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PYRALIN

POLYIMIDE COATINGS FOR ELECTRONICS

David Kleinfeld
Room 6H-424
ATT Bell Laboratories
600 Mountain Avenue
Murray Hill, N.J. 07974

Bulletin #PC-6 Rev. 4/82

T-9035 THINNER

T-9035 is a highly purified thinner, filtered through a 0.2 μ absolute filter and controlled to less than 1 ppm sodium. It is designed to provide excellent processing properties without unusual handling problems.

Processing advantages are:

- Thin Films 1500A – Pinhole free
- Minimizes edge crawlback
- Excellent surface wetting
- Good shelf stability even with high dilution ratios
- Compatible for use with all PYRALIN* polyamic acid solutions.

TYPICAL USE

T-9035 thinner is used to reduce viscosity and solids content of PYRALIN solutions to obtain desired film thickness. For example, diluting 1 part PI-2555 with 2 parts T-9035 yields 1500A films on a 3" silicon wafer spun at 5000 rpm.

The thinned solution should be allowed to age 12 hours at 70°F before use. This time is needed for the solution to reach equilibrium conditions. T-9035 does not need to be stored in a refrigerator, but mixed solutions should be stored in a refrigerator after the initial 12 hour aging period.

T-9035 is hygroscopic so it is critical that mixed solutions be brought to room temperature before opening container to avoid moisture condensation. Moisture can attack and degrade the polyamic acid polymer in the PYRALIN formulations.

TOXICITY/HEALTH HAZARDS

Adequate ventilation must be provided and skin contact should be avoided. Exposed areas should be flushed with water immediately.

Rubber gloves resistant to the solvents in PYRALIN Polyimide Coatings can be procured as follows: for general-purpose use, the "Buta-Sol" milled butyl rubber glove (Norton Company, Safety Products Division, P.O. Box 4367, Charleston, SC 29405); for light service, the "Wil-Gard" No. 26-640 tan latex industrial glove (Edmont-Wilson Division, Becton Dickinson and Company, 1300 Walnut Street, Coshocton, OH 43812); and for service requiring greater resistance to wear, the Natural Latex Rubber glove No. 2911 (B.F. Goodrich Engineered Systems, 500 S. Main Street, Akron, OH 44318).

Data supplied by the General Aniline and Film Corporation indicate that animals exposed to air saturated with N-methyl-2-pyrrolidone for six hours daily for ten days tolerated the conditions of the experiment and gained weight normally. Other animals subjected to 20-day dermal toxicity studies had no specific degenerative changes and did not have a remarkable degree of skin irritation.

Note that this material also contains 2-ethoxyethanol (cellosolve).

AVAILABILITY

Available in one-half kilo, one-kilo or four-kilo containers from:

Du Pont Company
F&F Department
85 Mill Plain Road
Fairfield, Connecticut 06430
Attn: B.T. (Brian) Lynch.
Phone: (203) 259-3351, Ext. 247.

For additional technical information, call:

V.S. (Vic) Bowers
(302) 774-0259,
Telex #83-5420
Cable address: FABFINISHES

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*Du Pont Trademark

E-47927 Printed in U.S.A.

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PYRALIN™

POLYIMIDE COATINGS FOR ELECTRONICS

Bulletin #PC-23
(E-52138)
4/82

PRODUCT SPECIFICATION
T-9035 THINNER

TEST	T-9035	TEST METHOD
Density (25°C)	0.97 ± 0.1 g/cc	Du Pont TM II G
Solvent System	NMP/Cellosolve 50/50 ± 3%	Du Pont TM II D
Chloride Content*	4.0 ppm max.	Du Pont TM II C
Sodium Content*	0.5 ppm max.	Du Pont TM II B
Potassium Content*	0.3 " "	
Copper Content*	0.05 " "	
Iron Content*	0.03 " "	
Filtration	0.2 micron abs.	

*Based on total sample.

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DU PONT

PYRAL

POLYIMIDE COATINGS FOR ELEC

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Room 6H-424
ATT Bell Laboratories
600 Mountain Avenue
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Bulletin #PC-15 Rev. 4/82

CLEAN-UP PROCEDURE FOR PYRALIN* FORMULATIONS

Polyamic acid may pose clean-up problems primarily because it is not soluble in most common organic solvents. The recommended solvent for clean-up is NMP (N-methyl-2-pyrrolidone). NMP can be used to clean up metal screens, metal catch basins and glassware without harm to those items. It is recommended that after cleaning with NMP, a mixture of 50/50 NMP/acetone (or isopropyl alcohol) be used to clean and dry the items.

NOTE: When using glassware with PYRALIN, simply place the glass item to be cleaned under running tap water until a milky white film develops. At this point, pour off the water and lift out the conforming film and deposit in a wastebasket. Caution: This will not work with metal containers.

PYRALIN polyamic acid can be disposed of by incineration. If the waste PYRALIN is mixed with photoresist, as in a spinning operation using the same spinner, the waste can be disposed of in like manner. It is not advisable to bury the waste because of the possibility of solvent leakage into groundwater.

Glass, polyethylene, polypropylene and stainless steel are suitable container materials when NMP solvents are involved.

TOXICITY/HEALTH HAZARDS

Adequate ventilation must be provided and skin contact should be avoided. Exposed areas should be flushed with water immediately.

Rubber gloves resistant to the solvents in PYRALIN Polyimide Coatings can be procured as follows: for general-purpose use, the "Buta-Sol" milled butyl rubber glove (Norton Company, Safety Products Division, P.O. Box 4367, Charleston, SC 29405); for light service, the "Wil-Gard" No. 26-640 tan latex industrial glove (Edmont-Wilson Division, Becton Dickinson and Company, 1300 Walnut Street, Coshocton, OH 43812); and for service requiring greater resistance to wear, the Natural Latex Rubber glove No. 2911 (B.F. Goodrich Engineered Systems, 500 S. Main Street, Akron, OH 44318).

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NMP can be obtained from local chemical supply houses or in larger quantities from GAF Corp., Dyestuff & Chemical Division, 140 West 51 Street, New York, NY 10080.

Printed in U.S.A.

**Du Pont
Semiconductor
Materials**

E. I. du Pont de Nemours & Co. (Inc.)
Photosystems & Electronic Products Department
Electronic Materials Division
Barley Mill Plaza, Reynolds Mill Building
Wilmington, DE 19898

Tel: 1-800-441-7543
TWX: 835420

Dear Customer:

As requested, enclosed are copies of Material Safety Data Sheets for specific products.

If you have any questions, please call on 800-441-7543.

Very truly yours,

L. M. Schafer

L. M. Schafer

LMS:ivd
Enclosure

David Kleinfeld
Room 6H-424
AT&T Bell Laboratories
600 Mountain Avenue
Murray Hill, N.J. 07974

L SAFETY 04/23/82
SHEET PI 2555
TO OSHA-20)

***** SECTION I *****

TRADE NAME/SYNONYMS
N.A.

MANUFACTURER
E. I. DU PONT DE NEMOURS & CO., INC
F & F DEPARTMENT
WILMINGTON, DE 19898

TELEPHONE
(302) 774 2421

CHEMICAL FAMILY
BROWN POLYIMIDE RESIN

FORMULA
PI 2555 801024

***** SECTION II - HAZARDOUS INGREDIENTS *****

SOLVENT	APPROX WT %	TLV (PPM)
AROMATIC PET DIST	16	100
METHYL PYRROLIDONE	65	25

***** SECTION III - PHYSICAL DATA *****

APPROX BOILING RANGE (F)
302-395
VAPOR PRESSURE PRINCIPAL SOLVENT (MM HG)
<1.0
VAPOR DENSITY PRINCIPAL SOLVENT (AIR=1)
3.40
SOLUBILITY IN WATER
Miscible
APPEARANCE AND ODOR
SEMI-VISCOUS LIQUID WITH CHARACTERISTIC ODOR
SPECIFIC GRAVITY (WATER=1)
1.049
PERCENT VOLATILE BY VOLUME
85.86
EVAPORATION RATE
SLOWER THAN ETHER

***** SECTION IV - FIRE & EXPLOSION HAZARD DATA *****

FLASH POINT (METHOD)
BETWEEN 100 - 140 F (CC)

APPROX FLAMMABLE LIMITS	LEL	UEL
	1.10	7.00

EXTINGUISHING MEDIA
FOAM, CARBON DIOXIDE, DRY CHEMICAL
SPECIAL FIRE FIGHTING PROCEDURES
WATER FROM FOG NOZZLES MAY BE USED TO COOL
CLOSED CONTAINERS TO PREVENT PRESSURE BUILD-UP.

PROTECTIVE GLOVES
    PROLONGED OR REPEATED CONTACT
EYE PROTECTION
    USE SAFETY EYEWEAR
OTHER PROTECTIVE EQUIPMENT
    USE APPROPRIATE INDUSTRIAL HYGIENE PRACTICES

***** SECTION IX - SPECIAL PRECAUTIONS *****

PRECAUTIONS TO BE TAKEN IN HANDLING AND STORING
    KEEP AWAY FROM HEAT, SPARKS AND OPEN FLAME.
    CLOSE CONTAINER AFTER EACH USE. DO NOT STORE ABOVE 120 F.
OTHER PRECAUTIONS
    WASH THOROUGHLY AFTER HANDLING AND BEFORE EATING OR SMOKING
    OBSERVE LABEL PRECAUTIONS. CONTAINERS SHOULD BE GROUNDED WHEN POURING.

NOTICE FROM DUPONT

THESE DATA RELATE ONLY TO THE SPECIFIC MATERIAL DESIGNATED HEREIN AND DO NOT RELATE TO USE IN COMBINATION WITH ANY OTHER MATERIAL

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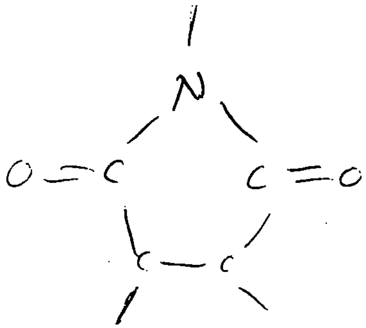
Basic Chem

PHOTODEFINEABLE POLYIMIDES: CHEMISTRY AND PROCESSING

R. S. BENTSON AND J. L. MARKHAM



imide ring

APPLICATIONS FOR POLYIMIDES

PROPERTIES OF POLYIMIDES

POLYIMIDE CHEMISTRY

POLYIMIDE PROCESSING

APPLICATIONS OF POLYIMIDES

α PARTICLE PROTECTION

PASSIVATION

MECHANICAL PROTECTION

MOISTURE BARRIER

INTERLAYER DIELECTRIC

DIE BONDING

PLANARIZATION

PROPERTIES OF POLYIMIDES

FILM FORMATION

HIGH T_G

HIGH THERMAL STABILITY (400°C)

LOW DIELECTRIC CONSTANT (3.5)

GOOD CHEMICAL RESISTANCE

PURITY

RELIABILITY

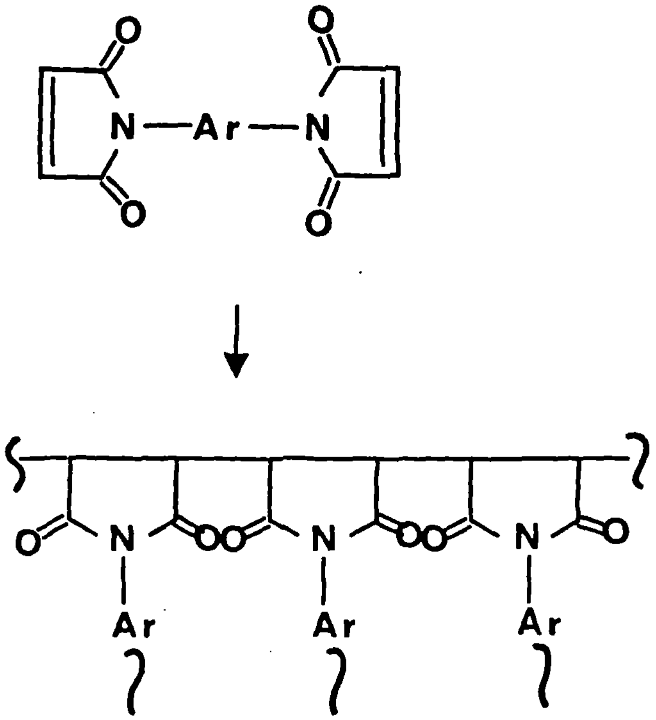
THREE TYPES OF POLYIMIDES

ADDITION POLYIMIDES

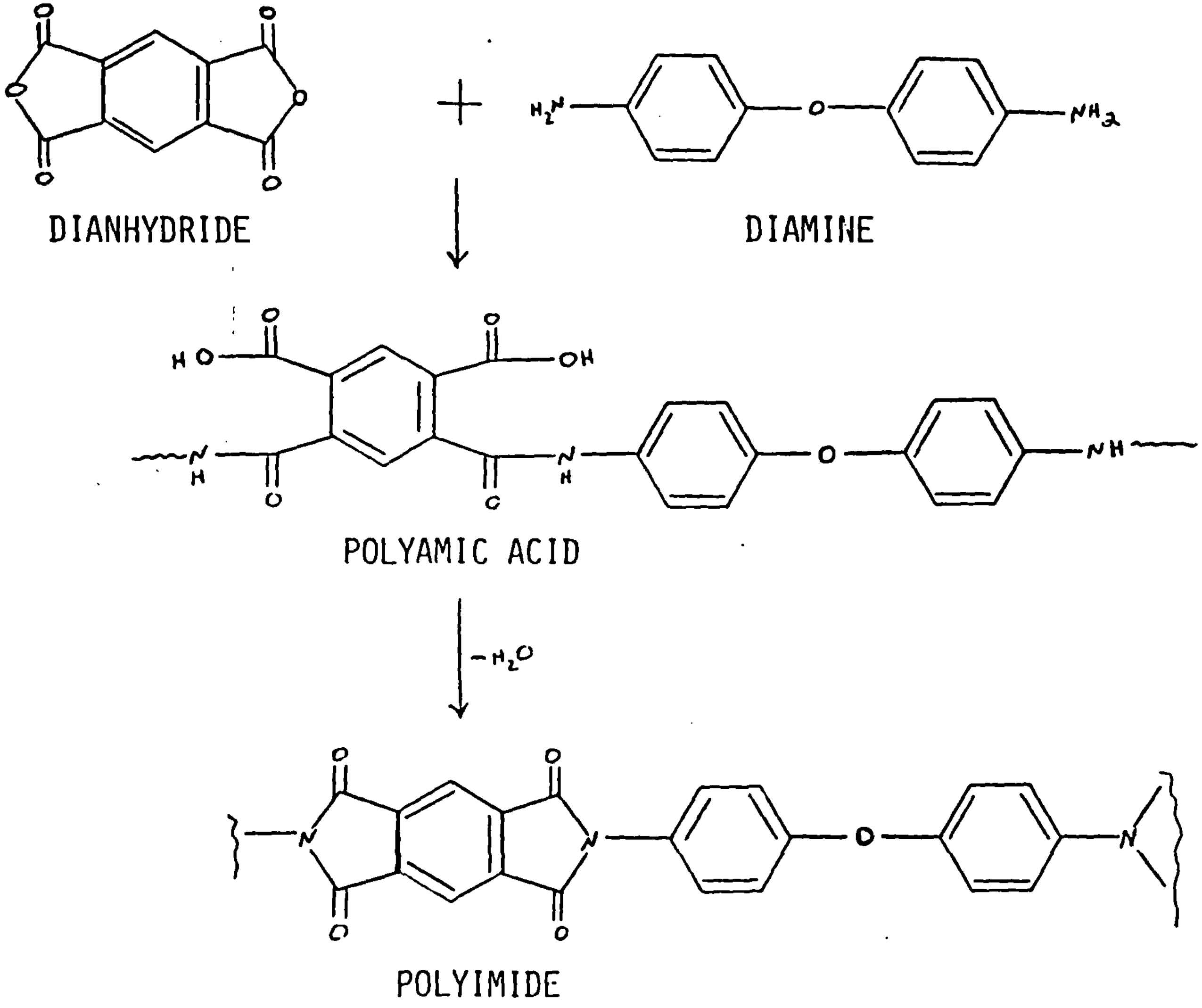
CONDENSATION POLYIMIDES

PRE-IMIDIZED POLYIMIDES

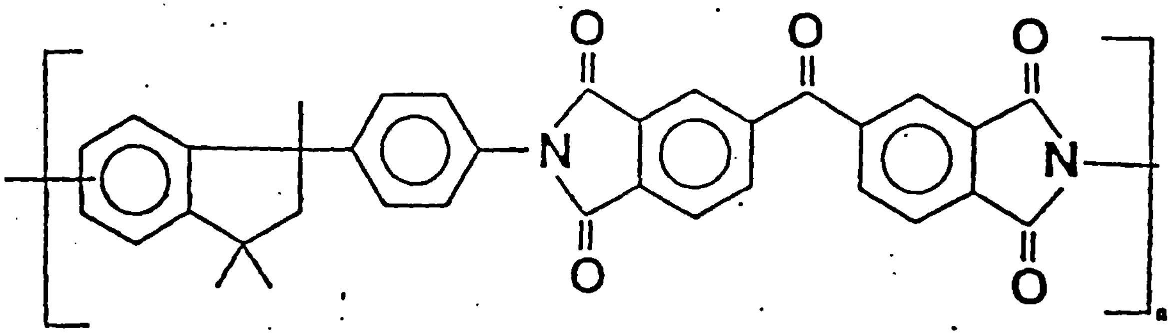
BISMALEIMIDE



POLYIMIDE CHEMISTRY

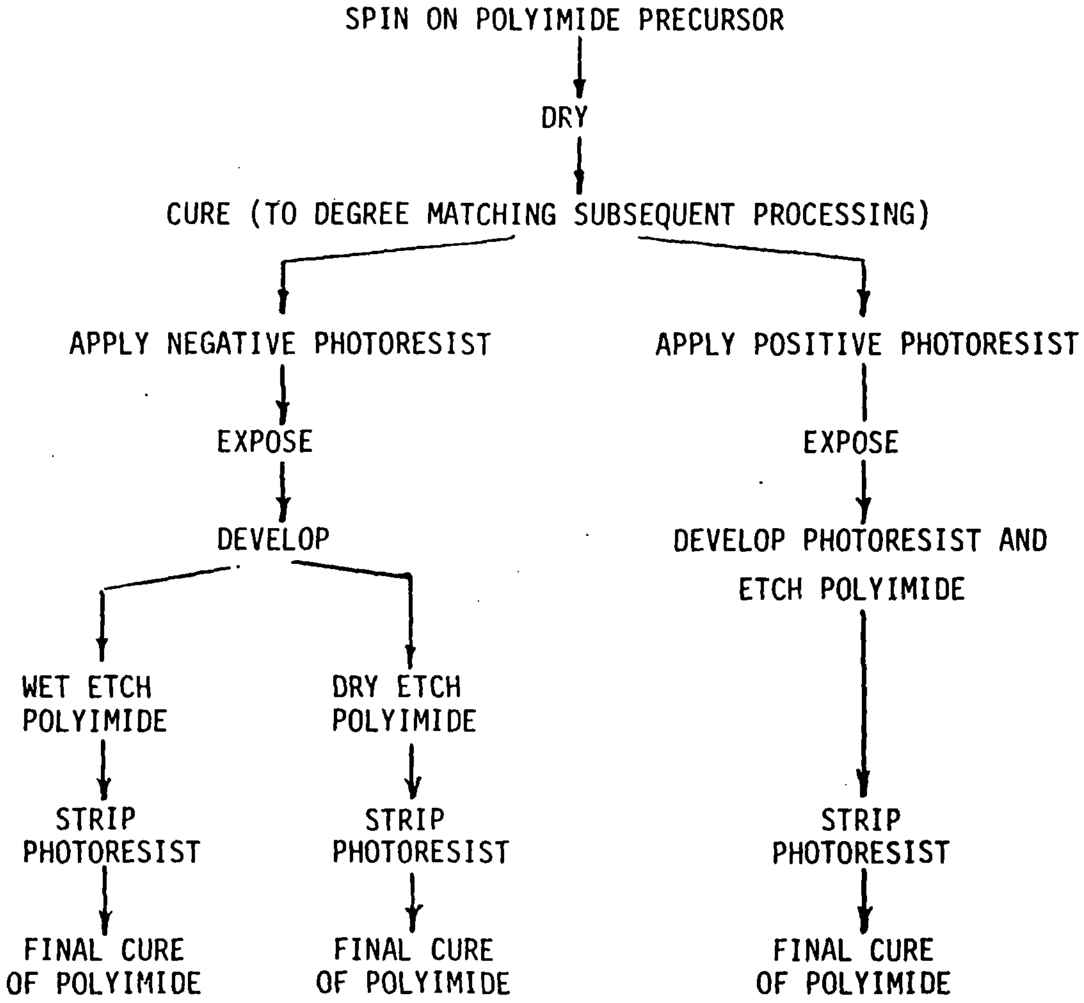


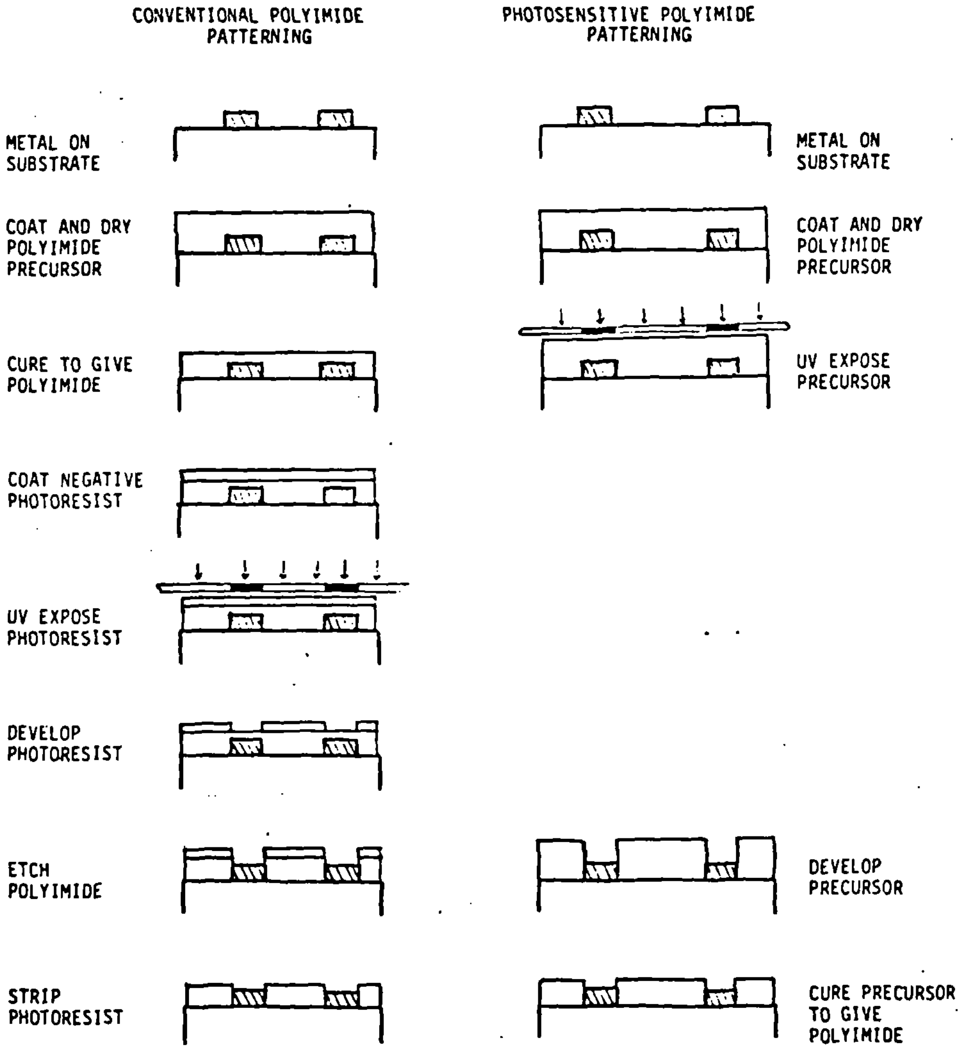
CIBA-GEIGY



POLYIMIDE XU 218

CONVENTIONAL POLYIMIDE PROCESSING




CONVENTIONAL POLYIMIDE PATTERNING
PHOTOSENSITIVE POLYIMIDE PATTERNING
METAL ON SUBSTRATE
METAL ON SUBSTRATE
COAT AND DRY POLYIMIDE PRECURSOR
COAT AND DRY POLYIMIDE PRECURSOR
CURE TO GIVE POLYIMIDE
UV EXPOSE PRECURSOR
COAT NEGATIVE PHOTORESIST
UV EXPOSE PHOTORESIST
DEVELOP PHOTORESIST
ETCH POLYIMIDE
DEVELOP PRECURSOR
STRIP PHOTORESIST
CURE PRECURSOR TO GIVE POLYIMIDE

PHOTOSENSITIVE POLYIMIDE PROCESS SEQUENCE

ADHESION PROMOTER

COAT POLYIMIDE PRECURSOR

PREBAKE TO REMOVE SOLVENTS

UV EXPOSURE

DEVELOPMENT

CURE

COMPARISON OF PHOTOSENSITIVE POLYIMIDES

MATERIAL	SENSITIZER	SOLVENT	DEVELOPER	ADHESION PROMOTER
HITACHI PL-1000	AZIDE (N_3)	NMP	NMP	ALUMINUM OXIDE
EM SELECTILUX HTR-2	ACRYLATE & INITIATOR	NMP/ CYCLO-PENTANONE 1:1	CYCLO-PENTANONE ISOPROPANOL	VINYL SILANE
DUPONT PIH 71710	ACRYLATE & INITIATOR	NMP/ CELLOSOLVE	BUTYROLACTONE/ TOLUENE 1:1	AMINO SILANE
TORAY PHOTONEECE UR 3140		NMP/METHYL CELLOSOLVE	DV-500	AMINO OR EPOXY SILANE

ADHESION PROMOTERS

EM CHEMICALS SELECTILUX HTR-2:

VINYL SILANE; SPIN COAT; AIR BAKE @ 130°C FOR 15 MIN.

DUPONT PIH 71710:

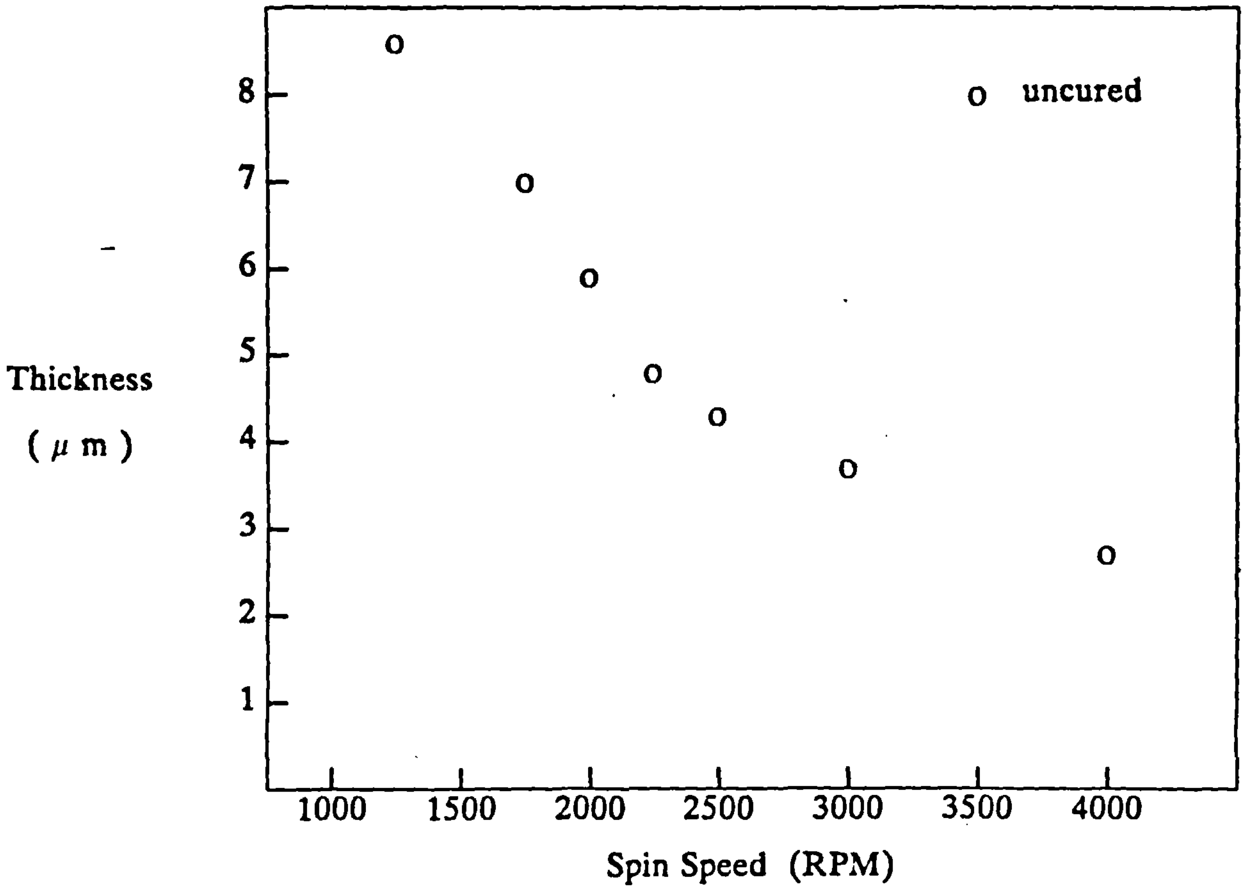
AMINO SILANE; SPIN COAT

HITACHI PL 1000

ALUMINUM CHELATE; SPIN COAT; AIR BAKE @ 350°C FOR 30 MIN.

