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PEOPLE'S REPUBLIC OF CHINA

Technical Report: Assistance in the Analysis and Detection of Photoresists*

Prepared for the Government of the People's Republic of China
by the United Nations Industrial Development Organization
acting as executing agency for the United Nations Development Programme

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1. ABSTRACT

The goal of this work was to strengthen the Beijing Institute of Chemical Reagents in order to enhance the technical capability in research, development, manufacture, analysis and detection of photoresists.

In the course of my stay in BICR methods of testing including necessary equipment were suggested to the control of photoresist quality. Experimental work was focused on the negative working photoresist containing cyclized polyisoprene, futher on its preparation and testing. Lectures and discussions were devoted to the chemistry of light-sensitive compounds and polymers and tc the futher demands on materials for lithography.

On the basis of this experience following principle recommendations were suggested:

Technical measures

- Complete instruments in analytic department
- Establish a high clean laboratory for photolithograph. c testing of photoresists
- Reconstruct organic department and equip it with modern devices

Photoresist development

- Ensure research and experimental production of photoresists for semiconductor technology
- Investigate the needs of photoresists for printed circuit boards and chemical milling
- Work out project for photoresist production plant

Training recommendation

- Ensure special training in photolithographic testing and NMR measurement
- Improve information system.

2. SUMMARY OF CONCLUSIONS AND RECOMMENDATIONS

Technical Measures

a/ New Site

Conclusion: Conception of new BICR buildings is suitable for protoresist research

Recommendations:

1. Consult the project of air condition on the first floor for extraordinary clean laboratories (photolithographic laboratory, ICP and mass spectr. laboratories).
2. Separate clean and unclean rooms and work out a special regime for personnel.

b/ Analytic Department

Conclusion: Most of instruments are on the high and latest level

Recommendations:

Complete equipment with these instruments:

- Titrator according to Karl Fischer for water content determination (8 000 US $)
- Modern dynamic viscometer including thermostate (15 000 US $)
- Laminar flow boxes for lithographic laboratory, 4 - 5 pieces (10 000 US $ a piece)
- Unit for vacuum evaporation of metals (Al, Cr) (50 000 US $)
- Modern analytic balances (3 000 US $ a piece).

c/ Organic Department

Conclusion: The equipment does not correspond to the contemporary demands

Recommendations:

1. Reconstruct buildings, laboratories and power suppliers
2. Equip laboratories with modern laboratory glass, joints and other auxiliary instruments according to the specification in chapter 4.3.

Futher Photoresist Development

Recommendations:

1. Finish research on negative photoresist for semi-conductor technology
2. Start research on positive photoresist for step and repeat lithography (DSW) with projection exposure
3. Investigate possibility of research on photoresists for printed circuit boards with metallizing holes (positive photoresist with high viscosity).
4. Investigate possibility of research on negative photoresist for chemical milling
5. Investigate needs of chemical and galvanic baths for metallizing of printed circuit boards.
6. Finisch pilot plant construction and prepare project for photoresist plant production with capacity about 150 t of photoresists and 300 t of auxiliary solutions.

Training Recommendations

Conclusions:

1. The level of organic research and analytic chemistry is high.
2. Photolithographic testing in conditions of old buildings is not complete, some inspection methods cannot be performed.

Recommendations:

1. Ensure special training programme in photolithographic testing
2. Ensure special training for NMR-spectra measurement and their interpretation
3. Improve chemical information system.

3. INTRODUCTION

This report has been worked out as a result of my visit to the Beijing Institute of Chemical Reagents (BICR) according to the UNIDO Project in the People's Republic of China. Purpose of my visit was to strengthen the BICR in order to enhance national technical capabilities in all aspects of research, develcpment, manufacture and application of chemical reagents and fine chemicals, especially in the analysis and detection of photoresists. These new chemical products, which belong to the unconventional photographic materials, are used in semiconductor technology, in manufacturing of printed circuit boards and preparation of offset printing plates.

My briefing visit to UNIDO Vienna was organized on 26 and 27 September 1988, visit to the BICR from 28 September to 28 October 1988. I spent most of my time discussing the methods of photoresist analysis and inspection. Basis for these discussions was my introduction report "Survey of Methods" which I had worked out in advance. I also gave several lectures with long discussions about the statement and prospects of photoresists, their chemistry and application. On the request of the BICR management, I was directing the experimental work on the negative photoresist including its preparation and testing for the whole time of my visit.

I was well received, organization of my work passed according to detailed schedule and the BICR staff did their best for my successful work.

4. STATE OF THE ART RESEARCH OF PHOTORESISTS IN BICR

4.1 BICR Site

The Beijing Institute of Chemical Reagents became independent in 1985 and occupies two old buildings. The existing site is unsuitable for research on photoresists and their testing, because the working areas are not clean. This site will be left by the end of this year and buildings will be used for organic synthesis only. A general reconstruction of buildings and power supply is necessary.

The new site of the BICR is situated about 1 km from the existing site and consists of the main building and two pilot plants. The main building has four floors with laboratories; three of them are air-conditioned. The fifth will mainly serve for administration personnel. On the first floor, there are several laboratories equipped for dust particle class 10000 (Mass spectrograph, ICP, photolithographic laboratory). I recommend to consult the air circulation in these laboratories with experts for clean rooms. According to my opinion the air supply should be introduced evenly through the whole ceiling to achieve laminar streaming, not only through one or two holes in the ceiling. Also the clean zone should be separated from the unclean zone with a cloakroom.

The east end of the new site is a three floor building, two floor are used for power supply, the third is a lecture hall for about 200 persons.

The conception of the new BICR site corresponds to conditions for the research on the chemical materials for electronics.

4.2 Analytical Laboratory Equipment

Analytical department is well equipped and there are modern analytical instruments available such as mass spectrograph, ICP emission spectrometer, atomic absorption spectrometer, gel and gas chromatograph, UV/Visible spectrophotometer. I recommend to complete analytical department with following instruments:

- Titrator according to Karl Fischer - 8000 US $
  (Gas chromatography is not exact for determination of small amounts of water)
- Modern dynamic viscosimeter including thermostate - 15 000 $
  (Measurement of kinematic viscosity by means of Ubelohde viscosimeter is exact but not quick).
- New types of analytical balances - 3 000 US $ a piece

Also the instruments for photolithographic testing isavailable on the modern and high quality level. In the new site, it is necessary to equip the photolithographic laboratory with 5 or 6 pieces of laminar-flow boxes (10 000 US $ a piece), where the dust particle class 100 or better will be reached. The out-line of their dislocating is introduced in chapt. 5.3. All devices and auxiliary instruments must be distributed in such a way that the personnel need not leave the clean room. I recommend to complete the photolithographic equipment with a unit for the vacuum evaporation coating of metals (Al,Cr).

4.3 Laboratories for Organic Synthesis

Organic department is situated in old buildings and will not be moved to the new site. A reconstruction of the old site is recommended with the goal to adopt the rooms for organic synthesis. Following arrengement and measures should be done:
1. Building arrengement (replacement of window frames, new doors, tiling of walls etc).

2. New power supply (electric power supply, cold and hot water, vacuum, gas, steam).
3. Modern equipment for organic synthesis

On the request of the BICR management I presen some details to the point 3.:

I suppose that two floors of old BICR site will be adopted for organic synthesis, that is about 20 laboratories of 25 - 30 m^2 each, together about 500 m^2. I recommend to equip them as follows:

1. 10 Leboratories for organic synthesis with equipment:
- Two fume cupboard along the walls (together minimum 6 m^2)
- A bench with a wash basin, two-sided, situated in the middle of the laboratory
- supply of electric power, cold and hot water, gas, vacuum
- Leboratory equipment: flasks with grounded necks, reflux and Liebigs condensors, beakers, split flasks, conical flasks, funnels, stirrers, Büchner funnels etc.

2. Two laboratories for high pressure work

a/ Glass reactors , volume 1, 3 and 10 l to 12 atm.
b/ Stainless reactors , volume the same to 60 atm.

3. Glass pilot plants

- Stands or rack for 3 glass apparatus in volume 20 - 50 l with stirring, stea heated spirals or oil bath
- Laboratory bench with a wash basin
- Power supply see point 1.

4. Separation laboratory

a/ Rectification columns
b/ Chromatographic preparation colomns

(Furniture and other equipment according to the point 1).

5. Analytic laboratory for quick measurement

(Analytic department will be moved to the new site)
- Physical measurement (viscosity, solids content, density, melting point)
- Chemical analysis (titration, etc).

6. Two auxiliary rooms

- Direction of organic department
- Dining-recess and rest room for personnel

Note: Specification of glass equipment will be send separately.

4.4 BICR Staff, Information and Organization System

Beijing Institute of Chemical Reagents is an independent economic unit. There are experienced chemists and engineers in the head of the institute. Many skilled young chemists are working in the analytic and organic departments. The level of the photolithographic testing should improve after completing the new laboratory.

Two pilot plants are built in the new site. The production pilot plant with chemical equipment in volume 200 - 1000 l is available for photoresist manufacture. This is important for gaining project data for large production plant in the future. In this respect, relations with electronic and other chemical companies should deepen.

Education and research information system is expected to be improved in the new site. There is no chemical library in the institute at present. Some recommendation on this subject see chapt. 9.

