

INVESTIGATION OF PROCESS TIME-DELAY ON
POLYIMIDE WITH DIFFERENT THICKNESSES
FOR PHOTOLITHOGRAPHY PROCESS

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POLYIMIDE WITH DIFFERENT THICKNESSES
FOR PHOTOLITHOGRAPHY PROCESS

by

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the Degree of
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DECLARATION

I declare that the content presented in this dissertation is my own research work that was done at Universiti Sains Malaysia unless it is informed otherwise. This dissertation has not been previously submitted for any other degree.

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TABLE OF CONTENTS

ACKNOWLEDGEMENTS	ii
TABLE OF CONTENTS	iii
LIST OF TABLES	vii
LIST OF FIGURES.....	viii
LIST OF ABBREVIATIONS	xiii
ABSTRAK	xiv
ABSTRACT	xv

CHAPTER 1 INTRODUCTION

1. Polyimide	1
1.1 Classification of Applications (Applications of polyimide)	2
1.2 Polyimide Coating.....	3
1.3 Types of Polyimide	5
1.4 Problem Statement	10
1.5 Project Background.....	11
1.6 Objectives.....	12
1.6.1 Specific objectives:	12
1.7 Scope of Project	13
1.8 Project Outline.....	13

CHAPTER 2 LITERATURE REVIEW

2. Introduction	15
2.1 Photolithography Process	15
2.1.1 Photolithography for Photosensitive Polyimide.....	15
2.1.1.1 Photoresist	16
2.1.1.2 Coat	17
2.1.1.3 Softbake.....	18
2.1.1.4 Expose	18
2.1.1.5 Develop	18
2.2 Photosensitive and Non-Photosensitive Polyimide.....	19
2.2.1 Photosensitive Polyimide	20

2.3	Structure of Polyimide	22
2.3.1	Formation of Polyimide	23
2.3.1.1	Formation of Polyamic Acid (PAA)	23
2.3.2	Reactivity of Monomers	24
2.3.3	Polyamic Ester (PAE) Precursor	25
2.4	Photo Crosslinking by UV Light.....	26
2.4.1	Photoinitiator	26
2.4.2	The Mechanism of Free Radical Photopolymerization.....	27
2.4.2.1	Initiation	27
2.4.2.2	The Propagation Reaction.....	28
2.4.2.3	Termination.....	29
2.5	Thermal Imidization	31
2.5.1	First Order Reaction	33
2.5.2	Effect of Heating Rate	34
2.5.3	Imidization Rate	34
2.5.4	Solvent Effect on Curing of Precursor	35
2.5.5	Polymer Diffusion	37
2.5.6	Reversible Reaction of Polyamic Acid	37
2.5.6.1	Hydrolysis of Anhydrides	38
2.5.6.2	Dehydration of Dicarboxylic Acids	39
2.5.6.3	Soft Cure/ Soft Bake Studies	39
2.6	<i>N</i> -Methyl-2-pyrrolidone (NMP).....	40
2.6.1	Evaporation of Solvent.....	41
2.7	Rapid Imidization	41
2.8	Degree and Completeness of Imidization (Cyclization)	42
2.8.1	Beer-Lambert's Law	42
2.8.2	FTIR Spectrum	43
2.8.3	Determination of Degree of Imidization from FTIR Spectrum	47
2.9	Factors that Affect Film Thickness	48
2.9.1	Coat	48
2.9.2	Expose	50
2.9.3	Imidization	51
2.10	Characterization	51
2.10.1	Fourier Transform Infra Red Spectroscopy	51

2.10.1.1	IR Sampling Method	53
2.10.2	Scanning Electron Microscopy (SEM)	54

CHAPTER 3 EXPERIMENTAL

3.	Introduction	55
3.1	Sample Splits.....	55
3.2	Materials.....	56
3.2.1	Photosensitive Polyimide Precursor	56
3.3	Environment Conditions	57
3.4	Photolithography Process.....	57
3.5	Characterizations.....	59
3.5.1	Optical Microscope	59
3.5.2	Profilometer.....	60
3.5.3	Fourier Transform Infra Red Spectroscopy (FTIR).....	64
3.5.3.1	Degree of Imidization	65
3.5.4	Scanning Electron Microscopy (SEM)	66

CHAPTER 4 RESULTS AND DISCUSSIONS

4.	Introduction	67
4.1	Optical Microscope Inspection.....	67
4.2	Film Thickness	70
4.2.1	Error Bar of Film Thickness.....	70
4.2.2	Mean Film Thickness	72
4.2.2.1	Mean Film Thickness of 3 μm Samples	73
4.2.2.2	Mean Film Thickness of 6 μm Samples	74
4.2.2.3	Mean Film Thickness of 11 μm Samples	74
4.2.2.4	Mean Film Thickness of 16 μm Samples	74
4.2.3	Factors that Affect Film Thickness	77
4.2.3.1	Evaporation of Solvent	77
4.2.3.2	Photo Crosslinking During Expose.....	77
4.3	Results of FTIR	78
4.3.1	FTIR Spectrum.....	78
4.3.2	Factors that Affect Degree of Imidization.....	88
4.3.2.1	Elimination of Solvent at Lower Temperature	88

4.3.2.2	Reversible Reaction of Polyamic Ester.....	89
4.3.3	Degree of Imidization for Post Expose Delay (PED)	90
4.3.3.1	Degree of Imidization for 3 μm PED Samples	90
4.3.3.2	Degree of Imidization for 6 μm PED Samples	92
4.3.3.3	Degree of Imidization for 11 μm PED Samples	94
4.3.3.4	Degree of Imidization for 16 μm PED Samples	96
4.3.4	Degree of Imidization for Post Coat Delay (PCD)	99
4.3.4.1	Degree of Imidization for 3 μm PCD Samples.....	100
4.3.4.2	Degree of Imidization for 6 μm PCD Samples.....	102
4.3.4.3	Degree of Imidization for 11 μm PCD Samples	103
4.3.4.4	Degree of Imidization for 16 μm PCD Samples.....	105
4.4	Scanning Electron Microscopy (SEM)	111

CHAPTER 5 CONCLUSIONS AND RECOMMENDATIONS

5.1	Conclusions	119
5.2	Recommendations	122

REFERENCES.....	123
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APPENDIX

Appendix A Properties of NMP. (IPCS, 2001)

LIST OF PUBLICATIONS

LIST OF TABLES

Table 1.1	Applications of polyimide in electronic devices (Horie & Yamashita, 1995).....	2
Table 1.2	Examples of research works conducted by other researchers.	7
Table 2.1	FTIR absorption band of polyimide, amide group in polyamic acid and polyamic ester precursor. (Konieczny et al., 1997; Karamancheva et al., 1999; Hou et al., 1999; Coates, 2000; Nishino, 2000; Rabilloud, 2000; Xu et al., 2004; Hsiao et al., 2006; Nguyen et al., 2007; Vijayanand et al., 2007).....	46
Table 3.1	The sample split for Post Coat Delay (PCD) & Post Expose Delay (PED).	56
Table 3.2	Machine parameter setting from coat to develop.	57
Table 4.1	Summary of thermal imidization for 3 μm PED samples.	108
Table 4.2	Summary of thermal imidization for 6 μm PED samples.	108
Table 4.3	Summary of thermal imidization for 11 μm PED samples.	109
Table 4.4	Summary of thermal imidization for 16 μm PED samples.	109
Table 4.5	Summary of thermal imidization for 3 μm PCD samples.	109
Table 4.6	Summary of thermal imidization for 6 μm PCD samples.	110
Table 4.7	Summary of thermal imidization for 11 μm PCD samples.	110
Table 4.8	Summary of thermal imidization for 16 μm PCD samples.	110

