EFFECT OF PYROLYSIS ON SHRINKAGE PROPERTIES OF SU-8 POLYMER

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by

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LIST OF SYMBOLS AND ABBREVIATIONS

$(CH_3)_2CO$	Acetone
Ka	Acidityconstant
A°	Angstrom
Ar	Argon
AFM	Atomic force microscopy
C	Carbon
C-MEMS	Carbon-microelectromechanical systems
cm	Centimeter
CP	Centipoise
CSP	Chip scale package
Cr	Chromium
CTE	Coefficient of thermal expansion
Cu	Copper
Td	Decomposition temperature
°C	Degree Celsius
°K	Degree Kelvin
ρ	Density
DW	Distilled water
SU-8	Epoxy-based negative photoresist
FIB	Focused ion beam
GC	Gas Cromatography
GHz	Gigahertz
GPa	Giga Pascal
Tg	Glass-transition temperature

HAR	High aspect ratio
h	Hour
H	Hydrogen
IC	Integrated circuit
Fe	Iron
IPA	Isopropyl Alcohol
C_3H_8O	Isopropyl Alcohol
C_3H_7OH	Isopropyl Alcohol
Kg	Kilo Gram
KJ	Kilo Joule
$v\rho$	Kinematic viscosity
PH	Measure of the acidity of the solution
MHz	Megahertz
MPa	Mega Pascal
m^3	Meter cubic
m^2	Meter square
CH_4	Methane
MEMS	Micro electromechanical systems
μm	Micrometer
mm	Millimeter
MCM	Multichip Modules
nm	Nanometer
Ni	Nickel
HNO_3	Nitric acid
N	Nitrogen

O	Oxygen
PPM	Parts-per-million
PCM	Photochemical milling
PMA	Propylene glycol monomethyl ether acetate
PPF	Pyrolyzed photoresist film
RIE	Reactive ion etching
Ω	Resistance
Rpm	Rotation per minute
SEM	Scanning electron microscope
s	Second
Si	Silicon
SCCM	Standard Cubic Centimeters per Minute
THz	Terahertz
3D	Three dimensions
Ti	Titanium
TiO_2	Titanium Oxide
2D	Two dimensions
UV	UltraViolet
VUV	Vacuum UltraViolet
μ	Viscosity
V	Volume
W	Weight
XRD	X-ray Diffraction
XPS	X-ray - photoelectron spectroscopy
E	Young’s modulus

KESAN PIROLISIS TERHADAP SIFAT PENGECUTAN POLIMER SU-8

ABSTRAK

SU-8 telah menarik banyak perhatian pada dekad lalu kerana sifat-sifat mekanikal dan elektrikal yang memberangsangkan. Kajian menyeluruh mengenai sifat-sifat mekanikal fotorintang negatif SU-8 telah dijalankan sejak dekad yang lalu. Pelbagai usaha telah dijalankan di dalam membangunkan kaedah yang betul untuk menyifatkan ciri-ciri seperti kesan suhu pirolisis dan masa pirolisis terhadap sifat pengecutan dan morfologi SU-8. Dalam kajian ini, pola foto SU-8 telah direka di atas wafer silikon melalui proses putaran untuk kelajuan yang berbeza (langkah (1) 250 rpm dan masa 10 saat, (2) 450 rpm dan masa 30 saat (3) 0 rpm dan masa 5 saat), kemudian dipanaskan pada suhu 95 °C selama 4 minit dan dibiarkan menyejuk selama 10 minit. Pendedahan kepada ultraungu (UV) adalah perlu untuk mendapatkan bentuk topeng, meningkatkan kadar sambung silang di kawasan radiasi dan menstabilkan mereka terhadap tindakan pelarut semasa langkah pembangunan. Ketumpatan UV yang digunakan adalah 6 mW/cm^2 pada 365 nm dan masa pendedahan adalah 5min, manakala jumlah pembangun SU-8 40cm^3 selama 10min. Sampel telah dipotong menjadi dimensi 2cmx2cm. Pirolisis ini telah dijalankan dalam tiub relau kuarza tertutup dalam gas nitrogen lengai (N_2) mengalir pada 1500 piawaian sentimeter padu seminit (SCCM) dan parameter yang berbeza suhu (350 °C, 400 °C, 450 °C dan 500 °C) dan masa (10min dan 20 min). Pengelupasan SU-8 berlaku disebabkan oleh lekatan yang lemah daripada menentang kepada substrat, filem yang lebih tebal atau kadar pemanasan yang lebih cepat semasa pirolisis SU-8. Meningkatkan parameter pirolisis (suhu dan masa) menyebabkan pengecutan secara mendatar dan menegak yang lebih besar, lembaran rintangan yang lebih rendah dan kekasaran permukaan. Mikroskop Imbasan Elektron (SEM), Mikroskopi Daya Atom (AFM) dan profilometer telah digunakan bagi mengkaji pengecutan dan kekasaran SU-8, untuk mendapatkan pemahaman tentang bagaimana ia boleh memberi kesan kepada ciri-ciri pengecutan dan menentukan keadaan pirolisis yang optimum.

