LB-M devices with an aluminum top electrode positively biased. The emission current was enhanced by the development of the VCNR with a gold bottom electrode positively biased. As shown in Fig.(b), the electron emission started at a voltage about 5V, which was a voltage above the work function of aluminum. The emission pattern obtained by using the fluorescent screen was a similar shape of the M-LB-M junction. Moreover, no physical damage was observed on the surfaces of the aluminum top electrodes after measurements.

These results show that the electrons were emitted from a whole junction area through the aluminum top electrode. The electric field in the LB film has to be so high over a whole junction area of the M-LB-M device that the electrons gain the kinetic energy larger than the

work function of aluminum. This means that the electron emission in the M-LB-M devices is not due to the local structures in the LB films such as the field emission based on the rupture of metallic pathways. The electric conduction in the M-LB-M devices is dominated by the LB films themselves.

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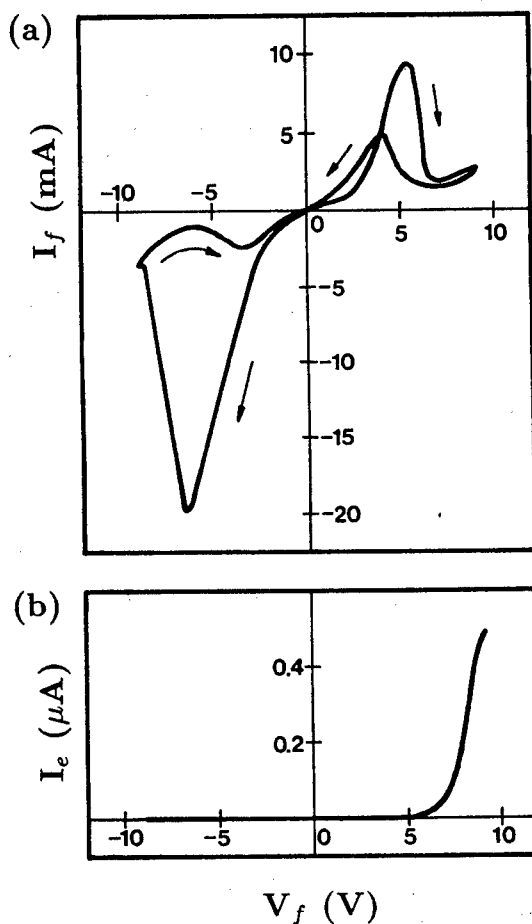


Figure Current-voltage characteristic (a) and emission current-voltage characteristic (b) in the formed Al-polyimide LB film-Au device under vacuum. A polyimide LB film is 9.6nm thick and an aluminum top electrode is 15nm thick. The positive quadrant corresponds to a positive bias to an aluminum top electrode.

MOLECULARLY ORIENTED POLYIMIDE ULTRA-THIN FILM PREPARED BY THE WATER SURFACE SPREADING METHOD

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[INTRODUCTION]

There has been a growing interest in the use of polyimides for various applications. In recent years, polyimide ultra-thin films have been prepared by the Langmuir-Blodgett technique and the vacuum deposition method. In the future, these can be used as electronic devices. In this report, we studied a new method to prepare polyimide ultra-thin films by spreading it on the surface of water. We also evaluated the molecular orientation of these polyimide ultra-thin films.

[EXPERIMENTAL]

Polyamic acid, which is a precursor of polyimide, is synthesized by the reaction of tetracarboxylic acid-dianhydride and aromatic diamine. Two techniques can be used for the spreading method: 1) a fixed amount of solution is spread on the water surface; 2) the polymer solution is continuously placed on the water's surface and the resulting ultra-thin film is continuously removed by a rotating film substrate (Fig.1). The molecular orientation of the ultra-thin films is evaluated by an FT-IR apparatus equipped with a polarizer.

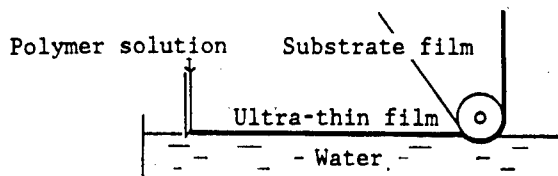
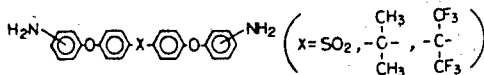


Fig.1 The apparatus for preparing ultra-thin film by continuously spreading polymer solution on the surface of water.

[RESULTS AND DISCUSSION]

A typical polyimide (KAPTON) precursor has strong hydrophilic groups and dissolves in solvents that are primarily water soluble. Therefore, it is difficult to spread on a water surface. We found that this precursor, which is silylated or neutralized by amines, spreads on the water's surface to form homogeneous ultra-thin film.

We also studied other precursors made from a diamine having four aromatic rings as follow:



These precursors can be easily spread by mixing them with a spread-aiding reagent such as asetophenone. The continuous-spreading (technique 2) results for one of the above mentioned precursors are shown in Fig.2. The thickness of the spread film decreased as film removal velocity increased. As a result, a thickness at about the 100Å level can be obtained for the polyimide precursor by using this method.

When the solid ultra-thin film is rapidly removed, it is supposed that the polymer solution regions are thinning and the flow stress orients the polymer molecules in the removing direction. The dichroic ratio (D) of successively spread thin films prepared from a polyimide precursor solution is plotted against the film removal velocity in Fig.3. The dichroic ratio increased linearly with this velocity. In this system, $D=1.0$ at a velocity of 3-4m/min. This indicates that the polymer solution spontaneously spreads on the water's surface at this velocity, and when the film removal velocity surpasses this rate, molecular orientation is obtained.

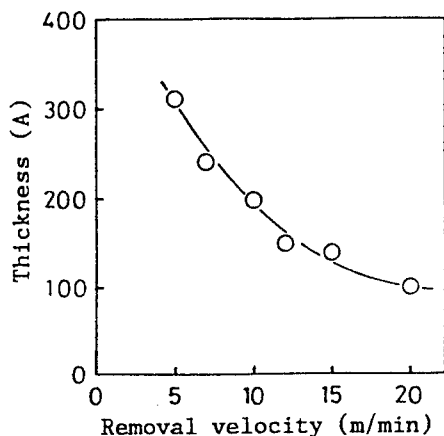


Fig.2 Relationship between the removal velocity and the resulting thickness of polyamic acid ultra-thin film.

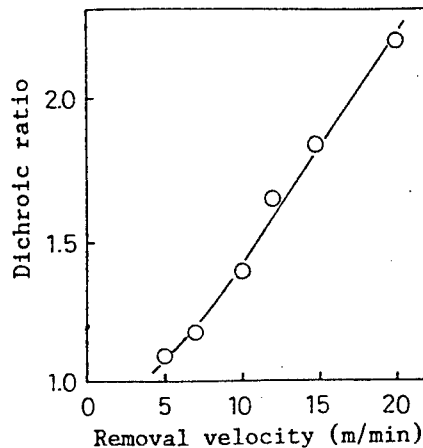


Fig.3 Effect of removal velocity on the dichroic ratio of polyamic acid ultra-thin film.

The orientation phenomenon in the film formation process is shown in Fig.4. In this system, film thickness decreased and the dichroic ratio sharply increased in the region between 20cm and 40cm from the point where the polymer solution was placed.