LIST OF FIGURES

Figure 1.1	Application of polyimide as stress-buffer coating (Ciba, n.d.).....	2
Figure 1.2	Applications of polyimides in the fabrication of high density integrated circuits (Rabilloud, 2000).	4
Figure 2.1	The photolithography process in wafer fabrication.	16
Figure 2.2	Polyimide patterning process. For non-photosensitive precursor, either positive or negative photoresist is used; for photosensitive precursor, no photoresist is needed. (Omote, n.d.)	17
Figure 2.3	(a) Imide group (b) Polyimide. (Strong, 2007).....	22
Figure 2.4	Mechanism of the formation of polyamic acid (PAA). (Takekoshi, 1996).....	23
Figure 2.5	The formation of polyamic ester (PAE). (<i>Photosensitive polyimide precursors</i> (Fujifilm Electronic Materials Manufacturer (FFEM), n.d.); Macomber, 1996).....	25
Figure 2.6	The initiation steps: the photogenerated free radical attacked the acrylate monomer to form an initiated monomer species (Koleske, 1989).....	28
Figure 2.7	The propagation steps (Koleske, 1989).	29
Figure 2.8	The termination step of acrylate monomer. (Koleske, 1989)	29
Figure 2.9	Crosslink of the photosensitive group. (<i>Photosensitive polyimide precursors</i> (FFEM), n.d.).....	30
Figure 2.10	Mechanism of thermal imidization for PAE. (<i>Photosensitive polyimide precursors</i> (FFEM., n.d.); Schwartz & Srikrishnan, 1998).....	31

Figure 2.11	Role of water in polyimide curing chemistry (Fjare & Roginski, 1993).	38
Figure 2.12	Hydrolysis of anhydride becomes dicarboxylic acid.....	39
Figure 2.13	IR spectrum indicatives of polyamic ester become polyimide after imidization (Nguyen et al., 2007).	44
Figure 2.14	IR spectrum of polyamic ester (Nguyen et al., 2007).....	45
Figure 2.15	The Michelson Interferometer (Smith, 1996).....	52
Figure 2.16	IR sampling method (Mark, 2004).	53
Figure 3.1	The photolithography process involved in the formation of polyimide.	58
Figure 3.2	Comparisons of the structure opening in the samples that is in good conditions versus structures that have residues of polyimide or defective pattern.....	60
Figure 3.3	Profile of a pad opening of the sample is plotted by the profilometer. (a) good profile (b) bad profile.....	61
Figure 3.4	Measurement locations of film thickness.	62
Figure 3.5	Measurement locations for FTIR.....	64
Figure 3.6	The footing of polyimide at the pad opening. The footing is good as it adhere properly to the substrate (Small circle showed resist slightly peeled due to cleavage during sample preparation).....	66
Figure 4.1	Images from optical microscope for 3 μm samples at 10X magnification.	68
Figure 4.2	Images from optical microscope for 6 μm samples at 20X magnification.	68

Figure 4.3	Images from optical microscope for 11 μm samples at 20X magnification.	69
Figure 4.4	Images from optical microscope for 16 μm samples at 20X magnification.	69
Figure 4.5	Error bar of film thickness vs. time delay for 3 μm PCD and PED samples.	70
Figure 4.6	Error bar of film thickness vs. time delay for 6 μm PCD and PED samples.	71
Figure 4.7	Error bar of film thickness vs. time delay for 11 μm PCD and PED samples.	71
Figure 4.8	Error bar of film thickness vs. time delay for 16 μm PCD and PED samples.	72
Figure 4.9	The difference in mean film thickness (%) for 3 μm films from the standard sample for each of the sample splits for PCD and PED.....	73
Figure 4.10	The difference in mean film thickness (%) for 6 μm films from the standard sample for each of the sample splits for PCD and PED.....	75
Figure 4.11	The difference in mean film thickness (%) for 11 μm films from the standard sample for each of the sample splits for PCD and PED.....	75
Figure 4.12	The difference in mean film thickness (%) for 16 μm films from the standard sample for each of the sample splits for PCD and PED.....	76
Figure 4.13	FTIR spectrum with the peak 1780, 1720 and 1380 cm^{-1} for 3 μm (a) PCD, (b) PED.	79
Figure 4.14	FTIR spectrum with the peak 1780, 1720 and 1380 cm^{-1} for 6 μm (a) PCD, (b) PED.....	80

Figure 4.15	FTIR spectrum with the peak 1860, 1780, 1720 and 1380 cm^{-1} for 11 μm (a) PCD, (b) PED.	81
Figure 4.16	FTIR spectrum with the peak 1860, 1780, 1720 and 1380 cm^{-1} for 16 μm (a) PCD, (b) PED.	82
Figure 4.17	FTIR spectrum with peak at region 3200-3400 cm^{-1} for 3 μm (a) PCD, (b) PED.	84
Figure 4.18	FTIR spectrum with peak at region 3200-3400 cm^{-1} for 6 μm (a) PCD, (b) PED.	85
Figure 4.19	FTIR spectrum with peak at 3200-3400 cm^{-1} and 2800-3000 cm^{-1} region for 11 μm (a) PCD, (b) PED.	86
Figure 4.20	FTIR spectrum with peak at 3200-3400 cm^{-1} and 2800-3000 cm^{-1} region for 16 μm (a) PCD, (b) PED.	87
Figure 4.21	Reversible reaction of PAE when water exists.	90
Figure 4.22	The degree of imidization and mean thickness for 3 μm PED samples.	91
Figure 4.23	The degree of imidization and mean thickness for 6 μm PED samples.	93
Figure 4.24	The degree of imidization and mean thickness for 11 μm PED samples.	94
Figure 4.25	The unreacted PAE and anhydride remained on the samples for 11 μm PED samples.	95
Figure 4.26	The degree of imidization and mean thickness for 16 μm PED samples.	97
Figure 4.27	The unreacted PAE and anhydride remained on the samples for 16 μm PED samples.	97

Figure 4.28	The degree of imidization and mean thickness for 3 μm PCD samples.	100
Figure 4.29	The degree of imidization and mean thickness for 6 μm PCD samples.	102
Figure 4.30	The degree of imidization and mean thickness for 11 μm PCD samples.	104
Figure 4.31	The unreacted PAE and anhydride remained on the 11 μm PCD samples.	104
Figure 4.32	The degree of imidization and mean thickness for 16 μm PCD samples.	107
Figure 4.33	The unreacted PAE and anhydride remained on the 16 μm PCD samples.	107
Figure 4.34	(a) The profile of polyimide at the opening area (b) the area that will be etch away and (c) the profile after etched.	111
Figure 4.35	The polyimide is not completely removed after developed.....	112
Figure 4.36	The profile of the footing of 6 μm polyimide obtained from SEM...	113
Figure 4.37	The profile of the footing of 16 μm polyimide obtained from SEM.	116

LIST OF ABBREVIATIONS

DMA	N, N-dimethylacetamide
DRAM	Dynamic random access memory
DSC	Differential scanning calorimeter
E_a	Electron affinity
FTIR	Fourier Transform Infrared
NMP	<i>N</i> -Methyl-2-pyrrolidone
ODA	Oxydianiline
PAA	Polyamic acid
PAE	Polyamic ester
PCD	Post coat delay
PEB	Post exposure bake
PED	Post expose delay
PI	Polyimides
PMDA	Pyromellitic dianhydride
PSPI	photosensitive polyimide
SEM	Scanning electron microscope
T _g	Glass transition temperatures
TGA	Thermal gravimetric analysis

KAJIAN TENTANG PENANGGUHAN MASA PEMROSESAN POLIIMIDA YANG BERBEZA KETEBALAN SEMASA PROSES FOTOLITOGRAFI

ABSTRAK

Poliimida (PI) terutamanya poliimida fotosensitif (PSPI) telah digunakan secara meluas dalam industri semikonduktor disebabkan sifat terma, mekanikal dan kimianya yang unggul. Semasa proses fotolitografi, terdapat penangguhan masa pemrosesan dari pelapisan fotoresis ke penyinaran UV dan ke proses pengembangan. Ini akan menyebabkan profail struktur terjejas dan sisa poliimida tertinggal dalam filem. Di Infineon teknologi, wafer akan disingkirkan jika masa penangguhan melebihi 5 jam dan kos terlibat untuk setiap kes ialah RM37500. Kajian ini bertujuan untuk mengkaji kesan penangguhan masa dalam proses fotolitografi terhadap filem poliimida. Berdasarkan keputusan, satu garis panduan akan diwujudkan dan pembuangan wafer boleh dielakkan. Sementara itu, ia juga memudahkan pengeluaran dan mengurangkan tenaga kerja. Dua jenis prekursor poliamik ester (PAE) yang memberi ketebalan poliimida berlainan telah digunakan. Mikroskop optikal, profilometer, spektroskopi inframerah transformasi Fourier (FTIR) dan mikroskop elektron pengimbasan (SEM) untuk keratan rentas telah digunakan untuk menganalisis sampel. Berdasarkan keputusan, tiada perubahan yang signifikan pada ketebalan akhir poliimida. Tiada kecacatan ketara atau sisa poliimida dalam filem poliimida. Namun, darjat imidisasi untuk sesetengah sampel terpengaruh. Terdapat PAE yang tidak bertindakbalas dan anhydride yang tertinggal dalam sampel 11 dan 16 μm . Ini adalah disebabkan oleh pelarut NMP yang mudah mengewap, boleh menyerap air dari udara sekeliling dan mudah bercampur dengan air. Reaksi berbalik PAE kepada PAA dan seterusnya anhydride telah berlaku.

