Combined *in situ* micromechanical cantilever-based sensing and ellipsometry

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Two cantilever-based chemical sensors are reported. First, a differential cantilever-based chemical sensor capable of sensitive surface stress measurements has been designed and implemented. The system uses two commercially available atomic force microscope cantilevers. The surface of one cantilever is functionalized to make it receptive to specific target analytes, while the second, passivated cantilever is used as a reference by subtracting undesired signals, resulting from mechanical and thermal noise, from the signal of interest. The second system is a combined cantilever-based sensor and ellipsometer capable of simultaneous *in situ* surface stress and film thickness measurements. Both sensors, operated in static mode, achieve a cantilever deflection measurement sensitivity of 0.2 nm and a surface stress resolution of 5×10^{-5} N/m. Molecular monolayer thicknesses are measured simultaneously with a 0.1 nm resolution. The real-time formation process of alkanethiol self-assembled monolayers on gold was investigated as a model system to characterize these instruments.
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I. INTRODUCTION

Micromechanical cantilever-based sensors are increasingly being used to probe nanoscale quantities of mass, heat, radiation, and surface stress.[1] These types of sensor are quickly gaining in popularity due to their high sensitivity (e.g., picogram, micro-Kelvin) and fast response (millisecond). Their potential as medical screening devices or as industrial monitoring sensors is currently driving research in this emerging field. For example, several groups[2–4] have already used these sensors for DNA sequence recognition in the hopes of improving on current sequencing technologies. Others[5] are using them as electronic noses by developing arrays of micromechanical sensors used for chemical mixture detection. However, if these micromechanical sensors are to become a useful technology, it is important to develop tools capable of accurately quantifying and characterizing the origin of the induced surface stress driving the cantilever's response.

We report on the development of a differential cantilever-based chemical sensor used for sensitive surface stress measurements. Furthermore, an adapted sensor capable of complementary ellipsometric measurements is also described. The combined cantilever-based sensor and ellipsometer is capable of simultaneous *in situ* surface stress and film thickness measurements associated with molecular adsorption. The self-assembly of alkanethiol monolayers on gold was investigated as a model system to characterize these instruments.

The use of alkanethiol self-assembled monolayers (SAMs) has rendered these sensors suitable to a wide variety of applications. Alkanethiol molecules can be functionalized such that the resulting SAM, when formed on the cantilever surface, becomes a receptive surface sensitive to specific molecular targets. For example, thiolated oligonucleotides are self-assembled onto the cantilever surface for DNA sequence recognition experiments, and alkanethiol molecules with carboxylic end groups can be used for PH measurements.[6] Furthermore, the sensors' attractiveness lies in the fact that the sensitive receptive layer is both selective (molecular specificity) and reactive (surface stress) to the presence of the target analyte.

II. DIFFERENTIAL CANTILEVER-BASED SENSOR

A. Setup

A custom-made differential micromechanical cantilever-based chemical sensor was designed and built. The system, as depicted in Fig. 1, is designed to accommodate two commercially available microcantilevers.[7] One cantilever is used as the active cantilever, and the second, passive cantilever is used as a reference. During an experiment, the active cantilever will deflect as a result of the adsorption of the target molecule onto its surface, but it will also deflect due to other factors. These parasitic cantilever deflections occur as a result of several effects, such as temperature changes (bimetallic effect), turbulent flow around the cantilever, environmental noise, non-specific binding, etc. These effects are particularly problematic when the system is used in liquid, as opposed to experiments carried out in a gas environment. In order to be effective, the reference cantilever must react to every stimulus the active cantilever reacts to, except to the presence of the target molecule of interest. This reference

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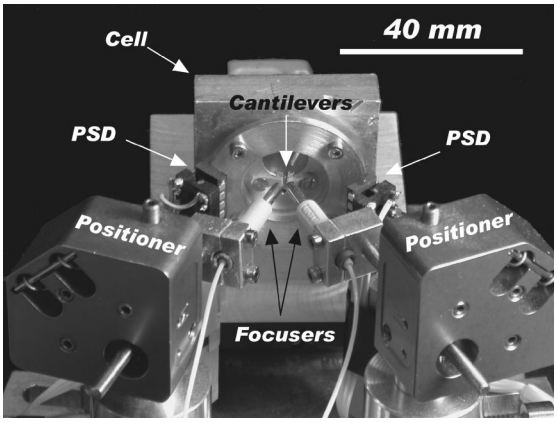

FIG. 1. Image of the differential cantilever-based chemical sensor. Highlighted in the image are the laser focusers, the cell holding the active and reference cantilevers, the PSDs, as well as the positioners used to focus the laser light onto the cantilever apex.

