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Photoresist: Fabrication, Characterization and Its Sensitivity on the Exposures of X-Ray and Ultraviolet

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Abstract. The epoxy resin-based photoresist is fabricated by mixing of resin (polymer), sodium acetate trihydrate and ethanol in mass variation using heated magnetic stirrer at 100 rpm speed and temperature of 75 °C. Sodium acetate trihydrate and ethanol each play role as photoactive compound (PAC) and solvent, respectively. Photoresist thin films were grown through spin coating method in voltage 5 V during the 60 s and heating temperature of 150 °C for 15 min. To determine photoresist sensitivity, ultraviolet and X-ray were exposed on the photoresist surfaces. The fabricated photoresist properties are densities of 1 g·mL^{-1} to 1.23 g·mL^{-1}, dynamic viscosities of 7 Cp to 22 Cp and kinematic viscosities of 7 Cst to 18 Cst. The absorbances of thin films are in the wavelength range of 350 nm to 1050 nm at the maximum absorbances of 0.2 to 0.5 in the wavelength g-line, h-line, and i-line. The generated maximum current achieved (1.84×10^{-8}) A. The microstructures of epoxy-based photoresist seem homogeneous. The sensitivities of UV exposures show a photochemistry reaction on photoresist occurred, however for X-ray exposure no reaction found.

Keywords. Epoxy, photoresist, and photosensitivity.

1. Introduction

Very fast microelectronic industry development requires sustainable raw materials supply [1]. One of the raw materials in microelectronic industries is resisted material, a material which is composed of four ingredients namely resin (polymer), photoactive compound (PAC), solvent and additive [2]. The photoresist is a complex polymer and additive with a low molecular weight which plays a role as photosensitive material and it is used in manufacturing printed circuit board [3].

The photoresist is classified into two kinds namely negative and positive photoresist. For positive one, the radiation-exposed area is soluble in photoresist developer; otherwise for a negative one, the exposed area remains to stay on the photoresist surface [4]. In the manufacturing process of a semiconductor, the radiation sources which are often used in a lithography process are ultraviolet (UV) and X-ray [5].

The epoxy-based resin is selected as an alternative due they are available on the broad market either in the liquid or solid. They have good adhesion on the semiconductor surface, high sensitivity and cheap [3]. Epoxy resin is copolymer thermosetting plastic which is often used in the composite polymer matrix. The epoxy resin is produced by chemical reaction process between epichlorohydrin and bisphenol-A compound [6]. The epoxy-based resin is used to make patterns by applying UV

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lithography technique, a method to transfer patterns of the master onto the substrate. As an example of epoxy-based photoresists is negative photoresist SU-8. Epoxy resins have advantages of good mechanical properties, good chemical resistance, and good electrical isolation as well as low cost [7]. The photoresist SU-8 is used in MEMS applications. All related parameters to produce a good photoresist image need to be optimized [8]. The uses of photoresist in the microelectronics industry are very broad so that the crucial aspects need to be investigated and developed to get good properties and performances such as sensitivity, resolution and contrast parameter. They both determine significantly the fabricated device density in the integrated circuit (IC) system. The contrast level of UV-lithography technique-developed image is affected by wavelengths of radiation sources. The higher the sensitivity of the material than the lithography process better because it easily absorbs radiation energy to perform photochemical reactions in forming patterns with high contrast levels. This research focuses on the manufacturing of epoxy resin-based photoresist, characterizing and testing photoresist sensitivity to UV and X-ray exposures.

2. Materials and methods

The used equipment in this research includes digital balance, heated magnetic stirrer, thermometer, beaker glass, measuring glass, screen filter, substrate glass, spin coater, oven, viscometer Ostwald, spectrometer ocean optic Vis-NIR USB 4000, I-Vmeter elkahfi 100 [9], microscope MS-804. The printed circuit board (PCB), aluminum foil, UV light, and X-ray machine. The used materials consist of photoresist (Aldrich), developer, de-ionized water, epoxy (polymer matrix), sodium acetate trihydrate (photoactive compound, PAC), and ethanol (solvent).

The samples are prepared of five composition variations of epoxy resin, and on the other hand, sodium acetate trihydrate was fixed as shown Table 1. The ethanol mass for each solution is selected as the independent variable and made to investigate their effects on the characterized material properties.

