Adsorption and detection of microparticles using silicon microcantilevers

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Abstract. This paper presents a droplet-based method for detecting the mass of fluid-based microparticles. The degree of wettability on silicon-based substrates is therefore investigated for enhanced adsorption of microparticles. Contact angles of 47.3° (pre-treatment) and below 9° (enhanced hydrophilicity upon oxygen plasma treatment) have been realized. Segments of mono-layered particles on the substrate and the possibility of homogenous distribution are also demonstrated. The volume and the surface-contact area of droplets on the substrate have been determined, hence empowering an envisaged optimized design of a particle-well cantilever. The determination of the mass of adsorbed microparticles on the cantilever has also been investigated.

1. Introduction

Development and miniaturization of various MEMS/NEMS-based sensors has gained great momentum in the recent past due to advancements in nanotechnology. Some of these sensors are proven to be useful for monitoring and measuring micro/nanoparticles (µ/NPs). Additionally, unwanted health-related and environmental impacts of such µ/NPs underlines the need of real-time measurement systems [1]. Consequently, a silicon-based microcantilever device has been developed for real-time monitoring and measurement of airborne NPs with a detection limit and quality factor (Q) of 5 µgm⁻³ and 4702, respectively [2]. However, detection of µ/NPs within liquid environment has been a great hurdle over past years with the main measurement challenge of low Q values due to high damping of the sensor. Recently, the possibility of detecting and scaling of dispersed µ/NPs with an improvement of Q has been demonstrated and accomplished using microfluidic channels [3]. These devices are however tagged with high cost, and require a lot of technological advancement in order to be realized. Hence, pegging the need for a simple fluidic particle detection approach.

Dispersed fluidic particles can be adsorbed onto a sensor’s sampling area. Here, the adsorption process depends on the surface properties of the material, i.e., its wettability, which correlates directly to surface energy [4], and depends upon surface topography, cleaning and etching procedures and surface treatment [5, 6]. The surface wettability can be quantified by determining the contact angle θ between a horizontal solid surface and a liquid droplet. For a hydrophilic surface (θ < 90°), the drop
contact radius $R_c$ remains constant during evaporation as the droplet mass (or contact angle) reduces. In contrast, the contact angle for hydrophobic surfaces ($\theta > 90^\circ$) tends to be constant with diminishing contact area during solvent evaporation [7]. Primarily, by observing the shape of the drop angle $\theta$ can be measured (figure 1). In this case, $\theta$ is the angle formed between the drop tangent and the solid surface at the tri-phase contact point of a simple spherical droplet. This can be done directly, or by calculating $\theta$ from the contact radius $R_c$ and the height $h$ of the sessile drop above the solid surface based on a simplified Young-Laplacian equation assuming a spherical shape of the drop, i.e., the half-angle method [4]:

$$\frac{\theta}{2} = \tan^{-1} \left( \frac{h}{R_c} \right)$$

(1)

The angle $\theta$ depends on the surface tensions between solid–liquid, solid–air, and liquid–air interfaces. Due to the dominance of surface tension over gravity on a small drop, a liquid drop tends to form a spherical cap shape to minimize total free surface energy. Consequently, this results in a capillary length defined as $L_c = (\gamma / \rho g)^{1/2}$ [8] where $\gamma$, $\rho$ and $g$ represent the liquid-vapor surface tension, the density of the liquid and the acceleration due to gravity, respectively. For water, at room temperature and standard pressure conditions, $L_c \approx 2.7$ mm [$\gamma = 0.0072$ Nm$^{-1}$, $\rho = 1$ gcm$^{-3}$ and $g = 9.8$ ms$^{-2}$].

![Figure 1. Schematic of contact-angle measurement using the half-angle method.](image)

In this study, we initially investigate and optimize the wettability of the $n$-type (100) silicon surface followed by the adsorption of liquid-dispersed microparticles on a piezoresistive cantilever sensor. Aqueous suspensions of polymethyl methacrylate (PMMA) and polystyrene (PS) microparticles (obtained from Sigma-Aldrich Inc.) with respective diameters of 1.96 $\pm$ 0.05 $\mu$m and 4.97 $\pm$ 0.05 $\mu$m were used in this study. The contact-surface area of the liquid droplet with the solid was also determined. Using these results, theoretical predictions and practical implementations of the adsorption process of particles on silicon material can be achieved. As a result, the mass of PMMA or PS particles deposited and adsorbed on a cantilever sensor can be precisely determined.