The micrographs in Fig.5 show the alignment of ferro-electric liquid crystal (FLC) in its cell when the ultra-thin films were used as an aligning layer. It is obvious that ultra-thin film with a high dichroic ratio can orient FLC homogeneously. We also obtained good FLC bi-stability in this cell.

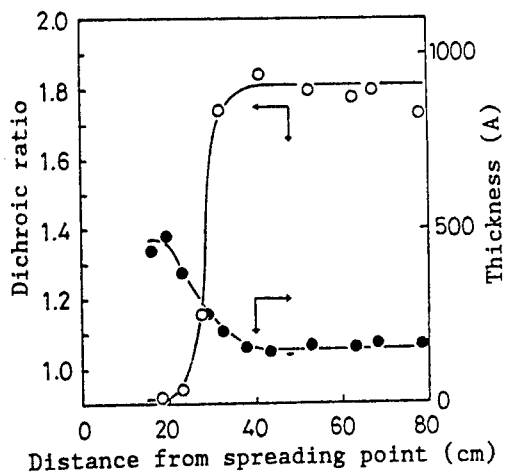


Fig.4 The formation process of molecularly oriented ultra-thin film.



Fig.5 Micrographs of FLC alignment on an aligning layer of ultra-thin film. Dichroic ratio of ultra-thin film: (a) below 1.1 ; (b) above 1.1

A NOVEL POSITIVE TYPE POLYIMIDE BASED ON PHOTOINDUCED ACIDOLYSIS

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Introduction

Polyimides are receiving wide interest in electronics industry owing to their excellent properties, e.g. high thermal and chemical stability and low dielectric constant. Recently, a number of photoreactive polyimides¹ and their precursors²⁾ have been reported. The authors also reported fluorene-containing photoreactive polyimide³⁾ which show improved optical transparency and solubility in common organic solvents.

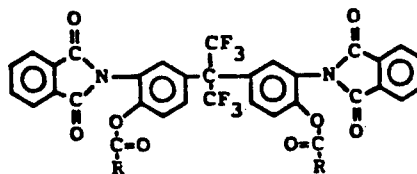
On the other hand, as an advanced design of photoresist in the field of microlithography, the systems involving chemical amplification recently has been attracting attention⁴⁾ because of its high sensitivity.

In the present paper, we will report the synthesis and lithographic evaluation of a novel positive type polyimide based on photoinduced acidolysis.

RESULTS AND DISCUSSION

In order to find the acidolytic facility of protecting groups, a series of model compounds corresponding to the unit of the polyimide was prepared and protected with various protecting groups (Figure 1).

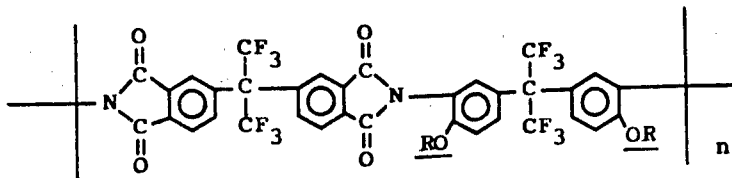
Figure 1 The structure of the model compounds corresponding to the unit of the polyimide. R=acylated group or alkyloxycarbonylated group.



0.1g of each model compound was dissolved in 3ml of N,N-dimethylacetamide with 1.6×10^{-3} mol of conc. sulfuric acid and 4.7×10^{-3} mol of water, then heated for 30min at several temperatures. The deprotecting ratio was measured by H-NMR spectrum. From this result, the acidolytic facility of protecting groups was in the order of $\text{COCH}_3 > \text{COCH}(\text{CH}_3)_2 > \text{COC}(\text{CH}_3)_3$ for the acylated series and $\text{OCOC}(\text{CH}_3)_3 > \text{OCOC}_2\text{H}_5 > \text{OCOC}(\text{CH}_3)_2 > \text{OCOC}_2\text{H}_4\text{CH}(\text{CH}_3)_2$ for the alkyloxycarbonylated series.

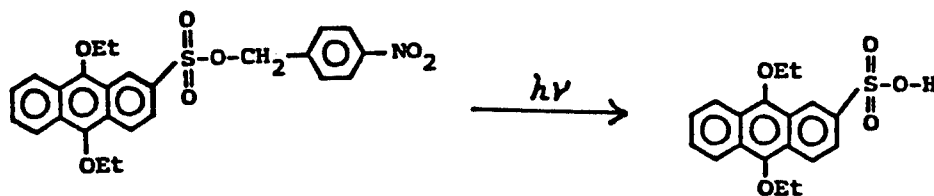
Based on the above result for the model compounds, the polyimide, 6F-t-BOC of which hydroxy group was protected by tert-butoxycarbonyl group, was synthesized (Figure 2). 6F-t-BOC showed high transmittance at the wavelength longer than 300nm. And 6FDA-AHHFP showed high solubility not only in common organic solvents but also in aqueous base or in mixed solution of alcohol and aqueous base depending on the molecular weight.

Figure 2 The structure of synthesized polyimides. R=t-BOC(6F-t-BOC), R=H(6FDA-AHHFP).



The lithographic performance of 6F-t-BOC was observed using p-nitro

benzyl-9,10-diethoxyanthracene-2-sulfonate (NBAS) as the photo-acid generator. The absorption band of NBAS extends until 436nm (g-line) and is photo-bleachable. NBAS is photochemically decomposed to give 9,10-diethoxyanthracene-2-sulfonic acid which is strongly acidic and deprotects the t-BOC group of the 6F-t-BOC (Scheme 1).



Scheme 1

The sensitivities (D°) and the contrasts (γ°) of the 1 μ m film of 6F-t-BOC with NBAS were evaluated by characteristic curves (Figure 3). D° and γ° were 270mJ/cm² and 4.2 to 365nm light, and 650mJ/cm² and 2.7 to 436nm light with postexposure bake (PEB) at 110 $^{\circ}$ C for 10min. Further, D° at 365nm was enhanced to 180mJ/cm² with PEB at 120 $^{\circ}$ C for 10min and γ° was 3.4. Figure 4 shows a scanning electron micrograph of the positive pattern formed from a 5 μ m thick 6F-t-BOC film. 6F-t-BOC offered high resolution with aspect ratio over 5.0 and good pattern profile.

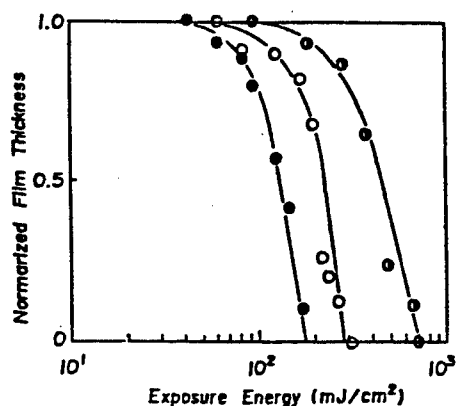


Figure 3 Characteristic curves for 6F-t-BOC/NBAS. Lines: (●): 436nm, 110 $^{\circ}$ C PEB, (○): 365nm, 110 $^{\circ}$ C PEB, (●): 365nm, 120 $^{\circ}$ C PEB.

