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A contact angle and ToF-SIMS study of SAM–thiol interactions on polycrystalline gold

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ABSTRACT

A process of chemical differentiation of neighboring Au features on a substrate (for biosensing applications) involves a step, where after electrochemical removal of a self-assembled monolayer (SAM) from one feature, another SAM is deposited onto it by incubation with a different thiol. During this incubation step, other undesorbed features are also exposed to this thiol which may lead to a partial SAM–thiol exhange, the extent of which is a function of time. Here, such surface reactions were followed on polystalline Au in both directions using contact angle measurements and time-of-flight secondary ion mass spectrometry (ToF-SIMS). The thiols involved were dodecanethiol (DDT) which forms SAM promoting adsorption of proteins and 11-mercaptoundecyl)tri(ethylene glycol) (TPEG) whose SAM prevents such adsorption. The surface reactions in both directions cannot be described by a simple pseudo-first-order kinetics. It was found that while the DDT SAM interaction with a TPEG solution leads eventually to a total replacement, the reverse process, TPEG SAM interaction with DDT, leads to no noticeable exchange over the first 3 h and then asymptotically approaches ~50% replacement.

1. Introduction

Thiol-based self-assembled monolayers (SAMs) on gold surfaces are workhorses for many platforms used in chemical sensing and biosensing [1–6]. In such platforms the gold surface is typically coated with a SAM terminated with groups promoting, either non-selective or, preferably, selective adsorption of a biologically active analyte, e.g., a protein [2–6]. Conjugation of SAMs with antibodies allows one to achieve very high specificity [1–3]. At the same time, the underlying thin layer of gold enables utilization of detection techniques such as surface plasmon resonance (SPR) [6–11] and surface enhanced Raman spectroscopy (SERS) [12].

Long-range surface plasmon polariton (LRSPP) waveguides [13] are potentially more sensitive for label-free biosensing due to the long optical interaction length with the adsorbed layer that is achievable [14,15]. An implementation consists of an integrated Mach-Zehnder interferometer (MZI) having Au arms that are coated with two chemically different SAMs one of which promotes adsorption (selectively or non-selectively) and the other prevents adsorption of the analyte [15]. Such differentiation can be achieved by a toposelective electrochemical desorption of SAM [16] from one (say, left) arm followed by incubation in the other thiol in order to form another SAM on the "clean" arm. The details of such process are given in ref. [17]. A possible issue with this approach is that during the secondary incubation in which thiol II forms a SAM on the left arm, the right arm is also exposed to this thiol. As SAMs are known to exchange with thiols in solutions [18–24], there is a distinct possibility of formation of a mixed SAM on this arm, increasing with the incubation time. This, in itself, is not necessarily a problem because some mixed SAMs may have better and more selective affinity to the analyte due to reduced steric hindrance [25,26]. At the same time, it is known that the quality of a newly-formed SAM improves with incubation time over several hours. Thus, we must trade off the quality of the SAMs on both arms by controlling the secondary incubation time. For this, we must know the kinetics governing formation of the mixed I/II SAMs in the system and this is the direct motivation of this study. Additionally, by studying the process in *either direction*, we may gain an additional measure of control by selecting the order of application of thiols I and II.

At the first sight, assuming that the mixed SAMs are formed by a SAM–thiol exchange ($R_1SAu + R_2SH = R_2SAu + R_1SH$) and that the bulk concentration [R_2SH] is practically constant the surface is uniform, the process should follow rather simple pseudo-first order

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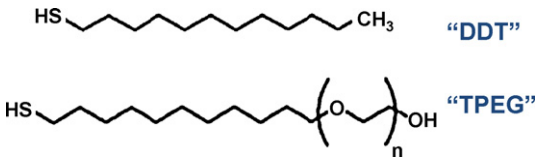

Fig. 1. The SAM forming thiols used in this study.

kinetics in which the ratio of the surface concentration $[R_2SAu]$ to the initial surface concentration $[R_1SAu]_0$ grows asymptotically to 1, *viz.*, as $1-\exp(-k[R_2SH])$. However, unlike with bulk reactions in dilute solutions where the rate constant k is independent of the composition, interactions between adjacent chains on the surface and at the surface-liquid interface would change as the reaction progresses and thus the pseudo-first order behaviour is not likely. Indeed, as described further, it was not observed even approximately.

