CONTROLLED PATTERNING OF SELF-ASSEMBLED MONOLAYER FILMS

by

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ABSTRACT

This paper is a critical review of three current methods used in patterning self-assembled monolayer films. It begins with an introduction to monolayer films and their potential uses. This is followed by a discussion of self-assembly and the various experimental methods used to form monolayer films. The discussion focuses mainly on silanes as the compounds used to form the films, but it also includes thiols and carboxylic acids. The mechanism for self-assembly is reviewed too.

Various characterization techniques are presented next. Wettability, ellipsometry, XPS, UV-vis spectroscopy, IR spectroscopy, Raman spectroscopy, SIMS, STM, and AFM are all presented and their applications to thin film characterization are mentioned.

Following the characterization techniques is a section on patterning. The three methods analyzed include patterning procedures by Kleinfeld and co-workers, Wrighton and Whitesides and co-workers, and Calvert and co-workers. It is concluded that the method by Kleinfeld and co-workers requires

too many steps and too much time; the method by Wrighton and Whitesides and co-workers does not produce in-plane patterns but rather stepped ones; and the method by Calvert and co-workers requires expensive equipment not readily available to all laboratories. In addition, none of these three patterning methods can create features any smaller than in the micrometer range.

Three more recent patterning methods by Wrighton and Whitesides are presented next. They are micromachining, microwriting, and "rubber stamping" and they are capable of producing pattern features in the hundreds of nanometers range. This is an improvement but it is still not the ideal of being able to pattern molecule by molecule.

Suggestions for future research follow the analysis of the patterning methods.

ACKNOWLEDGEMENT

I wish to extend my sincere thanks to my advisor, G. Alan Schick for his discussions, help, and patience. My special thanks goes also to James P. Wightman and John G. Dillard for their advice and service as committee members.

In addition, I would like to recognize some other people who were invaluable during my time at Virginia Tech. To Curtis, my most sincere thanks for putting up with it all and helping in every way. To Allison, my sincere thanks for helping me find the way. To my mother, Judith, my sincere thanks for proof-reading, moral support, and physical sustinence. To my father, Michael, my extreme appreciation for computer aid, professorial advice, and parental guidance. And to Ursa, Buck, Agnes, and all the others who have passed through, my thanks for a bit of light in dark times.

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by

Laura Sporakowski

INTRODUCTION

Organic thin films have been studied since Franklin noted the spreading of oil on a pond [1] and Pockels did monolayer experiments in a kitchen [2]. Another important early researcher in the thin film field, Langmuir first reported his research on molecular films formed at the gas-liquid interface in 1920 [3].

The field of molecular monolayer films has recently experienced an increase in interest. Recent reviews have been published on such films [4-7] and these often include suggested areas of needed research for further technological development. One such list may be found in a paper by Swalen, et al.,and includes the following suggested areas for research: 1)thin-film optics; 2)sensors and transducers; 3)protective layers; 4)patternable materials; 5)surface preparation and modification; 6)chemically modified electrodes; and 7)biomacromolecules [4]. These are just some of the areas of research that could prove to be useful for future technologies.

Patternable materials are an area of research interest as they can be used in resists and for information storage. While organic films are already being used as resist materials for forming circuits, technology is advancing and striving for greater resolution in smaller spaces. Smaller spaces require thinner pattern lines, which means that either thinner films or more ordered materials will be necessary [4]. Patterned films may also be helpful in surface preparation and modification as they can be used to design surfaces for the enhancement of adhesion, wetting, and lubrication. Attempts to understand biological systems can also utilize patterned films as a means to mimic naturally self-assembling proteins and binding sites that require specifically patterned receptors to function as biosensors [4]. Patterning thin organic films is an area of research that has great potential.

A critical review of self-assembled monolayers and their uses in patterning is undertaken in this paper. Various means of patterning with self-assembled monolayers are of great interest as we learn how to control the structure of the resulting two-dimensional assemblies. Three research groups in particular have provided various means of patterning with self-assembled monolayers. The first of these groups consists of Kleinfeld, Kahler, and Hockberger. Their 1988 paper discusses the use of patterned substrates to promote or inhibit adhesion of cells in an attempt to construct "simplified neural architectures in vitro." The patterning procedure results in coplanar "orthogonal" films [8]. The second group consists of Wrighton and Whitesides and co-workers. Their 1989 paper discusses the formation of alkyl-derivative monolayers on substrates with two different surface materials. This patterning procedure produces orthogonal systems with in-plane patterns [9]. Calvert leads the research efforts of the third group. Their 1991 paper describes deep ultraviolet irradiation of monolayer surfaces followed by subsequent self-assembly modification to produce patterned coplanar molecular assemblies [10]. These three techniques of patterning and their development over the past few years will be discussed in the pages that follow.

SELF-ASSEMBLY

Self-assembly is the spontaneous formation of molecular assemblies upon the immersion of a substrate into a solution containing an active surfactant in an organic solvent [6]. This method for the formation of thin organic monolayers was developed as an alternative to conventional Langmuir-Blodgett methods which were thought to be quickly reaching their limits of usefulness in the early 1980's [18]. During this time, Sagiv published the precursor to his "On the Formation and Structure of Self-Assembling Monolayers" series [19-21]. Entitled "Organized Monolayers by Adsorption", this paper presented adsorption onto solid substrates as a method for monolayer production that allowed for the control of in-plane molecular organization [18].

Given the limited amount of information and understanding about self-assembled films at the time, Sagiv and co-workers decided to do an in-depth investigation of the formation and basic structural features of such monolayers. The results of their intensive studies were presented through the above mentioned series. Using compounds like fatty acids, silane derivatives, phosphates and steroid derivatives, the group determined what reaction conditions (solvent, time, temperature, and concentration) produced the best monolayers based on analysis by ellipsometry, wetting-contact angles, FTIR, and ATR [18]. Such a procedure for the investigation of new compounds for monolayer formation continues to be quite effective.

The general preparation procedure for self-assembled monolayer films as presented by Sagiv and co-workers [6, 17] continues to be used today [23, 24]. The first step is the pre-treatment or cleaning of the substrate onto which the monolayer is to be adsorbed. This step is most important since the substrate plays an active role in the adsorption process. The surface of the substrate should be polar, hydrophilic after cleaning, and relatively smooth in order for the monolayer to form rapidly and with precise molecular packing and orientation [18]. For a substrate such as glass or quartz slides, the cleaning procedure could involve sonication in a detergent solution, soaking in a solution of NaOH, soaking in a solution of HCl, and thorough rinsing with distilled water, followed by drying in a stream of nitrogen gas [18]. For a substrate such as gold, which might be used in the self-assembly of alkanethiols, the preparation of a clean surface involves evaporating gold films onto a substrate and then using the freshly prepared surface soon afterwards [26]. For a substrate such as aluminum oxide, which could be used in the self-assembly of alkane carboxylic acids, the preparation of a clean surface involves the evaporation of aluminum onto a suitable substrate, followed by exposure to air which oxidizes the aluminum to aluminum oxide quickly [9].