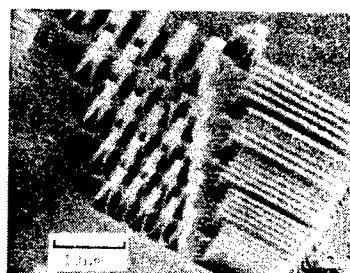


Figure 4 Scanning electron micrograph of positive image contact printed in 5 μ m thick film of 6F-t-BOC

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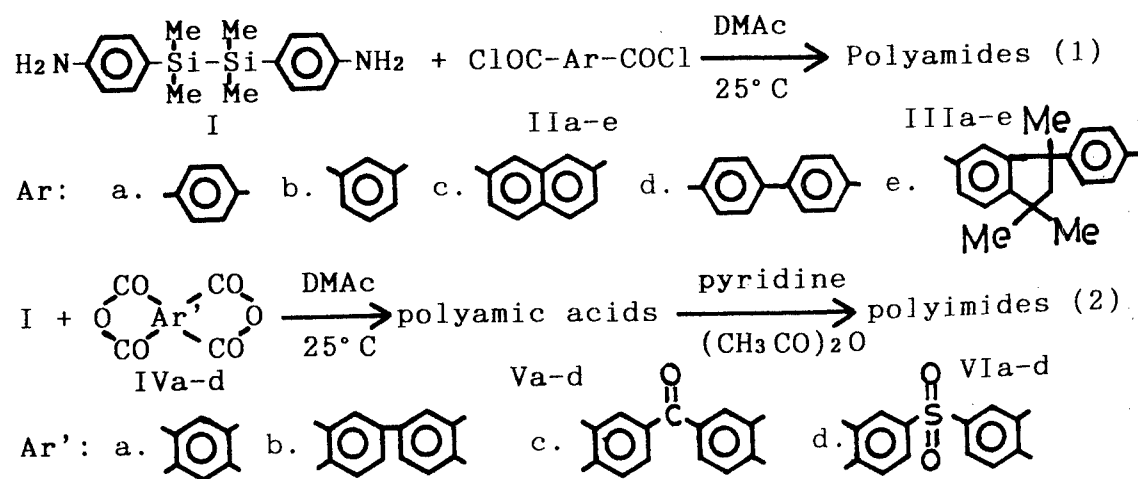
PREPARATION AND PROPERTIES OF DISILANE CONTAINING PHOTODEGRADABLE AROMATIC POLYAMIDES AND POLYIMIDES FROM BIS(p-AMINOPHENYL)TETRAMETHYLDISILANE

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Introduction: Recently, polysilanes have drawn considerable interest in the design of polymeric photoresist materials due to their unique UV spectral properties combined with oxygen-reaction ion etching resistance. Polymers such as poly(p-disilanylene phenylene)s¹⁾ undergo photodegradation upon UV light irradiation and has been reported as a potential candidate for positive working resist material. We thought that introduction of the UV chromophoric silicon-silicon moieties into aromatic polyamides and polyimides would give photosensitive polymers with additional advantages such as high T_g and thermal stability. The present work describes one such successful attempt using a new diamine, bis(p-aminophenyl)-tetramethyldisilane (I), obtained by the hydrolysis of 1,2-bis{[N,N-bis(trimethylsilyl)amino]phenyl}tetramethyldisilane which was previously synthesised by the reaction of 1,2-dichlorotetramethyldisilane and 4-[N,N-bis(trimethylsilyl)-amino]phenyllithium. The diamine had an absorption at 262 nm with a ϵ_{max} value of 3.6×10^4 .

Polymer Synthesis and Characterization: Polyamides III and polyimides VI were obtained by reacting I with various aromatic diacid chlorides II and dianhydrides IV according to equations 1 and 2, respectively.



The polymers were characterized by IR, NMR, and elemental analysis. The yields of the polyamides and the polyamic acids were above 85% and the inherent viscosity values were between 0.27 and 0.85 dL/g (Table).

Table. Synthesis and Thermal data of polymers III, V and VI

polymer code	yield (%)	η_{inh}^a (dL/g)	polymer code	Tg ^b (°C)	Ti ^c (°C)	
					in air	in N ₂
IIIa	99	0.70	IIIa	238	390	390
IIIb	85	0.27	IIIb	194	390	375
IIIc	90	0.31	IIIc	-	385	405
IIId	90	0.42	IIId	-	400	400
IIIe	95	0.35	IIIe	-	400	405
Va	99	0.85	VIa	-	410	421
Vb	99	0.69	VIb	255	448	464
Vc	100	0.52	VIc	235	419	426
Vd	100	0.82	VIId	250	392	379

a) Measured in DMAc at 30°C (0.5dL/g)

b) Measured on DSC at a rate of 10°C/min.

c) Initial degradation temp. measured on TG at 10°C/min.

Polyamides IIIa-d were soluble on heating in polar solvents such as NMP, DMF, and m-cresol. Polyamide IIIe was also soluble in pyridine, THF, CHCl₃ and acetone. The Polyamic acids Va-d were soluble in pyridine, DMAc, NMP and DMF. After imidization, polyimide VIId possessing diphenyl sulfone unit was found to be more readily soluble in the above mentioned solvents. The polymers had Tg's between 194 and 255°C and were stable up to 375°C in both air and N₂ atmospheres (Table).

Photodegradation Studies: The DMAc solution of polymer IIIe showed a decrease in both viscosity and molecular weight upon UV light irradiation. Polyamic acids Va-d and soluble polyimide VIa also showed a similar behavior, while a reference polyamic acid synthesised from pyromellitic dianhydride (PMDA) and bis(p-aminophenyl) ether (ODA) showed no such decrease. This suggests the cleavage of the silicon-silicon bonds present in the polymers III, V and VI during UV light irradiation.

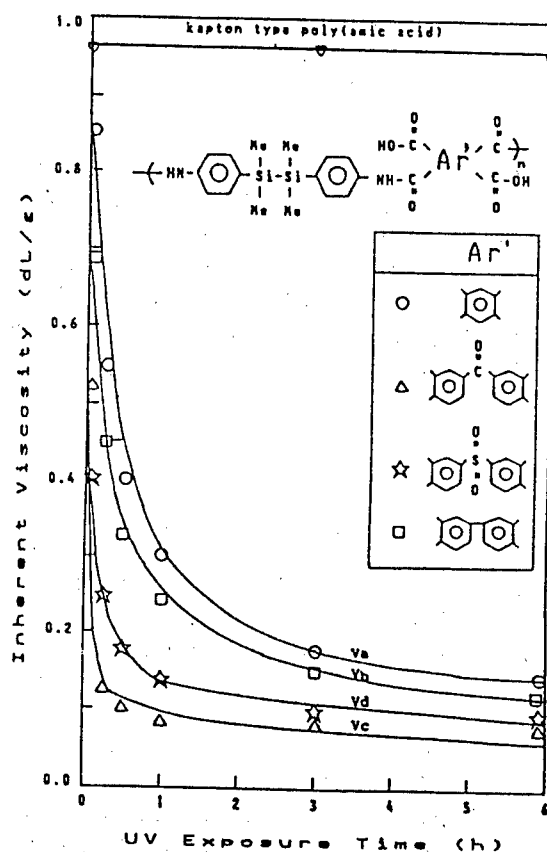


Fig. Effect of UV light irradiation on the inherent viscosity of polymer V in DMAc.

