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Preparation and surface analysis of ultrathin photoresist for microlithography

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ABSTRACT In integrated circuit (IC) technology the demand for faster and increased memory storage capacity has led to a continuous refinement of microlithograhic techniques for producing smaller circuit elements. Thus this requires submicron resolution which necessitates a move from conventional photolithography to techniques involving X rays, and electron or ion beams. The ultrathin film of ω-tricosenoic acid (30 – 1000Å) obtained by LB technique has been reported to have acceptable resolution, sensitivity and contrast to produce very small feature sizes. These monomolecular photoresists have found the application in the area of electron beam lithography. Here, the study focused on the preparation of these films in order to produce a uniform and controllable thickness of films suitable for high-resolution electron beam irradiation. Surface analysis of the films have shown that besides other factors such as type of deposition, temperature of the water subphase, speed of the barriers, the degree of adherence of Langmuir film to different substrates could also be detrimental to the film quality.

(Microlithograhic, Photolithography, Irridation, X-ray, Langmuir-Blodgett)

INTRODUCTION

There has been a considerable interest for some years in the use of LB technique in producing ultrathin electron resists as an alternative to spin coating method. Langmuir-Blodgett (LB) technique can produced LB films with excellent uniformity and homogeneity in thickness of less than 10 nm, which is far beyond the capabilities of the conventional spin-coating method of depositing photoresist. Amongst the substances proposed as LB resists, ω-tricosenoic acid ($C_{22}H_{43}COOH$) is by far the most promising. It is a fatty acid with 22 carbon atoms of hydrophobic chain and a double bond C at the terminal. The unsaturated group of double bond is the centre of chemical reactivity and is particularly important as polymerizable group. LB resist of ω-tricosenoic acid is capable of sensitivity and contrast [1] required by microlithograhic processes [2] and that its resolution of 60 nm [3] far surpasses foreseeable device requirement. Molecules of ω-tricosenoic acid can be deposited onto suitable substrates at the faster rate of 0.5 cm s^{-1}, so that the film preparation time is similar to that required for spin coated resists [4] .The fast dipping rate achievable with this material is attributed to the greater freedom of movement as a result of the presence of the double bond.

In order to achieve very high resolution in microlithography, the following criteria must be fulfilled. The resist film should be homogenous with constant thickness, impermeable to plasma with very low pinhole density and highly compact to serve as plasma-resistant films.

EXPERIMENTAL DETAIL

The fully automated Langmuir trough used is of the single compartment type with the Wilhelmy plate for monitoring the surface pressure. The water subphase was distilled and Millipore-filtered (resistivity > 18 MΩcm) at room temperature. Compact monolayer can be achieved by the symmetric compression of the two moving water surface barriers. The surface pressure versus area isotherm was recorded after the solvent evaporated. The film was compressed to a surface pressure of 30 mNm^{-1} and film transfer to clean substrate was carried out at 5.0 mm per minute. Constant pressure was maintained using an electronic servo-feedback

system. The surface morphology was investigated by scanning electron microscope, SEM (Leica Cambridge S360) and atomic force microscope, AFM (Burleigh-ARIS 3300).

RESULTS AND DISCUSSION

Successful fabrication of LB film of ω-tricosenoic acid was obtained on the following substrates; glass slide, Si wafer and SiO_2 coated wafer. Isotherm test carried out at four temperatures (20 °C, 25 °C, 30 °C and 35 °C) showed that 20 °C is the optimum temperature as it produced condensed monolayer. According to the stability test, the monolayer is most stable at the surface pressure of 37 mNm^{-1}.

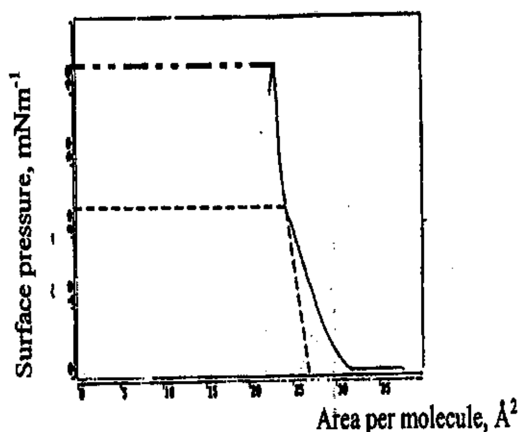


Figure 1. Isotherm of ω-tricosenoic acid monolayer on water subphase at 20 °C with collapse pressure (shown by - --of 44 mN/m and area per molecule of 26.5 $Å^2$ (shown by ---).