5. METHODS OF ANALYSING OF PHOTORESISTS, NECESSARY EQUIPMENT

The first group of physical and chemical methods is described briefly, becaues these procedures are common for many other compounds and chemical products. Therefore, I confine myself to the comments, notes and particulars which are specific for photoresists. On the other hand, the photolithographic estimation and testing are introduced in details.

5.1 Physical and Chemical Methods of Analysis

Photoresists are solutions of organic light-sensitive compounds and high-molecular polymers or resins in organic solvents. Application of photoresists in photolithographic process, especially in semiconductor technology demands the exact reproduction of micron petterns without impurifying of silicon wafers. To fulfil this condition, the photoresist composition, physical properties and content of impurities must be maintained in a very narrow tolerance and must not vary from the batch to batch. Usually these physical and chemical properties are controlled and tested:

- Photoresist viscosity
- Solids content
- Density
- Residue on ignition (ash content)
- Determination of inorganic ions
- Water content
- Content of the light-sensitive compound
- Auxiliary solution control

Viscosity

1. Principle and Significance

The viscosity of photoresists together with their solids content determines the layer thickness which must be reproduced with an accuracy of 0,05 µm. The viscosity is guaranteedby the producer in tolerance ± 10%of a given value, for exacting applications ± 5%.

Two principles of viscosity measurement exist: kinematic and dynamic. Both are well-known and described in every textbook of physical chemistry.

2. Devices and Auxiliary Instruments

Höpler viscometer	(dynamic viscosity)
Rotational viscometer	"
Ubelohde viscometer	(kinematic viscosity)
Stop-watch	

3. Procedure

Viscosity measurements are performed in many branches of applied chemistry and are described in standards of every country. Therefore I present only some remarks:

- The viscosity of photoresists is strongly dependent on temperature which must be maintained during measurement in narrow limits ± 0,1°C.
- Most of photoresist producers state dynamic viscosity in mPa.s. Applying of rotational viscometers is quicker than that of Höplers viscometers. Measurement of kinematic viscosity is more labourious but more exact.

4. Evaluation

Every viscometer has its own constant for evaluation of viscosity. Accuracy of viscometers must be tested regurally by means of standard liquids.

Solids Content

1. Principle and Significance

The solids content of photoresists together with their viscosity determines the layer thickness which must be reproduced with accuracy of 0,05/um. Thats why the solids content of every production batch must be reproduced in a very narrow tolerance.

Solids content is determined by baking of the liquid photo resist to the constant weight.

2. Devices and auxiliary instruments

Analytical balance (up to 200g ± 0,1/um)
electric oven
aluminium or porcelain bowls
glass sticks

3. Procedure

Solids content is determined in many types of solutions and the procedure of its determination is described in various standards. Some special rules should be kept with photoresists:

- Every weighing must be performed at the same time after the sample is taken out from the oven.
- The accuracy of weighing is ± 0,1 mg.
- Baking is carried out in two temperature levels. The higher temperature is to be chosen according to properties (thermal stability) of the measured photoresist.
- Positive photoresists contain novolac resins which are very difficult to dry completely. We recommend to mix up the photoresist with a poro - material e.g. silicagel or sea sand before drying.

4. Evaluation

Solids content /x/ is expressed as a percentage dried mass /b/ of the original liquid mass /a/ according to the relation:

$$x = \frac{b}{a} \cdot 100$$

Note: The difference between two parallel measurements should not be bigger than 0,2%.

Density

1. Principle and Significance

As the photoresist composition must be hold in a very narrow tolerance , the value of its density is constant and need not be contolled from batch to batch. Pycnometric method available for all liquids can be used.

2. Devices and Auxiliary Instruments

Glass pycnometer for liquids
Thermostat
Analytical balance (accuracy $\pm$ 0,1 mg(

3. Procedure

Density measurement is based on the weight comparison of water and measured liquid. Pycnometer of known volume is filed by water, tempered in thermostat and weighed. This procedure is repeated with photoresist.

4. Evaluation

Photoresist density is evaluated according to the equation:

$$\rho_{io} = \frac{m_1 + A}{m_2 + A}$$

where ρ_{io} is photoresist density
m_1 weight of photoresist in pycnometer
m_2 " water "
ρ_{H_2O} 0,9982 (20°C)
A $\rho_a \cdot m_2$
ρ_a 0,0012 (density of air)

Residue on Ignition
(Ash Content)

1. Principle and Significance

The residue on ignition gives us information about the entire content of anorganic impurities. Ash content is determined by burning of the liquid photoresist.

2. Devices and Auxiliary Instruments

Analytical balance (up to 200g ± 0,1 mg)
electric heater
laboratory furnace
porcelain bowls

3. Procedure

Place ca 10g of photoresist into a porcelain bowl weighed beforehand. Evaporate carefully solvents on a boiling water-bath. Burn the residue on the bowl in the flame and than in an electric laboratory furnace at 900° for two hours.

4. Evaluation

The residue on ignition /x/ is calculated according to the relation:

$$x = \frac{m_1 . 100}{m}$$

where m is the original mass of sample
m_1 the mass of burnt residue

Determination of inorganic ions

1. Principle and Significance:

Boron content in all the cases is settled by means of emission spectrography method.

The content of Na, Mg, K, Ca, /Li/ is determined by means of atom absorption spectrometry method /AAS/ with atomization in flames. Solutions of the searched samples are analysed in solvents. The evaluation is done by means of standard addition method of oil-soluble standard solutions /e.g. Merck, see the table/.

The content of Al, Cr, Mn, Fe, Ni, Sn is determined by means of atom spectrometry method with electrthermal atomization graphite furnace /AAS - ETA/. Solutions of the searched samples are analysed in solvents. The evaluation is done by means of standard addition method of oil-soluble standard solutions.

It is possible to check alternatively the content of Al, Cr, Mn, Fe, Ni, Sn by means of emission spectrography method.

Table 1. Survey of methods and standards used

	Standard Merck kat.	AAS flame	AAS - ETA	Spectrography
B	10980			x
Na	6428	x		
Mg	5822	x		
Al	10572		x	/x/
K	4988	x		
Ca	2054	x		
Cr	10502		x	/x/
Mn	5936		x	/x/
Fe	10503		x	/x/
Ni	6713		x	/x/
Sn	10579		x	/x/

2. Procedures and Devices.

2.1. Boron determination by means of emission spectrography:

2 ml /or a dump of about 2 g / of the sample in a quartz crucible are mixed in 2 ml of ethanol, 0.1 ml of 1M NaOH solution and 100 mg of spectral pure graphite powder. At first the mixture is evaporated under infralamp to dryiness and then, it is warmed up for an hour on an electrical heater /maximum heating/.
At the same time, the blank experiment and confrontation samples containing 0.6; 2; 6; 20 /ug B in 100 mg of graphite powder. The powders then fill graphite electrodes /e.g. SU 319/ which are exposed to complete burning up in D.C.-arch. The photographic registration /ORWO WU 3/ of a spectrum /spectrograph PGS - 2, II order, 240-340nm/. Intensities of lines B I 249, 77 nm are compared. The standard with 2 /ug B corresponds to the limit of 1.10^{-4}%.

2.2. Determination of Ca, K, Mg, Na, /Li/ by means of AAS method with atomization in flames.

To 4 ml /or a dump of about 4g/ of the sample add in PTFE or polypropylene bottle 20 ml of relevant solvent and the solution is taken up into nebouliser and burner of the instrument./1 - metoxy -2- acetoxyethane is necessary to refine, e.g. by keeping above a ion exchanger./ Parallelly, samples with standard additions of 10 and 20 /ug of the given metals are perpared and relevant absorptions are measured. When solvents are analysed /e.g. developer SCR 21/, the sample is analysed too /without dilution/ and it is evaluated also by means of addition method.
It is advantageous to work with an instrument with automatic compensation of non-selective absorption which might occur with some samples on carbon particles carried away in flames.
/Our equipment: Perkin-Elmer 4000, in all the cases PTFE nebouliser and burner for N_2O /.

Table 2. Determination of Ca, K, Li, Mg, Na with atomization in flames:

Element	Line /nm/	Flame
Ca	422,7	C_2H_2 - N_2O
K	766,5	C_2H_2 - air
Li	670	C_2H_2 - air
Mg	285,2	C_2H_2 - air
Na	589,0	C_2H_2 - air

2.3 Determination of Al, Cr, Mn, Fe, Ni, Sn by means of AAS-ETA method.

The same solution as for atomization in flames are analysed. The used concentrations of additions in dosed solution are presented together with the other conditions in table 3 . 25 /ul of the solutions are dosed, compensation of possibly non-selective absorption is used. The evaluation is done by means of standard addition method. If there is a determined element in the blank experiment /the used solvent/, it is necessary to determine its content from the additions to the blank experiment, and then, to subtract it from the result.

Element	Line/nm/	Furnace	Thermal arrangement /°C/	Atomization /°C/	Standard addition /ug/ml/
Al	309,3	pyro	900	2700	0.25; 0.50
Cr	357,9	pyro	900	2700	0.025; 0.05
Mn	279,6	pyro	900	2700	0.01; 0.02
Fe	248,3	pyro	900	2700	0.025; 0.050
Ni	232,0	pyro	900	2700	0.05; 0.1
Sn	224,6	standard	700	2700	0.1; 0.2

After solvent is evaporated /130°/, 25 /ul of NH_4OH /1:10/ solution in water is added into the furnace.