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J. Appl. Polym. Sci., 34, 2445, (1987)

PRESENT STATUS OF i-LINE LITHOGRAPHY

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1. Introduction

It is well recognized that photolithography is one of the most important technologies in the manufacture of LSIs. This technology has progressed with the advancement of ICs in the order: contact/proximity, 1:1 projection and reduction projection printing. In particular, g-line (436 nm) reduction projection steppers have greatly advanced and are widely used in LSI industry. To make further progress, many attempts are being made.

As well known, the resolution (R) and depth of focus (D) of a reduction projection stepper are expressed as:

$$R = k_1 \lambda / NA \quad (1)$$

$$D = k_2 \lambda / (NA)^2, \quad (2)$$

where k_1 and k_2 are constants depending on resist materials and their process parameters, λ is the wavelength of irradiation light, and NA is the numerical aperture of the lens. These equations show that there are two features for improving the performance of steppers. One is improvement in the optical system, which corresponds to the optimizations of λ and NA. The other is improvements in resists and their processes, which are, as mentioned above, directly related to k_1 and k_2 .

2. Steppers

Equation (1) indicates that both shortening λ and enlarging NA are effective for improving the resolution. It is, however, obvious in view of the depth of focus, that is, from Eq. (2) that shortening λ is superior to enlarging NA. Therefore, i-line (365 nm) lithography has, in principle, an advantage over g-line lithography.

As a matter of fact, however, i-line steppers were inferior to g-line ones because of lack of high quality i-line lens systems and because the i-line technology was "young". In recent years, the quality of i-line lens systems has been greatly advanced by continuous efforts to improve lens materials and related technologies.

Now, i-line steppers capable of resolving 0.6 μ m patterns are commercially available and further advancement will be expected in the near future. Several LSI manufacturers began to introduce i-line steppers in their production lines.

3. Resists

As explained above, resists also play an extremely important role in lithography. i-line resists have been improved with the appearance of advanced i-line steppers. Now, many kinds of i-line resists are commercially available. In addition, many methods for improving resolution and depth of focus such as contrast enhanced lithography, multilayer resist systems, phase-shifting mask method, etc. have been devised. We can, therefore, expect further improvement by the combination of these techniques with advanced resists. Following this introductory talk, the details on the newest i-line resists will be presented by leading resist suppliers.

4. Summary

The status of i-line lithography has been briefly reviewed. Both g-line and i-line lithographic technologies are probably employed in manufacturing advanced LSIs. The latter technology is, however, still "young", in which some room remains for improvement and we can expect further progress in it.

High Resolution Positive Resist for i-Line Lithography

Y.Yamamoto, S.Itami, Y.Masaki, R.Yoshizawa

CHISSO PETROCHEMICAL CORPORATION

5-1,GOIKAIGAN,ICHIHARA-CITY
CHIBA,JAPAN

Features

"CPR-17001" has been developed as a high resolution resist for i-Line lithography by CHISSO PETROCHEMICAL CORPORATION.

"CPR-17001" is composed of a novolak type resin and a naphthoquinone diazide type sensitizer, which is applied to i-Line and shows high resolution on submicron lithography.

Characteristics of CPR-17001

Resist Property

Resolution	0.4 μm
Sensitivity	116 mJ/cm ²
Heat Proof	140 °C (3 μm Line)

Process Condition

Exposure	NSR-150516A(NA0.45)
Pre-Bake Temp.	80 °C / 90 sec
PEB Temp.	100 °C / 90 sec
Developer	TMAH-aq
Developing Condition	23 °C / 60 sec

Application

Positive Resist for i-Line, high resolution lithography with high sensitivity and good heat proof.

Yoshiaki Yamamoto

I-LINE POSITIVE PHOTORESISTS: FH-6100 AND FHi-3100
(FUJI HUNT ELECTRONICS TECHNOLOGY CO. LTD.)

Shinji Sakaguchi, Kazuya Uenishi and Tadayoshi Kokubo
Research Laboratory of Yoshida-minami Factory, Fuji Photo Film Co. Ltd.
4000 Kawashiri, Yoshida-cho, Haibara-gun, Shizuoka, Japan 421-03

The following two series of i-line positive photoresists have been developed and are available from Fuji Hunt Electronics Technology Co.Ltd.

FH-6100 is an i-line / g-line compatible resist which performs well with advantages of high contrast and particularly of high photospeed. The resist provides good resolution as well as good depth of focus with both of the exposure tools and is suitable for g/i-mixed match process.

FHi-3100 is an advanced i-line resist which exhibits excellent resolution and profile. The resist has low A and B values at 365 nm. The values are reduced down to 0.55 and 0.02 respectively, which are very close to the values typically used at g-line processes. This allows the resist to generate steep side-wall angle, small contact hole and to have reduced optical bulk effect.

These resists were formulated using a novel PAC backbone which was designed to give high transparency at 365 nm. The structure of the PAC has been adequately optimized in view of resist dissolution discrimination which contributes strongly to the quality of the resulting image.

Processing Condition:

Substrate: Silicon
Resist Thickness: 1.20 μ
Soft Bake: 80°C 90 sec.
PEB: 110°C 60 sec.
Development:
TMAH 2.38% 60 sec.
Single puddle

Performances:

(by Hitachi LD-5010i; NA=0.40)
=== 0.6 μ Geometry ===

Resist	FH-6100	FHi-3100
Photospeed (Eopt)	120	210 mJ/cm ²
Mask Linearity	0.50	0.47 μ
1:1 Resolution	0.47	0.45 μ
CD change: $\pm$ 10% E	0.06	0.05 μ
DOF (L/S): $\pm$ 10% CD	2.5	3.0 μ
DOF(Hole): $\pm$ 10% CD		2.5 μ
Side-wall Angle	85	88 deg.

SEM Pictures of FHi-3100:
(by Nikon 1505i6A; NA=0.45)
210 mJ/cm²

Geometries
(μ)
0.60



0.50



0.45



0.40



JSR HIGH RESOLUTION I-LINE POSITIVE
PHOTORESIST - PFR IX SERIES -

Y.YUMOTO, M.EBISAWA, and T.MIURA

Japan Synthetic Rubber Co., Ltd.,
Development Center
100 Kawajiri-cho, Yokkaichi, Mie, 510 JAPAN

We present a newly developed i-line positive photoresist with highly lithographic performance.

The most technological problem in i-line positive photoresists composed of novolac resins and naphotoquinonediazides based photoactive compounds (PAC) is known to be more poor photobleaching characteristics compared with that in g-line exposure. PAC derived from conventional benzophenone have significant absorbance around 365 nm even after exposure.

Thus, We have applied a none-benzophenone structure as a starting material of PAC. And We also have designed novolac resins to match the new PAC. The monomer(not m-/p-cresol), molecular weight, molecular weight distribution and so on, have been investigated detail. As a result, a high resolution i-line positive photoresist has been developed by the most suitable composition of the new PAC and resin. This new i-line positive photoresist has high resolution capabilities and good profile even at half-micron patterns shown in Fig.1, and also the wide process latitude.