EFFECT OF PYROLYSIS ON SHRINKAGE PROPERTIES OF SU-8 POLYMER

ABSTRACT

Epoxy SU-8 has drawn a lot of attention during the last decades due to its promising mechanical and electrical properties. Extensive research regarding the mechanical properties of negative photoresists SU-8 has been carried out during the last decades. A lot of effort has been put into developing methods to properly characterize features such as effect of pyrolysis temperature and the pyrolysis time on shrinkage properties and morphology of SU-8. In this work photo patterned SU-8 were fabricated on silicon wafers by spin process for different speed steps (step (1) 250rpm and time 10sec, step (2) 450rpm and time 30sec, step (3) 0rpm and time 5sec), then Soft baked at 95°C for 4min before cooling for 10min. Exposure to ultraviolet (UV) light was necessary to obtain the shape of the mask, increase crosslinking degree in the irradiated areas and stabilizes them against the action of solvents during development step. The density of UV used was 6 mW/cm^2 at 365 nm and exposure time was 5min, while the volume of SU-8 developer was 40cm^3 at 10min. Samples were cut into 2cmx2cm dimensions. The pyrolysis was carried out in a closed quartz tube furnace in an inert nitrogen gas (N_2) flow at 1500 standard cubic centimeters per minute (SCCM) and different parameter of temperature (350^{o}C, 400^{o}C, 450^{o}C and 500^{o}C) and time (10min and 20min). Peeling of the SU-8 occurs due to a poor adhesion of the resist to the substrate, thicker films or faster heating rates during the pyrolysis of SU-8. Increasing pyrolysis parameters (temperature and time) lead to larger vertical and horizontal shrinkage, lower sheet resistivity and roughness. The scanning electron microscope (SEM), atomic force microscopy (AFM) and profilometer were used to examine the shrinkage and roughness of SU-8, in order to gain an understanding of how it can affect the shrinkage properties and determine the optimized pyrolysis conditions.

CHAPTER 1

INTRODUCTION

1.1 Background

Polymers are popular materials used for many industrial products due to light weight, ease in processing, low cost of raw materials and processes for producing polymers, high corrosion resistance, high electrical resistance, poor electric conductivity, high flexibility in structures, high dimensional stability and low melting point. Thermoplastics and thermosets are common industrial products, where thermosets have higher mechanical strength even at temperature of up to 350°C (Singh *et al.*, 2002). SU-8 is a kind of epoxy-based thermoset UV-curable negative photoresist. The first SU-8 products were introduced commercially by MicroChem in 1996. Cured SU-8 has excellent chemical and thermal stability because of the highly cross-linked matrix in the exposed material (Feng *et al.*, 2003). Several important properties of SU-8 make it suitable for many applications such as micro electromechanical systems (MEMS), sensor and lithium batteries.

First of all, the material has a low molecular weight enabling it to be dissolved in a variety of organic solvents to form highly concentrated solutions (72%–85% solids by weight). Secondly, the absorption for SU-8 in the UV spectrum is very low, thus allowing the patterning of thick coatings. It is well known that if the optical absorption of a photoresist is too high, even high doses of UV light will fail to penetrate a thick resist layer to generate clean, sharp images (Lee *et al.*, 1995). Since the resist has high functionality, a high degree of cross-linking can be obtained, permitting a high aspect ratio and straight sidewall to be achieved in lithographic applications. Also because of the high functionality, the resist has high chemical and thermal resistance as well as good mechanical properties. The reported glass-transition temperature (Tg) is over 200°C and the decomposition temperature (Td) is about 380°C for fully cured SU-8 (Zhang *et al.,* 2001). The excellent mechanical properties of this material make it capable of providing structure and support for microstructures. Finally, SU-8 is non-conductive and thus can be used as a dielectric in electroplating. SU-8 is not only used for masking and pattern transfer, but is also directly used as a polymeric material from which to fabricate micro-mechanical components (Bertsch *et al.,* 1998). However, the properties of SU-8 are very sensitive to the processing conditions. A wide variation in values for the processing parameters has been reported (Despont *et al* 1997 & Feng *et al.,* 2003).

