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Phase controlled surface reaction – reaction of a monolayer at the gas–water interface

G. FARISS, J. B. LANDO, S. E. RICKERT
Department of Macromolecular Science, Case Western Reserve University, Cleveland, Ohio 44106, USA

A new technique for esterification of an acid monolayer at the gas–water interface has been introduced. This novel process termed phase controlled surface reaction (PCSR), utilizes Gibbs' surface energies to ensure reaction in an environment that would normally inhibit it. Because surface energies are important in numerous environments, PCSR should work with many condensation reactions. The addition of a benzyl alcohol subphase to water leads to a concentration of excess benzyl alcohol at all water interfaces including the gas–water interface. This surface enriched benzyl alcohol zone reacts with a polymerized monolayer present at the gas–water interface. FT–IR characterization of the deposited reacted monolayer shows that up to 70% of the monolayer molecules have been reacted. Further experiments indicate that the degree of conversion is dependent on the pH of the water subphase. Preliminary studies of electron lithographic patterning of the deposited product indicates that it is more electron sensitive than the original monolayer. PCSR may thus be a method by which chemical changes can be made in an existing monolayer, without altering its structure.

1. Introduction

1.1. Background

One possible technique for forming resists for precise circuit patterning on semiconductor surfaces is the Langmuir–Blodgett technique of film formation. The films formed by this method are an order of magnitude thinner than conventional spin cast films. These extremely thin films can possess excellent uniformity and are suitable for a number of possible applications, as reviewed by Vincett and Roberts [1] and Breton [2].

A major drawback in the application of Langmuir–Blodgett films for resist production or any other purpose is the inability of many materials to form a stable monolayer, the basic building block of multilayer films. We have designed a method by which a monolayer can be reacted after it is formed on the gas–water interface, greatly increasing the different types of molecules that can be used to create multilayers and decreasing the cost of producing new amphiphiles. This method will be discussed in detail and initial results in support of the method will be shown. An example of the advantages offered by this technique will also be discussed.

1.2. Langmuir–Blodgett films

Langmuir–Blodgett film formation utilizes the tendency of an amphiphilic molecule such as a fatty acid or soap to form a monolayer at a gas–water interface. Rayleigh [3] first theorized the existence of a monolayer in 1890. Pockels [4] introduced the handling and manipulation of monolayers, later to be refined by Langmuir [5], whose extensive works are the background upon which conventional experiments are based [6–8]. Langmuir designed a balance (Fig. 1), making possible the measurement of a number of monolayer characteristics. Blodgett [9], in collaboration with Langmuir, further expanded our knowledge of such films, especially the development of a method to deposit them onto solid substrates. More recent work on monolayers is too extensive to cover in detail but several

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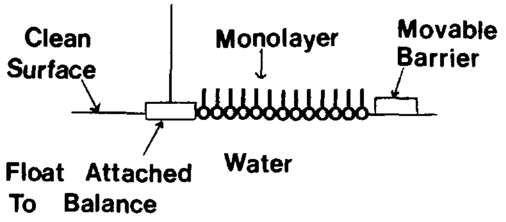


Figure 1 Langmuir film balance. Movable barrier compresses the monolayer film to a certain pressure which is measured by the floating barrier. The monolayer is oriented as pictured.

excellent review articles are available, including Adam [10], Harkins [11], Davies and Rideal [12], Gaines [13], and Fromherz [14].

Fatty acids and soaps were the first materials known to form monolayers. Since then, Gaines has divided monolayer-forming materials into two classes [15].

1. Simple, non-polymeric substances which are substantially insoluble, but whose molecules have sufficient attraction for the subphase to permit them to spread and disperse at the surface.

2. Polymeric materials which are positively adsorbed at the liquid–gas interface.

An important fact concerning Langmuir–Blodgett films is that certain non-polymeric monolayers can be polymerized, either at the gas–water interface [16] or after they have been deposited to form multilayers [17]. The polymerization of Langmuir–Blodgett films renders a monolayer or its subsequent multilayer more stable, allowing it to be used commercially.