The literature on thiol-SAM exchange, despite experimental difficulties due to a rather small amount of a thiol involved in monolayer surface coverage, is relatively extensive. Self-exchange, the simplest case free of chain length and type difference effects was studied using radiolabelling with $^{35}S^{18}$ and partial labelling with deuterium using IR external reflection spectroscopy [19]. In these studies the concentration of only one partner was followed through the decrease of ^{35}S activity on the surface [18] and the decrease of a carbon chain CH_3 stretching mode [20], respectively, and thus inferring that a simple replacement of one species by the other occurs. In a number of studies, thiols with different hydrophilicity were used and the exchange was followed with contact angle measurement [20–22]. XPS spectra were used similarly [20,22] Data thus obtained have a statistical character and only the relative ratio of surface concentrations of the SAMs can be assessed. A more direct approach to following the surface concentrations of SAM involved laser-desorption Fourier transform mass spectrometry (LD-FTMS) [27] where the exchange of two similar hydrocarbon thiols could be followed but was apparently complicated by the presence of oxidation products. Thus, in general, spectroscopic and/or labelling methods can be considered semi-quantitative only. For instance, they cannot distinguish between exchange and addition processes as the cause of formation of mixed SAMs.

Time-of-flight secondary ion mass spectrometry (ToF-SIMS), a more recent semi-quantitative tool for surface analysis, has found applications in the study of thiol SAMs on gold [28–38]. Recently, we demonstrated the usefulness of the technique to follow the formation and electrochemical desorption of SAMs [39]. To the best of our knowledge, the technique has not yet been utilized to study the equilibria or kinetics of thiol-SAM systems on gold.

Contact angle goniometry is a simple technique which was previously applied to thiol/SAM exchange kinetics [22]. In order to achieve enough resolution the two SAMs should significantly differ in their surface properties. In our study geared towards the development of LRSPP biosensors we use a SAM based on dodecanethiol $CH_3(CH_2)_{11}SH$ ("DDT") as a non-specific promoter of protein adsorption, and a SAM based on 11-mercaptoundecyl)tri(ethylene glycol) $HS(CH_2)_{11}(OCH_2CH_2)_3OH$ ("TPEG") as a protein adsorption blocker. The former is very hydrophobic and the latter quite hydrophilic, thus being perfectly suitable to a contact angle study of chemical interaction between SAMs and thiol solutions. The structures of the two thiols are shown in Fig. 1. However, contact angles cannot distinguish between exchange and addition, providing only relative amounts of the individual components of mixed SAM. Being aware of this limitation and also due to the fact that in our applied work we also use thiols with intermediate hydrophilicity (e.g., carrying a biotin moiety specific for streptavidin), we also carried out a preliminary study utilizing ToF-SIMS taking advantage of the fact that we have previously elucidated fragmentation data for the three types of SAMs [17,39].

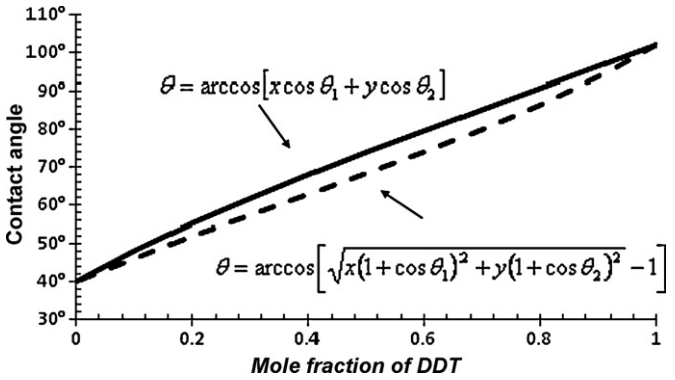

Fig. 2. Comparison of expected contact angles of mixed DDT/TPEG self-assembled monolayers as a function of composition based on the Cassie (solid line – Eq. (1)) and Israelachvili–Gee (dashed line – Eq. (2)) approaches, based on the measured water contact angles fot the two pure SAMs.

