Surface Characterization of Thin Polymer Films Deposited By Plasma Enhanced Chemical Vapor Deposition (PECVD) Using Water Contact Angle Measurements

Semienawit B Ghebrezadik, Chemical Engineering
Dr. John F. Evans Department of Chemistry
University of Minnesota Duluth

ABSTRACT

The purpose of this experiment is to explore the use of plasma polymerization in the preparation of thin polymer thin films for microelectronic, and sensor applications ranging from the fabrication of organic and inorganic optoelectronic structures to implantable medical devices. This method provides for the preparation of conformal coatings of predictable chemical structure and functionality by appropriate choice of film precursor (monomer) and operating conditions for the plasma discharge. The purpose of the coating is to either limit or promote the tissue growth when the device is implanted in human body depending on the application. Issues relating to adhesion, selective permeation and protection of the sensor or electronic structures can be addressed through the wide range of properties which can be imparted to the layered structure of such systems.

Of particular importance to the understanding of the stability and performance characteristics of such films within the ultimate device structure is the surface energy, surface tension and solvent compatibility of the plasma polymerized thin films. A practical approach to characterize the surface properties and energetics, along with compatibility of the films in the host environment in the long term involves the use of the sessile drop method of contact angle (CA) measurement, using the appropriate testing water on Teflon-like surface film precursors for fluorocarbon films and 1-octen (1-OT) for hydrocarbon films which were introduced in the gas run on sentence break into 2 or 3 phase into a plasma reactor powered at 13.56 MHz through a capacitively coupled external electrode. Where transform IR (FT-IR) experiments allow for the analysis of the bulk of the deposited films, contact angle measurement using water as the test liquid probe the surface polarity and stability of those materials. In all cases, the surface energies and solvent compatibilities can be measured immediately after preparation by contact angle measurements, and their stability over time can also be evaluated conveniently by this technique.
Contact angle measurements have also been applied to surface characterization of thin polymer films deposited on silicon and indium tin oxide substances.

**Introduction**

*Plasma polymerization.* The plasma state is one of the four states of matter (solid, liquid, plasma and gas). The plasma state is a gas that heated to the point where it begins to release electrons. Although plasmas occur naturally on the sun and other stars, it is artificially produced in fluorescent lights and plasma displays by electrically charging gas in order to release ultraviolet light. Partially that is full ionized gas consisting of equal numbers of positive ions, and negative ions and a different number of un-ionized neutral molecules. To maintain a stable numbers of electron and ion densities, the recombination process has to be balanced by an ionization process i.e. an external energy source is required and this particular energy sources is electric field which can act directly on the charged particles only.

Electric glow discharges are a type of plasma that are formed by passing a gas or noble gas or it could be made by applying a potential between two electrodes in a gas. Glow discharge technology is used in variety areas of lighting, TV, plasma physics and etc. It is most often operated in direct current mode, but it also can be operated in radio-frequency mode.

When ion and electrons hit the wall of the vessel containing the plasma they combine together and are lost. Because electrons have much higher velocities than ions, they are lost faster and leave the plasma with a net of positive potential compared to the wall. The sheath is formed by the interaction of the plasma with boundary material. The contact layer of charged particles which exist between plasma and its surrounding walls, electrodes, or other plasma is called sheath. A plasma sheath forms around a spacecraft during reentry and interrupts or interferes with communication with the ground.

A plasma discharge can be use to energy to activate or fragment gaseous or liquid monomers, often containing a vinyl group, in order to initiate polymerization. In this case plasma polymerization is used to deposit polymer thin films and by selecting monomer types and the energy density, the chemical composition and structure of resulting thin films can be varied over a wide range.

*Surface tension:* It is caused by the attraction between the molecules of the liquid, due to various intermolecular forces. In the bulk of the liquid each molecule is pulled equally in all directions by neighboring liquid molecules, resulting in a net force of zero. At the surface of the liquid, the molecules are pulled inwards by other molecules deeper inside.
the liquid, but there are no liquid molecules on the outside to balance these forces, so the surface molecules are subject to an inward force of molecular attraction which is balanced by the resistance of the liquid to compression. There may also be a small outward attraction caused by air molecules, but as air is much less dense than the liquid, this force is negligible. Surface tension is measured in Newton’s per meter ($\text{N} \cdot \text{m}^{-1}$), is represented by the symbol $\sigma$ or $\gamma$ or $T$ and is defined as the force along a line of unit length perpendicular to the surface or work done per unit area. The force, $F$, involved in stretching a film is: $F = \gamma L$ where $\gamma =$ surface tension (a constant of the material undergoing deformation). This means: $\gamma = F/L$ i.e. force/unit length (Units: N/m or mN/m).