STORE UNDER N_2

DELIVERY TO SUBSTRATE THROUGH FILTER UNDER LOW PRESSURE N_2



PL 1000: SPIN SPEED vs THICKNESS

SUBSTRATE COATING

THICKNESS COATED DEPENDANT ON:

- SPIN SPEED
- VISCOSITY

VISCOSITY CAN BE ADJUSTED WITH SOLVENT BUT NOT ALWAYS STABLE

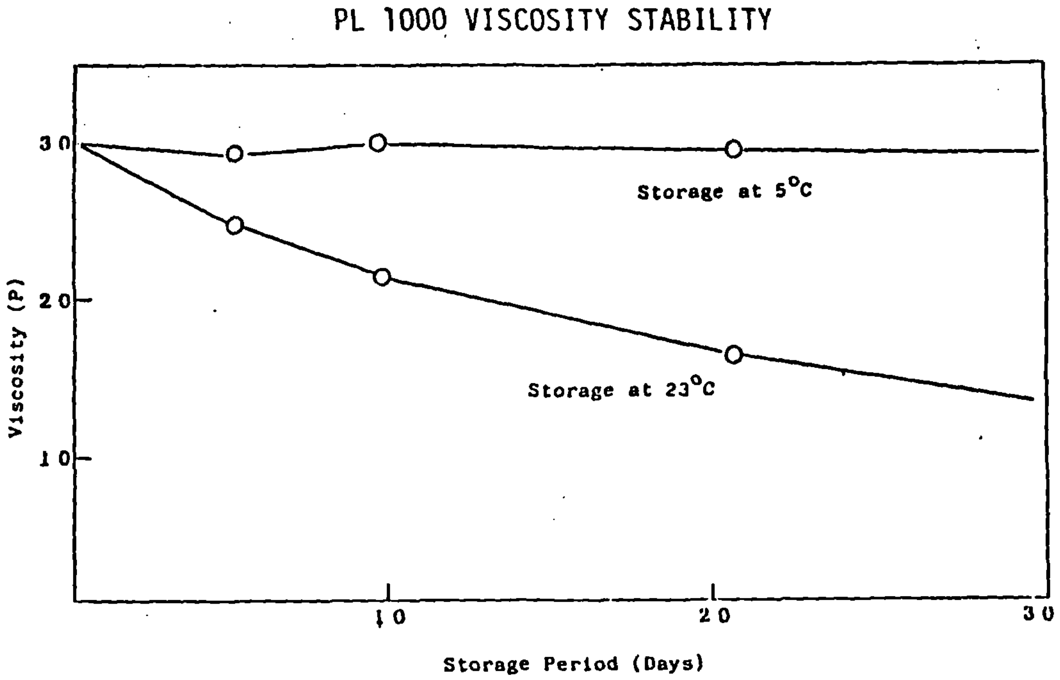


Fig. 5. Storage stability of PL-1000

PREBAKE METHODS

OVEN HEATING

IR HEATING

HOTPLATE HEATING

PREBAKE CONDITIONS TO ACHIEVE A DRIED FILM 4μM THICK OF:

EM SELECTILUX HTR-2

PREBAKE 2 HOURS AT 65°C

DUPONT PIH 71710

PREBAKE 90 MIN. AT 55°C

HITACHI PL 1000

PREBAKE 45 MIN. AT 70°C

UV EXPOSURE

EM CHEMICALS SELECTILUX HTR-2

80 MJ/CM^2/μM THICKNESS

DUPONT PIH 71710

FOR A 4μM THICK COATING $\approx$ 30 SEC. @ 5 MW/CM^2

HITACHI PL 1000

FOR A 4μM THICK COATING $\approx$ 12 SEC. @ 5 MW/CM^2

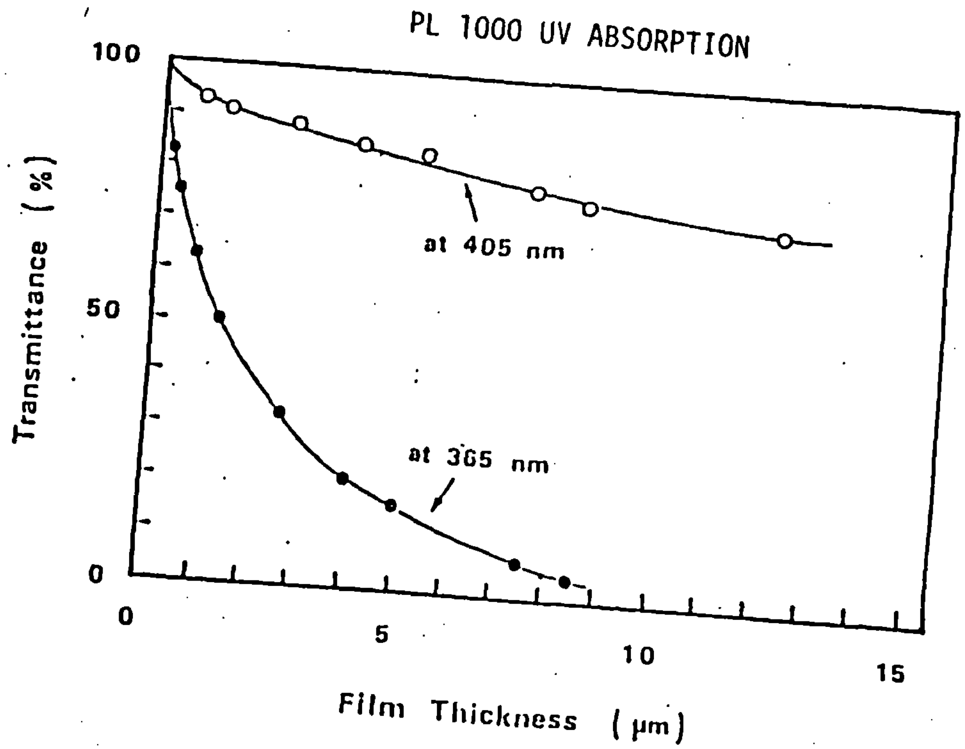
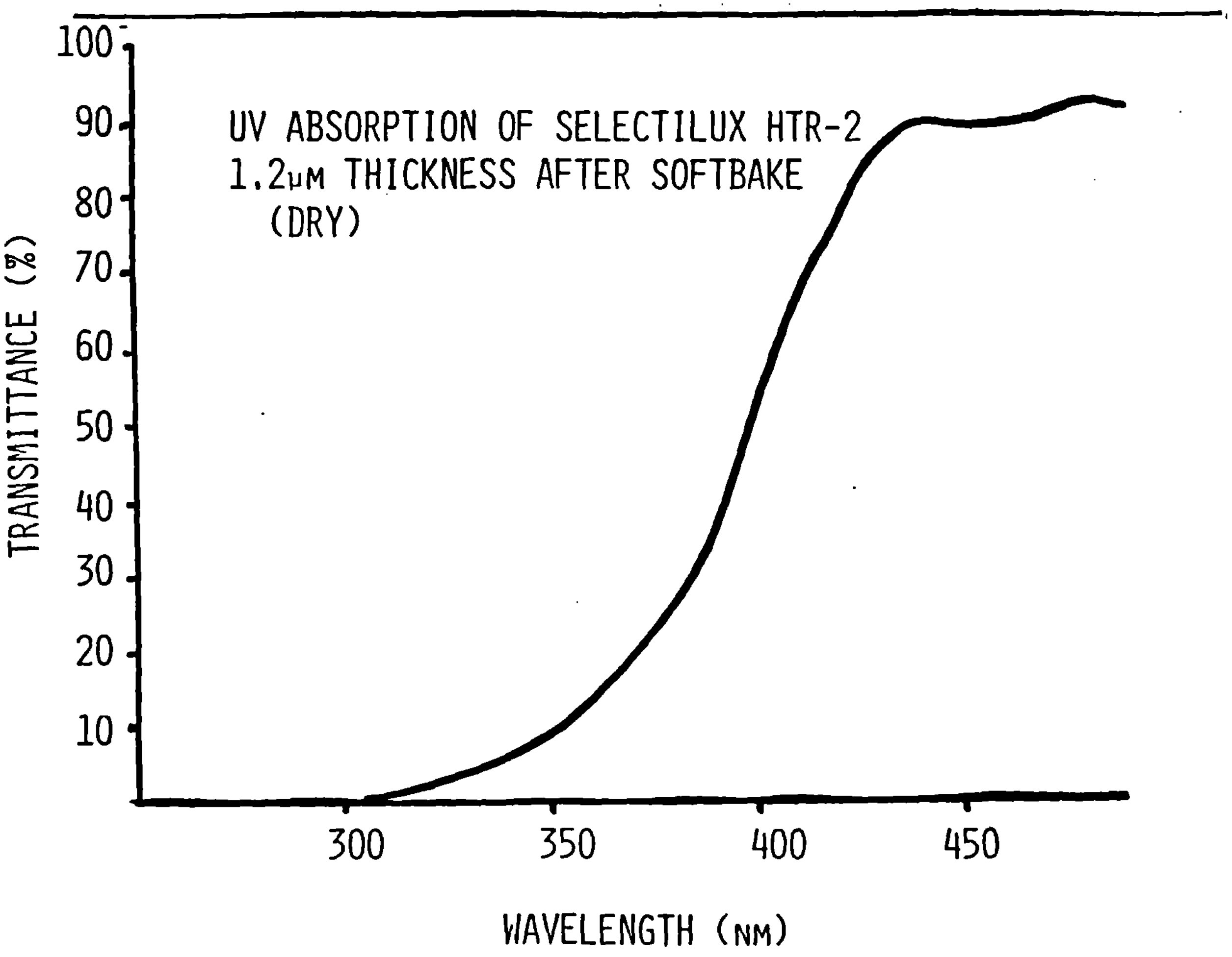


FIGURE DEPENDENCE OF FILM THICKNESS FOR THE UV ABSORPTION OF PAL.



UV ABSORPTION OF SELECTILUX HTR-2
1.2μM THICKNESS AFTER SOFTBAKE
(DRY)

PATTERN DEVELOPMENT
FOR 4μM DRIED FILMS

SELECTILUX HTR-2

CYCLOPENTANONE AND ISOPROPANOL

$\approx$ 20 SEC.

DUPONT PIH 71710

BUTYROLACTONE AND TOLUENE

$\approx$ 15 SEC.

HITACHI PL 1000

N-METHYL PYRROLIDONE

$\approx$ 8 MIN.

THICKNESS LOSS DUE TO DEVELOPMENT

SELECTILUX HTR-2	≈ 5%
PIH 71710	≈ 2%
PL 1000	≈12%

DATE PREPARED ______

SPEAKER ______

MEETING ______

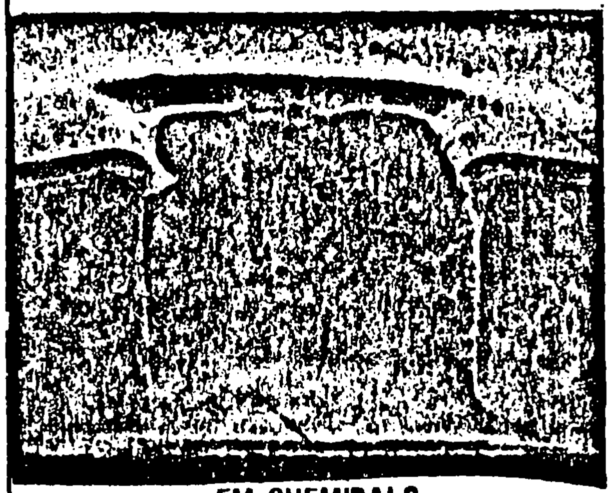
DATE ______

SPEAKER ______

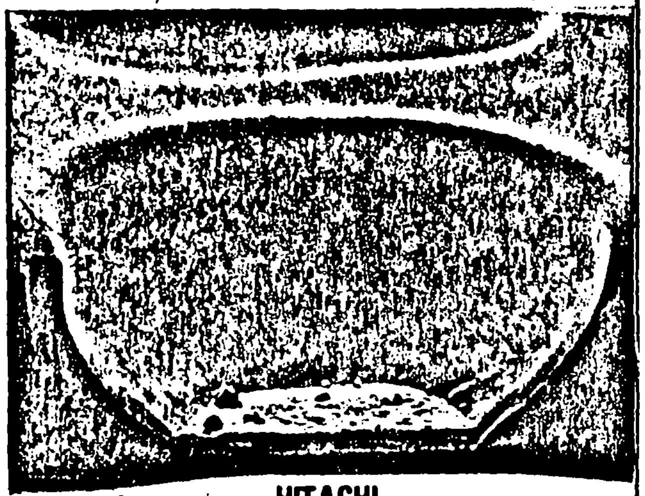
MEETING ______

DATE ______

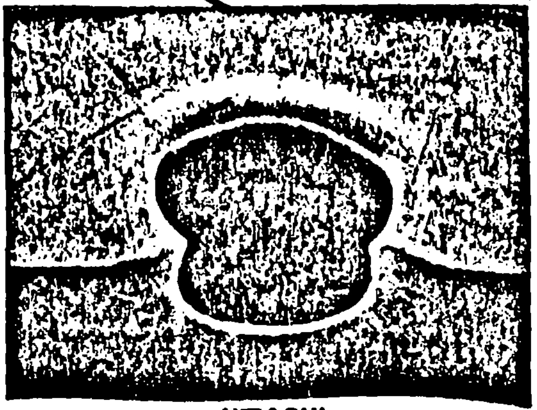
NOTES



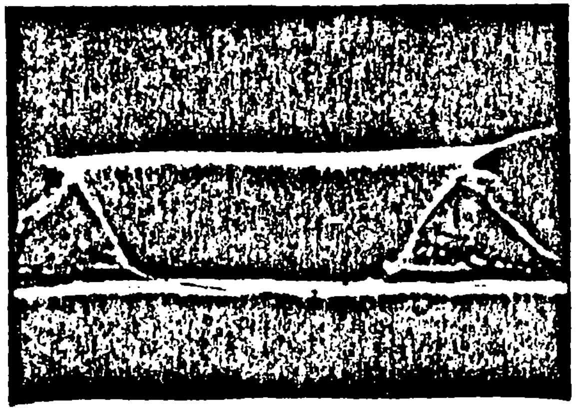
EM CHEMICALS
SELECTILUX HTR-2



HITACHI
PL 1000



HITACHI
PL 1000



HITACHI
PL 1000

AT&T TECHNOLOGIES, INC. - PROPRIETARY
Use pursuant to Company Instructions

H-7438

AT&T Technologies

CURE CONDITIONS FOR
PHOTOSENSITIVE POLYIMIDES

$200^{o}C$ IN AIR 30-60 MIN.

$400^{o}C$ IN N_2 60 MIN.

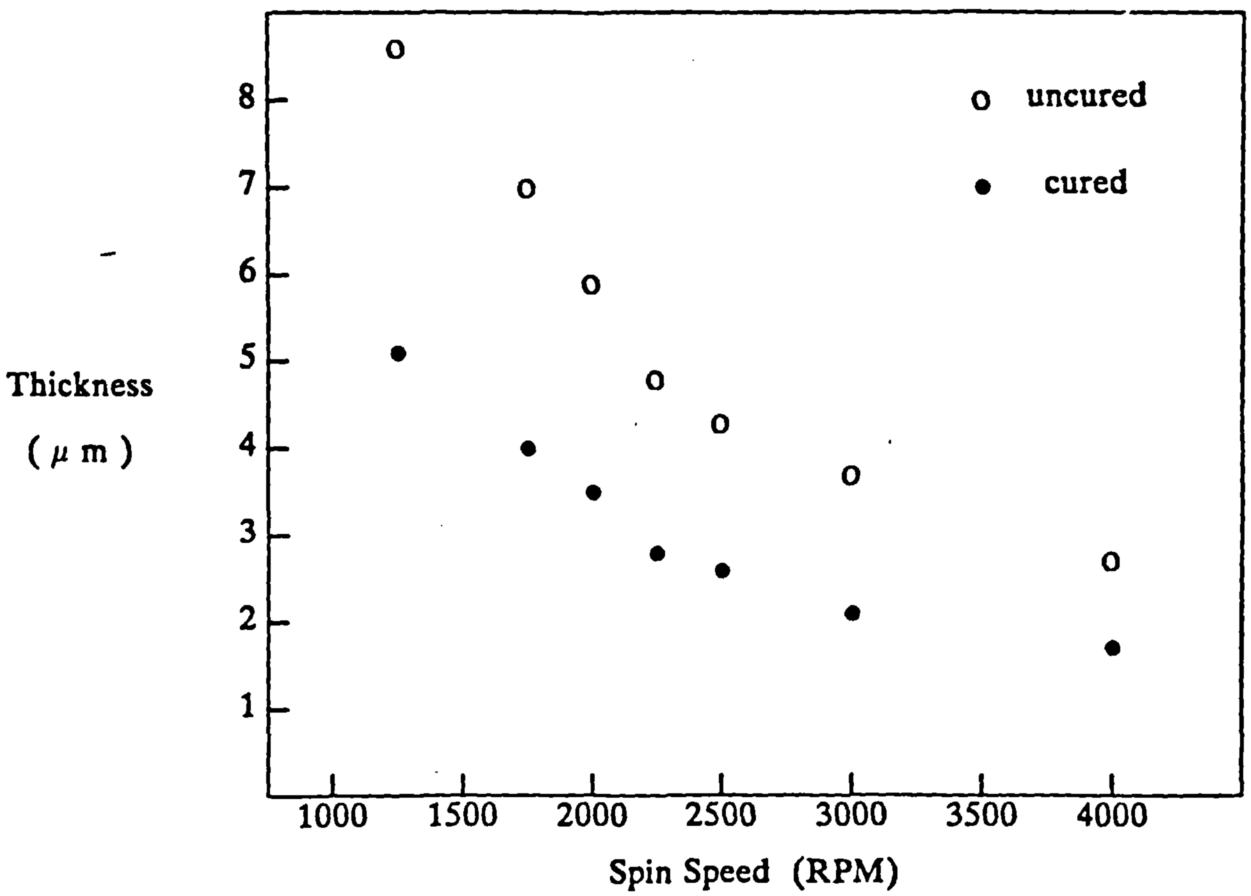
THICKNESS LOSS DURING DEVELOPMENT AND CURE

SELECTILUX HTR-2:

DEVELOPMENT LOSS	CURE LOSS	TOTAL
≈ 5%	≈ 60%	≈ 62% OF DRIED THICKNESS

PL 1000:

DEVELOPMENT LOSS	CURE LOSS	TOTAL
≈10%	≈ 40%	≈ 46% OF DRIED THICKNESS



PL 1000: SPIN SPEED vs THICKNESS

CAREFUL PROCESS CONTROL IS NECESSARY TO OBTAIN:

- UNIFORMITY OF DESIRED COATING THICKNESS
- PREBAKE UNIFORMITY
- DEVELOPMENT UNIFORMITY

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PYRALIN

POLYIMIDE COATINGS FOR ELECTRONICS

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Murray Hill, N.J. 07974

Bulletin #PC-7 Rev. 4/82

VM-651 ADHESION PROMOTER

VM-651 is an organosilane which is used to improve the adhesion of all types of PYRALIN* polyimide coatings to wafers (Si or SiO_2 surfaces). VM-651 is easy to apply and effective at very low concentrations. Among all the organosilanes that possess either amino or epoxy groups, alpha-amino propyltriethoxysilane was found to give the best and most consistent overall results.

Table I shows the experimental results when this silane compound is used as the adhesion promoter. These results show that the adhesion is not affected when the concentration of silane varied between .01% and .1%. No difference in adhesion was observed between air drying the silane or prebaking it at 130°C.

TABLE I
VM-651 CONCENTRATION RANGE
.01% TO - .1%

WAFERS

15 mil thick, 3" diameter (381 microns, 76MM)
P-Type boron doped
1,1,1 polished, any resistivity

PYRALIN CONTROL (No Adhesion Promoter)		
1 min. boiling water	:	0% peel(1)
5 min. boiling water	:	50% peel
10 min. boiling water	:	88% peel
30 min. boiling water	:	100% peel

PYRALIN OVER AIR DRY VM-651		
1 min. boiling water	:	0% peel(1)
10 min. boiling water	:	0% peel
60 min. boiling water	:	0% peel
30 min. Pressure Pot(2)	:	0% peel
120 min. Pressure Pot(2)	:	0% peel

PYRALIN OVER VM-651 BAKED AT 130°C FOR 10 MINUTES		
60 min. boiling water	:	0% peel
120 min. Pressure Pot	:	0% peel

NOTES:

(1) Peel Test Method: 1/8" cross-hatch and peeled with "MYLAR" pressure sensitive adhesion tape

(2) Pressure Pot conditions: 250°F, 15 psi (121°C, 104 x 10^3 Pascals)

VM-651 may also be used to promote adhesion between PYRALIN and glass and a variety of inorganic substrates.

Experimental results indicate that only a monomolecular layer is needed to promote adhesion. These results indicate that a Si-O bond is formed with the substrate.

When the PYRALIN solution is applied to the surface, ionic bonds are formed between the PYRALIN and the amine groups in the VM-651. Although these bonds may not survive subsequent processing steps, they have already served the purpose of bringing the PYRALIN coating into intimate contact with the substrate. Intimate contact is essential to developing good adhesion.

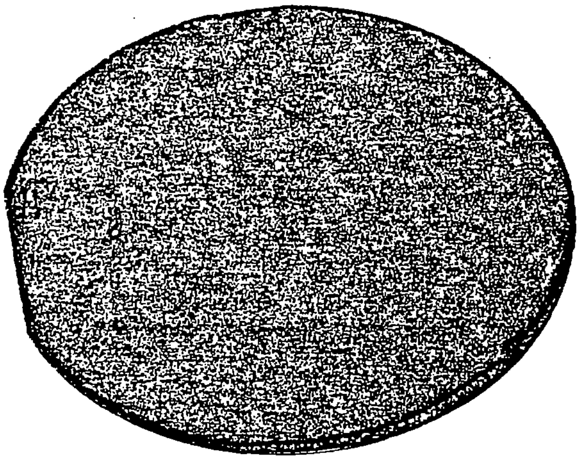
SOLUTION PREPARATION

VM-651 as received must be diluted to effectively react with the wafer surface. The following steps are suggested.

1. Prepare a mixture of 95% methanol and 5% deionized water.
2. Add VM-651 to obtain .1 to .01% solution of VM-651 in mixture of Step 1. (In 1000 milliliter Methanol/Water, add .5 milliliter VM-651.)
3. Stir until mixed.
4. Close container and let stand for 12 hours before use.
5. Mark date on container.
6. Discard after 20 days and prepare fresh batch. Do not use material older than 20 days — poor adhesion will result.

APPLICATION

Flood surface of wafer with the diluted solution of VM-651. It is suggested that the solution be filtered through a 0.2 micron filter at the time of application. Spin for 20 to 50 seconds to allow air drying. Spin time will vary with spin speed and wafer size. A 3" wafer at 5000 rpm will require 20 seconds of spin time. No bake is required. The wafer is now ready for application of the desired PYRALIN polyimide coating.



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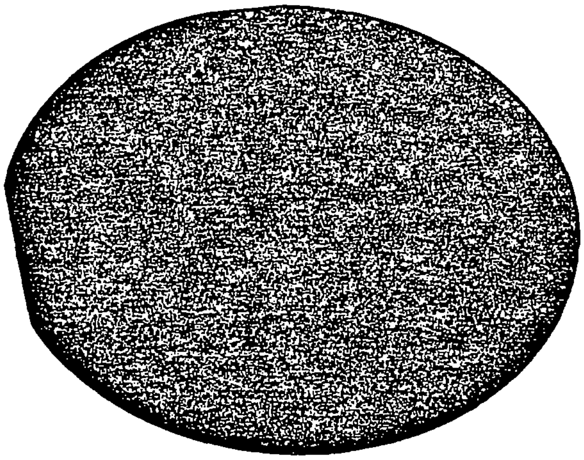

B

RESULTS

The photo shown above illustrates that the adhesion promoter changes the surface characteristics of the wafer and helps to obtain a uniform, blemish-free coating. The coating in "A" shows the effect of using PYRALIN* PI-2555 diluted 5 parts PYRALIN to one part of T-9035 thinner. The wafer in "A" is not treated with VM-651. You will note some edge pull back and surface blemishes.

The picture "B" shows the same PYRALIN formulation coated on a wafer that was treated with VM-651. This wafer shows no edge pull back or surface blemishes. Coating thickness on both wafers shown is 1 micron.

SPECIFICATIONS

Color — Water white
Specific Gravity — 0.945 25/25°
Flash Point — 160° F (closed cup)
Percent Volatile by Volume % — <1.0

SHIPPING

VM-651 is classified as a corrosive material by the Department of Transportation. The material is packaged in a 500 gram DOT 2E plastic container. This container is then packaged in a metal can and surrounded with vermiculite. A metal cup with six safety clips seals the metal can. A DOT 12A cardboard container holds the metal can. This package meets all DOT regulations for shipping by air, rail, or truck.

SAFETY

VM-651 adhesion promoter can cause eye damage and skin burns. In case of skin contact, flush with water and then wash thoroughly with soap and water. In case of eye contact, immediately flush eyes with water for 15 minutes. Consult a physician.

Use in a well ventilated area. Rubber or plastic gloves should be worn as should a face shield or eye goggles.

Keep container tightly sealed — water will cause VM-651 to polymerize slowly.

AVAILABILITY

Available in 500 gram containers from the Du Pont Company, F&F Department, 85 Mill Plain Road, Fairfield, Connecticut 06430, Attn: B.T. (Brian) Lynch. Phone: (203) 259-3351, Ext. 247. For additional technical information, call V.S. (Vic) Bowers, (302) 774-0259. Telex #83-5420. Cable address: FABFINISHES

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*Du Pont trademark.

DU PONT

PYRALIN™

POLYIMIDE COATINGS FOR ELECTRONICS

Bulletin #PC-24
(E-52139)
4/82

PRODUCT SPECIFICATION
VM-651 ADHESION PROMOTER

TEST	VM-651	TEST METHOD
Density (25°C)	0.946 ± 0.1 g/cc	Du Pont TM II G
Chloride Content*	6.0 ppm max.	Du Pont TM II C
Sodium Content*	1.5 ppm max.	Du Pont TM II B
Potassium Content*	0.5 " "	
Copper Content*	0.5 " "	
Iron Content*	0.05 " "	

NOTE: It is recommended that final filtration be done at the dispensing point. VM-651 is used at concentrations of 0.01% to 0.1% in a solution of 95% methanol and 5% deionized water. Final filtration should be done after the solution is prepared to be sure that the methanol and water is also filtered.

*Based on total sample.

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Polyimides in Semiconductor Manufacturing

Polyimides are finding a broad, new range of applications in the manufacture of integrated circuits.

By Ron Iscoff, West Coast Editor

Formerly used chiefly in the printed circuit industry, new polyimide formulations are being incorporated into the fabrication and packaging cycles of integrated circuits.

Major applications for polyimides today include their use as alpha particle barriers, coatings for passivation and mechanical protection, interlayer dielectrics and self-patterning passivation and high-temperature photoresists.

Alpha particle barrier coatings

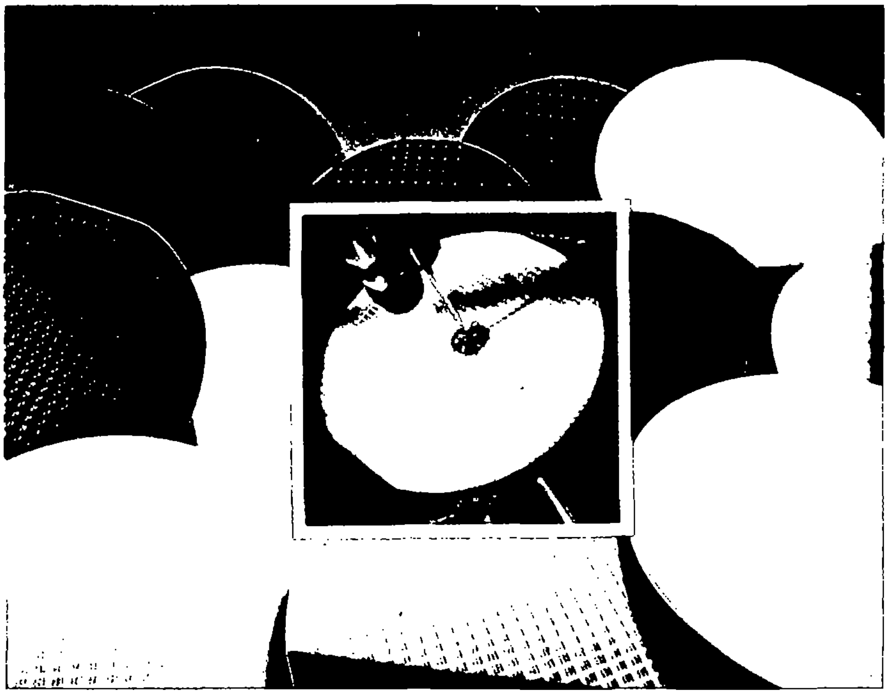
A significant and growing use for polyimides is their application as an alpha particle barrier. The barrier consists of a 75 to 80 μm polyimide coating applied to the die and cured just before packaging.

