

Electrowetting Technique for Measuring the Thickness of Spin-Coated Hydrophobic Fluoropolymer Films

Jumi Lee¹, Minkyu Kim², Hyojin Ko¹, Jihye Kim¹, Yongjun Kim¹, Heesuk Kim¹, Chan-Hee Jung³, Jae-Hak Choi⁴, Oh-Sun Kwon^{1,*}, and Kwanwoo Shin^{1,*}

¹Department of Chemistry, Institute of Biological Interfaces, Sogang University, Seoul 121-742, Republic of Korea

²Department of Chemistry, Seoul National University, Seoul 151-742, Republic of Korea

³Advanced Radiation Technology Institute, Korea Atomic Energy Research Institute, Jeongseup 580-185, Republic of Korea

⁴Department of Polymer Science and Engineering, Chungnam National University, Daejeon 305-764, Republic of Korea

ABSTRACT

For use as an analysis tool, the electrowetting technique was explored for measuring the thickness of thin hydrophobic dielectric films that were prepared by spin-coating a fluoropolymer resin in various weight percents on glass substrates coated with conductive tin-doped indium oxide (ITO-glass). We found that the film thickness was well fitted to a power law, yielding an exponent of 1.5, and that the results were in good agreement with those from the empirical deposit equation for the spin-coating technique. The X-ray reflectivity measurement also supported this method being very precise with a relative uncertainty of 9.2%, because this uncertainty is on the order of the roughness. These results indicate that this method can be used to find the thickness of thin hydrophobic and dielectric films on various conducting substrates. Conversely, the results of this report support the fact that the classical Young-Lippmann equation well describes the electrowetting on thin hydrophobic films well.

KEYWORDS: Thickness, Electrowetting, Contact Angle, Hydrophobic Film, Reflectivity.

1. INTRODUCTION

Although the thickness of a thin polymer film is very highly desired information that need to be known quickly in surface science, most sophisticated tools having nano-scale resolution require not only large-scale dimension but also a special care during sample preparation, so generally a long time is needed to do the measurements and the data analysis. For example, ellipsometry of an optical technique¹ and secondary ion mass spectroscopy of particle beam technique^{2,3} are common techniques that are used to characterize the structures of polymer films in the laboratory. Synchrotron X-ray and neutron reflectometries of scattering techniques, which are as powerful tools for investigating the dynamic behavior, as well as the static surface structure, of a thin polymer film, perform measurements on a site-scale, unfortunately. Even worse, these state-of-the-art tools cannot avoid a pre-scheduled wait time of at least a few week to obtain a specific beam time. Because of this, if a quick, small-scale method, such as a

desktop-scale method were available, it might definitely be helpful for investigating thin polymer films speedily, especially because information on a film's thickness is very often required in the polymer surface science.^{4,5} Here, we introduced an easy, simple and small-scale electrowetting technique to obtain quickly and reliably thickness information, especially for hydrophobic, amorphous fluoropolymer films spin-coated onto ITO-glass. This method may be potentially extended to other numerous dielectric films as long as those films are hydrophobic and have been deposited onto various conductive substrates.

Electrowetting on dielectrics (EWOD) has been used to control the degree of spread of a conducting liquid drop on dielectric film coated onto a rigid electrode substrate as a function of the electric potential, so we can reversibly vary the contact angle (CA, θ) of a drop by varying the voltage between the drop and the counter-electrode underneath the dielectric film (Fig. 1).^{6–8} Although the EWOD technique was introduced only two decades, it has been widely used in numerous applications, such as micro-fluidic lab-on-a-chip,^{9–11} liquid lenses¹² and liquid displays,^{13,14} especially in optoelectronic devices, but the structure of the dielectric film, in which we are now interested, has not been studied much.

*Authors to whom correspondence should be addressed.

