Synthesis of organic photoresist of *Hibiscus tiliaceus* L. flowers for patterning with X-Ray and UV exposure

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Abstract. Photoresist is an essential chemical used in patterning the microelectronic devices. To ensure the sustainability of the supply of raw materials of microelectronics industry such as photoresists need to look for alternative materials that are more eco-friendly. This study used natural ingredients of *Hibiscus tiliaceus* L. flowers extract. The manufacture of photoresists carried in four stages, the manufacture of *Hibiscus tiliaceus* L. flowers extract, the manufacture of thin film *Hibiscus tiliaceus* L. flowers extract, the manufacture of resist and the manufacture of thin film photoresist. The manufacture of *Hibiscus tiliaceus* L. flowers extract is done with mass fraction variations using distillation methods. The optical properties of *Hibiscus tiliaceus* L. flowers extract was characterized using ocean optic Vis-NIR USB 4000. The functional group was characterized using the Perkin Elmer Frontier FT-IR, while the surface structure was characterized using the Digital CCD Microscope MS-804 Scopeman and the electrical properties were characterized using the Elkahfi 100 I-V Meter. The density of the resist is characterized by the mass per volume method. Thin film of photoresist is grown through the spin coating method with a voltage of 10 V for 60 s and heating to a temperature of 200°C for characterization of surface structures and optical properties. Photoresist is tested for sensitivity by giving exposure to UV and X-ray radiation sources to photoresist material. The resulting photoresist has a value of absorbance that is located in the wavelength range of 350 to 1050 nm with a maximum absorbance value of 0.07 to 0.3 at the wavelength of the g-line, h-line and i-line.

1. Introduction

The development of the microelectronics industry in the world is rapidly increasing the need to ensure the sustainability of the supply of raw materials [1]. To ensure the sustainability of the supply of raw materials of the microelectronics industry such as photoresists need to look for alternative materials that are more environmentally friendly. Photoresist plays a crucial role in ‘micro-miniaturization’ of semiconductor circuits [2], semiconductor processing, liquid crystal display (LCD) processing [3]. They are widely used for the manufacture of printed circuit boards, silk screen printings, optical disks [4], color filter resists [5], fabrication of integrated circuit (IC) [6] and so on. In semiconductor device manufacturing, the light source for lithography are ultraviolet (UV) and X-rays [7].

Indonesia is one of the megadiversity countries in the world with rich and unique biodiversity [8]. Plants are one of the diversities that has many contents of beneficial substances such as pigments. Based on the constituent material the pigment is divided into two, namely organic pigment (dyes) and inorganic pigment. *Hibiscus tiliaceus* L. flowers is an organic pigment producer of anthocyanin...
pigment. These compounds are included in phenolic compounds which are collectively called flavonoids. Cyanidin-3-gluco side is the main anthocyanin found in Hibiscus tiliaceus L. flower [9].

In the future, negative photoresists are developed through new materials and processes with combining different materials, such as organic and inorganic compounds, to obtain improved performance is an important trend for developing new materials [10]. Negative photoresist consists of a binder, photosensitive polyfunctional monomer, photoinitiator, solvents and pigments [5]. SU-8 is a type of epoxy-based negative photoresist. While in general, photoresist consists of four components are resin (polymer), a photoacid generator (PAG), solvents and additives [11]. Polyomers function to assist the formation of film and improve the mechanical properties of the resist. Photoactive compound (PAC) or (PAG) is a photoactive material in the photoresist that produces acids when exposed to radiation exposure. As the name implies, the photoacid generator (PAG) forms a strong acid when exposed to Deep-UV light. Irradiation causes decomposition of a photoacid generator (PAG) to generate strong acid in the irradiated areas [12]. The solvent used for the manufacturing of photoresist materials is ethanol (C₂H₅OH) [13] [1], toluene (C₆H₅CH₃) and so on.

The contrast level of the image developed by UV-lithography technique is influenced by the wavelength of radiation sources. The higher the sensitivity of the material than the lithography process is better because it is easy to absorb radiation energy to carry out photochemical reactions in forming patterns with high contrast levels. The study focuses on the creation of organic photoresist from Hibiscus tiliaceus L. flowers, characterization and testing photoresist sensitivity to UV and X-ray exposure.