Alpha particle protection is necessary for high-density memory devices to prevent soft errors. High-density devices may suffer soft errors when alpha particles, which are emitted from trace quantities of thorium or uranium in packaging materials, strike the active surface.

High-purity polyimides are virtually free of radioactive emitters, and can withstand the IC packaging process without deterioration, according to Dr. J.C. Chevrier of E.I. DuPont in Wilmington, Del.

Chevrier, product manager for Semiconductor Materials, maintains that incorporation of the polyimide barrier can reduce the constraints of circuit design in the development and manufacture of smaller size dynamic memory devices.

While overall use of polyimides in the integrated circuit industry is quite low, the use of the polyimides for alpha particle protection could represent a high percentage of its use, according to Chevrier.



Coating the wafer with polymide.

"The main suppliers of 64K dynamic RAMs use polyimides extensively for alpha barrier protection of the plastic packages. I would almost say for this application, polyimides have become recognized as an industry-accepted solution," Chevrier reported.

Passivation coatings

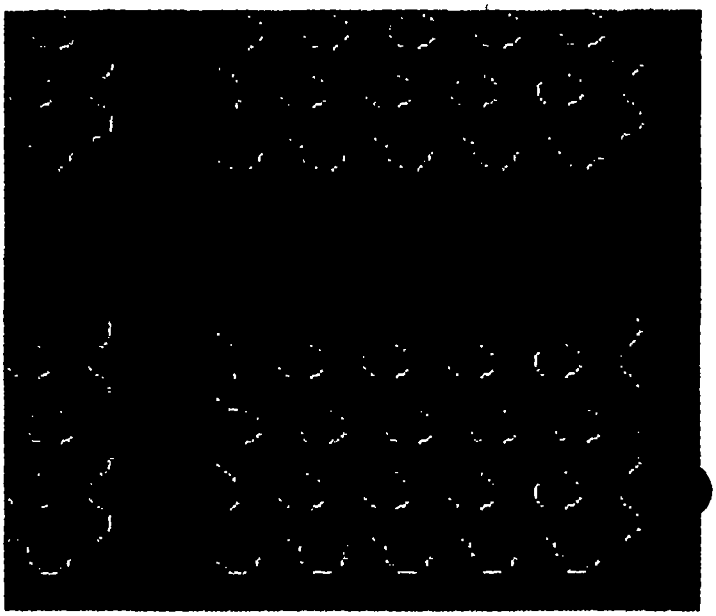
The most popular use for polyimides today is to passivate integrated circuits, according to Chevrier.

"Applied to wafers, polyimides provide excellent moisture barriers and protect devices from mechanical damage. The latter is especially important in automated packaging lines which can prove hazardous for fragile inorganic coatings.

"A thin but tough layer of polyimide, applied over inorganic layers, seals any cracks or pinholes that may form during inorganic deposition," according to Chevrier.

DuPont claims that polyimides also trap sodium ions migrating from packaging materials or other sources,

The actual pattern, in photo resist, on the wafer.



Overlay showing the relationship of the original CAD design geometry to the corrected CAD and the actual photoresist pattern.

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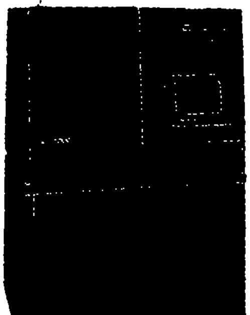

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and offer good moisture absorption, as well. "It has been shown that devices passivated with polyimide — compared with those protected only with inorganic coatings — perform better in humidity testing," Chevrier added.

The passivation layer may work as a moisture getter and prevent condensation of water molecules, thereby preventing corrosion.

Yield improvement

Integrated circuit manufacturers are now applying a thin polyimide coat over the die as a buffer against stresses that build up during thermal cycling, according to Chevrier. Open circuit failures can be reduced by the application of a thin coat of high-purity polyimide. The polyimide acts to protect the wire bonds against the rigors of packaging and thermal cycling. The secondary passivation of the polyimide, i.e., a polyimide passivation layer over standard inorganics, can improve the yields of packaged devices by as much as 10%, according to Du Pont.

William N. Bolster of M&T Chemicals, Rahway, N.J., agrees that polyimides are gaining acceptance as a passivation medium for integrated circuits. Bolster, a commercial development specialist for the polyimide producer, said that in terms of economics, polyimides probably represent "either a wash or a slight savings over silicones" when used as a replacement.

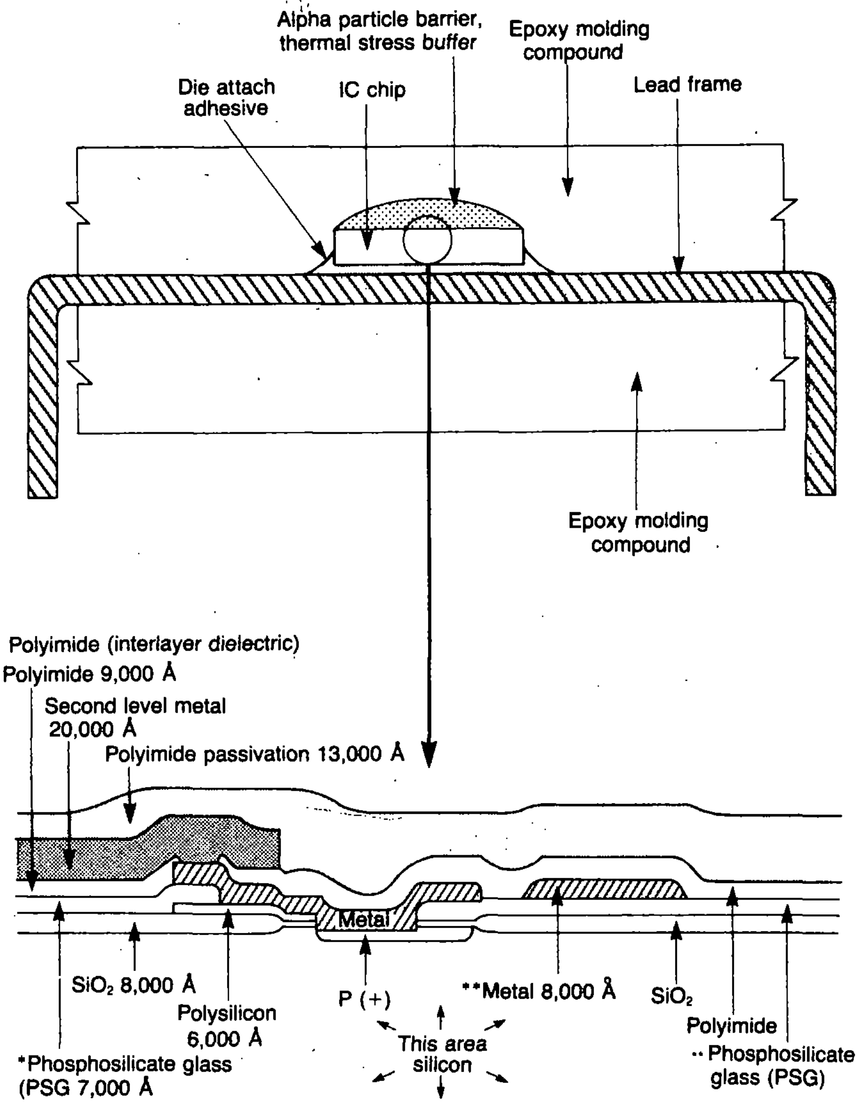
Not everyone agrees that polyimides are becoming a popular replacement for silicones and other materials, however.

Ken Uchihara, marketing director for Sumitomo Plastics in Santa Clara, Calif., reported, "About three or four years ago, many people were working on multilayer metalizations using polyimides. However, now it seems that nitrides or other inorganic chemicals are dominating the market for metalization."

In Japan, junction coatings using either silicones or polyimides are not popular, according to Sumitomo's Uchihara. He said the major applications for polyimides in Japan are for power transistors and power linears, primarily to enhance moisture performance in the encapsulation step.

Uchihara added that although the company produces and distributes polyimides in the U.S. and Japan, molding compounds represent a larger market. He feels that silica-epoxy molding compounds, which Sumitomo produces, can offer alpha particle protection equal to the polyimides.

Cross-sectional View of Polyimides Being Used as Alpha Particle Barrier Coding



*Polyimide can be used as a dielectric in place of PSG.

** Photosensitive polyimide can be used as a self-patterning, high temperature photoresist to produce any of the dielectric or conductor layers in the wafer.

DuPont's Chevrier concedes that overall use in the semiconductor industry of polyimides is small and that increased usage depends heavily on educating the industry about the benefits of polyimides.

He pointed out that polyimides are commercially available in very high purity forms, are extremely stable and have "excellent electrical, chemical and mechanical properties. Their thermal and electrical characteristics are superior to previous low-molecular-weight addition and silicone polyimides."

Interlayer dielectrics

Another application where polyimides are finding favor is their use as the interlayer dielectric in multilayered integrated circuits.

Chevrier noted that, "As the size of components gets smaller, it becomes extremely difficult to maintain adequately planar surfaces with inorganic dielectrics such as chemically vapor deposited silicon dioxide.

"Sharp surface relief at via sites and at metal lines can cause thinning of subsequent insulator and metal layers, leading to increased failures due to inadequate coverage."

Polyimide films, which are less than 1.5 µm thick, can be made as planar as necessary because they are dispensed as liquids and spincoated, according to Chevrier.

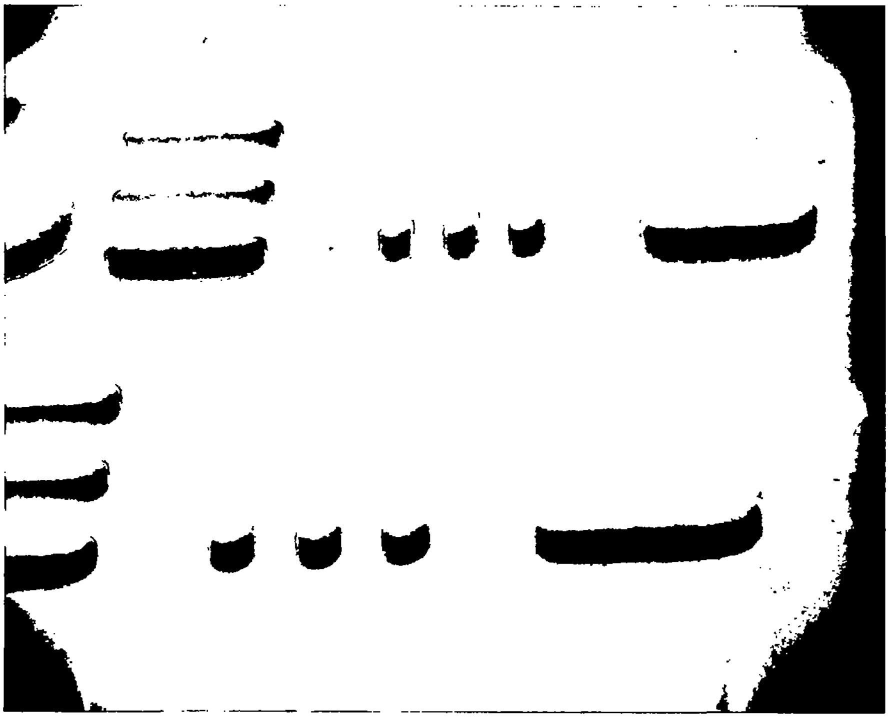
He said they make ideal interlayer dielectrics because of their high dielectric strength, low defect density, ease of etching and controllable via profiles. Lower residual stress in polyimides allows the use of thicker layers without cracking. The defect density is typically less than seven defects on a 100 mm wafer, according to Du Pont.

Andy Nakayama, sales manager for the Hitachi Chemical Co., New York, N.Y., reported that the leading applications for polyimides are as interlayer dielectrics and for passivation uses.

Table 1. Typical Process for Patterning 2 Micron Cured Film

1. Clean and dry wafer surface.
2. Surface preparation adhesion promoter coating: 4000 rpm, 30 sec., 0.1% VM-651
3. PSPI coating: 5 gm/wafer 3000 rpm, 30 sec.
4. PSPI prebake: 55°C, 45 min. (in air) Film thickness after prebake 4 pm
5. UV exposure: (contact aligner) 8mW/cm² at 365 nm for 15-20 sec.
6. Developing: 1/1 Butyrolactone/Xylene Dip for 15-20 sec.
7. Rinsing: Xylene dip, 25°C, 10 sec. spin dry in air 4000 rpm 20 sec.
8. Post Bake: 250°C, 30 min. in air
   400°C, 30 min. in air or N_2

   Film thickness after cure 2.0 µm



A semiconductor test pattern, made with a 1.8 µm coating of Dupont photosensitive polyimide, shows clearly defined 3.75 and 5.0 µm lines and spaces.

Hitachi is the largest producer o polyimides in Japan, and the second largest in the U.S. Du Pont is the leader domestically.

Arthur M. Wilson of Texas Instruments, Dallas, Texas, has reported that polyimide films, used as high-temperature planarizing insulators for multilevel interconnection systems, may be the key to high-yielding bipolar and MOS VLSI circuits.[1]

Wilson, of TI's Linear Circuits facility, noted that, "The small feature size now possible in silicon, and in other semiconducting phases in which the active component is built, has placed severe pressure on the design rules of interconnection systems in particular, and on thin-film engineering and processing personnel in general.

Connection of a large number of components on an integrated circuit with single-level (final thermal oxide/ conductor/passivating overcoat) interconnection systems consumes more chip area for interconnections than for activ components. If we recognize highly-doped silicon tunnels as part of the passive interconnection system, the active semiconductor area is even smaller: about 10% or less of the total chip area in bars of very large area (greater than 4×10^{-10} in^2).

So that advanced lithography tools can be used to produce chips with small feature sizes, a planarized interconnection process must be used, and polyimide insulation technology provides the interconnection systems with planarizing capability, according to Wilson.[2]

Photosensitive polyimides

A photosensitive polyimide, which Du Pont introduced at Semicon West this year, has properties which make it suitable for passivation and high-temperature masking. Because it eliminates processing steps, it is said to increase yields and productivity whil reducing semiconductor fabricati costs.

In passivation applications, the mask is placed directly on the negatiye-working photo-definable polyimide film, eliminating the photoresist step. T cured polyimide becomes a mechanical tough film which provides reliable electrical, mechanical and moisture protection as well as stability and rigidity to the wafer, according to Du Pont.

The company claims the material has mechanical properties which are superior to those found in inorganic materials. A typical process for patterning 2 μm cured film is shown in Table 1.

Du Pont points out that unlike some inorganic films, polyimides have very low residual stresses, and can be deposited over a wide range of thicknesses, from a 0.8 μm layer for an interlayer dielectric, to a 3.0 μm passivation film, to a 75 μm coat for alpha particle protection. Figure 1 shows a 1.8 μm coating of photosensitive polyimide.

Scientists at the Massachusetts Institute of Technology Lincoln Laboratory have been working with polyimides for high resolution ion implantation masking for several years.[3]

T.O. Herndon, et al, reported that "in evaluating alternatives (for high energy ion implants) we found that photoresist masks could provide reasonably good resolution, but that the mask profile degraded at implant doses as low as 1×10^{15} cm^{-2}, and that the resist was difficult to strip after higher dose implants.

"Plasma etched aluminum was found to provide good resolution and masked profiles did not degrade. However, control of undercutting during aluminum etching has been a problem. In response to these difficulties, reactive ion etched polyimide was evaluated as a reliable, high-resolution implant mask process.

"Reactive ion etching can provide negligible undercutting," Herndon continued. Furthermore, since polyimide is a high-temperature material, it should withstand the large temperature rise which occurs during heavy dose implantations, responsible for the degradation observed in photoresist."[4]

Herndon concluded that oxygen plasma etched polyimide, using a photoresist etch mask, provides a simple process for masking geometries on the order of 3 microns or larger. Reactive ion etched polyimide, using a thin aluminum etch mask, provided reproducible masking of micron and submicron geometries.

"In contrast to photoresist masks where profile degradation was observed at implant doses as low as 1×10^{15} cm^{-2}, polyimide mask profiles exhibited very little change after implants of 1×10^{16} cm^{-2} at 200 KeV," Herndon reported.

Screenable polyimide

Several companies, including DuPont and M&T Chemicals are working on a silk screenable polyimide which will allow users to employ applications such as alpha particle protection coating at the wafer stage, as opposed to applying the protection at the die dispense mode at the packaging station.

"That may provide an economic advantage for the customer," DuPont's Chevrier said.

M&T Chemicals is sampling a version of its siloxane polyimide resin for use in screenable applications for passivation and alpha particle barrier coating.

The chemical producers are watching with interest as polyimides displace silicones and other material. (See Table 2.)

M&T's Bolster feels that polyimides will not replace most older applications, but rather new applications, in areas where there are problems with the current materials. "Historically, this is where changes take place," he remarked. ☐

Table 2. Polyimide Uses as Substituted/Complementary Chemicals

Polyimides Uses	Replacing/Complementing
On Wafer	
Passivation	Silicon dioxide or PSG Silicon nitride Sputtered quartz
Dielectric (interlayer)	Silicon dioxide Silicon nitride
Alpha Particle barrier (memories)	Silicones "Cold" epoxy molding compounds
Thermo mechanical isolation from package	
Multichip Interconnects	
Passivation	Glass (thin film hybrid technology)
Dielectric (interlayer)	Glass (thin film hybrid technology)
IC Packaging	
Die-attach (Silver-filled polyimides)	Gold eutectics Silver epoxies
IC Process Aids	
Ion-implant mask	
Metal lift-off mask	
Support for X-ray mask	

References:

1. A.M. Wilson, "Polyimide Insulators for Multilevel Interconnections," *Thin Solid Films,* 83 (1981) p. 145.
2. *Ibid,* p. 147.
3. T.O. Herndon, et al, "Polyimide for High Resolution Ion Implantation Masking, unpublished paper," p. 1.
4. Ibid, p. 5.

For more information direct from the manufacturers of basic polyimides, circle the appropriate number found on the reader service card in this issue.

Company	Circle No.
CIBA-Geigy	235
Du Pont	236
Hitachi Chemical Co.	237
M&T Chemical Co.	238
Sumitomo Plastics Co.	239

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Bulletin #PC-1
(E-47943)
Rev. 4/82

PYRALIN* SEMICONDUCTOR GRADE PRODUCTS

The product line involves a number of different chemistries. All are polyamic acid solutions which convert to fully aromatic polyimide coatings when exposed to heat. The cure properties, adhesion, solubility, and application conditions vary slightly with each product.

The viscosity/solids characteristics are unique for each product. All are high-purity formulations, controlled for metallic ion content (sodium less than 2.5 ppm) and filtered through 0.1 micron nominal medium. In additional, PI-2545, PI-2555, and PI-2562 are filtered through 0.2 micron absolute filters, as is the PYRALIN* thinner, T-9035.

Other products include PI-2540, PI-2550, and PI-2560 which are higher solids/higher viscosity versions of their counterparts listed above. PI-2566 is an optically clear solution and PIH-61454 is a thixotropic formulation, suitable for application by screening.

Processing

The basic process is to dilute the polyimide coating (if necessary), filter, spin dry, apply photoresist, develop, etch, strip, and cure.

The following steps apply directly to PYRALIN* products PI-2540, PI-2545, PI-2550, and PI-2555. See product bulletins PC-3, PC-4, and PC-5 for processing modifications concerning PYRALIN* PI-2560, PI-2562, PI-2566, and PIH-61454.

- Apply Adhesion Promoter

  The adhesion of PYRALIN* coatings to SiO2 can be greatly enhanced by the use of an adhesion promoter. Du Pont recommends its VM-651 adhesion promoter. This material must be reduced to a 0.1% to 0.01% solution in water/methanol before applying to the wafer. Allow the solution to normalize for 12 hours before using. The use of too weak or too strong a solution can cause problems. To prepare a 0.05% solution in a methanol/water system, mix 200 ml of 95% methanol and 5% deionized water. To this 200 ml, add one drop of VM-651. Once reduced, the adhesion promoter should be discarded after twenty days.

  Puddle onto wafer and spin at 5000 rpm for 30 seconds. This will air dry the material. Tests have shown that baking is not required. See PYRALIN* Bulletin PC-7 (Du Pont Bulletin E-45525) for more details.

- Apply PYRALIN*

  Apply the PYRALIN* to the wafer and spin. The type 2540 and 2550 will yield a film thickness of about 2.5 microns at 5K speeds for 30 seconds, while the 2545 and 2555 will yield thicknesses of about 1 micron. Thickness can be controlled by varying the spin speed or diluting the PYRALIN* with Du Pont's T-9035 thinner.

  The spinning should be done in an environmentally controlled room just as photoresist is handled. Changes in humidity can cause variations later in the process. See PYRALIN* Bulletin PC-2 (Du Pont Bulletin E-45524) for more details.

- Partially Cure

  The polyimide film etches more easily in a dry, partially cured state. The rate and profile depend on the degree of cure or imidization which, in turn, is a function of temperature. The greater the imidization, the slower the etch rate. Note that PI-2550 and PI-2555 imidize more quickly at the same temperature than PI-2540 and PI-2545. Experimentation will determine the best cure. To start, try 135°C for 30 minutes.

  If the process calls for plasma etch instead of a wet etch, the polyimide film should first be cured at least one hour at 300°C after the lower temperature bake.

- Apply Photoresist

Use normal procedures. Make sure the partially cured polyimide film has returned to ambient temperature after bake. If applied to warm film, some reaction between certain resists and the film will occur. Many users prefer a positve photoresist because it contains fewer steps than negative photoresist. The positive photoresist and the PYRALIN* can be developed and etched in one step.

- Align & Expose

Normal procedures, depending on your photoresist, should be followed.

- Develop Resist and Etch

Several types of materials have been successfully used to etch the partially cured polyimide film.

When positive photoresists such as AZ-111, AZ-1350J, and AZ-1375 are used, development of the photoresist and etching of the polyimide are accomplished simultaneously. Developers such as AZ-351 or MF-312 are used. Other etchants for polyimide film include NaOH, KOH, and tetra alkyl ammonium hydroxide. The developer or etch solutions should be maintained at 0.25N and 30°C for best results.

Negative photoresists have also been used successfully. The same etchant is used as for positive photoresist. An intermediate bake (200°C for 30 minutes) may be necessary to imidize the polyimide sufficiently to withstand the strong strippers used. A spin spray or straight spray developer system should be used to develop and etch.

If plasma etch is used, oxygen is the preferred gas. The polyimide must, in this case, be fully cured before application of the resist. The resist thickness must be greater than the polyimide because it will etch faster during the plasma treatment.

- Via Clean-Up

After wet/dry etching, it may be necessary to clean the vias to remove residual material which results in high ohmic resistance. The following methods of clean-up are listed in order of effectiveness:

1. Reverse sputtering.
2. If SiO_2 or Si_3N_4 is used over metal in the via before polyimide deposition, removal of the glass will provide clean vias.
3. Clean-up may also be obtained by use of chemical means, i.e. sulfamic acid/phosphoric acid followed by a heat treatment of 450°C for 5 minutes.
4. Low pressure O_2 plasma.

- Neutralize

Depending on the etching process, it may be good practice to neutralize with a 1% acetic acid solution and deionized water rinse. Titration of the rinse water will show length of rinse time needed to remove all traces of the acetic acid.

- Strip Resist

Typical positive photoresists are stripped using butyl acetate/isopropanol or other strippers. Negative strippers often contain phenol and sulfuric acid. A spray system is recommended.

- Final Cure

A final cure is required to develop maximum properties. This can be accomplished by baking for one hour at 350°C or 30 minutes at 400°C.

PI-2550 and PI-2555 can also be cured at temperatures as low as 180°C in some extreme cases. Films of 25 microns, cured for 2 hours at 180°C, exhibit tensile strengths and elongation equivalent to films cured at higher temperature conditions. The dissipation factor of films cured at 180°C is higher, typically 0.003-0.004 due to small residual amounts of NMP retained in the film. Curing conditions will vary for different applications. For best results, a convection oven should be used. Cures above 400°C should be done in non-oxidizing atmospheres.

- Metallization

For multilayer metallization designs, the process is repeated. When applying polyimide over polyimide, use PI-2550 or PI-2555 as the first coat and the same or PI-2540 or PI-2545 as the second coat. No adhesion promoter is required between coats.

If two coats of PI-2540 or PI-2545 must be used, the first coat should not be completely cured or the second coat will not adhere well. If full cure between coats is necessary, an oxygen plasma roughening of the surface will enhance adhesion.

Storage Stability

PYRALIN* polyimide coatings are sensitive to heat and should be refrigerated at 4°C maximum. Freezer storage (-18°C) will practically eliminate any viscosity drift and prolong shelf life significantly. When exposed to heat, PI-2540 and PI-2545 will first drop in viscosity, then increase and eventually gel. PI-2550 and PI-2555 polyimide coatings are more stable. Viscosity curves are found on Page 9.

Moisture contamination is detrimental to stability and must be avoided. Containers should be brought to room temperature before opening to avoid moisture of condensation.

TABLE 1: LIQUID PROPERTIES**

	PI-2540	PI-2545	PI-2550	PI-2555
Solids (2 gms, 2 Hours @ 200°C)	15%	14%	25%	19%
Viscosity (LVF #3 @ 12 RPM)	40-70 poise 4.7 Pascal second	10-12 poise 1-1.2 Pascal second	40-70 poise 4-7 Pascal second	12-16 poise 1.2-1.6 Pascal second
Solution Density	1.06 g/cc	1.05 g/cc	1.08 g/cc	1.06 g/cc
Solvent	NMP[1]/aromatic hydrocarbon	NMP[1]/aromatic hydrocarbon	NMP[1]/acetone	NMP[1]/aromatic hydrocarbon
Flash Point (Closed Cup)	64°C	64°C	-7°C	64°C
Filtration	0.1 micron nominal	0.2 micron absolute	0.1 micron nominal	0.2 micron absolute

[1] NMP: N-methyl-2-pyrrolidone

**Typical properties, not to be used for specification purposes. See product specification bulletins.

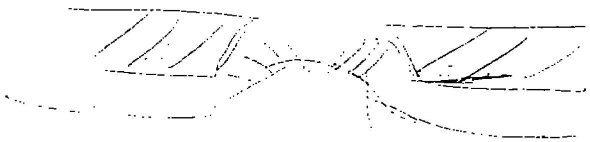
TABLE II: FILM PROPERTIES **

When fully cured, Pyralin* polyimide films are extremely heat resistant, mechanically tough, chemically resistant, and possess good electrical properties.