2. Experimental

The non-textured Au (typically known as polycrystalline) surfaces used consisted of vacuum-evaporated 30 nm thick Au on 4.5 nm Cr on p-type Si wafers. The wafers were cleaved into dies of ~0.5 to 1 cm^2 surface area. 1-Dodecanethiol $CH_3(CH_2)_{11}SH$ (≥98%, Arkema Inc.), 11-mercaptoundecyl)tri(ethylene glycol $HS(CH_2)_{11}(OCH_2CH_2)_3OH$ (95%) were purchased from Sigma–Aldrich Canada Ltd. De-ionized water (18 MΩ cm) was prepared in a Zenopure Quatra 90LC machine and 2-propanol (semiconductor grade, Puranal®) was obtained from Riedel-de Haën.

The Au surfaces were degreased with 2-propanol, rinsed with de-ionized water and placed in a Novascan PSD-UV UV-ozone cleaner (5 min UV irradiation followed by 20 min ozone action). To obtain initial SAM specimens, the dies were incubated in a 2 mM solution of the appropriate thiol in 2-propanol for 18–19 h. The kinetics studies of SAM formation as well as SAM–thiol solution interaction were carried out at room temperature for a prescribe time using the same solutions.

Contact angles were measured using a VCA Optima™ goniometer from AST Products Inc. De-ionized water was used and with each sample, the reported contact angles and their standard deviations were obtained from 3–6 droplets deposited on different areas of the die.

The surface morphology of the bare Au film as well as the thiol SAMs was evaluated using the dynamic force mode of a Park Systems XE-100 AFM. A silicon cantilever having a nominal spring constant of 40 N/m and a tip radius of 10 nm was used. The details were described elsewhere [17,39].

An ION-TOF (Gmbh) TOF-SIMS IV equipped with a Bi liquid metal ion source was employed to probe the surface structure. A 25 keV Bi_3^+ cluster primary ion beam with a pulse width of 12 ns (target current of ~1 pA) was used to bombard the sample surface to generate secondary ions from the surface. The secondary ions were extracted by an electric field (2 kV), mass separated, and detected via a reflectron type time of flight analyzer. The cycle time for the processes of bombardment and detection was 100 μs. A pulsed, low energy (~18 eV) electron flood was used to neutralize sample charging; the current was maintained below ~20 μA maximum to avoid sample damage. For the thiols we dealt with, the negative secondary ion mass spectra were much more informative than the positive ones in providing molecular ion fragments and their association with gold atoms [39]. Therefore, we only used negative