**Surface Energy:** Surface energy quantifies the disruption of chemical bonds that occurs when a surface is created. Surface must be intrinsically less energetically favorable than the bulk of a material; otherwise there would be a driving force for surfaces to be created, and surface is all there would be. The surface energy is related to the work required to produce the surface: $dW = dG = \gamma L\, dx = \gamma \, dA$. This means: $\gamma = dG/dA$ (i.e. free energy/unit area with units of J/m² = N/m). The surface chemistry and surface morphology are correlated with the surface energy as indicated by contact angle measurements.\(^{11}\)

**Contact Angle:** Contact angle measurements have been applied to surface characterization of thin polymer films deposited on silicon and indium tin oxide (ITO) surfaces. This technique allows for the direct measurement of surface energetics through the use of drop of test liquid placed on the surface of the material of interest. Contact angle measurements are a simple-to-adopt method for surface analysis related to surface energy and tension. The contact angle is the angle which encloses the tangent line on the drop shape from the three-phase point to the base line on the solid surface (see fig. 2). The contact angle is a measure of the wettability of a surface or interface with a different liquid phase; the smaller the contact angle the better the wettability. When drawing a tangent line from the droplet to the point where the test liquid touch as the
solid surface, the contact angle is the angle between the tangent line to the drop surface of the and the solid surface.

![Diagram of contact angle measurement](image)

Figure 2. Depiction of a contact angle measurement.

Figure 2 above shows that a contact angle is formed in the three phase contact between air, liquid and solid surface. The difference between the advancing and receding contact angle values is called hysteresis. It has been used to help characterize surface heterogeneity, roughness and mobility. It can be measured in four different ways on a horizontal surface.

1. The instant contact angle where the liquid drop is released from a capillary and the contact angle are directly measured.

2. Advancing contact angle, where the capillary is put inside the droplet and liquid is continuously pumped into the droplet.

3. Receding contact angle, where the liquid is withdrawn from the droplet.

4. Equilibrium contact angle. It is very hard to define when the drop has reached its equilibrium. For some systems it can take hours for the drop to relax to thermodynamic equilibrium. In these cases it is problematic because the drop has surely been evaporated by then.
Normally the contact angle can be measured within a few degrees. The accuracy is depending on the surface chemical heterogeneity and the surface roughness. Generally contact angle increases with increasing surface roughness on hydrophobic surfaces. The technique is extremely surfaced sensitive and hence sensitive to surface contamination. Very soft surfaces can be deformed in the three phase contact and cause wrong evaluation of contact angle.

Young’s Equation \( \theta_{SV} - \theta_{SL} = \theta_{VL} \cos \theta \)

Young equation interrelate contact angle and surface tensions of the liquid and solid phases. [5] The interfacial tension of water/air \( (\theta_{L_A}) \), water/solid \( (\theta_{L_S}) \), and solid/ air \( (\theta_{S_A}) \) determines the contact angle of water droplet on a given film surface and it is define by the Young’s equation. [27]

“According to Young’s equation, the maximum contact angle can be attained by lowering the surface energy of a flat surface and also the equation can only be applied to a smooth and homogeneous surface.” [27]

**Background on the Application of Contact Angle Measurements**

The discovery of wetting as a topic of physical science dates back two hundred years, to one of the many achievements of the eminent British scholar Thomas Young. He suggested a simple equation relating the contact angle between a liquid surface and a solid substrate involving the interfacial tensions. In 1805 Thomas Young in the *Philosophical Transactions of the Royal Society of London*, that is when he defined contact angle as “the interaction between the forces of cohesion and the forces of adhesion which determines whether or not wetting, the spreading of a liquid over a surface, occurs”. If wetting does not occur, then a bead or drop of liquid will form, with a contact angle which is a function of the surface energetics of the system.

Today when we refer too non-spreading liquid we mean that \( \theta \neq 0^\circ \), and when the liquid spreads freely or wets the surface to indicate that the \( \theta = 0^\circ \). Because there is always some adhesion of any liquid to any solid wettability differs to extreme of \( 0 < \theta < 180^\circ \). Because the ability for the liquid to spread increases as \( \theta \) decreases, the contact angle is useful or helpful to invest the measure of spreadability or wettability.

The contact angles of sessile drops were experimentally investigated in the electric field. It was found that contact angle of polar
liquid such as alcohols increase in the electric field. Increasing in contact angle is a manifestation of the effect of the electric field on interfacial tensions, due to the lack of mobility of the molecules of shift in contact angles. Therefore, it is believed the observed shift in contact angle is consequences of change in liquid interfacial tensions. It was found that the shift in contact angle of alcohols in an electric field is larger for liquids with long-chain molecules.