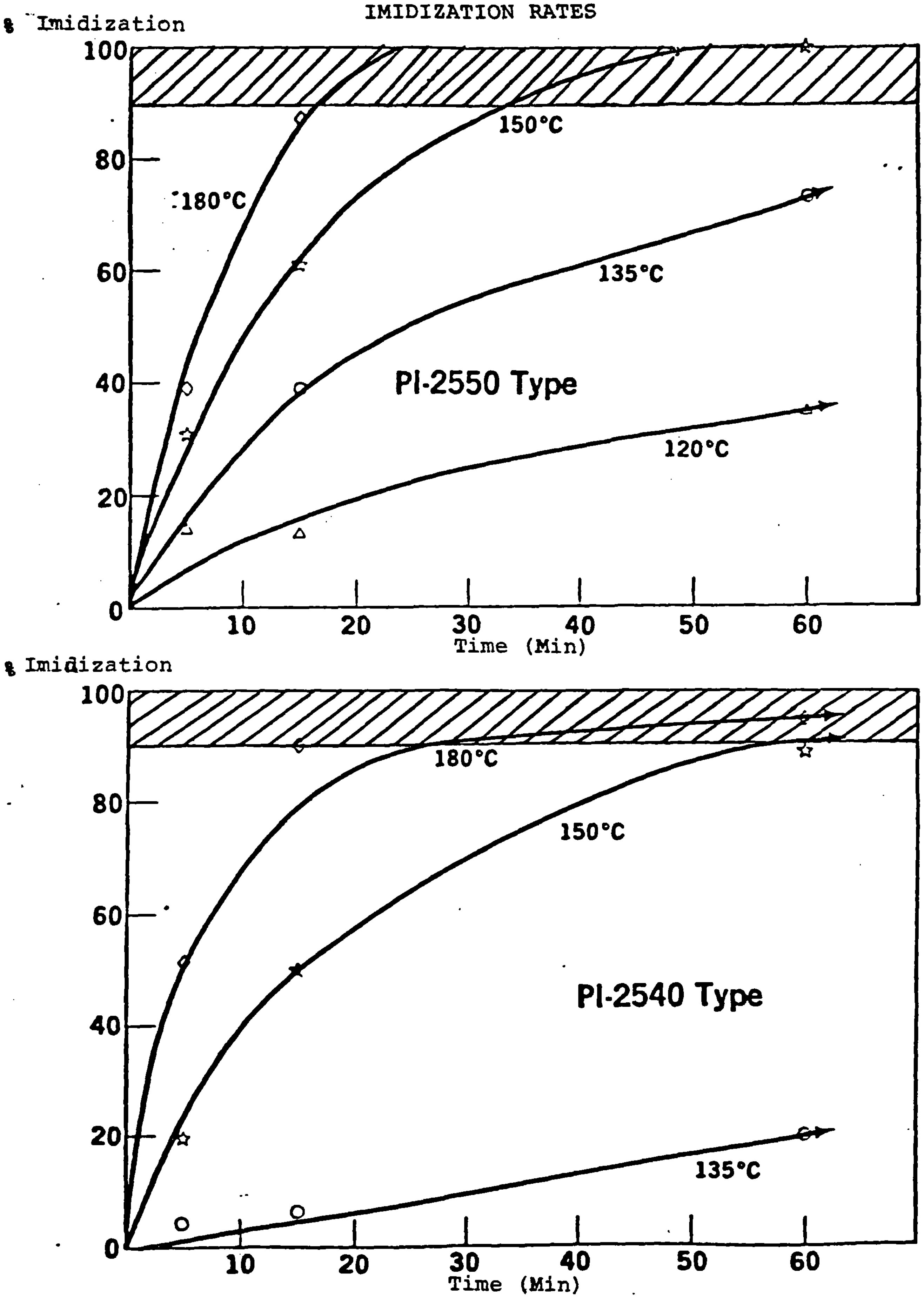
	PI-2540 (PI-2545)	PI-2550 (PI-2555)
Physical		
Tensile Strength (ultimate)	17,000 psi (1.17×10^8 Pascal)	19,000 psi (1.31×10^8 Pascal)
Elongation	25%	10%
Density	1.42 gms/cc	1.39 gms/cc
Refractive Index (Becke Line)	1.78	1.70
Flexibility	180° bend, no cracks	180° bend, no cracks
Thermal		
Melting Point	None	None
Weight Loss @ 316°C in air, after 300 hrs.	4%	4%
Final decomposition temperature	560°C	560°C
Coefficient of thermal expansion	$2.0 \times 10^{-5}/^{\circ}C$	$4.0 \times 10^{-5}/^{\circ}C$
Coefficient of thermal conductivity	$37 \times 10^{-5} \frac{\text{cal}}{(\text{cm})(\text{sec})(^{\circ}\text{C})}$	$35 \times 10^{-5} \frac{\text{cal}}{(\text{cm})(\text{sec})(^{\circ}\text{C})}$
Flammability	Self-extinguishing	Self-extinguishing
Specific heat	0.26 cal/gm/°C	0.26 cal/gm/°C
Electrical		
Dissipation Factor (1KHz)	.002	.002
Dielectric Strength	4000 volts/mil	4000 volts/mil
Volume Resistivity	10^{16} ohm-cm	10^{16} ohm-cm
Surface Resistivity	10^{15} ohm	10^{15} ohm
Dielectric Constant (1KHz)	3.5	3.5

*Du Pont Trademark

**Typical properties, not to be used for specification purposes. See product specification bulletins.

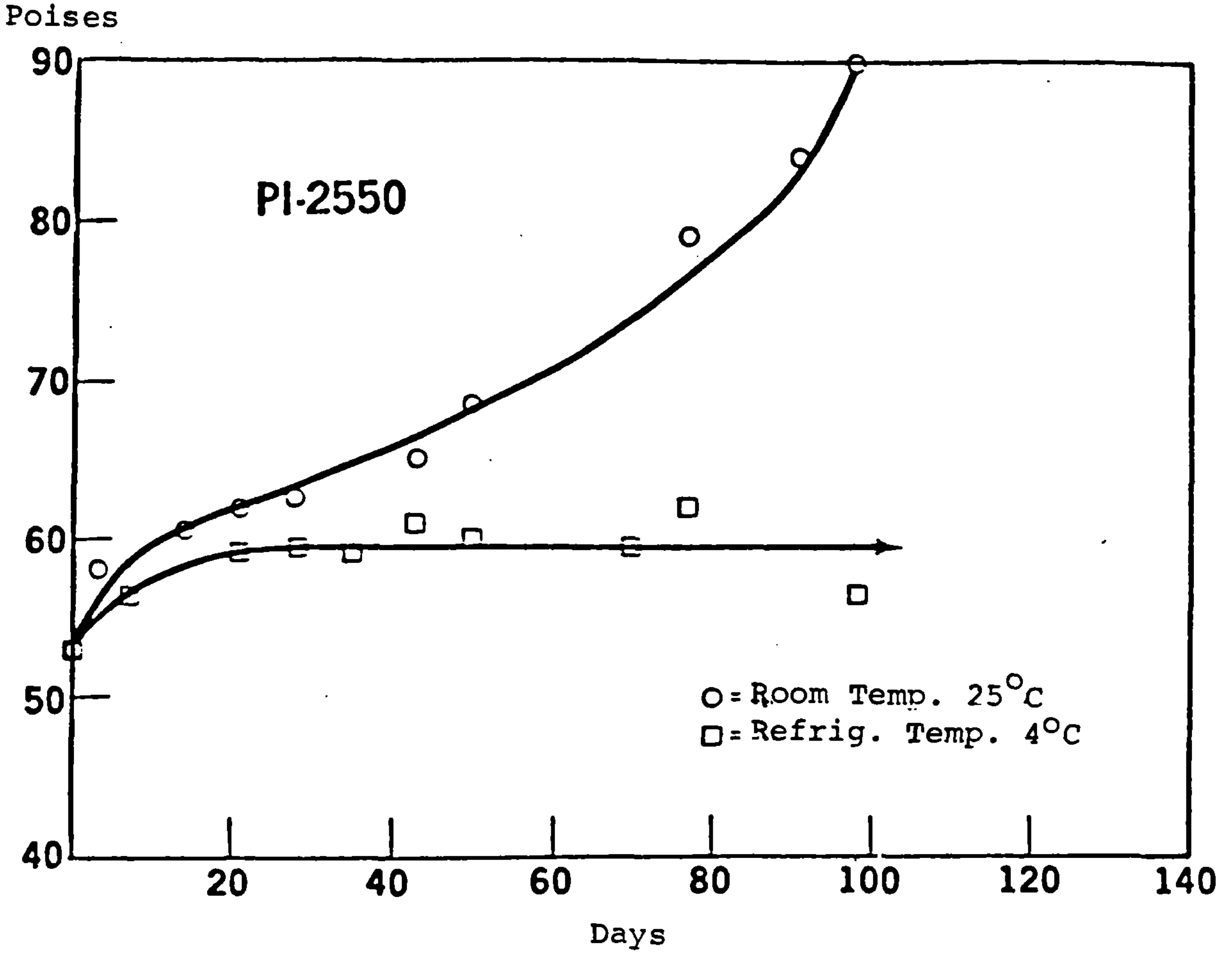


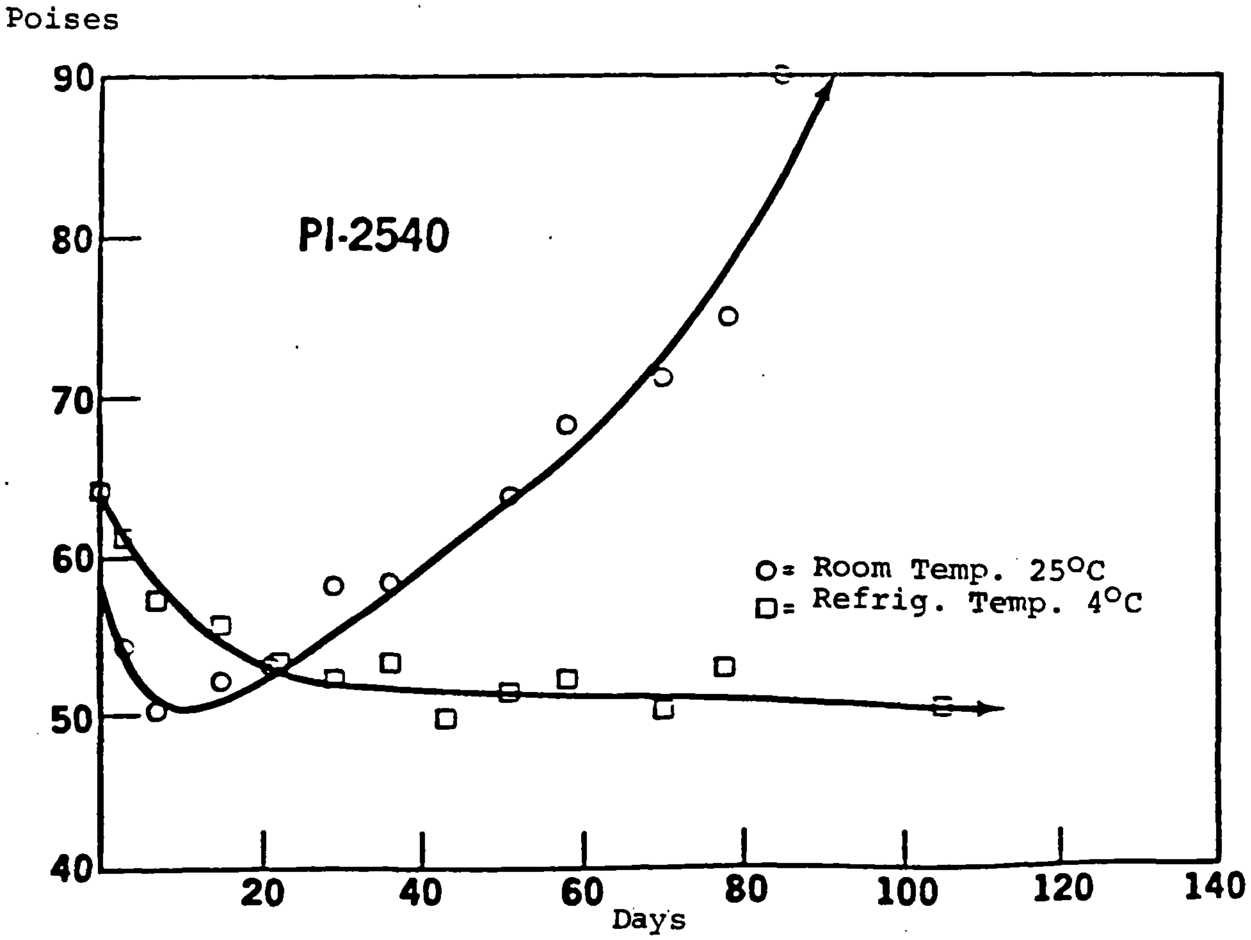
IMIDIZATION RATES



<u>Note:</u> These curves were generated using IR scanning techniques. This method does not adequately identify imidization levels above 90%. The electrical dissipation factor test should be used to determine if complete imidization has occurred.

VISCOSITY STABILITY





TOXICITY/HEALTH HAZARDS

Adequate ventilation must be provided and skin contact should be avoided. Exposed areas should be flushed with water immediately.

Rubber gloves resistant to the solvents in PYRALIN* Polyimide Coatings can be procured as follows: for general-purpose use, the "Buta-Sol" milled butyl rubber glove (Norton Company, Safety Products Division, P.O. Box 4367, Charleston, SC 29405); for light service, the "Wil-Gard" No. 26-640 tan latex industrial glove (Edmont-Wilson Division, Becton Dickinson and Company, 1300 Walnut Street, Coshocton, OH 43812); and for service requiring greater resistance to wear, the Natural Latex Rubber glove No. 2911 (B.F. Goodrich Engineered Systems, 500 S. Main Street, Akron, OH 44318).

Data supplied by the General Aniline and Film Corporation indicate that animals exposed to air saturated with N-methyl-2-pyrrolidone for six hours daily for ten days tolerated the conditions of the experiment and gained weight normally. Other animals subjected to 20-day dermal toxicity studies had no specific degenerative changes and did not have a remarkable degree of skin irritation.

VM-651 adhesion promoter can cause eye damage and skin burns. In case of skin contact, flush with water and then wash thoroughly in soap and water. In case of eye contact, immediately flush eye with water for 15 minutes. Consult a physician.

Use in well ventilated area. Rubber or plastic gloves should be worn as should a face shield or eye goggles.

Keep container tightly sealed - water will cause VM-651 to polymerize slowly.

AVAILABILITY

Available in one-half kilo, one kilo, or four kilo containers from Du Pont Company, F&FP Department, 85 Mill Plain Road, Fairfield, Connecticut 06430, Attn: B.T. (Brian) Lynch. Phone (203) 259-3351, Ext. 247. For additional technical information, call V.S. (Vic) Bowers, (302) 774-0259. Telex #83-5420. Cable address: FABFINISHES.

972-2592

DU PONT

PYRALIN

POLYIMIDE COATINGS FOR ELECTRONICS

David Kleinfeld
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Murray Hill, N.J. 07974

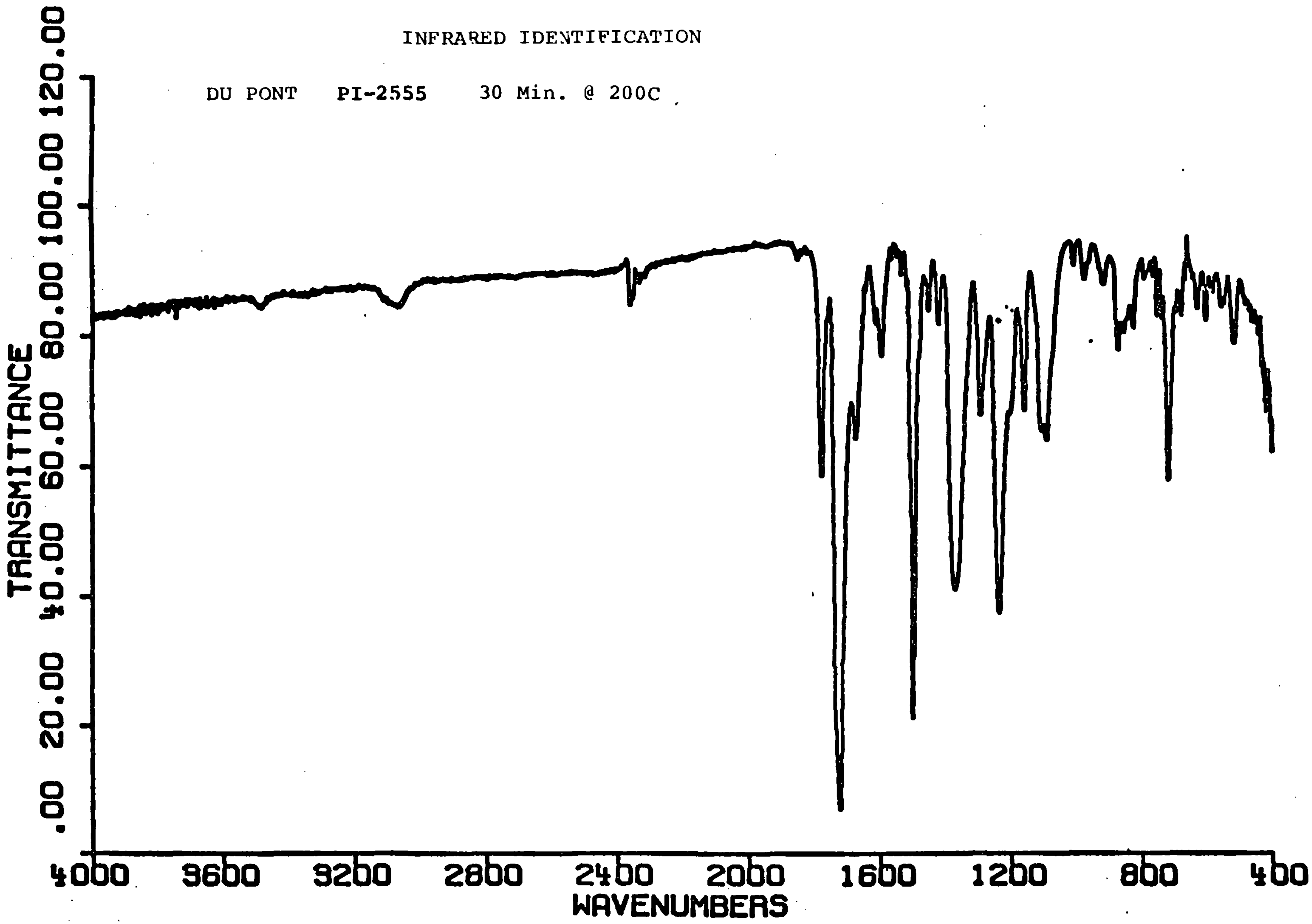
Bulletin #PC-10
(E-52127)
10/20/81

PRODUCT SPECIFICATION
PI-2555

TEST	PI-2555	TEST METHOD
Solids	19 ± 1%	Du Pont TM II A
Viscosity	12-16 poises	Du Pont TM II H (#3 spindle 12 rpm)
% Ash	0.1% max.	Du Pont TM II F
Density (25°C)	1.06 ± 0.1 g/cc	Du Pont TM II G
Infrared Identification	Compare after 30 minute bake @ 200°C	(See Reverse Side)
Solvent System	N-Methyl-2-Pyrrolidone/ Aromatic Hydrocarbon 80/20 ± 5%	Du Pont TM II D
Chloride Content**	10 ppm max.	Du Pont TM II C
Sodium Content**	2.5 ppm max.	Du Pont TM II B
Potassium Content**	1.0 " "	
Copper Content**	1.0 " "	
Iron Content	1.0 " "	
Total Metals	10 ppm max.	Du Pont TM II J
Filtration	0.2 micron abs.	

**Determined on total sample.

Printed in U.S.A.



INFRARED IDENTIFICATION

DU PONT

PYRAL

POLYIMIDE COATINGS FOR ELE

David Kleinfeld
Room 6H-424
ATT Bell Laboratories
600 Mountain Avenue
Murray Hill, N.J. 07974

Bulletin #PC-4
(E-47945)
Rev. 4/82

PYRALIN* PI-2566

PYRALIN* PI-2566 is a formulation designed to yield cured coatings of greater optical clarity than those obtained with other PYRALIN materials.

The index of refraction (Becke Line) is 1.56 vs. 1.78 for the PI-2540 series and 1.70 for the PI-2550 series.

Potential applications where clarity is required include:

- Opto Couplers and Isolators
- Alignment coatings for Liquid Crystal Displays

as well as special integrated circuit devices where quality control inspection must be done through the coating.

PI-2566 processing and cured film properties are similar to the PI-2550 series described in Bulletin PC-1; however, special techniques and conditions are required for consistent wet processing.

PI-2566 offers excellent electrical properties and low moisture absorption.

Printed in U.S.A.

LIQUID PROPERTIES**

	PI-2566
Solids (2 gms, 2 hours @ 200°C)	18%
Viscosity (LVF #3 @ 12 RPM)	50-70 poise 5-7 Pascal second
Weight	
per gallon	8.80 lbs.
per liter	1.06 kg
Solution Density	1.06 g/cc
Solvent	NMP[1]/aromatic hydrocarbon
Flash Point (Closed Cup)	64°C (147°F)
Filtration	1 micron

[1] NMP: N-methyl-2-pyrrolidone

**Typical properties; not to be used for specification purposes.

STORAGE STABILITY

PYRALIN* polyimide coatings are sensitive to heat and should be refrigerated at 4°C maximum. Freezer storage (-18°C) will practically eliminate any viscosity drift and prolong shelf life significantly.

TOXICITY/HEALTH HAZARDS

Adequate ventilation must be provided and skin contact should be avoided. Exposed areas should be flushed with water immediately.

Rubber gloves resistant to the solvents in PYRALIN* polyimide coatings can be procured as follows: for general purpose use, the "Buta-Sol" milled butyl rubber glove (Norton Company, Safety Products Division, P.O. Box 4367, Charleston, SC 29405); for light service, the "Wil-Gard" No. 26-640 tan latex industrial glove (Edmont-Wilson Division, Becton Dickinson and Company, 1300 Walnut Street, Coshocton, OH 43812); and for service requiring greater resistance to wear, the Natural Latex Rubber Glove No. 2911 (B.F. Goodrich Engineered Systems, 500 S. Main Street, Akron, OH 44318).

Data supplied by the General Aniline and Film Corporation indicate that animals exposed to air saturated with N-methyl-2-pyrrolidone for six hours daily for ten days tolerated the conditions of the experiment and gained weight normally. Other animals subjected to 20-day dermal toxicity studies had no specific degenerative changes and did not have a remarkable degree of skin irritation.

AVAILABILITY

Available in one kilo or four kilo containers from:

Du Pont Company
85 Mill Plain Road
Fairfield, Connecticut 06430
Attn: B.T. (Brian) Lynch
Phone: (203) 259-3351, Ext. 247

For additional technical information, call V.S. (Vic) Bowers, (302) 774-0259. Telex: 83-5420. Cable address: FAB-FINISHES.

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Bulletin #PC-3
(E-47944)
Rev. 4/82

PYRALIN* PI-2560 AND PI-2562 SEMICONDUCTOR GRADE

PYRALIN* PI-2560 is a polyamic acid solution designed to provide thicker coatings with one application than is normally possible with other PYRALIN solutions. The product combines a high solids content (37%) with a moderate viscosity.

PI-2562 is a diluted version of PI-2560 which has undergone 0.2 micron absolute filtration.

Typical potential applications include die bonding, mechanical protection, and/or alpha protection coating.

These coatings also offer:

- Excellent step coverage for metallization systems.
- Pinhole and crack-free, mechanically tough films.
- Compatibility with semiconductor fabrication and packaging.
- Controlled metallic ion content; sodium less than 3 ppm.

LIQUID PROPERTIES(1)

	PI-2560	PI-2562
Solids (2 gms, 2 hours @ 200°C)	37%	25.5%
Viscosity (LVF #3 @ 12 RPM)	15-30 Poises 1.5-3.0 Pascal Second	75-200 Centipoises 0.075-0.2 Pascal Second
Solution (Density)	1.13 g/cc	1.07 g/cc
Solvent	NMP(2)/Xylene	NMP/Xylene/Cellosolve
Flash Point (Closed Cup)	40°C	40°C
Filtration	0.1 Micron Nominal	0.2 Micron Absolute

FILM PROPERTIES(1)

	PI-2560 and PI-2562
Physical	
Tensile Strength (ultimate)	19,000psi (1.31x10^{8} Pascal)
Elongation	9%
Density	1.39 gms/cc
Refractive Index (Becke Line)	1.70
Flexibility	180° bend, no cracks
Thermal	
Melting Point	None
Weight Loss @ 316°C in air, after 300 hours	4%
Final decomposition temperature	560°C
Coefficient of thermal expansion	4.0 x 10^{-5}/°C
Coefficient of thermal conductivity	$35 \times 10^{-5} \frac{cal}{(cm)\ (sec)\ (°C)}$
Flammability	Self-Extinguishing
Specific Heat	0.26 cal/gm/°C

---

(1) Typical properties; not to be used for specification purposes. (See PC-11 and PC-12)

(2) N-methyl-2-pyrrolidone

FILM PROPERTIES(1) (cont'd)

Electrical	
Dissipation Factor (1KHz)	.002
Dielectric Strength	4000 volts/mil
Volume Resistivity	10^{16} ohm-cm
Surface Resistivity	10^{15} ohm
Dielectric Constant (1KHz)	3.5

PROCESSING

PI-2560 and PI-2562 are similar to the PI-2550 PYRALIN* series in rate of imidization. The processing conditions described in Bulletin PC-1 will generally apply to PI-2560 and PI-2562 for dry etch only.(3) However, the coating thicknesses derived from this material may be of the order of 1 mil, greater in most instances than with other formulations, so that an increase in prebake or final cure is necessary to deal with the extra thickness.

Prebake before etch should be 30 minutes at 80°C, 30 minutes at 105°C, and 30 minutes at 125°C. A final cure of 30 minutes at 180°C and 30 minutes at 300°C or higher is needed to achieve full imidization. Bubbles appearing during or after the final 300°C cure indicate a longer exposure at 180°C is necessary.

STORAGE STABILITY

PYRALIN* polyimide coatings are sensitive to heat and should be refrigerated at 4°C maximum. Freezer storage (-18°C) will practically eliminate any viscosity drift and prolong shelf life significantly. Viscosity stability of PI-2560 is similar to PI-2550. Viscosity curves are found on Page 9 of Bulletin PC-1.

Moisture contamination is detrimental to stability and must be avoided. Containers should be brought to room temperature before opening to avoid moisture of condensation.

---

(1) Typical properties; not to be used for specification purposes. (See PC-11 and PC-12)

(3) PI-2560 is difficult to wet process consistently with known etchants. Therefore, wet processing is not recommended

TOXICITY/HEALTH HAZARDS

Adequate ventilation must be provided and skin contact should be avoided. Exposed areas should be flushed with water immediately.

Rubber gloves resistant to the solvents in PYRALIN* polyimide coatings can be procured as follows: for general purpose use, the "Buta-Sol milled butyl rubber glove (Norton Company, Safety Products Division, P.O. Box 4367, Charleston, SC 29405); for light service, the "Wil-Gard" No. 26-640 tan latex industrial glove (Edmont-Wilson Division, Becton Dickinson and Company, 1300 Walnut Street, Coshocton, OH 43812); and for service requiring greater resistance to wear, the Natural Latex Rubber Glove No. 2911 (B.F. Goodrich Engineered Systems, 500 S. Main Street, Akron, OH 44318).

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AVAILABILITY

Available in one-half kilo, one kilo, and four kilo containers from:

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For additional technical information, call V.S. (Vic) Bowers, (302) 774-0259. Telex: 83-5420. Cable address: FAB-FINISHES.

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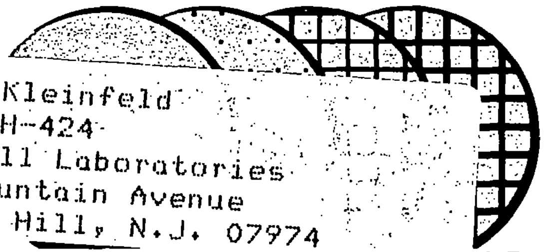

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Bulletin #[illegible]-2 Rev. 3/82

PRELIMINARY INFORMATION BULLETIN
SPIN COATING TECHNIQUES

PYRALIN can be applied to semiconductor wafers using standard photo resist spin coating techniques. Spin coating provides uniform, pinhole-free coatings and can be controlled in thicknesses between 1000 Angstroms and 35,000 Angstroms.

Most development work done to date has used 3 inch wafers. Data are being generated using larger diameter wafers.

Each of the following variables will affect the uniformity and overall quality of the final film and should be controlled to obtain consistent results:

1. Wafer preparation
2. Adhesion promoter
3. Dispensing
4. Spin speed
5. Cure

1. WAFER PREPARATION

The purpose is to provide a clean, dry surface. One process which yields good results is:

- Degrease in Freon® for 1 to 2 minutes with agitation.
- Air dry
- Rinse in deionized water at room temperature for 3 minutes.
- Rinse in isopropyl alcohol for 20 seconds.
- Air dry
- Bake for 20 minutes at 300°C to insure dryness and cleanliness.
- Cool wafer to room temperature.

2. ADHESION PROMOTER (VM-651)

Spin apply as detailed in PYRALIN Bulletin PC-7 (Du Pont Bulletin E-41093).

3. DISPENSING PYRALIN*

A three-inch wafer was used for tests. Similar information must be developed by the user for wafers four inches or larger.

Dispense 1 cm^3 of PYRALIN on 3 inch wafer. It is very important that the amount of material dispensed remain constant for each wafer. Most manufacturers of spinning equipment offer pumps for PYRALIN solutions which control accurately the amount dispensed.

Variations in the amount of solution dispensed can cause variation in average film thickness at any given spin speed. In general these variations will show up more at spin speeds below 4000 rpm and will be minimized as speeds approach 6000 rpm.

The best results have been obtained by dispensing onto a wafer at rest and then bringing the wafer up to speed as rapidly as possible. A final filtration of PYRALIN as the material is dispensed is recommended.

4. FINAL SPIN SPEED

For best control, final spin should be maintained between 4000 and 6000 rpm. The PYRALIN solution viscosity can be adjusted with T-9035 thinner so that operations can be maintained in this speed range. If PYRALIN is thinned, it should be allowed to stabilize at least 12 hours before using.

The film as deposited on the wafer is a wet film and will shrink about 75% during cure.

Chart 1 (on page 2) shows the relationship between spin speed of a 3 inch wafer and final dry film thickness of PYRALIN 2555 after curing at 400°C.

Charts 2 through 7 show the percent solids vs. viscosity of all commercial PYRALIN solutions. Solids content are listed on the product sheet. To use Charts 2 through 7, start with the original solids of the material, multiply by the original volume and divide by the reduced volume. This calculation will give the reduced solids content. This reduced solids figure on the charts will give the reduced viscosity.

The final film thickness of any of the PYRALIN solutions should be close to those figures shown on Chart 1. There will be some difference due to solids content; however, this will serve as a guide or starting point in developing the exact film thickness desired.

The best results have been obtained by spinning for 60 seconds. This length of time partially dries the film and minimizes edge pull back and eyeholing.

5. FILM CURE

To obtain an accurate thickness measurement, the wet film on the wafer should be fully cured. A typical method would be 30 min. bake at 135°C, one hour at 300°C and 10 min. at 400°C. Details on curing methods are listed in PYRALIN* Bulletin #PC-1.

Once the desired dried film thickness has been obtained and the operating spinning parameters determined, wafers may be coated and the other operating variables studied.