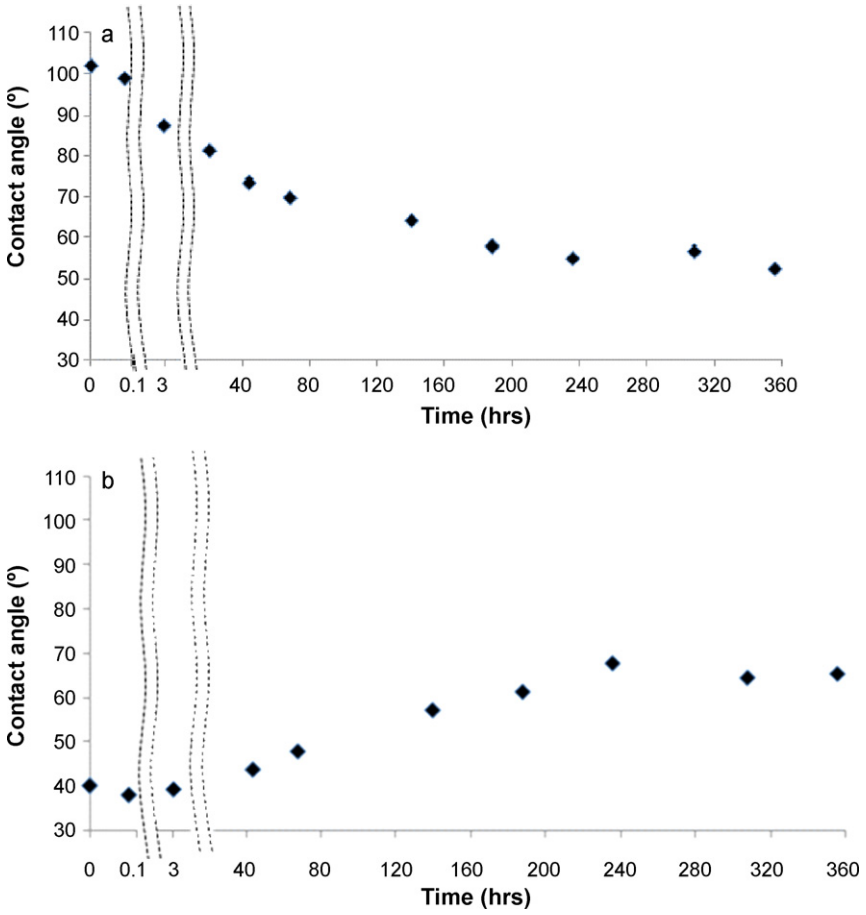

Fig. 3. Interaction of SAMs on polycrystalline Au with a 2 mM thiol solution in 2-propanol as a function of time: (a) Contact angle of DTT SAM exposed to TPEG solution, (b) Contact angle of TPEG SAM exposed to DTT solution.

secondary ion mass spectra for molecular identification of the thiols on gold surfaces. For each sample, spectra were collected from 128×128 pixels over an area of $500 \times 500\ \mu m^2$ for 120 s. The spectra were calibrated using, H^-, C^- and CH^-. The mass resolution at CH^- and $^{34}S^-$ were ~4000 and 6000, respectively.

3. Results and discussion

3.1. Contact angle measurements

A series of dies coated with DDT-based SAM and TPEG-based SAM were prepared by incubation with 2 mM thiol solutions in 2-propanol for 18 h and 19 h, respectively. After cleaning, the DDT coated dies were immersed in the 2 mM TPEG solution while the TPEG coated one were immersed in the 2 mM DDT solution. Samples were withdrawn periodically and their contact angles measured.

The contact angles were used to infer SAM relative surface compositions. Two models are known from the literature to express the contact angle dependence of a mixed surface composition. The older model, proposed by Cassie [40], relates the contact angle of a surface of mixed composition to those of pure ones as

$$\cos\theta = x\cos\theta_1 + y\cos\theta_2 \quad (1)$$

where θ is the water contact angle on the mixed surface, θ_1 and θ_2 are the contact angles related to the pure SAMs, formed in our case from DDT and TPEG respectively, and x and y are their corresponding surface molar fractions ($x + y = 1$). An alternative model was given by Israelachvili and Gee [41]

$$\left(1+\cos\theta\right)^2 = x\left(1+\cos\theta_1\right)^2 + y\left(1+\cos\theta_2\right)^2 \quad (2)$$

where the symbols representing the same quantities as in Eq. (1). According to the authors [41], Eq. (1) applies only to heterogeneous surfaces with patchwork coverage by SAMs 1 and 2, while Eq. (2) should be used where SAM mixing approaches the molecular level. In Fig. 2, the two models are compared for the particular case studied here for which we measured the contact angles of the DDT-based SAM and the TPEG-based SAM on non-textured gold to be $102.0 \pm 2.1^\circ$ and $40.1 \pm 2.1^\circ$, respectively.

We can see in Fig. 2 that for a given composition, the Cassie model predicts a larger value of θ than that of Israelachvili–Gee, but the difference is not very large. In fact, it is not much larger than the standard deviation of contact angle measurement. With our system, it also means that for a given experimental angle, the Cassie model suggests lower DDT and higher TPEG contributions than the Israelachvili–Gee model does.