Once clean, the substrate is ready for monolayer adsorption. This involves soaking in a solution of the desired adsorbate in an organic solvent such as bicyclohexyl, hexadecane, or chloroform for silanes. For thiols and carboxylic acids, solvents such as isooctane and degassed ethanol may be used [9, 26]. The concentration of the adsorbate, the time of soaking, the temperature, and the solvent used all depend upon the compound with which one desires to make a monolayer. These factors are optimized for the deposition of the specific monolayer and, as such, they prevent multilayer formation. Once the soaking is complete, the substrate is removed from the solution. Often, only the samples that emerge unwetted or oleophobic from the deposition solution are considered for further characterization since lack of wetting indicates full coverage of the substrate [18].

The mechanism for monolayer formation via self-assembly is controlled by the spontaneity of the process as it proceeds towards the minimum free energy for the system [21]. Such deposited monolayers are presumed to be either covalently bonded (irreversibly adsorbed) or physisorbed (reversibly adsorbed) to the substrate. An example of the covalent bonding mechanism for silane monolayers is found in Figure 1. The monolayers formed are highly oriented and closely packed with the possibility of intermolecular hydrogen-bonding or even polymerization. However, until recently, this mechanism has been presumed due to the lack of direct experimental evidence to support the formation of such covalent bonds [18-21].

More current research by Tripp and Hair has concluded that alkylchlorosilanes do not react directly with surface silanols based on IR spectroscopy data [31, 58, 59]. At the solid/gas interface, the silane studied (trichloromethylsilane or TCMS) physisorbs onto dehydrated silica. When the silica surface has water adsorbed onto it, the TCMS forms methyltrisilanol which does not polymerize on the surface nor condense with the surface silanols. At the solid/liquid interface, the TCMS reacts with water to form methyltrisilanol also. The trisilanol then adsorbs to the silica surface where it subsequently condenses to form a polymer [58]. In contrast, previous studies show that another trichlorosilane, OTS, does not adsorb to silica surfaces unless greater than monolayer amounts of surface water are present. The difference is due to steric hinderance from the long hydrocarbon tail in the OTS system [31, 58].

Once the self-assembled monolayer has been adsorbed onto the substrate, it is ready for further analysis.

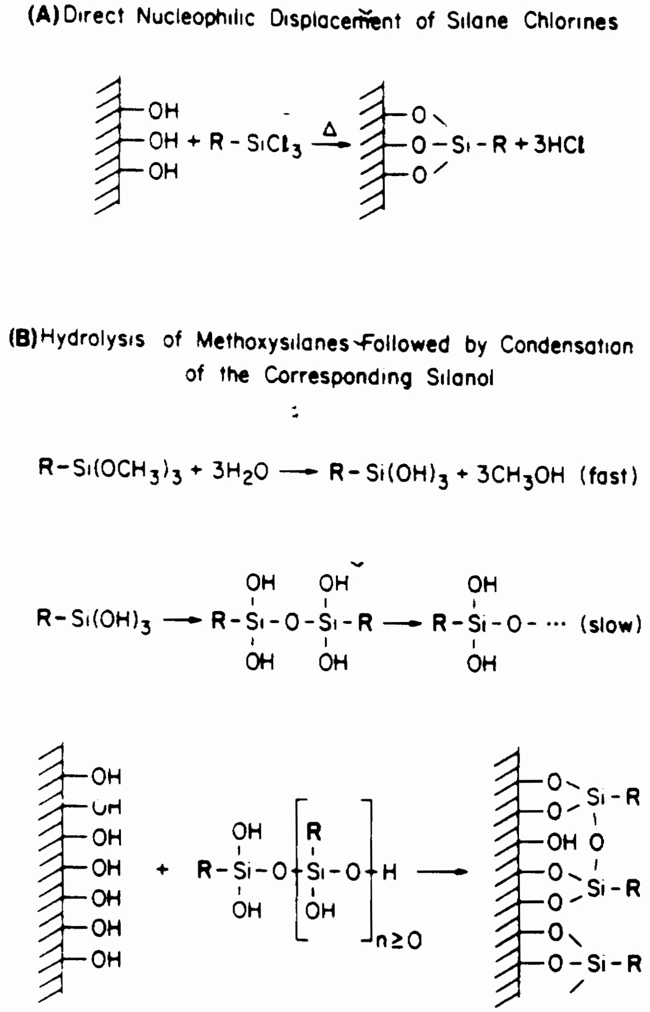

FIGURE 1 : Schematic of silanes covalently bonding to substrates to form monolayers [8].

CHARACTERIZATION TECHNIQUES

Having prepared self-assembled monolayer films, the next step would be to analyze the prepared samples. Some of the properties that are necessary to check in order to determine how "good" the film is include wettability, thickness, orientation, elemental composition, and other structural characteristics. It is preferable that the analytical techniques used to elucidate such information be non-destructive, as the films being analyzed often go on for further modifications and testing. Some of the more common methods of characterization for self-assembled films include wettability testing, ellipsometry, x-ray photoelectron spectroscopy (XPS), UV-visible and IR spectroscopies, Raman spectroscopy, and scanning tunneling microscopy and atomic force microscopy (all of which are non-destructive) and secondary ion mass spectroscopy (SIMS) (which is destructive) [4, 5, 16, 17, 30]. These techniques will be discussed briefly below.

Wettability: This technique provides some information about the surface structure and functionality of thin organic films. By measuring the contact angles of stationary water drops, one can use Young's equation to determine interfacial free energy ratios as shown in Figure 2(a) [5, 30].

This is the simplest information about the surface in question that can be acquired from this technique. By expanding the technique to include experimental parameters such as pH dependence, probe liquid variation, and advancing and retreating contact angles, and by comparing measurements of similar systems, this method can become a valuable tool for investigating the surfaces of self-assembled monolayers [17].

Contact angle measurements can be used to determine the polarity of the surface functional groups. This can be done by comparing contact angle values using different liquids and different compounds as monolayers as shown in Figure 2(b). Films will show varying contact angles depending on their own surface group polarity and that of the liquid being used for the measurement. If one film has greater contact angles than another using the same liquid, the former film has more polar surface groups. Such measurements also respond to structural details of surfaces and can thus be used to detect inconsistencies and flaws in the prepared films. These can be detected by studying the contact angles and their variations on a single sample. Too much variation within a sample tends to indicate poor film quality. Characteristics like the energies of spreading and the hysteresis of contact angles may provide future information as they become better understood [17].

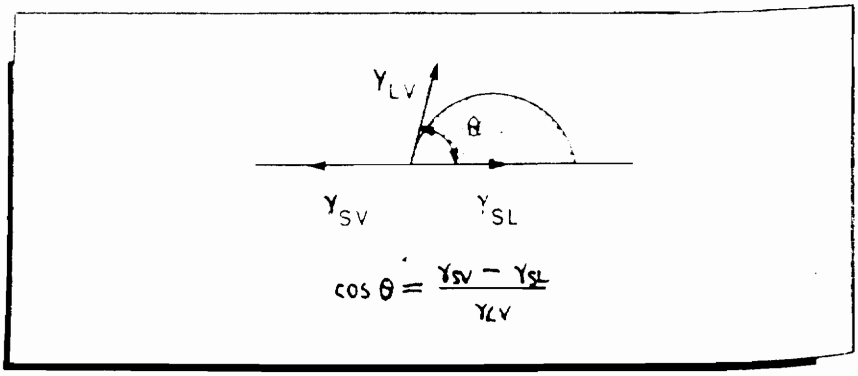

FIGURE 2(a) : Schematic representation of Young's equation [5].