LB deposition was carried out on treated and untreated glass slides, Si wafers and SiO_2 coated wafers. Transfer ratio of the monolayer onto the substrate showed that this material can be deposited as Y -type LB films. Results also showed that treated substrates had better transfer ratio compared to untreated substrates. This is due to the increase in the hydrophobicity of the substrates when they were treated with CCl_3CH_3 and $Si(CH_3)_2Cl_2$. Hydrophobic surfaces are essential for good quality LB film as intervening water layer caused by improper drainage during LB deposition could break and filled any microvoids or irregularities on the substrate surface. When these water droplets evaporated, the LB film would be disrupted and respread to the water subphase.

Another conclusion that can be drawn from the results of transfer ratio is that Si wafer used as solid substrate for deposition of ω-tricosenoic acid had the highest average transfer ratio. Glass slide on the other hand had the lowest average transfer ratio. This is an indication that treated Si wafer made the best solid substrate for the LB deposition of ω-tricosenoic acid. Moreover, increasing the number of monolayers deposited onto the substrate would decrease the average transfer ratio of the deposition of ω-tricosenoic acid.

Structural characterization was conducted to further understand the morphology of the deposited ω-tricosenoic acid onto various substrates. SEM images depicted in Figure 2, showed that treated glass slide, with the purpose to enhance hydrophobicity, had less pinholes on the surface of deposited monolayers.

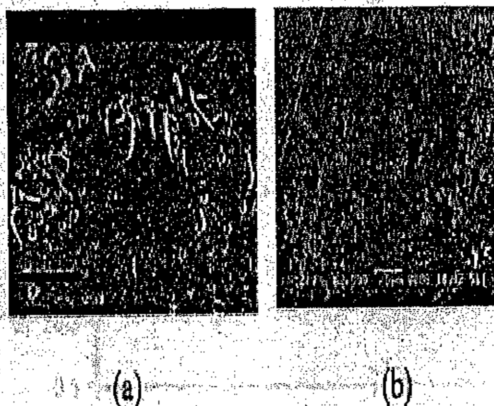


Figure 2. SEM images of 39 layers of LB film on (a) untreated glass slide at a magnification of 5000 x (b) on treated glass slide at magnification of 3000 x.

SEM images of LB films on Si wafers (Figure 3) showed a homogeneous and smooth deposition without much topographical texture. However, deposited ω-tricosenoic acid on untreated Si wafer showed pinholes on the surface. Pinholes are not visible for ω-tricosenoic acid LB film deposited on treated Si wafer.

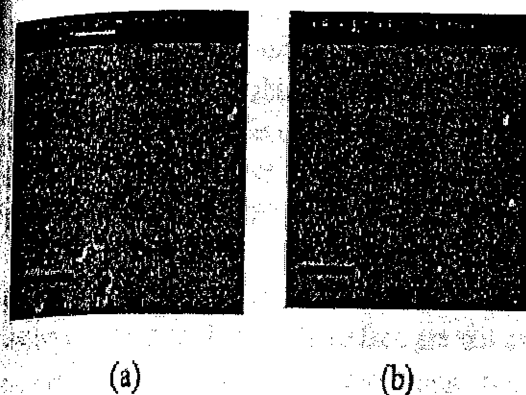


Figure 3. SEM images of 20 layers of ω-tricosenoic acid on (a) untreated Si wafers and (b) treated Si wafer at a magnification of 10000 x.

Although Si wafers are naturally hydrophobic, but when wafer exposed to moisture, either from air or postcleaning rinses, surface condition changes to a hydrophilic one [5]. Hydrophilicity affects the deposition of LB material onto untreated Si wafer, worsening the quality of the films. Therefore, Si wafer treated with CCl_3CH_3 and $Si(CH_3)_2Cl_2$, has its hydrophobicity enhanced giving better quality LB films.