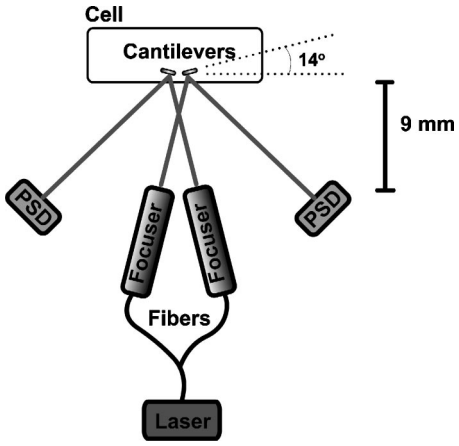

FIG. 2. Top view of the optical beam deflection sensing setup. The laser light is coupled to a single mode fiber, and then split into two fibers. The emerging light is focused onto the cantilever apex using two focusers. The reflected light is monitored using two PSDs. The working distance between each focuser and their respective cantilever is approximately 9 mm.

signal is then subtracted from the active cantilever's signal to give a measurement of surface stress that is purely due to the adsorption of the target molecules onto the active cantilever's surface.

Several deflection sensing schemes can be used to monitor the cantilever deflections. For example, piezoresistive[8] or capacitive[9] cantilevers have been used by others. Unfortunately, these types of cantilevers tend to have a higher spring constant than typical silicon or silicon nitride cantilevers, which makes them less suitable for sensing applications in the static mode. Furthermore, care must be taken to isolate the deflection sensing electronics from the chemical environment surrounding the cantilevers. Fiber interferometry[10] is also used for deflection sensing, but is not recommended due to its fragility and the difficulty associated with cleaning the fiber between experiments. A laser beam deflection technique similar to the one commonly used in atomic force microscopes (AFMs) was used in our systems. This method has the main advantage that all the deflection sensing components are kept out of the cell environment.

Although the system utilizes two independent cantilevers, a single laser light source was used in order to subtract any laser intensity noise that might influence the deflection measurements. For this purpose, a laser diode[11] operating at 635 nm was coupled to a FC-connectorized single-mode fiber. This wavelength was chosen to minimize the amount of absorbed power by the gold-coated cantilevers, while remaining in the visible range to facilitate alignment. This laser light was then split into two single-mode fibers using a 50/50 coupler.[11] These two fibers were then fitted with small lenses, which focus the laser light to a spot size of $\sim 16\ \mu$m at a working distance of 9 mm.[12] These focused laser beams are easily aligned onto the apex of the two cantilevers using a five-axis positioner.[13] The displacement of the reflected optical beams is then monitored using linear position sensing (photo)detectors (PSDs).[14] Figure 2 shows a top view of the cantilevers, along with the components needed for the optical beam deflection sensors.

PSDs were utilized instead of four-quadrant photodetectors commonly used in commercial AFMs. PSDs have the advantage that there is no need to align the reflected beam with the center of the detector, since linearity is maintained over most of their active surface (>80%). Although four-quadrant detectors typically have a larger bandwidth, we opted to use PSDs since deflection measurements (static mode) are done, as opposed to frequency (dynamic mode) measurements, and adequate sensitivity is achieved. Furthermore, PSDs are less sensitive to oddly shaped reflected spots since the position signal follows the centroid of light impinging on the PSDs photoresistive surface, which spans the area between two electrodes.