2.4. Determination of Al, Cr, Mn, Fe, Ni, Sn by means of emission spectrography method

2 ml /or a dump of about 2g/ of the sample are mixed in a platinum bowl with 100 mg of spectral pure carbon powder. The mixture is evaporated to dryiness under infralamp, warmed up for an hour in an owen heated up to 500°C. Electrodes SU 319 are filled with dry carbon powder. Parallelly, the blank experiment is prepared together with standards containing 0.6; 2; 6 and 20 mg of each element in 100 mg of powder graphite. Spectrum is excited in D.C.- arch under the same conditions as with boron determination. The use of spectral line is presented in table 4.

Table 4.

Element	wave length /nm/
Al	309,27
Cr	283,56
Mn	279,48
Fe	302,06
Ni	305,08
Sn	284,00

The evaluation is done by semiquantitative visual comparison of blackening of the corresponding lines at the exposition of the sample and the standard. Also quantitative evaluation is possible by means of densitometer, in this case an addition of the internal standard would be suitable, e.g. Pt.

3. Conclusion.

In the present stage /the limits of volumes in order 10^{-5-10}%/, we take as optimum the maximum use of the direct determinations

by means of AAS methods, or determination of moveable ions by means of the direct AAS with atomization in flames, guarantee of heavy metals volume by means of emission spectrography method with simple comparison of intensities. In case of need of more exact determination of these metals, it is possible to apply AAS - ETA method with spraying of organic solutions.

Water Content

1. Principle and Significance

Method of determination of water content according K. Fischer is based on the reaction of iodine and SO_2 in medium of methanol and water. Electrometric titration must be used for indication (not visual).

2. Devices and Auxiliary Instruments

Apparatus for electrometric titration according to K. Fischer
K. Fiischer's reagent
Methanol

3. Procedure

Exact procedure is discribed in international standards (e.g. SRV 1489-79). The reagent must be daily controlled.

4. Evaluation

Water content /x/ is calculated according to relation:

$$x = \frac{TV_4}{V_5 \varrho} \cdot 10$$

where T is factor of Fischer's reagent
V_4 volume of F. reagent used
V_5 volume of sample
ϱ density of sample

Note: Water content in positive photoresists should be < 0,5%, in negative photoresists < 0,05%.

Content of the Light Sensitive Compound

1. Principle and Significance

The sensitizer quantity in photoresist solution influences its light-sensitivity, contrast and other photochemical properties. The sensitizer content should be maintained in solution with accuracy of ±0,1%.

Spectrophotometric method is used for this purpose. Extinction of the photoresist solution is measured in maximum of the last absorption peak.

2. Devices and Auxiliary Instruments

Spectrophotometer (200-700nm range)
Thinner of photoresist
Sensitizer standard

3. Procedure

Photoresist is diluted with thinner to the concentration which is optimum fot the respective photometer used. Absorption curve of diluted solution is meesured.

4. Evaluation

The value of extinction at wavelength of the last absorption maximum is determined from the record of the absorption curve. A purified sensitizer standard is used for calibration and concentration reckonning of the light sensitive compound.

Auxiliary Solutions

The auxiliary solutions serve for processing or preparation of the light-sensitive layer. Their composition must be adjusted to the specofic properties of the respective photoresist.

These types of auxiliary solutions are used in the photolithographic process:

- Developers

Thinners

Strippers

Adhesion promotors

Deystoff solutions

The quality and purity of auxiliary solutions must correspond to the level of the photolithographic process. The most exacting demands are put on the solutions for semiconductor technology.

Following parameters are stated and inspected:

- Density
- Refractive index
- Water content
- Metal content
- Chemical composition (alcalinity)
- Residue on evaporation
- Dust particle content

Determination methods do not differ from methods used for other liquids of semiconductor purity grade (e.g. mineral acids, organic solvents). Chemical composition is controlled in some cases only (alcalinity of positive developers, absorbance of dyestoff solution).

NMR Spectrometry of polyisoprene cyclicity

1. Principle and Significance

Polymers having different cyclicity have influence on the quality of the photoresist produced from them. Different degree of cyclicity can be measured by ^1H NMR spectroscopy.

2. Devices and Auxiliary Instruments

High resolution NMR spectrometer for measurement of ^1H

3. Procedure

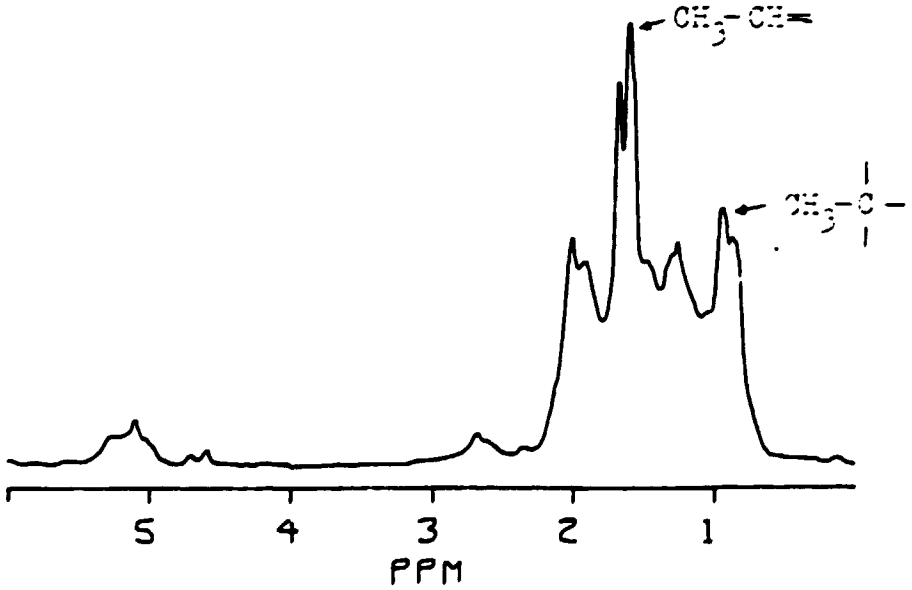
The NMR spectra of cyclized rubber are measured in deuteriochloroform with tetramethylsilane / 2% / as internal standard. Signals of $CH_3-\overset{|}{\underset{|}{C}}-$ group and $CH_3-CH=$ group are followed.

4. Evaluation

Degree of cyclicity is evaluated according to the eqution:

$$N = \frac{I/0.94/}{I/1.59/}$$

N is degree of cyclicity
I/1.00/ is height of NMR signal $CH_3-\overset{|}{\underset{|}{C}}-$ group 0.94 ppm
I/1.64/ is height of NMR signal $CH_3-CH=$ group 1.59 ppm



552 . Photolithographic Properties

Testing of physical and chemical photoresist properties does not completely manage the quality control by application in semiconductor technology with a user. It must be completed with a series of photochemical and photolithographic measurements:

- Thickness and quality of the light-sensitive layer
- Pinhole testing
- Light sensitivity measurement, contrast
- Quality of development
- Thermal flow
- Resolution
- Adhesion and undercutting

Procedure for all these tests is common, can be described together and then specified for every method.

1. Principle and Significance

Photolithographic testing of photoresists is based on performing of the whole photolithographic process in laboratory conditions. These measurements give a guarantee for the photoresist ability of application in semi-conductor production.

2. Devices and Auxiliary Instruments

-Air-conditioned laboratory with parameters:

Particle class	10 000
Humidity	40-50%
Temperature	22±2°C
Yellow illumination	500nm

- 4p. Laminarflow-boxes class 100
- UV-exposure device (Thinn film mask aligner) with a high mercuri lamp
- UV-Light intensity-power meter
-Centrifugal coating device (whirler) with adjustable revolutions in the range of 2000 - 10 000 rpm.

- Electric contact oven, temperature range 50-200°C ± 2°C
- Contact profilograph for thicknesses of 0,2 - 5um ± 0,05 /um
- Microscope magnifying 50 - 800fold
- High vacuum coater for thermal evaporation of metals (Al)
- Test masks
- Auxiliary chemicals

3. Procedure

Photolithographic process can be devided into several steps:

a/ Preparation of silicon wafers (with 500nm SiO_2-layer)
Wafers are cleaned in a mixture of sulphuric acid and hydrogene peroxide (3:1) at 130-140°C and several rinsed in pure water. Then the wafer surface is activated in an oven at 250-300°C. In special cases can be the SiO_2 layer hydrophobized in hexamethyldisilazan vapours.

b/ Coating
The silicon wafer is put on the rotary of the whirler, flooded with photoresist and spin coated at 2000 - 5000 rpm for 30-60s.

c/ Prebaking
The light-sensitive layer is dried in a contact oven at temperature given by photoresist producer, usually at 70 - 90°C for 20min.

d/ Exposure
The light sensitive layer on silicon wafer is illuminated through a test mask by a Hg-lamp placed in a mask aligner in vacuum. Light intensity must be checked by means of UV-power meter. The exposure time is experimentally determined.

e/ Development
Process of development is carried out according to instructions of photoresist producer in developer delivered to photoresist.

f/ Postbake
is performed for improvement of etch resistance. Temperature depends on the layer thermal stability and keeps within 110-140°C for positive photoresists and 140-180°C for negative ones.

g/ Etching
Immerse the developed and dried silicon wafer into the etch-bath

(mixture of HF and NH_4OH, etching rate 700nm/min) at 30°C. Etching is finished when the surface of wafer loses its wettability in water. Plasma etching can be carried out too, but usually by the user only.

h/ Stripping

Rests of the photoresist layer, that remained on the wafer surface after etching are removed in the mixture of sulphuric acid and hydrogenperoxide (3:1) at 120-140°C. Positive photoresist rests can be solved in organic solvents.