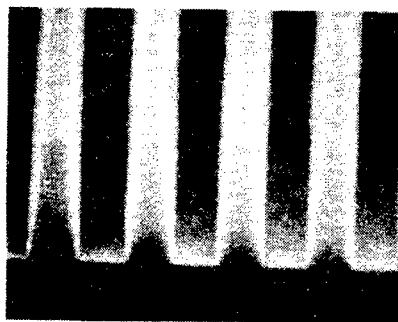


Fig.1.SEM photograph of $0.40\mu\text{m}$
L/S patterns obtained by i-line
exposure (NA=0.45).

Half Micron I-Line Processing Using EL 2015

D. W. Johnson, E. Shalom
MACDERMID INCORPORATED
WATERBURY, CT 06702 USA

M. Kataoka
TORAY INDUSTRIES, INC.
OTSU-SHI, SHIGA, 520 JAPAN

Abstract

ULTRAMAC^R PR1024MB developed by MacDermid, Inc. was the first i-line resist for high resolution applications using the emerging i-line lithographic equipments. This product is still used by a number of equipment vendors for qualifying their i-line and mid-UV equipment, as well as being used for the development of eximer laser equipment and processes. It is also widely known that this resist has low thermal properties and does not hold up well in aggressive etch process. These needs led to the development of MacDermid's ULTRAMAC^R EL 2015 positive photoresist series. This is a high contrast high resolution photoresist series based on the same chemical concepts used in the PR 1024MB resists. This new resist contains a 2,1,5-naphthoquinone diazide sulfonate ester of a special novolak resin as its photoactive component. EL 2015 is a versatile positive resist uniquely optimized for g-, h-, i-, and broad band exposure tools. The broad benefits of this product can be ascribed to its complete bleachability upon exposure down to 320nm. This product also uses ethyl lactate as the coating solvent for improved safety. Resolution of better than 0.50 μ m has been routinely obtained with current 0.40 NA i-line steppers and 0.40 μ m resolution at best focus, EL 2015 contrast greater than 4 can be obtained in standard type metal ion free developers. A focus latitude of greater than 1.5 μ m for 0.5 μ m images with an exposure latitude of 10-20% has been demonstrated on i-line equipment. Resolution of better than 1 μ m has also been obtained in almost 2 μ m of resist using standard scanning projection equipment. Finally, the thermal stability and plasma etch resistance of EL 2015 has been found to be far superior to our older PR 1024MB and comparable to current high resolution g-line photoresists.

M CPR i 100

Yasuhiro Kameyama, Tomoyo Yamada and Tameichi Ochiai
Mitsubishi Kasei Corporation Research Center
1000, Kamoshida-cho, Midori-ku, Yokohama, 227, Japan

Sensitivity ¹⁾	210 mJ/cm ²
Resolution	0.40 μ m
CD Linearity ²⁾	0.45 μ m
Depth of Focus ³⁾	± 0.75 μ m

Table 1. Evaluated Results of
M CPR i 100
(Film Thickness: 1.17 μ m; NA=0.45)
1) Fig 1. ; 2) Fig 2. ; 3) Fig 3.

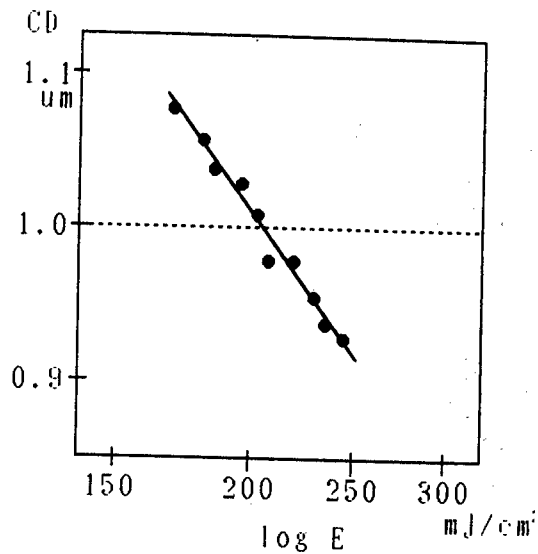


Fig 1. CD vs. log E
(1.0 μ m l/s)

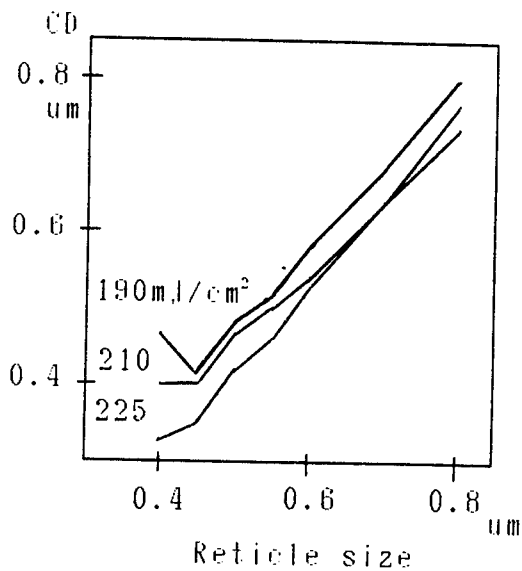


Fig 2. CD Linearity

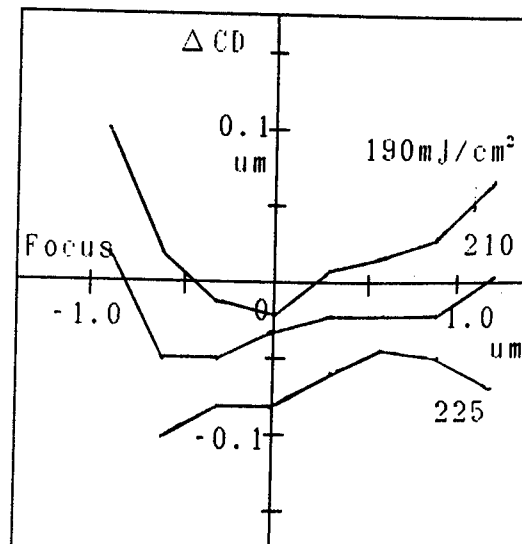


Fig 3. CD vs. Focus
(0.5 μ m l/s)

NAGASE High Resolution Resist A 1 8 E X

TAKESI KOTANI , YUTAKA SAITO, YOSHIAKI HORIUCHI

NAGASE ELECTRONIC CHEMICALS Ltd. 236 Nakai Tatuno City Hyogo JAPAN

Recently, devices with half micron structure is tried using both i and g-line stepper. To generate half-microne level pattern, the photoresist will be required capability of 0.4μ resolution. And it is necessary that non-linear optical responsibility is given to resist to achieve this requirement. We started to develop resists with high resolution at the view point of three items below.

- (1) Lower dissolution rate of the resist surface.
- (2) To reduce resist optical parameter B .
- (3) Excellent stability of long time storage.

To give these characteristics to resist, we selected novel PAC(Photo Active Compound) system different from conventional PAC and novolac resin.

The characteristics of NPR A 1 8 E X are shown below.

- (1) Excellent resolution, 0.4μ l/s pattern is generated using i-line or g-line high NA stepper.
- (2) Rectangular Profile, smaller CD variation between top and bottom is also expected on contact hole.
- (3) Wider process margin, especially concerning with exposure and development.
- (4) High performance on the topographical substrate, good step coverage, steep profile. When used as a dyed resist ,this resist is very useful .
- (5) Excellent storage stability, compared with other conventional PAC system.