Photo-litho-graphy in Latin meaning light-stone-writing is an optical technique for transferring patterns from a glass photo mask onto a semiconductor substrate. Types of lithography: (a) Photolithography (or optical lithography) uses UV radiation; (b) X-ray lithography uses X-ray; (c) Electron-beam lithography uses electron beam; (d) ion beam lithography uses ion beam. Performance of a photolithographic process is determined by its resolution, the minimum feature size that can be transferred with high fidelity; the registration, how accurately patterns on successive masks can be aligned; and throughput, the number of wafers that can be transferred per hour (a measure of the efficiency of the lithographic process) (Feng *et al.,* 2003). Upon pyrolysis under a reducing (i.e., oxygen-free) environment, the photoresist becomes a hard carbon due to its highly cross-linked molecular structure. Elemental analysis of pyrolyzed photoresists shows that the oxygen to carbon ratio is 0.06 for carbon films pyrolyzed between 800°C to 1100°C (Kostecki *et al.,* 2001). Furthermore, the crystalline structure of the material resulting from this process is comparable to commercial glassy carbon (Ranganathan *et al.,* 2000). Hard carbons usually deliver capacities beyond that of the typical of graphitic carbons (Liu *et al.,* 1996). In this sense, hard carbons can be a powerful candidate for a lithium-ion battery anode material. The drawbacks are a higher irreversible capacity and occasionally a higher de-intercalation voltage. Specific conductivities and shrinkage rates of SU-8 derived carbons as well as their use in lithium batteries have been already reported (Park *et al*., 2005 & Genis *et al.,* 2008).

1.2 Problem statement

Current trend in tactile sensing has shown inclination towards using microelectromechanical system (MEMS) technology to improve signal resolution, ease of signal extraction, as well as packaging. The MEMS structures are typically prepared from silicon and few uses metals and polymer. The problem with silicon is the ability to withstand impact due to its brittleness. Alternative to silicon in MEMS is glassy carbon which can be produced from the pyrolysis of photoresists film, and this technique is commonly used in electrochemical applications. The beauty of using photoresist film is its potential to be patterned to any shape at desired thickness and size can vary due to substantial shrinkage during pyrolysis for small structures. The shrinkage of polymer to glassy carbon turns micro size structures into nano size, and this can be manipulated to produce an array of tactile sensors with spatial resolution comparable to the human mechanoreceptors.

1.3 Objectives

The main objective of this study is to fabricate MEMS by coating SU-8 over the silicon wafer. In order to complete this study, various approaches in fabricating and characterizing the MEMS were implemented to find the most suitable parameters to fabricate the MEMS. The other objectives of this study are:

I. Design of the mask to predict the magnitude of shrinkage based on the sensor application.

II. To study the effect of pyrolysis temperature and time on the shrinkage properties of SU-8 photoresist.

III. To observe the morphology of yield carbon of SU-8 photoresist after pyrolysis.

1.4 Scope of study

Research on tactile sensing is still an ongoing process with potential wide application in engineering. It is hoped that future sensor will be able to attain a tactile performance comparable to that human skin. The scope of study for this project is to obtain low percentage of shrinkage under different parameter of temperature and time. SU-8 polymer will be patterned by lithography process and then undergo pyrolysis process. After pyrolysis the carbon obtained will be measured to determine its shrinkage, the carbon films were extensively characterized. Carbon film properties like the structure, shrinkage and morphology of the film were tested by using scanning electron microscope (SEM), atomic force microscopy (AFM) and profilometer. Low shrinkage during polymerization is necessary for dimensional accuracy and to avoid film stress.

CHAPTER 2

LITERATURE REVIEW

2.1 SU-8 polymer

The first SU-8 products were introduced commercially by MicroChem Corporation in 1996. The resist is available in a wide range of formulations to cover a film thickness range from 2 to 300μm in a single coating process or to 3mm by multi coating processes (Lorenz *et al.,* 1998). The SU-8 series is formulated with gamma-butyrolacton as a solvent. Figure 2.1 shows the general chemical structure of SU-8, there are eight epoxy groups in each molecule on average, so it is named SU-8, and the functionality of the molecules is eight. SU-8 films with thickness below 2μm can be obtained by diluting the resist solution with the solvent. More recently, a new generation of SU-8 resist, the SU-8 2000.