The PSD's photocurrent signals originating from the two electrodes are amplified using low-noise transimpedance amplifiers ($I-V$ converters).[15] The amplified voltages are then processed by an analog dividing chip[16] in order to convert the signal into a voltage that is independent of laser intensity.[17] The circuit diagram used is shown in Fig. 3. The output voltage is directly proportional to the position of the reflected beam on the PSD, which in turn is directly proportional to the cantilever deflection. The PSD signal is acquired

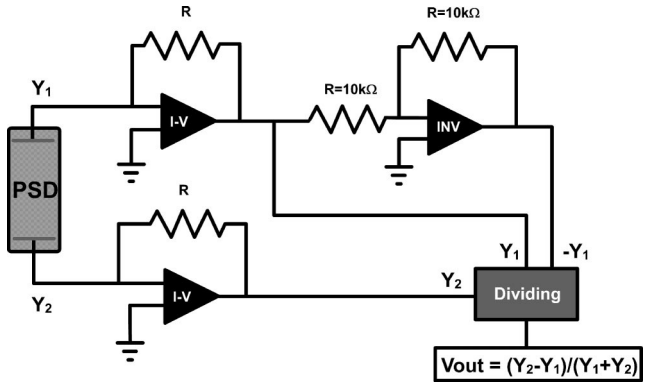

FIG. 3. Electronics used to convert the PSD electrode photocurrents to a voltage proportional to the laser spot position on the PSD surface. The photocurrents are processed by current-to-voltage converters ($I-V$). The gain of the $I-V$ is determined by R. The Y1 voltage is inverted (INV). The two signals are then fed into a dividing chip. The gain of the $I-V$s was determined by the feedback resistor. The value of R was selectable (100 kΩ, 220 kΩ, 470 kΩ, and 1 MΩ). The two feedback resistors were matched to better than 0.01%.

using a 16-bit analog-to-digital data acquisition card[18] interfaced to a computer.

In order to accurately quantify the surface stress causing a deflection, it is important to precisely relate the PSD signal with the cantilever's deflection, and then to convert this deflection to a surface stress. We have reported elsewhere[19] on a method to quantify the surface stress from the measured PSD signal, the results of which are summarized here. First, the deflection measurement is calibrated using a complementary fiber interferometer. Second, the surface stress, $\Delta\sigma$, is inferred from the cantilever deflection, Δz, as expressed by Eqs. (1) and (2):

$$\Delta\sigma = \frac{4}{3(1-\nu)} \frac{l}{Wt} k_{\text{rect}} \Delta z \tag{1}$$

for rectangular cantilevers, and

$$\Delta\sigma = \frac{2}{3(1-\nu)} \frac{l^2}{\left[Wtl_1 + \frac{tb}{4l}(l-l_1)^2 \right]} k_{\Delta} \Delta z \tag{2}$$

for V-shaped cantilevers, where k_{rect} and k_{Δ} are the measured spring constants of the rectangular and V-shaped cantilever, respectively. W is the cantilever leg width, t is its thickness, l is its length, l_1 and b are the V-shaped cantilever's intermediate length and base width, respectively. V-shaped silicon nitride cantilevers were used in the experiments described here. Given a cantilever deflection resolution of about 0.2 nm, a surface stress sensitivity of $\sim 5 \times 10^{-5}$ N/m is achieved.[20]

There are several parameters that must be considered when designing the sensor's cell. In particular, both the active and the reference cantilevers must be as close to each other as possible, the cell material must be nonreactive and easily washed between experiments to prevent contamination, and the back of the cantilevers must be accessible for calibration.[19] The front of the cell is sealed with glass pressed against a Teflon o-ring. The glass is necessary to allow for the focused laser beam to enter the cell towards the cantilevers. The two cantilevers are separated by ~ 2 mm. This minimum separation is constrained by the width of the chip onto which the cantilevers are mounted. The cantilevers are angled away from each other by an angle of 14°, as shown in Fig. 2. This angle is necessary due to space restrictions so that the reflected laser beams do not hit the opposing focuser. Prototypical cells were made of aluminum, PEEK[21] and KEL-F.[22] Aluminum was used for the alkanethiol experiments described below; KEL-F proved to be difficult to clean from alkanethiol contamination. The aluminum cell was cleaned between experiments by soaking in a boiling ethanol/chloroform (50/50) solution for 5 min followed by 30 min of ultrasonication in the same solution. *Boiling ethanol/chloroform using a hotplate can be a fire hazard. The use of an explosion-proof heater in a fumehood is strongly advised.*

The introduction of analytes into the cell can be done either using a flow or a closed-volume method. In the flow method, analytes (liquid or gas) are flowed into the cell via an inlet hole and exit the cell through a second outlet hole.