The contact angles as a function of incubation times are given in Fig. 3. In the absence of a preffered surface model for our system, we decided to fit the values of Fig. 3 to both models abd the results are shown in Fig. 4. Here, for each exchange, both sets of data (diamonds – the Cassie model, squares – the Israelachvili–Gee model) are based on the same measured contact angles. In our system for a given experimental angle, the Cassie model suggests lower DDT and higher TPEG contributions than the Israelachvili–Gee model but th diffence is not very large. In fact, it is not much larger than the standard deviation of conatct angle measurements. Neither short-time or long-time results obrtained this way could be fitted to the

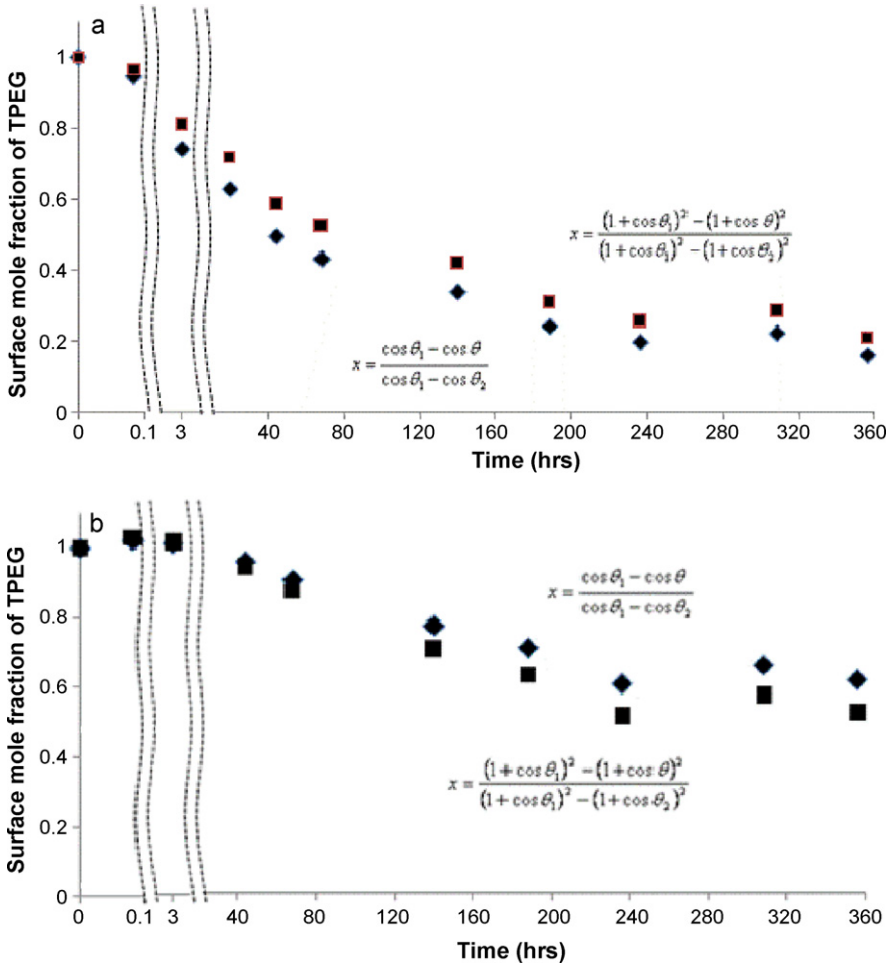

Fig. 4. Composition of mixed SAMs on polycrystalline Au calculated with contact angle data of Fig. 3: (a) Surface mole fraction of DTT SAM exposed to TPEG solution, (b) surface mole fraction of TPEG SAM exposed to DTT solution. The diamonds are computed using the Cassie model (Eq. (1)) and the squares are computed using the Israelachvili–Gee model (Eq. (2)).

pseudo-first-order kinetic model. Aparently, no single rate constant (or even two) is sufficient to describe the system since the molecular interactions change as the reaction progresses, as discussed in the introduction.