RSH	$\theta_a(H_2O)$	$\theta_a(HD)$
$HS(CH_2)_2(CF_2)_5CF_3$	118	71
$HS(CH_2)_{21}CH_3$	112	47
$HS(CH_2)_{17}CH=CH_2$	107	39
$HS(CH2)_{11}Br$	83	0
$HS(CH2)_{11}Cl$	83	0
$HS(CH2)_{11}OCH_3$	74	35
$HS(CH_2)_{10}CO_2CH_3$	67	28
$HS(CH_2)_8CN$	64	0
$HS(CH_2)_{11}OH$	0	0
$HS(CH_2)_{15}CO_2H$	0	0

FIGURE 2(b) : Contact angle measurements (using water and hexadecane) showing differences due to surface functional groups of thiol monolayers on gold [5].

Ellipsometry: This technique allows the researcher to determine the average thickness of the self-assembled film. The thickness of the film is estimated by measuring the ratio of the reflection coefficients of the parallel and perpendicular components of plane-polarized light, usually from a He-Ne laser. The plane-polarized monochromatic light is polarized at an angle A. These values are achieved from the plane-polarized light being resolved into its two components which are then reflected and combined to form elliptically polarized light. This light then goes through a compensator and the angle B by which the beam has been polarized is determined by an analyzer as is shown in Figure 3. The phase shift between angles A and B is then computed and the desired ratio is achieved and related to the film thickness [5, 16]. By comparing film thickness to an estimated monolayer thickness, one can determine if the film is close to a monolayer or not.

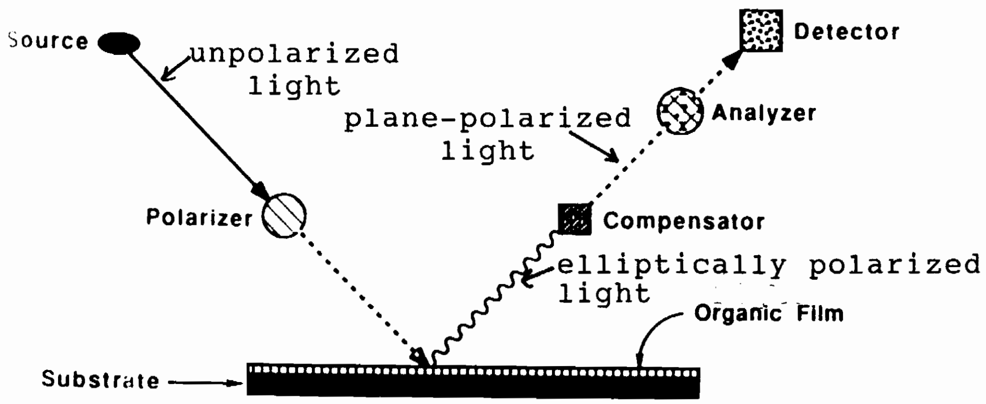

FIGURE 3 : Schematic of an ellipsometer [5].

XPS: This technique allows for the indirect determination of surface functional groups. A sample of the film is irradiated with known-energy (hv) X-rays which cause photoelectrons to be emitted as shown in Figure 4(a). The kinetic energy (E(kin)) of these can be analyzed via their velocities and then used in the equation

$$E(kin) = hv - E(i) - \Phi(sp)$$

(where $\Phi(sp)$ is the work function characteristic of the instrument used) which is used to calculate the binding energy (E(i)). This binding energy is characteristic of the atom from which the photoelectron was emitted. The bonding between the surface elements can be determined from the chemical shifts that occur with these binding energies [24].

An example of XPS determining surface functional groups is found in Figure 4(b). Two separate spectra show monolayers of octanethiol and dioctyl disulfide, both on gold, have the same surface functionality. It is a thiolate moiety that occurs with the main peak at 162.0 eV. The main peak occurs at 163.3 eV for docosanethiol, at 163.0 eV for didocosyl disulfide, and at 162.5 eV for hexadecyl thiolate [39]. These differences in the binding energies of the core atom between functional groups are due to variations in the valence charge distribution. The binding energies of atoms reflect the electronegativity of the atoms. The more strongly an atom attracts it's core electrons, the greater the binding energy.

For a molecule, the binding energy of a specific atom is shifted from it's normal position due to the influence of the valence electrons on the nuclear charge [60]. These differences due to electronegativities should allow one to assign relative binding energies to related functional groups. For the above example used to explain Figure 4(b) all of the compounds have binding energies less than that of elemental sulfur, which has the main peak at 168 eV [60]. This is because the sulfur is the most electronegative atom in those compounds. As such, it attracts electrons from the other atoms and creates a partial negative charge for itself as a result. The partial negative charge repells the core electrons so that they are less strongly bound to the sulfur thus decreasing the binding energy. The two thiolates have the lowest binding energies because of the added effect of the negative charge on the sulfur atoms. The disulfide has a somewhat higher binding energy as the sulfur atoms are attached and they are not negatively charged as the thiolates are. The thiol has the highest binding energy because it experiences the least amount of donated electron density from it's substituents.

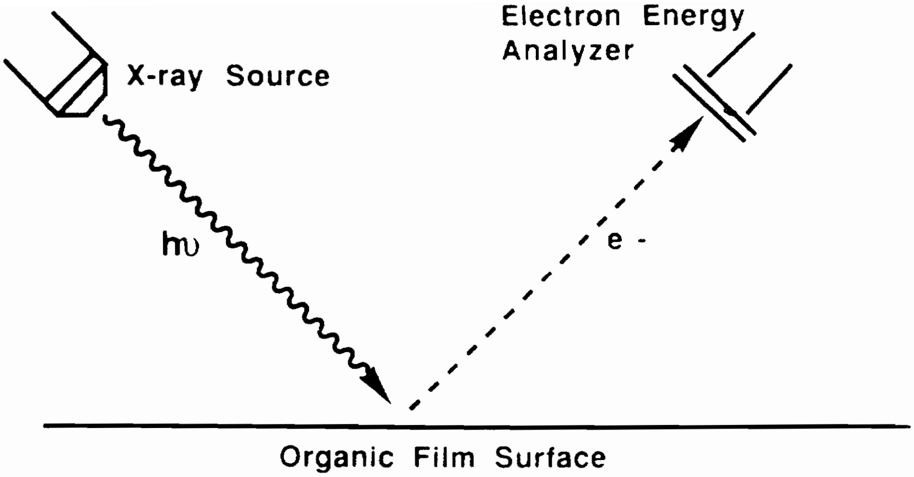

FIGURE 4(a) : Schematic representation of XPS set-up [28].