Several other requirements than those listed above must be met in order for the material to remain a monolayer. If a monolayer is to be stable, it must experience a decrease in free energy during its formation [18]. In other words, there should be a sufficient attraction between the water and the polar end group to spread the material on the surface. Dispersion between the carbon tails can add another degree of stability to the monolayer. Last, the material should be neither soluble nor volatile to any significant extent.

The requirements for a material to form a monolayer are thus quite confined and rigid. These requirements severely limit the number of materials that can form monolayers, especially polymerizable monolayers. This chemical limitation directly limits the number of applications of Langmuir–Blodgett films. The development of a method which increases the number of chemically different monolayers that are certain to form multilayers would therefore increase the number of possible applications of Langmuir–Blodgett films.

1.3. Esterification

The amphiphile used in this initial study of PCSR was alpha-octadecyl acrylic acid (ODAA, Fig. 2) which forms a stable monolayer with the acid group adjacent to the water and the carbon tails protruding from the water, perpendicular to its surface. While ODAA proved to be highly electron sensitive for both polymerization and degradation [19], we have attempted to increase its electron sensitivity through the preparation of a more photosensitive material via PCSR.

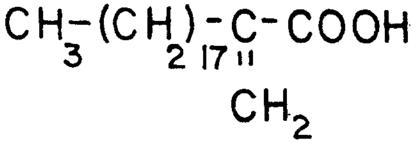
One species that is known to be highly electron sensitive is an aromatic group. An aromatic ester can be produced from the acid group of ODAA by running an esterification reaction with ODAA and an aromatic alcohol. This chemical modification of ODAA should result in a more electron sensitive resist.

It would have been preferred to run the esterification reaction while the ODAA was unpolymerized. However, polymerization of ODAA is not possible if it already exists as an aromatic ester, due to a change in the packing at the gas–water interface. Thus, it was necessary to polymerize the ODAA at the gas–water interface before reacting it.

Running a bulk esterification reaction of an acid in the presence of excess water is impossible. Consider the typical esterification reaction [20]:

$$\mathrm{RCOOH} + \mathrm{R'OH} = \mathrm{RCOOR'} + \mathrm{H_2O} \qquad (1)$$

The above reaction shows that esterification consists of reacting an acid and an alcohol in an



$$\mathrm{CH_3{-}(CH_2)_{17}{-}\underset{\underset{\displaystyle CH_2}{\|}}{C}{-}COOH}$$

α-octadecyl acrylic acid

Figure 2 Chemical structure of alpha-octadecyl acrylic acid (ODAA). ODAA is composed of three parts: (1) a hydrophobic carbon tail; (2) a hydrophilic acid head, and; (3) a vinyl group, all of which are important in this experiment.

acid medium to produce an ester. However, water is a by-product of the reaction. Since the reaction is reversible and, for an acid monolayer, would be carried out in a water environment, one might expect little, if any, ester to be produced.

1.4. Phase controlled surface reaction

We have developed a method by which esterification of an acid monolayer can be carried out. Phase controlled surface reaction (PCSR) is a technique based on two phenomena which occur in a monolayer environment:

1. Polymerization induced fixed configuration of a monolayer.
2. Concentration of excess solute at an interface.

The polymerization of a monolayer at the gas–water interface provides a degree of stability not found in a monomer monolayer (Fig. 3). The reaction of the vinyl groups limits the possible configurations the molecules can attain. The bonded molecules are no longer able to spread or flow freely on the water surface.

The theory behind PCSR is based on Gibbs' laws of surface free energies [21]. Gibbs states that the addition of an organic solute to a water solution leads to a tendency for the solute to concentrate at all interfaces. This tendency to concentrate at the interfaces is driven by the surface free energy of the solution which must be maintained at a minimum. Thus, diffusion of the solute of all interfaces will continue until such a minimum is reached.