Emails: kwshin@sogang.ac.kr, oskwon@sogang.ac.kr

Received: 11 January 2014

Accepted: 30 January 2014

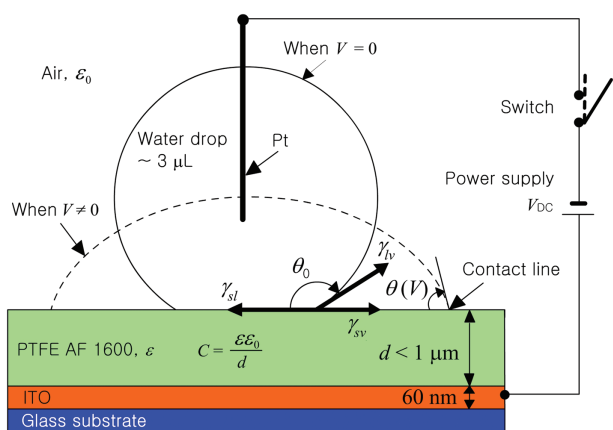


Fig. 1. Schematic view of the EWOD experimental setup to measure Lippmann's CA, $\theta_L(V)$. The CA of a drop at the contact line is determined by the balance of the horizontal components of surface forces (bold arrows) at the equilibrium state, as described by Eq. (1).

According to the formal thermodynamic approach, the variation of CA with the voltage at the triple contact line, which is the boundary of three phases, usually vapor, liquid and solid, is well described by using so-called, Young-Lippmann equation:

$$\cos \theta_L(V) = \cos \theta_Y + \frac{1}{2\gamma_{lv}} CV^2 \quad (1)$$

where θ_Y is the initial Young's equilibrium CA under no voltage, θ_L is the Lippmann's CA at applied voltage V , γ_{lv} is the interfacial tension between the liquid and the ambient vapor, C is the capacitance of the dielectric film, and V is the external voltage across the capacitance C . Classically, the capacitance C in Eq. (1) can be well approximated by using a simple model of the capacitor consisting of double parallel plates as Lippmann described at first. Under the assumption that the drop is a perfect conductor, the electric charges induced in the drop form an electric double layer (EDL) with a negligible Debye length of the order of a few nanometers at the interface,⁷ resulting in an equivalent charged capacitor with the approximated distance of only the dielectric film's thickness. Thus, the capacitance can be given by

$$C = \frac{\varepsilon \varepsilon_0}{d} \quad (2)$$

where ε and ε_0 are the dielectric constant of the dielectric film and the permittivity of air, respectively.

Herein, we will employ the above two theoretical equations to obtain the thickness of a spin-coated dielectric film by fitting the measured Lippmann's CA, $\theta_L(V)$. The CAs were obtained by using a simple zoomed camera (J1, Nikon), possibly a cellular phone with a zoom lens, as shown in Figure 1, to take cross sectional images of a water drop (Fig. 2) and subsequently performing an image-processing analysis.

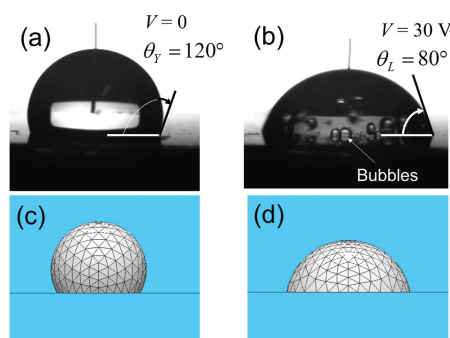


Fig. 2. (a) and (b) photo images, and (c) and (d) corresponding simulated images obtained from Surface Evolver program, to measure Lippmann's CA. Note that near the saturated voltage of 30 V, bubbles appear due to the electrolysis of water, implying imperfect water resistance of the film.

2. EXPERIMENTAL DETAILS

Unpolished, flat, glass slides pre-coated with ITO of 60 nm in thickness were cleaned by using sonication in ethanol, acetone and de-ionized water (DIW) for 30 minutes and were then dried in a laminar flow of nitrogen gas. Polytetrafluoroethylene (PTFE, $\varepsilon = 1.93$), which is an amorphous fluoropolymer (AF 1600) based on copolymers of 2,2-bistrifluoromethyl-4,5-difluoro-1,3-dioxole (PDD), was purchased from Sigma-Aldrich. It was dissolved in FC-40 (3M) solvent by stirring for four days in the ambient environment. Four different solutions with low concentrations of 1.0, 1.5, 2.0 and 2.5 wt%, respectively, were prepared to provide different film thicknesses. Each solution was spin-coated onto a cleaned ITO-glass substrate under fixed conditions, spin-coating at 2000 rpm for 120 seconds, and were kept at 90 °C for 10 minutes to evaporate the solvent, after which they were annealed at 170 °C, a temperature slightly higher than the glass transition temperature of 160 °C, for 30 minutes.