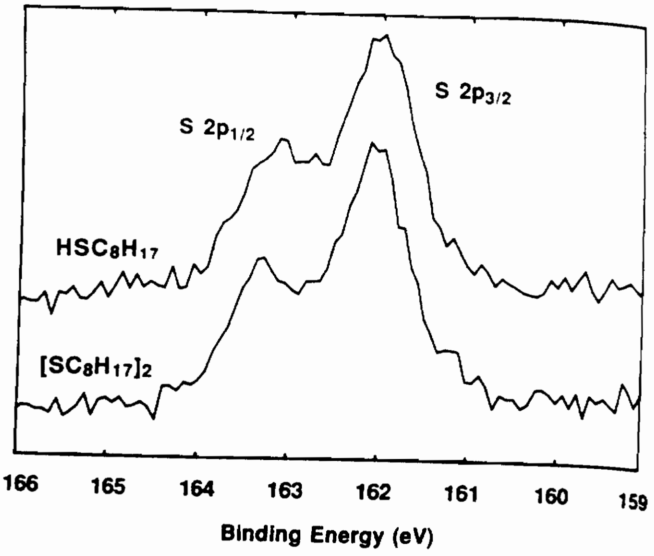

FIGURE 4(b) : XPS spectra of octanethiol and dioctyl disulfide monolayers on gold [39].

UV-vis: This technique allows for the determination of concentration, molar absorptivity, absorbance, or, qualitatively, changes to electronic transitions of the compound. A sample of concentration (c) in a suitable solvent is placed in a cuvet of known width (b). Another cuvet of the same width is filled with the solvent only and serves as the reference cell. A beam of light of known power (Po) is directed at the sample and reference cells, and the power that is transmitted (P) through the sample is measured on the other side. The percentage of the original power that passes through the sample is the transmittance (T) and is related to absorbance (A) as seen in the following equations:

$$T = P/P_o$$

$$A = -\log T$$

The absorbance is important as it is directly related to the concentration of the light-absorbing chromophore species in the sample. Beer's Law provides this relationship:

$$A = \varepsilon bc$$

where ε is the molar absorptivity (or extinction coefficient) [25]. The extinction coefficient can be used by comparing it to the estimated value for full monolayer coverage in an effort to determine if the sample is a molecular monolayer or not.

Chromophores in monolayers lend themselves to being studied via UV/Vis spectroscopy. They tend to have very characteristic absorption spectra which can provide averaged orientation and organization data about the monolayer.

The spectra will vary in strength of transmittance depending on the polarization and incidence of the radiation going through the sample as shown in Figure 5. The lack of a peak for the normal incidence and the s polarization spectra indicates a vertical orientation of the transition moment [53, 54]. Potential problems may occur in that there may be no absorbance or transmittance for specific combinations of light polarization and molecular orientation. One example occurs if the molecule being investigated has many substituents. All of the dipole moments within the molecule may cancel when the substituents are properly oriented. The polarized light being sent through the sample might not interact with such molecules and thus show no absorption or transmission.

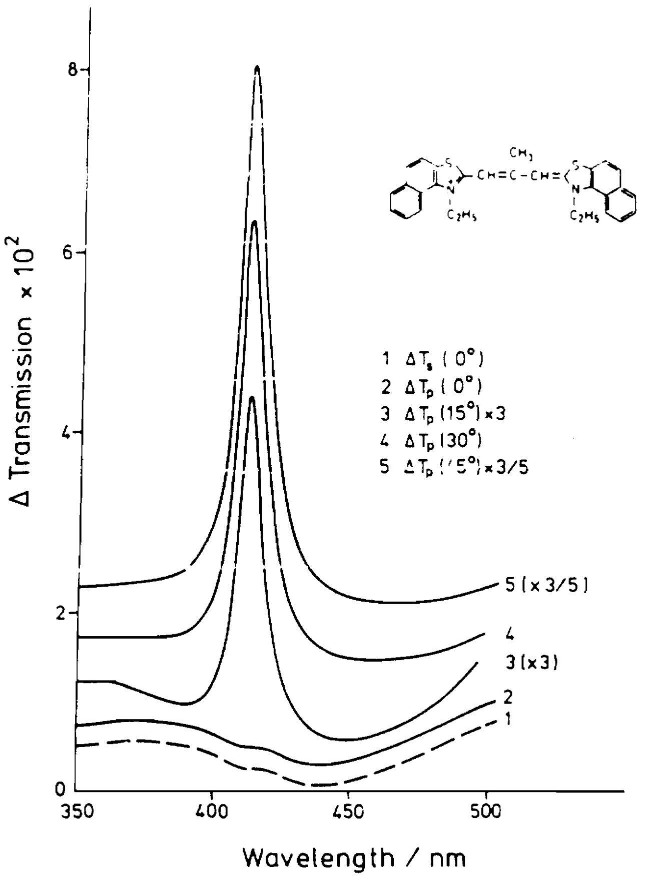

FIGURE 5 : UV/Vis spectra of CY3 (a cyanine dye) showing differences due to angle of incidence and polarization of radiation [54].

FTIR: This technique can provide information about molecular orientation within a sample. The IR spectra can also indicate packing density of the adsorbate and provide information on bonding between the adsorbate and the surface [16, 34].

The Michelson interferometer is the basic model for most interferometers used in IR spectrometry today. It is a device that is capable of splitting a beam of radiation into two paths and then recombining the two beams once a difference in their paths has been introduced. The path differences cause interference between the two beams to occur and, upon recombination, the resulting beam exhibits intensity variations from the original beam. These variations in intensity can be measured as a function of the path differences and this data will ultimately provide the spectral information [33].

Infrared external reflection spectroscopy (IR-ERS) is quite suitable for studies of monomolecular assemblies [34]. This specific technique can probe the spatial arrangement, or orientation, and the composition of monolayer films at surfaces that have either high or low IR reflectivities. The equation used to quantitatively calculate the average spatial orientation for interfacial surface structures is presented below:

$$\cos\ \theta = A(obs)/(3 * A(calc)).$$

The absorbances (A), both observed and calculated, are of a specific vibrational mode. The angle of orientation, Θ, is of the same vibrational mode with respect to the surface normal and is related to the molecular axis of the adsorbate in order to achieve the spatial orientation of the surface structure as desired [34].

Tripp and Hair demonstrated the usefulness of IR in their study of octadecyltrichlorosilane on silica. They were able to show that there is no direct reaction between the silane derivative and the surface hydroxy groups. As shown in Figure 6, the difference spectra (c and d) from the spectra of OTS and outgassed silica (a and b) show no spectral changes to the surface hydroxy groups upon adding OTS [31]. These IR spectra give no evidence that a covalent bond is formed as was previously thought.