Table 1. Composition of Photoresist

Sample	Epoxy Resin (g)	Ethanol 96% (g)	Sodium Acetate Trihydrate (g)
A	20	12	4
B	20	14	4
C	20	16	4
D	20	18	4
E	20	20	4

The photoresist was fabricated using epoxy resin as a polymer matrix, sodium acetate trihydrate as PAC and ethanol as solvent. The mixing was done using magnetic stirrer accompanied heating process up to 75 °C. The photoresist was spin-coated on the substrate at 150 °C during 15 min.

The manufactured photoresist liquids were measured to determine their densities and viscosities. The photoresist films on glass substrates were characterized to determine absorbances, generated currents and voltages, and thin film surface structures. The thin films which were tested their sensitivities and contrast spin-coated on the PCB were exposed by UV and X-ray radiation.

3. Results and discussion

Densities of photoresist solutions are plotted in Figure 1, as the ethanol mass increases the density increases as well. In this research, the ethanol amount was optimized to obey the best performance of manufactured photoresist and applicable for lithography.

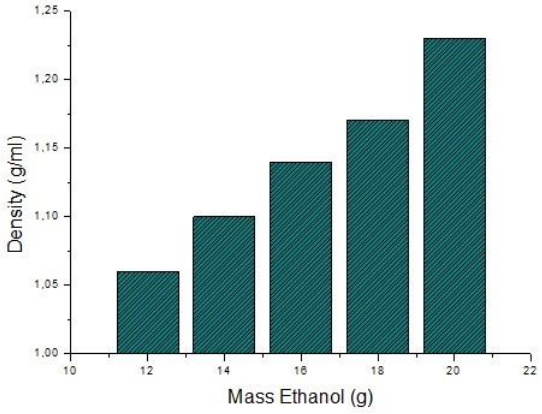

Figure 1. Graph of Densities of photoresist at different pH

Viscosities of photoresist solutions were measured using Ostwald viscometer. First, they were sucked using capillary pipe **B** (lower level) up to **A** (upper level). Then they were allowed to flow freely from line **A** down to line **B** using a stopwatch, and noted times were used to determine viscosities based on the following Equation 1.

$$\frac{\eta^\circ}{\eta} = \frac{\rho^\circ \cdot t^\circ}{\rho \cdot t} \tag{1}$$

η° = Standard liquid viscosity/Water viscosity (Poise)
η = Sample viscosity (Poise)
ρ° = Standard liquid density/ Water density $\left(g \cdot mL^{-1}\right)$
ρ = Sample density $\left(g \cdot mL^{-1}\right)$
t° = Average time for standard liquid movement / water movement (s)
t = Average time for sample movement (s)

Table 2. Dynamic viscosities of photoresist solutions

Sample	Dynamic Viscosity (Cp)
A	22.21
B	16.75
C	15.05
D	10.57
E	7.42

Based on Table 2, dynamic viscosity sample **A** is highest of all. Kinematic viscosity is determinable using ratio viscosity and density [10]. On Table 3, kinematic viscosity sample **A** is highest of them, and sample **E** viscosity equals to 18.05 Cst. To achieve deeper submicron device geometries, lithography plays an important role in the semiconductor manufacturing. It needs tighter resist thickness uniformity to control linewidth. The low viscosity photoresists for less than 7000 Å film thickness is available to produce the higher degree of substrate planarization and need for an improved lithographic solution. Khrisna et al. (1998) have used low viscosity photoresist (10 Cp) for lithography process [11].

Table 3. Kinematic viscosities of photoresist.

Sample	Kinematic Viscosity (Cst)
A	18.05
B	14.32
C	13.20
D	9.61
E	7

The kinematic viscosity of photoresist is affected by its ingredients, as the epoxy resin increases the viscosity increases as well. The epoxy resin increases mean the solution becomes smaller, and the otherwise conditions will occur. The photoresist strength depends on the viscosity.

