Chapter 2

Experimental Techniques

This chapter describes experimental arrangement for studying electrowetting phenomenon on planar electrode and interdigitated wire free geometry. The essential electronic and optical arrangements are also discussed. The dip-coating technique used for deposition of insulators on conductive electrodes is discussed in length. The detailed information regarding contact angle (CA) measurement with optical contact angle (OCA) goniometer is given. The measurement of surface tension using pendant drop techniques is also added. In the later part of this chapter, various characterization techniques like ATR-FTIR, AFM etc are discussed in brief.
2.1 Electrowetting (EW)

Various electrode geometries are used to implement EW for basic studies as well as in the microfluidic applications. All these geometries are generalization of two generic geometries namely planar electrode and interdigitated electrode geometry which are described in the following section.

2.1.1 Planar electrode geometry

The schematic of electrowetting set up for planar electrode geometry is shown in figure 2.1. Here hydrophobic dielectric is deposited on a conducting surface such as Indium doped Tin Oxide (ITO) glass. The deposition of dielectric insulator can be carried out by adopting various techniques such as spin-coating, dip-coating, Chemical Vapour Deposition (CVD), Physical Vapour Deposition (PVD), Atomic Layer Deposition (ALD) etc. As mentioned earlier, low surface energy dielectric is essential for high CA at zero voltage so that a large CA tuning range is realized. Also flat surface topology is essential to reduce contact angle hysteresis (CAH) so that droplet can move without pinning on the surface. The liquid droplet mainly water is made conducting by adding suitable amount of salt like KCl or NaCl and a small volume is dispensed on the dielectric surface. The size of the droplet is kept below capillary length to avoid the effects due to gravitational force. The voltage source is connected between liquid drop and bottom electrode by means of thin wires. Due to sufficient conductivity of liquid, the charges are accumulated at the liquid-solid interface and the image charge of opposite polarity is generated at the bottom electrode. So the system becomes analogous to parallel plate capacitor.

The direct current (DC) or alternating current (AC) voltage can be applied as per the requirement. Nevertheless, applied AC voltage has some advantages over to DC voltage. The AC voltage continuously perturbs the force balance at contact line that leads to depinning of the contact line from the surface. Hence CAH is less for AC voltage as compared to DC voltage.\(^1\)\(^-\)\(^3\) It is observed that contact angle saturation in EW occurs at higher effective voltage for AC rather than DC voltage.\(^4\)\(^-\)\(^6\) It has been observed that the ion adsorption at the liquid–solid interface is reduced by applying AC instead of DC voltage.\(^3\)\(^,\)\(^7\)

In the present study DC voltages were applied by means of Keithley 2400 source meter. The amplitude modulated AC voltages were generated through a
function generator (HP 33120 A) and further amplified using high voltage amplifier. The contact angles were measured with optical contact angle (OCA) goniometer and analyzed using software from DataPhysics, Germany.

Figure 2.1: The schematic of planar electrode geometry set up employed for studying EW phenomenon.

2.1.2 Interdigitated electrode geometry

There is another popular geometry for electrowetting viz. interdigitated geometry. This is also called wire-free geometry because wire is not required to make electrical connection to the liquid droplet hence this geometry is extensively used in EW based applications particularly in microfluidic devices. The schematic of interdigitated electrode is shown in figure 2.2. The electric field in this geometry is non-uniform as shown. The conducting/dielectric liquid can be placed on insulating surface and the voltage is applied between the sets of electrodes as shown in figure 2.2. If EW is realized on dielectric liquid under high frequency AC signal then the phenomenon is also called as dielectrowetting.\(^5\) The voltage dependent CA change additionally depends on the liquid dielectric constant and electrode spacing along with applied voltage.

Figure 2.2: The schematic view of electrowetting setup on interdigitated geometry. The distribution of electric field lines across the electrodes is also shown.
2.2 Dielectric coating by dip-coating technique

We have extensively used a dip-coating technique for coating the dielectric layer on planar and interdigitated electrodes. In dip-coating method there is less wastage of solution and it offers a fair control over the film thickness.\(^9\) Initially the polymer solution is prepared in a suitable solvent. The solution concentration can be adjusted by the weight of polymer and volume of the solvent. The cleaned substrate is allowed to dip into solution bath with a controlled velocity. After that the sample is rested in solution bath for the specified time (in our case it is 5 sec.). The substrate is then retracted from the solution with a specific speed. The retracting speed mainly decides the film thickness. Landau and Levich showed that the thickness \(d\) of the entrained film is given by

\[
d = 0.94 \, l_c \, C_a^{2/3}
\]

where \(l_c = \sqrt{\frac{\gamma}{\rho g}}\) is the capillary length (\(\gamma\) and \(\rho\) are surface tension and density of the liquid solution respectively, \(g\) is gravitational acceleration) and \(C_a = \frac{\eta v}{\gamma}\) is capillary number (\(\eta\) is liquid viscosity and \(v\) is substrate velocity).\(^9-11\) Figure 2.3 shows the schematic of dip-coating process.