3.2. Two basic differences are noticed between the two directions of the exchange

The long-term data indicate that when DDT SAM is interacting with TPEG solution (in shorthand, "DDT to TPEG"), the exchange should be expected go to completion if the process is carried out long enough (Fig. 4(a)). On the other hand, the reverse process ("long term TPEG to DDT") seems to level off to a 40–50% exchange (Fig. 4(b)). The reason for this behaviour difference is not completely clear even though its long term character seems to point to thermodynamics rather than kinetics. One possibility would be the presence of stable hydrogen-bonded structures with PEG moieties on the more ordered areas of gold not easily replaced by the hydrocarbon based DDT. Another possibility could be related to the relative size of TPEG chains which are much longer than those of DDT. The stability of SAMs is known to increase with the chain length [1] although a direct comparison cannot be drawn due to the composition difference between DDT and TPEG. A similar behaviour was observed with exchange of a hydroxy terminated SAM in solution but not in a gas phase [22]. More surprisingly, a similar behaviour was observed on polycrystalline gold with what is essentially a self exchange [19] despite a large excess of the reagent in solution which would suggest a kinetic regime. At the short time scale, the DDT to TPEG process behaves as expected, while in the TPEG to DDT process no exchange could be observed within experimental error for at least the first 3 h. Such a phenomenon is referred to in chemical kinetics as an "induction period" [42], and indicates that the product is not directly formed from the reagents but from an intermediate [43]. Here, it could mean that a certain reorganization of TPEG on the surface is required such that the TPEG network is disrupted forming an intermediate structure before the exchange process with DDT commences. Atomic force microscopy of the substrate used with our samples [39] indicates that the gold has a structure which could be referred to as polycrystalline but, probably more accurately, as non-textured. Thus, different types of surfaces can be observed locally, *i.e.*, concave and convex ones. One can speculate that when covered with a TPEG SAM, some of these areas will undergo an exchange with DDT after the initial reorganization and on the other areas the TPEG SAM will not undergo an exchange at all due to a strong surface network. Similarly, grain boundaries in another type of polycrystalline gold were postulated to be the site of a fast SAM–thiol exchange [22]. Thus, the peculiar behaviour at both the short and long time scales can be explained for the TPEG-to-DDT exchange, albeit only speculatively.

The results discussed above clearly indicate a preferred process direction for the chemical differentiation of small Au features [17] as discussed in the introduction. If we want to avoid any mixed SAMs on either of the arms, the initial incubation step should be in TPEG solution, followed by its electrochemical desorption from the

first feature, and then by incubation of the die with DTT. This secondary incubation can be carried on for several hours, long enough to ensure good quality of the DTT SAM without jeopardizing the quality of the SAM on the other arm.

3.3. ToF-SIMS measurements

There are two basic ways of reporting peak intensities in ToF-SIMS measurements: absolute intensities, and normalized vs. an internal standard thus reflecting the relative probability of formation of a given ion. This internal standard may be, e.g., the "total ion intensity" (TII) or a selected peak (e.g., Au^- which can be reasonably assumed to be relatively independent of the surface composition). It is worth stressing here, that the TII does not exhaust all the possible ionization and fragmentation processes as there are also positively charged and neutral species formed (in fact, the vast majority of the fragments are neutral species). As long as we are dealing with one species, both approaches are equally valid. The situation changes, however, when analyzing the mass spectrum of a mixture of two or more SAMs on the surface. In this situation, the total ion count is likely a function of the relative proportion of each thiol and is thus unsuitable as a reference point.

