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Application of Ultrasonic Shear Wave Measurements for the Assessment of Surface Hydrophobicity and Drying Dynamics of Aqueous Droplets

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Summary:
The paper describes the application of ultrasonic shear wave measurements for the assessment of hydrophobicity of various surfaces and real-time non-destructive monitoring of the process of aqueous droplet evaporation. This research focuses on the quantification of surface hydrophobicity expressed through aqueous droplet contact angle and the study of the kinetics of droplet evaporation including evaporation modes (pinned and unpinned) and the characterization of watermarks left after drying.

Keywords: Surface Hydrophobicity, Contact Angle, Shear Wave Ultrasonic Spectroscopy, Admittance Analysis, Drop Shape Analysis

Background, Motivation and Objective

Wettability and droplet evaporation plays an important role in nature, daily life, and many technological applications, manufacturing engineering, chemical and medical products. Understanding the interaction and wetting dynamic of droplets with various surfaces, and the complex mechanisms of drying processes is essential [1, 2]. Moreover, the formation of drying defects and watermarks (WM), after the wet cleaning procedures in the semiconductor industry, has been identified as a serious problem [3]. Quantification of these phenomena and correlation of surface properties (i.e., roughness) and drying defects (i.e., watermarks) will provide in-depth information on the quality of the materials and cleaning liquids. This requires efficient real-time, non-destructive techniques for precision monitoring of the droplet drying process.

The current paper describes the application of shear wave ultrasonic spectroscopy for studies of aqueous droplet shape and dynamics of drying on surfaces with different hydrophobicity. This spectroscopy includes the principles usually described as Quartz Crystal Microbalance (QCM) technique [4, 5]; however, with add-on multifrequency and energy loss analysis.

Description of the Method

The shear wave spectroscopy probes the 'bottom' part of the droplet, which is in contact with the surface studied. A generated shear wave propagates through the material into the liquid and attenuates in a very thin layer of liquid that resides on top of the surface, thus providing information on the surface area and the properties of the system (surface and thin layer of liquid attached). The effective thickness of the probed liquid layer can be changed from the micron to nanometer range by changing the frequency of the wave. This allows for quantitative assessment of surface hydrophobicity and real-time characterization of different amounts of liquid positioned on the surface during the drying process, distinguishing the pinned and unpinned modes of evaporation (see Fig. 1).

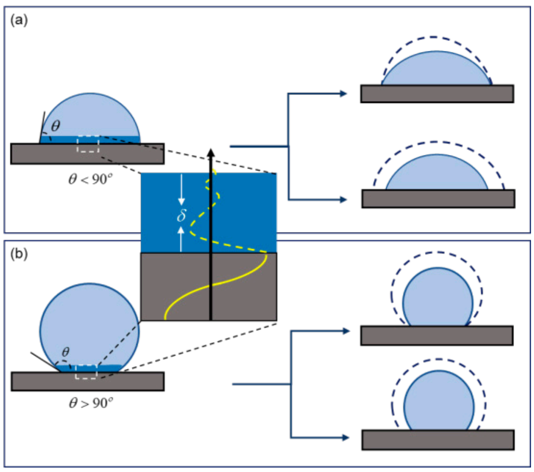

Fig. 1. Schematic illustration of the measuring principles of sessile droplets on surfaces showing the decay length (δ) and the two modes of evaporation (pinned and unpinned contact line) on; (a) hydrophilic, and (b) hydrophobic surfaces. The grey rectangle represents the piezoelectric sensor covered by the surface studied. Measurements of complex admittance produce the crystal resonance frequencies and energy losses characterized by the crystal Q factor.

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Analysis of size and shape characterization of impurity depositions (i.e., 'water marks') formed, possible slip phenomena for hydrophobic surfaces, can be included as well. Figure 1 illustrates the measuring principles of characterization of droplet hydrophobicity and monitoring of the dynamics of drying for different, pinned, and unpinned, modes of evaporation.

Results

Figure 2 illustrates an example of monitoring of the evaporation process, compiled of pinned and unpinned mode, on a hydrophobic surface, represented by the difference of the resonance frequencies, δf , of the sensor with an aqueous droplet on its surface and without the droplet. The weight of the droplet decreases nearly linearly over the whole time period (high-precision gravimetric measurements). The initial value of the frequency shift can be recalculated into the amount of surface area covered by the droplet, or into the droplet contact angle.

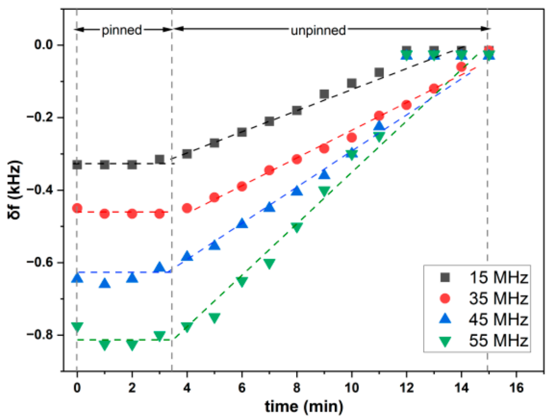

Fig 2. Experimental results of the frequency shift, δf, of a 2 μL water droplet on the hydrophobic surface (PTFE spray-coated sensor) measured in various frequencies as a function of time at room temperature.

The pinned mode of evaporation, corresponding to constant frequency shift, is observed at the time period of 0 to approximately 3.5 min (see Fig. 2). Unpinning mode occurs after this phase until the end of the drying process. Further drop shape analysis offered important information on the geometry of the droplet (height, volume, diameter), and energy loss analysis (at various frequencies) provided knowledge on viscous damping effects from the droplets, during different times of evaporation. Finally, the drying kinetics of aqueous droplets allowed for the quantification of impurity depositions on the surfaces and the characterization of watermarks formed.

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