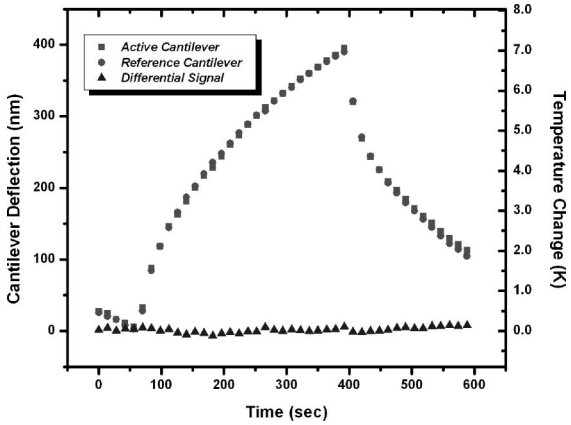

FIG. 4. Both the active and the reference cantilevers deflect due to an increase and a decrease in temperature. The differential signal is unaffected by temperature variations.

We will focus on describing our closed-volume system as most of our experiments were performed under these conditions.

In the closed-volume cell, the analyte is introduced into the cell by injection through a Teflon-lined septum at the back of the cell. For our surface stress measurements associated with SAM formation onto the gold-coated cantilever from the vapor phase, pure liquid dodecanethiol was injected at a specific location in the cell. The volatile liquid droplet then evaporated and the dodecanethiol vapor concentration at the gold surfaces increased up to saturation.

B. Results and discussion

In order to measure the surface stress induced by the formation of alkanethiol SAMs on gold from the vapor phase, one side of the active cantilever was coated with gold by thermal evaporation.[23] In this case, one side of the reference cantilever was also coated with gold to make it equally sensitive to temperature variations, but, in addition, an alkanethiol SAM was grown *ex situ* prior to the start of any experiment. This process protected the gold surface of the reference cantilever by preventing additional alkanethiol molecules from binding to the gold. In essence, the reference cantilever is now completely unreactive to the presence of alkanethiols, but is still sensitive to other environmental effects. The SAMs grown on the reference cantilevers were prepared by incubating the gold-coated cantilever in a 1 mM dodecanethiol/ethanol solution for 24 h. Furthermore, using commercially available cantilevers that are mounted on separate chips facilitates the passivation of the reference cantilever independently from the active cantilever.

In order to characterize the effectiveness of the reference cantilever in our differential system, we monitored both the active and the reference cantilevers' deflection as we varied the ambient air temperature surrounding the cantilevers. Figure 4 shows a graph of the cantilevers' response to a varying temperature. It is clear that both cantilevers react similarly to variations in temperature. Similar tests showed that the reference cantilever successfully subtracted mechanical noise from the measurement. In another test, dodecanethiol was injected in the cell. The gold-coated active cantilever deflects

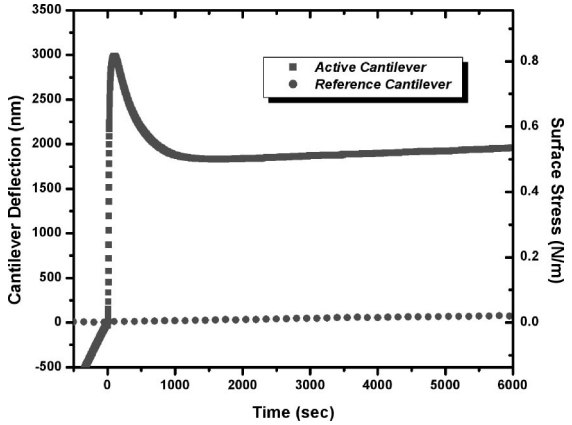

FIG. 5. Active gold-coated cantilever deflects when exposed to vapor dodecanethiol at time=0 s. The reference cantilever, precoated with a dodecanethiol SAM, is unaffected by the introduction of dodecanethiol. The deflection of the active cantilever prior to the injection of dodecanethiol is attributed to a contamination (exposure to air) of the freshly evaporated gold layer.

due to the surface stress induced by the growth of the dodecanethiol SAM on the cantilever surface, as shown in Fig. 5. Meanwhile, the SAM-coated reference cantilever does not react to the introduction of the dodecanethiol. This shows that the reference cantilever is behaving as it should; it is unreactive to the presence of alkanethiols, but still response to other stimuli that also induce a deflection.

