

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/224765717>

Imaging of Surface Heterogeneity by the Microdroplet Condensation Technique

ARTICLE *in* LANGMUIR · JUNE 2001

Impact Factor: 4.46 · DOI: 10.1021/la001200r

CITATIONS

14

READS

12

3 AUTHORS, INCLUDING:



Marcus Textor

ETH Zurich

333 PUBLICATIONS 14,041 CITATIONS

SEE PROFILE



Nicholas D Spencer

ETH Zurich

403 PUBLICATIONS 11,621 CITATIONS

SEE PROFILE

Notes

Imaging of Surface Heterogeneity by the Microdroplet Condensation Technique

R. Hofer, M. Textor, and N. D. Spencer*

Laboratory for Surface Science and Technology, Department of Materials, Swiss Federal Institute of Technology (ETH), CH-8092 Zurich, Switzerland

Received August 21, 2000. In Final Form: March 16, 2001

1. Introduction

Condensation figures (CFs) enable the imaging of surfaces, delineating regions with different wettabilities (different interfacial free energy). The use of CFs as a method for detecting contamination on homogeneous surfaces was first described by Lord Rayleigh¹ and subsequently used by Méricoux.² Water from a humid atmosphere condenses more readily on contaminated, polar,^{3,4} or angular (rough) regions with a high wettability⁵ compared to clean, apolar, and flat surfaces showing reduced wettability. If a surface is inhomogeneous in its physicochemical properties, the droplet patterns reflect its heterogeneity.⁶

To illustrate the use of the microdroplet condensation technique, we describe here its application on flat Ta₂O₅ surfaces, modified by self-assembled monolayers (SAMs) based on octadecyl phosphate (ODP) and mixed SAMs of hydroxy dodecyl phosphate and dodecyl phosphate.^{7–9} The images were used to estimate the quality of these surfaces in terms of both large scale and local surface properties, as well as their homogeneity/heterogeneity, by quantitatively evaluating the microdroplet density (μ dd, droplets per unit surface area). This paper aims at providing information on the relative importance of different surface properties (chemical composition/wettability, structural properties/roughness) in relation to the experimentally observed value of the μ dd.

2. Materials and Methods

2.1. Microdroplet Density. The μ dd apparatus (Figure 1) consists of a metal sample table placed in a transparent humidity chamber made of polystyrene. The metal table is first thermally stabilized with water at 25 °C, and the air in the humidity chamber is saturated with water vapor, also at 25 °C. Condensation is initiated by switching to flowing ice water. The analyzed surfaces were imaged by a CCD camera (Panasonic, model WV-

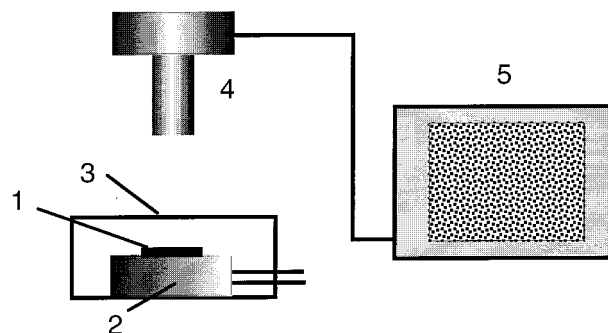


Figure 1. Schematic drawing of the microdroplet density apparatus: The object (1) is placed on a temperature-controlled table (2) within a transparent box (3). An atmosphere saturated with water vapor is achieved by the presence of water on the bottom of the box. Ice water is pumped from outside the box through the sample table. The growth of condensed water droplets is monitored via a CCD camera system (4 and 5).

BP 310/6, Matsushita Communication Deutschland GmbH, Germany) coupled to a microscope (Zeiss, Carl Zeiss (Schweiz) AG, Switzerland) having 2.5 \times and 6.3 \times objectives. The quantification of the μ dd was performed using video-capture software (Ulead VideoStudio, Video Capture, version 2.0, Ulead Systems, Inc.).