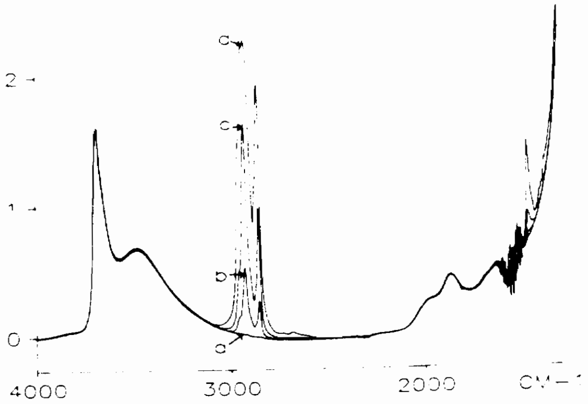

FIGURE 6(a) : IR spectra of the addition of varying amounts of OTS to degassed Aerosil 380 [31].

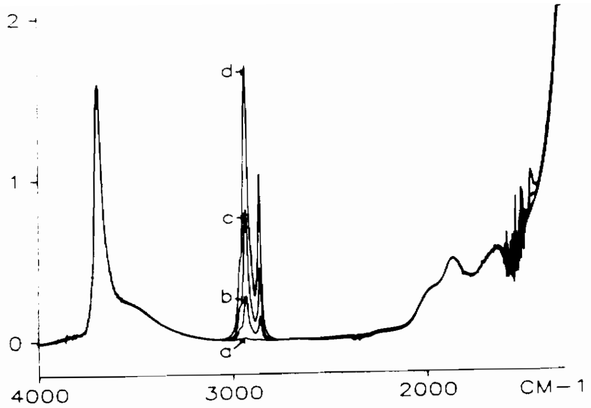

FIGURE 6(b) : IR spectra of the addition of varying amounts of OTS to degassed Aerosil 380 [31].

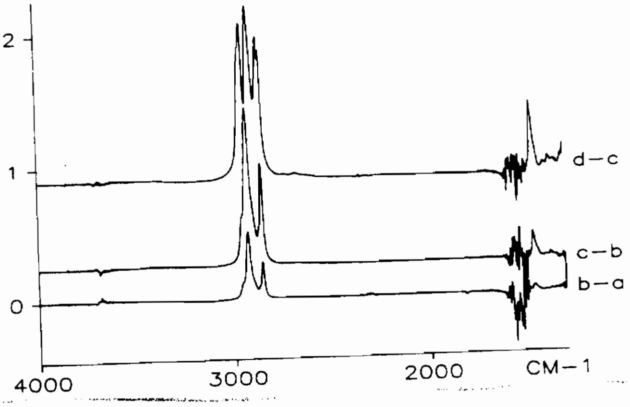

FIGURE 6(c) : Difference spectra for curves in Figure 6(a) [31].

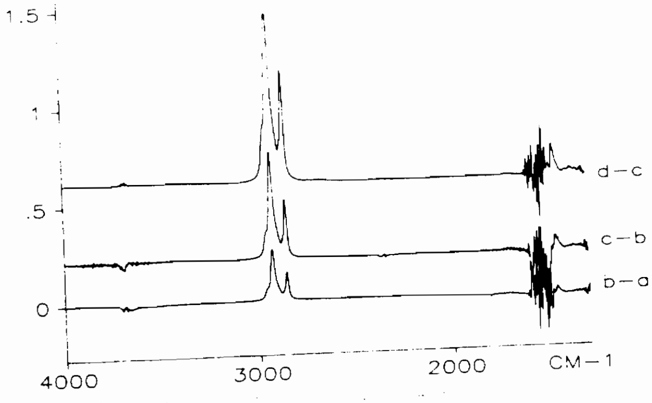

FIGURE 6(d) : Difference spectra for curves in Figure 6(b) [31].

Raman: This spectroscopic technique is similar to FTIR in the information it can provide. Based on Raman scattering, Raman spectroscopy can give details on thin film conformation, orientation, structure, and interfacial intermolecular interactions such as bonding [16, 35, 36].

The Raman effect is, simply, a light scattering effect. Upon interacting with some material, a beam of monochromatic light will acquire a change in the frequency of some small percentage of its intensity. This will cause either a new frequency signal to appear or an already present signal to increase somewhat. The change in frequency is a result of coupling between the incident radiation and usually the molecular vibrational energy levels, but possibly also the electronic and rotational energy levels [35].

Harrand has presented a series of papers on the polarized Raman spectra of monolayer films [55-57]. The author discusses the need for careful interpretation of polarized Raman spectra for thin films as the exciting beam into the sample is rarely strictly perpendicular to the scattered beam. This presents the researcher with complex spectra that must be analyzed appropriately [55, 56]. Even with such complexity, the author is able to show that such Raman spectra can give information on chain conformation [57].

The schematic for the more recent Waveguide Raman Spectroscopy (WRS) is presented in Figure 7. This specific technique is of value when studying thin films and monolayers because it increases the scattering volume and the optical field intensity inside the film. This provides a high signal to noise Raman spectrum, thus making the characterization of submicron films via Raman spectroscopy easier [36, 37].

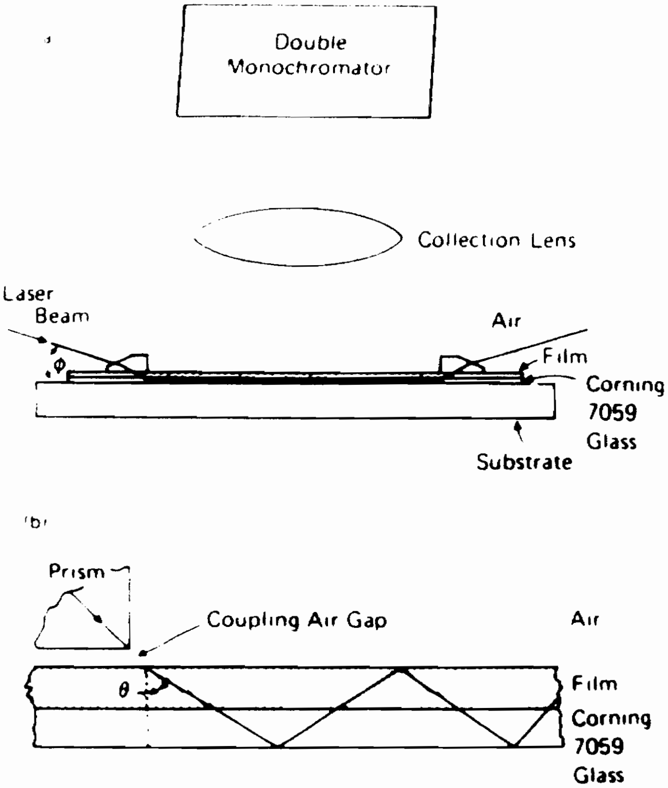

FIGURE 7 : Schematic of setup for WRS and actual wave propagation [36].

SIMS: Although destructive, this technique provides useful information about molecular surface structure. By bombarding a sample with a pulsed primary ion beam, secondary ions are released from the outermost layers of the surface [4, 16]. The primary particles can be electrons, photons, ions, or neutrons. The emitted species, as shown in Figure 8(a), can be neutral species, atoms, molecules, electrons, or atomic and cluster ions. The emitted particles are detected and analyzed by a mass spectrometer. A diagram of the equipment components needed for SIMS is presented in Figure 8(b). This analysis provides a mass spectrum of the surface from which the chemical composition of the surface is determined [38].