4. Evaluation

Evaluation of photolithographic process is stated further in descriptions of individual methods.

Thickness and Quality of the Light-sensitive Layer

1. Principle and Significance

Preparation of the quality layer is a basic assumption for the photoresist application. We evaulate:

- thickness of the layer
- flatness of the layer
- pinhole defects (are described extra)

2. Devices and auxiliary instruments

Photolithographic laboratory (see common chapter)

3. Procedure

Prepare the light-sensitive layer according to the points a/, b/ and c/ of the common procedure. Engrave with a wolfram needle three grooves into the light-sensitive layer. Place the stylus of the profilograph on the wafer and go through the entire surface including the grooves. Repeat this procedure on three various wafers.

4. Evaluation

From the record of the profilograph on the both sides of every groove we can determine the layer thickness as an arithmetic average of nine measurements. The photoresist layer thickness should not differ from batch to batch in the range of $\pm 0{,}05\,\mu m$. From the record on the smooth surface can be read off its flatness. The difference between maximum and minimum thickness cannot overstep $0{,}02\,\mu m$.

Pinhole Testing

1. Principle and Significance

Pinhole dfects in the light-sensitive layer are caused by dust particles which remained in photoresist solution in spite of its microfiltration.

Pinhole testing is based on etching of SiO_2 -layer, on enlarging and transferring holes int the Si-layer and microscopic counting of their number.

2. Devices and Auxiliary instruments.

Photolithographic laboratory (see common chapter)
SiO_2 - etchant
Si - etchant
Silicon wafers with crystallographic level /1,0,0/

3. Procedure

Photolithographic process is performed according to points a/ - h/ of common procedure. A pure glass is used for negative photoresists as a mask, positive photoresists are not illuminated. Etching time is twice longer than usually. After stripping the wafer is immersed into the Si-etchant for 5 min. and rinsed in pure water. Finally the wafer is etched in SiO_2-atchant once more, rinsed in water and dried.

4. Evaluation

Holes transferred from SiO_2 - layer into Si are counted by means of microscope by magnification 50 - 80 fold. Their number is expressed per cm^2. The min.area of 20 cm^2 is evaluated.

Note: Pinhole defects can be also tested by measuring electric resistance. In this case the etched SiO_2 - layer is covered with aluminium instead of Si - etching.

Light Sensitivity Measurement, Contrast

1. Principle and Significance

Photoresist sensitivity control plays an important role in reproduction of very small structures (5 /um). Exact exposure dose is a condition for high resolution.

Sensitivity measurement consist in illumination of the light-sensitive layer by various light-doses. The sensitivity is evaluated from the relationship of the development rate (positive photoresists) or of the crosslinked thickness (negative photoresists) on the exposure energy.

2. Devices

Photolithographic laboratory equipment (see common chapter)

3. Procedure and Evaluation for Positive Photoresists

Apply the common procedure according to the points a/ - f/. A black mask with ring-hole of 5 mm diameter is used by exposure. Measure the thickness of the layer with a profilograph. Exposure energy, the intensity of which is measured with a UV-power meter, is dosed from 0 to 200 mJ/cm^2 in about 10 intervals. Immerse the wafer into developer and follow the time till the ring exposed hole is developed according to the change of colour between naked SiO_2-surface and undeveloped layer. From the measured time reckon the development rate (in /um/min).

Plot on the graph the relationship of development rate on exposure energy. The photoresist sensitivity is determined with exposure energy which is necessery for achieving the chosen development rate (e.g. for 1 /um/min or for thickness used in praxis).

Contrast is a gradient of the above described curve. In some cases the ratio of maximum development rate and development rate of unexposed layer is evaluated as contrast.

4. Procedure and Evaluation for Negative Photoresists

Common procedure described for positive photoresists including exposures in ten doses is performed. Development process (temperature, period, rinsing) is carried out according to the supplier instructions. After postbaking the thickness of the crosslinked layer remained on the support is measured on a profilograph.

The relationship of the crosslinked layer thickness on the exposure energy is plotted on the graph. The exposure enrgy, which is necessary for achievment of chosen layer thickness, usually one half of initial thickness, is a criterion of sensitivity.

Contrast is the gradient of this curve.

Quality of Development

1. Principle and Significance

In the course of development process some disorders in the quality of the image reproduced can occur. Rests of the photoresist layer can remain on the developed spots or cracks appear in some structures. Microscopic inspection is used for this purpose.

2. Devices

Photolithographic laboratory equipment (see common chapter)
Resolution mask

3. Procedure

Apply the common procedure according to the points a/ to f/. The estimation of development quality is performed simoultaneously with resolution test. After development the silicon wafer is inspected under a microscope at magnification 600 fold.

4. Evaluation

The developed naked spots must be pure without any remains of photoresist layer and dust particles. The surface of reproduced structures must be smooth. without any crocks, the edges shlould be straight.

Thermal Flow

1. Principle and Significance

Thermal flow test characterizes the stability of developed structures by heating during the second drying (postbaking). The test consists in microscopic measurements of the difference between the stricture size after and before postbaking.

2. Devices

Photolithographic laboratotory equipment (see common chapter)
Silicon wafers with SiO_2 layer
Resolution mask

3. Procedure

Apply the common procedure according to the points a/ - f/. Resolution mask with one to ten /um strips is used at exposure. After development two wafers aredrying at temperature of the first baking (80 - 90° usually), two wafers are postbaked at temperature examined (140 - 180°C). The sizes of 5 /um stripes on all wafers are measured by means of microscopic measurement with measuring eyepiece.

4. Evaluation

Sizes of postbakes wafers shloud not differ from those not-postbaked more than o,3 /um. Otherwise the postbake temperature is too high.

Resolution

1. Principle and Significance

With increasing number of electronic units (bites) in integral circuits demands for the photoresist resolution are always more exacting. We understand, as resolution, the smallest structure which can be reproduced in the photolithographic process.

2. Devices and Auxiliary Instruments

Photolithography laborytory equipment (see common chapter)
Resolution mask

3. Procedure

Apply the common procedure according to the points a/ - f/. The resolution mask contains a system of lines, the sizes of which diminishe from 10 to 1 /um. The developed and dried silicon wafer is inspected under a microscope at magnification 600 fold.

4. Evaluation

We estimate the smallest lines which are reproduced without any interruption or other demage. The width of stripes and gaps between them should be equal.

Note: Photoresist resolution is influenced by the exposure system used. For instance better results are obtained with project exposure system than with contact system.

Adhesion - Undercutting

1. Principle and Significance

Some theoretical methods of adhesion measurements of the photoresist layer to various supports cannot give us a satisfying response about the photoresist avaibality to practical appllication. Therefore the entire photolithogrphic process must be performed including etching- Undercutting is evaluated as a measure of adhesion.

2. Devices and Auxiliary Instruments

Photolithographic laboratory equipment
Resolution mask
SiO_2-etchant, auxiliary chemicals

3. Procedure

Apply the common procedure according to the points a/ - h/. The resolution mask is used at exposure. The width of 4 /um stripe is measured after development and postbaking (points e/ and f/) and then once more after etching and stripping (points g/ and h/) om the bottom edge of the structure. Size measurements are carried out by means of microscope with magnifying 600 fold and by means of measuring eyepiece.

4. Evaluation

The difference in width of 4 /um stripe after development and after etching should be 1 /um maximum.

Note:
This procedure can be used for various types of surfaces used in semiconductor technology . For Al - surface, however, it is better to estimate adhesion by means of overdevelopment (2 -4 times longer period of development than necessary) without etching.