Consider now the addition of benzyl alcohol to the monolayer trough. Because it is only slightly soluble in water ($\simeq 4\%$) and is heavier than water (density = 1.045), the majority of the benzyl alcohol immediately sinks to the bottom of the trough. This benzyl alcohol forms a reservoir below the water phase. Some of the benzyl alcohol that is dissolved will inevitably diffuse to the surface of the water, driven by the surface free energy.

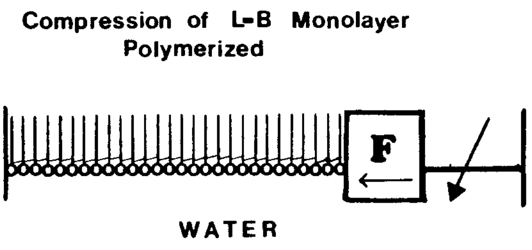


Figure 3 Polymerized monolayer of ODAA at the gas–water interface. The bonds between the molecules give the molecules a higher configuration stability.

Thus, the surface of the subphase will contain a higher concentration of benzyl alcohol than in the bulk solution. Due to the excess concentration of the benzyl alcohol in this reaction zone, an esterification reaction as in Equation 1 would be driven more to the right. Since the monolayer at the gas–water interface exists as a solid, its activity is one at the reaction site. Production of an ester from the acid and alcohol would thus be greatly enhanced, provided some catalyst (H^+) is present.

The reaction of the alcohol with acid produces an ester and water, immediately lowering the concentration of benzyl alcohol in the reaction zone. However, since the surface free energy must be maintained at a minimum, diffusion of benzyl alcohol from the reservoir into solution occurs. The total volume of benzyl alcohol in solution thus remains the same, enabling continued concentration of benzyl alcohol at the interfaces. The surface free energy also compels any water produced to diffuse to the bulk solution, thereby maintaining a certain concentration of benzyl alcohol in the reaction zone, leading to further reaction. Therefore, the esterification reaction must necessarily continue to a much higher degree than normally expected.

2. Experimental details

2.1. Equipment

The monolayer trough used was made of teflon-coated steel and contained a deep well [22]. A strip of teflon, to which nylon string was attached, was used for the movable barrier. Weights were hung on the string (by means of a pulley) in order to supply a certain pressure to the film. The entire apparatus was placed in a glove box to provide an inert atmosphere during the polymerization of the monolayer.

The water used for the subphase was doubly-distilled tap water. The first distillation flask removed the inorganics. The second flask contained potassium permanganate ($KMnO_4$) which oxidized any organic contaminants. The water received had a pH of 6.9 to 7.1 and remained at that pH for several weeks if bottled.

2.2. Spreading of the monolayer

A dilute solution (in the range of 0.5 mg ml^{-1}) of ODAA in heptane was made and spread on the clean water surface dropwise by means of a micropipette (about 20 μl per drop). The heptane in each drop was allowed to evaporate before the next drop was added. Drops were added until the unweighted barrier moved back to the fully expanded position. At this point selected weights were hung on the barrier to compress the film to a desired surface pressure.

The polymerization was carried out after purging the glove box for 30 min with nitrogen. A small ultraviolet (UV) lamp was placed in the glove box about 3 inches above the monolayer. Exposure of the monolayer to the UV irradiation lasted 1 h while a positive pressure of incoming nitrogen was maintained. Polymerization of the monolayer was generally carried out at a surface pressure of $2 \times 10^{-2}\,\mathrm{N\,m^{-1}}$ ($20\,\mathrm{dyn\,cm^{-1}}$) due to a difficulty in obtaining a stable film at higher pressures with the described apparatus.

2.3. Reaction

The addition of benzyl alcohol was accomplished after the polymerization was completed. A volumetric pipette was used to deliver a predetermined volume of benzyl alcohol below the water surface. The benzyl alcohol was added behind the movable barrier (Fig. 3, arrow) in order not to disturb the polymerized monolayer. The addition of benzyl alcohol continued until the majority of it concentrated in the well as a second phase, directly under the monolayer. The amount of benzyl alcohol added was usually in the range of 8 to 12% total volume. The trough remained undisturbed for 36 h to permit ample time for diffusion and reaction of the benzyl alcohol molecules, while the room temperature was kept at 23.5 + 0.5° C.