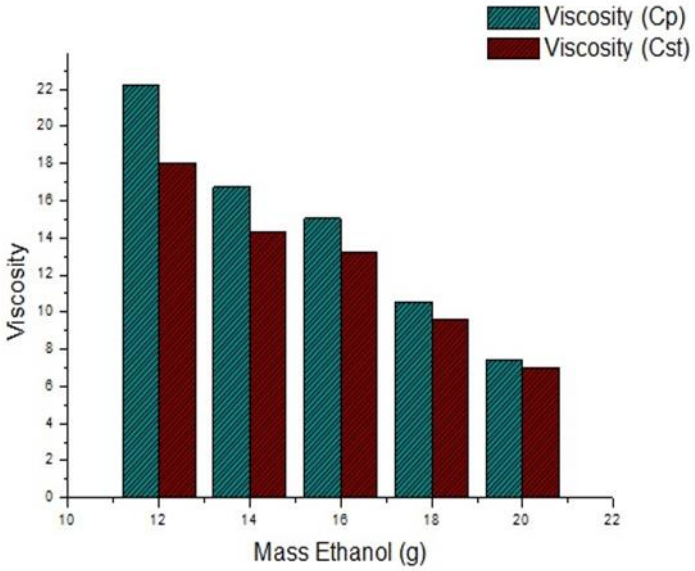

Figure 2. Dynamic and kinematic viscosities at the different mass of photoresist

In Figure 2, the higher concentration of photoresist solution the higher density. The absorbances were measured using spectrometer ocean optic Vis-NIR USB4000 and calculated based on the Equation 2.

$$\mathrm{OD} = \log\left(\frac{1}{\mathrm{T}}\right) = -\log\left(\mathrm{T}\right) = \mathrm{A} \tag{2}$$

where OD (Optical Density), A (Absorbance) and T (Transmittance). The absorbances of photoresist thin films with a different wavelength of incident light are shown in Figure 3.

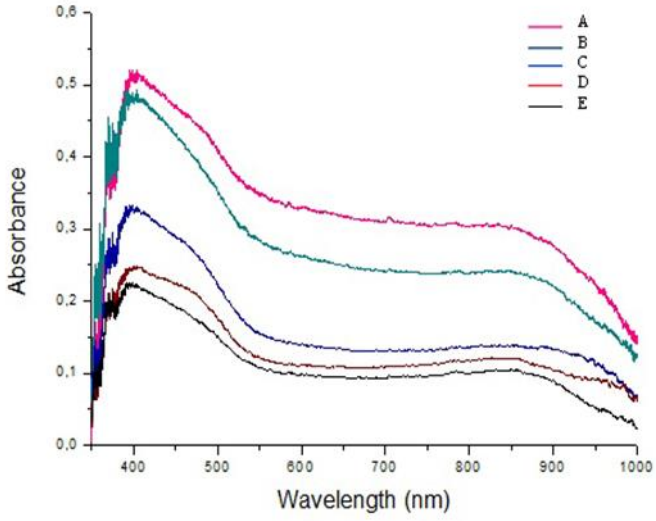

Figure 3. Graph of absorbances of photoresist thin films with a different wavelength of incident light

Based on Figure 3, absorbances of photoresist thin films are in the range of wavelengths 350 nm to 1050 nm, and the highest absorbance is in the wavelength range of 350 nm to 450 nm. Sample **A** was photoresist thin film which was heated at 75 °C and performed the highest absorbance, the maximum absorbance of light existed at 404.62 nm equals to 0.51 and sample **E** existed at 391.15 nm, it performed the lowest absorbance (0.22). The higher absorbance of photoresist thin film the higher photoresist sensitivity [12]. In the lithography, lights with wavelengths of 365 nm, 405 nm, and 436 nm were used to determine absorbances at i-line, h-line, and g-line, respectively [13] as shown Table 4.

Table 4. Absorbances for each i-line, h-line, and g-line epoxy resin-based photoresist.

Sample	i-line (365 nm)	h-line (405 nm)	g-line (465 nm)
A	0.15	0.21	0.18
B	0.14	0.24	0.21
C	0.21	0.32	0.27
D	0.32	0.47	0.41
E	0.30	0.51	0.45

The generated current of light exposed photoresist thin films are shown graphically in Figure 4. The highest one, (1.84×10^{-8}) A, is generated by sample **A**, and the lowest one, (5.71×10^{-10}) A. For the different composition of photoresist, the generated current is also different.