DIW ($\gamma_{lv} = 72$ mN/m and resistivity 18.2 M $\Omega \cdot$ cm at 25°) was used as the conductive liquid sample. A water drop (~ 3 μ L) was put on the substrate, and the Lippmann's CAs were measured after a 50 μ m diameter platinum wire electrode (thin enough to not affect the surface tension of the drop) had been inserted into the drop and connected to a DC power supply (Keithley 2400), as shown in Figure 1. When a voltage was applied to the drop, the cross sectional images of the deformed drop were captured by using a zoom camera, as shown in Figures 2(a) and (b). To support the approximation that the drop's shape was a truncated circle, we simulated the three-dimensional images for the same system by using Surface Evolver program based on the method of interfacial energy minimization.¹⁵ The simulated shape also showed a truncated circular shape, indicating that the two classical approaches, the thermodynamic Young-Lippmann equation and the minimization of the interfacial energy of the system, equivalently well describe the EWOD for a tiny water drop.¹⁶ The images were analyzed by using

ImageJ published by the National Institutes of Health with DropSnake plug-in Refs. [17, 18].

3. RESULTS AND DISCUSSION

Under zero voltage, the initial Young's CA of a water drop on each of the four PTFE AF 1600 films was measured to be ca. 120° regardless of the thickness, as shown in Figure 2(a). Such a relatively high value of the CA independent of the thickness indicates that no matter what concentration of PDD dioxole monomer is dissolved in the AF 1600, within 1.0–2.5 wt%, the solidified surface shows a good hydrophobic property because the non-polar covalent C—F bonds very effectively produce a low surface energy for PTFE. This high initial CA does allow a wide controllable range of the CA as a function of the applied voltage. As the voltage was increased, thus, the contact angles for our four films decreased smoothly, as we expected, and all of them reached a saturated angle of $\theta_{\text{sat}} = 80^\circ$ at corresponding limited voltages, V_{sat} , between 30 and 60 V depending on the film's thickness (Fig. 3), indicating that the CA does not vary even though voltage is increased. Thus, by using the voltage we can adjust the variation in the CA just within $\Delta\theta = 40^\circ$.¹⁹

Because the four curves in Figure 3 are apparently parabolic, to obtain the thicknesses of the AF 1600 films easily, we converted them to linear curves with respect to the squared voltage (Fig. 4). In addition, for obtaining the best-fitted curve with its slope proportional to the film's thickness, we excluded the low-voltage data below 10 V because the initial CAs at those voltages showed no apparent changes due to the hysteresis of the CA. According to direct observations by using the atomic force microscopy (AFM) images of surface as shown in Figure 5, the hysteresis of the CA can be attributed to the drop's being pinned due to the mostly to the lack of surface uniformity on the spin-coated thin film. We also excluded the data

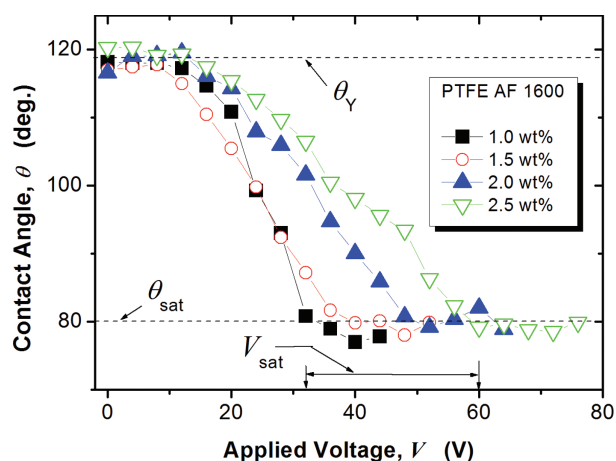


Fig. 3. θ versus V for ITO-glass substrates coated with different concentrations of AF 1600.