![Schematic of dip-coating technique.](image)

**Figure 2.3: Schematic of dip-coating technique.**

2.3 Characterization techniques

2.3.1 Contact angle measurement

The contact angle measurement is one of the basic characterization tools for measurement of surface energy of the substrate. Also the contact angle depends on
surface roughness and chemical composition. So the change in contact angle entails the change in surface roughness or chemical composition or combination of both. The contact angle is measured using optical contact angle (OCA) goniometer. Figure 2.4 shows a photograph of the system. The image of sessile drop is captured with a CCD camera (Watec-902 B) which is equipped with an adjustable magnifying lens. The contact angle is measured using software from DataPhysics, Germany.

![Figure 2.4: The photograph of OCA goniometer.](image)

In the drop shape analysis method a sessile drop is casted on the surface. The magnification and the focusing are manually adjusted for the best image. Firstly baseline i.e. the boundary of the surface is set manually. The ellipse fitting method is used for calculation of the contact angle. The fitted drop profile touches the baseline giving two points. The points of intersection between fitted drop shape and baseline correspond to the three-phase contact points of the system. The lines which pass through three phase contact points are drawn tangentially to the elliptical curve, fitted to drop image. The angle between these tangent lines and the baseline are measured inside the droplet giving left and right contact angles. The mean of these two angles is considered as a contact angle. Figure 2.5 (a) shows a snapshot of the contact angle measurement. Figure 2.5 (b) shows a schematic of contact angle measurement.
In case of AC as well as DC EW the applied voltage across the electrodes is varied in discrete steps using voltage ramp and at the same time contact angle is measured by a synchronized OCA system with voltage source. Figure 2.6 shows a photograph of the synchronized automated OCA system.

**Figure 2.5:** (a) The snapshot of contact angle measurement using ellipse fit to the drop profile. (b) Schematic of contact angle measured inside the droplet.

**Figure 2.6:** The photograph of a synchronized automated system for optical contact angle measurement.

### 2.3.2 Surface tension measurement by pendant drop method

The surface tension of liquid is an important property when wetting is concerned. In the present work we have measured surface tension of liquid by pendant drop method. A drop of the liquid is formed at lower end of the dosing needle called
as pendant drop. The surrounding medium can be gas or liquid. The shape of pendant drop is a result of two forces, the gravitational force, which elongates the drop and the surface tension force, which holds it in spherical form to minimize the surface area. The drop size is taken as big as possible. In the equilibrium state both the forces are balanced. The excess pressure $\Delta p$ inside the droplet is given by Young-Laplace equation as follows:

$$\Delta p = \gamma \left( \frac{1}{R_1} + \frac{1}{R_2} \right)$$

where $\gamma$ is surface tension and $R_1, R_2$ are radii of curvature.\(^{12}\)

At equilibrium the image of pendant drop is taken with the help of CCD camera. The magnification and focus are adjusted for the best image. Figure 2.7 shows snapshot of the pendant drop. For the mathematical analysis of drop shape the effect of gravity, which influences the drop, needs to be taken into account. Therefore, the knowledge of density difference between drop phase and surrounding medium is necessary. So the drop phase and ambient are defined along with the density values. Furthermore, the absolute drop volume must be known. Therefore, a length calibration is necessary. This is done taking the needle diameter as a reference length scale. Then the shape of drop is detected by carrying out image profiling. Eventually the surface tension is measured by Axisymmetric Drop Shape Analysis (ADSA) method.\(^{13,14}\)

![Figure 2.7: The snapshot of axisymmetric pendant drop.](image)
2.3.3 Thickness measurement by profilometer

The thickness of insulator film is an essential parameter that is needed to be known to estimate various parameters e.g. capacitance, electric field etc. The thickness measurement was accomplished using KLA Tencor P-16+ stylus profilometer. A sharp step of the film on substrate is required to carry out thickness measurement. Care is to be executed during deposition so that a sharp step of the film on the substrate is achieved. This stylus profilometer uses a diamond stylus for advanced profiling applications. The stylus is allowed to move laterally across the surface for a specified distance. While scanning, the stylus remains in constant contact with the sample surface by means of a user-specified force.\textsuperscript{15} The measuring principle is that a stylus is moved across the feature to be measured and the vertical displacement of the stylus is converted to a height value in Z-equivalent to the step height in the feature studied. By dragging the stylus over the surface the cantilever will move in Z-direction (up/down) and the force that the stylus impinges over the sample is controlled by counter-weight system. The linear Z-displacement is converted to the electric signal for measurement. This process involves some mechanical and electronic devices in order to perform the conversion.\textsuperscript{16}