INVESTIGATION OF PROCESS TIME-DELAY ON POLYIMIDE WITH DIFFERENT THICKNESSES FOR PHOTOLITHOGRAPHY PROCESS

ABSTRACT

Polyimides (PI), particularly photosensitive polyimide (PSPI) has wide applications in semiconductor industries due to their good thermal, mechanical and chemical properties. During photolithography process, there might be time delays from coat to expose and from expose to develop. The time delay could change the profile of the structures and residues of precursor might leave on the film. In Infineon technologies, those wafers are scrapped if time delay exceeded 5 hours and every scrapped cost RM37500. As such, a study is carried out to investigate the effect of time delay in photolithography process to the cured polyimide film. Based on the results, a guideline is established and unnecessary wafer scrapped can be prevented. Meanwhile, it also eases the production and reduce work force. Two types of polyamic ester (PAE) precursors that give different thicknesses involved in this study. Optical microscope, profilometer, Fourier Transform Infrared (FTIR) spectroscopy and cross-sectional scanning electron microscope (SEM) is used to characterize and investigate the polyimide. Based on the results, the time delay did not significantly changed the final thickness of polyimide. There are no significant defects or residues remained. However, degree of imidization for some of the samples are affected. There are unreacted PAE and anhydride left on the film of 11 and 16 μm thick samples. This is caused by NMP, which is highly miscible with water, easily evaporates and absorbed moistures from the environment. The PAE can reverse to polyamic acid (PAA) and subsequently become anhydride.

CHAPTER 1

INTRODUCTION

1. Polyimide

Polyimides (PI) have found very important applications in semiconductor industries due to high thermal stability, low dielectric constant, excellent mechanical and chemical properties (Ghosh & Mittal, 1996). It is a class of the highest heat-resistant polymer whose properties as a passivant or dielectric meet the requirement of semiconductor industries (Horie & Yamashita, 1995). The excellent mechanical properties at high temperatures are due to the rigid structures, which result in high glass transition temperatures (Kim & Hay, 1993). Another property that makes polyimide popular is it has excellent ability to planarize topographical substrates (Horie & Yamashita, 1995). This property is attributed to the fluidity of polyimide precursor solution that makes it possible to be spin-coated on a substrate followed by thermal curing to convert to polyimide (Horie & Yamashita, 1995). Originally, polyimides are used as interlayer dielectric for multilevel metalized transistor (Horie & Yamashita, 1995). By the midst of 1970s, there are patents claiming the use of polyimide films as passivation layer for integrated circuits. Hitachi PIQ has been the first to be evaluated as the uppermost protective layer, coated over a silicon dioxide passivation layer, pretreated with a silane coupling agent (Rabilloud, 2000). At the same time, IBM started to use polyimide as buffer coating for final chip passivation, before incorporating polyimide films as insulator and passivation layers for metal-gated dynamic random access memory (DRAM) production.

1.1 Classification of Applications (Applications of polyimide)

Polyimides have been used in many applications in electronic devices. There are two main categories. One is a passivating protection while another one is an interlayer dielectric in integrated circuits (ICs). The former can be further subdivide into junction-coating, buffer coating, passivation and α -ray shielding (Horie & Yamashita, 1995). Table 1.1 gives examples of the location and purpose of polyimides.

Table 1.1 Applications of polyimide in electronic devices (Horie & Yamashita, 1995).

Classification		Location	Purpose
Protection	Junction-coat	PN Junction	Prevention of contamination
	Passivation	Surface of device	Surface protection
	Buffer coat	On the passivation	Relief of mechanical stress
	α -ray shielding	On the passivation	Prevention of soft errors for memory devices
Interlayer dielectric		Between wire and wire	Insulation between wire and wire

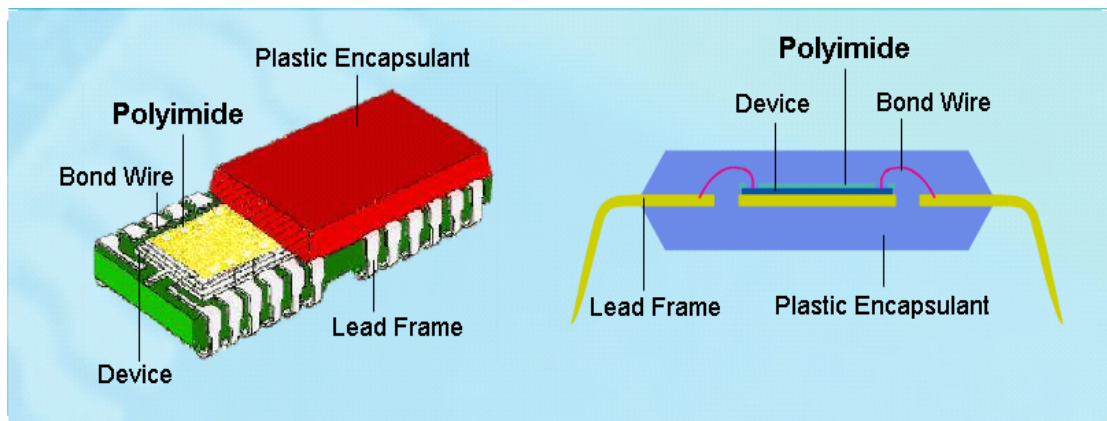


Figure 1.1 Application of polyimide as stress-buffer coating (Ciba, n.d.).

The main application of polyimide is a stress-buffer coating for devices in thin and ultra-thin packages as shown in Figure 1.1 (Rabilloud, 2000; Ciba, n.d.).

These devices include large-die devices packaged in plastic molding compounds, for example dynamic random access memory (DRAM). Modern packaging design of integrated circuits involves a lot of process that induce significant amount of stress on the chips. These stresses are resulted from the difference in thermal expansion of silicon chips, lead frames and plastic packages. Subsequently, these may lead to cracking of the package or the protective passivation layer, exposing them to contaminants such as moisture and ionic particles (Flack et al., 2001). Imparted stress may also lead to metal or wire-bond deformation, possibly altering device parameters. In both cases, device reliability and yield may be severely degraded (Flack et al., 2001). Thus, polyimide overcoat at passivation help absorb the interfacial stresses and prevent from passivation crack and electrode displacement.

On the other hand, polyimide is also used as passivation layer. Usually, the die passivation is made of a brittle glass film, such as silicon dioxide, phosphosilicate glass (PSG), or silicon nitric (Pecht, 1994). During inner lead bonding, the center of a bump is dented. This causes the pressure by bump to be concentrated at the passivation film under the periphery of the bump. The passivation film under the bump may crack unless there are special design of the bump structure and bonding conditions. One of the solutions to this problem is to use a relatively ductile polyimide film as the passivation layer, which provides good protection against bonding pressure and temperature (Pecht, 1994).