2. Methods

The tools used in this study include digital precision balance, spatulas, pipettes, graduated cylinder, beaker, distillation tools, filter tools, filter paper, heated magnetic stirrers, thermometers, substrate glass, ultrasonic cleaner Branson model 1510, spin coater, oven, ocean optic Vis-NIR USB 4000 [14], scopeman digital CCD Microscope MS-804, Perkin Elmer FT-IR Spectrometer Frontier, I-V Meter Elkahfi 100 [15], printed circuit board (PCB), aluminum offset, UV light, and X-ray machine. The used materials consist of Hibiscus tiliaceus L. flowers, distilled water, acetic acid (CH₃COOH), ethanol (C₂H₅OH) 96% (solvent), epoxy resin (polymer), sodium acetate 3-hydrate and Hibiscus tiliaceus L. flowers extract (PAC), acetone, DI water, nitrogen, negative photoresist (Sigma-Aldrich) and developer solutions.

Hibiscus tiliaceus L. flowers will be extracted by the distillation method. This method is also used to musa acumina bracts extract [16]. Hibiscus tiliaceus L. flowers that have been cut are mixed with a solvent composition of 20 grams of distilled water and 100 grams of ethanol, and 4 grams of acetic acid. In this study, Hibiscus tiliaceus L. flowers extract samples were divided into 5 types of samples with different fraction values as shown in Table 1. The fraction value of 0,025; 0,05; 0,075; 0,100; 0,125. With a variety of Hibiscus tiliaceus L. flowers mass in a row of 3,18 grams; 6,53gram; 10,05 grams; 13,78 grams; 17,71 grams.

| Fraction | Hibiscus tiliaceus L. flowers (g) | Solvent (g) |
|----------|----------------------------------|-------------|
| 0,025    | 3,18                             | 124         |
| 0,050    | 6,53                             | 124         |
| 0,075    | 10,05                            | 124         |
| 0,100    | 13,78                            | 124         |
| 0,125    | 17,71                            | 124         |

Each fraction of Hibiscus tiliaceus L. flowers extract that has been dropped on a substrate glass which has been washed with acetone, ethanol 96%, DI water respectively and dried with nitrogen. The substrate was dropped of Hibiscus tiliaceus L. flowers extract and then rotated using a spin coater for
1 minute. The substrate is dried and heated for 10 minutes. The resulting thin film was then characterized by electrical properties, absorbance values, and the surface structure of the films of each fraction extract.

After the extraction process is complete, then the process of photoresist synthesis from *Hibiscus tiliaceus* L. flowers. The samples are prepared of six variations of hibiscus extract as photoactive compounds (PAC) which as shown in Table 2. PAC can affect the absorbance and sensitivity of photoresist thin films to radiation.

| Epoxy Resin (g) | Ethanol 96% (g) | Sodium Acetate 3-hydrate (g) | *Hibiscus tiliaceus* L. flowers extract (g) | Percentage (%) |
|----------------|----------------|-----------------------------|-----------------------------------------|----------------|
| 20             | 10             | 4,73                        | 1,05                                    | 3              |
| 20             | 10             | 4                           | 1,78                                    | 5              |
| 20             | 10             | 3,23                        | 2,55                                    | 7              |
| 20             | 10             | 2,42                        | 3,36                                    | 9              |
| 20             | 10             | 1,58                        | 4,20                                    | 11             |
| 20             | 10             | 0,70                        | 5,08                                    | 13             |

Sodium acetate 3-hydrate mixed with *Hibiscus tiliaceus* L. flowers extract, epoxy resin and ethanol. The materials are mixed accompanied by stirring the material using a heated magnetic stirrer to temperature of 75 °C. After the temperature reaches 75 °C the heating is stopped and stirring continues for up to 15 minutes. The photoresist was spin-coated on the substrate at 200 °C for 15 min. The manufactured photoresist liquids were measured to determine their densities. The photoresist films on glass substrates were characterized to determine absorbances and 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. UV light exposure is carried out for 5 minutes then immersed in developer solution for 5 minutes to develop film and water as a stopper. X-ray exposure is carried out for 0.125 seconds then immersed in developer solution and water as above. The step is also carried out for negative photoresist Sigma Aldrich.