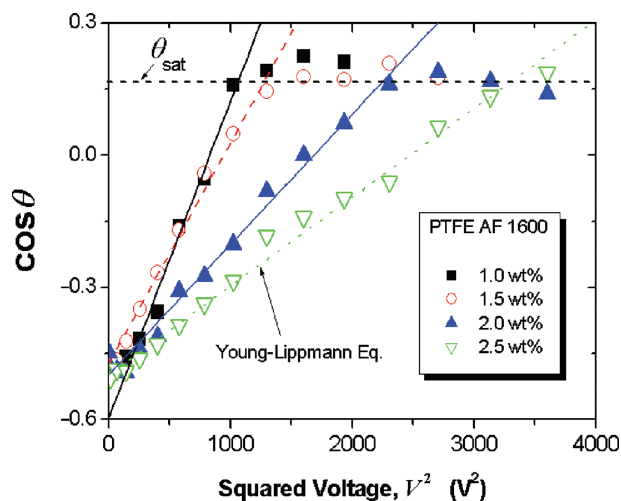


Fig. 4. $\cos\theta$ versus V^2 . The film's thickness is correlated to the slope of each fitted straight line. The θ_{sat} was the same, regardless of the thickness.

showing an asymptotic behavior appeared after the saturation of the CA because those data deviated greatly from linearity. With only these selected CA data, we obtained good linear straight lines having different slopes. Because this linearity was consistent with Eq. (1), we equated the slopes obtained from Figure 4 to the coefficient of the second term of Eq. (2). The film's thickness was calculated using $d = \epsilon\epsilon_0/2\gamma_{lv}/(\text{slope})$, where the dielectric constant of the AF 1600 is, $\epsilon = 1.93$, and the permittivity of air is, $\epsilon_0 = 8.854 \times 10^{-12}$ F/m.

To ensure the confidence of the measured thickness obtained by using the electrowetting method, we compared our results to the empirical hydrodynamic power law, which has been commonly used to estimate a film's thickness, especially for a spin-coated polymer film. To determine clearly the dependency of the film's thickness on the concentration of AF 1600, in Figure 6(a), we plotted the data as a function of the concentration of AF 1600, and we fitted to the plot to the power law,

$$d = Ac^B \quad (3)$$

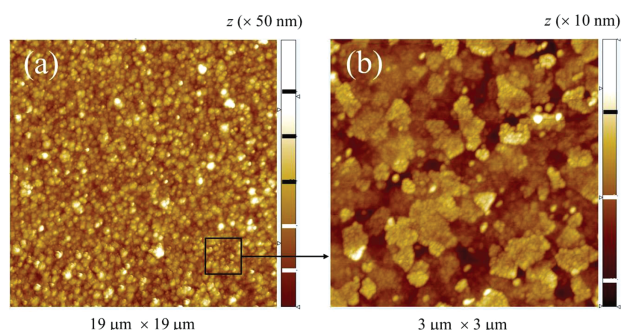


Fig. 5. AFM topographic images of the surface of AF 1600 of 1.0 wt% in the tapping mode: (a) $19 \mu\text{m} \times 19 \mu\text{m}$ and (b) zoomed to $3 \mu\text{m} \times 3 \mu\text{m}$.

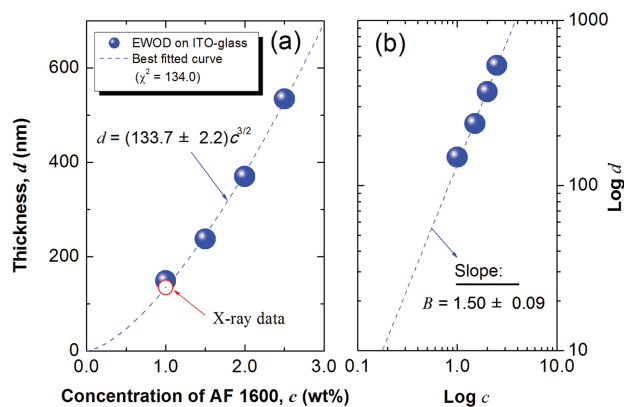


Fig. 6. (a) Empirical equations obtained from the fitted curves for the thickness data obtained from the EWOD measurements and for the blank circle obtained from the X-ray reflectometry profile (see Fig. 6). (b) A plot on log–log scale clearly shows a common exponent of 3/2.

where A and B are the free degrees of freedom for the fitting parameters and d and c are the thickness and the concentration of AF 16000, respectively. In this way, we achieved a good empirical result with the fitting parameters: $A = 133.7 \pm 2.2$ (Fig. 5(a)) and $B = 1.50 \pm 0.09$ (Fig. 5(b)) and a minimal least square, $\chi^2 = 134.0$.