1.2 Polyimide Coating

Figure 1.2 shows the different layers in a transistor including the potential use of polyimide in integrated circuit. Silicon substrate 1 with active device 2 is insulated with a thin layer of silicon dioxide 3. Then, level 1 metal pad and conducting lines 4 are patterned by photolithography and chemically etch. A layer of intermetallic

dielectric is formed by spin-coating of a polyimide film 5 which is subsequently patterned and etched to open through holes or ‘vias’. The second metallization level (metal 2) 6 is then deposited over the structure and patterned to create conducting lines interconnecting the active devices. (Rabilloud, 2000)

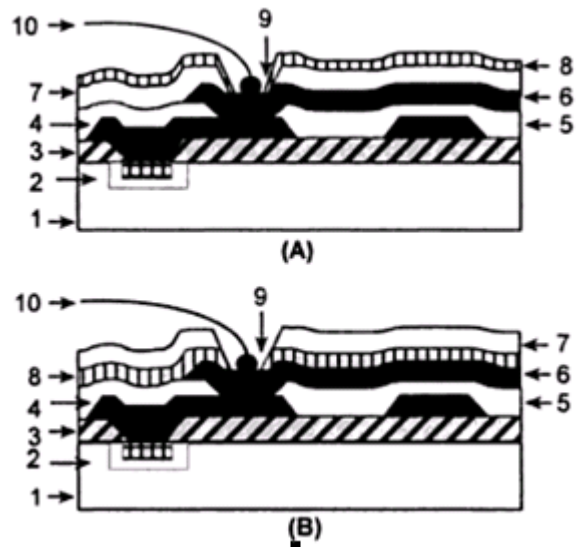


Figure 1.2 Applications of polyimides in the fabrication of high density integrated circuits (Rabilloud, 2000).

There are two ways of the use of polyimide as the final passivation. In Figure 1.2A, the top protective coating include polyimide film 7 covered with silicon nitride 8 that are both patterned and etched to open windows over metal pads 9. These pads are electrically connected to the chip package by bonding metal wires 10. The opposite sandwich is shown in Figure 1.2B where silicon nitride 8 is coated over the metallization and protected by an uppermost layer of polyimide 7. (Rabilloud, 2000) The latter way is more advantage as the polyimide layer can fills the pinholes and cracks of the underlying inorganic film. After openings have been defined over the metal pads, the individual dice are separated and are attached to their lead frames. They are electrically connected by wire bonding and then coated with a second layer of polyimide (Rabilloud, 2000). The shrinkage of the plastic moulded package,

which have thermal expansion coefficient that is greater than the silicon chips and lead frames induces force on the inner layer (Horie & Yamashita, 1995). Thus, the second layer of polyimide act as buffer coating to reduce structural deformation in interconnects.

1.3 Types of Polyimide

Most of the polyimides are not process able because of their rigidity, high glass transition temperature and almost insoluble in most common solvent (Ghosh & Mittal, 1996). Therefore, they are processed in their soluble precursor forms and thermally or chemically imidized to become polyimide (Matsumoto & Kurosaki, 1997). Various kind of polyimides have been reported since the last 2 decades, including the soluble polyimide and photosensitive or non-photosensitive polyimide that are either negative or positive type (Horie & Yamashita, 1995).

DuPont R & D has made early attempts in the 1950s to use the dianhydrides and aromatic diamines directly react in the melt or in solution. It resulted in precipitation of intractable low molecular weight polyimides (Takekoshi, 1996). However, by 1956, Dr. A. Endrey at DuPont had successfully pioneered the invention to obtain polyimides. It is a two steps reaction of soluble intermediates polyamic acid. Polyamic acid precursors are most widely used to obtain polyimide. In 1967, Boldebuck and Klebe (1967, cited in Oishi et al., 1991) has applied the N-silylated diamine method to the synthesis of polyimides. This method is found to produce a high molecular weight polyimide (Oishi et al., 1991).

Kerwin and Goldrick reported the first photosensitive polyimide in 1971 (Hou et al., 1999). The PSPI was obtained by adding sodium dichromate, which is a photoreactive group to polyamic acid. However, this material had too short of shelf

life to be practical because of the instability of the polymer solution and contamination by residual chromic ions.

Rubner and his co-workers first reported, in 1976, a practical system, which is a negative-type photosensitive polyimide precursor (Higuchi et al., 1991). A photoreactive methacryl group was introduced to the polymer side chain by esterification of carboxyl groups of a polyamic acid (Berrada et al., 1996). This ester-type system showed excellent storage stability and better solubility than PAA (Houlihan, 1989). There are researchers that synthesized positive type photosensitive polyimide precursor, for example, precursor that based on nitrobenzyl ester, nitro-p-xylylene structure and alkaline-developable polyimide with diazonaphthoquinone as a photosensitive compound (Kubota et al., 1989 cited in Higuchi et al., 1991; Feng et al., 1996; Seino et al., 1998).

In contrast, Yoda and Hiramoto (1984) demonstrated a different way of introducing the photoreactive groups, which is by ionic bonding (Berrada et al., 1996). In their material, an amino compound with a photoreactive methacryl group is added to a polyamic acid as a photoreactive additive, and the methacryl group is incorporated by a salt formation reaction between the amino groups of the photosensitive additive with the carboxylic acid group of the polyamic acid (Berrada et al., 1996). Kataoka et al. (n.d) described highly photosensitive materials containing aromatic azide compounds as a photosensitive additive (Berrada et al., 1996).

After the pioneered inventions of polyimide, many researches were continuing on the studies of different aspect of polyimide. Some researchers had synthesized and characterized the soluble polyimide (Omote et al., 1990; Higuchi et al., 1991; Kim & Hay, 1993; Matsumoto & Kurosaki, 1997; Ree et al., 1997; Chung

& Kim, 2000). Many researchers have investigated on the thermal cyclization include the variation in curing temperature for polyamic acid (PAA) precursor (Colburn & Pottiger, 1991; Fjare & Roginski, 1993; Konieczny et al., 1997; Li et al., n.d cited in Rabilloud, 2000; Chang & Park, 2000; Nishino et al., 2000). On the other hand, there are researches that did investigations on PAE. (Pottiger et al., 1988; Houlihan et al., 1989; Becker & Schmidt, 1992; Huang et al., 1997; Hou et al., 1999; Choi et al., 2010). Kajzar and Swalen (1996) and Rabilloud (2000) have study on the thermal imidization temperatures and the mechanism to cure PAE precursor. Bhattacharya and Blaosale (1996) had explored and reported the viscosity and stress dependent mechanisms of some commercially available polyimides in order to characterize the best softbake cycle for each polyimide. Ishida et al. (1980) had done intensive spectroscopic studies on polyimide and their related component to know their configurational change. Others applied FTIR to study the imidization of polyimide, degree of imidization and their concentration (Cheng & Wunder, 1996; Karamancheva et al., 1999; Nguyen et al., 2007). Table 1.2 shows some examples of PAA and PAE studies conducted by researchers.

Table 1.2 Examples of research works conducted by other researchers.

Author	Year	Research work
Fukukawa & Ueda	2010	Reported on chemically amplified PSPI, the advances in the molecular design as well as potential properties of PSPIs and poly(benzoxazole)s (PSPBOs).
Choi et al.	2010	Synthesized & characterized a PAE from a PAA, determined the best post exposure bake (PEB) temperature, imidization temperature and the weight loss of PAE.
Chang et al.	2009	Synthesized a photosensitive polyimide - nanocrystalline titania optical thin films with high refractive index. Demonstrated a novel approach to produce a high refractive index photosensitive hybrid material with patternability.

Table 1.2 Continued.

