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Chemical Communications

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Water on Au sputtered films

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Transient changes in the contact angle, $\Delta\theta \sim 10°$, of water on gold (Au) reveal reversible wetting of near hydrophobic Au films. The recovery time is temperature dependent. Surface flatness is investigated using AFM and profilometry.

Au is increasingly used as a platform for many bio and chemical reactions because it is regarded as inert, so-called noble, with low biological and chemical activity. Consistent with such inactivity, it is the only metal which does not form an oxide on heating in air or oxygen at least up to 900 °C [1,2]. Such properties are critical to the production of reliable, reproducible and repeatable interfaces capable of both disposable and multiple uses. Many commercial products now incorporate Au nanoparticles because such low activity inhibits bacterial and fungal growth – for example, Au nanoparticle films are thought to act as ideal barriers between skin and dental implants [3]. As a high energy coating it is used for the self-assembly of monolayers [4,5] and is suitable for catalyzing, or enhancing catalysis of, various important reactions [6-10]. The ability to form monolayer or nanoscale, films from various deposition techniques or from nanoparticle self-assembly also makes it attractive for biosensing applications [11]. Yet, despite this extensive use and application, the surface properties of Au are not well understood and questions remain about the implicit inert activity of Au. Crucial to all of these applications is the wetting nature of the gold surface which continues to raise ambiguity in the literature. Most literature suggests the pure Au surface is hydrophobic, consistent with thermodynamics of gold oxidation, and this property is even used to reduce the wetting of other noble metals such as platinum by adding gold [12]. Yet despite its high thermodynamic oxidation state, gold is easily turned hydrophilic by chemical means through the formation of AuO when anodized in the presence of an acid [13]. Many standard laboratory cleaning procedures for generating highly pure or clean surfaces, such as those required for accurate force measurements, also oxidise Au. Preparations such as cleaning in piranha solution, UV/Ozone cleaning, and water or oxygen plasma cleaning all generate highly hydrophilic surfaces (with a contact angle as low as

$\theta \sim 7°$) suggesting the presence of AuO [14]. Much of the reported hydrophilic and wetting observations are therefore attributed to the presence of gold oxidation or in unclean environments due to surface contamination. Interestingly, the subject of the measured contact angle, θ, of water on thin Au films within the literature also reflects a degree of uncertainty. It is nearly always measured to be hydrophilic or wettable ($\theta < 90°$) and rarely hydrophobic. Early and systematic work typically reports $\theta \sim 66°$ [15], consistent with early theories [16,17], whereas many (though not all) recent works report $\theta \sim 76°$ [18,19] about 10° higher. Variations around these are also reported and may be attributed to the type and quality of gold surface.

Provided many of the cleaning aspects described above are considered, it would appear overall Au is an inert platform ideal for many applications. Hydrogen peroxide cleaning, for example, is thought to avoid oxidation [20]. These aspects are increasingly important given the growing consideration of ultra-sensitive surface wave spectroscopies as local tools for quick, potentially low cost, chemical and biodiagnostics on gold.

In this work, however, we find that the situation is more complicated still. In addressing the issue of potential reuse of a gold sample, the history of the sample becomes important. Even less susceptible to oxidation issues than hydrogen peroxide cleaning, the use of pure water can often be sufficient to remove material, seemingly avoiding oxidation altogether. Given that in nearly all cases $\theta < 90°$, we would expect that the surface is wetted under such conditions and drying is often undertaken using nitrogen. Here, we show that simple soaking and drying of pristine Au films on borosilicate slides with water alone lead to an immediate but non-permanent change in the wettability of the film. The timescale of recovery to that of the pristine case is found to be temperature dependent, a direct indication that a molecular layer of water is weakly attached to the gold, resisting initial drying under nitrogen at room temperature. The effect of this molecular layer on subsequent sessile drop formation, despite weak attachment, demonstrates properties that differ from the water making up the sessile drop.