One noticeable feature in the comparison of the concentration dependencies is the fact that the slope of straight lines in Figure 6(b), which is plotted on log–log scale, yields an exponent of $B = 1.5$. As we expected, this power is well consistent with the conventional technical equation for spin-coating with the exponent of 1.5 as a function of the concentration which has been known to be closely related to the viscosity of the solution.²⁰

To verify the thickness data obtained from the EWOD technique and to support our confidence in the empirical power law further, we performed a high-resolution thickness measurement on the sample with 1.0 wt% AF 1600, by using X-ray reflectometry (D-8, Bruker). The X-ray reflectivity profile obtained using the wavelength of $\text{CuK}\alpha_1 = 1.5417 \text{ \AA}$ showed an oscillating series of maxima and minima that characterized the film's thickness (so-called Kiessing fringe) as a function of the scattering vector, q_z , as shown in Figure 7. By fitting the reflectivity profile to a uniform layer model for the X-ray scattering length density of AF 1600 on an ITO-glass substrate, we deduced the thickness ($d = 2\pi/\Delta q_z$, where Δq_z is the difference between two successive minima) to be $135 \pm 6 \text{ nm}$ for the blank circle in Figure 6(a), which is in good agreement with the EWOD's value, within the relative uncertainty of 9.2%. If the EDL approximation and the roughness of the surface and the interface of the film are considered, the error might be negligible.

We believe that the electrowetting method, which is a quick, easy-to-use tool for thickness measurements, may be extended to any hydrophobic dielectric films coated on planar electrode surfaces, such as Teflon, Cytod and Hyflon polymer resins, for which such measurements are

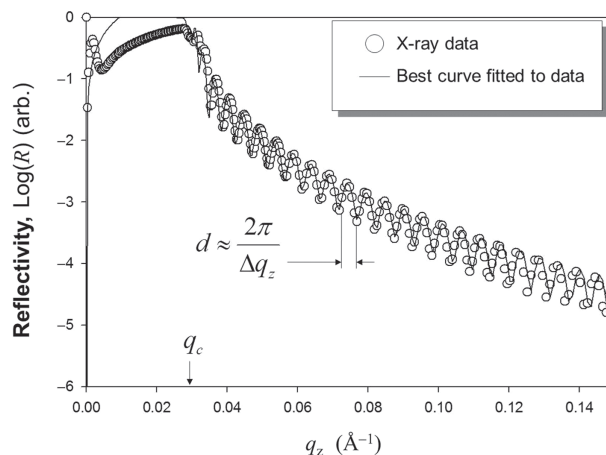


Fig. 7. Specular X-ray reflectivity profile to characterize the thickness for a 1.0 wt% AF 1600 film on an ITO-glass substrate.

hardly accessible when using large-scale equipment, such as ellipsometry, impedance analyzer, and X-ray or neutron reflectometry.

Finally, it is worthy to note the observation of the undesirable bubbles frequently appeared inside the water drop even before saturation. Though they did not affect the measurement of the CA of a water drop, they must be suppressed or removed to obtain accurate CA data. In most cases, because the bubbles were observed at the surface of AF 1600 positioned just below Pt-electrode after other bubbles had appeared on the bare Pt-wire conductor, we hypothesized that they were created by electrolysis. According to Cooney et al.²¹ the pinholes generated by electric breakdown enable water to penetrate very thin AF 1600 film (cf. the electric breakdown voltage of AF 1600 is 21 kV/mm) and allow a leak current to flow through the pinholes to the underlying counter-electrode, easily causing electrolysis.²² In fact, in general EWOD experiments, another layer with a strong dielectric breakdown (ca. 200 kV/mm), such as parylene-C, Al_2O_3 and SU-8, is commonly inserted between the AF 1600 and the counter ITO electrode, in order to prevent such undesirable electrolysis. In this case, the usage for thickness measurements of the EWOD technique perhaps requires an analysis of a double-layer consisting of a hydrophobic film and a dielectric film by using a simple model of a serial-connected capacitance. This is left as our interesting future work.