2. Substrate preparation and surface treatment

The substrates (~15×15 mm$^2$) used for this study were diced from $n$-type (100) silicon wafers (Siegert Wafer GmbH, Germany) with resistivity and thickness of 1-10 $\Omega$cm and (275 ± 15) $\mu$m, respectively. Cleaning was done by boiling the substrates for 5 min in an oxidant solution containing a mixture of sulfuric acid ($H_2SO_4$, 96%) and hydrogen peroxide ($H_2O_2$, 30%) in a volume ratio of 1:1. Subsequently, the substrates were immersed in a water bath for 5 min and then rinsed with deionized (DI) water and blow-dried with nitrogen. Upon cleaning, the substrates were then dipped in HF solution for 5 s and immediately treated by O$_2$ plasma (100-E, Technics Plasma GmbH) for 2 min at an RF power of 220 W. Measurement of the water contact angle $\theta$ followed right after the cleaning and treatment process respectively, for two different sets of substrates.

Measurement of $\theta$ was carried out by the sessile-drop method using a dispensing system integrated with an imaging apparatus. The latter consisted of a light source, a collimating mask, an adjustable
stage, and a digital microscope camera (Mz-902, Oowltech). The diameter of the dispensing needle was ~0.15 mm, and a low pressure (~0.1 bar) was applied to dispense a droplet at room temperature. Subsequently, the profile of the drop image was extracted by an image-fitting method using the Low Bond Axisymmetric Drop Shape Analysis program (LBADSA) [8]. The LBADSA approach is based on the half-angle method (figure 1) and allows for calculation of $\theta$ from sessile drop images based on equation (1). In the LBADSA method, $\theta$ is approximated based on a perturbation solution of the Laplacian equation for the contour of a sessile drop, and assumes gravity as the only external force [9]. With this approach, contact angles of 47.3° ± 2.7° and less than 9° were respectively measured on silicon substrates prior to and after O$_2$ plasma treatment (2 min). It is obvious that surface treatment with O$_2$ plasma yielded enhanced hydrophilicity, comparable to the previously reported values of 9° ± 1.6° ($t_{O_2\text{-plasma}} \approx 5$ min) [5] and 24.5 – 46.5° ($t_{O_2\text{RIE-plasma}} = 1 – 20$ min) [10]. This can be attributed to the measurement of contact angles immediately after O$_2$ plasma treatment. In the case of this study, the short time gap between O$_2$-plasma treatment and contact-angle measurement does not compromise the results, which can be otherwise a consequence of buildup of static charges. Moreover, for our evaluation of the experimental contact angle, we assume a negligible effect of gravity and a constant droplet volume.

3. Droplet on substrate: Determination of volume and surface-contact area

In determining the volume $V_d$ of a drop containing monodispersed microparticles, a theoretical volume ($V_t = \pi d^3/6 \approx 1.8$ nL) of a spherical-shaped droplet was initially assumed and estimated. Moreover, the diameter $d$ of the deposited droplet was also assumed to be equivalent to that of the dispensing needle (~0.15 mm). Subsequently, DI water droplets were deposited on the pre-treated substrates and drop images were captured thereof. Through drop-image extractions based on the LBADSA technique, the volume of water droplet $V_d$ was found to be 3.44 ± 1.52 µL. From the measured volume, our initial assumption of the equivalence of $V_t$ with $V_d$ was thus rendered invalid. Consequently, we kept constant the measured drop volume and substituted the DI water with an aqueous suspension of monodispersed particles. In this work, our target particles were PMMA and PS particles with a mass concentration of about 0.01 g per mL. Each particle solution was thoroughly mixed in an ultrasonic bath before drawing a test sample. This was necessary to ensure uniform particles concentration in the sampled droplet(s).