2.2. Laboratory Equipment

Devices which are necessary for the measurements of individual parameters were stated in the description of determination(see chapt. I and II). According to the nature of the measurements, various laboratories shlould be arranged:

1. Laboratory of physical chemistry
(Solids content, viscosity, density, residue on ignition, water content)

2. Spectrophotometric laboratory
(Content of light-sensitive compounds, other spectrophotometric measurements connected with research on photoresists)

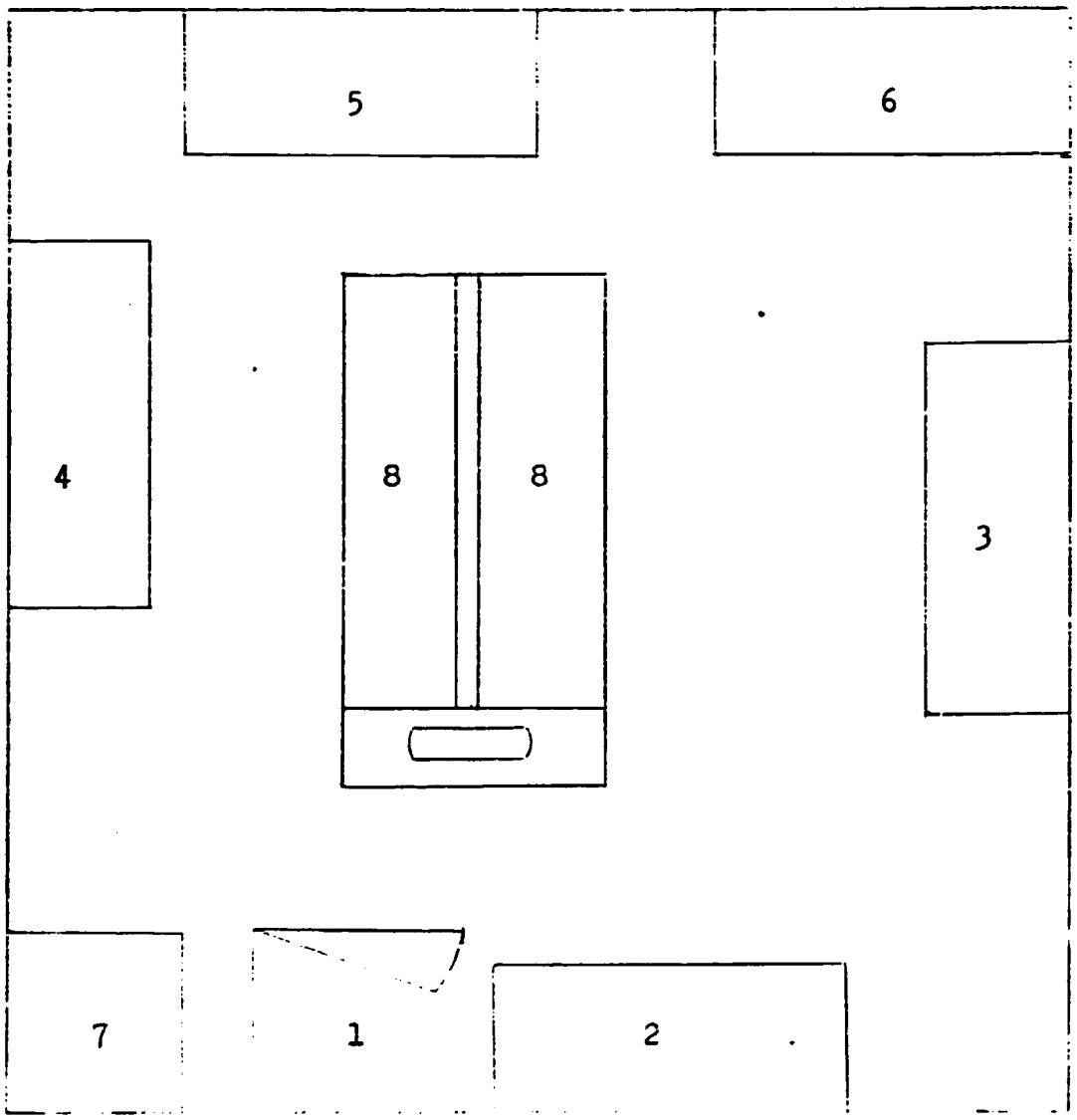
3. Laboratory of atomic absorption and emission spectrometrie
(Inorganic impurities)

4. Photolithographic laboratory
(All photolithographic properties, see p. 15)

The first three laboratories can be common for the control and measurements of other chemical products (chemical for diagnostics, chromatographie, electronics etc.). That's why the details are not stated.

A photolithographic laboratory must be arranged for the research on photoresists. Proposal of laboratory equipment and their locating is introduced in following scheme.

Scheme of Photolithographic Laboratory



1 : 40

Legend:

1 - Door
2 - Laminar flow box for coating and drying:
Centrifugal coating device
Electric contact oven
3 - Laminar flow box for illumination
UV- exposure device (Thinn film mask-aligner)
UV-Light intensity-power meter
4 - Chemical laminar flow box
Auxiliary instruments for development
Auxiliary instruments for etching
5 - Laminar flow box for drying and baking
Electric contact oven
Electric laboratory furnace
6 - Laminar flow box for microscopic inspection
Microscope magnifying 50 - 800times
7- High vacuum coater for thermal evaporation of metals (Al, Cr)
8 - Laboratory bench two sided with a wash basin
Contact profilograph
Balances
Other auxiliary instruments and chemicals

Examples of possible equipment described in trade literature are enclosed.

Energy, gas and water supply:
- el. power points 220 and 380 V
- compressed air
- compressed nitrogen
- central vacuum
- cold and warm water
- demineralized water
- chemical drains

Specification of Instruments for Photoresist Testing

Handed to B I C R

Dynamic Viscosity Measurement:

1. HAAKE Viscosimeter
2. HAAKE Thermostate

Water Content Measurement

3. Mettler Titration
4. Methothrom Programme 1988/89

Metal Content Determination

5. The Guide AS - Perkin Elmer
6. The Graphite Furnace AAS Technique
7. AAS 1100B - Perkin Elmer
8. AAS 3030 - Perkin Elmer

UV-Visible Spectrophotometer

9. UV/VIS/NIR - Spectrophotometer - Perkin Elmer
10. PU 8800 UV/VISIBLE Spectrophotometer-Pye Unicam
11. Spectra AA - 30/40 - Varian

Photolithographic Testing

12 Laminar Flow Boxes - Prettl
13. Clean Air Benches - Kojair Finland

Mask Aligner

14. MA 45 - K. Süss NSR
15. MA 33S - dtto

Matallization

16. LLS 801 Load Lock Sputtering System - Balzers
17. BAS 450 PK Planar Magn. Sputtering System - Balzers
18. UNIVEX 300/450 Leybold

Microscope

19. Leitz MPV CD
20. Leitz Secolux 6x6
21. Leitz MPV CD 2
22. Leitz Ergolux

6. LECTURES AND DISCUSSIONS

Three lectures were presented in the course of my assistance in BICR:

1. Photoresist Chemistry and Application
2. Polymers for Photo- and Electron Beam Resists
3. Technical Development and Futher Demands on Materials for Lithography

The shortened text of these lectures see Appendix III.

Long discussions were devoted to the conclusions of my lectures and experimental work:

- Perspectives of polyvinylcinnamate photochemical system (KPR).
- Synthesis of cyclized rubber and reproduction of its properties.
- Influence of substituents on the properties of o-naphtoquinonediazides
- Methods of positive photoresist purifying
- Photo-sensitivity measurements
- Determination of boron content in organic solutions by means of ICP method.
- Modern equipment for organic synthesis
- Synthesis of new organic compounds and testing their properties.
- Modern methods of investigation optimum technological conditions

7. EXPERIMENTS

On the request of the BICR senior staff I was directing experimental work for all the time of my stay in BICR. Experiments were focused on the negative photoresists, their preparation, reproduction and testing their properties.

a/ Experiment Description and Results

The aim of this experimental work was to find a way how to control the reaction course of polyisoprene cyclization; this polymer is used in negative photoresists and its molecular weight and distribution must be maintained in a very narrow tolerance. The relationship between the viscosity and solids content of polyisoprene solution was taken as a criterion of cyclization degree. If the solids content is always constant during the reaction, we can follow the reaction course (reaction rate, cyclization degree) by voscosity measurements.

Four experiments were performed; three of them were successful and the reaction was stopped in the viscosity range of 1 cP. One batch was spoilt because of higher temperature during cyclization than it was recommended. After purifying and filtration through 0,2/um filter, the sample of negative photoresist was prepared and tested. Results of chemical analysis proved the high purity of the photoresist sample (all metals measured less than 1 ppm, boron was not determined). Only the resolution and quality of development were tested from the photolithographic properties. The layer thickness and sensitivity measurement could not be determined, because the profilograph failed. Resolution 1,5/um that was reached by testing is very suitable in this photoresist system.

b/ Recommendations

- Precise the relationship between the viscosity and solids content as a function of

$$\log \quad = Ac + B$$

where is dynamic viscosity in mPa.s /cP/

c solids content in % mass

A,B constants which must be experimentally measured

This relationship can be used for photoresist diluting to the exact standard viscosity.

- Introduce measurement of dynamic viscosity instead of kinematic viscosity.
- Work out a method for boron determination in photoresists.
- Introduce the sensitivity measurement, pinhole testing and undercutting.