Author	Year	Research work
Grabiec et al.	2009	Synthesized 2 new series of polyimide using Poly(amide imides) and Poly(ether imides) Containing 1,3,4-Oxadiazole or Pyridine Rings. The structure of polymer is characterized and their optical properties are studied.
Kim	2009	Discussed further improvement of polyimide as buffer coating, the pre-established processes and the considerations affecting the design of future PSPI materials. The next generation of PSPI buffer coating processes is briefly described.
Saito et al.	2009	Developed a highly refractive sulfur-containing PSPI with photoacid generator. A clear negative-tone line-and-space pattern with 8- μ m resolution is formed.
Fukuda et al.	2009	Synthesized a PSPI with two types of highly sensitive photobase generator and investigated on their applicability in photolithography process.
Jin & Zhu	2008	Investigated the Influence of curing temperature on the optical properties of fluorinated polyimide thin films.
Choi et al.	2006	Synthesized negative PAE, study effect of post exposure baking temperature, amount of photoinitiator and exposure dose on photosensitivity. Evaluated photolithography process by using mercury lamp.
Fukukawa et al.	2006	Investigated the direct patterning of negative type PAA and low-temperature imidization using a photo-base generator.
Saeed & Zhan	2006	Studied on the effects of monomer structure and imidization degree on mechanical properties, viscoelastic behavior. Two types of polyimide that cast from polyamic acid (20 and 50 μ m thick polyimide) are used.
Choi et al.	2005	Synthesis of negative-type PAA based on cyclobutane-1,2,3,4-tetracarboxylic dianhydride and the characterizations: degree of planarity, transmittance, thermal stability after photoirradiation.
Hsu & Fan	2004	Synthesis of negative aquos based PAE and characterized using FTIR, H-NMR. Different photosensitizer, photoinitiator and crosslinker has been added.
Xu et al.	2004	Studied the structure and properties of polyimide films based on PMDA/ODA during a far-infrared-induced imidization process.
Chang & Park	2000	Investigation on the thermal cyclization of polyamic acid (PMDA and Benzidine) and their thermal, mechanical and morphological properties.

Table 1.2 Continued.

Author	Year	Research work
Nishino et al.	2000	Study the residual stress and microstructures of aromatic polyimide with different imidization processes.
Chung & Kim	2000	Soluble polyimides from unsymmetrical diamine with trifluoromethyl pendent group.
Hou et al.	1999	Synthesized of negative type PAE, investigated the influence of main chain structure and molecular weight on their photosensitivity.
Karamancheva et al.	1999	FTIR spectroscopy and FTIR microscopy of vacuum-evaporated polyimide thin films.
Stoffel et al.	1998	Imidization and interdiffusion of poly (amic ethyl ester) precursors of PMDA/3,4*-ODA
Lee & Murarka	1998	Studied the various parameters that affect the imidization process and characterization of low k-fluorinated polyimide film during thermal curing.
Huang et al.	1997	Synthesis and characterization of a series of poly(amic methyl ester)s from five aromatic dianhydrides and a diamine, 4,4*-oxydianiline (ODA).
Konieczny et al.	1997	Curing reaction of the para, meta and 50/50 mixed isomers of PMDA/ODA based polyamic ethyl ester 30 μm thick.
Miwa et al.	1997	Investigated the effect of precursor structure and imidization process on thermal expansion coefficient (TECs) of BPDA/PDA. Included the effect of drying condition on thermo-mechanical properties and morphology.
Berrada et al.	1996	Synthesis and characterization of soluble PSPI by chemical imidization.
Flack et al.	1996	Investigation of the properties of ester and ionic type photosensitive polyimide.
Cheng & Wunder	1996	NMR and FTIR investigations of the solution imidization kinetics of model compounds of PMDA/ODA polyamic ethyl ester.
Rich et al.	1996	Curing study of a preimidized photosensitive polyimide.
Kim et al.	1995	Investigated the thermal imidization of BPDA-ODA & BPDA-PDA by TGA.
Kim et al.	1993	Studied the kinetics of imidization reaction for PAA in solution.
Kim & Hay	1993	Synthesis of soluble poly(ether imide)s from bis(ether anhydride)s containing bulky substituents.
Becker & Schmidt	1992	Synthesis and imidization study of para-linked aromatic poly(amic ethyl ester)s: precursors to rod like aromatic polyimides.

Table 1.2 Continued.

Author	Year	Research work
Okamoto et al.	1992	Studied the sorption and diffusion of water vapor in polyimide films.
Houlihan et al.	1989	Synthesis and characterization of the tert-butyl ester of the oxydianiline/pyromellitic dianhydride polyamic acid.
Pottiger et al.	1988	Studies the processing and cure film properties of PMDA/ODA and BTDA/aromatic diamine based polyimide.
Laius & Tsapovetsky	1984	Studied the kinetics of the imidization reaction for PAA in solid state.
Ishida et al.	1980	Spectroscopic studies of poly[N,N' bis(phenoxyphenyl)pyromellitimide]. Studied the structures of the polyimide and three model compounds.

1.4 Problem Statement

Although polyimide is widely used in the semiconductor industries, none of the researchers has study on the effect of time delay during the manufacturing process. Many of the researchers synthesized and characterized various kind of polyimide. Likewise, many of them also investigated on their characterization such as the mechanical, chemical and electrical properties of different polyimides. However, the variation in manufacturing process is also important to study because they might affect the conditions of the precursor to continue process and subsequently affect the properties of polyimide.

The precursor of polyimide (PAE precursor) consists of 60% of solvent, which is *N*-Methyl-2-pyrrolidone (NMP). Hilfiker (2006) has mentioned that NMP is hygroscopic which means it can takes water easily from the environment. At the same time, NMP is volatile (International Programme on Chemical Safety (IPCS), 2001). Mckeen (2006) and Xu et al. (2004) have proved that NMP can easily evaporate at room temperature and at temperature below 100°C. However, Lee and Murarka (1998) mentioned that solvent is important for imidization process.

Therefore, it is important to know whether the polyimide is still in good conditions after some time delay.

It is common that in manufacturing, the wafers are not process immediately from one process to another process. This may be due to some complicated situations such as machine breakdown, congestion at certain machine, shortage in work force, materials and so on. With the prolonged time delay, residue of the precursor may remain on the wafer and the structures profile might change. This happens in the factory almost every day and many wafers were scrapped. In addition, polyimide is the last layer in wafer fabrication, the lost is huge, which is equivalent to RM1500 per wafer. One box of wafers contains 25 wafers, each scrapped of a box cost RM37500. Since there is no proven data on the duration of delay time that the polyimide will in good condition, many wafers have been scrapped to ensure only products with good quality are shipped to customers.

Thus, the study of time delay will serve as a guideline for the company to process the wafer within a safe delay time and prevent unnecessary scrap of wafers. This guideline will gives more flexibility to production and reduce work force to ensure the wafers are process within a very tight period.

1.5 Project Background

In wafer fabrication, polyimide is the last photolithography layer, which serves as passivation layer. The photolithography process for polyimide layer has time restrictions from coat to expose and from expose to develop. Post Coat Delay (PCD) is the time delay after coat before expose while Post Expose Delay (PED) is the delay time after expose before develop. The standard process, which is represented by the standard sample, is to have a time delay of 30 minutes after expose to allow the PAE precursor to polymerize or crosslink before continue to

another process. Based on the information from the precursor supplier, the restriction time is less than 24 hours for both of the process. The company has an internal control of less than 5 hours for each PCD & PED. A study is carried out to investigate the impact or process ability of the precursor if exceeding the restriction time. Based on the results, a guideline of allowable process window can be established to ensure a better production flow and no scrapped of good wafers.

1.6 Objectives

1. To study the effect of post coat delay (PCD) and post expose delay (PED).
2. To establish a guideline for process time delay of polyimide during photolithography process.

1.6.1 Specific objectives:

1. To observe whether there are residues of PAE precursor left on the film, which indirectly explain whether the fixed curing temperature and time used is able to imidize the films after the time delay.
2. To study the effect of post coat delay (PCD) and post expose delay (PED) on film thickness.
3. To evaluate the degree of imidization of polyimide after post coat delay (PCD) and post expose delay (PED).
4. To determine whether there are unreacted PAE precursor remained in the film after imidization.
5. To observe the footing of the polyimide after post coat delay (PCD) and post expose delay (PED).

1.7 Scope of Project

The maximum time delay for this study is 50 hours for both PCD and PED. Two types of PAE precursors that give different thicknesses were used to examine the effect of process time delay. One of the PAE precursors, Durimide from Fujifilm Electronic Materials Co. Ltd. is used to obtain thicker polyimide, which is the 6, 11 and 16 μm polyimide while another precursor, Asahi from Asahi Kasei Corporation is used to obtain thin polyimide, which is the 3 μm thick polyimide. These four thicknesses were used because they cover thin, medium and thick polyimide that were used in the factory. The four thicknesses of polyimide have different reticle design, which is having different patterns. Each thickness has 12 samples with different split as shown in Table 3.1. The actual final film thickness for each thickness is based on the thickness obtained by the standard sample of each thickness.