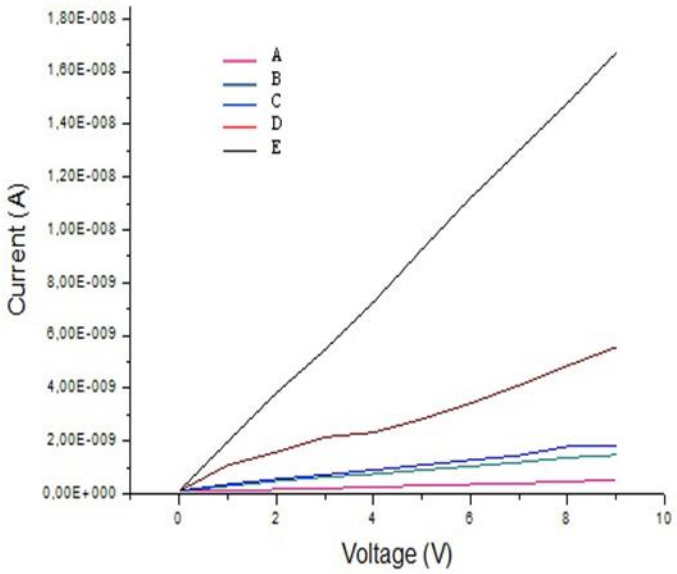

Figure 4. Graph of generated currents of photoresist thin films corresponds to source voltages

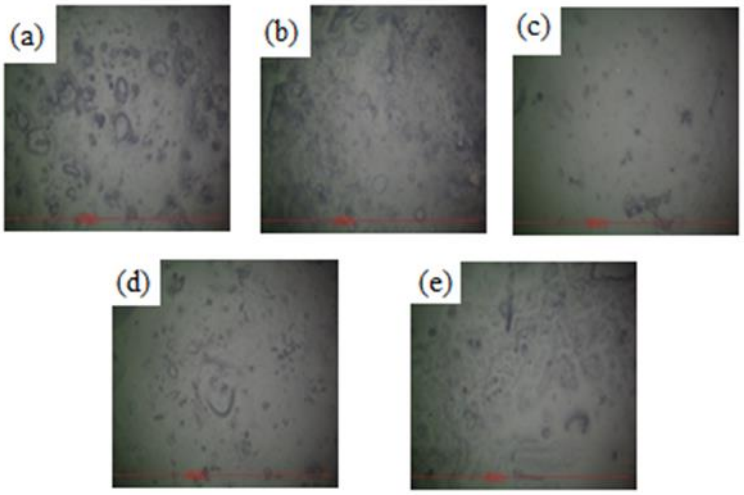

Figure 5. Structures of photoresist thin films.

Structures of photoresist thin films for all samples are shown in Figure 5. The photoresist thin films seem homogeneous. The solvent fraction increase in the solution leads to photoresist thin film coagulates on the substrate surface. Inversely, the solvent fraction decrease in the solution produces photoresist thin film more homogeneous, here sample **A** is the most homogeneous. The covered area is un-exposed, while the uncovered one is exposed, and after development, they show different results, as shown in Figure 6.

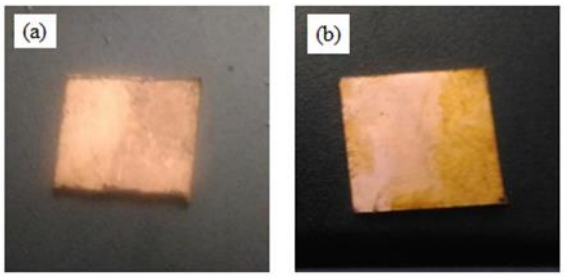

Figure 6. Photoresist spin-coated on the PCB: (a) Epoxy resin-based photoresist (Experiment result); and (b) Commercial photoresist (Sigma Aldrich).

The patterns can be developed on the epoxy resin-based photoresist and photoresist (Sigma Aldrich), although which were developed on the epoxy resin-based photoresist are less contrast. This contrast level difference is affected by solution and developer.

4. Conclusions

Epoxy resin-based photoresist (densities of 1 g·mL^{-1} to 1.23 g·mL^{-1}) is fabricated by mixing epoxy resin, ethanol, and sodium acetate trihydrate. The dynamic and kinematic viscosity of manufactured photoresist equal to 7 Cp to 22 Cp and 7 Cst to 18 Cst, respectively. The absorbances of epoxy resin-based photoresist exits in the range of 350 nm to 1050 nm with their absorbances of 0.2 to 0.5, respectively and the generated currents are as much as (5.71×10^{-10}) A to (1.84×10^{-8}) A. Their surface structures seem homogeneous and voids found of ethanol residual. The developable patterns were found on both photoresists exposed using UV. The different sensitivities depend on PAC and developer. The X-ray developed photoresist unable produce patterns.

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