8. RECOMMENDATIONS ON FUTHER PHOTORESIST DEVELOPMENT

Contemporary state of photoresist development and manufacturing in BICR can be characterized as an initial stage which should be futher gradually developed. The average production level of the world photoresist producers makes hundreds of tons of photoresists and several thousand tons of auxiliary solutions, financially expressed about 50 million s US $. Chinese market surely reaches this level in the future. Photoresist research should prepare conditions for such a development and step by step should solve technology of new photoresists and introduce them into the market. In this respect I recommend to involve following topics in the programme of futher BICR research and development:

a/ Photoresists for Semiconductor Technology

- Finish research works on negative photoresists, work out procedure for several photoresist concentrations and complete photolithographic testing methods and include them into the standards.
- Start research on positive photoresist for step and repeat lithography with projection exposure system (DSW). This direction appears to be extraordinary perspective for the next ten years.
- Prepare a survey of the last communications and patents in the field of polymers for X-ray and electron beam lithography.

b/ Other Applications of Photoresists

There are many other applications of photoresists in technical practise. I recommend, therefore, to investigate needs of Chinese market in this respect and if necessary to extend the range of photoresists:

- Positive photoresist with high viscosity (150cP) for two- and more-sided printed circuit boards with metallizing holes.
- Negative photoresist for chemical milling (manufacture of miniature parts from metal sheets by means of photo-etching).
- Chemical and galvanic baths for metallizing of circuit boards and other surfaces (Co-plating, Sn-plating), cleaners, etching baths and other auxiliary solutions for circuit boards manufacture.

c/ Production Development of Photoresists

Research results should be fluently introduced into production. For this purpose, it is necessary to prepare projection data and to constuct gradually production plants:

- Prepare glass pilot plant in volume 10 - 50 l during reconstruction of the old BICR site.
- Finish stainless pilot plant in volume 200 - 1000 l and introduce the photoresist production on it.
- Prepare project data for plant production with capacity 100-200 t of photoresists and 300-500 t auxiliary solutions.
- Investigate systematicly needs of Vhinese electronic industry.

9. TRAINING RECOMMENDATIONS

During my stay in BICR I had an oppurtunity to get aquinted with many research workers on occasion of my lectures, discussions and experiment performance. There are many young people, recently graduated, who have prospects to become outstanding experts in analytic, physical or organic chemistry. Puther training should be aimed at the internal schooling in BICR as well as external stay in foreign institutes.

a/ Internal Schooling

- Complete chosen analytic methods and procedures (water content determination, dynamic viscosity, boron content etc.).
- Improve methods of organic synthesis
- Improve knwledge of English in special English courses

b/ External Training

There are some areas where the special training in foreign institutes is necessary for increasing level of research in BICR:

- NMR spectra measurement and their interpretation
- Photolithographic testing of photoresists
- Information system in chemistry

Training according to the two first points can be realized in Czechoclovakia provided that it will be filed into the UNDP Training Programme (two workers for two months).

APPENDIX I

DIARY

September 28	Meet at airport
September 29	Meet UNIDO Officer
	Meet Director of BICR
September 30	Discuss schedule and inrotriducing the BICR Staff"
October 1-3	National Days - Sightseening
October 4	Discuss experiments, visit laboratories
Ocrober 5	Lecture I, discussing
Oct 6-8	Work in lab.
Oct. 9	Sightseeing
Oct 10	Work in lab., siscussing experiments
Oct. 11	Lecture II , Discussing
Oct. 12-13	Work in lab.
Oct. 14	Discussing experiment results
Oct. 15	Sightseeing
Oct. 16	Holiday, prepare lect III
Oct. 17	Work in lab.
Oct. 18	Lacture III, Discussing to lecture III
Oct. 19-20	Work in lab.
Oct 21 - 22	Discussions on experiment results
Oct. 23	Sightseeing
Oct. 24-25	Work in labo.
Oct. 26-27	Final discussing and sum.
Oct 28	Meet UNDP Beijing, departure

APPENDIX II

Senior Staff of BICR

Mrs SUN SHI-MING	Director
Mr PAN BANG-DI	Chief Engineer
Mr MA CHUN-SHU	Chief of Research Department
Mr LIO PAI-XIAN	Engineer
Mrs WANG WEI	Advanced Engineer
Mr LI JIAN GUO	Engineer
Mr YANG KUANG	Engineer
Mr SHI XIANG-MIN	Engineer
Mrs ZHANG XIO-WEN	Advanced Engineer
Mrs ZHENG GUAI-LIN	Advanced Engineer
Mr LIO SHI-RONG	Engineer

APPENDIX III

Adolf MISTR

L E C T U R E S O N P H O T O R E S I S T S

Worked out for Beijing Institute of Chemical Reagents as a part of discharging the UNIDO Programme

Beijing October 1988

Ackowledgement
My thanks to Mr. PhD. Yang Kang for his valuable assistance in translation to Chinese and completing this survey

L E C T U R E I

Photoresist Chemistry and Application

1. Introduction

Photoresists belong to the unconventional photographic systems. Their light-sensitivity is based on organic compounds which undergo a photochemical reaction(decomposition, cross-linking) on irradiation. Photoresist consist of three main parts: - Light sensitive organic compound

- Film-forming polymer or resin
- Solvents

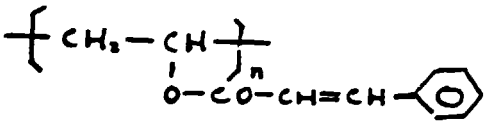
The function of photoresists consists in the change of solubility on illumination. This change is used by development; the illuminated spots either lose the solubility (negative photoresists) or gain solubility (positive photoresists).

2. Chemistry of Photoresists

According to the chemical structure we can devide the light-sensitive compounds into several groups:

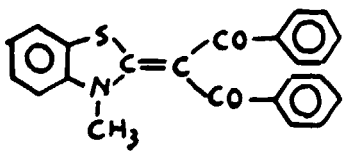
a/ Compounds with active -C=C-C=O double bonds

The high-molecular ester of cinnamic acid is the most important representative of this group:

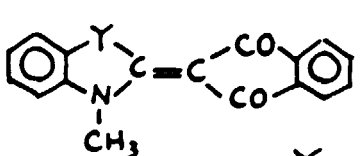


(I)

On irradiation two cinnamic ester groups dimerize (cross-linke) and the layer loses solubility. The spectral sensitivity is unfavourable for practical use (short wavelength) and must be spread by addition of sensitizers(see examples II,III,IV):

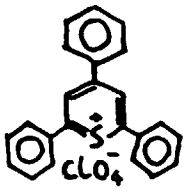


(II)



Y = -S- ; -Se- ; -O-

(III) Phtalons

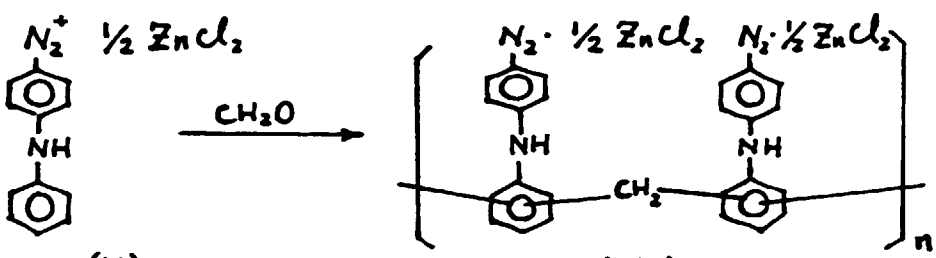


(IV) Thiopyrylium Salts

The industrial application of this photochemical system was worked out by Eastman Kodak Co (Kodak Photo Resist) in printed circuit board manufacturing and chemical milling. For semiconductor technology are not suitable (insufficient adhesion to SiO_2).

b/ Diazo-compounds

The light-sensitivity of diazo-group is well-known for 60 years. The high-molecular diazo-resin is used for photoresist preparation:

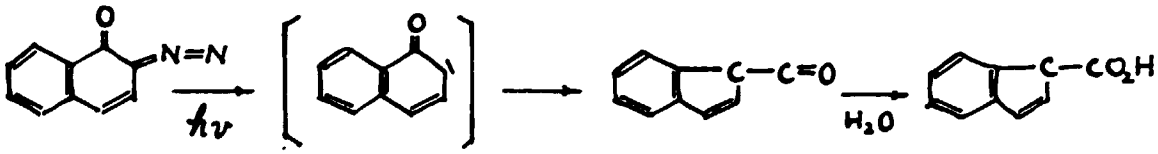


(V) (VI)

Use: Negative offset printing plates, development in water or water solutions.

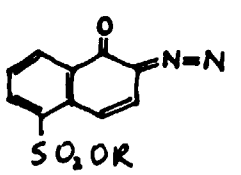
c/ o-Quinone Diazides

The mechanism of their photochemical decomposition was explained by Oscar Süs:

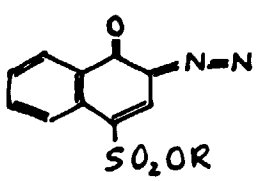


(VII) (VIII) unstable (IX) (X)

The arising molecule of indencarbon acid X causes, that the irradiated layer is soluble in alcaline solutions. In practise the esters XI or XII are used.



(XI)

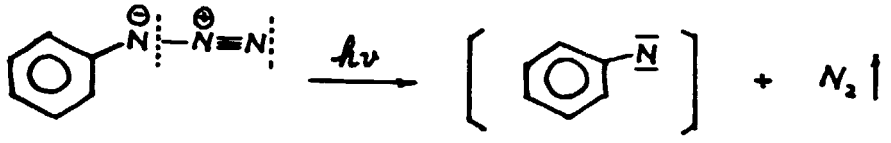


(XII)

o-Naphtoquinone diazides play a great role in technical practise. All positive photoresists are founded on them.