4. CONCLUSION

In summary, we tried to apply the EWOD theory and technique for measuring the thickness of hydrophobic dielectric AF 1600 films that had been spin-coated with different weight percents onto a conductive substrate. The thickness data followed a power law, which is in good agreement with the deposit equation for the spin-coating technique. The result also agreed, within 9.2% relative error, which may be ignored when considering the film's roughness,

with that measured by the X-ray reflectometry in high resolution. Thus, as a supplement to our previous work,²³ this tool may be used as a quick, easy and small-size experimental tool to find a film's thickness, especially for any spin-coated hydrophobic polymer film.

Acknowledgments: This work was supported by the Nuclear Research R&D Program and the Radiation Technology R&D Program (2013M2A2A6043677) through Advanced Radiation Technology Institute and the Advanced Research Center for Nuclear Excellence (2011-0031932), the Mid-career Researcher Program (2011-0017539) and Basic Science Research Program (2013R1A1A2010265) through the National Research Foundation of Korea funded by the Ministry of Education, Science and Technology, and the Ministry of Science, ICT and Future Planning.

References and Notes

- R. M. A. Azzam and N. M. Bashara, *Ellipsometry and Polarized Light*, North-Holland Publishers, New York (1977).
- E. Phillip, *Rapid Communication in Mass Spectrometry* 4, 123 (1990).
- S. J. Whitlow and R. P. Wool, *Macromolecules* 22, 2648 (1989).
- T. P. Russell, *Mat. Sci. Rep.* 5, 171 (1990).
- M. Tolan, *X-Ray Scattering from Soft-Matter Thin Films*, Springer Tracts in Modern Physics, Springer, Berlin (1999), Vol. 148.
- G. Lippmann, *Ann. Chim. Phys.* 5, 494 (1875).
- C. Quilliet and B. Berge, *Curr. Opin. Colloid Interface Sci.* 6, 34 (2001); F. Mugele and J.-C. Baret, *J. Phys.: Condens. Matter* 17, R705 (2005); U.-C. Yi and C.-J. Kim, *J. Micromech. Microeng.* 16, 2053 (2006).
- O. Kwon, M. Kim, T. Kim, C. Lee, S. Han, J. Kim, J. Jung, J. Choi, and K. Shin, *J. Nanosci. Nanotechnol.* 11, 7132 (2011).
- M. G. Pollack, R. B. Fair, and A. D. Shenderov, *Appl. Phys. Lett.* 77, 1725 (2000).
- H. Moon, S. K. Cho, R. L. Garrell, and C.-J. Kim, *J. Appl. Phys.* 92, 4080 (2002).
- T. Pfohl, F. Mugele, R. Seemann, and S. Herminghaus, *Chem. Phys. Chem.* 4, 1291 (2003).
- B. Berge and J. Peseux, *Eur. Phys. J. E* 3, 159 (2000).
- R. A. Hayes and B. J. Feenstra, *Nature* 425, 383 (2003).
- J. Heikenfeld, K. Zhou, E. Kreit, B. Raj, S. Yang, B. Sun, A. Milarcik, L. Clapp, and R. Schwartz, *Nat. Photon.* 3, 292 (2009).
- K. Brakke, *Exper. Math.* 1, 141 (1992).
- N. A. Patankar and Y. Chen, *Technical Proceedings of the Fifth International Conference on Modeling and Simulation of Microsystems Nanotech.*, Puerto-Rico, USA, April (2002).
- W. S. Rasband, ImageJ, U. S. National Institutes of Health, Bethesda, Maryland, USA, <http://rsb.info.nih.gov/ij/>, 1997 (2011).
- A. F. Stalder, G. Kulik, D. Sage, L. Barbieri, and P. Hoffmann, *Colloid Surface A* 286, 92 (2006).
- H. Moon, S. K. Cho, R. L. Garrell, and C. J. Kim, *J. Appl. Phys.* 92, 4080 (2002).
- D. Meyerhofer, *J. Appl. Phys.* 49, 3993 (1978).
- C. G. Cooney, C.-Y. Chen, M. R. Emerling, A. Nadim, and J. D. Sterling, *Microfluid. Nanofluid.* 2, 435 (2006).
- DuPont, <http://www2.dupont.com> (2011).
- H. Ko, M. D. Phan, D. Khatua, C.-H. Jung, J.-H. Choi, O.-H. Kwon, and K. Shin *J. Biomed. Nanotechnol.* 9, 1 (2013).

Copyright: American Scientific Publishers