The Au films used in this work were produced by sputtering. Commercial films (Supplier: PHASIS, Sweisse) made up of Au ($\phi \sim$ 50 nm) sputtered onto a thin layer of titanium (Ti: $\phi \sim$ 5nm) on borosilicate slides to help improve attachment was compared with locally sputtered Au directly onto borosilicate slides. The local films were sputtered using an Emitech K550X sputterer (0.1 mbar Ar, $I =$ 25 mA) and a Au target ($\phi \sim$ 60mm, 1mm thick). Given the potential contribution from surface variations, both types were scrutinized using atomic force microscopy (AFM - Asylum Research Cypher S) for high resolution examination of local surface properties, and profilometry (Veeco Dektak 8 Programmable Surface Profilometer) to determine longer range surface roughness and variation.
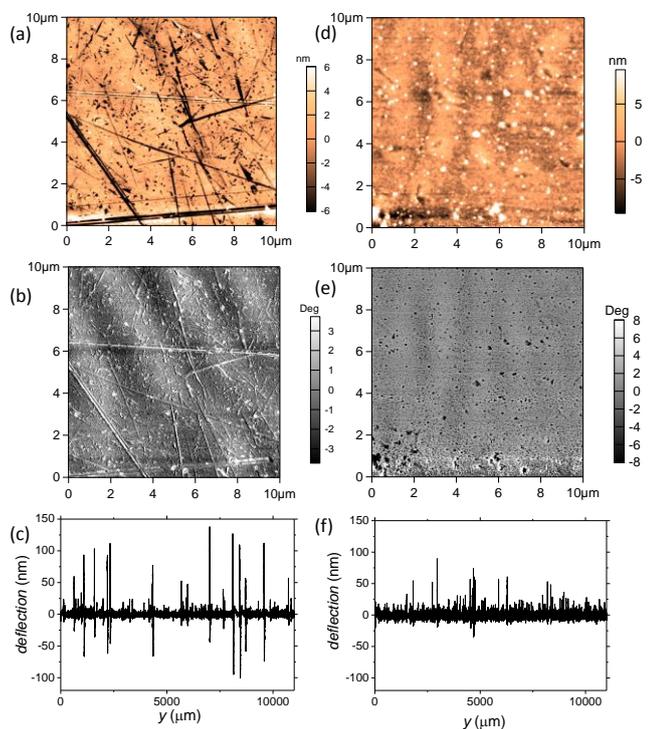
Fig 1. AFM and profilometer characterisation of Au films: (a-c) commercial film and (d-f) local film. (a) and (d) are AFM height profiles with 2 nm xy spatial resolution; (b) and (e) are phase renditions of (a) and (d); (c) and (f) show the surface variations along one axis measured over 10 mm using a profilometer with $\sim$ 3 μm xy spatial resolution. Low frequency variations have been filtered out to extract R_A.

Figure 1 summarises results. The differences in local surface features are distinct with the commercial sample showing cracking of the Au, attributed in part to differences in thermal expansion coefficient with the underlying titanium to which it is strongly attached; it may also reflect the surface topography of the Ti layer. The phase image shows up slight but periodic undulations with a pitch on the order of $\Lambda \sim$ 3 μm. By contrast, the locally sputtered material appears to have clusters of Au distributed across the surface and has a weaker undulation with pitch slightly shorter $\Lambda \sim$ 2 μm. These undulations are very slight ($\sim$ 1 nm in height) suggesting overall very low surface roughness. These undulations may contribute to the coupling mechanism for the recently reported near orthogonal excitation of surface plasmon resonances [21]. The profilometer results indicate that the films have similar surface roughness with values of $R_A \sim$ (1.9 - 14.8) nm measured over 10 mm for the commercial Au film. Given the large individual scattering that appear to arise from crack edges, when these are removed the lower value of 1.9 nm is dominant,