### 3. Results and Discussion

*Hibiscus tiliaceus* L. flowers are extracted with a variety of *Hibiscus tiliaceus* L. flowers mass that is adjusted to each fraction. The formula used to compute the mass fraction is as the following.

\[
x = \frac{a}{a+b}
\]

where x = mass fraction; a = mass of *Hibiscus tiliaceus* L. flowers (g); b = mass of solvent (g) [17]. Fraction mass variation is 0.025; 0.050; 0.075; 0.100; dan 0.125, respectively, obtained the mass of *Hibiscus tiliaceus* L. flowers to be extracted, 3.18 gram, 6.53 gram, 10.05 gram, 13.78 gram, dan 17.71 gram. From the fraction 0.025 to 0.125, it appears that the higher the concentration of *Hibiscus tiliaceus* L. flowers, the higher the absorbance value. The results of the absorbance of *Hibiscus tiliaceus* L. flowers extract can be seen in Fig. 1. Absorption is a quantity that states the ability of a material to absorb light.
Figure 1. Graph of absorbances of *Hibiscus tiliaceus* L. flowers extract

Based on figure 2, that the five samples have almost the same spectrum structure. Referring to the study [18], obtained the peak of the spectrum of the five samples, 3445.29 cm\(^{-1}\) in the fraction of 0.025; 3436.52 cm\(^{-1}\) in the fraction of 0.050; 3503.93 cm\(^{-1}\) in the fraction of 0.075; 3435.7 cm\(^{-1}\) in the fraction of 0.100; 3429.74 cm\(^{-1}\) in the fraction 0.125 indicates the presence of -OH bonds that are considered to be from the alcohol group (3650 - 3200) cm\(^{-1}\). Vibration absorption also occurs at wave number (1350 - 900) cm\(^{-1}\) which is a stretching vibration of C-O alcohol. This confirms that anthocyanin from hibiscus extract has a hydroxyl (OH) functional group.

Figure 2. Graph of FTIR of *Hibiscus tiliaceus* L. flowers extract

The electrical properties of thin films of extract are characterized using I-V meter V1.0 ELKAHFI 100 with two point probe method and input voltage [19]. The results of testing the electrical properties of the thin film of *Hibiscus tiliaceus* L. flowers in Fig.3. show that the current value at each fraction is different. Thin-film of *Hibiscus tiliaceus* L. flowers with mass fraction of 0.125 had the highest current value that was raised at 2.71 x 10\(-7\) A and the lowest current value generated at 1.88 x 10\(-7\) A on thin-film of *Hibiscus tiliaceus* L. flowers extract with a mass fraction of 0.025. The greater the conductivity value, the better the material is to be applied as a photoresist photoactive material.
Figure 3. Graph of generated currents of *Hibiscus tiliaceus* L. flowers extract thin films corresponds to source voltages.

The surface structure of the *Hibiscus tiliaceus* L. flowers extract thin film can be seen using the Digital CCD Microscope MS-804 Scopeman. The five samples have a less homogeneous structure as shown in figure 4.

![Surface structure thin film of *Hibiscus tiliaceus* L. flowers extract with mass fraction](image)

**Figure 4.** Surface structure thin film of *Hibiscus tiliaceus* L. flowers extract with mass fraction (a) 0.025; (b) 0.050; (c) 0.075; (d) 0.100; (e) 0.125

The density value in the solution affects the physical and mechanical properties of photoresist material. The value of resist density as shown in figure 5 when compared to the density of the epoxy-based photoresist SU-8 3000 in Table 3 has a density value that tends to be the same as the photoresist SU-8 3005 and SU-8 3010. The density value Resistant fluid produced in the study ranged from 1.047 g / ml to 1.110 g / ml while the value of photoresist SU-8 3005 and SU-8 3010 were 1.075 g / ml and 1.106 g / ml.
Figure 5. Graph of densities of organic photoresist

Table 3. The value of photoresist SU-8 3000 densities

| Photoresist SU-8 3000 | Density (g/ml) |
|-----------------------|----------------|
| 3005                  | 1.075          |
| 3010                  | 1.106          |
| 3025                  | 1.143          |
| 3035                  | 1.147          |
| 3050                  | 1.153          |

The microstructure of thin-film photoresist, as shown in figure 6, tends to be homogeneous sample of 13% to 3%, so the more percentage composition of Hibiscus tiliaceus L. flowers extract photoresist microstructure of thin film tends to be homogeneous. This condition is influenced by the spin coating process and the prebake process.