The hydrogen ions needed for catalysis of the esterification were supplied prior to the addition of the monolayer. Hydrochloric acid was added to the water subphase, lowering the pH to a desired level. Several experiments were run to determine the effect of pH on the degree of conversion.

2.4. Horizontal dipping

Polymerization of a monolayer renders vertical dipping [8] of the substrate impossible for deposition of the resulting continuous film. Vertical deposition relies on free movement of the monolayer into uncovered regions caused by the removal of material during the previous dipping in order to reform a contiguous film. Unfortunately, polymerization limits this movement by bonding the molecules, thus fixing their configuration. Vertical deposition thus is not possible following polymerization.

A different method of deposition has been developed for the direct purpose of depositing a polymerized monolayer [23]. Instead of passing the substrate vertically through the water surface, it is now passed through horizontally, depositing the first layer (Fig. 4). After passing it through the monolayer, the substrate is inverted while still in the water. This inversion places the deposited layer(s) on top of the substrate. The substrate is now moved to a new position below an undisturbed area of the monolayer and brought up through the monolayer horizontally. This uptrip deposits a second layer on the substrate. Additional layers can be deposited by subsequent horizontal passes, which should result in a Y-structure of multilayers [24]. In all cases, care must be taken to pass the substrate through an undisturbed area of the monolayer, or no deposition will occur.

Deposition of ester monolayers was done on germanium plates for the purpose of Fourier transform (FT)–IR characterization. When electron lithography patterns were to be drawn on multilayers, the substrate employed was ⟨1 1 1⟩ silicon coated with 130 nm silicon oxide on one side [9].

3. Results and discussion

3.1. FT–IR characterization

The esterification of the monolayer was followed through the use of a Digilab FTS-20E for FT–IR spectroscopy of deposited multilayers. The instrument was sensitive enough to detect three multilayers of deposited product, though in most cases 30 to 40 layers were deposited.

ODAA can be characterized by the FT–IR spectrum in Fig. 5a. Existence of peaks at 3440 cm^{-1} (OH bond stretch), 2915 cm^{-1} and 2850 cm^{-1} (CH_2, CH_3 stretch), 1685 cm^{-1} (COO– acid stretch), 1625 cm^{-1} (C=C stretch), and 1480 cm^{-1} (CH_3 bend) support the structure

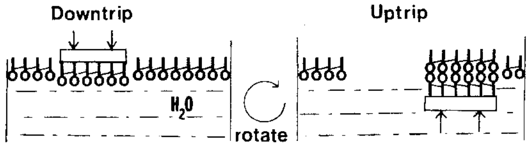


Figure 4 Horizontal deposition of monolayer at the gas–water interface. This deposition method is necessary due to the bonding between the polymerized molecules.