The effect of the time delay is study in terms of the physical properties, the degree of imidization and the process ability of the polyimide in photolithography process after time delay. The physical properties includes the condition of the pattern formed after develop, the film thickness and the profile of the structures after cure. The process ability refers to whether the wafers are physically in good condition to continue to next process. The wafers are physically in good condition if there are no residues of polyimide left on the wafers and the pattern is well formed even with the time delay.

1.8 Project Outline

Chapter 2 illustrates the overall photolithography process from coat to develop, the introductions of photosensitive and non-photosensitive polyimide as well as the structure of polyimide. It covers the theoretical explanations and findings

from other researchers, which include the formation of PAA, PAE precursor, photocrosslinking by UV light, thermal imidization and the factors that affect film thickness. Besides, the solvent, *N*-Methyl-2-pyrrolidone (NMP) and the effects were explained. The elucidation of the degree of imidization based on Beer-Lambert's Law and details of findings from others as well as characterization using Fourier-Transform Infra red spectroscopy (FTIR) and Scanning electron Microscopy (SEM) were presented. Chapter 3 depicts the samples splits, sample preparations, tool settings for the processes and formulas for the various calculations. Besides, the characterization test used and the methods were explained. Chapter 4 comprises of the results of the optical microscope inspection, the thicknesses and Fourier Transform Infra Red (FTIR) spectrum that showed whether the polyamic ester precursor has completely changed into polyimide. Apart from that, the degree of imidization is determined to understand the polymerization of the precursor become polyimide. The degree of imidization, effect of solvent and the absorption of moistures from environment are further discussed. Chapter 5 is the conclusion of the findings and recommendations for future works.

CHAPTER 2

LITERATURE REVIEW

2. Introduction

This chapter introduces the steps involved in the photolithography process and the introductions of the photosensitive as well as non-photosensitive polyimide. Most of the reviews are surrounding with the photosensitive polyimide. It provides explanation about the formation of polyamic acid (PAA), polyamic ester (PAE) precursor and the formation of polyimide after the precursor is thermally cured (imidization process). At the same time, it depicts the process of thermal imidization to form polyimide. It also includes finding and theoretical explanations proposed by others. Important findings from others are the effect of solvent and the chemical reaction during imidization, the evaporation of solvent and the method to get the degree of imidization. The last part exemplifies the main characterization test, which is the determination of degree of imidization by Fourier Transform Infra Red (FTIR) and the scanning electron microscopy (SEM) that is used to observe the surface of polyimide.

2.1 Photolithography Process

2.1.1 Photolithography for Photosensitive Polyimide

Photolithography is the process of transferring circuit patterns from masks or reticles to a thin layer of photosensitive material called photoresist covering the surface of a semiconductor wafer via optical method (Levinson, 2001). The

photolithography process involves three main processes, which are coat, expose and develop. Figure 2.1 gives the overview of the photolithography process:

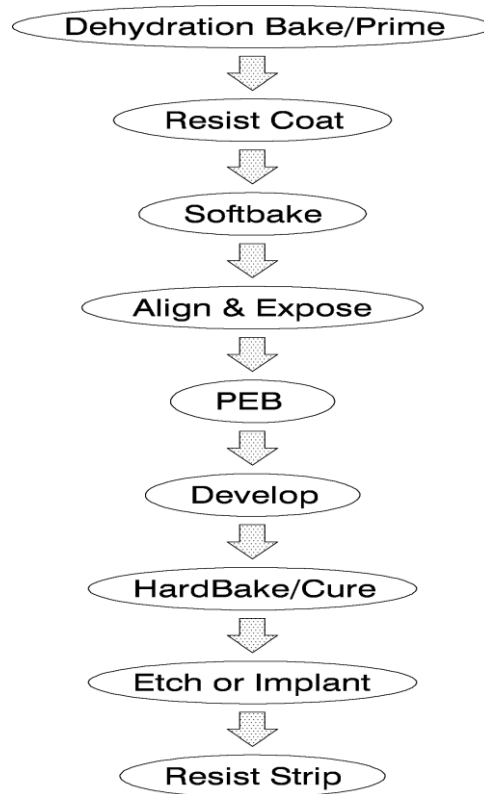


Figure 2.1 The photolithography process in wafer fabrication.

2.1.1.1 Photoresist

Photoresist or simply resist is a radiation-sensitive compound that can be classified into positive or negative (Figure 2.2), depending on how it response to radiation. For positive resists, exposure process changes the chemical structure of the resist so that it becomes more soluble in developer. Thus, the area that is exposed to ultraviolet (UV) light will be removed. Negative resists behave in just the opposite manner. Exposure to UV light causes the negatives resist to polymerized and is difficult to dissolve. Therefore, the negative resist remains on the surface and the developer solution removes only the unexposed portions. The compositions of

photoresist are polymers, sensitizers, solvents and additives. Polymers provide physical resistance to etch while sensitizers modify the photosensitivity for the resist. Solvents keep the resist liquefied for spin application whereas additives improve sensitivity to developer.

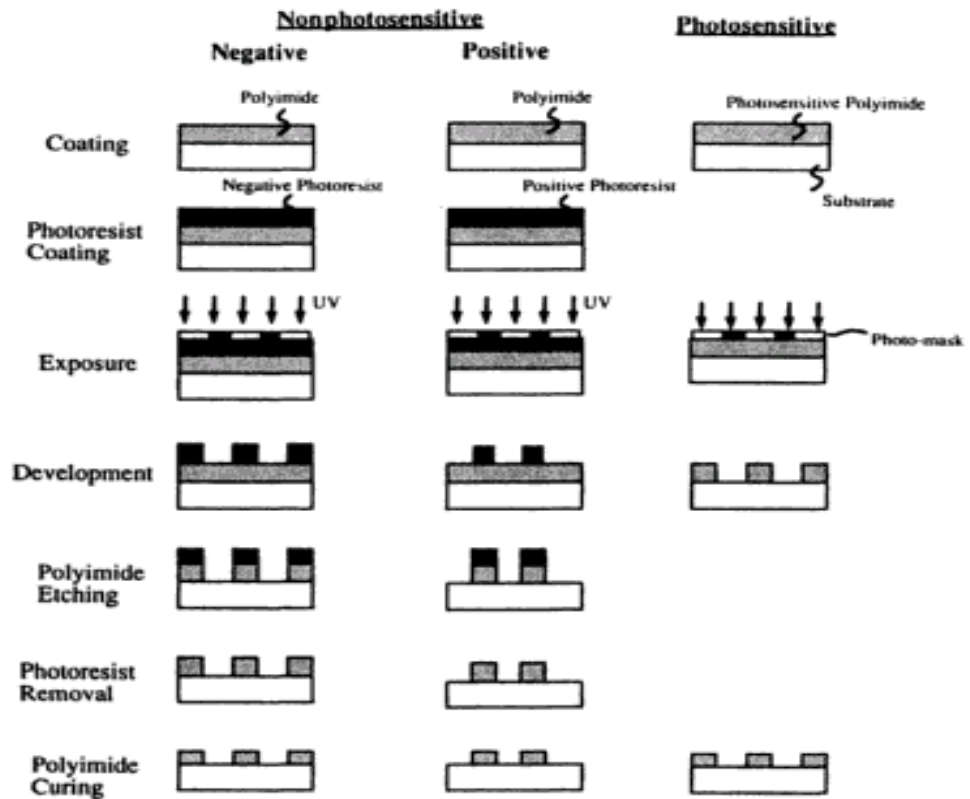


Figure 2.2 Polyimide patterning process. For non-photosensitive precursor, either positive or negative photoresist is used; for photosensitive precursor, no photoresist is needed. (Omote, n.d.)

2.1.1.2 Coat

Coating is to produce a uniform photosensitive material and polymeric film for mask patterns. The coating methods include spin coating, spray coating and dip coating. For spin coating, the process has four stages. The first stage is deposition where excess resist is spun onto the substrate. Next, the coater will spin-up to wet the entire wafer with excess resist. After that, the excess resist is removed from the

substrate surface by the spin-off process and lastly is the solvent evaporation that drives off some of the solvent and solidified the film. The evaporation of solvent occurs from the top surface, while the simultaneous rotation forces the fluid to flow uniformly outward (Haas & Quijada, 2000).