On hydrophobic surfaces, it is not essential to take pictures after an exactly defined time of condensation. Once water has started to condense, one sees the condensed droplets continuing to grow rather than new droplets nucleating at the surface; therefore, the number of droplets per unit area remains constant for typically 1 min, after which coalescence of droplets starts to occur.

It is more difficult to measure μ dds on hydrophilic surfaces, because condensed droplets tend to coalesce in the course of the condensation experiment. For hydrophilic, surfaces it is therefore essential to carefully cool at a low cooling rate of the order of 10 K/min to prevent complete water film coverage of the surface by coalescence.

2.2. Contact Angle Measurements. The wettability of surfaces was investigated by measuring the advancing water contact angle (Contact Angle Measuring System, with Kontaktwinkel Messsystem G2/G40 2.05-D software, Krüss GmbH, Hamburg, Germany).

2.3. Surface Modification. (a) Substrate. Surface modifications were performed on tantalum pentoxide films deposited by physical vapor deposition onto a Corning glass substrate. Details are given in refs 9 and 10.

(b) Self-Assembled Monolayers. Octadecyl Phosphate Monolayers. Octadecylphosphoric acid ester (ODP) was synthesized as described by Okamoto¹¹ and dissolved in *n*-heptane (UVASOL) and 2-propanol (UVASOL) from Merck in a 100:0.4 (v/v) mixture at a 0.5 mM concentration. SAM formation on cleaned Ta₂O₅-coated glass chips was carried out according to details given in a separate paper.¹⁰ The chips were immersed for a time between 0 and 48 h.

Dodecyl Phosphate/Hydroxy Dodecyl Phosphate Mixed Monolayers. Aqueous solutions of ammonium salts of dodecyl phosphate (DDPO₄(NH₄)₂) and hydroxy dodecyl phosphate (OH-DDPO₄(NH₄)₂) at a concentration of 0.5 mmol/L were prepared and used

* To whom correspondence should be addressed.

(1) Lord Rayleigh, *Nature* **1911**, 66, 416.

(2) Méricoux, R. *Rev. Opt.* **1937**, 9, 281.

(3) Frisbie, C. D.; Rozsnyai, L. F.; Noy, A.; Wrighton, M. S.; Lieber, C. M. *Science* **1994**, 265, 2071.

(4) Aizenberg, J.; Black, A. J.; Whitesides, G. M. *Nature* **1998**, 394, 868.

(5) Blanchard, A. P.; Kaiser, R. J.; Hood, L. E. *Biosens. Bioelectron.* **1996**, 11, 687.

(6) López, G. P.; Biebuyck, H. A.; Frisbie, C. D.; Whitesides, G. M. *Science* **1993**, 260, 647.

(7) Brovelli, D.; Hähner, G.; Ruiz, L.; Hofer, R.; Kraus, G.; Waldner, A.; Schlösser, J.; Oroszlan, P.; Ehrat, M.; Spencer, N. D. *Langmuir* **1999**, 15, 4324.

(8) Poirier, G. E.; Pylant, E. D. *Science* **1996**, 272, 1145.

(9) Hofer, R.; Textor, M.; Spencer, N. D. *Langmuir*, **2001**, 17, 4014.

(10) Hofer, R. Surface Modification for Optical Biosensor Applications. Ph.D. Thesis No. 13873, ETH Zurich, Zurich, Switzerland, 2000.

(11) Okamoto, Y. *Bull. Chem. Soc. Jpn.* **1985**, 58, 3393.

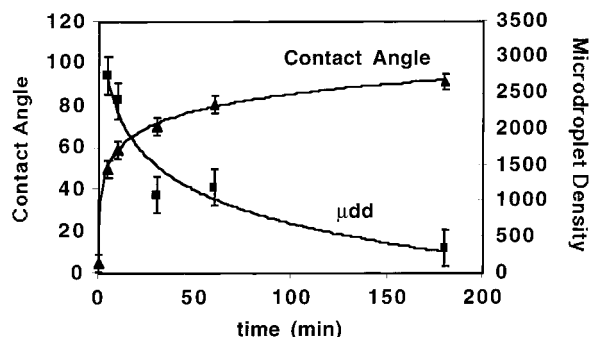


Figure 2. Water contact angle (triangles) and microdroplet density (squares) variation with assembly time from a 0.5 μ M solution of ODP in *n*-heptane/2-propanol (100/0.4 v/v). Logarithmic trendlines are applied on both data point sets.

for SAM formation on Ta₂O₅ chips as described by Hofer et al.^{9,10} The alkyl phosphate and hydroxyalkyl phosphate solutions were mixed in different molar ratios from 0 to 100% with respect to the amount of OH-DDPO₄(NH₄)₂. The chips were immersed for 48 h in the solution for self-assembly.

