Colloids and Surfaces A: Physicochem. Eng. Aspects 449 (2014) 42–50

Contents lists available at ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

journal homepage: www.elsevier.com/locate/colsurfa

"Coffee ring" formation dynamics on molecularly smooth substrates with varying receding contact angles

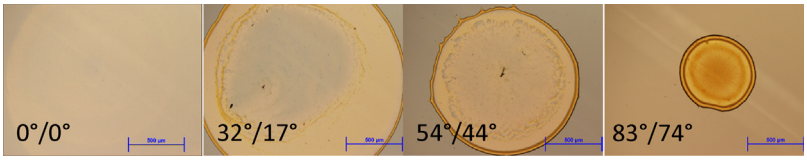
Lanhe Zhang, Yen Nguyen, Wei Chen *

Chemistry Department, Mount Holyoke College, South Hadley, MA 01075, USA

HIGHLIGHTS

- Molecularly smooth substrates were chemically tailored for drying dynamics studies.
- Substrate receding contact angle dictates the number and duration of drying stages.
- A secondary pinning stage is identified for the first time.
- "Coffee ring" can be eliminated on a superhydrophilic substrate.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 2 January 2014
Received in revised form 9 February 2014
Accepted 14 February 2014
Available online 24 February 2014

Keywords:
Drying dynamics
Coffee ring
Molecularly smooth substrate
Receding contact angle
Secondary pinning
Superhydrophilic

ABSTRACT

A systematic study of "coffee-ring" formation dynamics was carried out using chemically and physically well-controlled substrates and colloids. Clean silicon wafers were reacted with tris(trimethylsiloxyl)chlorosilane in the vapor phase to yield molecularly smooth substrates with advancing and receding contact angles up to 84°/74° (θ_A/θ_R) and a constant hysteresis of $12 \pm 2°$. Monodisperse gold nanoparticles (AuNPs) of 15 nm in diameter were stabilized and functionalized with poly(vinyl alcohol) (PVOH) of 9 nm in thickness in aqueous solution. The evolution of contact angle and contact diameter of water and colloid-containing drops on clean and modified silicon wafers was assessed as sessile drops evaporated. PVOH-AuNPs in the colloid-containing drop increase the energy barrier for contact line depinning and the pinning force. There are up to four drying stages for colloid-containing drops, initial pinning, depinning, secondary pinning, and final evaporation. The contribution of each stage to evaporation depends on substrate receding contact angle. It is established in this study that the secondary pinning is unique for colloid-containing drops and is only observed on substrates with receding contact angles greater than 35°. "Coffee rings" are formed on all modified silicon wafers, but not on clean silicon wafers with contact angles of 0°/0°.

1. Introduction

"Coffee-ring" formation dynamics have received considerable interest in the scientific community [1–20]. Controlled deposit patterns of colloidal particles from sessile drops have important applications in the printing industry, assembling heterogeneous catalysts on solid supports, lithography, manufacturing microassay arrays, and solution-based sample preparation for microscopy. Both the macroscopic deposit pattern depicting the overall particle distribution across the deposit region and the organization of neighboring particles are important [1].

The deposit pattern of an evaporated sessile drop can be a ring [2–4], a spherical cap [1], a uniform deposit [5–7], or a more complex structure [8–13]. The observed patterns result from Brownian motion (small particles), gravitational force (large particles), particle–particle [7], surface–particle interactions [14], and mode

* Corresponding author. Tel.: +1 413 538 2224; fax: +1 413 538 2327.
E-mail address: weichen@mtholyoke.edu (W. Chen).

http://dx.doi.org/10.1016/j.colsurfa.2014.02.043
0927-7757/

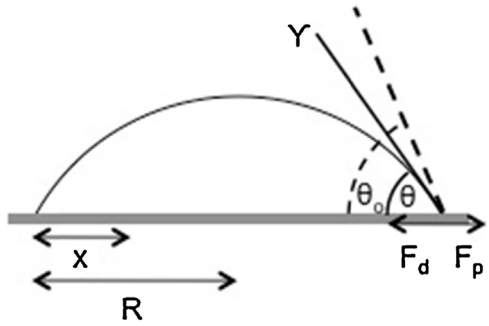


Fig. 1. An evaporating sessile drop with surface tension of γ: the shape of the drop is defined by the contact angle at the solid–liquid–vapor contact line, θ; the dimension of the drop is characterized by the distance from the edge to the center, R.

of evaporation [4,15]. A schematic of an evaporating sessile drop in open air is shown in Fig. 1.

