



Role of surface morphology on desorption kinetics of water molecules from uncoated silicon microcantilever



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ABSTRACT

Desorption kinetics of water molecules from uncoated silicon microcantilevers (MC) is studied, by measuring resonance frequency, with Relative Humidity (RH) varying in the range of 50–15%. Shift in resonance frequency of MC was used to estimate the desorbed mass, which over-estimated the number of monolayers desorbed between the RH values of interest and followed a single exponential decay model. Moreover, desorption rate is found to be higher for $RH > 25\%$ compared to $RH < 25\%$. However, the Q factor describing the sensitivity of the MC and computed from the resonance spectrum is found to decrease by $\sim 3\%$. These results are explained on the basis of complex surface coverage during desorption of water molecules and is supported by topographical image of MC surface clearly showing quasi 3D nanofeatures. The bending of uncoated MC during desorption, due to the generation of differential surface stress, further confirms the presence of these surface features.

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1. Introduction

Physical or chemical adsorption onto the surface of microcantilevers (MC) is the basis for a rapidly growing field of several chemical and biological sensing in the mechanical domain [1–3]. The MCs are usually coated with a sensitive layer whose purpose is to selectively sorb the analyte of interest, resulting in either a deflection due to the generation of differential surface stress (static mode) or a shift in the resonant frequency due to the added mass (dynamic mode) [4]. However, the coated MCs primarily possess disadvantages such as poor reproducibility of results and the influence of the coating material itself [5]. In the case of polymer coated MC, the surrounding medium is known to affect the sorption properties. A thermal drift in the output signal is often observed due to temperature dependence of Young's modulus of the polymer. Moreover, the limited long term stability of the viscoelastic coatings and the resulting aging also affect the reliability of the sensor [6]. Taking these aspects into consideration, recently there are attempts to use uncoated MCs for various sensing applications [6–10].

Understanding the interaction of target molecules on the surface of MC is of vital importance to both basic research and technological applications. For example, the adsorption/desorption kinetics

of MC would be of interest, which would be useful in determining the response time of the sensor [11]. Also knowledge of the MC surface features and their role on adsorption/desorption kinetics would help in designing the MC surface that would maximize the sensitivity [7,12]. Several experimental studies reported in literature, show that surface features are indeed crucial to understand the evaluation of adsorption induced surface stress, resulting in MC bending [5,13].

While it is well known that adsorption/desorption of molecules results in resonance frequency shift, the sensitivity of the resonant MC to detect the same also depends on its spectral resolution, which is directly related to the Q -factor. Q -factor is defined as the ratio of the stored energy to the dissipated energy and is associated with damping and energy dissipation. The larger the value of Q , the higher the sensitivity of the resonance system is to external perturbations and is a measure of sharpness of resonance peak [14]. It is therefore pertinent and imperative to understand the dependence and role of Q in adsorption/desorption studies. Q -factor of the MC is determined by various mechanisms like losses due to fluid interaction and surface defects, attachment losses and losses due to phonon scattering, etc. [15]. Ergincan et al. [16] have performed a systematic study on the dependence of Q -factor on the surface of commercial MCs at various gas pressures, covering the entire range from the free molecular up to continuous regime (ambient pressures ~ 1 atm). They have shown that, in the molecular regime Q scales with pressure P as $1/P$, while in continuous regime the scaling changes to $\sim 1/\sqrt{P}$.

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In the present work, we have studied the desorption kinetics of water molecules on an uncoated Si MC with a native grown SiO₂ layer, in dynamic mode. Resonance frequency of MC was measured at regular RH intervals and Q-factor was estimated from the measured resonance spectrum. We present experimental evidence to show that the presence of complex surface features on MC surface revealed by AFM morphology, is the reason for the nonlinear desorption behavior of uncoated MCs. These results are further supported by MC bending measurements, which is a result of presence of surface features on the MC. Information obtained from the present studies can be vital in the design of MC based humidity sensors under ambient environmental conditions.

2. Experimental details

Commercially available, rectangular shaped, tipless silicon n-type (Model no: SICON-TL, M/s AppNano, USA) MCs, which are made of single crystal n-type silicon with antimony doping, were used in the present work. Physical dimensions of the MC were 450 μm long (±1 μm), 40 μm (±1 μm) wide and 2.5 μm (±0.5 μm) thick with a spring constant of 0.21 N/m (±0.006). An AFM head (M/s NT-MDT Ntegra Prima, Russia) along with the MC, was placed inside an airtight chamber and was purged with nitrogen gas in order to reduce the RH from 50% to 15%. N₂ flow rate was kept constant to avoid any artifacts due to gas flow. Prior to conducting actual experiments, several test runs were conducted, to zero in on the limits over which the RH needs to be varied and the reversibility process (see Supporting information S1). The RH level of chamber was measured using a standard RH meter with an accuracy of ±3.5% RH. The rise in temperature in the chamber was ~2°C during RH change from 50% to 15%.