The absolute intensity of a given ion produced from each thiol is a function of the probability of its formation, but it may change due to changes in primary beam and analyzer conditions; thus, it alone cannot be used directly to assess the relative amounts of the molecular types on the surface. Using samples with only one SAM on the surface, we can define, for each SAM, the probability of formation of an ion in a given ion bombardment condition as the ratio of its intensity to the total ion intensity (or another internal standard peak, such as Au^-) of the pure SAM on gold (its normalized intensity). We assume, initially, that the probabilities p_A and p_B of formation of ion A (originating exclusively from DDT) and of ion B (originating exclusively from TPEG) may be determined as the respective normalized ion intensities. Under this assumption, the probabilities p_A and p_B do not depend on neighbouring chains, and the intensity of ions from the mixed SAM are given as $I_A = p_A x (I_{total})_m$ and $I_B = p_B y (I_{total})_m$ where $(I_{total})_m$ is the total ion intensity of the mixed SAM. For pure A and B SAMs the mole fractions are unity and thus $p_A = I_A/(I_{total})_A \equiv \left(I_A^N\right)_{pure}$ and $p_B = I_B/(I_{total})_B \equiv \left(I_B^N\right)_{pure}$ where the superscript N stands for normalization vs. total ion intensity. Thus, it should be possible to calculate the actual fractions x and y in the mixed SAM as:

$$x = \frac{1}{p_A}\left(\frac{I_A}{I_{total}}\right)_m = \frac{\left(I_A^N\right)_m}{\left(I_A^N\right)_{pure}} \text{ and } y = \frac{1}{p_B}\left(\frac{I_A^N}{I_{st}}\right)_m = \frac{\left(I_B^N\right)_m}{\left(I_A^N\right)_{pure}} \quad (3)$$

In other words, x and y are given as the *ratio of two normalized intensities, the one in the mixed SAM to that in the pure SAM*. If exchange is the dominant process, we should have $x + y = 1$.

We have previously identified and reported characteristic ion fragments in the ToF-SIMS spectra of DDT and TPEG SAMs on the polycrystalline Au used also in this study [17,39]. For DDT SAM, the molecular ion fragment of DDT, $[DDT\text{-}H]^-$ (or $C_{12}H_{25}S^-$), is characteristic. For TPEG SAM, the high intensity ion fragment CH_3O^- is characteristic to the ethylene glycol moiety. Only the short-term ToF-SIMS results (up to 18 h) were collected following the $C_{12}H_{25}S^-$ and CH_3O^- ions and are given in Fig. 5, where the mole fractions computed using Eq. (3) as a function of incubation time are plotted. On the zero time sample which was not subjected to any further processing and only contained DDT SAM on Au, traces of the CH_3O^- signal are attributed to oxygen contamination (which was found on every surface exposed to air in the lab). Therefore, the data shown in Fig. 5(a) were corrected for this trace CH_3O^- signal. Results obtained by following gold-containing molecular ion