Flux per unit area along the drop, $j(x)$, can be quantified according to Eq. (1) [2,3,16],

$$j(x) \approx \frac{D_{\text{vap}}(c_{\text{sat}} - c_{\infty})}{\rho_{\text{water}} x^{a} R^{1-a}} \quad (1)$$

where D_{vap} is the diffusion coefficient of water vapor in air, c_{sat} is the saturated concentration of water vapor in air, c_{∞} is the concentration of water vapor in air at a large distance from the drop, ρ_{water} is the density of water, and $a = (\pi/2 - \theta)(\pi - \theta)$. Based on Eq. (1), for a pinned drop with a contact angle of smaller than 90°, the evaporation rate near the edge is faster than that at the center, which creates an outward convective flow resulting in accumulation of solutes at the contact line. Eq. (1) also indicates that the extent of convective flow depends on humidity in the environment and substrate contact angle/surface chemistry, which is consistent with the work by Hu and Larson [17]. The drying dynamics is commonly believed to consist of three stages. In the initial stage, the contact line stays pinned while the contact angle of the drop decreases from the initial contact angle, θ_o, to the receding contact angle of the substrate, θ_R. As evaporation continues, the contact line recedes or depins while the drop maintains its receding contact angle. In some systems, the "stick-slip" process can repeat many times to produce interesting features in the deposit patterns [8–11]. In the very last stage of drying, the contact line pins again and contact angle of the drop decreases further. Therefore, the contact angle, specifically the receding contact angle of a substrate has a significant impact on the drying process and the deposit pattern of colloidal particles [1]. When θ_R is low, a deposit pattern in the form of a ring is expected due to contact line pinning, which is formed by the accumulation of particles at the periphery of the drop [2–4]. On the other hand, when θ_R is high, shrinking contact area in the drying process can concentrate particles in the center of the drop [1]. Humidity [18], particle size [16,19], particle concentration [1,10,20], particle and substrate charge [14], and temperature [20], also affect deposit patterns by modulating drying rate, particle mobility, and solid content.

The energy barrier for contact line to depin, which depends on substrate–drop interactions and surface defects, plays a significant role in the drying dynamics. The magnitude of the energy barrier dictates how much a drop deforms from its initial contact angle and how long the contact line stays pinned before the depinning stage is reached. The pinning force per unit length (F_p) has been used to quantify the energy barrier for contact line depinning in a published report [10]. The pinning force per unit length is equal in magnitude to the depinning force per unit length (F_d) at the onset of the depinning stage and the latter is caused by the deviation of the drop contact angle from its initial value, or $F_p = F_d = \gamma(\cos\theta - \cos\theta_o)$, where γ is the surface tension of the drop (Fig. 1). The pinning force has been shown to be much larger when colloids are present in the drop [10].

The existing body of work on drying dynamics makes conjectures concerning the importance of substrate surface chemistry and substrate–colloid interactions, however, most of them exploited native substrates, including metal oxides [3], silicon [3,10,17], glass [2,3,5–7,10,13,14,16,19,20] and polymers [3,10]. A dried deposit formed from a sessile drop typically has a contorted circumference resulting from localized contact line pinning by surface dust particles, roughness, and chemical heterogeneity. These "defects" increase the energy barrier for depinning and complicate the underlying correlation between substrate energetics and drying dynamics. It is thus important to use defect-free, molecularly smooth substrates with readily modifiable surface chemistry and energetics. There are limited previous studies that used substrates with controlled wettability. One of them involved the preparation of a series of self-assembled monolayers consisting of different ratios of alcohol and alkyl groups on gold-coated mica [21]. The advancing and receding contact angles (θ_A/θ_R) of the substrates varied from c.a. 20°/10° to 110°/100° with a constant hysteresis ($\theta_A - \theta_R$) of c.a. 10°. Drying dynamics studies were carried out using only water drops on these substrates. Two other studies examined drying dynamics on different substrates (polymers, native and modified glass slides, native and coated silicon, etc.) with discrete contact angles values [1,10]. Silicon wafers are ideal substrates to study coffee-ring formation because they are easy to clean, molecularly smooth, and more importantly, modifiable using silanes with controlled chemical composition. Circularity of sessile drops and dried deposits on clean and modified silicon wafers allow the focus to be placed on the effect of substrate wettability on drying dynamics, deposit dimension, and distribution of particles in the deposit.

In this study, a system consisting of physically and chemically well-controlled substrates and colloids was designed and prepared for the first time to elucidate factors affecting drying dynamics and criteria for coffee-ring formation. Clean silicon wafers were chemically modified with tris(trimethylsiloxyl)chlorosilane to afford a series of atomically smooth substrates with varying (receding) contact angles. Poly(vinyl alcohol) (PVOH) chains were adsorbed onto gold nanoparticle (AuNP) surfaces to impart steric stabilization, especially at high colloidal concentrations, and offer surface chemistry control. Drying dynamics of water as well as colloid-containing drops containing PVOH-AuNPs were compared and correlated to substrate wettability. New insights into the drying dynamics are gained from the carefully tailored experimental design.

2. Materials and methods

2.1. Materials

Poly(vinyl alcohol) (PVOH) (M_w = 13–23 kDa, 98% hydrolyzed) and hydrogen tetrachloroaurate(III) trihydrate were obtained from Aldrich; sodium citrate and tris(trimethylsiloxy)chlorosilane (trisTMS-Cl) were purchased from Fisher Scientific and Gelest, respectively; HPLC-grade organic solvents were attained from Pharmco. All reagents were used as received without further purification. Water was purified using Millipore Milli-Q Biocel System (Millipore Corp., resistivity ≥18.2 MΩ/cm). Silicon wafers (100 mm in diameter, thickness 475–575 μm, P/B doped, resistivity 1–10 Ω cm) were purchased from International Wafer Service. All glassware was cleaned in a base bath (potassium hydroxide in isopropyl alcohol and water), thoroughly rinsed with distilled water, and stored in a clean oven at 110 °C until use.