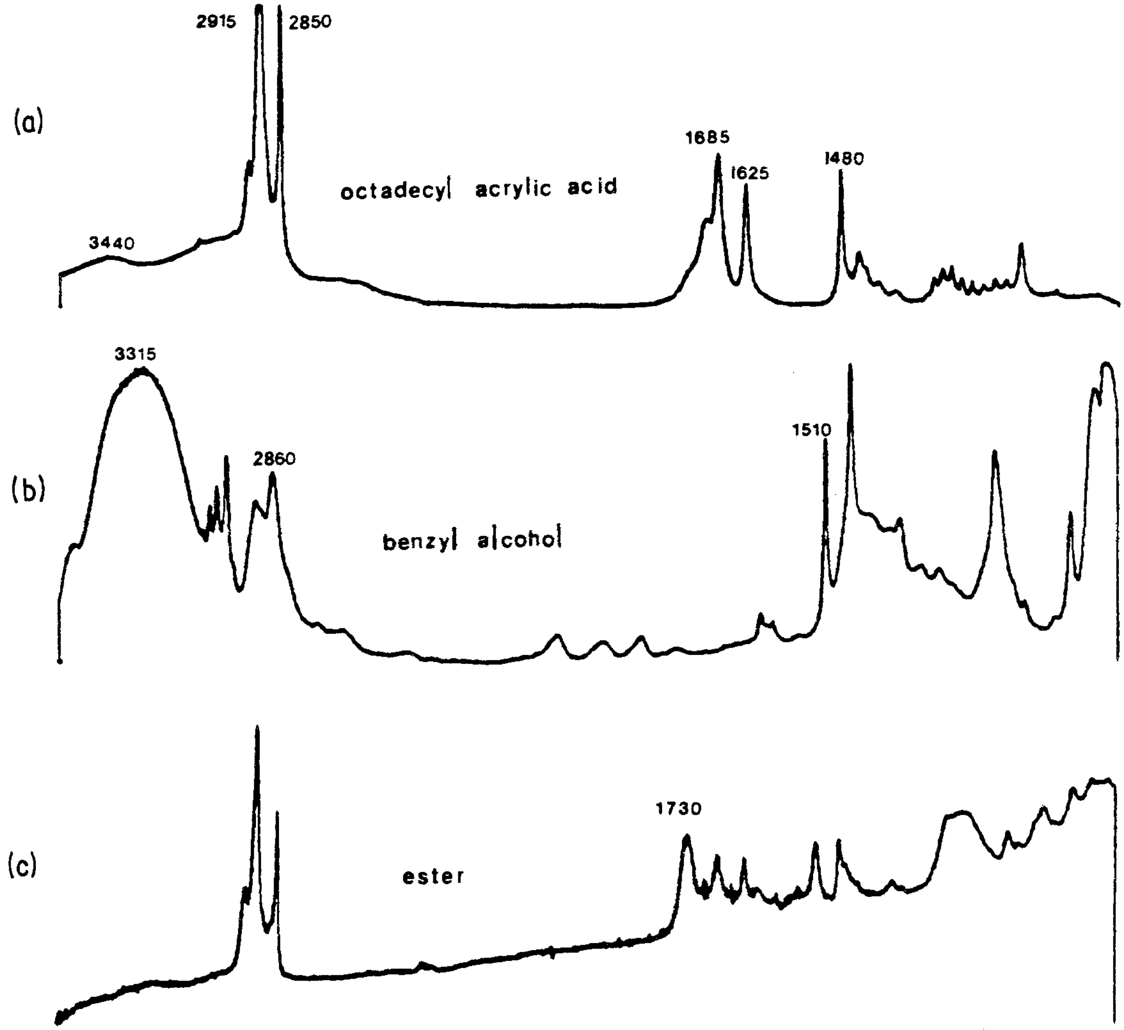


Figure 5 (a) FT–IR spectrum of ODAA, which can be characterized by the presence of peaks at 3440, 2915, 2850, 1685, 1625 and 1480 cm^{-1}. (b) FT–IR spectrum of benzyl alcohol, which can be characterized by the presence of peaks at 3315, 2860, 1510 cm^{-1} and peaks at lower wavelengths. (c) FT–IR spectrum of ester multilayers. The backbones of ODAA and benzyl alcohol are shown to be present and are coupled by an ester linkage (peak at 1730 cm^{-1}).

of ODAA in Fig. 2. FT–IR characterization of benzyl alcohol (Fig. 5b) shows peaks at 3315 cm^{-1} (bonded OH stretch), 2860 cm^{-1} (CH_2 stretch), and 1510 cm^{-1} and lower wavelength peaks (aromatic ring stretches). Any ester formed from the coupling of these two materials would be characterized by a combination of these spectra, except for a decrease in the hydroxy and acid bands and the necessary formation of an ester peak.

Fig. 5c is a spectrum of such a combination. Peaks are present at 2715, 2850, 1685, 1625 and 1480 cm^{-1}, indicating the presence of the backbone of ODAA. Likewise benzyl alcohol is shown to be present as indicated by absorbances at 1510 cm^{-1} and lower wavelengths. While both materials are present, neither one is in its pure state, as can be seen by a lack of an OH– stretch in the range of 3300 to 3500 cm^{-1}. There also exists a new peak at 1730 cm^{-1}, due to the existence of an ester group [20]. Thus, the spectrum in Fig. 5c is one of an ester formed by the coupling of benzyl alcohol and ODAA. Therefore, a successful reaction was accomplished through the use of PCSR.