In our setup, the separation distance between the injected alkanethiol droplet and the cantilevers can be controlled. The time constant associated with the increase up to saturation of the alkanethiol vapor concentration at the gold surface is proportional to the square of the droplet-to-cantilever distance. In a first system modification, cylindrical extensions added at the back of the cell, as depicted in Fig. 6, made it possible to control this time constant. The droplet can also be located at the front of the cell for a rapid increase in alkanethiol vapor concentration. In all cases, enough liquid alkanethiol was injected to ensure that the droplet did not completely evaporate before the vapor reached saturation. Figure 7 shows the induced surface stress as a function of time for droplet-to-cantilever distances of 3, 23, 96, and 246 mm, corresponding to cell volumes of 3, 3, 12, and 32 ml, respectively.[23] It is interesting to note that the surface stress profiles are quite different for the separations of 3 and 23 mm, even though the cell volumes were identical (3 ml). The cell's geometrical dimensions, not just volume, must be well defined in order to achieve reproducible results. These results highlight the need to use complementary techniques in order to characterize the resulting SAM.

III. COMBINED SENSING AND ELLIPSOMETRY

Very precise surface stress measurements associated with molecular adsorption can be achieved with a micromechanical cantilever-based chemical sensor but in order to gain insight into the origins of the surface stress developed during the formation of various molecular structures, it is important to use other complementary techniques to characterize these resulting thin films.[23,24] As another system modification, a combined cantilever-based chemical sensor and ellipsometer was designed and implemented. This system is capable of providing simultaneous *in situ* surface stress and thickness measurements associated with molecular adsorption. This combined system was used to investigate the real-time growth kinetics of dodecanethiol SAMs on gold. It is then possible to correlate the surface stress with the different structural phases that occur during monolayer formation.

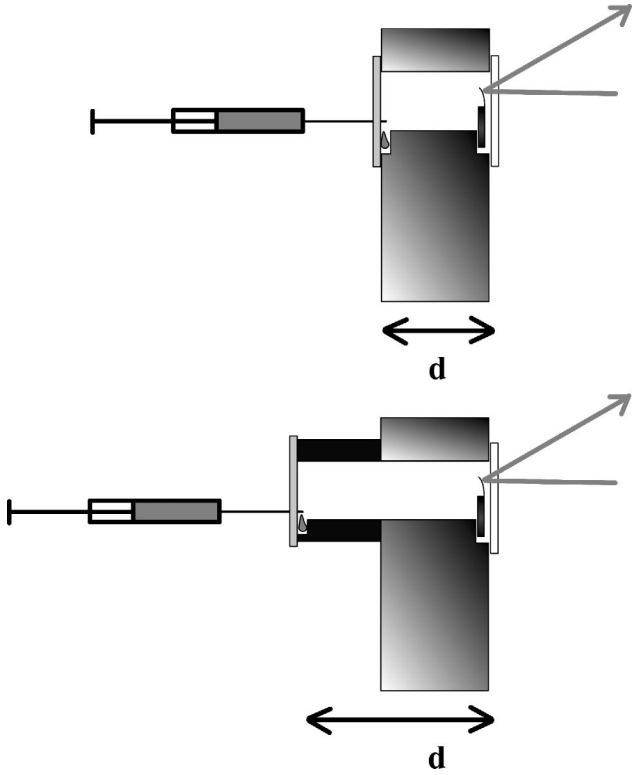

FIG. 6. Separation distance between the cantilever and the alkanethiol droplet, *d*, is controlled using a series of cylindrical extensions. The liquid analyte is injection through a Teflon-lined septum at the back of the cell (left). The deflection sensing components are located at the front of the cell (right). The laser light accesses the cantilever through glass.