An electret state, formed as a result of modification, can an increase in the surface energy\(^1\). Surface charge densities and contact angles of dielectric polymer whose surface were activated under identical conditions, could be measured.

**Experimental**

A diagram of the plasma reactor used in all the plasma experiments is shown in Figure 3. The substrate sits on the substrate holder and can be adjusted to control the position of the substrate within the reactor.

![Figure 3: Diagram of the plasma reactor used during the experiments.](image-url)
A vacuum pump, flow controller, power supply, matching network, HFPO, HFP and 1-octene were used to control and maintain the glow discharge. Electronic grade silicon was used as the substrate for deposition experiments.

The substrate positions for the HFP experiments were located at 0, 6, 8, 9, 10, 11 and 12 cm with respect to the furthest downstream point. The substrate position for the HFPO experiments were at the 0 cm position. The hot electrode (band in Fig. 3) was located at 12 cm on this scale.

Fourier transform infrared spectroscopy (FT-IR) was used to characterize the chemical composition of the polymerized thin film. Integration of selected peaks in the FTIR spectrum was used for analysis. In particular, integration of fluorocarbon region (~900-1500 cm\(^{-1}\)) and hydrocarbon region (~2850-3000 cm\(^{-1}\)) in the FT-IR spectra.

All contact angle measurements were made using de-ionized, distilled water as the test liquid. A digital camera (Canon model S2 IS) was used to capture contact angle information. The macro/manual focusing capability of this camera is an essential feature which enables quality measurements to be made. The contact angle apparatus (Figs. 4 and 5) was set up to make sure the drop of water is leveled up to the camera. The inclusion of a razor blade allowed for convenient focusing of the camera lens system on the middle of the water drop. To capture the image with out having light from the camera flash and the light from the back ground affecting it, we use a piece of card board to limit the light from the surrounding. Also to make sure there was enough light, we use stand light from the top and sometime from the side to make sure the image would turns out to be to light or back. The tools use to make to apparatus were very flexible to move around for focus.
The unique macro focusing features of the camera made the experiment very easy to work with and generally 5% relative uncertainties in the measured contact angles were found. Images were transferred to a laptop computer from the camera memory, enhanced using Adobe Photoshop and the angles measured after superimposing the tangent to the water drop at the point of contact with the surface of interest. A typical result is shown in Fig. 6, below.
Results and Discussion

We have investigated the application of contact angle measurement to characterize the surface energetics of a variety of plasma-treated surfaces. These include indium-tin oxide (ITO) and thin polymer films deposited from plasma discharges. In the later category, we have examined three different polymer film types: 1) hydrocarbon films deposited using 1-octene (OT), 2) fluorocarbon films using hexafluoropropene (HFP) and hexafluoropropene oxide (HFPO) and 3) copolymer films prepared using a mixture of OT and HFPO as the discharge gases. Furthermore, the use of a grid placed over the substrate (single crystal silicon) to minimize the role of ion bombardment was also explored in the case of films derived form plasma discharges conducted in HFPO. In some cases the use of reducing plasmas where hydrogen was used as the discharge gas, or oxidizing plasmas in which air was fed into the discharge was examined to explore the further modification of the plasmas-deposited hydrocarbon, fluorocarbon or copolymer film surfaces. In many cases the effect of exposure to atmospheric oxygen after deposition was also explored to ascertain the extent to which the surface composition was stable. In all cases contact angles are reported for a 95% confidence interval.

Cleaning of ITO surfaces using air plasmas. Plasma cleaning of ITO using reactor settings of 50 W power, 6.4 sccm air flow rate, 300 mT steady state pressure for 5 minutes, gave rise to significantly decreased water contact angles. After cleaning the average contact angle was found to be 57.1 ± 3.6° (n = 17). This indicates that a highly polar (high energy) surface results from this treatment. It suggests that the non-polar, hydrocarbon surface contamination normally found on this surface can be very effectively removed by plasma cleaning. Future work will evaluate the long term stability of this clean surface upon prolonged exposure to laboratory air, which is naturally contaminated with low levels of hydrocarbon.

Hydrocarbon polymer films deposited using OT as the precursors. Plasma deposition of a hydrocarbon film at the 9 cm position using reactor settings of 10 W power, 360 mT steady state pressure for 60 minutes gave high water contact angles indicative of a low energy (non-polar) surface. Immediately after deposition the average of contact angle was found to be 100.3 ± 1.7° (n = 11). These results indicate that a highly non-polar surface is prepared under these conditions. Future work will investigate the affect ageing of these films in air over time.