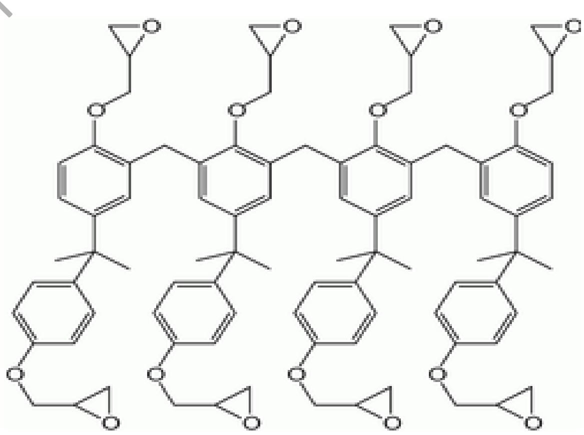

Figure 2.1: SU-8 molecule (Baughman *et al.,* 2002)

SU-8 2000 is a high contrast, epoxy based photoresist designed for micromachining and other microelectronic application, where a thick, chemically and thermally stable image is desired. SU-8 2000 is an improved formulation of SU-8, which has been widely used. The use of a faster drying, more polar solvent system results in improved coating quality ad increase process throughput. SU-8 2000 is available in twelve standard viscosity. Film thickness of 0.5 to > 200µm can be achieved with a single coat process. The exposed and subsequently thermally cross linked portions of the film are rendered insoluble to liquid developer. SU-8 2000 has excellent imaging characteristics and is capable of producing very high aspect ratio. SU-8 2000 has very high optical transmission above 360nm, which makes it ideally suited for permanent applications where it is imaged, cured and left on the device (Wang *et al.*, 2004). This series is formulated with cyclopentanone as solvent and has improved coating and adhesion properties and faster processing times. This is particularly important in thick coatings, where one photolithographic cycle may take more than 2 h. Table 2.1 shows the typical values of the processing parameters for the commercially available variants.

SU-8 type	**Viscosity (cp)**	**Thickness (µm)**	**Development (min)**
SU-82	45	1.5-5	1
SU-85	290	5-15	1-3
SU-810	1050	10-30	2-5
SU-825	2500	15-40	3-6
SU-850	1250	40-100	6-10
SU-8100	51500	100-250	10-20
SU-82002	7.5	2-5	1
SU-82005	45	6-7	1
SU-82007	140	8.5-10	2-3
SU-82010	380	13-15	2-3

SU-82015	1250	21-25	3-4
SU-82025	4500	41-75	5-7
SU-82035	7000	35-110	5-10
SU-82050	14000	50-165	6-12
SU-82075	22000	110-225	7-12
SU-82100	45000	100-260	10-20

Table 2.1: SU-8 characteristic processing times (in minutes) for different variants and film thicknesses (Lorenz *et al.*, 1998)

SU-8 is a negative tone, chemically amplified resist. It contains acid–labile groups and a photo acid generator. Irradiation generates a low concentration of a strong acid which will act as a catalyst of the cross-linking process. Subsequent heating of the polymer activates cross-linking and regenerates the acid catalyst. As a consequence, the sensitivity of the resists is significantly increased. These protonated oxonium ions are available to react with neutral epoxides in a series of cross-linking reactions after application of heat (Kostecki *et al.*, 2001). Each monomer molecule contains eight reactive epoxy sites and therefore high degree of cross-linking can be obtained after photo thermal activation giving a negative tone. This results in high mechanical and thermal stability of the lithographic structures after processing.

In fact, fully cross-linked SU-8 has a glass-transition temperature around 200°C, degradation temperature around 380°C and a Young's modulus (E) range of 4–5 GPA. SU-8 is a very viscous polymer that can be spun or spread over a thickness ranging from <1µm up to >300µm and still be processed with standard contact lithography. It can be used to pattern high aspect ratio (>20) structures. Its maximum absorption is for ultraviolet light with a wavelength of 365nm. When exposed, SU-8's long molecular chains cross link causing the solidification of the material (Hebert *et al.*, 2003). SU-8 was originally developed as a photoresist for the microelectronics industry, to provide a high-resolution mask for fabrication of semiconductor devices. It is now mainly used in the fabrication of microfluidics (mainly via soft lithography, but also with other imprinting techniques such as nano imprint lithography) and micro electromechanical systems parts. It is also one of the most biocompatible materials known which is often used in bio-MEMS (Lorenz *et al.*, 1998). The physical and electrical and mechanical properties of SU-8 are listed in Table 2.2, 2.3 and 2.4.