A more recent development known as static SIMS (or SSIMS) may allow for the determination of chemical structure as well as elemental composition [38]. Static SIMS refers to the fact that the primary ion beam used has a much lower current density. The low current density means less damage to the monolayer surface and causes the secondary ions to be emitted from previously undamaged regions [38].

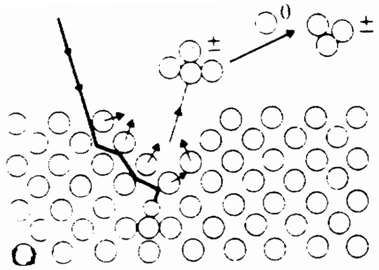

FIGURE 8(a) : Schematic of secondary ions emitted during SIMS [38].

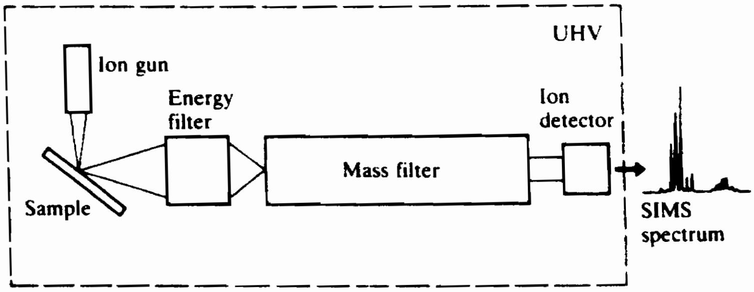

FIGURE 8(b) : Schematic of SIMS equipment setup [38].

STM and AFM: Scanning tunnelling microscopy, instead of providing information based on whole-sample averages, is capable of determining characteristics at an atomic level. This technique uses an extremely sharp tip (ultimately one atom in size) that is conductive and can image a similarly conductive surface at the atomic level. Control of this tip is achieved using a piezoelectric x,y,z scanner. The amount of space between the sample surface and the tip of the microscope is controlled by a voltage to the z piezo element. The distance is monitored and controlled by a feedback circuit which measures the current caused by electrons tunneling across the space between the sample and the tip as shown in Figure 9(a). All of this allows the STM to provide a three dimensional image of the sample surface [27, 32].

Atomic force microscopy, like STM, provides atomic level characterizations. The major advantage of AFM over STM with respect to organic films is that it does not require a conductive sample. Topographic imaging in AFM is achieved by a spring-mounted diamond tip and a sensor that measures the deflection of the spring as shown in Figure 9(b). The spring deflection is due to the interatomic forces between the sample and the tip [27].

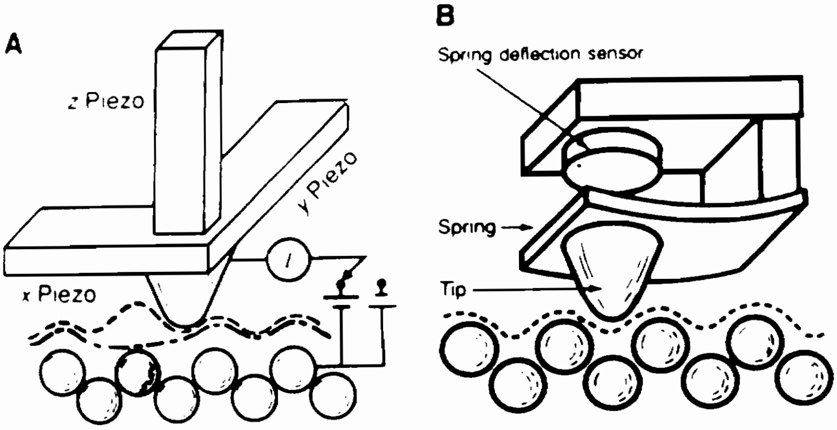

FIGURE 9 : (A) Schematic of the piezoelectric scanner used in STM [27].
(B) Schematic of the spring-deflection scanner used in AFM [27].

PATTERNING

Three reported methods of controlled patterning using self-assembled monolayer films will be discussed in this review. The three methods differ in the processes used to form the pattern as well as in the molecular orientation of the system that is created. Resists and conventional lithographic processing are used in one method to form coplanar assemblies [8]. These assemblies form patterns in the plane of the substrate. Simultaneous coadsorption onto a substrate of two different surface materials is used to form orthogonal systems in the second method. These assemblies form stepped patterns on the substrate [9]. The third method, which uses deep ultraviolet irradiation, is another way to form coplanar molecular assemblies [10]. Though the procedures and end products vary, the patterned films have similar potential applications.

Patterning Methods of Kleinfeld and Co-workers

The first patterning method to be discussed is the one initially presented by D. Kleinfeld, K.H. Kahler, and P.E. Hockberger in The Journal of Neuroscience (November 1988, 8(11): 4098-4120). The authors were trying to control the outgrowth of neurons by using substrates patterned with small organic molecules. The molecules provided selective adhesive properties with respect to the dissociated neurons. Such a setup would allow the scientists to reintroduce some two-dimensional order into the cell cultures which have lost the three-dimensional cytoarchitecture found in living tissue. Using this method, the authors were able to create patterns from 50 um down to less than 10 um.

To produce such selectively adhesive patterns, both photolithography and surface chemistry methods were performed. The surfaces chosen for this work were silicon or quartz and the small organic molecules chosen to promote or prevent adhesion were silane derivatives. These choices were probably due to the facts that silanes adsorb well to silica and that silane chemistry is well documented in the literature [11-15]. (See Figure 1 for the general reaction of chlorosilanes with a silicon surface [8].) To design regions of selective cell adhesivity, the silicon or quartz surfaces were coated with a photoresist, lithographically exposed using a mask of the desired pattern, and etched to remove the resist from the exposed areas to provide a lithographically defined surface. Once the resist was removed from these areas, the exposed silicon surface could have the selected silane chains bound to it to form low cell-adhesivity patterns. Then the remaining resist was stripped from the silicon surface and amine derivatives were bound in the newly exposed areas to create regions of high cell-adhesivity. This procedure, as shown in Figure 10 , created a chemically defined surface for cell adhesion.

This first patterning method produces a coplanar system (with respect to the plane of the substrate) of orthogonally oriented self-assembled films with fairly small features (10-50 um). This resulting coplanar pattern is a relatively new achievement, and since control over the patterns out of the plane of the substrate is very precise, this new method allows for further versatility in creating patterns. One of the biggest drawbacks to this procedure is the large number of processing steps required to produce a usable patterned surface [10]. This could limit its potential usefulness when there are constraints on time and materials.