Several other observations can be made from the spectra in Fig. 5c. First, the presence of the vinyl peak at 1625 cm^{-1} indicates that polymerization did not proceed to 100%. From the relative peak area it can be calculated that approximately 70% of the vinyl groups in the monolayer are reacted during polymerization.

Second, conversion of the acid to the ester was not complete. The deposited multilayers contained acid groups, as revealed by the peak present at 1685 cm^{-1}. Assuming that the extinction coefficients of the acid group and the ester group are the same (as they are in most cases), the esterification via PCSR is about 70% complete. Such a conversion ratio is still much higher than one would expect in a water solution.

3.2. Polymerization against surface pressure

The 70% polymerization of the monolayer was thought to be rather low. In previous work [23], close to 100% polymerization had been achieved with diacetylenes. Experiments were run varying the surface pressure is $3.5 \times 10^{-2}\,N\,m^{-1}$ (35 dyn during different polymerizations, with results shown in Fig. 6. These experiments were run on a Lauda Filmwaage Balance [19], which was not suitable for PCSR. It can clearly be seen that the polymerization increases too close to 100% when the surface pressure is $3.5 \times 10^{-2}\,N\,m^{-1}$ (35 dyn cm^{-1}). It appears that as the vinyl groups in the ODAA molecules get closer to one another, it becomes easier for them to react with each other. This increased pressure may also lead to a change in the packing of the monolayer, further enabling polymerization.

3.3. PCSR conversion against pH of subphase

The dependency of the degree of conversion for PCSR on the pH of the water subphase is shown in Fig. 7. At higher concentrations of hydrogen ions, a greater percentage of acid groups react with benzyl alcohol. A critical value for the pH appears to be around 3.7, below which the degree of conversion increases dramatically before levelling off below a pH of 2.8. This dependency of the degree of conversion on pH is expected, since the esterification is acid catalysed. The inflection point appears to depend upon the extent of polymerization.

Other variables upon which the degree of conversion may be dependent include temperature and surface pressure of the monolayer. Initial results indicate that a low degree of polymerization of the monolayer may cause limitations upon the degree of PCSR conversion. These limitations may be due to the inability of the unpolymerized molecules to react. Future work should be able to determine whether or not this is true.

3.4. Resists using esters

Deposition of the ester monolayer was carried out on clean ⟨1 1 1⟩ silicon chips [19] in order to test the material as a possible electron resist. 20 layers of ester monolayer were deposited using the previously described horizontal dipping method. A novel, computer-controlled electron microscope (Digital Minc-JEOL JEM-100B) was used to produce the patterning [19]. Because the ester had already been polymerized, it was only possible to work with it as a positive electron resist.

The ester produced proved to be an extremely electron sensitive material (Fig. 8). Line resolutions of 80 nm were obtained, somewhat compar-

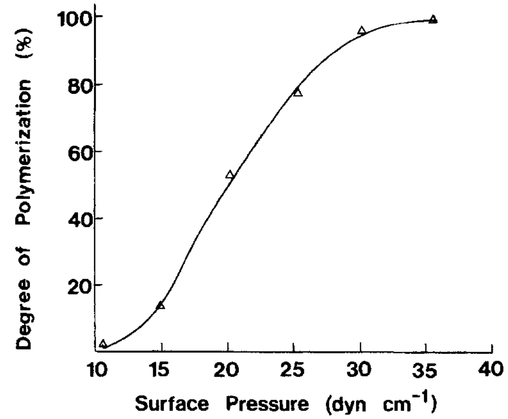


Figure 6 Graph plotting percentage polymerization of ODAA against surface pressure. Polymerization approaches 100% at a surface pressure of $3.5 \times 10^{-2}\,N\,m^{-1}$ (35 dyn cm^{-1}).