The thickness of resist is determined primarily by the resist viscosity and secondarily spinner rotational speed.

2.1.1.3 Softbake

The softbake process is to harden the resist and to remove residual solvent without imidized or cure the film. Bhattacharya and Blaosale (1996) found a decrease in the viscosity of the precursor, which is due to degradation or chain scission happened (Reichmanis & Thompson, 1989) for some polyimide during softbake. While some other polyimide, the viscosity increases because of the polymer crosslinked and solvent evaporation phenomena.

2.1.1.4 Expose

Exposure or imaging is a process to transfer the latent image of integrated circuit (IC) design from photo mask onto resist coated wafer using UV light. The process involves the absorption of radiation and subsequent photochemical change (PAC) of the resist resulting in modification of dissolution properties.

2.1.1.5 Develop

Development is the process to removes all of the resist that has been patterned without removing the unpatterned resist. The pattern dimensions should be precisely produced and the original resist thickness should be kept. The time required to resolve the patterned coating depends on the coating thickness (Pottiger et al., 1998).

2.2 Photosensitive and Non-Photosensitive Polyimide

The introduction of photosensitive polyimide (PSPI) is a major advance in polyimide technology and it has attracted considerable attention in the semiconductor industry due to its direct patternability. It integrates the passivation and photolithography processes into one process. The standard polyimide photolithographic process frequently utilizes a trilayer film consisting of an adhesion layer, a polyimide film, and photoresist (Omote, n.d.). This standard process uses a non-photosensitive polyimide and is shown in Figure 2.2. During photolithography process, a layer of polyimide is spin-coated on the wafer and a layer of photoresist is coat on top of the polyimide. After that, the wafer is exposed using a photolithography tool. The photoresist is then developed to remove the uncrosslinked area, which is usually accomplished by a wet etch process (Omote, n.d.).

As shown in Figure 2.2, the photoresist used is either a negative or a positive photoresist. For positive resists, exposure process changes the chemical structure of the resist so that it becomes more soluble in developer. Thus, the area that is exposed to UV light will be removed. Negative resists behave in just the opposite manner. Exposure to UV light causes the negative resist to become polymerized and is more difficult to dissolve. Therefore, the negative resist remains on the surface and the developer solution removes only the unexposed portions. This non-photosensitive wafer fabrication approach has a significant level of process complexity, as well as limited resolution and poor sidewall profile quality resulting from the isotropic polyimide etches process (Omote, n.d.).

Therefore, a negative-type photosensitive polyimide (Omote, n.d.) has been widely used in the semiconductor industries because it simplifies complicated patterning process by direct exposure and development without the use of additional

resist (Nguyen et al., 2007). This decreases cost and cycle time by elimination of the entire photolithography level in the manufacturing cycle (Flack et al., 1996).

2.2.1 Photosensitive Polyimide

Photosensitive polyimide (PSPI) can be classified into polyimide precursors with photoactive groups (PSPI precursors) and the inherently photosensitive polyimide (preimidized PSPI) (Rich et al., 1996; Han et al., 1998). Polyamic ester (PAE) precursor is the first type of PSPI precursors developed (Rubner et al., 1979 cited in Rich et al., 1996). A PSPI precursor has inherently higher solubility in solvents. Therefore, they do not have limitation in the backbone chemistry. They can be further formulated with photosensitizers and photocrosslinkable monomer to enhance their photolithographic performance (Han et al., 1998). The PSPI precursors need high temperature to remove solvent and convert from a precursor to polyimide. In contrast, a preimidized PSPI is already in the converted state and they gel upon exposure to UV. Rich et al. (1996) mentioned that much work have published on the performance and physical properties of the preimidized PSPI. They showed how the material changed physically and chemically, by thermal and UV curing without involves ring closure of the imide ring.

Most of PSPI are found to have high shrinkage of more than 20%, swell in the developing solution, resulting in poor resolution characteristic. Berrada et al. (1996) developed a new soluble PSPI to overcome this. Besides, thermal curing will induced excessive of film shrinkage that distort the image patterned using the PSPI precursor (Higuchi et al., 1991). Omote et al. (1990) and Higuchi et al. (1991) have synthesized soluble polyimides that do not required thermal imidization and thus are expected to be storage-stable and non-shrinking. However, it is difficult to design a fully imidized photoreactive polyimides that have higher sensitivity due to the

rigidity and strong electron-acceptor property of the imide carbonyl. The rigidity prevents migration of free radical and significantly hinders the rate of polymerization (Omote et al., 1990). Ree et al. (1992 cited in Han et al., 1998) found that the photochemically generated crosslink would affect the mechanical properties.

On the other hand, many researchers had synthesized and characterized the PSPI precursor based on the poly amic ester (PAE). Kim et al. (1995) have synthesized a PAE precursor by poly(4,4'-oxydiphenylene biphenyltetracarboximide) (BPDA-ODA) & poly(p-phenylene biphenyltetracarboximide) (BPDA-PDA). They have investigated on their thermal imidization thermally and non-thermally by TGA. Huang et al. (1997) synthesis and characterization of a series of poly(amic methyl ester)s from five aromatic dianhydrides and a diamine, 4,4'-oxydianiline (ODA). Huang and Ding (1999) had synthesized the poly(amic methyl ester)s based on 3,3',4,4'-biphenyl dianhydride (BPDA) and 4,4'-oxydianiline (ODA) to study the imidization behavior of poly(amic ester) precursors, in particular, the difference of polymer chain architecture on the ring-closing reaction. Kotera et al. (2000) has analyzed in detailed about the imidization process of PAA and its effect to glass transition temperature by using temperature modulated DSC.

Other authors have studied on the photolithographic performance of PSPI (Han et al., 1998). Terrones and Pearlstein (2003) have investigated on the photopolymerizations to understand the relationship between the processing parameters for instance the photoinitiator concentration, incident light intensity, reaction time, layer thickness and the material properties. Lin et al. (1988) had studied on the cross-linking mechanism of benzophenone-containing polyimides. They described the hydrogen abstraction by triplet benzophenone and subsequent

coupling of the radicals so formed. Hou et al. (1999) investigated the influence of main chain structure and molecular weight on the photosensitivity.

2.3 Structure of Polyimide

The imide group is a ring structure containing nitrogen and two carbonyl groups. Rings having more than one type of atom, such as the imide ring, which contains both carbon and nitrogen atoms, are called heterocyclic. When linked with an aromatic molecule, the molecule can be called an aromatic heterocyclic (Strong, 2007).

The imide group can bond to other atomic groups in the main chain of polymer as backbone (Fahim et al., 2001) (Figure 2.3b). The aromatic-heterocyclic polymer chain is highly aromatic. It conjugates the electrons from the aromatic ring with the electrons in the oxygen-carbon bonds of the imide group. Imide has high thermal stability because it is very stiff and generally planar with few backbone bonds around which rotation can occur. In addition, it is composed of only strong bonds (Strong, 2007).

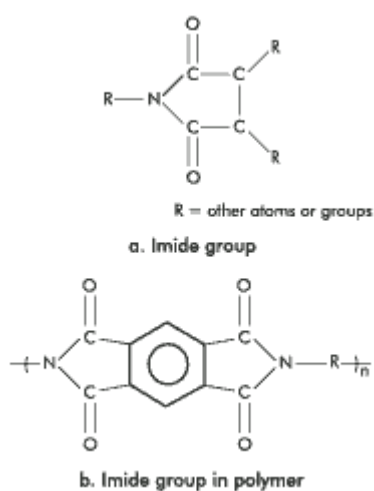


Figure 2.3 (a) Imide group (b) Polyimide. (Strong, 2007)

2.3.1 Formation of Polyimide

Being insoluble in most common solvents, photosensitive polyimides are usually processed in the form of their precursor polyamic acid. The traditional synthetic route for these materials is a two-step method, where the first step is the synthesis of the polyamic acid (PAA) and the latter step is the subsequent thermal or chemical imidization of PAA (Saeed & Zhan, 2006). The cycloimidization reaction is not limited to the acid precursor but also several derivatives of the PAA-polyamic alkyl ester (PAE) (Volksen, 1991 cited in Becker & Schmidt, 1992), for example, the polyamic ethyl ester, were developed (Cheng & Wunder, 1996).