Given that the mass concentration of both PMMA and PS was the same (0.01 gmL$^{-1}$), different number of particles per droplet would therefore be expected due to the variance in particle densities and sizes. A summary of the number of individual microparticles per droplet is shown in table 1. The number of particles in each droplet is simply determined from the ratio of total mass to the corresponding single particle mass i.e. ~ 4.65 pg (PMMA) and ~ 67.49 pg (PS). These values were determined from the product of the respective particle density and volume (of a spherically shaped particle). The densities of the 1.96 $\mu$m PMMA and 4.97 $\mu$m PS particles were, respectively, 1.18 g cm$^{-3}$ and 1.05 g cm$^{-3}$ [11].

| Table 1. Estimates of the mass and number of microparticles per droplet. |
|---------------------------------|------------------|------------------|
| Particle solution              | Mass of microparticles (ng) | Number of microparticles |
| [0.01 g mL$^{-1}$]             | $V_t$      | $V_d$       | $V_t$ | $V_d$ |
| PMMA                           | 18.53      | 34400       | 3984  | 7394513 |
| PS                             | 18.53      | 34400       | 275   | 509684  |

Similarly, based on the LBADSA method, the average droplet surface-contact area $S_C$ on Si substrates was determined. The contact area on pre-treated Si substrates was 8.77 ± 2.34 mm$^2$, whilst on substrates treated with O$_2$ plasma (2 min) the area was indeterminate due to $\theta < 9^\circ$ (i.e. the optical detection limit of our setup). Nevertheless, the surface-contact area on treated substrates was observed to be much larger than the pre-treated ones, i.e., $S_C$ was therefore evidently shown to depend on the
degree of hydrophilicity. The intention of measuring the droplet contact area on different substrates was to assess the practicality of fitting the droplet on a defined position of our mass sensors whose possible particle collection areas were about 0.139 mm$^2$ and 0.248 mm$^2$ for cantilevers with rectangular and triangular free-end configurations [12, 13], respectively. From the obtained results, it is quite evident that the sensor particle collection areas are much smaller than the average $S_C$ of pre-treated silicon substrates, whose surface properties actually closely resemble that of the cantilever sensor. Thus, making it impractical to directly align, deposit and perfectly adhere the droplet onto the surface of a cantilever. A small-sized droplet is desirable, and an optimized geometrical design of a cantilever containing a differentially treated surface is therefore intended.

4. Droplet evaporation and microscopic characterization of adsorbed microparticles

To further compare and validate the volume-based estimates of the number of particles per droplet (table 1), $\mu$Ps were adsorbed on $n$-type (100) Si substrates and observed using scanning electron microscopy (SEM). Firstly, a droplet of known volume $V_d$ was deposited on a pre-treated substrate, and the solvent was evaporated for about 20 min at ambient conditions, i.e., with temperature and relative humidity of about 23.8 $^\circ$C and 43%, respectively. Secondly, the adsorbent was initially analyzed with an optical microscope and subsequently with the SEM to determine particle distributions with an aim of counting the number of particles.

The adsorbed PMMA $\mu$Ps on pre-treated samples are closely packed and mostly multilayered (figure 2a). However, the drop profile (figure 2b) of the adsorbed $\mu$Ps on treated Si substrates consisted of a cluster of segments of a multilayer (along the edge or ring of the droplet, figure 2c) and a monolayer (spatially distributed from the center of the droplet, figure 2d). The thickness of the monolayer is approximately equal to the particle size, i.e., $1.90 \pm 0.07$ µm (PMMA) and $4.66 \pm 0.21$ µm (PS). The degree of uniform distribution of the monolayer on the treated substrates was higher compared to the pre-treated samples. The SEM micrographs from treated substrates were analyzed with ImageJ [14] to determine the number of adsorbed microparticles per droplet. But, the observed segment of multilayers was a hindrance in determining the precise number of the adsorbed particles. In order to obtain homogeneous distribution of mono-layered $\mu$Ps on treated Si substrates, further optimizations through spin coating processes of the particle-laden droplet is intended.

Figure 2. SEM images of adsorbed $\mu$Ps: (a) on pre-treated Si substrates showing a cluster of multilayered particles, (b) on treated Si substrates, with (c) a clustered multilayered ring and (d) a segment of monolayer particles.