3. Results and Discussion

SAMs are ideal systems to modify the chemical properties of surfaces in a defined manner and to study the effect of surface chemistry on the physicochemical properties. Alkane phosphates have been shown by a variety of surface-analytical techniques to form ordered monolayers with the terminal phosphate group bound to the Ta₂O₅ layer, while the terminal CH₃ groups are exposed at the SAM surface, forming strongly hydrophobic surfaces.^{7,12} This SAM system is used here to test the usefulness of the μ dd technique for the determination of surface properties and their heterogeneity across the surface.

3.1. Microdroplet Density Measurements as a Function of Alkane Phosphate Self-Assembly Time. A series of ODP-SAM chips were prepared as described in section 2. The SAM formation on Ta₂O₅-coated chips in a 0.5 μ M ODP solution was investigated after different immersion times. Advancing water contact angle and μ dd were measured, and the data were plotted as a function of immersion time (Figure 2).

A few chips were immersed for only 30 min in the ODP solution, and the rest were immersed for 48 h. Water contact angle and μ dd were measured. The water contact angle of the chips immersed for 30 min is $109^\circ \pm 2^\circ$, whereas the chips with the longer immersion time reached the maximum value of $112^\circ \pm 2^\circ$, which is typical for a well-ordered ODP SAM.^{7,12} The μ dd pictures show that the surface of a chip immersed for 30 min is very

inhomogeneous (Figure 3, left). The μ dd of homogeneous regions on these chips was much higher than for chips following an immersion time of 48 h. All chips with the longer immersion time showed a homogeneous distribution of condensed microdroplets at a low droplet density. ODP apparently assembles at the surface in the form of islands within a short time (minutes). However, in order for a SAM to become homogeneous, hours or days are necessary to complete the formation of a densely packed monolayer with an ordered arrangement of the adsorbed alkyl phosphate molecules (Figure 3, right).

An obvious first conclusion from the results presented in Figure 3 would be that the μ dd value correlates with the overall or local wettability properties (contact angle values), thus making the technique potentially useful for determining wettability properties or surface energetics on a much more local scale (down to the micrometer level) than is possible with conventional sessile-drop contact angle measurements. However, in view of the fact that both contact angle and molecular order/surface homogeneity are known to increase with immersion time (i.e., alkane phosphate adlayer coverage), it could not be decided from these experiments alone to what extent surface energetics (contact angle) and nanostructural properties (molecular order/disorder, heterogeneity, nanoscale roughness) are responsible for the observed variations in droplet density. Therefore, a second series of experiments was carried out in order to answer the question of whether molecular order/disorder and structural heterogeneity are other important factors in the context of the microdroplet density observations.

3.2. Microdroplet Density of Mixed OH-DDPO₄/DDPO₄ SAMs. Mixed, complete monolayers of dodecyl phosphate and hydroxy dodecyl phosphate were prepared, as described in section 2, so as to produce 11 samples that displayed different contact angle values.¹¹ In this set, the samples were morphologically similar and uniform but chemically distinct. The total molecular coverage of the SAMs across the different compositions is very similar as judged by X-ray photoelectron spectroscopy.^{9,10} As can be seen in Figure 4, while the measured contact angle varies monotonically from approximately 110° (pure DDPO₄) to 50° (pure OH-DDPO₄), the μ dd value remains low (around $100\text{--}200$ droplets mm^{-2}) and essentially unchanged over the whole compositional range, because it is relatively insensitive to contact angle over the range studied but highly sensitive to morphological heterogeneity. The conclusion from these experiments is that molecular order/disorder is more important than the wettability properties (contact angle) for the experimentally observed microdroplet density.