Fluorocarbon films prepared using HFP as the precursor. Thin fluoropolymer films freshly deposited from HFP discharges with the substrate at the 0 cm position gave higher contact angles than those for freshly deposited hydrocarbon films (from OT, above), as would be
expected for a fluorocarbon material. Using reactor settings of 50 W power, 20.0 sccm flow rate of HFP and a 630 mT steady state pressure for 60 minutes gave a water contact angle of. Immediately after deposition the average of contact angle was found to be $96.5 \pm 1.4^\circ$ (n = 35). Aging of films in the laboratory ambient overnight showed no statistical change in the water contact angle ($99.3 \pm 2.9^\circ$, n = 8). When these films are modified using a brief air plasma treatment, which is known to introduce polar, oxygen-containing functionality on the surface, the contact angle decreases dramatically ($43.4 \pm 3.2^\circ$, n = 6).

**Fluorocarbon films prepared using HFPO as the precursor.** Thin fluoropolymer films freshly deposited from HFPO discharges (Using reactor settings of 50 W power, 20.0 sccm flow rate of HFPO and a 610 mT steady state pressure for 60 minutes) with the substrate at the 0 cm position also gave high contact angles ($97.9 \pm 4.6^\circ$, n = 6). Overnight aging again showed no loss of this low energy surface condition from post-plasma exposure to the lab ambient ($103.7 \pm 1.6$, n = 7). Intentional introduction of polar surface groups from an air plasma treatment, as above, also indicated conversion to a high energy surface similar to that seen for the HFP films ($46.2 \pm 5.7^\circ$, n = 4). Subsequent reduction in a hydrogen discharge (25 W power 20.0 sccm flow rate of HFP and a 300 mT steady state pressure for 3 minutes) gave higher water contact angles ($65.3 \pm 3.7^\circ$, n = 8) suggesting that the effect of air oxidation is only slightly reversible under these conditions.

**Fluorocarbon films prepared using HFPO as the precursor-modified deposition procedure.** It was found that the linear structure of the fluorocarbon films using HFPO as the precursor could be improved by placing a medium mesh stainless steel grid over the substrate during deposition. The grid was used to minimize cross-linking thought to arise from ion bombardment of growing film. For fluoropolymer films prepared under optimal conditions, which gave FT-IR spectra which were indistinguishable from conventionally prepared Teflon, the water contact angle measurements yielded results consistent with a linear chain structure ($104.8 \pm 2.2^\circ$, n = 7). The stability of these films is in question, however, as the water contact angle decreased slightly as the aged in the lab ambient ($99.7 \pm 1.4^\circ$, n = 13). This is consistent with the observation by others of high free radical content in these materials. Water in the lab abient is expected to react with these radicals, causing the introduction of polar functional groups such as hydroxyl and carbonyl functionality. While FT-IR spectra did not show appreciable signal in regions where these groups are expected to absorb, the contact angle measurements are more surface sensitive, that the FT-IR spectra due to the fact that the infrared beam sample s the entire thickness of the deposited films.
Co-polymer films prepared using a mixture of OT and HFPO. Preliminary experiments on copolymer films prepared using a mixture of OT and HFPO precursors (plasma conditions: no grid, $P_{\text{ss, HFPO}} = 400$ mT, $P_{\text{ss, OT}} = 150$ mT, 25 W, 30 min. deposition time) gave high contact angle results ($104.1 \pm 3.9^\circ$, $n = 6$), suggesting the resulting surface is more fluorocarbon-like than hydrocarbon-like. This hypothesis requires further scrutiny, however, owing to the small difference in water contact angle expected for these two surface types. Other test liquids, which are known to more readily discriminate between CH and CF surfaces, such as diiodomethane will be employed in future work on these copolymer films.

Summary and Conclusions

The utility of water contact angle measurements for the surface characterization of plasma-treated or plasma-deposited materials has been demonstrated using an apparatus based on a Canon digital camera. The results are consistent with parallel spectroscopic (FT-IR) analysis, yet provide additional surface sensitivity due to the more intimate interactions between the test liquid (water) and the region of primary interest (outermost surface). Contact angles measured on these thin films compare favorably with published values reported for bulk materials.

Acknowledgements

This publication is dedicated to my beloved family and friend (Quinnita Morris) and Colleagues (Research groups) at UMD who made the writing process easier in one way or another. Special thanks to Professor John F. Evans for giving me the chance to work with him and also for bringing out the hidden talents in me. For that I’m thankful for having him as my mentor and advisor. Last, but not least, I want to thank the McNair Staff at the University of Wisconsin-Superior for working hard and for giving me the opportunity to be a part of this experience.
Literature Cited


99