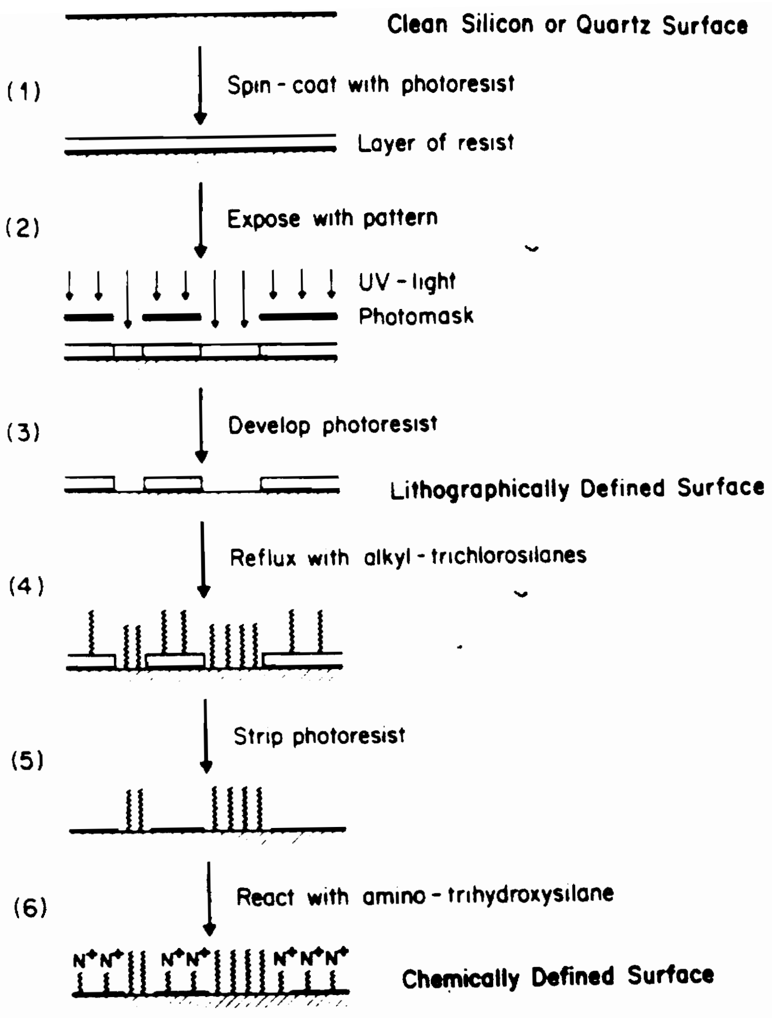

FIGURE 10 : Schematic representation of the steps involved in the Kleinfeld, Kahler, and Hockberger patterning method [8].

Patterning Methods of Wrighton and Whitesides and Co-workers

The second method for patterning self-assembled monolayers comes from P.E. Laibinis, J.J. Hickman, M.S. Wrighton, and G.M. Whitesides in Science (August 1989, 245: 845-847). The authors were trying to simultaneously control orthogonal self-assembly of alkanethiols on gold and of alkane carboxylic acids on alumina. They were also hoping to achieve patterns in the plane of the monolayer. Using this particular method, the authors were able to create patterns of dimensions on the order of one micrometer.

To get this coadsorption to work, a substrate with two different surfaces had to be produced. To do this, a gold substrate was masked and aluminum was evaporated onto the gold. The aluminum oxidized to aluminum oxide upon exposure to air and the end product was a substrate with patterns of gold and aluminum oxide. This substrate was then soaked in a solution containing both alkane carboxylic acid and alkanethiol in isooctane. Upon removal from the solution, the substrate had preferentially adsorbed the thiol compound in the gold regions and the carboxylic acid compound in the aluminum oxide regions [9]. This procedure is represented in Figure 11.

This patterning procedure produces not only patterns out-of-plane with respect to the monolayer, but it also produces patterns that are in-plane with respect to the monolayer.

However, one drawback to this method is that the patterns created are not truly coplanar with respect to the monolayers due to the metal "steps" that are formed when the aluminum is evaporated onto the gold in a thickness of about 500 Å [9]. Another drawback is that monolayers made from compounds with similar surface attachment chemistry need a single material substrate [10]. Such a substrate is not possible with this method since it utilizes a surface with different material regions.

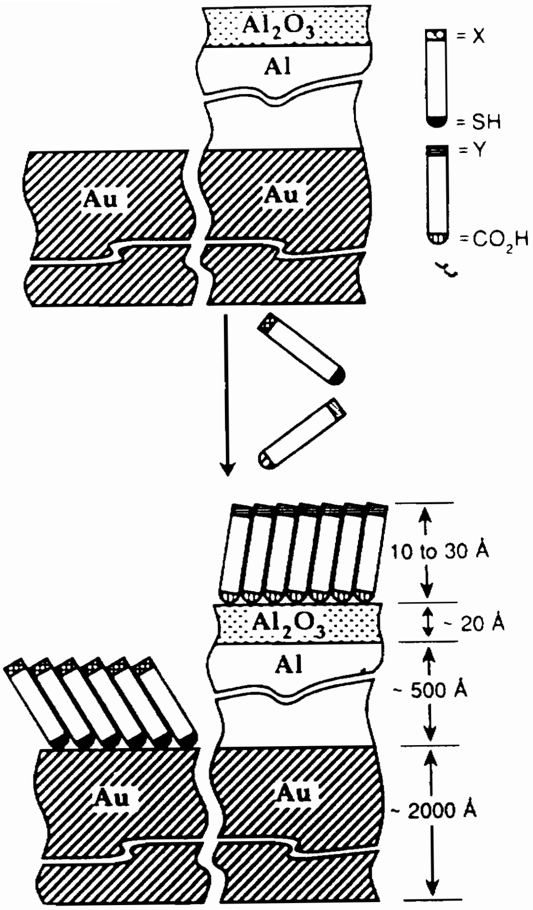

FIGURE 11 : Schematic of the steps involved in the Wrighton and Whitesides patterning method [9].

Patterning Methods of Calvert and Co-workers

The third and final method for patterning self-assembled monolayers comes from C.S. Dulcey, J.H. Georger,JR., V. Krauthamer, D.A.Stenger, T.L.Fare, and J.M. Calvert in Science (April 1991, 252: 551-554). In their paper, the authors were trying to improve upon the above two methods and produce patterns that were not only orthogonal in nature, but also truly coplanar - and all through a simpler, quicker method. The materials to be patterned were organosilanes on substrates of glass or fused silica slides, silicon wafers, and platinum films on silicon substrates. Using this method, the authors were able to create patterns in the tens of micrometers dimension range.

To produce these patterns, the cleaned substrates were soaked in solutions of the organosilanes in an organic solvent. This put down a self-assembled monolayer of whatever compound was desired as shown in Step 1 of Figure 12. Next, the samples were irradiated with deep ultraviolet light from one of two excimer lasers having either a 248nm or 193nm light source as shown in Step 2(a). The irradiation was done through a mask to provide both exposed and unexposed regions which would be reactive and unreactive, respectively. The phenyl rings of the monolayer absorbed the irradiation and were removed from the film in the exposed areas as shown in Step 2(b). Upon exposure to air, the film absorbed moisture to form hydroxy groups in the exposed regions as shown in Step 2(c). The unexposed phenyl rings are unreactive to further monolayer deposition while the hydroxy groups readily react with silanes for subsequent self-assembly. This allows for the deposition of another film in the exposed areas and thus creates the in-plane (with respect to the substrate) pattern as shown in Step 3 of Figure 12. Out-of-plane patterns could also be built using organosilanes or other compounds that adsorbed to the various regions of the sample [10].