Figure 6. Surface structure of organic photoresist

The important physical-optical properties of pigments are therefore their light-absorption and light-scattering properties [20]. The absorbance results of organic photoresist material from Hibiscus tiliaceus L. flowers extract as shown figure 7 that the highest absorbance value of the six samples is at
a wavelength of 350 to 450 nm. The results of absorbance characterization showed that the percentage composition of *Hibiscus tiliaceus* L. flowers extract of 11% had the highest absorbance value, so the maximum light absorption was at a wavelength of 400.57 nm with absorbance of 0.318. At the percentage of 13% and 5% have the lowest light absorption because it only reaches 0.074 which is located in the wavelength range of 416.13 nm and 394.36 nm. Graph of absorbance spectrum shows that the maximum absorbance of 3% is 0.136 at a wavelength of 379.14 nm, the maximum absorbance of a percentage of 7% is 0.112 at a wavelength of 395.86 nm, the maximum absorbance of a percentage of 9% is 0.147 at a wavelength of 403.13 nm. The higher absorbance of photoresist thin film the higher photoresist sensitivity [21]. The i-line, h-line, and g-line values of each sample have been made to determine the wavelength range for lithography applications as shown in Table 2. In the UV lithography the exposure from g-line (436 nm) to h-line (405 nm) and then to i-line (365 nm) [22].

![Graph of absorbances of organic photoresist](image)

**Figure 7.** Graph of absorbances of organic photoresist

The i-line, h-line, and g-line values of each sample have been made to determine the wavelength range for lithography applications as shown in Table 4. In the UV lithography the exposure from g-line (436 nm) to h-line (405 nm) and then to i-line (365 nm) [20]. Thin film organic photoresist of *Hibiscus tiliaceus* L. flowers extract has an absorbance value of 0.1-0.3 which qualifies for photoresist absorbance. In general, the value of the photoresist absorbance is 0.1-3 [23].

| Percentage | i-line (365 nm) | h-line (405 nm) | g-line (465 nm) |
|------------|----------------|----------------|----------------|
| 3%         | 0.09232        | 0.12653        | 0.12944        |
| 5%         | 0.05293        | 0.07221        | 0.06558        |
| 7%         | 0.06401        | 0.11056        | 0.09074        |
| 9%         | 0.09315        | 0.1457         | 0.13217        |
| 11%        | 0.14597        | 0.31347        | 0.26768        |
| 13%        | 0.05037        | 0.07143        | 0.06292        |

The results of the sensitivity test of organic photoresist and Sigma Aldrich's negative photoresist solution can form patterns on the PCB substrate after exposure to UV light. Organic photoresist gives a lower level of contrast compared to the Sigma Aldrich’ negative photoresist as shown in figure 8. The difference in the level of contrast is influenced by the color of the solution and the developer solution (developer) [13]. As for the results of the sensitivity of organic photoresist from *Hibiscus tiliaceus* L. flowers and Sigma Aldrich, photoresist solution cannot form patterns on the PCB substrate after being given X-ray exposure.
Figure 8. The results of the sensitivity test after exposure to UV light a. organic photoresist b. negative photoresist (Sigma Aldrich)

4. Conclusions

*Hibiscus tiliaceus* L. flowers extract has anthocyanin pigment. This pigment shows the response to light which is shown with different absorbance values according to the concentration of extract. The same thing applies when samples are tested for conductivity values. Based on the results of FTIR characterization showed the presence of hydroxyl (OH) functional group vibrations and vibration vibrations of C-O alcohol. *Hibiscus tiliaceus* L. flowers extract has the potential to be used as a photoresist photoactive material.

Organic photoresist from *Hibiscus tiliaceus* L. flowers has the same density value as epoxy-based photoresist in the market, which ranges from 1,047 g / ml to 1,110 g / ml. The more the percentage composition of *Hibiscus tiliaceus* L. flowers extract, thin-film photoresist of microstructure tends to be more homogeneous. The resulting photoresist has a maximum absorbance value of 0.07 to 0.3 at the g-line, h-line, and i-line wavelengths. The resulting organic photoresist can form patterns after exposure to UV light but does not form patterns after exposure to X-rays.

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