References

1. F.L. Givens and W.J. Daughton – Recent News Paper 381 presented at the Electrochemical Society Meeting, Pittsburgh, Pennsylvania, October 15-20, 1978.
2. Bulletin #PC-7 Du Pont Bulletin 41093.
3. Du Pont Bulletin, PYRALIN PC-1. Adhesion Promoter (VM-651).

CHART #1 **PI-2555** FULLY CURED AT 400°C

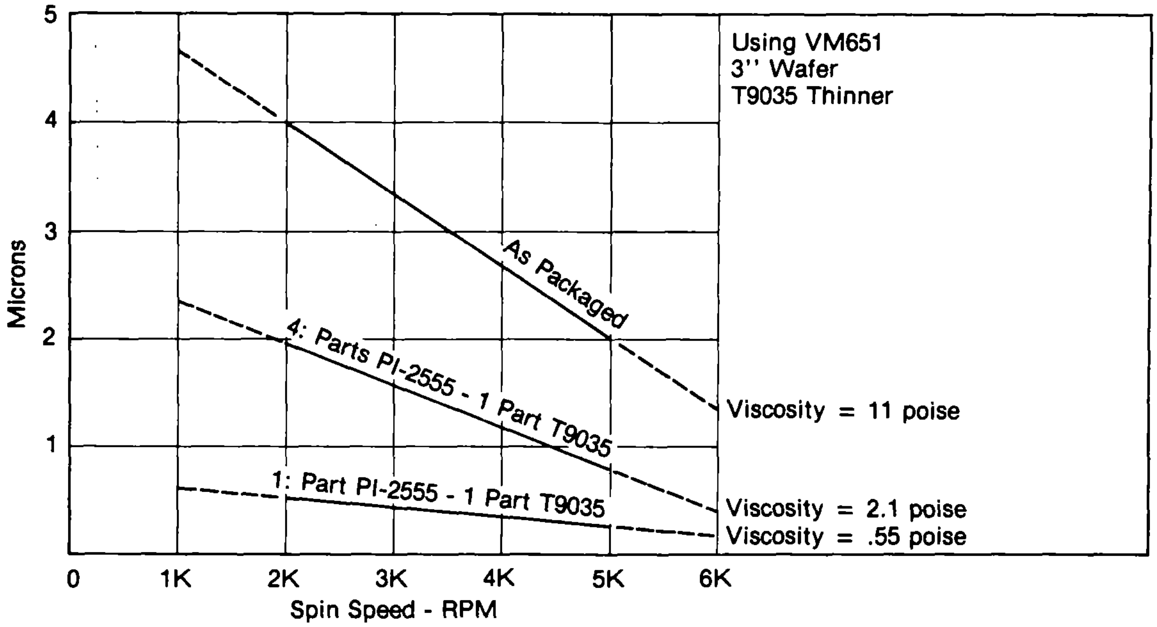


CHART #2 **PI-2555** REDUCED WITH T-9035

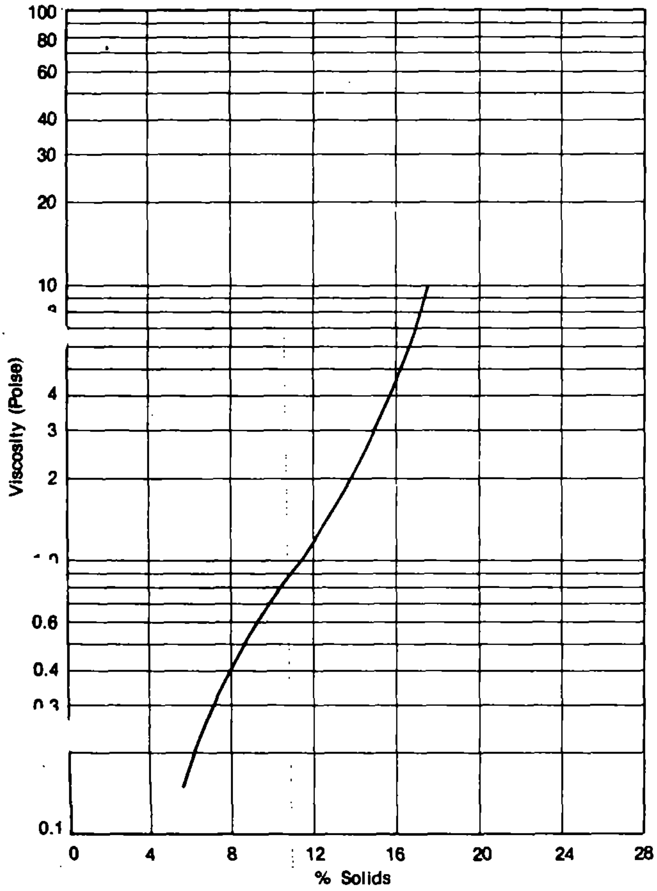


CHART #3 **PI-2550** REDUCED WITH T-9035

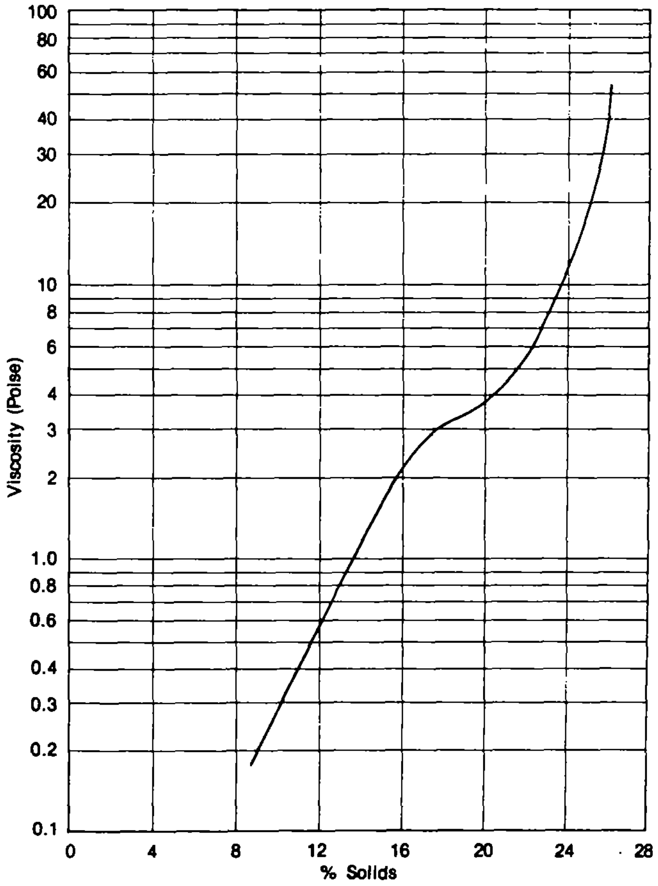


CHART #4 **PI-2560** REDUCED WITH T-9035

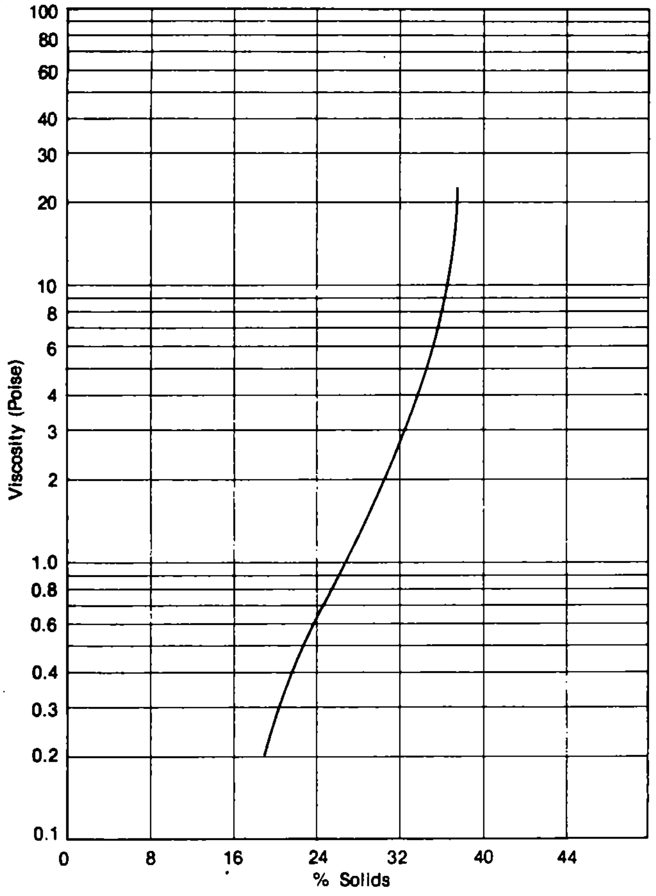


CHART #5 **PI-2566** REDUCED WITH T-9035

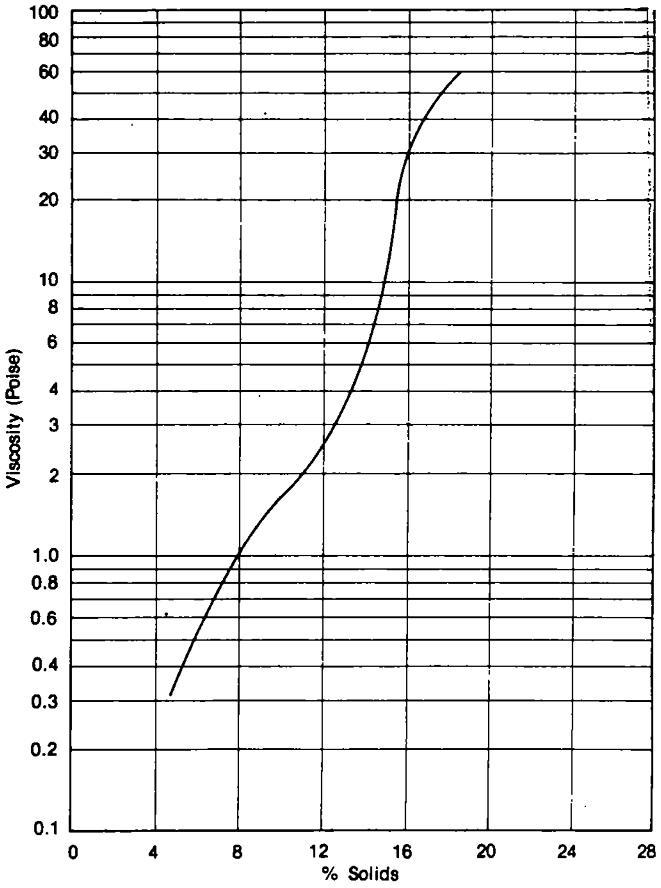


CHART #6 **PI-2540** REDUCED WITH T-9035

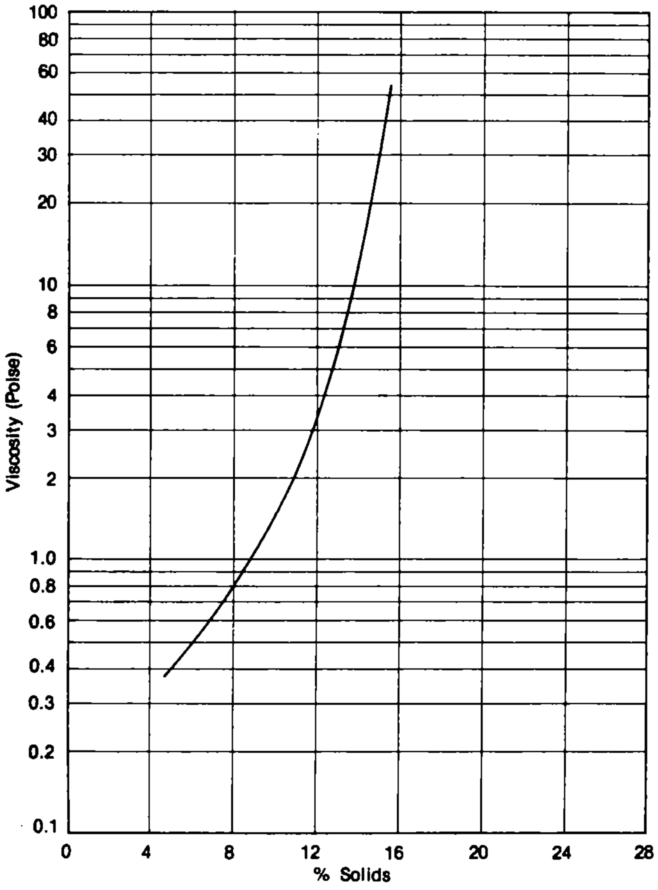
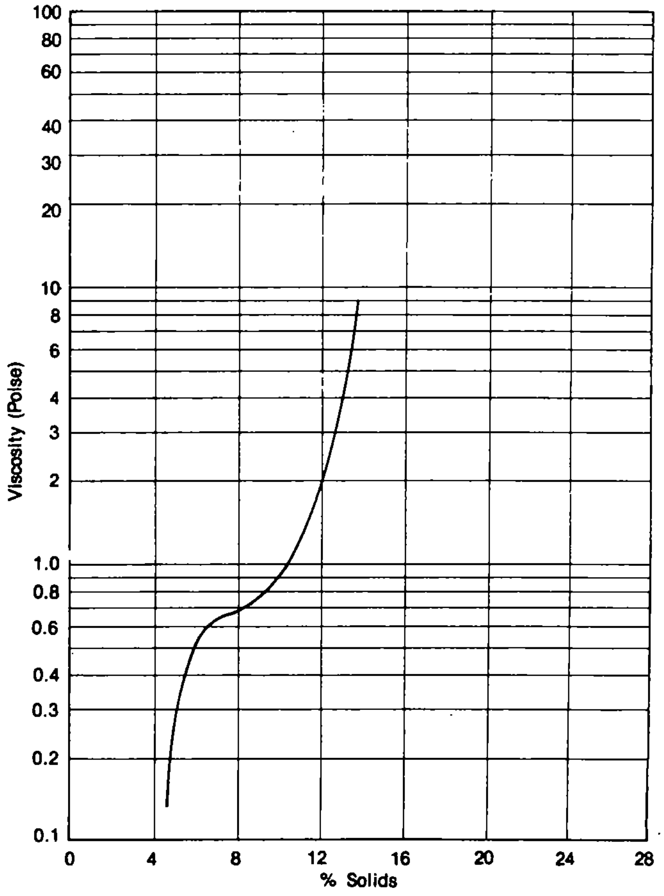


CHART #7 **PI-2545** REDUCED WITH T-9035



PROCESSING DIRECTIONS
PI-2555 - 1.5 MICRONS THICK
PASSIVATION LAYER

Positive

1. Clean Wafer - Blow clean using nitrogen for 4 seconds at 2500 RPM.

2. Apply 3 ml VM-651 adhesion promoter solution.

   Mix (every two weeks) a solution of 95% methyl alcohol and 5% DI H_2O. To this, add 0.1% VM-651 adhesion promoter. Mix by shaking or stirring. Allow mixture to normalize 12 hours before using. (See Bulletin PC-7 for further details.)

3. Spin wafer 30 seconds at 3000 RPM.

4. Adhesion promoter is used only over Si, SiO_2, or CVD surfaces, not on a previous polyimide coating.

5. PI-2555 can be dispensed as received or it can be thinned with T-9035 Thinner (8 parts PI-2555 to 1 part T-9035). Apply 3 ml to center of the wafer (4") while wafer is stationary. Bring spinner up to full speed (3500 RPM) immediately. (See Bulletin PC-2, Rev. 3/82, for further details.)

   IMPORTANT: PI-2555 removed from freezer or refrigerator should be allowed to equilibrate to room temperature before the container is opened.

6. Soft bake wafer for 30 minutes at 140°C. A hot plate or recirculating air oven is preferred. Infrared may be used, but remember IR is absorbed and the temperature of the film may exceed the temperature setting of the oven and cause poor results.

7. Let wafer cool for 10 minutes.

8. Wafers should be coated with photoresist within 24 hours.

9. Blow clean with N_2 for 5 seconds at 3500 RPM.

10. Apply HMDS adhesion promoter for photoresist if desired.

11. Spin apply Shipley AZ1350J, AZ4210, or equivalent.

12. Soft bake resist 20 minutes at 90°C.

13. Expose in any standard contact, or proximity printer. Length of exposure will depend on light energy available from equipment.

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14. Use Shipley MF312 or other desired developer to develop the photoresist and at the same time etch the PYRALIN*. The developer should be diluted with DI H_2O so that it has a normality of .25N to .3N. We suggest a spin spray develop for best results. Second choice is a spray, then agitated dip, and last choice is a straight dip.

15. Etch should be complete in less than 30 seconds in a spin-spray piece of equipment. Slightly higher temperatures (30°C) will speed up etch rate.

16. Strip photoresist with 60% butyl acetate, 40% isopropanol solution at room temperature. Spray stripping is best. If any cracking of the PI is seen, increase the soft bake (Step 6) in 5°C increments until cracking is no longer present.

17. Rinse for 30 seconds at 1000 RPM with DI H_2O.

18. Blow dry in N_2 for 30 seconds at 3000 RPM.

19. Full cure 30 minutes at 300°C)
    30 minutes at 400°C) In Nitrogen

PROCESS FOR DEPOSITING A 1.5 MICRON PYRALIN* FILM ON A 4" WAFER AND OPENING VIAS BY A NEGATIVE WET ETCH PROCESS

1. Clean wafer. Use RCA or Pirannah clean or a Freon* Method. Bake at 180°C for 10 minutes.

2. Prepare and apply adhesion promoter in accordance with Bulletin #PC-7, Rev. 4/82.

3. Apply approximately 3cc of PI-2555 (PI-2545) thinned with T-9035 (8 parts PI-2555 to 1 part T-9035) to center of wafer on spinner. Note: Dilution should be made 24 hours in advance of use. Wafer should be at rest. Bring to full 3500 RPM immediately. Spin for 60 seconds. See Bulletin #PC-2, Rev. 3/82, for further details.

4. Soft bake wafer 30 minutes at 125°C. We suggest a hot plate or recirculating air oven. Infra-red may be used but remember that polyimide absorbs infra-red and the temperature of the film may exceed the temperature setting of the oven and cause poor results.

5. Let wafer cool for 5 minutes.

6. Apply HMDS adhesion promoter for resist if needed.

7. Spin apply a negative resist such as 747 Kodak. Caution: To achieve a 45° via wall slope, the photoresist should be applied, developed, and the polyimide etched within one hour. Long delays bwtween application of the photoresist and developing and etching can cause change in the slope of the via walls.

8. Soft bake the photoresist 30 minutes at 90°C.

9. Expose in any standard contact or proximity equipment. Length of exposure will depend on photoresist used and light energy available from equipment.

10. Develop following photoresist manufacturing instructions.

11. Hard bake resist for 20 minutes at 135°C.

12. Use Shipley MF312 to etch PYRALIN*. The MF312 should be diluted with deionized water so that it has a normality of .25N to .3N. We suggest a spin spray etch for best results. Second choice is spray, and last choice is straight dip.

13. Etch should be completed in about 30 seconds in a spin spray piece of equipment. Vias can be held to 3-4 microns. Slightly higher temperatures (30°C) will increase etch rates.

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14. Bake for 30 minutes at 160°C.

15. Strip photoresist with standard stripper like 712D or J100 at 80-85°C. If the stripper attacks the PYRALIN*, increase the bake in Step 14 by 10°C increments until attack disappears.

16. Rinse with deionized water - 5 minute dip, 5 minute spray for 2 cycles.

17. Fully cure at:

30 minutes	300°C)	in Nitrogen
30 minutes	400°C)	
10 minutes	450°C)	
5 minutes	500°C)	

18. Neutralize with a 1-3% acetic acid solution. Then rinse as in Step 16.

This should provide an adequate film that will withstand second layer metal deposition temperatures.

Back sputtering or low pressure oxygen plasma clean should be used to clean vias before second metal deposition.

If second layer metal adhesion is poor, a 5 minute low pressure oxygen plasma will roughen the PI surface and improve adhesion.

VSB/lgb
8/20/82

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DRY ETCHING PYRALIN*

Attached are two excellent papers covering both plasma etching and Reactive ion etching of polyimide films. I believe one word of caution is necessary whenever plasma or RIE is discussed. No two etch reactors behave exactly the same even though they are the same size, model number, or share the same specifications. Information on dry etching techniques can and should be used as a guide, but exact results probably cannot be duplicated on similar equipment.

A Guide to O_2 plasma etching fine line geometries follows:

1. Best results are obtained etching fully cured, PI films.

2. For etching small vias, a mask other than photo resist should be considered. This mask can be a metal mask, silicon nitride, or a spin on glass. T. O. Herndon's paper reports good results using spin on glass. This may be more economical than the other alternatives.

3. After mask imaging a neutralization rinse in 1% to 3% acetic acid is suggested to neutralize any sodium ions which if allowed to remain on the surface, can cause non uniform etch rates across the wafer surface. The neutralization is followed by a DI water rinse.

4. To etch almost straight walls, in a single wafer parallel plate etcher, a power of 100 watts and 50 millitorr can be used with straight O_2 gas. Etch rate will be about 900 A/min.

5. Faster etch rates may be obtained by using higher power, pressures, and temperatures. 3500 A/min. etch rates have been demonstrated at 300 watts and 50 millitorr. If, at 300 watts, pressure is allowed to rise to 2000 millitorr and temperature to 180°C, the etch rate is too fast to control.

6. Another approach being used is to etch at high power (300 watts) and high pressure (1500 millitorrs) to obtain an isotropic etch halfway through the PI film. The pressure and power is then lowered to 50 millitorr and 50 watts to obtain an anisotropic etch speed, a 45° angle through part of the film and straight walls through the remaining film for good metal step coverage.

VSB/mmc
Attach.

Intermetal Polyimide Via Conditioning and Plasma Etching Techniques*

T.O. Herndon, R.L. Burke, W.J. Landoch
MIT Lincoln Laboratory, Lexington, MA 02173

Polyimide has numerous advantages as an intermetal insulator for integrated circuits including self-levelling, low defect density, a large range of useful thicknesses and ease of application. The high resolution required for the via openings utilized in VLSI has stimulated the study of factors which directly affect via dimensions and via contact resistance including: etching power and pressure, photoresist characteristics, premetal cleanup and thermal curing. In these experiments the polyimide used was DuPont PI2555 and the vias were etched by O_2 plasma in a 7" diameter parallel plate reactor with aluminum electrodes spaced 1.5" apart.

The standard procedure for eliminating so-called "invisible shield"[1] involves etching 80% of the P.I. thickness at 250 millitorr and finishing the etch at 50 millitorr, both at 50-100 watts[2]. This final etch at low pressure eliminates the redeposition which is found to occur at higher pressures. Attempts to simplify this schedule by etching the full P.I. thickness at 50 millitorr, using 300 watts R.F. power in order to increase the etch rate, has been found to cause several problems. The standard schedule etches both the P.I. and the Shipley AZ photoresist at 1,000 Å/min. This rate drops to 250 Å/min. for the 50 watt, 50 millitorr condition. Etching at 300 watts, 50 millitorr increased the polyimide etch rate to 3,000 Å/min., but the photoresist etch rate increases even more to 4,300 Å/min. A second undesirable effect of increasing power from 50 watts to 300 watts is that the etching of the P.I. and photoresist, which are anisotropic at the low power, become isotropic at high power. Thus, the via dimensions enlarge at a considerably greater rate at the high power level with the sidewall in the P.I. via becoming rough and tapered at approximately a 45° angle due to the photoresist erosion. Furthermore, the amount of residue left in the bottom of the completed vias is considerably greater than in the case of etching at 50 watts and 50 millitorr. This residue which is clearly visible in SEM images, can be removed by continuing the etch at 50 watts and 50 millitorr, and it can be removed in buffered HF. SEM studies of the resist/P.I. layers etched at the 300 watt, 50 millitorr pressure conditions indicate the high etch rates and pronounced roughening of the resist surface/ P.I. via sidewalls are probably due to sputtering which is augmenting the normal O_2/polymer chemistry. This sputtering is also thought to be responsible for the residue left at the bottom of the via openings which is caused by knocking off chunks of resist/P.I. It is concluded that successful plasma etching of P.I. using photoresist masking requires completing the etch at low r.f. power and low pressure to eliminate these problems.

---

*This work was sponsored by the Department of the Air Force
The U.S. Government assumes no responsibility for the information presented.

Positive photoresist on polyimide requires long exposure times due to the absence of back-reflection from the light absorbing underlayer. It is also limited as a mask for O_2 plasma etching since the resist erodes at least as fast as the P.I.[2] The use of aluminum or chromium as a non-erodable mask for P.I. has been demonstrated but the added complexity of depositing metal is a drawback. We have investigated spin-on glass as an easily applied and removed noneroding mask. In this case, Silicafilm from Emulsitone Co. is spun on fully cured P.I. at 10,000 rpm and baked for 15 minutes at 250°C. This produces a pinhole free glass layer approximately 1300 Å thick. AZ resist is spun on to a thickness of 1 to 1.2 microns, exposed and developed using normal techniques. The glass is then plasma etched in $CF_4 + O_2$ at 250 millitorr pressure and 50 watts power in a parallel plate reactor with an etch rate of 450 Å/min. This etch is reasonably selective, relative to the photoresist, and does not etch the P.I. at all. Following the glass definition, the P.I. can then be etched in O_2 plasma during which time the photoresist is completely removed. The spin-on glass can be stripped either with $CF_4 + O_2$ plasma or in 100:1 HF. The benefits of the spin-on glass are its ease of application and removal, its complete resistance to O_2 plasma, which permits etching thick P.I. sections, and the absence of residue in the via after etching regardless of plasma power.

A third major factor affecting via yield is surface preparation prior to metallization. The use of buffered HF immediately prior to second level metal has been described[3]. However, some applications cannot tolerate HF, and we have found that a 90 second dip in a 1:1 mix of Shipley MF 312 and water is a reasonable substitute for HF to effect aluminum oxide removal. On the other hand the use of argon sputter cleaning after resist removal, while it gives consistently low via contact resistance, leads to very poor adhesion of metal to P.I.. Examination of SEM photos indicates that the argon sputter process breaks up the P.I. surface into either a very fine powder or loosely bound particles, which causes such poor adhesion that the top metal may fall off nearly spontaneously. If argon sputter cleaning is used, it must be prior to resist removal to prevent this problem.

A final area of difficulty has been bubbling of the overlying metal during 450°C sinter. This occurs only in large (100 mm^2), unpatterned areas such as those which remain at the outer edges of DSW exposed wafers. Experiments have verified this is due to outgassing of the P.I., probably caused by absorbed liquid from HF dip and rinse steps. It has been demonstrated that baking the P.I. at 300-400° for half an hour prior to application of metal eliminates this bubbling. However, it has also been found that baking the P.I. at temperatures above 150°C prior to metallization leads to very poor via contacts. There is Auger evidence that outgassing from the via sidewalls or surface of the P.I. deposits an insulating carbonaceous material at the bottom of the via. Elimination of metal bubbling can be achieved without this deleterious premetallization bake by increasing the sinter temperature gradually in 15 minute-long increments at 150° 300° - 400° - 450°C.

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2. D.R. Day, R. Whitten, S.D. Senturia, "Invisible Shield in Polyimide Vias — An Auger Analysis," E.C.S. Meeting, Denver, CO, Oct. 1981.

3. T.O. Herndon, R.L. Burke, J.A. Yasaitis, "Use of Polyimide in VLSI Fabrication," E.C.S. Meeting, Denver, CO, Oct. 1981.

DRY ETCHING: REACTIVE ION ETCHING

The processing of semiconductor devices involves the use of a variety of organic films. Mainly these films are photoresists used for masking purposes. More recently, organic films such as polyimide are being used as insulators. Therefore, the etching characteristics of organic films is of importance. The literature has mainly dealt with the stripping of resists in an oxygen plasma. This part of the course will deal with the reactive ion etching of organic films in both O_2 and CF_4 plasmas.

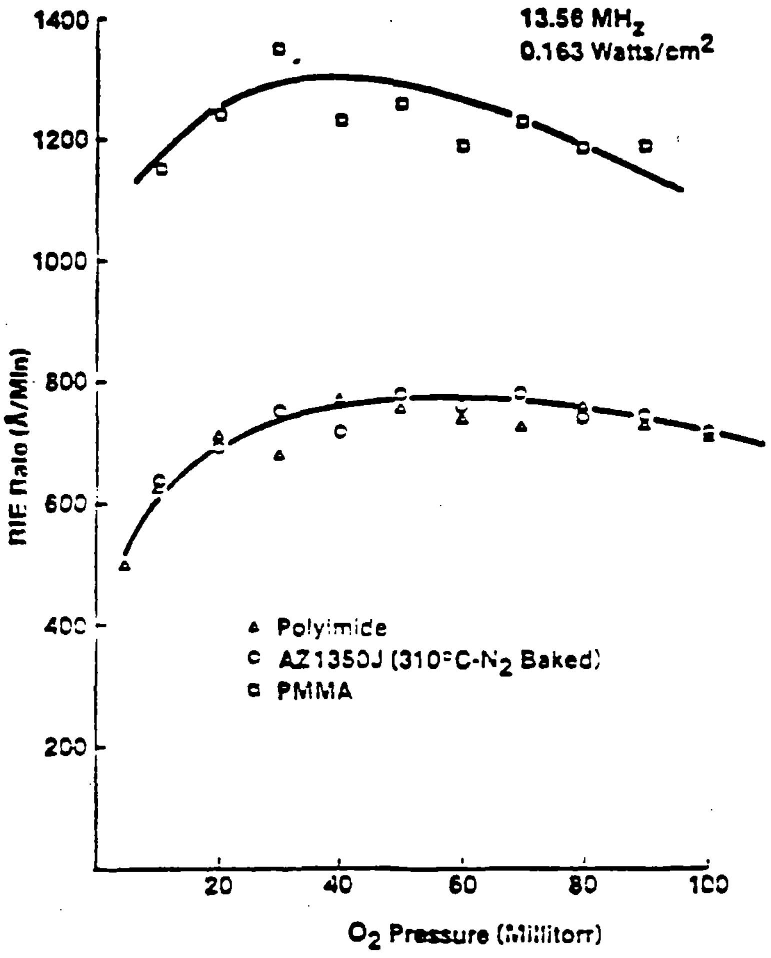
The organic films investigated are AZ1350J, KMR, PMMA, polyimide and polysulfone. Etch rate data as a function of system parameters are presented. Despite the structural differences in these organic films, all the materials with the exception of PMMA etch at the same rate under the same conditions.