5. Resonant frequency measurements

The frequency responses of the adsorbed microparticles on an electrothermally actuated piezoresistive microcantilevers (excited in-plane mode) were measured and evaluated. These rectangular cantilevers
$(l \times w \times t = 1000 \times 170 \times 15 \, \mu m^3)$ are fabricated in-house from $n$-type (100) silicon wafers by a bulk-micromachining process [13]. Initially, a clean bare cantilever was mounted on a sample holder, and its resonant frequency $f_0 \approx 202099$ Hz was measured as shown in figure 3(a). Subsequently, the cantilever was tilted ($\sim 60^\circ$) and a droplet ($V_d \approx 3.44 \, \mu L$) was carefully deposited at a point on the sensing surface a few microns from the edge of the free-end. This was necessary to avoid spilling of the solvent at the edge of the cantilever during the drop impact. Upon adhesion of the droplet, the cantilever was then tilted back to its normal horizontal position. The solvent (i.e. water) was then evaporated and resonant frequency of the cantilever with the adsorbent (inset in figure 3b) was monitored over time (for at least 5 min) at ambient conditions.

The adsorbent on the cantilever show a distributed mass over the entire sensing area, and causes a shift in resonant frequency $\Delta f$, which corresponds to the mass $(\Delta m)$ of the adsorbed particles. The frequency shift $\Delta f$ can be determined from the following relation:

$$
\Delta f = \frac{f_0}{2m_0} \Delta m
$$

The parameter $f_0/2m_0$ in equation (2) is equivalent to the sensitivity ($\sim 24.78 \, Hz/ng$) of the cantilever mass sensor. We find cantilever resonant frequencies (figure 3) of $f_0 \approx 160.723 \, kHz$ at about 5 min and $f_0 \approx 160.725 \, kHz$ after 25 min. Therefore, droplet evaporation period of at least $\sim 5$ min was reasonably allowed prior to the measurement of the resonant frequency response of the adsorbent. The shift $\Delta f$ of the adsorbent was calculated to be $41.515 \, kHz \pm 6 \, Hz$, which corresponds to about $394786$ PMMA particles. This number considerably deviates from the previous volume-based particle estimates ($\sim 7394513$), where the same droplet ($V_d \approx 3.44 \, \mu L$) was assumed. The difference in the measured and expected number of $\mu$Ps could be attributed to non-uniformity in particle distribution due to random adsorption [15], and a variance in concentration is further supposed.

![Figure 3](image.png)

**Figure 3.** Measured resonant frequency responses of cantilever sensor (a) without particles, and (b) with adsorbed PMMA particles (monitored with evaporation time).

Furthermore, the Q-factor values of the thermally actuated cantilever prior to and after particles adsorption were computed to be 2098 and 1224 respectively. The measured lower quality factor upon adsorption of particles may be partly due to damping arising from the particle layer on the cantilever. The precise values of $f_0$ and $Q$ were extracted out of the asymmetric resonance curves based on the Fano-fit method [12]. The cantilever sensors used in this study were generally cleaned after each adsorption- and frequency-measurement cycle so as to regenerate it. The cleaning process involved immersing a particle-laden cantilever in ethanol mixed with DI water for $5 \, min$, followed by thorough
rinsing with DI water. Upon cleaning, the resonant frequency of cantilever was again measured and compared with the pre-adsorption $f_0$ value, leading to $f_0 \approx 202.099$ kHz.

6. Conclusion

This study investigated the wettability of $n$-type Si substrates by water-based suspensions of µPs for a defined deposition on piezoresistive microcantilever sensors. The substrates which were cleaned in an oxidant solution of $\text{H}_2\text{SO}_4$ (96%) and $\text{H}_2\text{O}_3$ (30%), 1:1 (v/v), resulted in hydrophilic surfaces ($\theta \approx 47.3^\circ$), whereas those treated with O$_2$ plasma (2 min) exhibited enhanced hydrophilicity ($\theta < 9^\circ$). The profile of particles on treated substrates was also observed to have segments of mono-layers and multi-layers, while pre-treated substrates were exclusively multi-layered. The volume ($\approx 3.44 \mu\text{L}$) of a single droplet and the mass of microparticles ($\approx 34.40 \mu\text{g}$) was also measured and calculated, respectively. The mass of the PMMA particles ($\approx 1673 \text{ng}$) for a single droplet adsorbed on a cantilever was realized using resonance-frequency response measurements. A marked deviation between the two experimentally determined mass values was though observed, and further investigation is intended.

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