consistent with commercial specifications ($\sim$ 2 nm) provided by the supplier. The locally produced Au film generates $R_A \sim$ (2.3 − 9.5) nm. On this scale it would appear that the films are not so different in terms of surface roughness although the local films are found to be a little rougher. Overall the profilometer measurements do show that the locally produced Au film has some long range undulations not seen in the commercial film (Figure 2); this has a significant effect on measuring contact angles because the surface is not flat and averaging of the data over several areas will lead to larger errors.
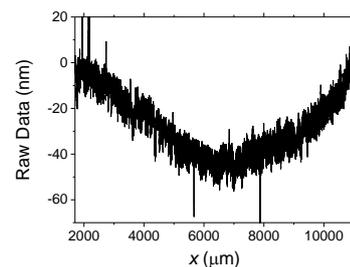
Fig 2. The raw surface profile measurement, over 10 mm, of the locally fabricated film. Relatively deep undulations are observed, at 50 nm greater than the film thickness $\sim$ 45 nm. These are not seen in the commercial film, and along with visual inspection, suggesting uneven deposition. The surface topography of the borosilicate slide may also be a great deal less flat than the underlying surface of the commercial slide.

The wettability of these films was measured as a function of contact angle, θ, of a sessile drop ($V = 2$ μL) imaged immediately after deposition at each time. To simulate repeated use of a slide, pristine slides were compared with slides immersed for 30 min in deionized water (pH $\sim$ 6) – sessile drops from the same deionized water were then placed on each sample and θ measured directly. The method of measurement involved imaging the drop from the side using a CMOS microscope camera and software to measure the contact angle. Initially measurements were repeated several times to ensure reproducibility were obtained between samples. 12 drops of similar volume were placed on each slide and measurements were obtained in steps of four, limited by the CMOS camera field of view. A standard deviation and error range was extracted from this data, reflecting to some degree the overall surface quality and uniformity. Measurements were again repeated to ensure reproducibility was maintained. Overall the data for the commercial film was consistent and within experimental error showed clear variations between pristine samples and water soaked samples. This data is summarised in Figure 3.
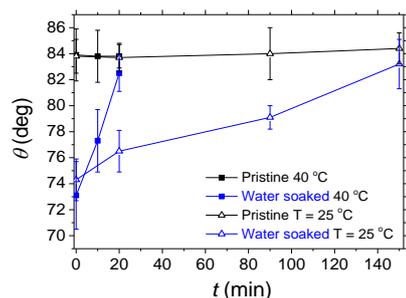
Fig 3. Contact angle, θ, over time for both pristine and water immersed commercial Au films at two temperature, 25 °C and 40 °C.

Contact angles were measured for both pristine and water soaked conditions at two temperatures, 25 and 40 °C. A little higher than in other work, the measured contact angle is $\theta \sim$ 84°, closer to the hydrophobic condition expected for pure Au and consistent with