Table 1 shows the ability of NPR A18EX1 and SEM's photos show the profile exposed by i-line stepper. By using NPR A18EX1, the device which has 0.5μ design rule can be manufactured sufficiently. However, with NA going up ,the problem of DOF (Depth Of Focus) becomes more serious, besides the request to other process margin would be severe. As there is much possibility of optimization for NPR A18EX, so the improvement of performance can be expected.

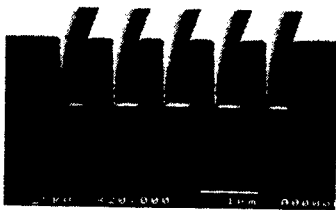


Fig 1 NPR A18EX1 SEM of 0.45μ L/S pattern in 1.2μ resist thickness with NSR1505i6A (NA=0.45).

Table 1 NPR A18EX properties in 1.2μ resist thickness with NSR1505i6A (NA=0.45).

	A 18EX1	A 18EX2* ¹
Eth (msec)	280	180
E ₀ (msec)	550	360
Resolution (μ)	0.4	0.4
DOF (μ) at 0.5μ l/s	± 0.9	± 0.9
Profile	Rectangular	Rectangular
Heat resistance ($^{\circ}$ C)	130	130

*¹ sensitivity up version of EX1

HIGH RESOLUTION POSITIVE I-LINE RESIST " SUMIRESIST[®] PFI-15 "

Makoto Hanabata

Sumitomo Chemical Co.,Ltd. Osaka Research Laboratory,3-1-98,Kasugadenaka,
 Konahana-ku,Osaka City,Osaka 554,Japan.

Sumiresist[®] PFI-15 is a positive i-line resist designed for use in the
 manufacture of 4-16 megabits DRAM class devices.

Sumiresist[®] PFI-15 has excellent lot-to-lot quality consistency,because all
 of the raw materials are produced by Sumitomo Chemical Co.,Ltd. itself and
 the evaluation of each lot is made with our new evaluation machines.

Advantages of Sumiresist[®] PFI-15

(1) High resolution

A resolution of as high as 0.45 μ m(with N.A.=0.40) and 0.40 μ m(with
 N.A.=0.45) is obtained with mask linearity.

(2) Wide focus latitude

Sumiresist[®] PFI-15 keeps good resolution even under defocused conditions
 with its wide focus latitude.

(3) Scumless sub-micron hole

Sumiresist[®] PFI-15 can make a scumless sub-micron hole with its large
 solubility change between exposed and unexposed parts.

(4) High heat resistance

This good heat resistance gives a good dry etching durability.

(5) Usable without PEB(Post Exposure Bake)

Although PEB is recommended as a standard process,Sumiresist[®] PFI-15
 can also be used without PEB.

(6) Usable with g-line(436 nm) exposure

Sumiresist[®] PFI-15 can be used with g-line exposure with high resolution
 and wide focus latitude.

Characteristics

Sensitivity	Eth	90mJ/cm ²
	E _{0p} (0.6 μ m L/S=1)	200 mJ/cm ²
Resolution(Mask	Linearity)	0.45 μ m
Focus Latitude	0.60 μ mL/S	$\pm$ 1.8 μ m
	0.50 μ mL/S	$\pm$ 1.2 μ m
	0.45 μ mL/S	$\pm$ 0.9 μ m

Above values are obtained under following conditions.

Exposure	: N.A.=0.40 i-line stepper
Development	: 60sec,puddle, SOPD(produced by Sumitomo Chemical)
Prebaking	: 90°C,60sec
Post Exposure Bake	:110°C,60sec
Film Thickness	:12550Å

TSMR-365i Series I-Line Resist

Kobun Iwasaki
Tokyo Ohka Kogyo Co., Ltd.
1-403, Kosugi-cho, Nakahara-ku, Kawasaki, 211, Japan

It has been conventionally considered that i-line and deep UV resists are positive photoresists composed with use of 4-diazoquinone. By utilizing the material for g-line photoresists to make i-line photoresists, TOK has succeeded in the development of the first domestic g-line & i-line dually applicable resist.

At present, TOK is manufacturing and marketing TSMR-365i series (for silicon and silicon dioxide) and TSMR-CRi series (for highly reflective substrates) as i-line photoresists.

Among these photoresists now available in the market, I would like to introduce the properties of our photoresists within my main emphasis on TSMR-365iB photoresist.

Flexible and Highly Adhesive Polyimide for Printed Circuit

Yasunori Sugita

Mitsui Toatsu Chemicals, Inc.
2-5, Kasumigaseki, 3-chome Chiyoda-ku, Tokyo, Japan

Features

- Polyimide ; it has excellent flexibility, high thermo-stability, good bond strength and dielectric properties.
- By being laminated directly onto the commercially available copper foils, this polyimide shows the excellent peel strength and durability.
- Therefore, it is widely applicable for printed circuits.

Characteristics

- As shown in Table 1, the film of this polyimide has better flexibility and tear strength than Kapton®.
- Electric properties are comparable to Kapton®.
- As shown in Table 2, the adhesion of the polyimide to copper foil is highly superior to ODA/PMDA derived polymer with maintaining the above mentioned mechanical properties of film.
- It is able to laminate film onto copper foil by casting method without any special surface treatment of copper foil, and the FCL(Flexible Copper Laminate) has an excellent bond strength as shown in Table 1.

Applications

- FCL • Flexible or metal based copper clad laminates
- Insulation coating for electric wire or shield wire

Table 1 ; Film Properties

Items	Unit		Method
Tensile Strength	[Kg/mm ²]	14	IPC-TM-650 2 · 4 · 9
Elongation	[%]	120	IPC-TM-650 2 · 4 · 9
Young's Modulus	[Kg/mm ²]	300	
Initiation Tear Strength	[g]	1,310	IPC-TM-650 2 · 4 · 16
Propagation Tear Strength	[g]	18	IPC-TM-650 2 · 4 · 17
Tg	[°C]	340	
Dielectric Constant (1MHz)		3.0	JIS C 6481
Dissipation Factor (1MHz)		0.007	
Volume Resistivity	[Ω cm]	>10 ¹⁶	IPC-TM-650 2 · 5 · 17

Table 2 ; FCL Properties

Items	Unit		Method
Bond Strength			
---as is	[Kg/cm]	>1.5	IPC-TM-650 2 · 4 · 9
---after 85 °C, 80%RH 1,000Hours	[Kg/cm]	>1.5	IPC-TM-650 2 · 4 · 9
---after 155°C 240Hours	[Kg/cm]	>1.5	IPC-TM-650 2 · 4 · 9
Flexural Fatigue (0.8mm mandrel) (500gr load)	[cycles]	750	JIS C 5016

POLYIMIDE FOR INTERLAYER DIELECTRICS

Mitumasa Kojima

Hitachi Chemical Co., Ltd. Yamazaki Works

4-13-1, HIGASHI-CHO, HITACHI, IBARAKI 317, JAPAN

Hitachi chemical is a pioneer of polyimides for electric components and IC devices, and can provide many kind of characteristic polyimides, particularly interlayer dielectrics.