The two major drawbacks to this patterning method are that the pattern features are still in the micrometer size range and that the equipment necessary for the patterning in expensive and not readily available to many laboratories.

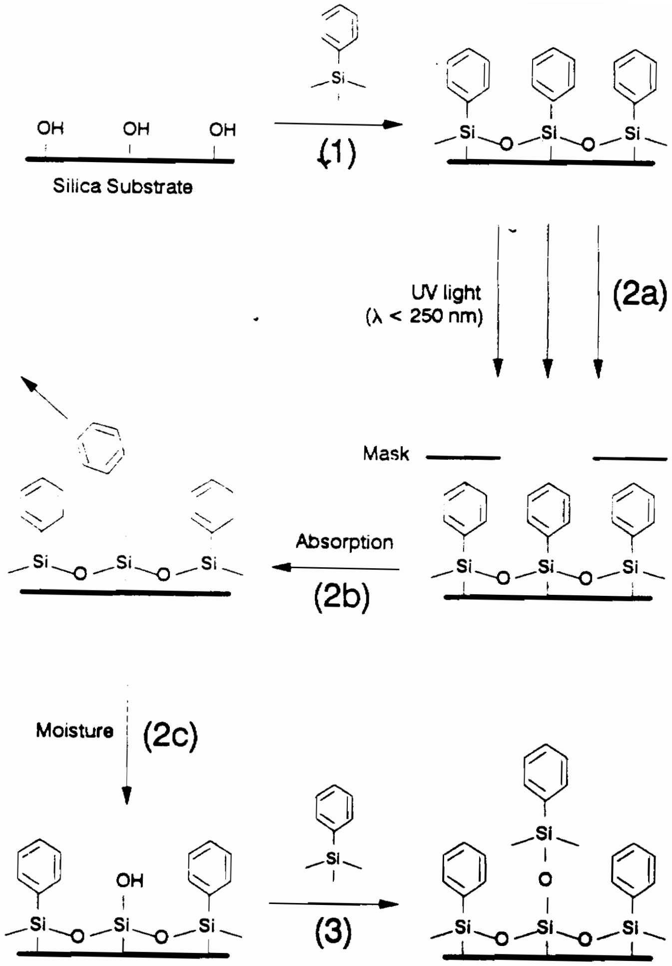

FIGURE 12 : Schematic of the steps involved in the Calvert patterning method [10].

Other Patterning Methods

Only two of the three self-assembled monolayer patterning methods presented in this paper have continued to appear in the literature. The method described by Wrighton and Whitesides was preceded by coadsorption, first of thiols on gold [26], and then of thiols and disulfides on gold [39]. More recent usage of this particular method has been directed towards patterning redox active molecules on platinum and gold [40]. The other method currently in use is the one described by Calvert, et al. This group continues to present their findings on deep UV lithography and photochemistry of self-assembled monolayers as a means of patterning [41-44].

One area of interest which these two methods seem to be converging on is biology. Both systems of patterning monolayer films are being utilized in studies of patterned biomolecular assemblies [45] for use in neuron cell adhesion [46] and protein adsorption [47]. Though their method was too cumbersome, Kleinfeld, Kahler, and Hockberger were apparently researching a topic that would become of much interest.

Whitesides and Wrighton are also currently working on new methods of patterning self-assembled monolayers. In addition to lithography, micromaching can be used to fabricate high-resolution patterns when combined with selective etching [48]. Figure 13 shows an example of how micromachining forms patterns. This method uses an alkanethiolate self-assembled monolayer on gold which is subjected to micromachining to expose bare gold regions. The exposed substrate areas are then covered by the formation of a second self-assembled monolayer [49]. The generated patterns are quite useful in manipulating wetting and adhesion at surfaces.

The most recent additions to the various methods of patterning self-assembled monolayers are microwriting and "rubber stamping" [50]. Microwriting currently has been done using a pen filled with long-chain alkanethiol which is used to draw single molecule thick line patterns on gold. This procedure is followed by a selective etch of the uncovered gold in order to make the lines permanent. The lines have been drawn as narrow as 1 um thick [50, 61]. The "rubber stamping" method involves transferring a lithographically defined pattern into a piece of polymer. The patterned polymer stamp is then dipped into alkanethiol as a source of "ink" and pressed onto a surface of choice. This transfers the pattern as a rubber stamp transfers its own inked pattern. The patterns produced have had features on the scale of hundreds of nanometers [50].

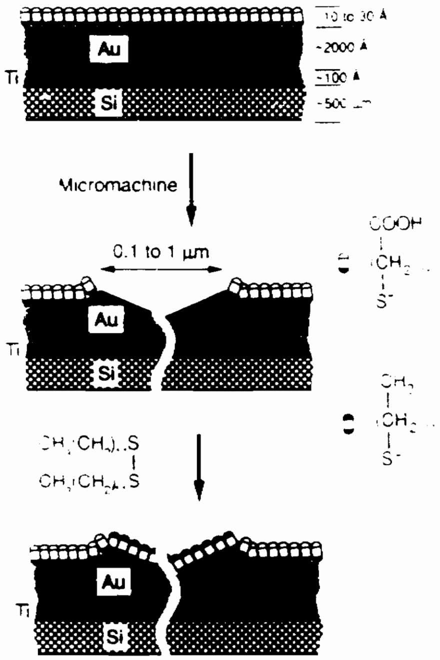

FIGURE 13 : Schematic of the steps involved in the micromachining patterning method [49].

SUGGESTIONS FOR FUTURE RESEARCH

All of these newer methods of patterning are useful as they do not require elaborate apparatus to which many labs have no access. This allows many more researchers to delve into this field as these procedures can be done in the open laboratory and they provide a high degree of precision which is comparable to the methods using the more expensive equipment [49, 50].

Continuing research on methods of patterning self-assembled monolayers is necessary. While the ability to pattern thin films and have some amount of control over their organization has been growing in huge steps, the knowledge about how the monolayers are actually forming at the surfaces seems to be miniscule [51, 52]. There is still no direct evidence for covalent bonding of the monolayers to the substrates [31]. Questions like "How are the molecules attaching to the surfaces?" and "How are the molecules interacting with each other to affect the properties of the films created?" still need to be answered in much greater depth. The first question of how the molecules of the monolayer are attaching to the substrate is beginning to be studied by Tripp and Hair. They are investigating various alkylsilane systems using IR spectroscopy [31, 58, 59]. Obviously, IR spectroscopy is one method that could be quite useful in studying other monolayers. NMR spectroscopy (perhaps of silicon) and XPS/ESCA might also be useful in characterizing surface attachments.

Ultimately, one might hope to be able to pattern features at a level much less than the currently available hundreds of angstroms. However, being able to create a pattern molecule by molecule is still in the future.

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References: Available upon request.

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