Mechanism for femtosecond laser pulse patterning of self-assembled monolayers on gold-coated substrates

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Abstract. Self-assembled monolayer (SAM) patterning on gold thin films was performed using 800 nm, 118 fs laser pulses. SAM removal was ablative and was observed at fluences near the multishot ablation threshold for the thin gold film. Line widths six times smaller than the 2 e-folding intensity beam diameter were observed demonstrating sub-diffraction limited patterning with femtosecond lasers. Similar experimental results in air and N₂ indicated that the removal process does not involve oxidation of the gold-sulfur bond as was claimed in the literature.

1. Introduction
Nanoscale engineering of surfaces with self-assembled monolayers (SAMs) is a relatively new technique that could extend the limits of current optical lithographic techniques to the nanometer scale. By using SAMs as etch resists, serial patterning of substrates using femtosecond pulses with SAMs could lead to rapid prototyping of micropatterns to avoid the expense of photolithography masks until the final mass production stage. We demonstrated and characterized for the first time micrometer scale patterning of SAMs of alkanethiols on a gold substrate to create barrier-free microfluidics channels using a continuous wave (CW) Argon ion laser [1-3]. With CW lasers, lateral feature sizes are limited to the micrometer scale with the minimum line width reached to date of 4 µm with a 10X objective (unpublished data). This methodology has been extended to femtosecond laser pulses to perform sub-diffraction limited patterning of SAMs of 1-hexadecanethiol (hydrophobic) on a 30 nm gold thin film substrate using fluences below the ablation threshold. The remaining bare region can be etched to create patterns similar to lithographic techniques or backfilled with 16-mercaptohexadecanoic acid (hydrophilic) as done in our work to tune the surface energy. Chang et al. [4] showed near-infrared femtosecond pulse SAM patterning on gold films and proposed that SAM removal was due to photo-oxidation of the gold-sulfur bond; however, no substantial argument or control experiment was presented. In this study we explored the roles of ablation and of ambient oxygen in the patterning of SAMs using 800 nm, 118 fs laser pulses below the ablation threshold fluence.

2. Experimental Procedure
The experimental setup, laser equipment and calibration techniques are described elsewhere [5] using a 15 cm lens in this case to focus the laser. The average pulsewidth was 118 fs full width at half maximum (FWHM) assuming a Gaussian pulse shape and varied over a range of 109 fs to 124 fs.
during the experiments. The pre-pulse contrast ratio was $3 \times 10^{-4}$ to $9 \times 10^{-4}$ measured after a half-wave plate and Glan polarizer combination, which was used for laser energy control. The contrast ratio varied within this range according to the setting of the half-wave plate due to the different polarizations of the pre-pulse and main pulse. Further energy selection was made using Schott NG absorbing glass filters. The repetition rate of the laser varied from single shot to 1 kHz and this range is not expected to alter the incubation coefficient. Femtosecond laser pulse interactions with materials at these intensities are expected to reach equilibrium conditions at most in a few µs after each pulse. The cumulative heating effects are expected to be small also since the average writing intensity at 1 kHz is around 100 W/cm² (300 µW average power), much less than CW writing intensities of 10 kW/cm² (80 mW) required for thermal writing of monolayers with a 10 cm lens [2, 3] (note that the incident beam diameters and divergences differ for each laser). Preparation of the monolayer target sample and solutions and the monolayer redeposition technique after laser scanning were similar to experiments discussed elsewhere [2].

For each experiment, the single-shot ablation threshold for the 30 nm gold thin film, $I_{th}(1)$, and its multi-shot incubation coefficient [6], $\xi$, were measured as these parameters provide details into the patterning mechanisms of the thin gold film during monolayer removal. The $I_{th}(1)$ calibration also provided the beam waist of the laser focal spot to calibrate the peak incident fluence for each experiment [5]. Line scans were made at a speed of 50 µm/s with a repetition rate of 1 kHz. After depositing the hydrophilic monolayer, scanning electron microscopy (SEM) images were made to image the two monolayer species on the surface and determine the line widths through contrast differences. A vacuum chamber was used to test removal of O₂ as a control for the previously proposed [4] photochemical reaction mechanism with oxygen.

3. Results and Discussion

SEM images of the thin gold film substrates after laser scanning showed the removal of the hydrophobic SAM within the focal region of the laser and the deposition of the hydrophilic SAM within the patterned region as in figure 1. The line width of the patterned region shown in figure 1 was approximately 10 µm, while the smallest line width observed was approximately 4 µm wide. Compared to the 2 e-folding intensity diameter of 24.8 µm for the laser, the minimum value indicates a six times reduction from the focal spot size of the laser to the resulting line width demonstrating the ability of femtosecond laser pulses to pattern SAMs on gold-coated substrates below the diffraction limited spot size. With this scaling, the smallest line widths achievable would be 170 nm for a 1 µm spot diameter, for example, using a 40X microscope objective.