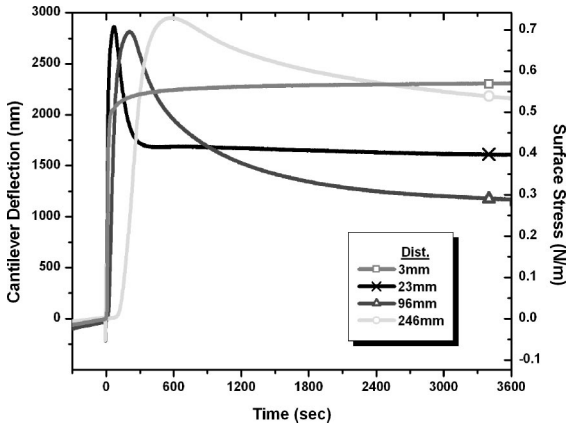

FIG. 7. Surface stress and cantilever deflection as a function of exposure time for different dodecanethiol droplet-to-cantilever separation distances. Separation distances of 3, 23, 96, and 246 mm correspond to cell volumes of 2.7, 2.7, 12.2, and 32.2 ml, respectively. Dodecanethiol was injected at time=0 s.

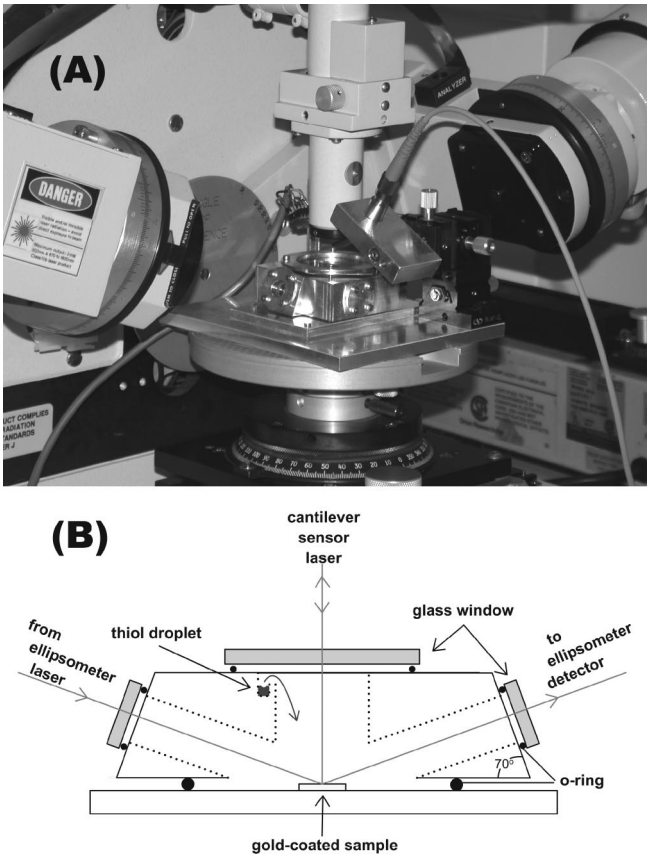

FIG. 8. Combined cantilever-based sensor and ellipsometer (A). The sensor was designed to fit on the stage of a commercial ellipsometer. The cantilever deflection is monitored using a laser beam, which enters the cell in a plane perpendicular to the plane of the ellipsometer laser. The schematic below (B) is a side-cut view of the cell. The distance between the alkanethiol droplet and the gold-coated samples is ~15 mm.

A. Setup

A custom-made cantilever-based surface stress sensor was integrated with a commercial ellipsometer.[25] A second aluminum cell was designed and built in order to accommodate the geometrical constraints imposed by both instruments. The cantilever-based sensor, designed to fit onto the ellipsometer stage, is shown in Fig. 8.

The ellipsometer laser spot size is 1.0 mm in diameter. Consequently, the minimum size of the sample used for the thickness measurement must be larger than this laser spot size. In some experiments, the ellipsometer laser was reflected off the chip onto which the cantilever was mounted. The typical chip size of commercially available cantilevers is approximately 1.6×3.6 mm. In other cases, a second gold-coated sample of mica was placed next to the cantilever for the ellipsometric measurement. In this case, the separation between the cantilever and the ellipsometer sample is minimized, and is usually less than 1 mm. This ensures identical adsorption conditions. If two separate samples are used, it is important to verify that the two substrates are as similar as possible. In our studies, both the silicon nitride cantilevers and the mica substrate were simultaneously coated with gold by thermal evaporation.[23] Scanning tunneling microscopy (STM) was performed *ex situ* on both gold surfaces to verify that their morphology was similar. Furthermore, x-ray diffraction revealed that the gold films deposited on the two different substrates both exhibited the Au(111) texture.