It should be pointed out that as the number of layers of ω-tricosenoic acid on treated Si wafer increases from 20 to 50, the stacking of molecules on top of each other becomes obvious as overturning of molecules became significant. This is evident from the SEM images (Figure 4) where several dark patches were seen. Surface analysis done by AFM revealed that surface roughness increased as the number of monolayers of ω-tricosenoic acid increased.

The surface roughness of these images was also measured by AFM. Figure 5 depicts the comparison of the surface roughness of Si wafer deposited with 20, 30, 40 and 50 layers of ω-tricosenoic acid LB film measured at a surface area of 7 x 7 μm.

It is observed that the surface roughness of the LB film increases as the number of mono layers increases. This outcome indicating the deterioration of the quality of LB film as the number of LB monolayers increases is supported by the SEM images and the values of transfer ratio. A possible explanation for this observation is that it may be due to reorganization of the molecules during transfer [6,7, 8] or while under water [9]. Due to the reorganization of the molecules, the LB film deposited onto substrate became unstable and spontaneously form islands and voids [10]. As the number of monolayers increases, the stacking to form monolayer islands becomes more prominent. These defects initially originate at isolated sites and quickly spread over the entire film.

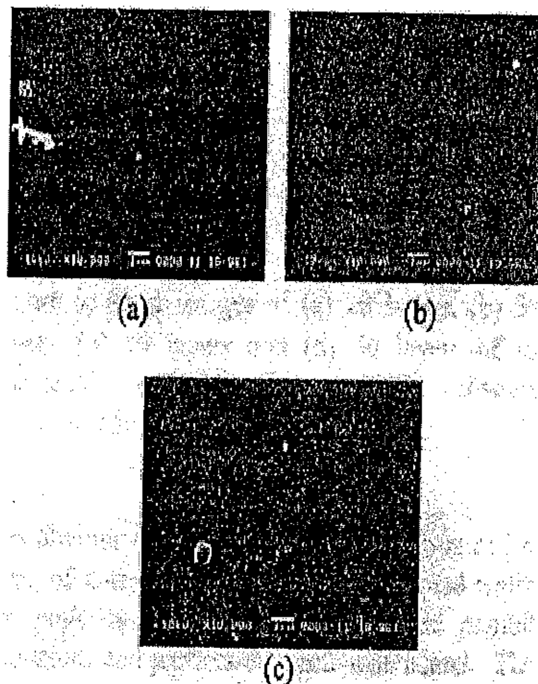


Figure 4. SEM images of (a) 30, (b) 40 and (c) 50 layers of ω-tricosenoic acid on treated Si wafers.

Researchers had proposed that one of the mechanisms responsible for reorganization is the overturning process [7, 8, 11]. Molecules in deposited LB films may not be in fixed or rigid state but had the potential for motion. When the attachment between monolayer-substrate or between monolayer-monolayer was not strong enough, molecules might overturn [6]. In overturning process, molecules on top monolayer folds back on themselves and bound with the molecules at the bottom monolayer.

Compared to Si wafer, ω-tricosenoic acid monolayers deposited on SiO_2 surface are not as homogeneous. LB film of ω -tricosenoic acid seemed to form continuous islands and domains. AFM results also showed that the surface was rougher than for ω -tricosenoic acid LB film on Si. This can be explained by the structure of the oxide layer, which is amorphous with much

space between molecules. Furthermore, the oxide layer thermally grown on Si was not uniform. This was proven by the thickness measurement of grown oxide layer by ellipsometer .The thickness of oxide measured was different at different points of the substrate. As a consequence, the LB film obtained on SiO_2 was not uniform and had pattern like structure (refer Figure 6 (c)).

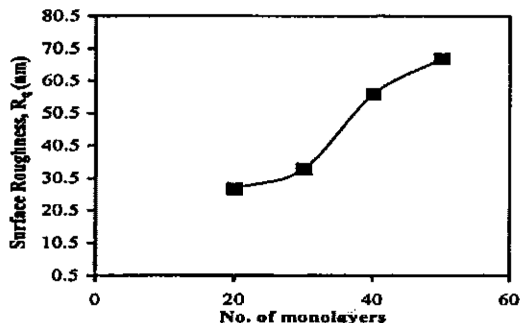


Figure 5. A plot of microroughness against the number of monolayers of ω-tricosenoic acid LB film on treated Si wafer.