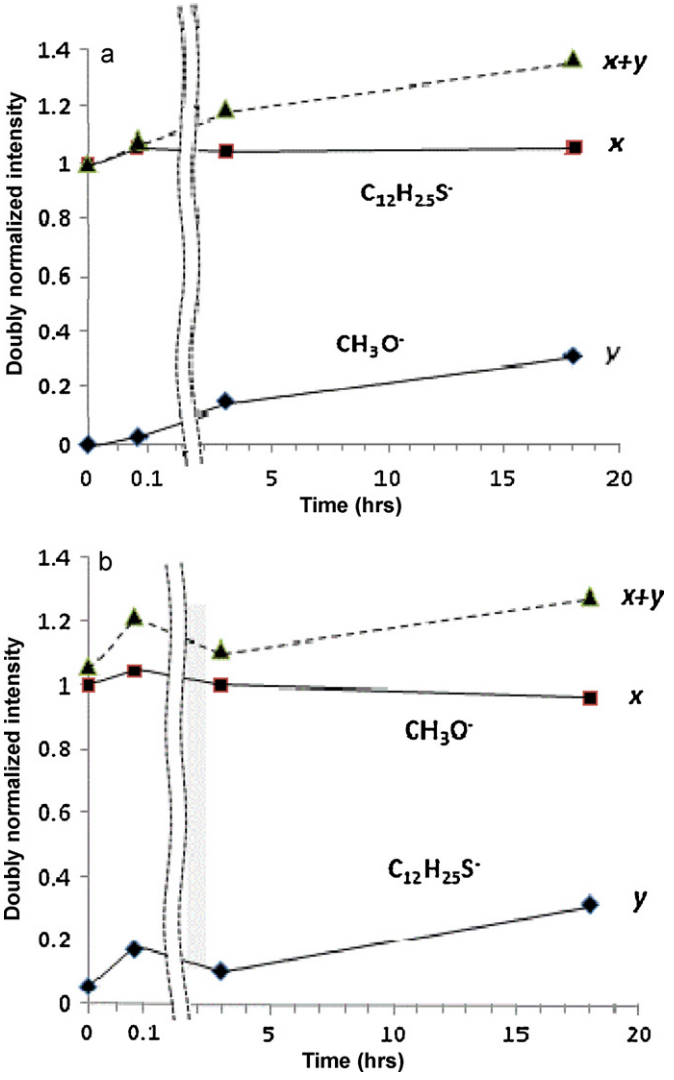

Fig. 5. Exchange of SAMs on polycrystalline Au with a 2 mM thiol solution in 2-propanol followed by ToF-SIMS: (a) DTT SAM ($C_{12}H_{25}S^-$) with TPEG (CH_3O^-); (b) TPEG SAM (CH_3O^-) with DTT ($C_{12}H_{25}S^-$). The lines connect experimental points only.

fragments (not shown), such as $[DDT\text{-}H + Au_2]^-$ (or $C_{12}H_{25}SAu_2^-$) for DDT, and $[TPEG\text{-}H + Au_2]^-$ (or $C_{17}H_{35}O_4SAu_2^-$) for TPEG, have similar trends to those shown in Fig. 5.

The results of Fig. 5(a) show that while the intensity of the "exchanging" thiol (TPEG) increases significantly, the ion intensity related to the bound thiol (DDT) surprisingly does not change appreciably and thus $x + y > 1$. Fig. 5(b) shows a similar behaviour for the case where TPEG is bound and DDT is the unbound compound. However, here, for the first 3 h hardly any process is observed at all, in agreement with the contact angle results described above.

These ToF-SIMS results suggest either addition [44] of the other thiol to the existing SAM, or the matrix effect [45] during ion fragmentation, where the intensity of one component is dependent on the presence of another nearby component, or a combination of both. Such uncertainties present difficulties when conducting quantitative analyses on the kinetics of thiol exchange using ToF-SIMS which is only a semi-quantitative analytical method. On the other hand, contact angle measurements, while easier to quantify, cannot distinguish between exchange and addition processes as they are only sensitive to the average composition of the surface. From the point of view of biosensing, where the selectivity vs. analyte is important, it is the average composition which is critical

and the difference between exchange and addition is of secondary importance.

Nevertheless, the ToF-SIMS results show the same trends as the contact angle results (except for the starting points at $t = 0$): x and y as calculated from Eq. (3), always add to a value greater than unity. This could indicate an addition process accompanying the exchange. As contact angles reflect only the average composition, we cannot distinguish between addition and exchange.

In conclusion, both water contact angle measurements and ToF-SIMS present a similar picture of the SAM–thiol interactions, although exact results are open to interpretation. From the point of view of biosensor development the most important result is that, when starting with TPEG, one can safely incubate the whole structure in DDT for a time long enough to ensure the formation of a good quality SAM, without any appreciable exchange occurring on other features. When performing the process in the opposite direction, the secondary incubation time should be much shorter to avoid the formation of a mixed SAM.

4. Conclusions

Our contact angle study of the SAM–thiol interaction in solution shows that the TPEG SAM-DDT exchange is characterized by a several hours long induction period and only tends to reach ca. 50% completion at long time scale. On the other hand, the DDT SAM-TPEG exchange shows neither the short time nor the long time anomalies. This result, also confirmed by ToF-SIMS, suggests an order of processing when making sensor structures in which micron-sized features are selectively differentiated by electrochemical desorption of one SAM and re-incubated with another thiol.

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