little AuO present. There is a clear and reproducible trend after soaking with water showing a reduction in contact angle of $\Delta\theta \sim 10°$ between pristine and water soaked samples; i.e. from $\theta \sim 84°$ to $\theta \sim 74°$, a figure closer to most reported data. Remarkably, this drop is consistent in magnitude with the difference between sets of literature and raises the possibility that the time of measurement of the contact angle is important. In our samples, we observe persistent recovery of this decrease over time – at 25 °C the recovery is longer than 150 min. Increasing the temperature to 40 °C reduces this recovery time dramatically, by more than a factor of 5, to < 30 min. In both cases, within experimental error, the recovery appears linear consistent with a simple equilibration process (e.g. $AuOH \cdot \cdot H \leftrightarrows Au + H_2O$). These observations suggest that water has directly interacted with the surface of Au rather than forming an oxide. Such an interpretation would be consistent with data showing little difference in surface potential between Au and AuO for a solution with pH 6 or higher [16], making AuO formation unlikely. For comparison, both a pristine sample and a water immersed sample were irradiated for ten minutes with UV light through exposure within a medicinal lamp cabinet (Starkeys Ultraviolet Steriliser; Phillips TUV T8 lamps: UV-C radiation – 4.9W); this approach generates ozone which in turn can oxidize the Au so allows a direct observation of oxide formation on local contact angle. The results are shown in Figure 4(a).
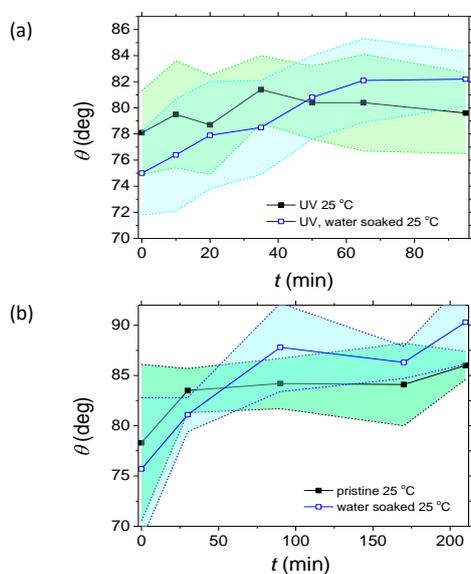
Fig 4. Contact angle, θ, over time for both pristine and water immersed Au films: (a) commercial Au under UV (UV-C band) irradiation with initial temperature at 25 °C; (b) Local Au under identical conditions to that used in Figure 3. Error bars shown in shadow format for clarity.

The large error distribution obtained from 12 drops distributed over the sample is plotted in shadow format for clarity and shows substantial variation. This variation probably reflects the variation in lamp irradiance over the sample. Nonetheless, within error the water soaked sample shows similar behaviour to the sample with no UV treatment, recovering from a lower contact angle of 82 ° in ~ 80 min, whilst the pristine sample shows little evidence of comparable change. Oxidation is ruled out as a significant factor. We note, on the other hand, such UV treatment ought to generate heat through absorption within both the sample and in the water. From Figure 2, this must contribute to a faster initial recovery time of the immersed sample during irradiation.

Figure 4(b) shows the contact angle data for the locally sputtered film. The large error variations may be attributed to the observed long range undulations and reflect the importance of the film quality and surface flatness for reproducible measurements. Surface quality can therefore explain some of the large measured variations in pristine metal contact angle reported within the literature; for example, Erb [15] reported $\theta \sim (55 - 85)°$ for Au. The large data error distribution therefore makes it difficult to interpret this data although a similar trend, and time, of recovery is observed for the sample immersed in deionized water compared to the results for the commercial film.

Conclusions

We have demonstrated that even in the simplest and most common case of water immersion of widely used Au films, there is evidence of direct water interactions with the surface which can recover over time in the presence of a sessile drop. Some wetting occurs despite the near hydrophobic measurements of a subsequent sessile drop on the film. This raises interesting propositions regarding the nature of wetting and the reliance on contact angles, where surface tensions and Marangoni flows occur, to describe wetting generally.

The temperature sensitivity is also consistent with weakly bound surface hydration, most likely water molecules attached, and probably oriented, via the oxygen. The difference in water structure accounts for the 10° change in contact angle. We propose that convective flow within the drop as it evaporates determines the recovery time in contact angle between pristine and water immersed Au. Given deionised water has a slightly acidic pH where some hydrogen peroxide is probably present, surface attachment may also proceed via a peroxide species. This water layer will therefore be charged.

The contact angle recovery with temperature allows for novel diagnostics. In the absence of other contributions to the recovery, it may be used as a novel and high resolution diagnostic for determining local temperature changes.

Focussing on the contributions of surface quality, we compared quite flat commercially sputtered film strongly bound to titanium with locally sputtered film without titanium. Using 12 sessile drops for each measurement distributed over the film we were able to ascertain a degree of film surface quality by the magnitude of the error size distribution. The long range undulating local film had much larger error variation sensitivity to the contact angle measurement, making measurements more difficult to quantify; nonetheless, this approach opens up another alternative to estimating surface quality that is easier and more rapid to undertake than either AFM or profilometry.

Notes and references

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