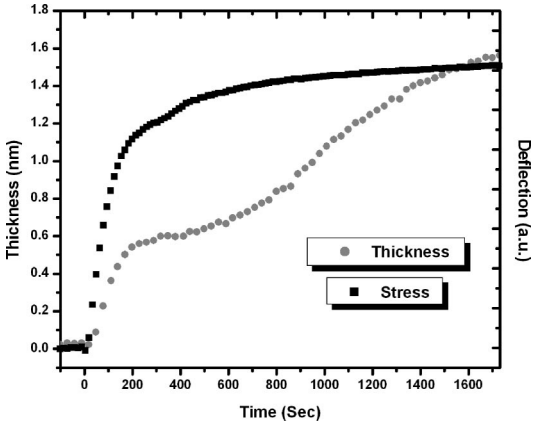

FIG. 9. Simultaneous measurement of the surface stress and monolayer thickness as a function of time associated with the formation of a dodecanethiol SAM on gold. Both measurements reveal the phase transitions that occur during SAM formation.

The cantilever-based sensor part of this system uses a single active cantilever without a reference. Therefore, it is imperative to minimize environmental effects that cause unwanted deflections of the cantilever. For this reason, the entire system was covered in a light-tight box with an air-cooling system designed to maintain the air temperature surrounding the setup constant. For the vapor phase alkanethiol experiments, we found that closed-volume experiments caused negligible cantilever deflections on reference cantilevers, compared to the active cantilever's large response to alkanethiol SAM formation. For experiments done under flow conditions or in a liquid environment, it would then be important to incorporate a second cantilever used as a reference, since unwanted deflections are much more difficult to eliminate.

B. Results and discussion

Simultaneous surface stress and monolayer thickness measurements were performed during the formation of dodecanethiol SAMs on gold.[26] Figure 9 reveals that both the surface stress and the thickness of the SAM undergo a two-step process before reaching equilibrium. In fact, others[24] have studied the formation process of alkanethiol SAMs on gold using several different techniques. These studies have found that the SAM undergoes several conformational phase transitions during formation.[27] Initially, the alkanethiol molecules lie with their alkyl chains parallel to the gold surface in a series of low density striped phases. At higher coverages, the alkanethiol molecules undergo a phase transitions into the standing-up phase, where the alkyl chains orient themselves at approximately 30° from the surface normal. The observed two-step process is associated with these phase transitions. The combined surface stress and ellipsometric measurement establishes the possibility to quantitatively associate surface stress values to specific structural phases.

The thickness measurement shown in Fig. 9 stabilizes at a value of 1.5 ± 0.1 nm, which is the expected thickness of a dodecanethiol SAM in the standing up phase. A constant

index of refraction of 1.459 (bulk liquid value) was assumed for all dodecanethiol SAM phases. As discussed elsewhere,[23] this assumption is not necessarily valid, since the index of refraction (dielectric constant) can be quite different depending on the orientation of the alkanethiol molecule. This makes the interpretation of ellipsometric measurements on alkanethiol SAMs nontrivial.

The complementary use of several experimental techniques is essential in understanding the mechanisms driving the sensor's response. We have shown an example of an adaptable cantilever-based surface stress sensor which is capable of simultaneous *in situ* film thickness measurements.

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[13] Positioners (9016) by New Focus.
[14] PSDs (1L10) by On-Trak.
[15] OPA111BM from Burr-Brown used as current-to-voltage converters. OPA627BP used for unity gain inverting amplification.
[16] MPY634KP from Burr-Brown used for analog division.
[17] The photocurrents from the two electrodes on the PSD are converted and amplified to a voltage, Y_1 and Y_2. The resulting processed PSD signal, $(Y_1-Y_2)/(Y_1+Y_2)$, is directly proportional to the cantilever deflection, and is independent of the laser intensity impinging on the PSD.
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