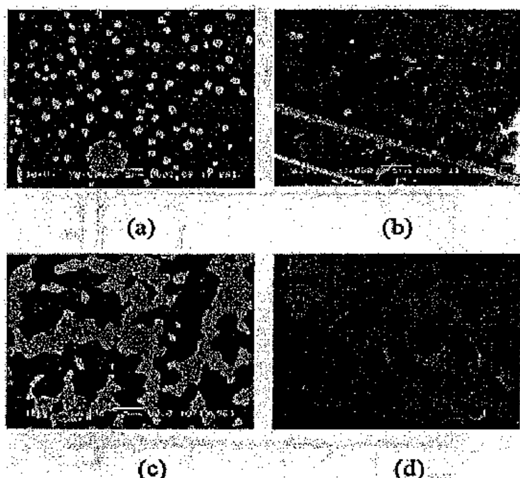


Figure 6. SEM images of (a) 20 layers, (b) 30 layers, (c) 40 layers and (d) 50 layers of (ω- tricosenoic acid LB film on SiO_2 substrate (magnification at 3000x).

It is obvious from Figure 6 that the surface of LB films of ω -tricosenoic acid on SiO_2 coated wafer are pinholes-free but not uniform and exhibit inclusions and patches of continuous island. The contrast shown is believed to be due to the thickness differences where darker areas are much deeper than the brighter patches of continuous islands. These patterns indicate extensive local rearrangement or depletion of the LB monolayers. The patches also seemed to form domains and the size of the domains becomes larger as the number of deposited monolayer increases. This infers that as the number of monolayers deposited increases the uniformity decreases and more molecules accumulate to form islands or patches. Further accumulation results in a continuous island. This observation is agreeable with the values of surface roughness obtained for 20, 30, 40 and 50 monolayers measured at a surface area of 7 x 7 microns (Figure 7).

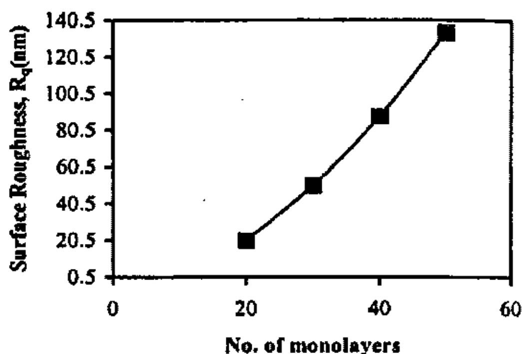


Figure 7. A plot of surface roughness against the number of monolayers on treated SiO_2 wafer.

Figure 7 indicates that the surface roughness increases as the number of LB monolayers on SiO_2 wafer increases. This fmding is similar to the LB deposition of ω-tricosenoic acid on Si wafer. However, the value of surface microroughness of monolayers deposited on SiO_2 was found to be higher than for Si wafer. This infers that Si wafer was more suitable for LB deposition of ω-tricosenoic acid compared to using SiO_2 and glass slide. The comparison of surface roughness of LB films on glass slide, Si wafer and SiO_2 wafer is shown in Table 1.

Table 1: Comparison of surface roughness of ω-tricosenoic acid LE film on different substrates.

Number of monolayers	Surface Roughness, R_q (nm)		
	Glass Slide	Si wafer	SiO_2 wafer
20	-	27.24	20.32
30	-	33.26	50.29
40	83.09	56.41	87.89
50	-	67.50	133.82

As discussed earlier, the presence of oxide layer on Si wafer affect the quality of LB monolayers. This might be due to the irregularity of the grown oxide layer during oxidation process or the natural amorphous structure of SiO_2 which are relatively open with voids in-between molecules.