2.3.1.1 Formation of Polyamic Acid (PAA)

The polyamic acid is rapidly formed when a dianhydride and a diamine are added into a dipolar aprotic solvent such as N, N-dimethylacetamide (DMA) or N-methylpyrrolidinone (NMP) at ambient temperature (Figure 2.4) (Fahim et al., 2001). This reaction is due to the nucleophilic attack of the amino group on the carbonyl carbon of the anhydride group, followed by the opening of the anhydride group to form an amic acid group, which is a carboxylic acid (Takekoshi, 1996).

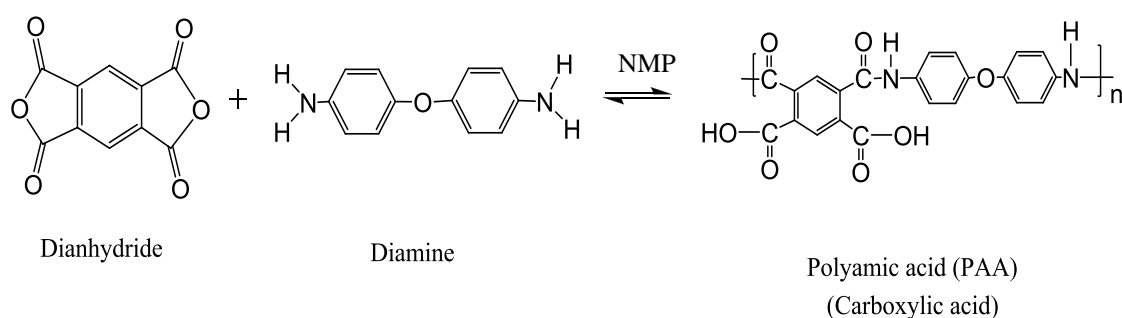


Figure 2.4 Mechanism of the formation of polyamic acid (PAA). (Takekoshi, 1996)

The formation of polyamic acid is an equilibrium reaction and it is reversible (Takekoshi, 1996). A high molecular weight polyamic acid hinders the reversible reaction, which decrease the rate of backward reaction. The high molecular weight

polyamic acid is formed when pure reagents are used and the difference between the reaction rates is large. In addition, the forward reaction is much faster by several orders of magnitude than the reverse reaction. Therefore, it is important to examine the driving force that favoring the forward reaction and shift the equilibrium to the right. Apart from that, the acylation reaction of amine is an exothermic reaction and the equilibrium is favored at lower temperatures (Takekoshi, 1996). The equilibrium is favored at high monomer concentrations to form higher molecular weight polyamic acid since the forward reaction is a second-order reaction while the back reaction is a first-order reaction (Takekoshi, 1996).

2.3.2 Reactivity of Monomers

The mechanism of the polyamic acid formation is the nucleophilic substitution reaction at one of the carbonyl carbon atom of the anhydride group with a diamine. Thus, it is expected that the reaction rate mainly depend upon the electrophilicity of the carbonyl groups of the dianhydride and the nucleophilicity of the amino nitrogen atom of the diamine (Takekoshi, 1996).

The electrophilicity of carbonyl carbon of dianhydride can be gauged using the term electron affinity (E_a), which is the tendency of the molecule to accept an electron. Polyimides based on pyromellitic dianhydride (PMDA) are among the polyimide that has the highest E_a value, which is 1.9 eV and is most reactive (Takekoshi, 1996). The existence of electron-donating group such as ether can decrease the reactivity of dianhydride. It is important to note that PMDA must be handled in strictly moisture-free conditions to prevent the decrease of reactivity. On the other hand, the reactivity of diamine depends on its basicity, pK_a (Rabilloud, 1999).

2.3.3 Polyamic Ester (PAE) Precursor

The polyamic ester (PAE) precursor (ester) is formed by the esterification of the polyamic acid (carboxylic acid) with methacrylate or acrylate that attached to a hydroxyl group (alcohol). Methacrylate or acrylate is the photosensitive group and is linked to the carboxyl group of the polyamic acid through an ester linkage to become a polyamic ester (PAE) precursor and this reaction is reversible as shown in Figure 2.5 (Macomber, 1996). In order to drive the reaction to the right, the water by-product should be removed or an excess of alcohol should be used (Macomber, 1996).

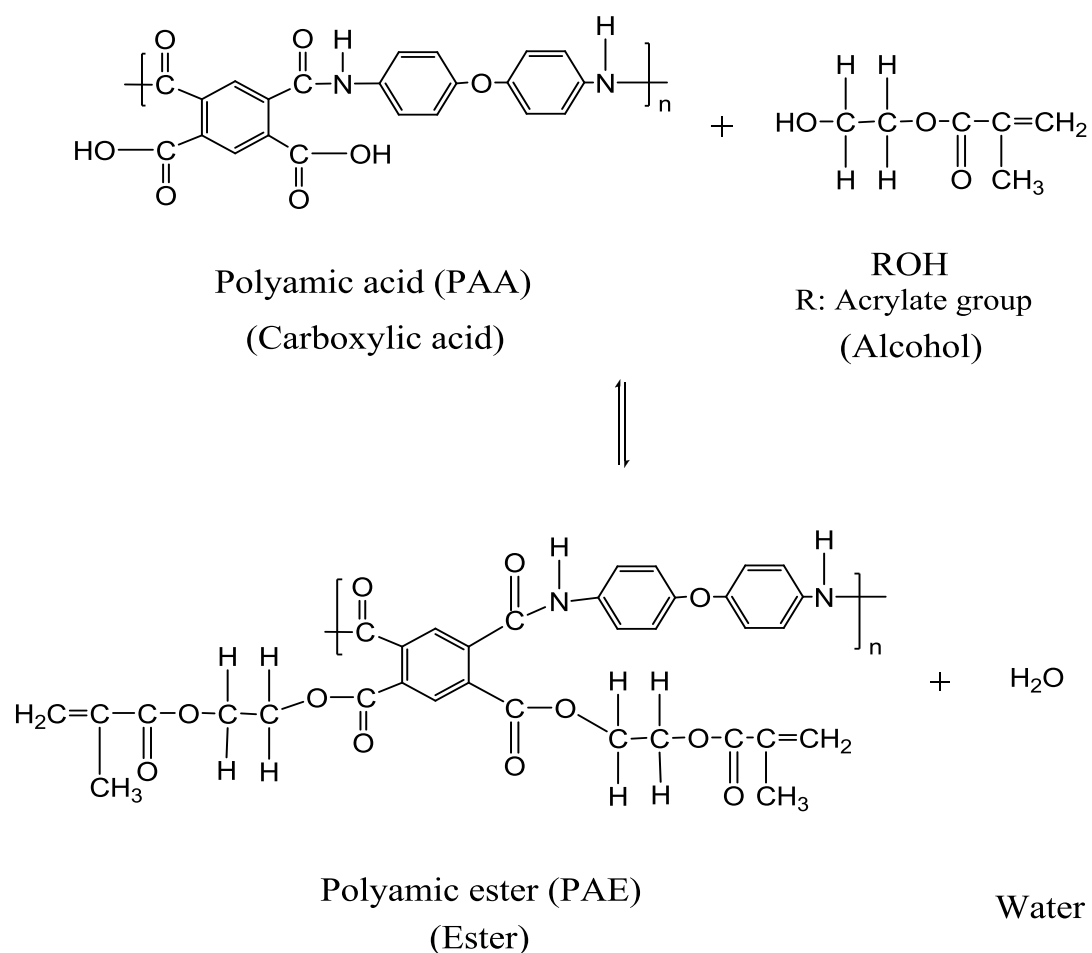


Figure 2.5 The formation of polyamic ester (PAE). (*Photosensitive polyimide precursors* (Fujifilm Electronic Materials Manufacturer (FFEM), n.d.); Macomber, 1996)