Many differences were observed in the etching of organic films in a O_2 plasma compared with a CF_4 plasma. In general the etch rates are lower in CF_4 than in an O_2 plasma. Loading effects occur in both plasmas but to different degrees. In a CF_4 plasma, a large decrease in the etch rate of the organic film is observed as the cathode is loaded with either organics or Si. A small loading effect is seen in an O_2 plasma with the addition of organics only. The influence of loading on etch rate uniformity will also be discussed.

Profiles of organic films etched in an O_2 plasma with a non-erodible mask are considerably different from profiles obtained in a CF_4 plasma. In an O_2 plasma, undercutting is observed as a function of pressure. Under the same conditions in a CF_4 plasma only vertical profiles are observed.

Surface roughening and residue are examined as a function of etching conditions, since the functional organic films are left in place. For the thermally stable organic materials such as polyimide, surface roughening and residue formation are related and are a function of pressure. Residue is produced by backscattering of sputtered inorganic material and also by inorganic particles in the organic films. Generally, as the pressure is increased more backscattering occurs. However, in an O_2 plasma the amount of undercutting which increases with the pressure, results in a smoother surface.

A process for forming vias in polyimide by reactive ion etching will also be discussed.


13.56 MHz
0.163 Watts/cm^2
1400
1200
1000
800
600
400
200
RIE Rate (Å/Min)
20
40
60
80
100
O_2 Pressure (Millitorr)
▲ Polyimide
○ AZ1350J (310°C-N_2 Baked)
□ PMMA

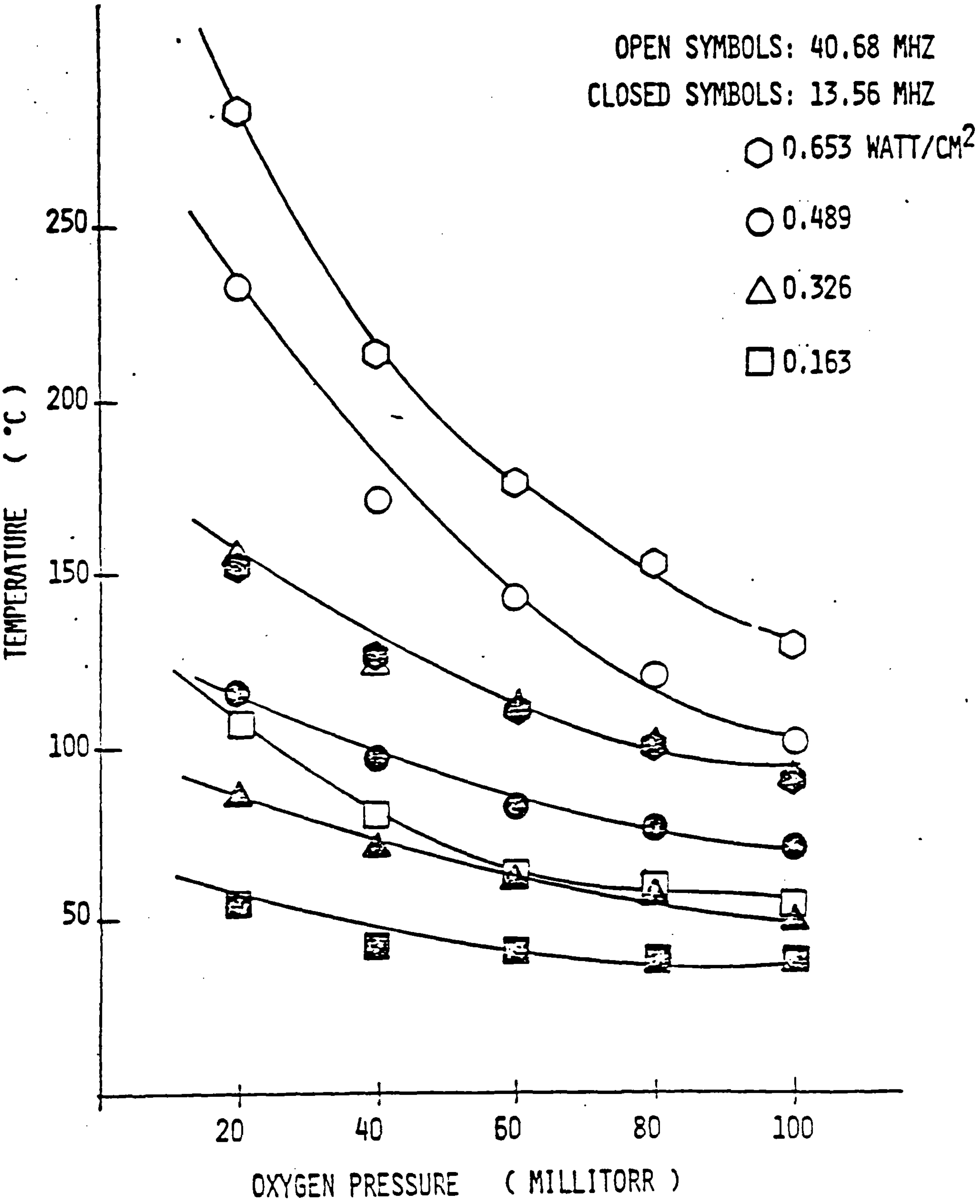
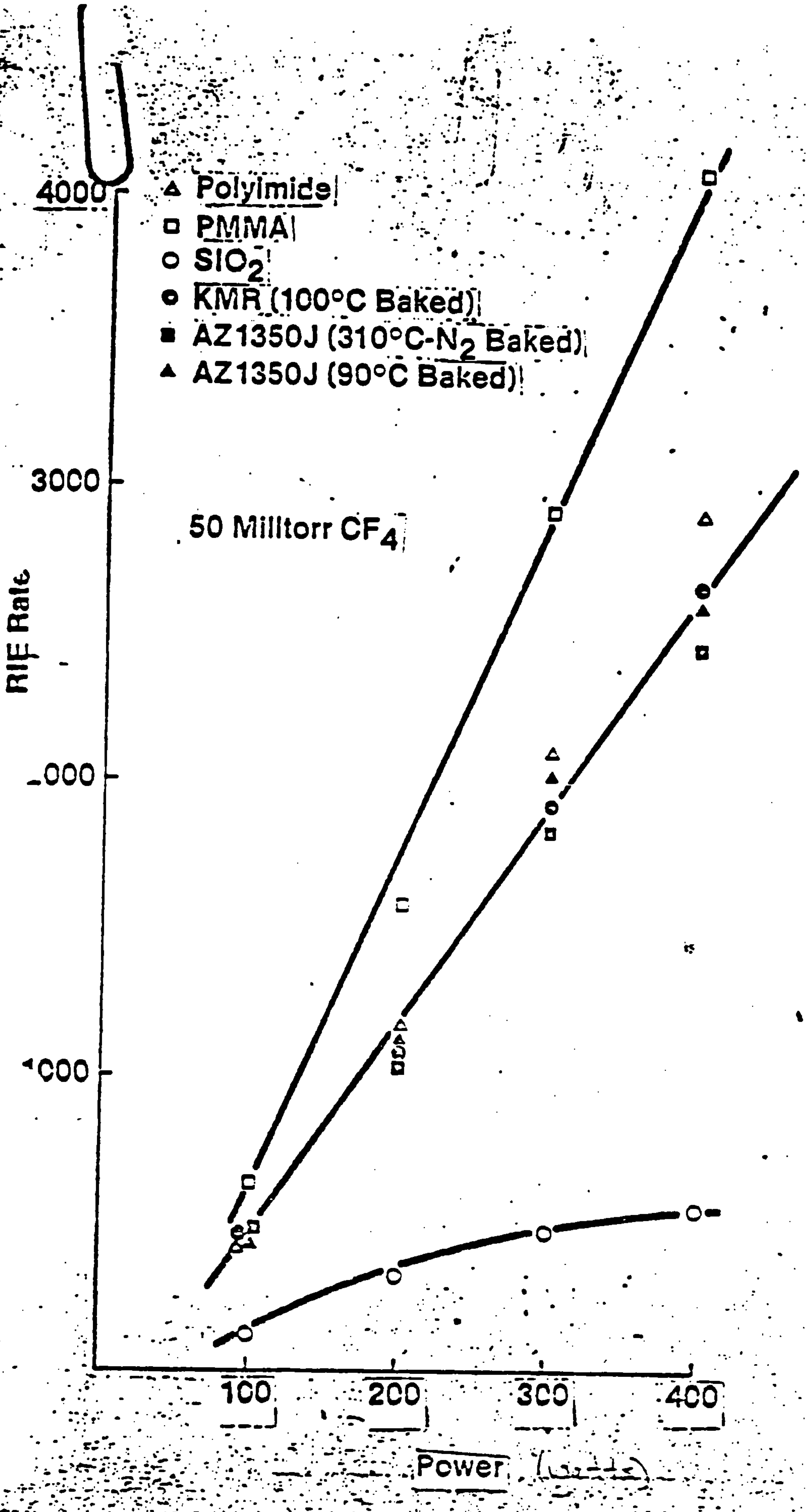
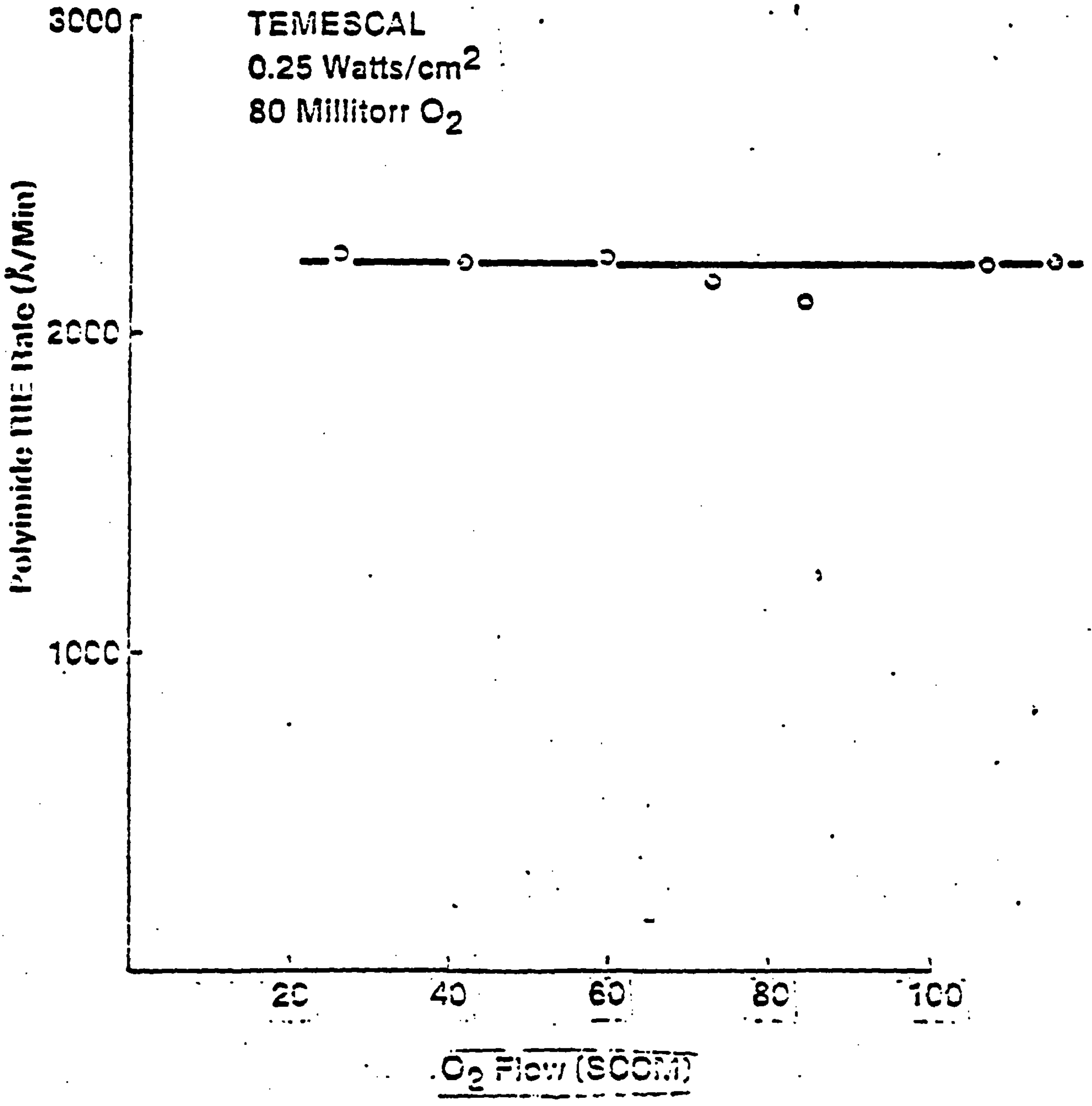
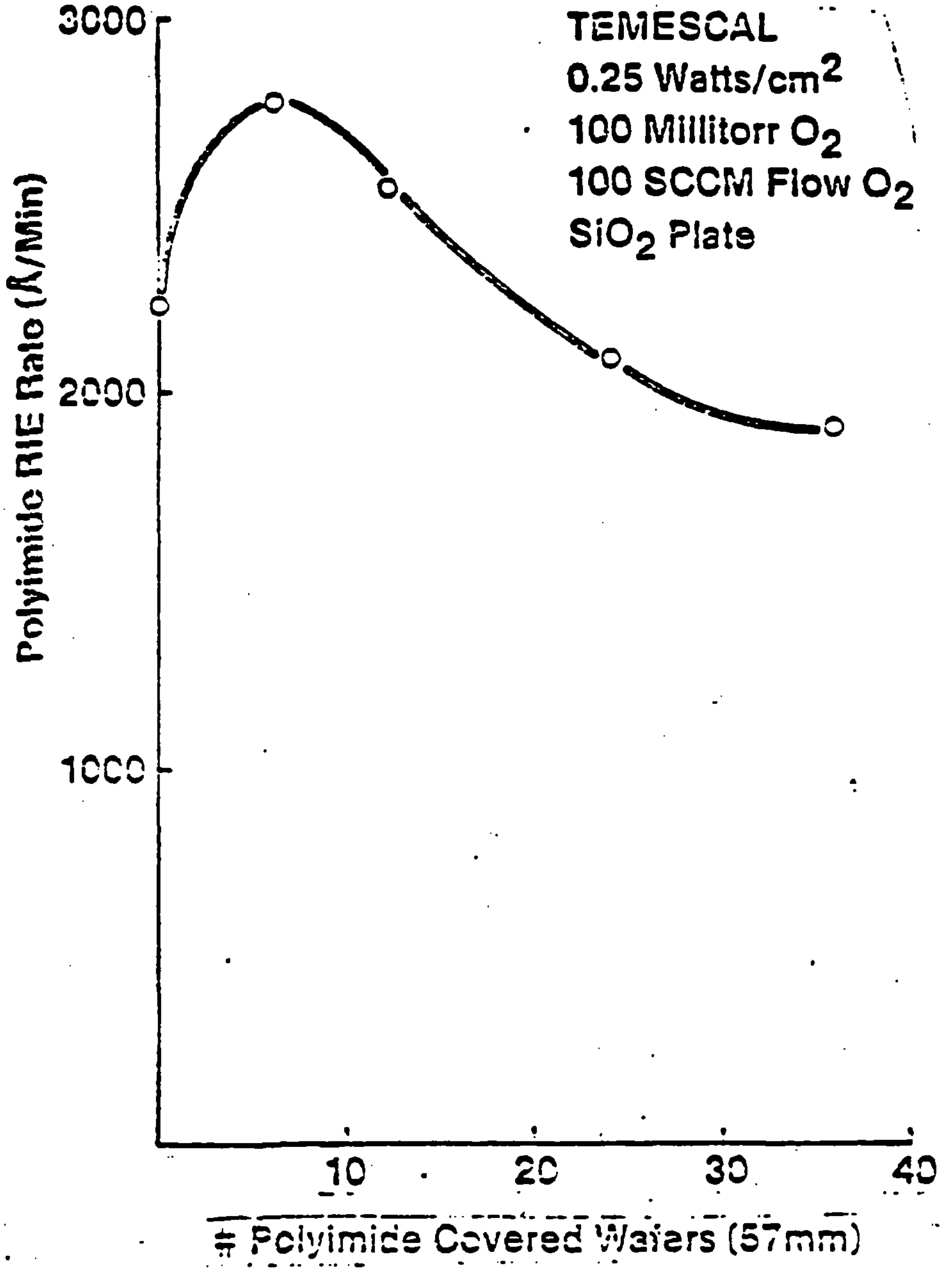
OPEN SYMBOLS: 40.68 MHZ
CLOSED SYMBOLS: 13.56 MHZ
0.653 WATT/CM^2
0.489
0.326
0.163
TEMPERATURE (°C)
250
200
150
100
50
20
40
60
80
100
OXYGEN PRESSURE (MILLITORR)

Fig.10

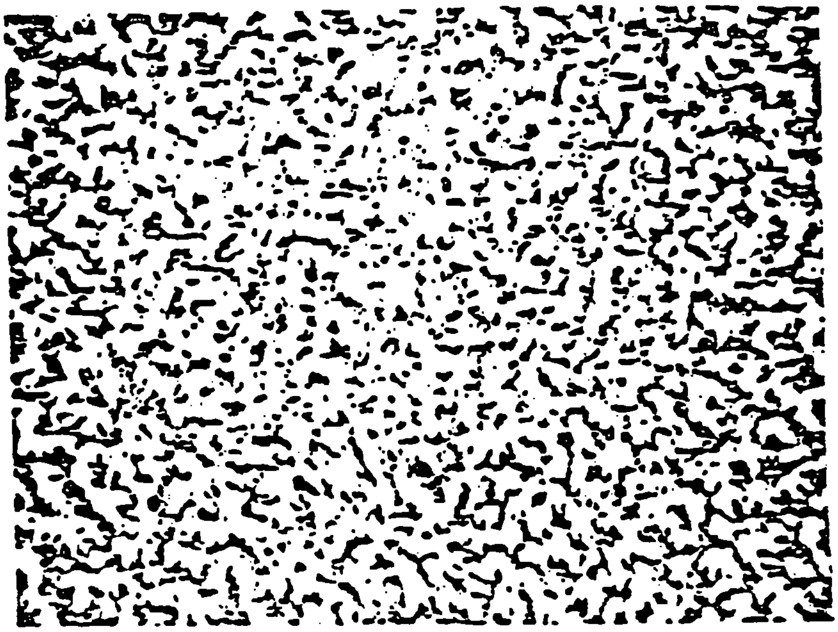

RIE Rate
4000
3000
-000
1000
100
200
300
400
Power
▵ Polyimide
□ PMMA
○ SIO$_2$
⊙ KMR (100°C Baked)
■ AZ1350J (310°C-N$_2$ Baked)
▲ AZ1350J (90°C Baked)
50 Millitorr CF$_4$

TRM-EF- 12

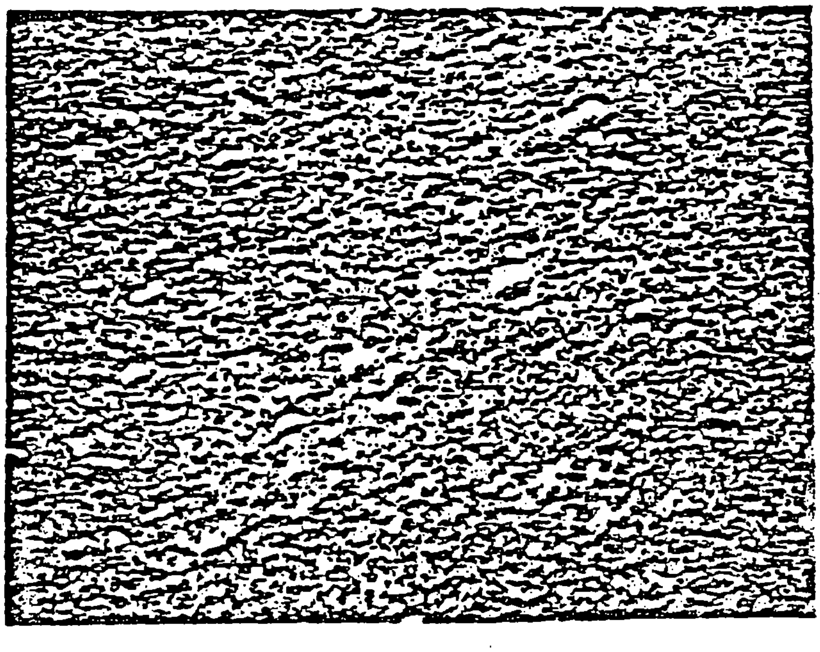

TEMESCAL
0.25 Watts/cm^2
80 Millitorr O_2
Polyimide RIE Rate (Å/Min)
3000
2000
1000
20
40
60
80
100
O_2 Flow (SCCM)


TEMESCAL
0.25 Watts/cm^2
100 Millitorr O_2
100 SCCM Flow O_2
SiO_2 Plate
Polyimide RIE Rate (Å/Min)
3000
2000
1000
10
20
30
40
Polyimide Covered Wafers (57mm)

RESIDUE AS A FUNCTION OF GAS

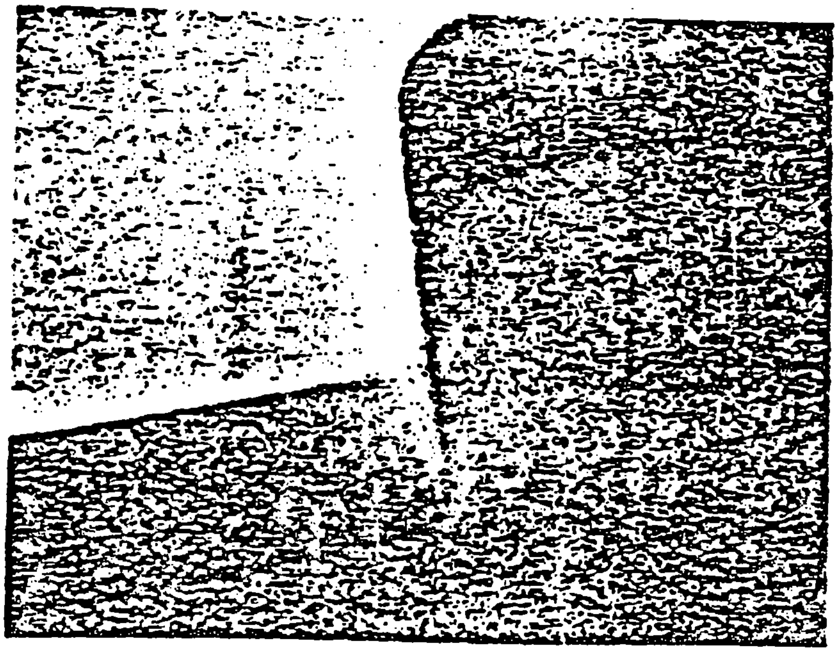


50 MILLITORR O_2



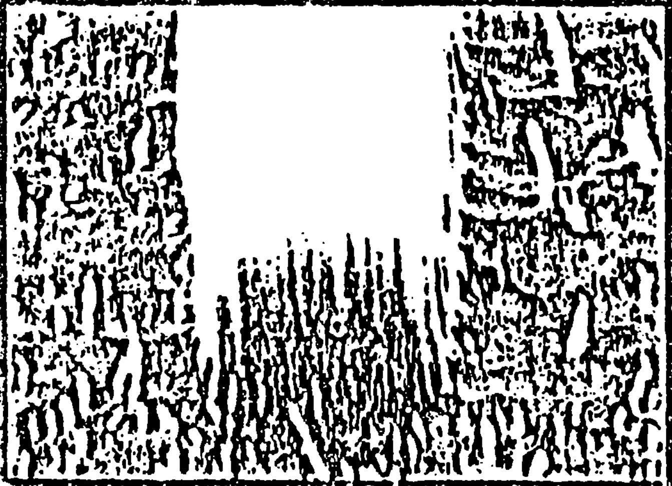
50 MILLITORR CF_4

AFTER RIE IN OXYGEN



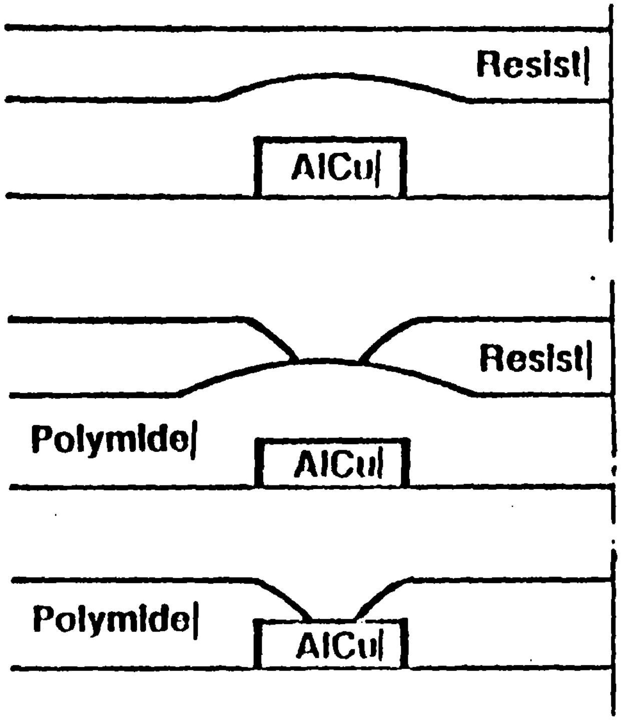
RESIDUE REMOVAL AFTER DIP IN BHF

Polymer Film with Non-Erodible Mask RIE at 100 Millitorr CF4



15,000x

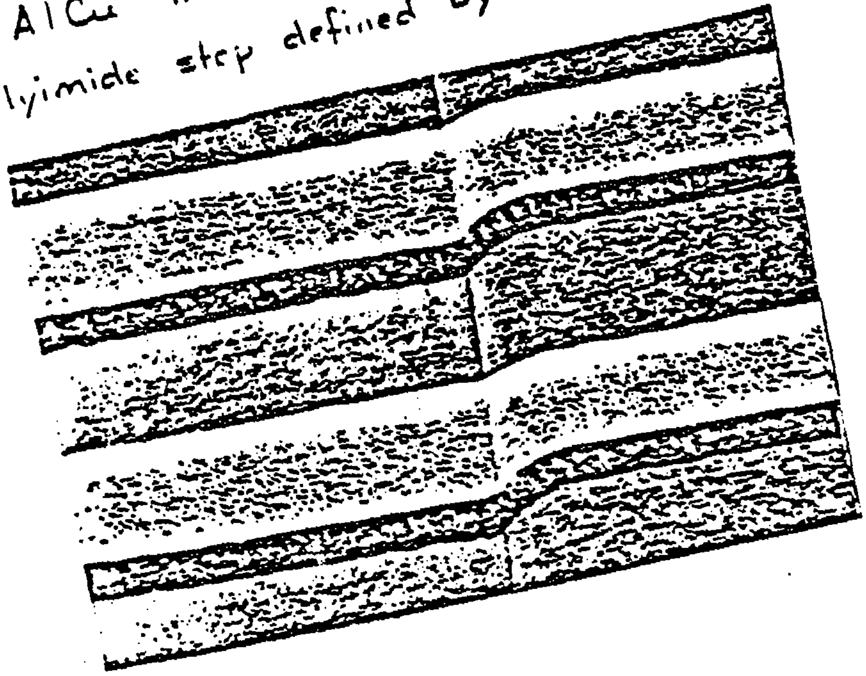
RIE of Vias in Polymide



1. Apply Polymide and Fully Cure
2. Apply Thick Layer of Resist (Must be Thicker than Polymide Layer)
3. Define Via Pattern in Resist
4. Post-Bake for 30 Minutes at 130°C
5. RIE in O_2 Plasma
6. Strip Resist in NMP at 60°C

INT

AlCu lines over Polyimide Step
(Polyimide step defined by reactive ion etching in O$_2$)



2400x

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Adhesion

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2. K. Kendall, J. Adhesion, Vol. 5, 179-202 (1973)
3. W. D. Bascom, Macromolecules, Vol. 5, No. 6, Nov.-Dec. (1972)
4. L. B. Rothman, J. Electrochem. Soc., Vol. 127, No. 10, Oct. 1980.