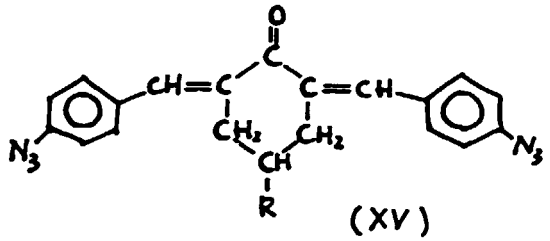
d/ Organic Azido compounds

Inorganic azido-salts are unstable and are use as explosives. The azido-group bound on an aromatic ring is stabilized. On irradiation, the azidogroup decomposes, a nitrogene molecule releases and the arising radical - phenylnitrene XIV reacts with the adjoining polymer molecules and cross-links them:

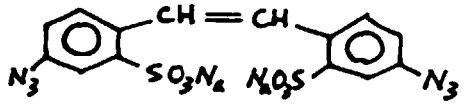


XIII (XIV) unstable

In technical practise compounds with two azido groups are used. Structure XV is suitable for organic solvents, compound VI can serve as example of water soluble sensitizer:

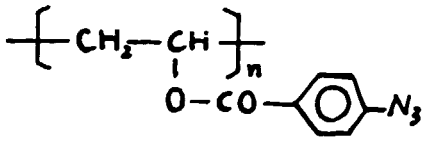


(XV)



(XVI)

Azidogroup can be bound also on a polymer; in this case the functions of sensitizer and film-forming polymer are connected (structure XVII):



(XVII)

This light-sensitive system is used in semiconductor technology with a negative photolithographic processing. The water soluble azido-compounds are applied in printing industry and by TV-colour tubes manufacturing (black stripes).

3. Photoresist Application and Producers

Photoresists belong to the modern chemical materials which influence and contribute to the development of many other economic branches. The first application appeared after the World War II in printing industry. Later they became indispensable in the manufacture of printed circuit boards and semiconductor integral circuits (IC). After 35 years development, the photoresists are applied in these main fields of technique:

- Offset printing plates. Application of photoresists enable to concentrate the production, improve the quality of printing and increase the number of copies (run).
- Printed circuit boards have become the basis of computers and other electronic devices. They are produced in large scale.
- Chemical milling is a new application by manufacturing of various metal sheets into miniature parts.
- Semiconductor technology is the most important application of photoresists. The most exacting demands on their quality are required for the photolithographic process.

Survey of the main world photoresist producers:

USA -Eastman Kodak Co - Negative Photoresists of series KPR, KMER, Microphotoresists

- Ollin Hunt - Series of Waycoat Photoresists, negative and positive for semiconductor technology
- Shipley Co-Positivephotoresists for IC and PC boards.

West Europe- Kalle-Hoechst Co - Positive photoresists for IC and PC boards. Series AZ 1350, 1450, 4000.

- E.Merck(WG) Negative and positive photoresists for IC
- Micro Image Technology (GB) - Negative and positive photoresists for IC

East Europe - Lachema Brno (CS) - Negative and positive photoresists for IC, PC boards and offset print.plates.

-Orwwo Berlin (EG) Positive photoresists for IC

Asia - Tokyo Ohka Kogyo (Japan) - Positive and negative photoresists for electronics (various applications).

L E C T U R E I I

Polymers for Photo- and Electron Beam Resists

1 Introduction

In the first lecture we briefly described the chemistry of light-sensitive compounds. The high-molecular compounds - polymers and resins form the second components used for photoresist preparation. The solvents are evaporated after coating and polymers together with sensitizers form a homogenous film. Properties of polymers influence the quality of the light-sensitive layer. While the sensitizers determine photo-chemical properties (sensitivity, contrast, absorption regionetc.), the choice of polymers is decisive for physical and mechanical properties such as:

- thickness and quality of the layer
- adhesion and undercutting
- temperature of softening
- etch resistance

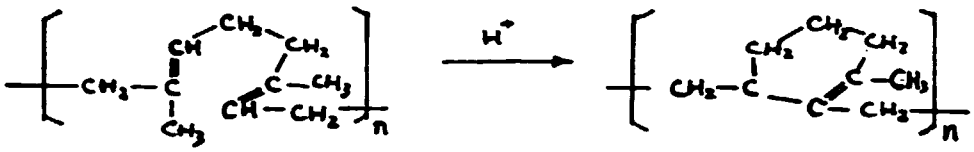
Demands on the quality of polymers: - high purity
- standard molecular weight and its distribution.

The purity of polymers can be ensured by purifying of monomers or which is sometimes more convinient, by adsorption of metal impurities on the ion exchangers in the course of photoresist preparation.

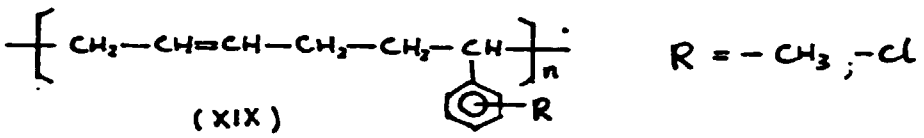
Standard molecular weight is usually controlled by gel chromatography measurement. The values of M_w and M_n are determined and their ratio M_w/M_n walculated, which characterizes the distribution. This measurement is important for photoresist research, but it is not suitable for the inspection and quick control of polymer synthesis. For this purpose we use watching of the relationship between the viscosity and solids content of the polymer solution. This relationship must be maintained in narrow tolerance, which must be strictly defined.

2. Polymers for Negative Photoresists

The derivatives of synthetic or natural rubber are used in semiconductor technology for photoresist preparation because of their high etch-resistance. From the various possibilities I present two examples of polymers used in technical practise: cyclized polyisoprene XVIII and copolymer of butadiene and substituted styrene XIX:



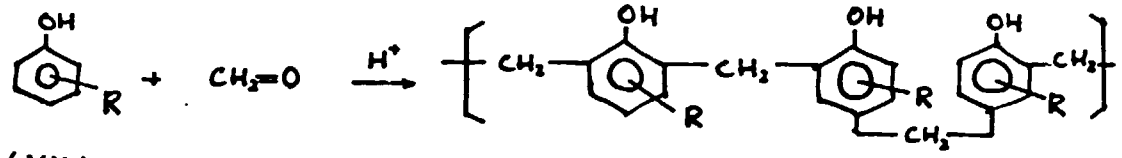
(XVIII)



(XIX)

3. Polymers for Positive Photoresists

Novolacks resins are mostly used for positive photoresist systems. They are prepared by condensation of phenol with formaldehyde in acidic environment (HCl, /COOH/$_2$). This reaction is more than 60 years old and novolacks resins became a basis of the backelite:



(XX) (XXI)

Nevertheless, in spite of this known and old procedure, the manufacturing of novolacks for positive photoresists has some problems in regard of reproduction their properties. Also in this case the relationship between novolacks solution viscosity and its solids content is the best and quickest production control. Solids content determination is usually connected with a big error because of imperfect evaporation of solvents. I recommend to perform this determination in mixture of some porous material (sea sand, silica). In respect of adhesion and contrast, the substituent R- in structure XXI plays an important role, but this question will be discussed in lect.III.

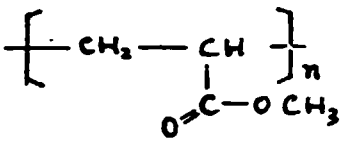
4. Polymers for Electron Beam Resists

During last five years, the new lithographic procedures have been introduced into the semiconductor technology with the aim of futher diminishing of resolution: - Deep UV lithography
- X-ray lithography
- Electron beam lithography

The chemistry of resists for these application is similar; we can discuss it commonly.

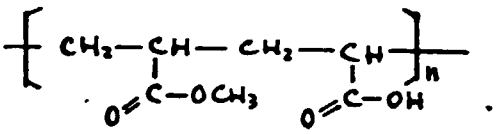
Positive resists

Positive resist system is based on depolymerisation reaction, which occurs on irradiation by rays with very short wavelength. Lowering of molecular weight enables to dissolve irradiated spots in a developer (organic solvents). Polymethylmetakrylate (PMMA) is the most well-known example (XXII)



(XXII)

The sensitivity of PMMA is rather low. Copolymer XXIII can serve as example how to increase the resist sensitivity.

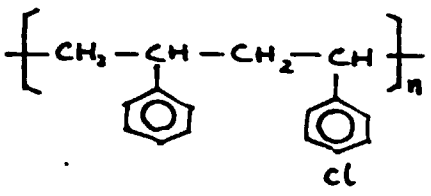


(XXIII)

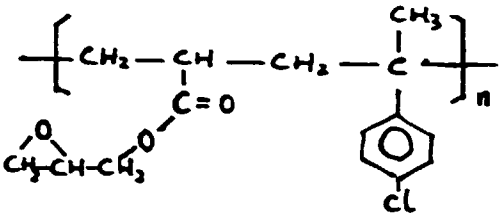
The layer is heated over 200°C after coating in order that some anhydride groups arise and molecular weight increases. The sensitivity is about 10 times bigger (10^{-6}C.cm^{-1}) than that of PMMA.

Negative resists

Crosslinking of polymer molecules is a result of chemical reaction, when the negative working layer is irradiated. Many polymers were described for this purpose. I present two copolymers which can be used in technical practise:



(XXIV)



(XXV)

XXIV - copolymer of styrene and 4-chlorstyrene

XXV - copolymer glycidylmethacrylate and α-methyl-4-chlorstyrene

These main demands are put on the electron beam resist properties

- resolution 0,2 /um
- sensitivity 10^{-6} C.cm^{-2}
- high purity : metal content < 0,5 ppm .
  microfiltration through 0,1 /um filter porosity.