Table 2.2: Electrical properties of SU-8 photoresist (Liu *et al.*, 2004)

Property	**Value**
Dielectric Constant, 1 GHz,	4.1
Dielectric loss, 1 GHz	0.015
Dielectric Strength (V/µm)	112
Volume Resistivity (Ω.cm)	2.8×10^{16}
Surface Resistivity (Ω.cm)	1.8×10^{17}

Table 2.3: Mechanical properties of SU-8 photoresist (Liu *et al.*, 2004)

Property	**Value**
Young's modulus	4400MPa
Poisson's ratio	0.22
Viscosity	15.0 Pa-s (70% SU-8 – 30% solvent)
Coefficient of thermal expansion	0.183 ppm /°C
Thermal conductivity	0.073 W/cm-°C
Glass transition temperature	200°C
Reflective index	1.8 at 100 GHz
Absorption coefficient	40/cm at 1.6 THz

Table 2.4: Physical properties of SU-8 photoresist (Liu *et al.*, 2004)

Characteristics	**Value**
Glass temperature(Tg)	50°C - 200°C
Degradation temperature(Td)	308°C
Coefficient of thermal expansion (CTE)	102/-5.1 ppm/K
Thermal conductivity	0.2 W/mK

Specific heat	1.5 KJ/KgK
Polymer shrinkage	7.5%
Density(ρ)	$1.2 Kg/m^3$
Viscosity (Dynamic or Absolute) μ	1.5Pa.s
Kinematic viscosity νρ	$0.001050\ m^2/s$

SU-8 is highly transparent in the ultraviolet region, allowing fabrication of relatively thick (hundreds of micrometers) structures with nearly vertical side walls. Table 2.5 shows different application of SU-8. After exposition and developing, its highly cross-linked structure gives it high stability to chemicals and radiation damage. Cured cross-linked SU-8 shows very low levels of outgassing in a vacuum. However it is very difficult to remove, and tends to outgas in an unexposed state. The main developer for SU-8 is methoxyl propanol acetate (Liu *et al.,* 2004).

Table 2.5: Possible application of SU-8 photoresist polymer (Liu *et al.,* 2004)

Microelectronics	Coils
	Capacitors
	Dielectric material
Micromechanics	Sensors
	Fast Prototyping
Microfluidics	Biochips & micro; TAS Micro pumps
Packaging	MCM 2D
	MCM 3D
	CSP
	Microconnectics
Magnetics	Magnets (by adding Ferro magnetics materials into the SU-8 Micro relays)
Others	Flat Panel Displays
	Microoptics
	Microwaves

2.2 Lithography

Within the space of 40 years, two developments in photography laid the foundations for the photoresists we use today. In (1742–1808) Geneva investigated the property of certain resins that become insoluble in turpentine after exposure to sunlight. Inspired by Senebier after experimenting with various resins in sunlight, managed to copy an etched print on oiled paper by placing it over a glass plate coated with bitumen (asphalt) dissolved in lavender oil (France, 1822 & Gates *et al.*, 2004). In 1827 using strong acid, the Lemaitre made an etched copy of an engraving of Amboise from a plate developed by Niepce. The latter copy represents the earliest example of pattern transfer by photolithography and chemical milling such as photochemical milling (PCM). The accuracy of the technique was 0.5–1mm. Lithography consists of the transfer of a pattern onto a substrate by means of an etching process. Resist lithography makes use of an irradiation source and a photosensitive polymer material to perform the pattern transfer (Hui *et al.,* 2004). Selective irradiation initiates a series of photochemical processes in the resist which alter the physical and chemical properties of the exposed areas such that they can be differentiated in a subsequent image development step (Gates *et al.,* 2005). Most commonly, the solubility of the film is modified by either increasing the solubility of exposed areas (yielding a positive image after develop) or decreasing the solubility to yield a negative-tone image.

Development of the imaged substrate reveals a pattern on the resist layer which corresponds to the geometry of the mask, pushed by the electronic industry; most developments in lithography have mainly been directed at shrinking the lateral dimensions of the imaged features (Wallraff *et al.,* 1999 & Singh *et al.,* 2002). The application of different resolution enhancement approaches (illumination sources with shorter irradiation wavelength, projection and immersion optics, phase-shifting masks,