Although the deposited LB film of ω-tricosenoic acid on treated SiO_2 surface was free of pinholes, a pattern like topographical structure was clearly seen on the surface. In addition, increasing the number of monolayers on SiO_2 increases the non-uniformity of the LB film and caused lower transfer ratio and rougher surface with islands and patches.

Here, the Energy Dispersive Spectrometer (EDS) which is attached to a SEM, was used not to quantitatively measure the composition of the LB monolayers of specific substrate but to confirm the existence of the LB monolayers. Figure 8 below shows the EDS energy peak for 50 layers of deposited LB film of ω-tricosenoic acid on Si wafer.

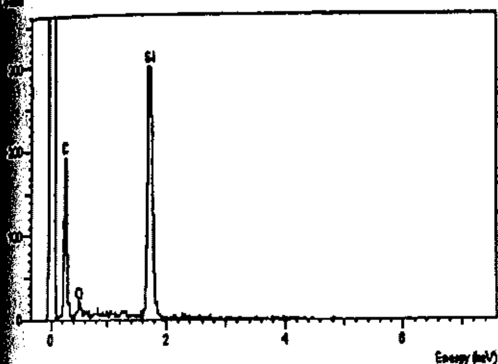
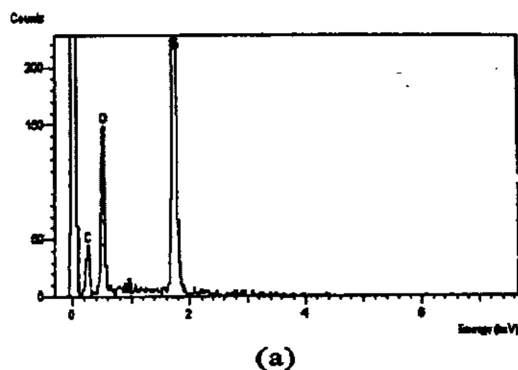
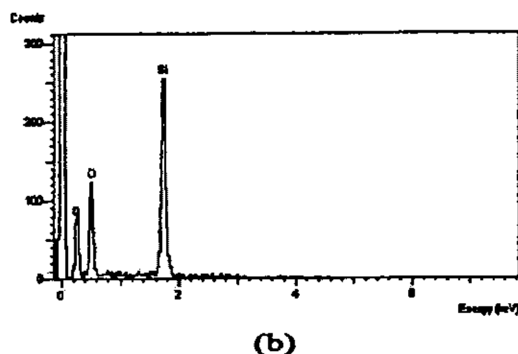


Figure 8. Characteristic EDS energy peaks of 50 layers of ω-tricosenoic acid LB film on Si wafer.

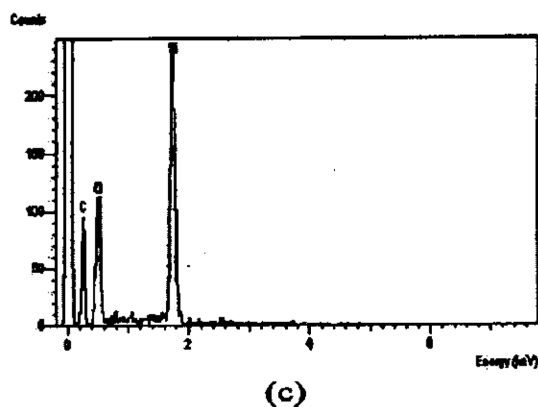
From Figure 8, on Si wafer covered with 50 layers of ω-tricosenoic acid, the energy peaks shown on the spectrum belongs to C, O and Si atoms. As the substrate is composed entirely of Si, the presence of carbon and oxygen in the spectrum can only be explained by the presence of deposited ω-tricosenoic acid. Carbon composition is seen to be much higher than oxygen as a molecule of ω-tricosenoic acid comprises of more carbon atoms compared to oxygen atoms (ratio of 23:2 carbon to oxygen).