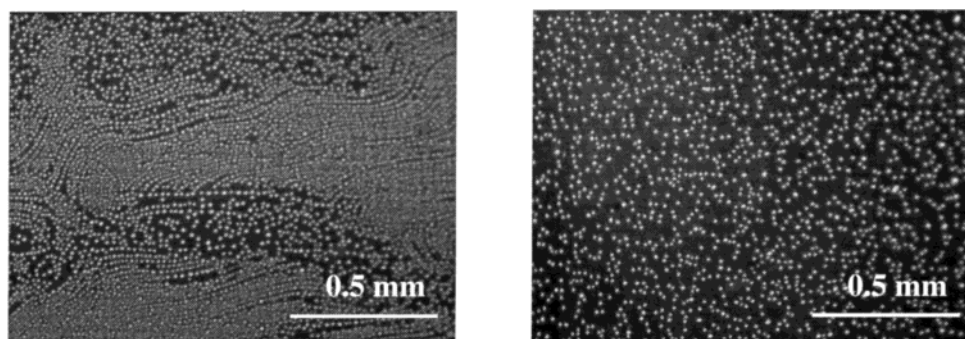


Figure 3. Microdroplet patterns (condensation figures) of self-assembled monolayers of octadecyl phosphate on Ta₂O₅: Ta₂O₅ chip immersed for 30 min (left) and 48 h (right). The droplet pattern indicates inhomogeneous SAM formation at the short exposure time. Full coverage, order, and homogeneity of the SAM is achieved after 48 h exposure to the SAM solution, resulting in a relatively homogeneous condensation figure at a low value for the microdroplet density.

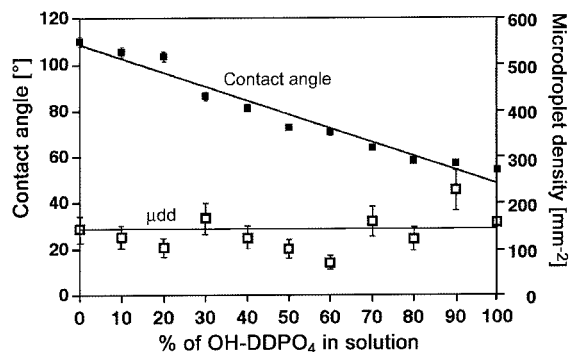


Figure 4. Water contact angle (filled squares) and microdroplet density (open squares) for a set of complete SAMs containing different proportions of DDPO₄ and OH-DDPO₄. % of OH-DDPO₄ denotes the molar percentage of OH-DDPO₄ in the mixed aqueous SAM solution. The total concentration of OH-DDPO₄ plus DDPO₄ is 0.5 mmol/L.

4. Conclusion

The quantification of the droplet density allows for the definition of a new surface property, called microdroplet density (μdd , number of droplets per mm^2). By use of the μdd technique, local variations in surface properties can

be readily observed in a few seconds by measuring a number of small areas at high magnification. Conventional contact angle data, on the other hand, provide only an average over the area that is in contact with the water (or another solvent) droplet or are limited to local single measurements.

Comparison of the μdd and contact angle behavior of the two sets of self-assembled monolayer samples discussed in this paper shows that the two methods yield complementary information, μdd being chiefly indicative of surface heterogeneity rather than wettability per se. Surface heterogeneity of hydrophobic surfaces can thus be investigated by monitoring condensation figures and calculating μdd values on both macroscopic (mm^2) and microscopic (μm^2) levels. It is a low-cost, nondestructive method for determining surface quality in a short time (minutes) and with reasonable reproducibility and therefore a useful method for applications in areas such as molecular self-assembly, chemical patterning, and microstructuring.

Acknowledgment. We thank Dr. M. Ehrat, formerly at Novartis Pharma AG Basel, for his support. Financial support by the Commission for Swiss Technology and Innovation (CTI) is gratefully acknowledged.

(12) Textor, M.; Ruiz, L.; Hofer, R.; Rossi, A.; Feldman, K.; Hähner, G.; Spencer, N. D. *Langmuir* **2000**, *16*, 3257.