At regular intervals of RH, resonance frequency of MC was measured using the laser and a photo diode arrangement of the AFM head. With the MC placed on a piezo-actuator, the out-of-plane vibrations were monitored using laser and a four quadrant photodetector system (ABCD). The piezo-actuator was excited vertically, and the photodetector output signal (AB–CD), proportional to MC vibrations, is detected using lock-in method. The frequency sweep was done in the range of 12–15 kHz with a step of 1.4 Hz and the data was fit to Lorentzian, from which resonance frequency (f_0) and band width (BW) were computed at every RH. The stability of frequency measurements and noise floor of the present experimental setup are given in Supporting information S2.

From the observed frequency shift (f_2) with reducing RH values, with respect to its value at 50% RH (f_1), the desorbed mass (Δm) during desorption was estimated using the equation,

$$\Delta m = \frac{k}{4\pi^2 n} \left(\frac{1}{f_1^2} - \frac{1}{f_2^2} \right) \quad (1)$$

where 'k' is the spring constant, 'n' is a geometric factor which is 0.24 for a rectangular cantilever in fundamental mode [17]. The associated Q-factor during desorption process was estimated using the relation, $Q = f_0/BW$.

MC bending measurements during desorption of water molecules were also carried out, using the same set up after the resonance frequency measurements. The deflection sensitivity of the present AFM head is measured by contacting the MC with a calibrated piezoelectric element in motion and is found to be 20 pA/nm. From the deflection data (Δz), differential surface stress ($\Delta\sigma$) is estimated using the modified Stoney's equation given by [18],

$$\Delta\sigma = \frac{ET^2}{4(1-\nu)L^2} \Delta z \quad (2)$$

where 'E' is Young's modulus, 'ν' is Poisson's ratio and 'L' and 'T' are length and thickness respectively of the MC used.

Prior to the above experiments, the MCs used in the present study were *piranha* cleaned and were loaded into the experimental chamber immediately. It is known that *piranha* cleaning removes the organic contamination on MC and a native oxide of about 5 nm that is grown [19]. This was confirmed by measuring the contact angle on the cantilever chip which was found to reduce from 95° to <10°. After the frequency and deflection experiments, the surface morphology of MC was examined using AFM in tapping mode. A gold coated cantilever (with tip) was used to scan the sample MC surface.

It may be noted that the MCs used in the present work are uncoated with only the presence of native oxide on its surface. This layer is prone to hydrophobic contaminants (hydrocarbons) when stored in air. It is indeed possible to study desorption kinetics with a more stable thermally grown SiO₂ film on MC surface. However, any potential experiment intending to grow SiO₂ on MC will alter the surface morphology and may introduce the residual intrinsic stress [20–22], which will influence the desorption kinetics.

Also, while studying the contamination on AFM cantilevers using Time of flight SIMS and contact angle measurements, Sirghi et al. [23] have pointed out that *Piranha* cleaning will leave the surface clean and at least it will take 5 days for the surface of MC to become contaminated again. Taking these aspects into consideration, uncoated MCs with only native oxide were used in the present work and the entire experiment was completed within 6 h.

3. Results and discussions

Fig. 1(a) shows the variation in resonance frequency and the associated desorbed mass estimated using Eq. (1), as a function of time, when humidity in the chamber was reduced from 50% to 15% over a time period of 400 min. It is clear from this figure that the resonance frequency increases as a function of time, till about 125 min, beyond which it remains almost constant. Desorbed mass was found to fit well to a single exponential decay model with a decay rate of 0.02 min⁻¹. This indicates that the MC surface coverage with water molecules during desorption is complex. The rate of desorption is generally expected to vary linearly with time for a constant rate of loss of water molecules which in turn is proportional to the total surface area. However, this is true only for planar surfaces, which is in contrast to real surfaces possessing a corrugation either due to intrinsic nature of formation or during deposition. In fact, similar exponential behavior has been observed by Muralidharan et al. [12] in desorption of TNT molecules from uncoated MCs. They however, found that their data fits well to a double exponential model and attributed it to the diffusional transport of TNT away from the MC surface and to the complex surface coverage involved. But, the same authors in a further study [7] reported that TNT desorption kinetics on similar uncoated MCs follows a linear decay model. This contradiction was explained on the basis of island formation at preferred sites which depends on the surface structure and could vary from cantilever to cantilever. However in both the studies, no experimental evidence was provided to support the argument based on MC surface. Further, Raghu et al. [24], have reported the desorption kinetics of H₂O molecules from native grown SiO₂ on Si surface using electron impact mass spectrometer. They also noticed an exponential decay during desorption and explained it on the basis of multilayer adsorption model. But this study also did not examine the role of morphology on kinetics.

To further understand the present experimental results, total desorbed mass is plotted with RH and is shown in Fig. 1(b). From this figure, it is evident that water molecules desorb with two different rates during RH variation. A faster rate having slope of 4.6 pg/RH% and a slower desorption rate of 0.2 pg/RH% are obtained, during high (>25%) and low (<25%) RH values respectively. This can be

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