Planarity

1. K. Sato, S. Harada, A. Saiki, T. Kimura, T. Okubo, and K. Mukai, IEEE Trans. Parts, Hybrids, Packag., Ph p-9 176 (1973)
2. A. Saiki, S. Harada, T. Okubo, K. Mukai and T. Kimura, J. Electrochem. Soc., 124, 1619 (1977)

RIE

1. G. C. Schwartz, L. B. Zielinski, T. Schopen, Proceedings Vol.- Etching for Pattern Definition" J. Electrochem Soc. (1976)
2. J. R. Hollahan & A. J. Bell (Editors), "Techniques and Applications of Plasma Chemistry," John Wiley, New York 1974.

LOW PRESSURE OXYGEN PLASMA

- TYPICAL OPERATING CONDITIONS:
  - 35×10^{-3} TORR PRESSURE
  - OXYGEN GAS
  - 500 WATTS R.F. POWER
  - 2 TO 3 MINUTES
  - BUFFERED HF DIP TO REMOVE AL OXIDE

- WHY THIS METHOD IS USED:
  - QUICK
  - RELATIVELY CLEAN
  - AL SINTERING PROBABLY NOT NEEDED
  - EXCELLENT IF PLASMA ETCHING PI

- CAN BE USED ON SOME DEVICES WHERE SPUTTERING CANNOT BE USED.

- MOST CUSTOMERS HAVE THE EQUIPMENT

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PHOTOREACTIVE POLYIMIDE PRECURSOR

"PAL"

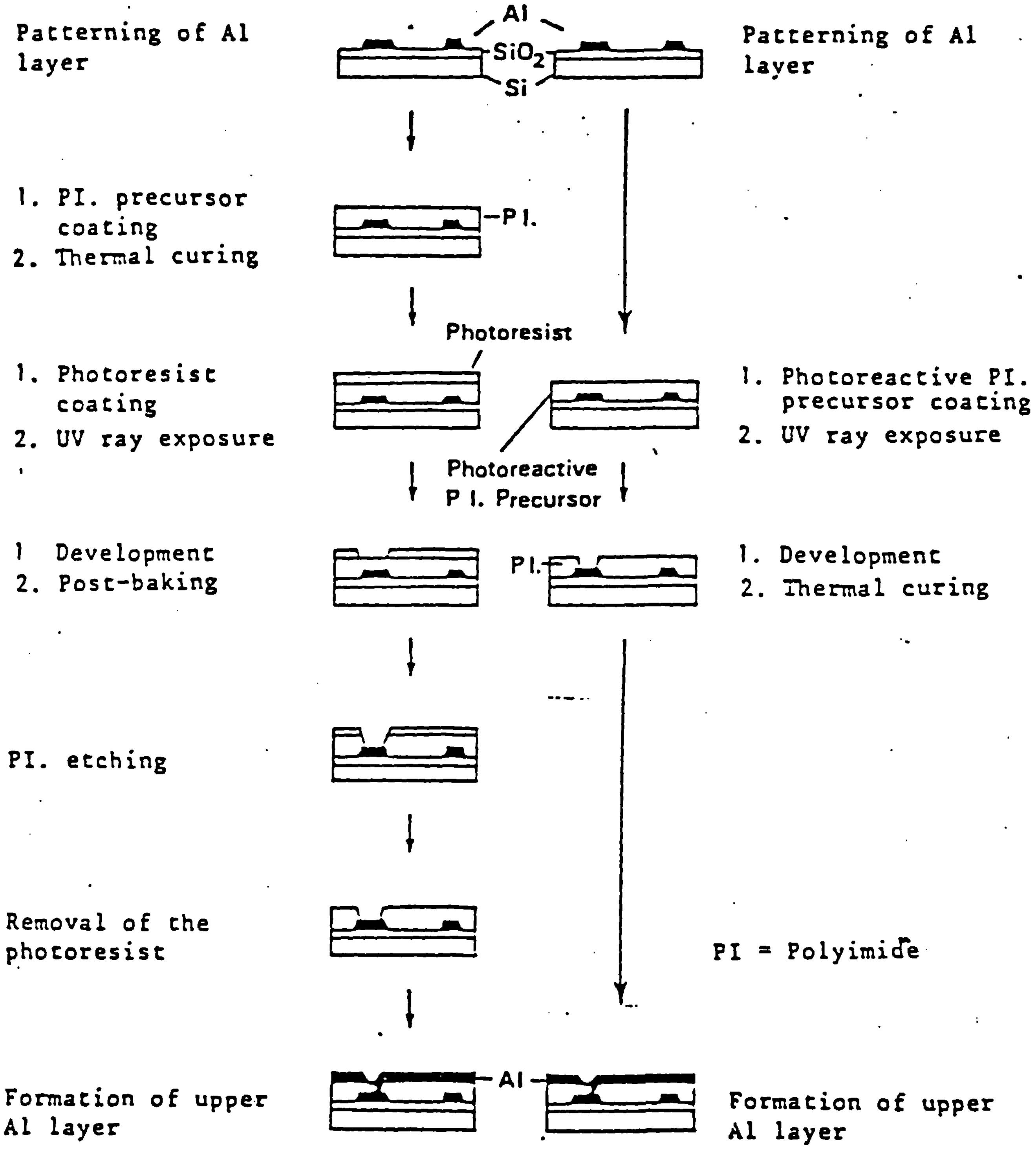
I. THE UTILITY OF PHOTOREACTIVE POLYIMIDE PRECURSOR IN MICROFABRICATION OF THE ELECTRONIC DEVICES

1) Shortening the Polyimide Layer Pattering Processes

2) No Need to Use Polyimide Etchant such as Hydrazine Hydrate Which has a Considerable Toxicity

Previous Works for Photoreactive Polyimide Precursors

1) R. W. Kerwin et al., Polymer Eng. and Sci., 11, 426 (1971)
2) R. Rubner, Siemens Forsch, u, Entwickl., 5, 92 (1976)
3) T. Hir moto et al., Denshizairyo, 47 (1981)



a) Patterning of an ordinary polyimide layer

b) Patterning of a polyimide layer by utilizing its photoreactive precursor

FIGURE 1. A COMPARISON OF THE POLYIMIDE PATTERNING PROCESS UTILIZING AN ORDINARY PRECURSOR WITH THE NEW PROCESS UTILIZING A PHOTOREACTIVE PRECURSOR

II. CHARACTERISTICS OF THE PHOTOREACTIVE POLYIMIDE PRECURSOR " PAL ".

(PAL = PHOTOREACTIVE POLYAMIC ACID FOR LITHOGRAPHY)

1) HIGH SENSITIVITY: 10-12 mJ/CM^2 AT 365 NM (THICKNESS: 3-6 μm)

2) HIGH CONTRAST: γ = 1.4-1.6

3) EXCELLENT FINE PATTERN PRODUCTIONABILITY
   RESOLUTION FOR LINES AND SPACES PATTERN IN 4.1 μm THICKNESS: 3 μm
   RESOLUTION FOR THROUGH-HOLE PATTERN IN 4.1 μm THICKNESS: 5 μm

4) ALMOST COMPLETE REMOVAL OF THE PHOTOREACTIVE GROUPS OR COMPONENTS AND CONCOMITANT IMIDIZATION WITH A THERMAL CURING TREATMENT

Table Liquid Properties of PAL

Item	Unit	Property
Viscosity	CPS	2500
Solid Content	%	14.2
Impurities Content	ppm	
Na		1.8
K		0.1
Fe		0.8
Cu		<0.1
Filtration	μm	1.0

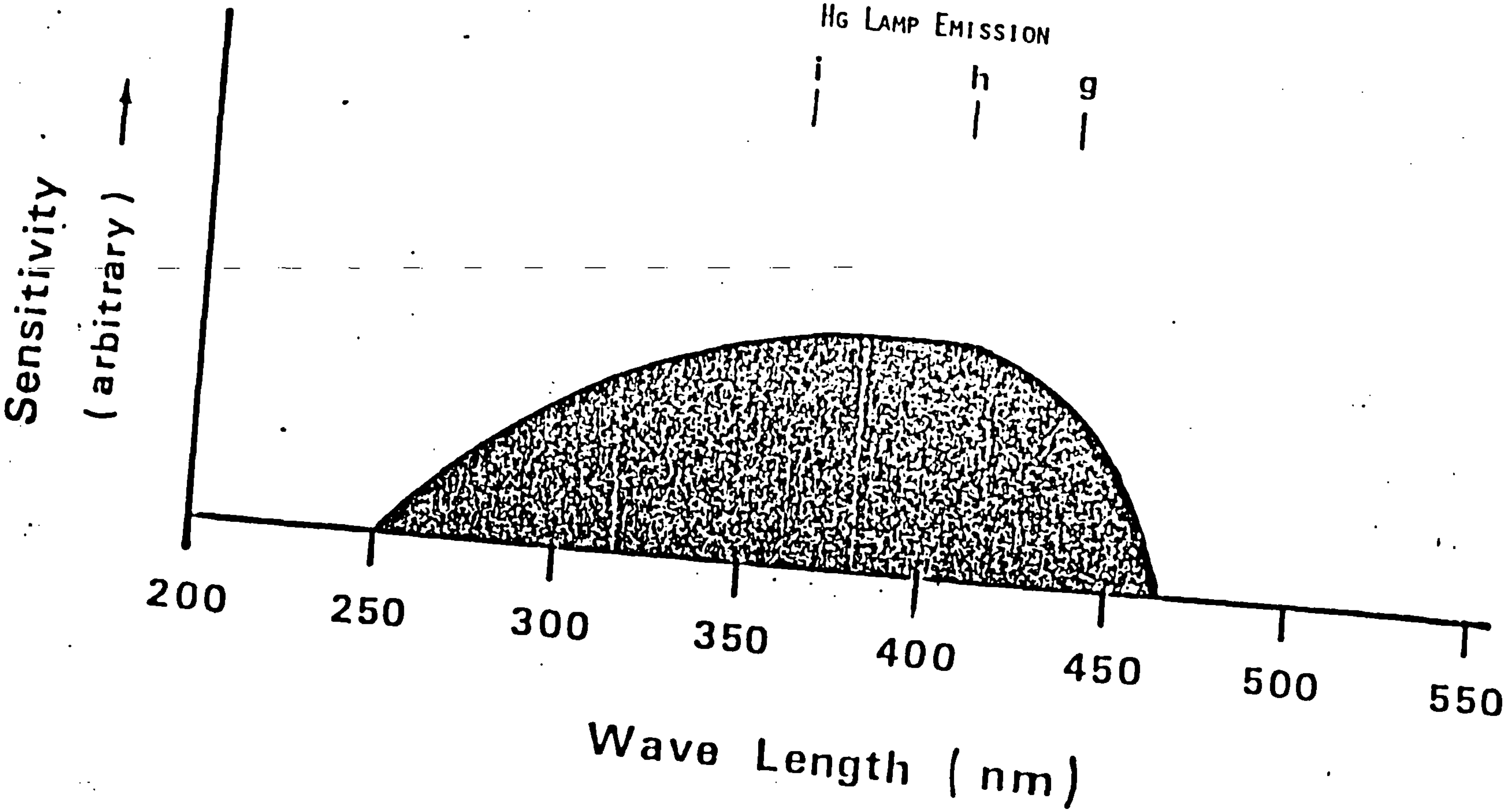


FIGURE SPECTRAL SENSITIVITY FOR PAL

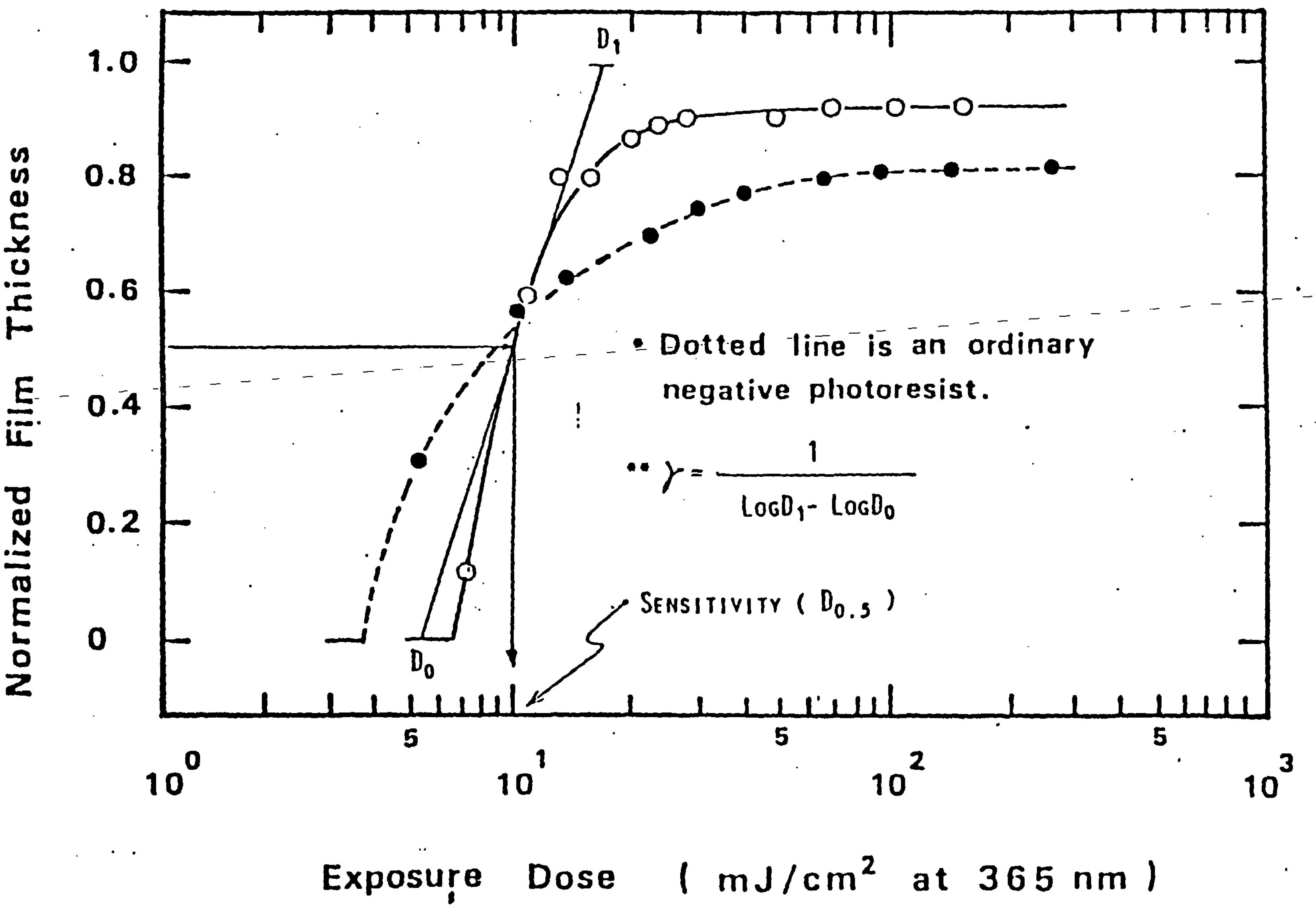


FIGURE EXPOSURE CHARACTERISTIC FOR PAL WITH UV RAY IRRADIATION.

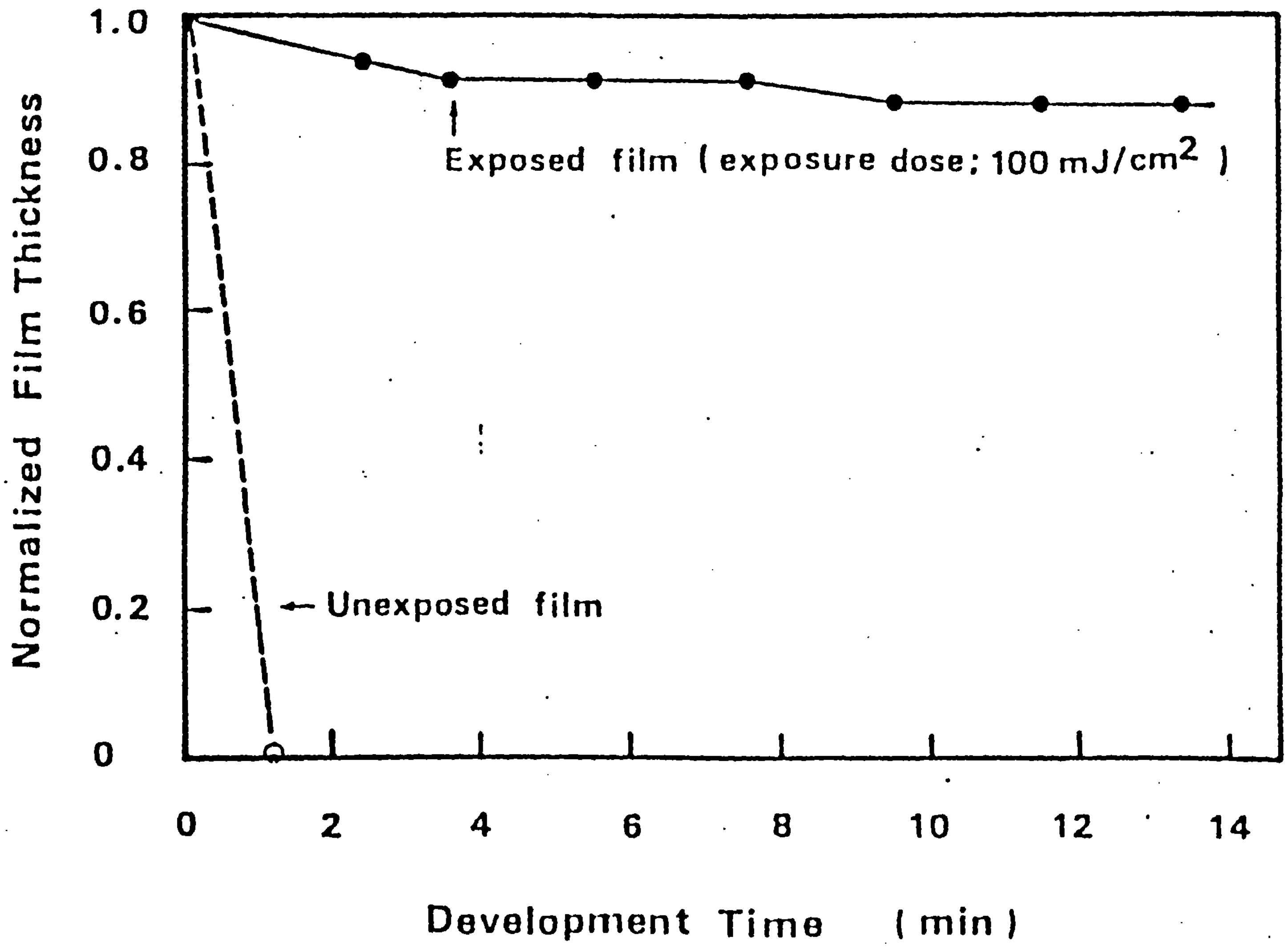


FIGURE DEPENDENCE OF DEVELOPMENT TIME FOR THE REMAINING FILM THICKNESS.

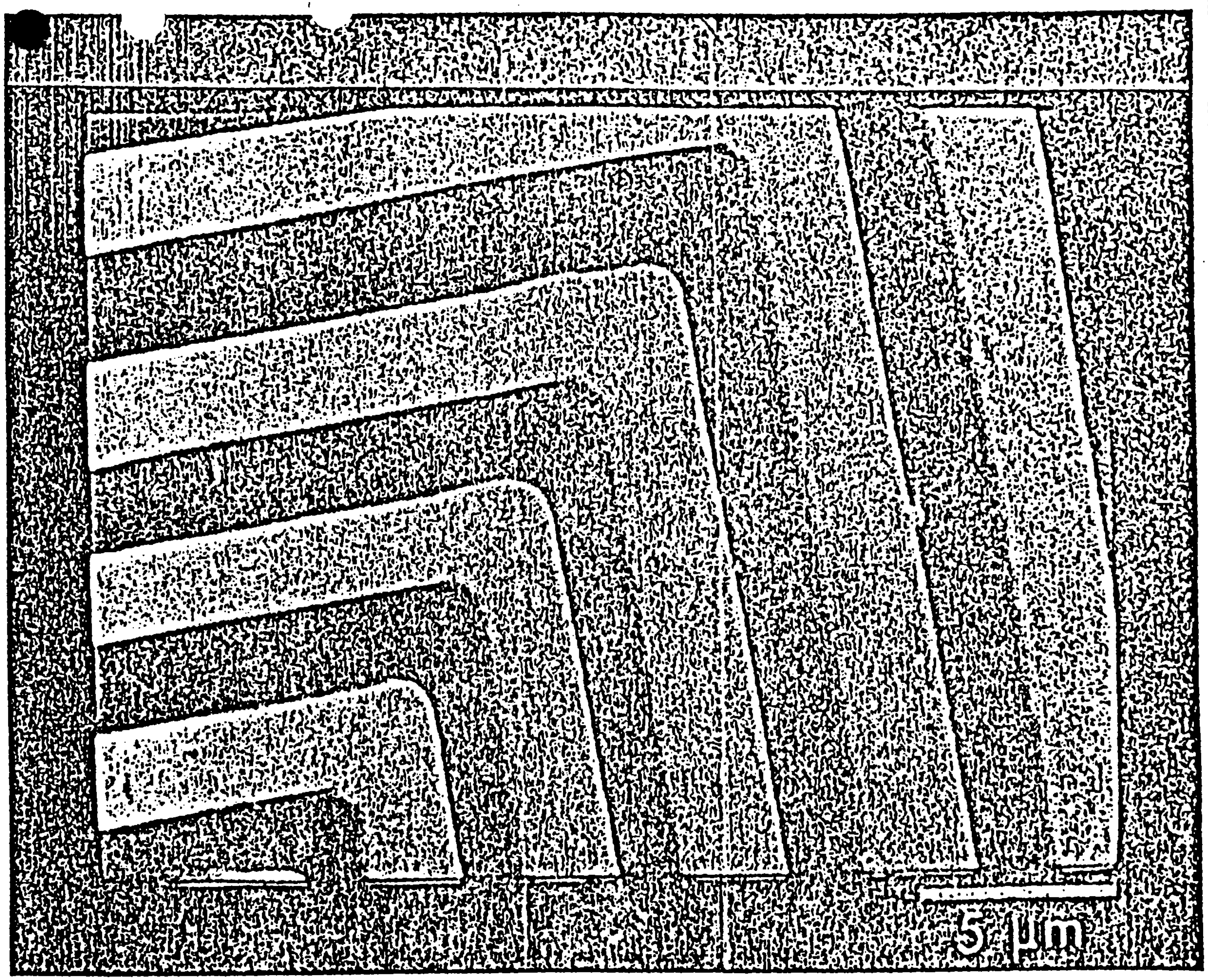


FIGURE PATTERNS IN 4.1 µm THICK PAL MADE WITH CONTACT PRINTING.

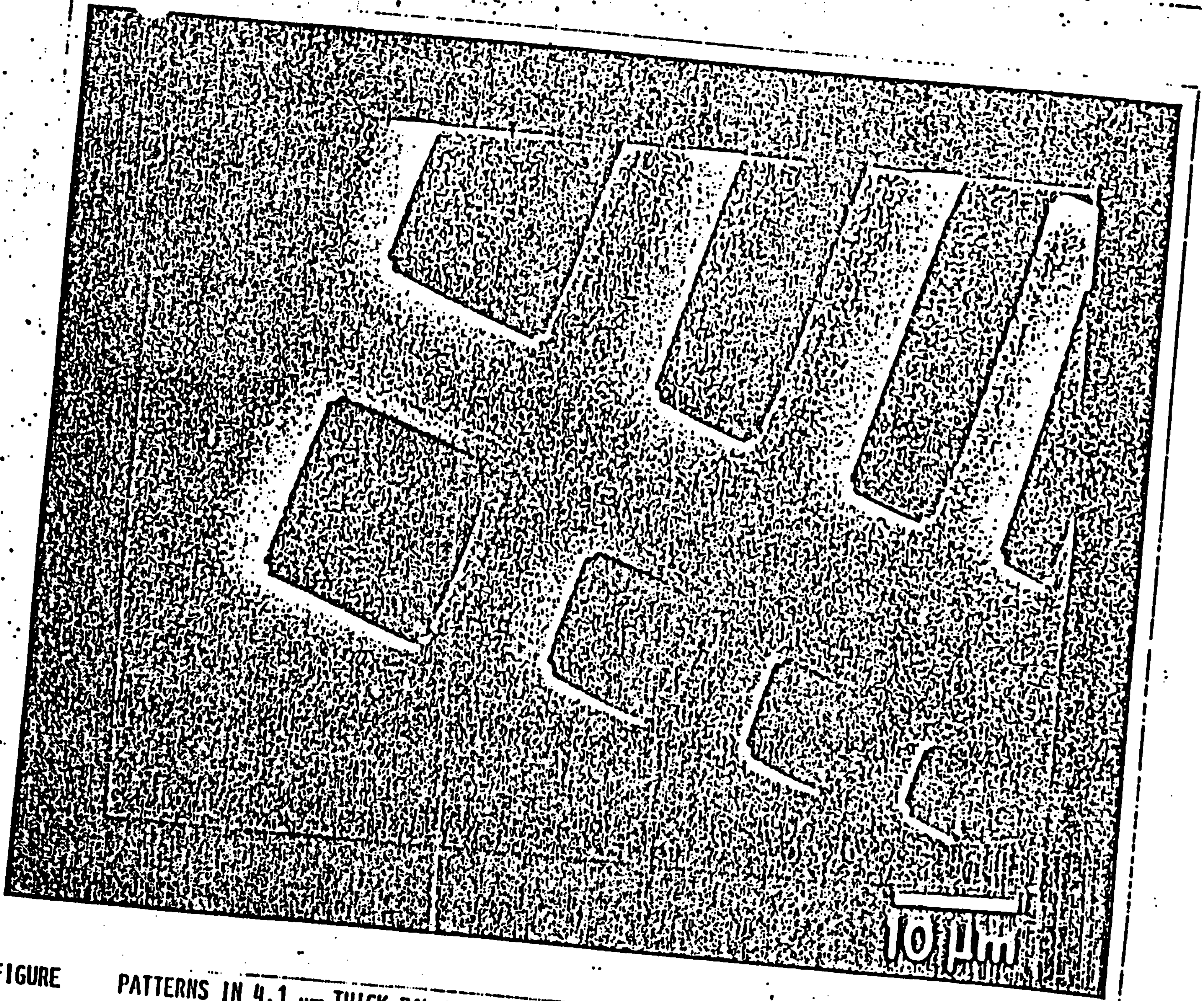


FIGURE PATTERNS IN 4.1 μm THICK PAL MADE WITH CONTACT PRINTING.

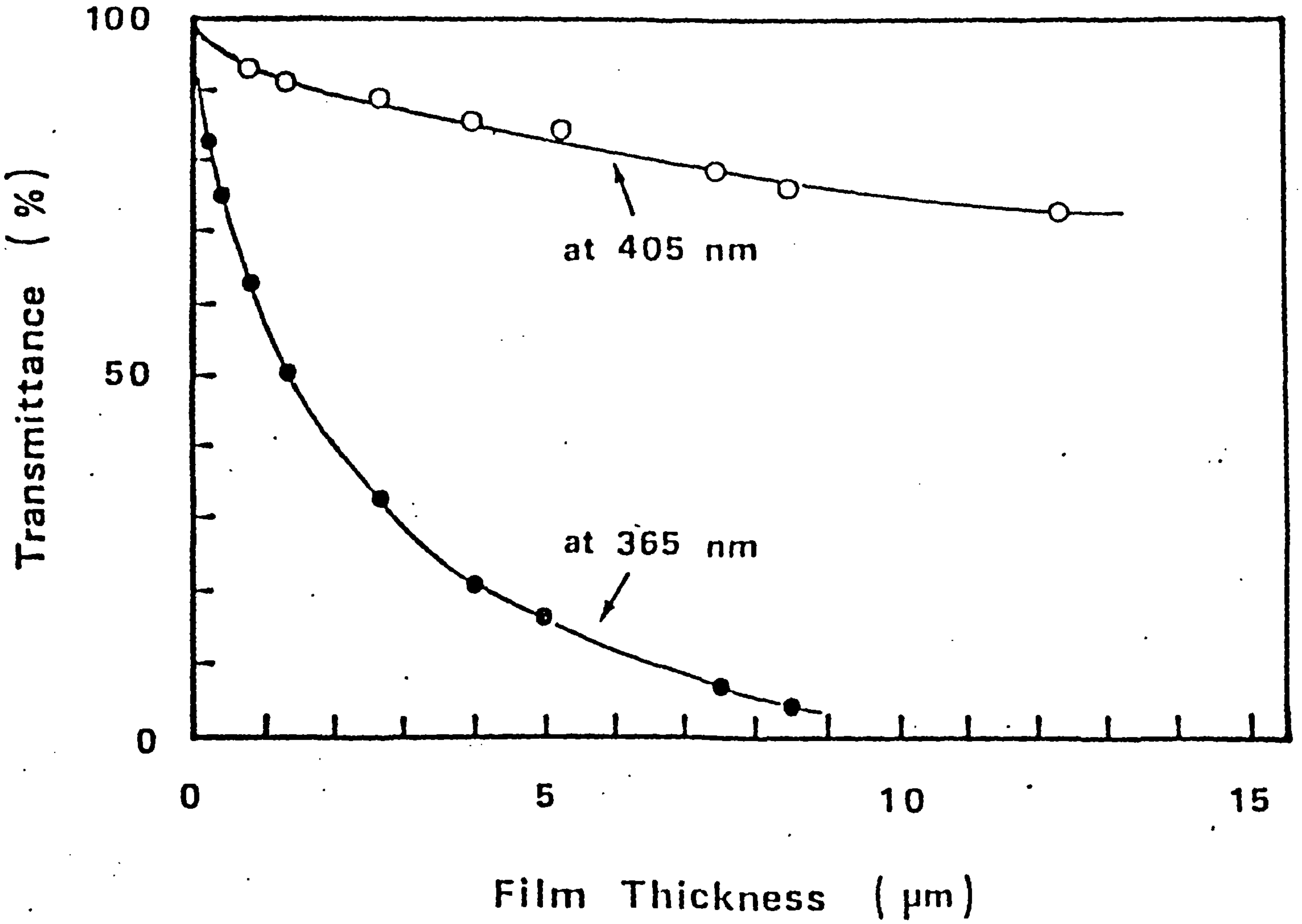


FIGURE DEPENDENCE OF FILM THICKNESS FOR THE UV ABSORPTION OF PAL.