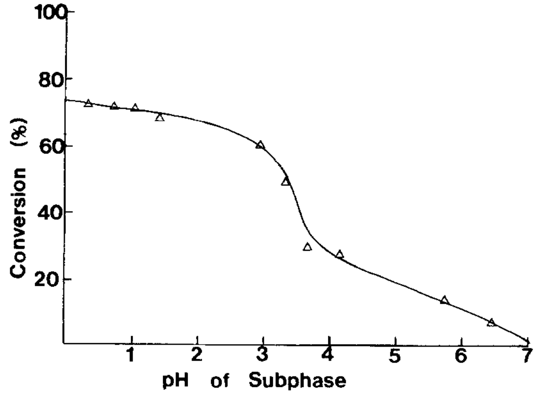


Figure 7 Graph plotting degree of conversion of acid groups to ester groups against pH of water subphase. A critical value for the pH exists at 3.7, below which a high degree of the acid groups react.

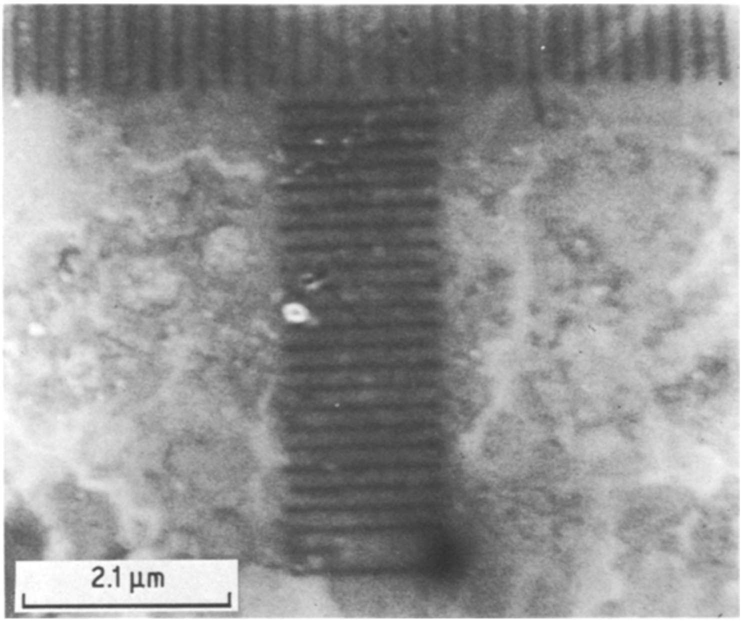


Figure 8 Positive resist from ester multilayers. The pattern is much darker than in previous work and was written in less than 2/3 the time needed before, while suffering only a slight loss in resolution.

able to the 50 nm resolution obtained with pure ODAA multilayers. Degradation appeared to be more complete with the ester while exposure time was only 2/3 as long. No development was necessary to see this pattern. We have thus produced, via PCSR, a more electron sensitive material capable of being a high resolution electron resist.

The non-uniformity of the horizontally deposited multilayers is due to the imprecision of the dipping method [25]. The silicon substrate had to be manipulated by hand, which is not the steadiest of all instruments. A mechanical device designed for the specific purpose of horizontally dipping a substrate should provide much more uniform films.

4. Conclusions

Gibbs' laws of surface free energies are the basis for a unique type of reaction. Phase controlled surface reaction relies on the tendency of an excess of an organic solute to concentrate at an interface of a water solution. This concentration drives to 70% completion a reaction that is usually unfavoured, esterification in an aqueous medium.

The reaction has been shown to be strongly dependent on the pH of the water subphase. As expected, PCSR conversion increases with the concentration of hydrogen ions in the subphase.

The most important application of PCSR includes chemical modification of a monolayer. This produces new, stable monolayers, unattainable by other means. Such monolayers can form unique multilayers of desired characteristics (e.g. a more electron sensitive multilayer resist). Also, it may be possible to attach desired characteristic groups, such as temperature sensitive groups, to monolayer material and thereby incorporate them into multilayer films.

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