Features and Characteristics

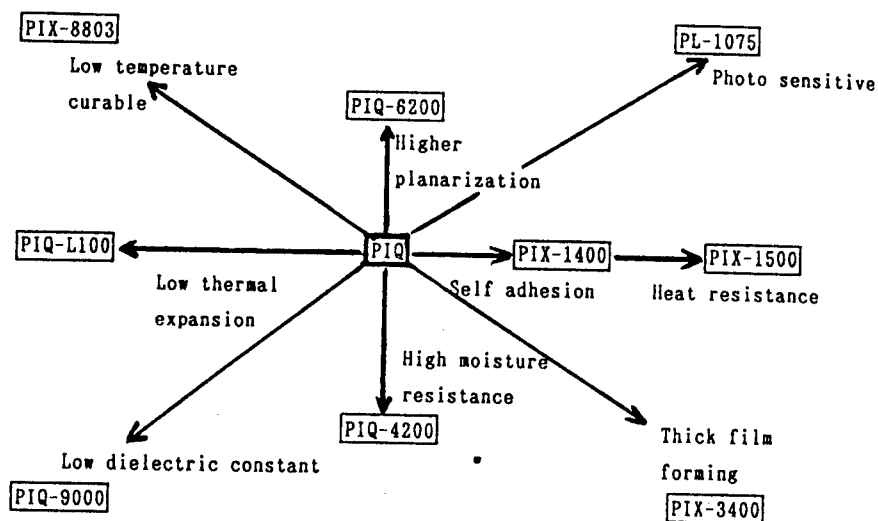


Table 1 Characteristics of New products

Product name	Property
PIQ-L100	Thermal expansion coefficient: $3 \times 10^{-6} / ^\circ\text{C}$
PIQ-6200	Solid content : 40 %
PIQ-9000	Dielectric constant : 2.7
PIX-8803	Curing temperature : 230 $^\circ\text{C}$
PL-1075	Resolution : $2 \mu\text{m}$

Application

- Inter layer dielectrics
- Buffer coating
- α -ray protection

POLYIMIDE ALIGNMENT FILM FOR LIQUID CRYSTAL DISPLAYS

HIROYOSHI FUKURO

Polymer Research Laboratory, Nissan Chemical Ind., Ltd.
11-1 Goiminamikaigai Ichihara-city Chiba-pref, Japan

1. Features

In high information liquid crystal(LC) displays, such as STN or TFT modes, polyimide materials play important roles in obtaining the stable molecular alignments of liquid crystals (LC). The polyimides, SUNEVER series, are widely utilized for these LC displays, their features are as follows:

- 1) Good transparency for visible light
- 2) Good printability
- 3) Pretilt angle controllable in the wide range of $0^{\circ}\sim 90^{\circ}$ with polyimide molecular designs
- 4) Generation of higher pretilt angle at a lower curing temperature ($\leq 200^{\circ}\text{C}$) for color LC displays
- 5) High RC-time for a TFT mode application

2. Characteristics & Applications

Characteristics of the typical polyimides for LC displays are shown in the following table:

polyimide	cure temp. ($^{\circ}\text{C}$)	pretilt (deg)	RC-time (sec)	Appl.
General PI	250	<2	<1	TN
SE-150	250	5	4	STN
SE-4110	250	6~7	-	STN
SE-610	250	8~10	-	STN
SE-7111	170	5~6	-	color STN
RN-733	170	5~8	-	color STN
RN-713	170	2	7	TFT
RN-718	170	5~6	7~8	TFT
RN-722	170	90	-	

LOW POLARIZATION POLYIMIDE FOR SEMICONDUCTOR DEVICES

TOYOHICO ABE

Polymer Research Laboratory, Nissan Chemical Ind., Ltd.

11-1 Goi Minamikaigan, Ichihara-city, Chiba-pref, Japan

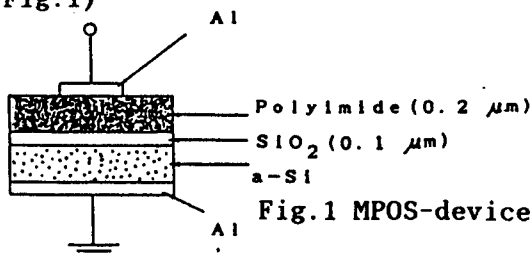
1. Features

Polyimides, having high thermal stability, are used for various insulation films of electronic devices. But Polyimides have one unsuitable property that they are polarized under high voltage. To solve this problem we have developed new type polyimides "RN-series", which have low polarization and high insulation properties under higher electric field. RN-812 is a standard type, and RN-809 is a low thermal expansion type. These polyimides also have superior transparency and colorless properties. Furthermore, they give excellent adhesivity to glass or silicon and can be easily patterned with posi-type resist, so they are useful for insulation films for semiconductor devices.

2. Characteristics

(1) Low polarization properties were tested by using MPOS model device

(Fig.1)



*Capacitance-Voltage curve of RN-812 shows no hysteresis. (Fig.2)

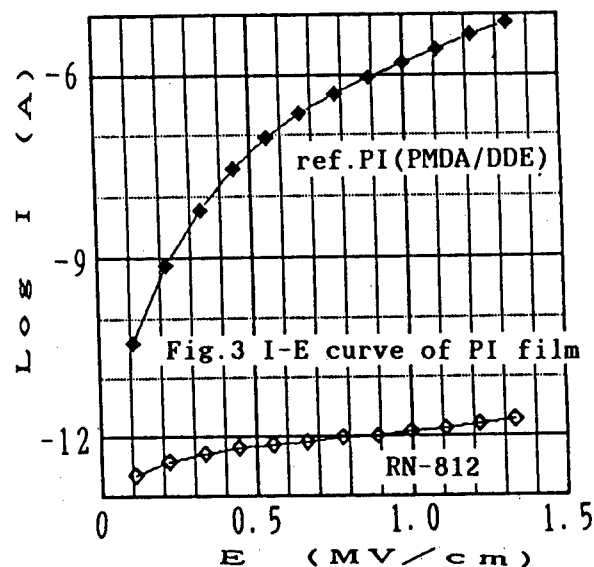
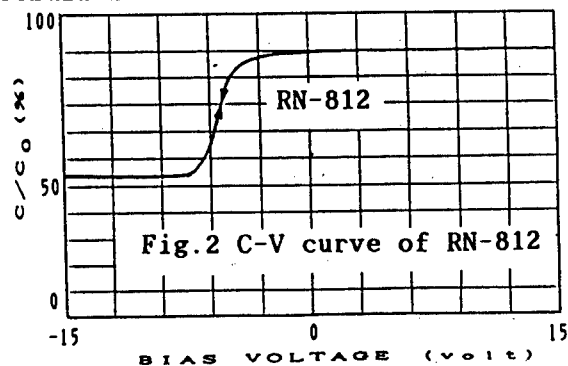
(2) High insulation properties were tested by measuring leak current through about $0.5\mu\text{m}$ film (Fig.3)

*Leak current of RN-812 is negligible under higher electric field.

3. Application

Interlayer insulation

Passivation film, Buffer coating



POLYIMIDES HAVING EXCELLENT ADHESION PROPERTY FOR MICROELECTRONICS

N.SASHIDA

SUMITOMO BAKELITE CO., LTD. - Fundamental Research Laboratory
495 Akiba-cho, Totsuka-ku, Yokohama, Kanagawa, 245 JAPAN

1, FEATURE

We have been developed two types of polyimides having excellent adhesion property for microelectronics. They are called "SUMIRESIN EXCEL CRC-6061 and 6081".