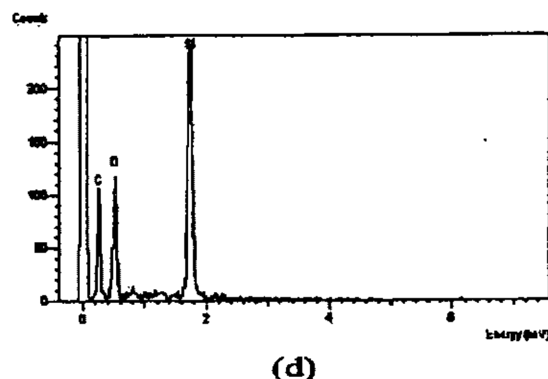
(a)



(b)



(c)



(d)

Figure 9. Characteristic EDS energy peaks of (a) 20 layers, (b) 30 layers, (c) 40 layers, (d) 50 layers of deposited ω-tricosenoic acid LB film on SiO_2 wafer.

Figure 9 (a), (b), (c) and (d) compares the EDS compositional analysis results of increasing number of layers of ω-tricosenoic acid deposited onto SiO_2. The results show that as the number of monolayers deposited onto SiO_2 increases the energy peak of carbon element increases. However, the energy peak of oxygen exhibits no trend when the number of monolayers increases. This is because the majority of the oxygen detected by EDS comes from the oxide layer as the composition of oxygen from ω-tricosenoic acid is rather low (two oxygen atoms per molecule of ω-tricosenoic acid).

With reference to Figure 8 and Figure 9(d), it is observed that the energy peak of carbon element is higher in deposited ω-tricosenoic acid on Si wafer than on SiO_2 wafer. This implies that more carbon atoms in the composition of the LB films on Si substrate than SiO_2 substrate, confirming the fact that more ω-tricosenoic acid molecule were transferred onto Si substrate. This is agreeable with the transfer ratio of 50 layers of ω-tricosenoic acid deposited onto Si, which is higher than the same number of layers of ω-tricosenoic acid deposited on SiO_2.

CONCLUSION

Omega tricosenoic acid has been successfully deposited as LB films on the substrates of glass slide, Si wafer and SiO_2 coated wafer, all with Y-type deposition. Among the substrate used, Si wafer was found to be the best substrate for good quality, homogeneous LB film with uniform thickness. LB films of ω-tricosenoic acid have been able to fulfil the criteria as the resist film for very high resolution. Film which are impermeable to plasma with very low density of pinholes can be obtained by subjecting the substrate to a treatment of CCl_3CH_3 and $Si(CH_3)_2Cl_2$ to render its hydrophobic property. Other contributing factors towards producing highly compact LB films would be to have the deposition conducted at the optimum temperature of 20°C and at the surface pressure of 37 mNm^{-1}. In order to produce smooth surfaces of LB films, it is proposed that monolayers deposited should not be too thick, as stacking with too many layers would increase the microroughness which can consequently cause degradation in the resolution.

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REFERENCES

1. Bean, K. E. (1978). IEEE Trans. *Electron Devices,* ED- **25**: 1185.
2. Martinot, H~Rossel, P. (1981). *Handbook On Semiconductors,* North-Holland Publishing Co.: 910.
3. Barraud, A., Rosilio, C. ~ Ruaudel- Teixier, A. (1980). *Thin Solid Films,* **68**: 91 -98
4. Peterson, I. R., Russel, a. *I.* ~ Roberts, a. a. (1983). *Thin Solid Films,* **109**: 371-378.
5. Van Zant, P. (1997). *Microchip Fabrication,* Third edition, McGraw Hill Book Co., New York. 6. Langmuir, I. (1938).
7. Honig, E.P .(1973). *J. Colloid Interface Sci.* , **43**, 66- 72.
8. Hasmonay, H., Vincent, M. and Dupeyrat, M. (1980). *Thin Solid Films,* **66**, 21-31.
9. Stephens, *I.F.* (1972). *J. Colloid Interface Sci.,* **387**,557-566.
10. Takamoto D.Y, Ter-Oveneysan, E., Schwartz, D.K., Viswanathan, R., Chiruvolu S., ~ Zasadzinski, *I.A.* (1998). *Acta Physica Polonica,* **93**,373-382.
11. Takamoto, D.Y., Aydil, E., Zasadzinski, *I.,* Ivanova, A., Schwartz, D.K., Yang, T. ~ Cremer, P. (2001). *Science,* **293**, 1292 - 1295.