The mechanism for the patterning of the SAMs using femtosecond laser pulses was found to be ablative, defined as removal of the SAMs as well as at least a few gold atoms. Reducing the peak incident fluence, $\phi_h$, showed that removal of monolayers occurred at the periphery of the visibly damaged gold spots and continued to occur even when visible damage to the film was not seen by SEM, as in figure 1. With continued reduction of $\phi_h$, the removal of the monolayers stopped. To

![SEM image of a region on the gold-coated substrate scanned with an incident peak fluence of 150 mJ/cm², a repetition rate of 1 kHz, and a scanning speed of 50 µm/s. With the incident elliptical Gaussian intensity beam radius of 14.0 by 12.4 µm and the major axis parallel to the scan direction, the overlap of the pulses effectively gives an irradiation of 560 pulses for any one pulse. The contrast is due to the presence of two different SAM species.](image)
determine whether the removal regime was ablative, measurements of $I_{th}(1)$ and $I_{th}$ were made as shown in figure 2. Measuring $I_{th}$ required additional measurements of the multiple-shot ablation threshold, $I_{th}(N)$, for $N = 10, 100$ and $1000$, where $N$ is the number of co-incident laser pulses on one spot. The measured $I_{th}(N)$ for the 30 nm gold thin film coated with the hydrophobic monolayer were $(553 \pm 45) \text{ mJ/cm}^2$ for $N = 1$, $(255 \pm 30) \text{ mJ/cm}^2$ for $N = 10$, $(183 \pm 16) \text{ mJ/cm}^2$ for $N = 100$, and $(135 \pm 10) \text{ mJ/cm}^2$ for $N = 1000$. This gave an incubation coefficient of $0.80 \pm 0.01$.

The presence of the hydrophobic monolayer on the thin gold film was not expected to perturb the ablation mechanism and alter the thresholds when compared to a clean gold thin film. Published values for the single-shot ablation threshold confirmed this hypothesis. Amoruso et al. [7] used 780 nm, 120 fs pulses at a $50^\circ$ angle of incidence to measure the electrons and ions removed from the surface of bulk gold (99.99 % purity). Scaling the ablation threshold of the vapourization regime of 460 mJ/cm$^2$ using tables for the complex index of refraction for gold at 800 nm [8] in the $p$-polarized state yielded 700 mJ/cm$^2$ for the single-shot ablation threshold. This threshold is higher than the value measured here; however, it has been established that the ablation threshold will decrease as the thickness of a metal decreases below the electron diffusion length with a critical thickness of $\sim 443$ nm for gold [9, 10]. Quartz crystal microbalance (QCM) measurements of the single-shot ablation threshold at 850 nm for a 250 nm thick gold electrode resulted in a value between 350 and 450 mJ/cm$^2$ [11]. This confirms our measured single-shot ablation threshold.

To our knowledge only one report on the incubation coefficient of gold exists: a value of 0.922 for gold films with thicknesses varying from 90 nm to 1500 nm [10]. These measurements were made at the 400 nm wavelength, which is above the resonant $d$-band absorption line for gold [12] and it is uncertain how this affects the incubation coefficient when scaling to 800 nm. Further investigations are planned for patterning at 400 nm and these fundamental ablation parameters will be investigated.

The $\phi_h$ range for patterning was 90 mJ/cm$^2$ to 190 mJ/cm$^2$ for line scans made at 50 µm/s at a 1 kHz repetition rate, which corresponded to irradiances of 510 to 560 pulses for any one spot. Above 190 mJ/cm$^2$ visible ablation damage was observed in the centre of the patterning region. The damage threshold for this pulse range varies from $134 \text{ mJ/cm}^2$ to $183 \text{ mJ/cm}^2$ using equation 4 in [5] including the errors. This places the patterning regime into the near-threshold ablation region, where nanomilling was measured in thin copper films just above the multishot ablation threshold [13].

To determine whether photo-oxidation was required for patterning in the femtosecond regime, we performed O$_2$ dilution experiments. By pumping down the vacuum chamber to $\sim 100$ mtorr and refilling to 633 torr with N$_2(g)$ from the blow-off of a liquid nitrogen tank sequentially three times, a
ratio of one oxygen molecule in the chamber per 10 million sulfur atoms on the monolayer surface was achieved. This assumed a (5 Å)² area per sulfur atom on the gold thin film surface and an initial 21 % partial pressure of oxygen at atmospheric pressure. Line scans were made at 50 µm/s between 130 ml/cm² and 190 ml/cm² and no measurable change in the contrast ratio or the line widths was detected by SEM for experiments done in an oxygen deprived atmosphere and in ambient air.

Considering the above discussion, the proposed mechanism for femtosecond laser patterning (800 nm, 220 fs) of SAMs on gold thin films as photo-oxidation [4] is not plausible. The peak incident fluence for the study in [4] would be ~ 1 J/cm² with 5 pulses overlapping (using their theoretical focal spot size of 1.6 µm and scanning conditions of 70 mm/s, 5.5 mW and 100 kHz). This fluence, well above $\phi_{th}(1)$ here, would lead to ablation of the sample as the dominant patterning mechanism. Furthermore, since no control experiment as described above was performed, the photo-oxidation proposal cannot be substantiated.

4. Conclusion
Patterning of SAMs on 30 nm thin gold films using 800 nm, 118 fs pulses was achieved using incident peak fluences between 90 ml/cm² and 190 ml/cm². The mechanism for patterning was ablative since the patterning fluences were near the ablation threshold for 510 to 560 consecutive pulses given by a single-shot threshold of (553 ± 45) ml/cm² and incubation coefficient of 0.80 ± 0.01. The previously proposed photo-oxidation mechanism in the literature was refuted by demonstrating monolayer removal in an oxygen deprived environment. Line widths were six times smaller than the 2 e-folding beam diameter, demonstrating the potential of this technique to achieve sub-diffraction limited nanometer scale patterning of SAMs for rapid prototyping of micro and nano-devices reliant on optical lithography techniques.

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