CRC-6061 contains siloxane units in Aromatic Polyimide backbone. For this reason, CRC-6061 can have excellent adhesion strength to SiO₂ and other materials for use in microelectronics without adhesion promoter. Naturally, CRC-6061 maintains inherent characteristics of the Aromatic Polyimides, such as heat resistance, and so on.

CRC-6081 is a photosensitive type polyimide. Direct patterns can be produced using common photolithography. Furthermore, CRC-6081 has high photosensitivity and good resolution by means of our novel photoinitiating system. CRC-6081 also has excellent adhesion strength, mechanical, electrical and thermal properties.

2, APPLICATIONS

Applications of CRC-6061 and 6081 include the following

- Passivation and buffer layer
- Interlayer dielectrics
- α -particle barrier

TABLE 1 Adhesion Property ¹⁾

Materials	CRC-6061	CRC-6081
SiO ₂	0/100	0/100
SiN	0/100	0/100
Al	0/100	0/100
Molding Compound ²⁾	0/100	0/100

1) Cellophane tape test(JISD-0202)
Count the number of separation
/Total,
After PCT(125 C/1.3atm)20hr

2) EME-6300

TABLE 2 Typical Properties of CRC-6061 and 6081

Test Items	Items	CRC-6061	CRC-6081
Physical			
Tensile Strength	kg/mm ²	12.0	11.0
Tensile Elasticity	kg/mm ²	280	270
Thermal			
Heat Decomposition Temp.	°C	550	550
Thermal Expansion Coefficient	ppm/°C	35	40
Electrical			
Volume Resistivity	Ω cm	1×10^{16}	1×10^{16}
Dielectric Constant	(1MHz)	3.5	3.5
Photoreactivity ¹⁾			
Sensitivity	mJ/cm ²	none	7
Resolution	μ m	none	5

1) thickness; 5 μ m (after curing)

A PHOTSENSITIVE LOW MODULUS POLYIMIDE

HIROSHI MAEDA

CHISSO CORPORATION

2, KAMARIYA-CHO, KANAZAWA-KU
YOKOHAMA, JAPAN

Features

PSI-P8351X has been developed as one of grades of PSI series by Chisso Corporation. This product is provided as a coating material for stress buffer of semiconductor devices.

PSI-P8351X has a low tensile modulus resulting from incorporation of siloxane segments into its molecule, which will bring the stress caused by the molding compound decrease in its application.

In addition PSI-P8351X has photoimageable characteristics.

Characteristics of PSI-P8351X

Varnish

Solvents	4-Butyrolactone/cyclopentanone
Solids	17-20 wt%
Viscosity	1000-2000 cps

Film properties

Tensile Modulus	90 Kg/mm ²
Tensile Strength	3.5 Kg/mm ²
Elongation	15%
Pencil Hardness	H
Thermal Decomposition temperature	320°C
Thermal Expansion Factor	$2.7 \times 10^{-4} \text{ }^{\circ}\text{C}^{-1}$
Volume Resistivity	$10^{12} \Omega \cdot \text{cm}$
Dielectric Constant (1KHz)	3.1

Photosensitive properties

Type	Negative type
Exposure energy	320 mJ/cm ²

Application

Coating material for stress buffer

**"PIMEL" PHOTSENSITIVE POLYIMIDE COATINGS
FOR ELECTRONICS**

S.Ogitani
Central Laboratory
Asahi Chemical Industry Co., Ltd.
Samejima 2-1, Fuji-shi, Shizuoka-ken Japan

Our photosensitive materials have been actually used in mass productions of semiconductor manufacturing, applied to buffer coatings and interlayer dielectrics. In addition, we've been developing new types of photosensitive polyimide which have unique characteristics. Here, both our existing grade "*G-6246S*" and newly developed "*Low Stress Photosensitive Polyimide*" are presented.

PIMEL™ G-6246S

The PIMEL™ G-6246S was designed to meet requirements of good adhesion to substrates and high amenability not only to mercury full spectrum but also to g-line only. This grade can allow us to obtain a high quality polyimide film stably through similar photolithographic procedure to those in the case of normal negative-working photoresist.

Feature (in case of final thickness = 5 μ m)

- Short Bake Time : 3 min. on Hotplate
- High Photospeed : 300mJ/cm² with g-line stepper
200mJ/cm² with contact aligner
- High Resolution : Aspect Ratio = 1 (via hole)
- Excellent Adhesion : PCT 1000 hr.< , @121 °C, 2atm, 100%R.H.
- High Tensile Strength : 150MPa<
- High Thermal Resistance: 450 °C

LOW STRESS POLYIMIDE

The low stress polyimide film will release you from stress-crack problem caused by the difference of the coefficients of thermal expansion. This new material is processed by almost the same manner as that of G-6246S except that the puddle development is employed.

Feature (in case of final thickness = 5 μ m)

- High Photospeed : 300mJ/cm² with g-line stepper
- High Resolution : Aspect Ratio 1< (via hole)
- High Tensile Strength : 240MPa<
- High Elongation : 15%<
- High Thermal Resistance: 510 °C
- Low Coefficient of Thermal Expansion : 8-10ppm
- Low Dielectric Constant: 2.9, @1kHz

PHOTOSENSITIVE POLYIMIDE FOR ELECTRONIC DEVICES
- "Photoneece"UR-4144 -

Masaya Asano
Toray Industries, Inc. Electronic and Imaging Materials Res. Labs.
2-1, Sonoyama 3-chome, Otsu-shi, Shiga, Japan

Features

A newly developed photosensitive polyimide, "Photoneece" UR-4144, can be easily patterned by conventional photolithographic process, for example by using ordinary wafer processors. "Photoneece"UR-4144 have the following features;

- o Easily cured (350 °C is sufficient for curing to get excellent film properties and adhesion; independent of curing atmosphere)
- o Low Young's modulus ($\sim 210 \text{ kg/mm}^2$)
- o Excellent adhesion to silicon substrates and molding compounds.

Characteristics

"Photoneece"UR-4144 have various kinds of characteristics, some of which are exemplified as follows;

- o High photosensitivity ($100 \sim 200 \text{ mJ/cm}^2$, g-line stepper)
- o High resolution (10 μm via holes can be resolved in 5 μm cured film)
- o Excellent physical and electrical properties of cured film (shown in table 1)

Application

"Photoneece"UR-4144 is the specially designed photosensitive polyimide coating for various kinds of electronic devices and is especially suitable for the following applications;

- o Buffer coatings and interdielectrics for LSI
- o Multilayer thin-film packages for computers
- o Line photosensors, thermal heads, etc.

Table 1 Film Properties

Properties	Item	Units	Typical Values
Mechanical	Tensile Strength	kg/mm^2	10
	Elongation	%	10
	Young's Modulus	kg/mm^2	210
Thermal	Melting Point	°C	None
	Glass Transition Temperature(Tg)	°C	280
	Coefficient of Thermal Expansion	1/°C	4.5×10^{-5}
Electrical	Dielectric Constant	(1kHz, 25 °C)	3.3
	Dissipation Factor	(1kHz, 25 °C)	0.002
	Volume Resistivity	$\Omega \text{ cm}$	1.0×10^{17}
	Surface Resistivity	Ω	10^{16}
	Dielectric Strength	kV/mm	250

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