III. CHARACTERISTICS OF THE POLYIMIDE PRODUCED FROM " PAL ".

1) RETAIN THE " PAL " PATTERNS SATISFACTORILY

2) HIGH HEAT RESISTIVITY

3) GOOD ELECTRICAL AND MECHNICAL PROPERTIES FOR THE APPLICATION OF THE MICROELECTRONIC DEVICES

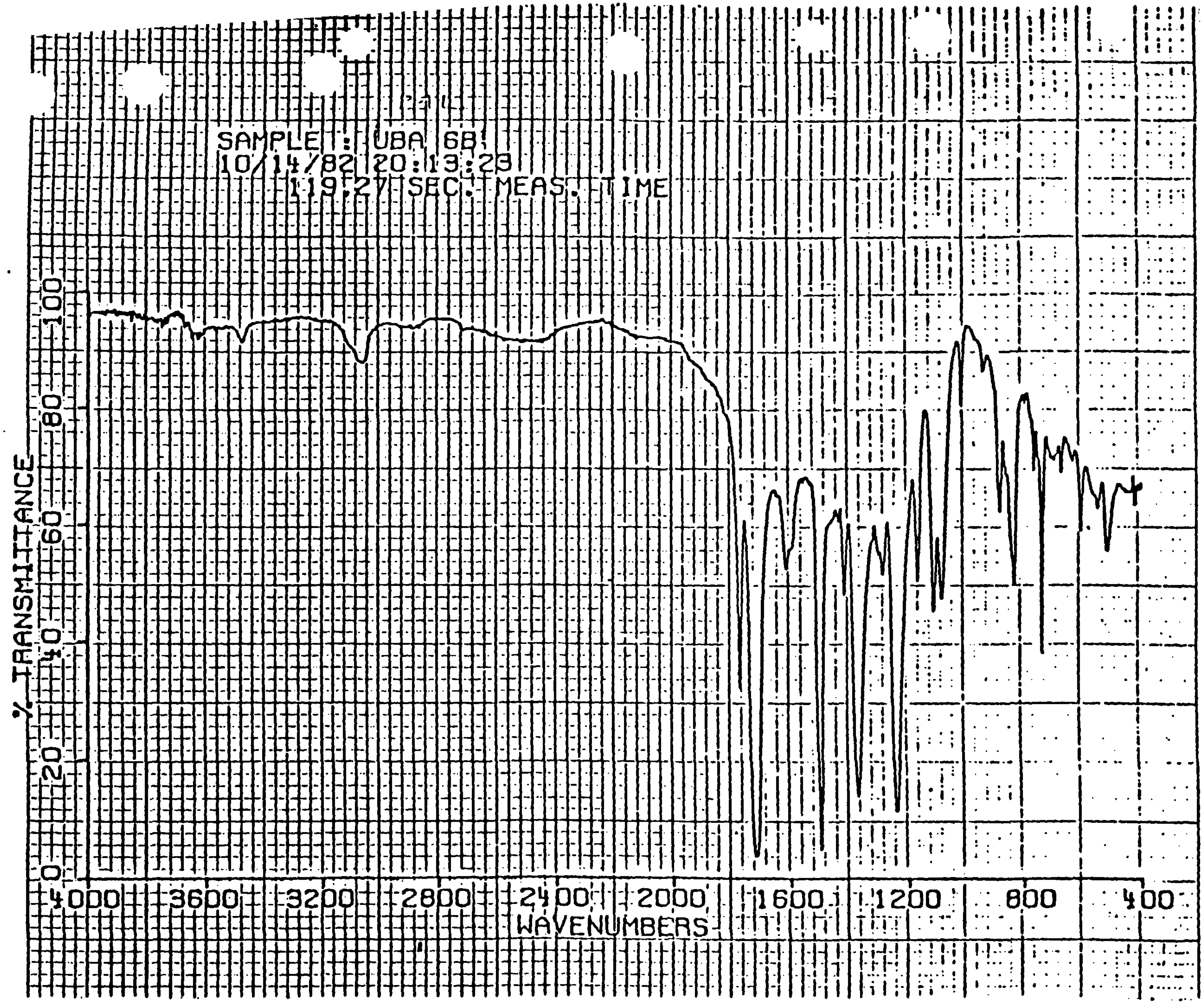


FIGURE FT-IR TRANSMISSION SPECTRA FOR THE POLYIMIDE PRODUCED FROM PAL.

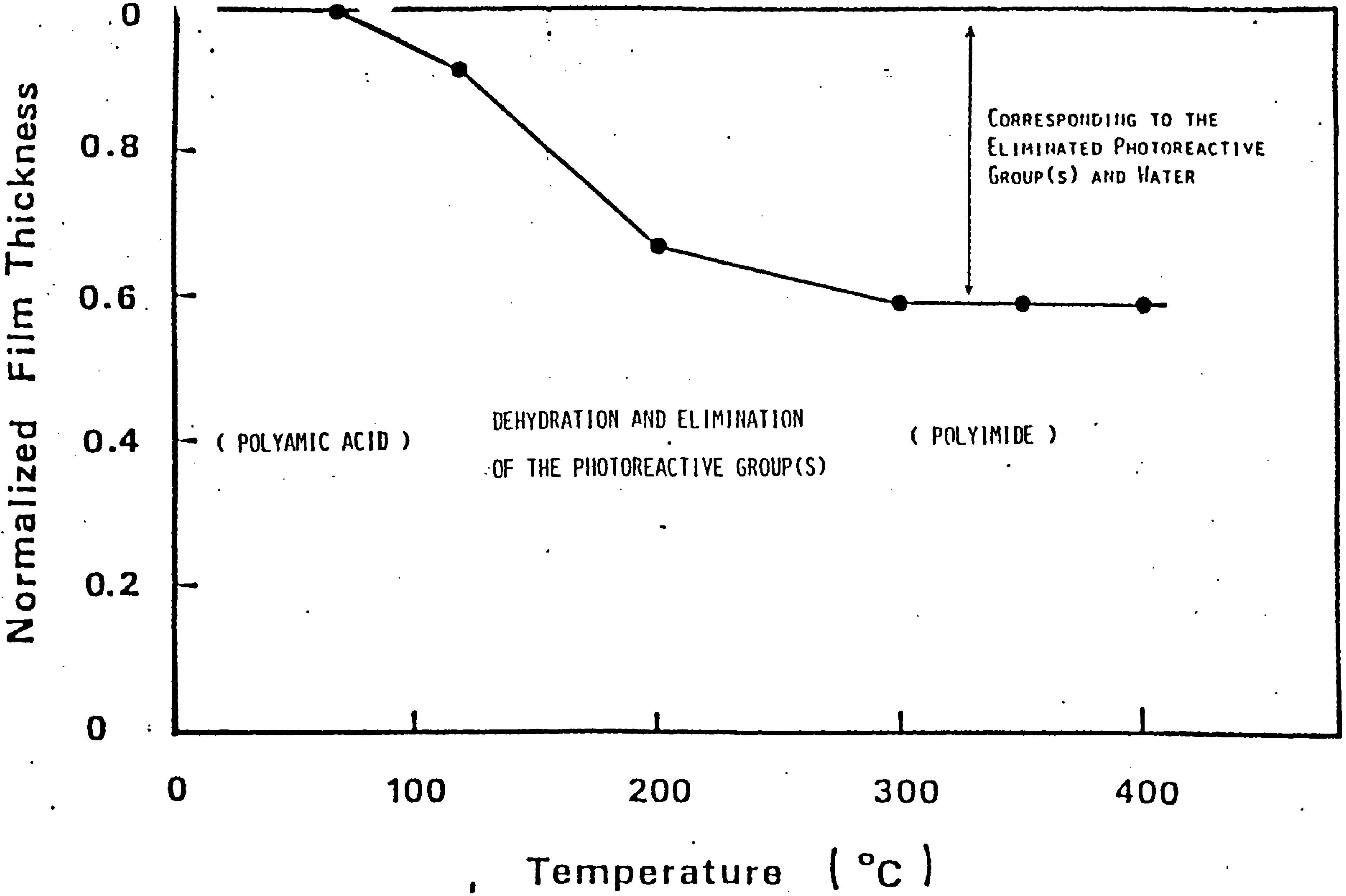


FIGURE 7. REMAINING FILM THICKNESS AFTER HEATING AT EACH TEMPERATURE FOR 30 MINUTES.

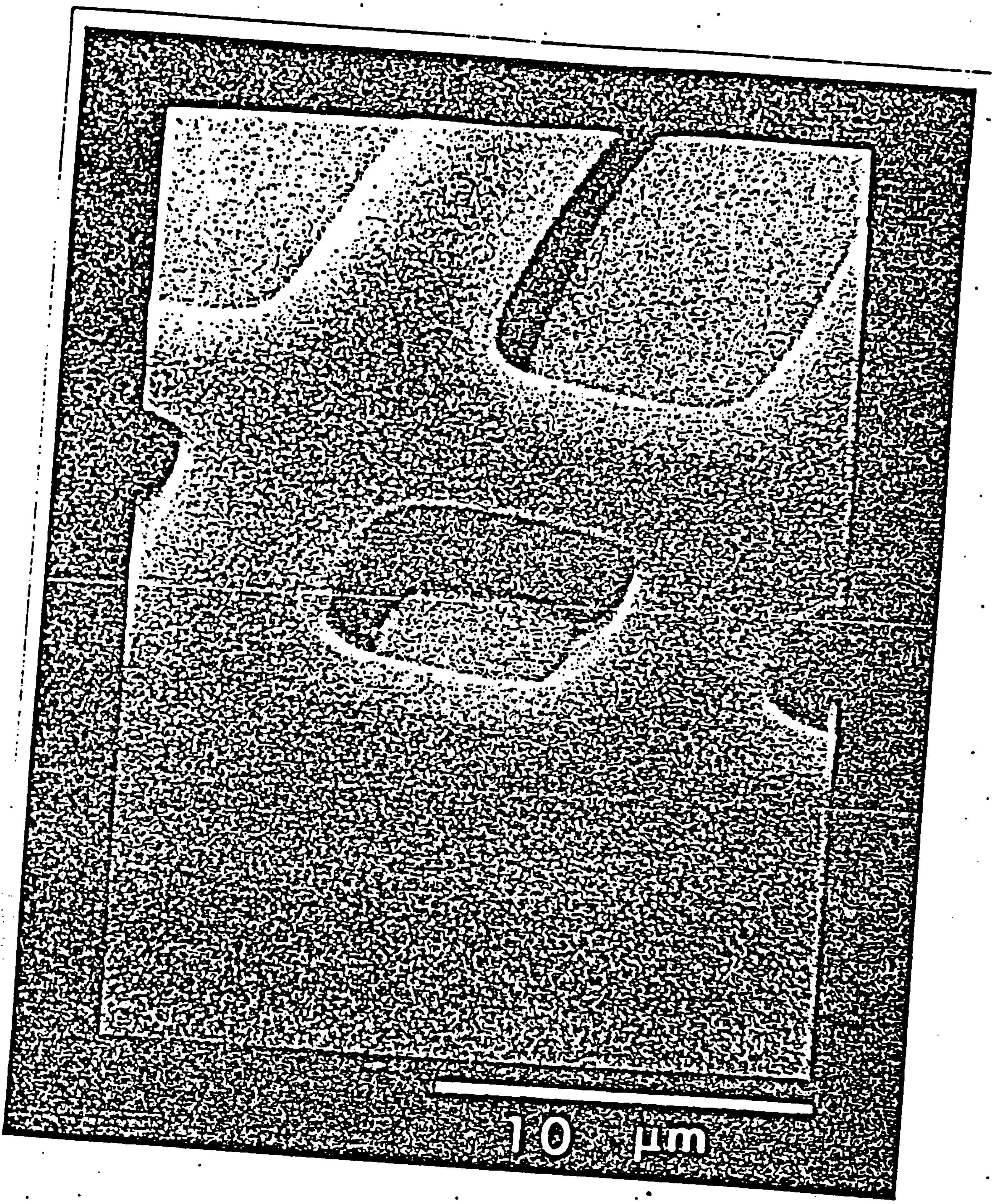


FIGURE PATTERNS OF POLYIMIDE OBTAINED DIRECTLY BY HEATING THE PAL PATTERNS.

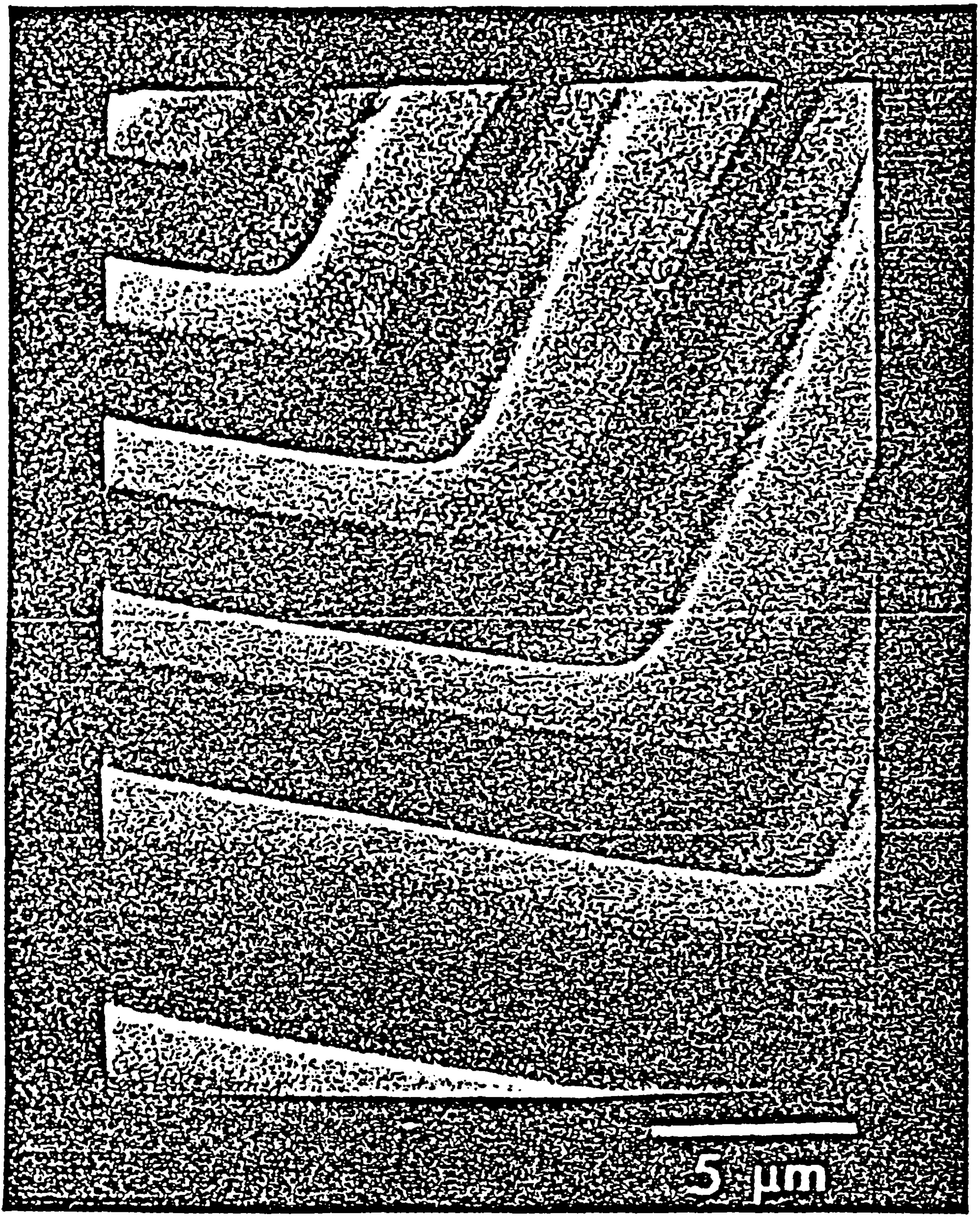
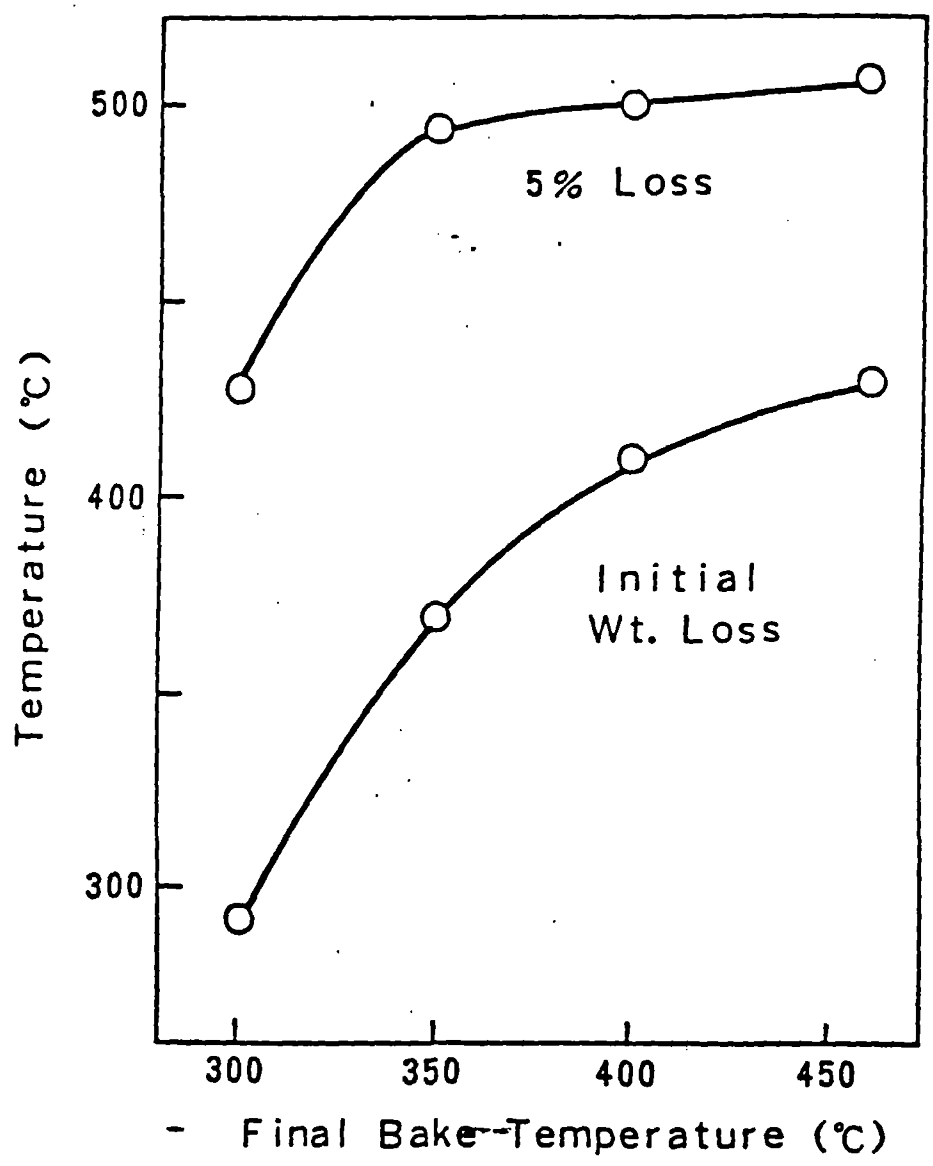


FIGURE PATTERNS OF POLYIMIDE OBTAINED DIRECTLY BY HEATING THE PAL PATTERNS.


500
400
300
Temperature (℃)
5% Loss
Initial
Wt. Loss
300
350
400
450
Final Bake Temperature (℃)

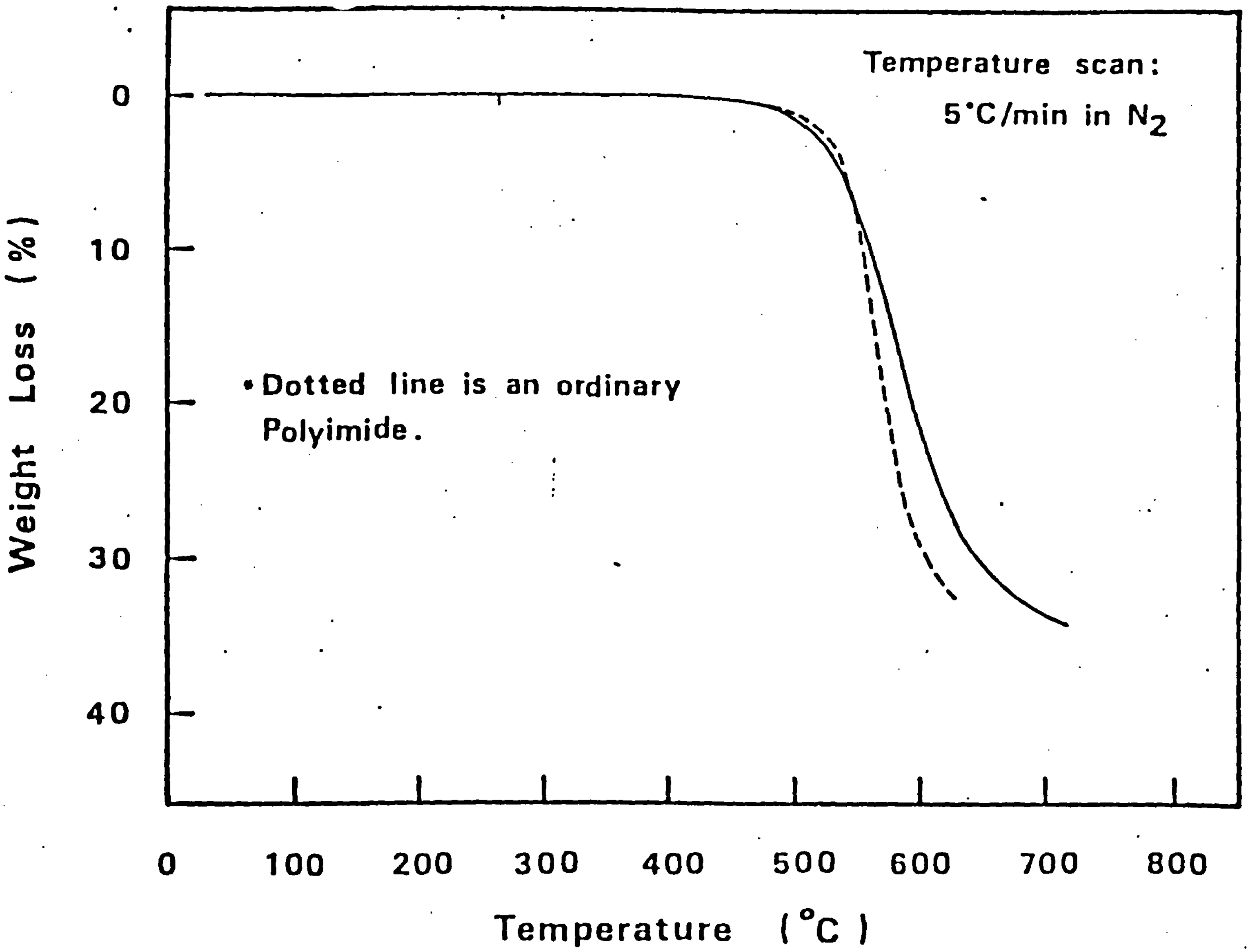


FIGURE THERMAL GRAVIMETRIC ANALYSIS OF THE POLYIMIDE PRODUCED FROM PAL AFTER HEATING AT 450°C FOR 1 HOUR IN N_2 FLOW.

TABLE 1. ELECTRICAL AND MECHANICAL PROPERTIES OF THE POLYIMIDE PRODUCED FROM PAL.

PROPERTIES	
ELECTRICAL	
DIELECTRIC STRENGTH, KILOVOLTS PER MM	275
DIELECTRIC CONSTANT AT 1 KILOHERTZ	3.0
DIELECTRIC LOSS TANGENT AT 1 KILOHERTZ, PERCENT	0.22
VOLUME RESISTIVITY, 10^{16} OHM-CENTIMETER	0.6
MECHANICAL	
TENSILE STRENGTH, KILOGRAM PER SQUARE MIL	377
TENSILE MODULUS, KILOGRAM PER SQUARE MIL	12.8
ELONGATION, PERCENT	10

TYPICAL PROCESSING CONDITION FOR OBTAINING 2.5um THICK FILM

Process	Condition
(1) Prebake of Wafer	1) 200℃-10min
(2) Coating Coupler	1) Coating of PIC-C-3
	amount of coupler : 3-5 g/wafer
	coating : 4000 rpm-30 sec
	2) Baking : 350℃-30min in air or O_2
(3) Coating PAL	1) Amount of PAL : 5-6 g/wafer
	2) Coating : 500 rpm-10 sec.
	+4500 rpm - 30 sec
(4) Prebake*	1) 70±3℃-30min, film thickness : ca. 5.0 um
(5) Exposure	1) Photomask : conventional glass mask
	2) Printer : contact UV printer
	3) Exposure : 100 mJ / cm^2 at 365 nm

* Keep prebake temperature below 75℃.

Process	Condition
(6) Development	1) PAL-Developer 2) Developing time : 180-240 sec by dipping method 3) Developing temperature : 23 - 25℃
(7) Rinsing	1) Ethanol : 15 sec 2) Drying in N_2
(8) Post Bake	1) 200℃ - 30min in air +>400℃-60min in N_2

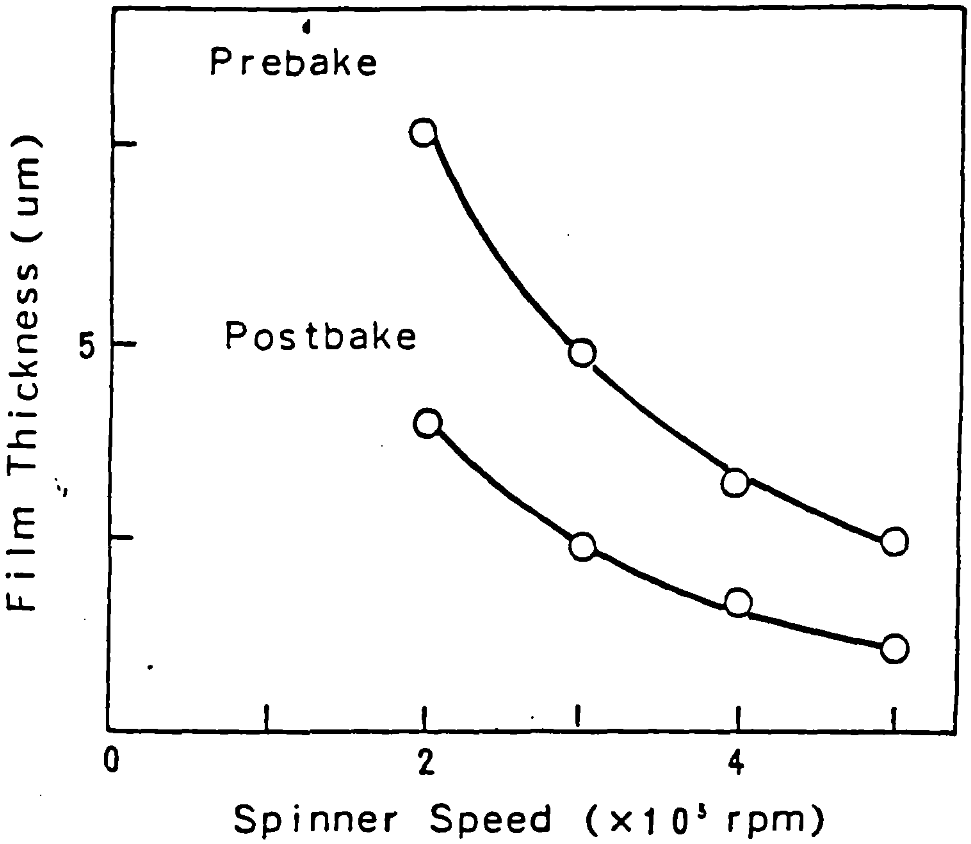


Fig. Coating Property of PAL

Prebake : 70℃−30min
Postbake : 200℃−30min+400℃−30min