L E C T U R E III

Technical Development and Futher Demands on Materials for Lithography

In this last lecture I should like to estimate future demands on photoresists in various fields of their application.

1. Offset Printing plates

We can state an increasing significance of offset technique in printing industry because of its quick and simple performance and possibility of computer setting (photocomposition). Following properties should be improved:

- Number of printed copies should increase to the range 150 - 250 thousand from one plate.
- Improvement of printing quality, resolution about 5 /um.
- Reproduction of all properties (sensitivity, contrast atc) in very narrow tolerance, in order that the mechanization of the whole process could be carried out.

Of course, these demands depend also on the quality of the aluminium support which must be improved and maintained standard. From the chemical point of view new processing of drying are searched. The layer is heated to the level of softening for several seconds (about 130°C). A glass hard layer is formed on the surface and the number of printed copies increases.

2. Printed Circuit Boards

Two and more-sided circuit boards with metallized holes together with integral circuits have become a foundation of computers and other electronic devices. Two ways of their manufacturing exist:

1. Positive photoresist of high viscosity (150cP) for roll coating (10 /um).
2. Dry photoresists

The technical advantage of dry photoresists is obvious from the following picture:

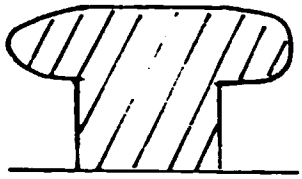


Fig.a. Liquid Photoresist.

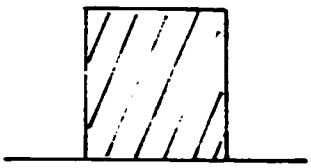


Fig.b. Dry Photoresist

The chemical and galvanic plating of boards follows after development and the metal layer of 30-40 /um is formed. In the case of liquid photoresists the layer thickness is only 10 /um high and so the metal layer has a form of a mashroom (fig. a). Circuit boards made by means of dry photoresists are perfect but much more expensive(fig.b). Derivatives of cellulose or polyvinylethers are used for the viscosity increasing. Dry photoresists are based on photopolymer system which consists of diester of acrylic acid, filmforming polymer and photo-iniciater (derivative of benzoine). They are negative working.

3. Semiconductor Technology

Gemmon Demands

The increasing level of semiconductor technology is presented in table 1.

Table 1

Year	Level K Bit	Resolution /um	
		required	available
1965	1	10	5
1972	4	8	5
1977	16	5	3
1980	64	2-3	1.5
1984	256	1.5-2	1.5
1987	1000	1	1

New perspective methods of lithography and equipment have been developed in the last years:

- Step and repeat printer (DSWO with projection monochromatic illumination (G-line 436nm, I-line 365nm, deep UV-laser 248nm).
- X-Ray lithography
- Electron Beam lithography.

Contamporary step and repeat system is the most important exposure equipment which enables to use commercial photoresists and improve resolution to the level 1 /um.

The future belongs to the X-ray lithography after solving problems connected with construction of exposure devices and with mask preparation. On the contrary, the electron beam lithography seems to remain for application in mask production only because of the long exposure time.

In addition new technologic processing have been introduced intc semiconductor technology:

- Dry etching (plasma chemical etching) replaces etching in solutions, surpresses side-etching and improves edge acuity.
- Ion implantation (new way of As, B, P - dopping)

Both processes demand higher temperature resistance of photoresists.

Estimation of the futher development of semiconductor circuits to the end of century is presented in table 2.

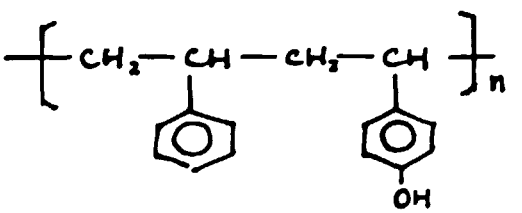
Table 2

Year	Level MBit	Resolution /um		Stepper technology
		required	reached	
1987	1	1	0.8	Opt. G-line 436nm
1989	4	0.7	0.65	opt. G-line 436nm I-line 365 nm
1991	16	0.5	0.5	Deep UV - 248 nm
1995	64	0.3	0.3	Deep UV, X-Ray
2000	1000	?	?	?

Futher Demands on Resists

Negative Photoresists

Simoultaneous commercial negative photoresists are not suitable for reproduction of structures $< 2/\mu m$, because of their swelling and deformation in organic developer. Some experiments are performed to remove this defect. Example XXVI presents a possibility how to replace organic developer with a water alcaline solution:



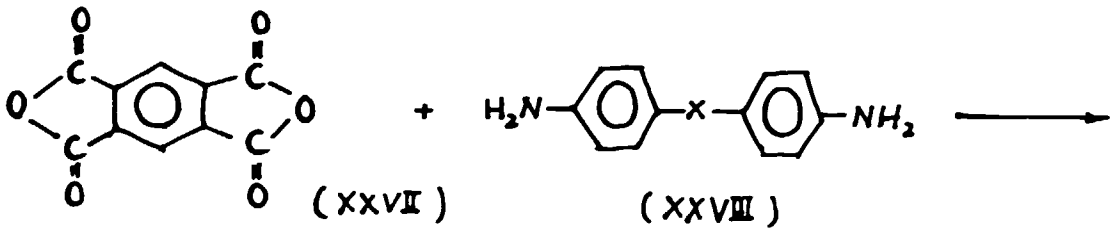
(XXVI)

Positive Photoresists

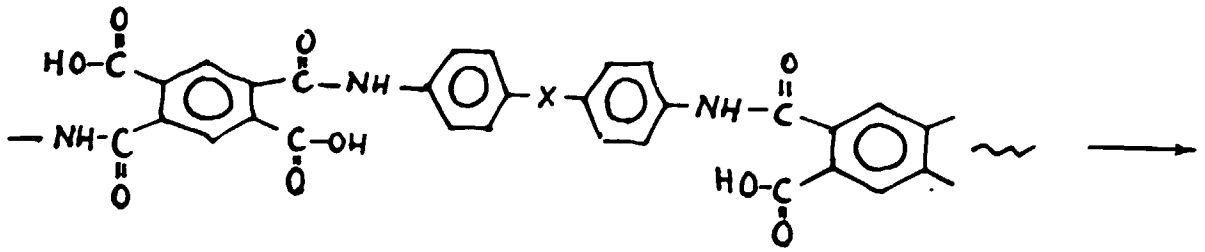
Positive photoresists are considered as perspective materials for step and repeat process. Investigations are focused to several streams:

- Addition of surface-actants to developers improves quality of development and edge acuity.
- Substitution of novolack resins (o-cresol, terc.butyl group) increases contrast.
- New modification of o-naphtoquinone derivatives without acidic -OH groups improves photo-chemical properties (resolution, contrast).
- Thermal hardening (special regime of drying) increases temperature of softening to 200°C.
- UV-Deep resist hardening has the same effect but it is quicker. Special devices for this purpose were developed.
- Image reversal - addition of organic basis causes insolubility of developed structures
- Multilayer procedure: The first layer smoothes the unevent surface after several etching processing.

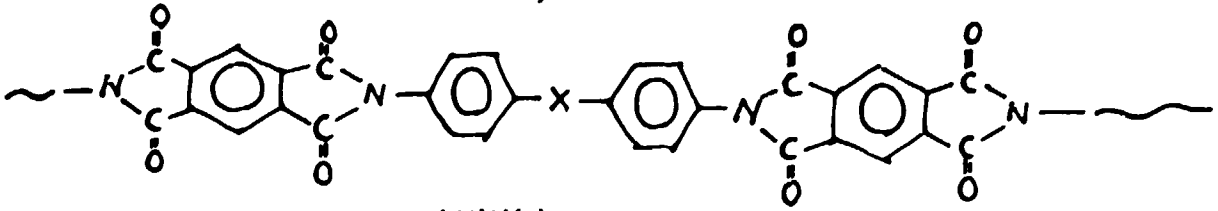
The second layer is a commercial photoresist layer. Polyimides are used for the smoothing; the first reaction step is performed by photoresist producer, the second step by photoresist user on the wafer by heating above 200°C.



(XXVII) (XXVIII)

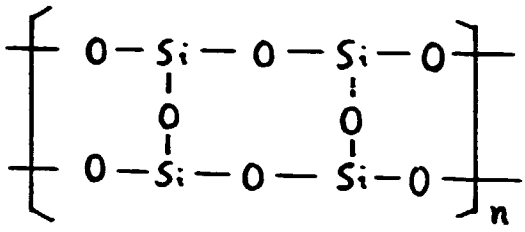


(XXIX)



(XXX)

- Addition of siloxanes and silanes to positive photoresists results higher resistance against plasma-etching (structure XXXI).



(XXXI)

- Addition of deystuff is used for reflex surfaces for absorption of reflective raes and for improvement of resolution, especially on aluminium.

The survey of photoresist chemistry and application at present and in the future demonstrates that this scientific and technical field develops quickly in many streams. We can, therefore, agree to G.E. Fuller's opinion[1]:"The future of optical lithography remains bright!"

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