2.3.4 Attenuated Total Reflectance-Fourier Transform Infrared (ATR-FTIR) spectroscopy

Infrared spectroscopy is the study of interaction of infrared light with matter. When a beam of infrared light is directed at a sample, the wavelengths absorbed are dependent on molecular vibrations of the substance. The multiple ways in which infrared light can be directed at samples and the range of detectors available, allow the analysis of a wide variety of samples. Attenuated Total Reflectance (ATR) is widely used FTIR sampling tool. ATR allows qualitative or quantitative analysis of samples with little or no sample preparation, which greatly speeds up the analysis. The major benefit of ATR sampling comes from very thin sampling path length and depth of penetration of IR beam into the sample. This is different from the traditional FTIR sampling by transmission where the sample is diluted with IR transparent salt, pressed into a pellet or a thin film, prior to analysis to prevent total absorption of the infrared spectrum. Hence we used ATR-FTIR to study surface chemistry of the samples.
ATR-FTIR spectroscopy involves directing the infrared light at an interface between an infrared transparent material with a high refractive index called the internal reflection element (IRE) or ATR crystal and a sample on the surface of the IRE. If the angle of incidence of IR beam is greater than the critical angle then total internal reflection occurs (figure 2.8). The critical angle \( \theta_c \) is given by

\[
\theta_c = \sin^{-1}\left(\frac{n_2}{n_1}\right)
\]

where \( n_1, n_2 \) are refractive indices of the crystal and sample respectively and \( \theta_c \) is critical angle. The IR beam reflects from internal surface of the crystal and creates an evanescent wave (zoomed part of figure 2.8), which propagates orthogonally into the sample in contact with the ATR crystal. Some part of energy of the evanescent wave is absorbed by the sample and remaining reflected radiation is returned back to the detector. The depth to which the evanescent wave penetrates a sample is defined by the depth of penetration \( d_p \), as given in the following equation.

\[
d_p = \frac{\lambda}{2\pi n_1 \left(\sin^2 \theta - \left(\frac{n_2}{n_1}\right)^2\right)^{1/2}}
\]

where \( \lambda \) is wavelength of light and \( \theta \) is angle of incidence of the IR beam relative to a perpendicular from surface of the crystal.\(^{17-19}\)

**Figure 2.8:** A multiple reflection ATR system.
2.3.5 Atomic Force Microscopy (AFM)

Atomic force microscopy (AFM) is one of the most versatile techniques known as scanning probe microscopy used for surface topology characterization. AFM has an advantage over STM that it could be used for insulating as well as conducting samples. The AFM covers a broad range of applications from surface science to biological and medical research. By virtue of the ability of AFM to image samples on an atomic scale, it has become an important technique in the field of nanotechnology. We have used AFM to study surface morphology of the dielectric surfaces.

In AFM the tip is attached to a cantilever and the tip-cantilever assembly is brought closer to the sample. Due to interaction between tip and sample the cantilever deflects and these deflections are detected using appropriate electronics to get the topography of sample surface. The forces experienced by the cantilever vary depending on the tip to sample separation. At small tip-sample separation close to interatomic distances, the repulsive force dominates and it increases exponentially with decreasing separation, while an attractive force (van der Waals force) dominates at larger separations. A physical probe raster scanning across the sample using piezoelectric ceramics is utilized in Atomic Force Microscope (AFM). A constant interaction between the probe and the sample is maintained by a feedback loop. The probe position and the feedback signal are electronically recorded to produce a three dimensional map of the surface. Figure 2.9 shows the schematic of AFM. The AFM can be operated in three modes of operation contact mode, non-contact mode and tapping mode.²⁰⁻²³

![Figure 2.9: The schematic diagram of AFM.](image)
I. Contact mode
In contact mode the tip contacts the surface through the adsorbed fluid layer on sample surface. The changing cantilever deflection is monitored by the detector and the force is calculated using Hooke’s law:

\[ \vec{F} = -k\vec{x} \]

where \( F \) is force, \( k \) is spring constant and \( x \) is cantilever deflection. The feedback circuit adjusts the probe height to maintain a constant force and deflection on the cantilever.\(^{21,24}\)

II. Non-contact mode
In this mode the cantilever is vibrated at a frequency close to resonant frequency. The tip oscillates just above the surface without making a contact with it. When the tip approaches the surface, the resonant frequency and amplitude of oscillating cantilever changes due to the interactions with long range forces and thus provides imaging of the surface. The amplitude or resonant frequency is maintained constant through the feedback loop. The motion of the scanner generates topographic image.\(^{21,23}\)

III. Tapping mode
The resolution using this mode is similar to contact mode but the applied forces are lower. Hence this mode is suitable for imaging of soft samples. The cantilever is oscillated near its resonant frequency but the oscillation amplitude is much greater than that of the non-contact mode. The tip taps on sample surface lightly during scanning for short time duration. The tip-sample interaction induces change in the amplitude, resonant frequency and phase angle of the oscillating lever.\(^{21,23}\)
References