

# Selective Oxidative Patterning of Self-Assembled Organothiol Monolayers on Gold

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## Abstract:

Ozone and ultraviolet light have been implicated in Self-Assembled Monolayer (SAM) oxidation. Although these agents have been successfully used to fabricate simple patterns of alternating oxidized and non-oxidized species at the micron scale, the full potential of oxidative patterning at the nanometer scale has yet to be explored. SAM oxidation chemistry is highly complex and the precise oxidation mechanisms are not yet fully understood.

Here, we report novel methods for: 1) elucidating the oxidation reaction dependence on oxidative agents and SAM functionality; and 2) fabricating oxidized surface-patterns. Our methods use commonly available tools, and afford ease and simplicity in comparison to conventional methods.

## Introduction:

The desire to develop simple techniques for the nanoscale patterning of SAMs has driven interest in understanding the complex processes of SAM oxidation. Although several research groups have used oxidative agents in conjunction with masks of various geometries to create oxidized patterns of SAMs [1], the specific nature of SAM oxidation remains unclear.

Researchers demonstrated that exposing SAMs to a broadband ultraviolet (UV) source in air results in SAM oxidation [2]. However, UV light of 185 nm in the presence of oxygen also generates ozone and it was uncertain whether 185 nm light directly oxidized SAMs by photo-oxidation or if the resulting ozone was the true oxidant. A few years later, it was found that ozone alone can induce SAM oxidation implying that ozonolysis is the responsible mechanism [3].

Most recently, however, researchers have demonstrated that a 254 nm ozone-free UV source can oxidize mercaptoundecanoic acid (MUDA), but not octadecanethiol (C18) [4]. These findings indicate that the terminal carboxylic acid functionality may play a role in another oxidation mechanism. Especially interesting is the possibility of selectively oxidizing different organothiols using various combinations of

oxidative agents.

Past studies used costly and laborious processes to research the effects of individual oxidants. We have developed a simple, readily available technique utilizing a UV clean instrument that can separate and manipulate oxidation variables. The UV clean instrument exposes samples to a broad-band UV source and generates ozone within a contained environment. Glass microscope slides, which block all UV irradiation, and quartz microscope slides which block deep UV but transmit 254 nm light, were used to mask the samples.

## Procedure:

Wafers of amorphous Au thermally evaporated onto silicon were submerged in 1 mM solutions of MUDA, mercaptohexadecanoic acid (MHDA) and C18 for 18 hrs to form ordered monolayers. A sample each of MHDA, MUDA and C18 was pressed against fresh quartz and glass slides and taped creating a "pocket" to minimize air infiltration. The covered samples were placed in a Boeckel 135500 instrument for 13 minutes, which was determined to be the ideal time span for exposure. Samples were removed and ellipsometric height was measured using a Gaertner Fixed Angle LSE Stokes Ellipsometer. Samples were then rinsed for one minute with 18 M $\Omega$  deionized water followed by a thirty second rinse in ethanol to remove any remaining oxidized species and ellipsometric measurements were retaken.

## Results and Conclusions:

**UV Clean/No Screen; Control:** Prior to UV clean, the MUDA monolayer measured approximately 18Å in height, 7Å higher than in previous experiments. The extra height may indicate the presence of interdigitated bilayers. After UV clean, the height dropped to 7Å followed by complete monolayer degradation after a water/ethanol wash (Figure 1). The monolayer removal after washing indicates that complete oxidation occurred during the UV clean and the 7Å visible before washing were likely the remnants

of oxidized species. We term the difference in height after UV clean but before washing as “volatile desorption.” The MHDA and C18 samples showed similar trends to MUDA; some degree of volatile desorption followed by complete monolayer removal after washing.

**No UV Clean/Glass Contact Screen:** A glass contact screen was placed on a sample each of MUDA, MHDA and C18 (without UV cleaning) to determine effects of the glass slide on monolayer thickness (Figure 2). The MUDA sample exhibited no change in height after removal of the glass contact screen but did exhibit a decrease in height after washing. This height decrease can likely be attributed to partial removal of the interdigitated bilayer during washing rather than any effects of the glass contact screen. The samples of MHDA and C18 showed no change in height before or after washing indicating that the presence of the glass microscope slide does not detectably influence monolayer height.

**UV Clean/Glass Contact Screen:** UV cleaned samples of MUDA, MHDA, and C18 with a glass screen displayed similar results to glass-screened samples which were not UV cleaned (Figure 3). This indicates that the glass contact screen protected the samples from UV and ozone exposure, preventing oxidation.

**UV Clean/Quartz Contact Screen:** After UV cleaning with a quartz contact screen, MUDA exhibited a 6Å loss in monolayer height and a further 7Å height loss after washing, indicating partial oxidation (Figure 4). These results are strikingly different from MUDA with a glass contact screen which exhibited no monolayer loss after UV cleaning. MHDA also exhibited a significant loss in monolayer height after UV cleaning whereas C18 demonstrated only minor height loss.

These results demonstrate clear differences in the oxidation of carboxylic-acid terminated SAMs (MUDA, MHDA) and alkyl-terminated SAMs (C18). The glass contact screen prevented the infiltration of UV light and ozone thereby preventing oxidation in all SAMs whereas in the case of the quartz screen which transmitted 254 nm light, partial oxidation was induced in MHDA and MUDA.

#### References:

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- [3] Zhang, Y.; R.Terrill; T.Tanzer; P.Bohn; JAmChemSoc.; (Communication); 1998; 120(11); 2654-2655.
- [4] Brewer, N. J.; Rawsterne, R.E.; Kothari, S.; Leggett, G.J. J. Amer. Chem. Soc. 2001, 123, 4089 - 4090.

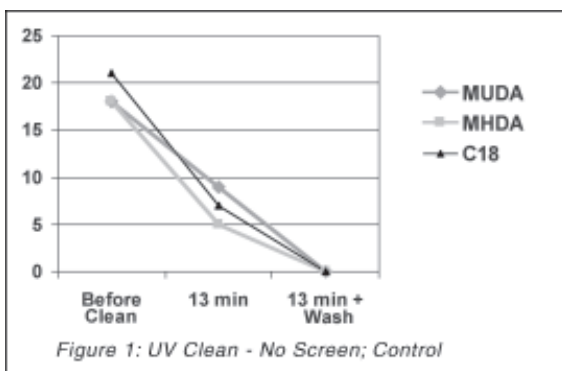


Figure 1: UV Clean - No Screen; Control

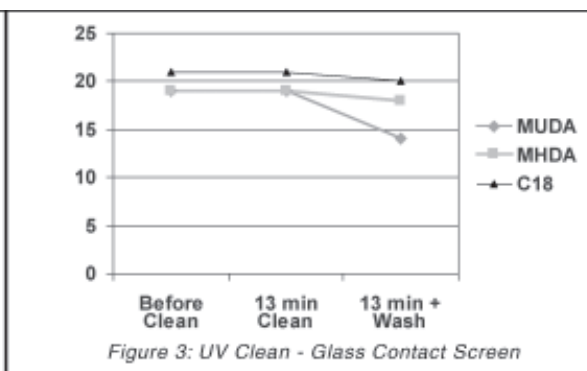


Figure 3: UV Clean - Glass Contact Screen

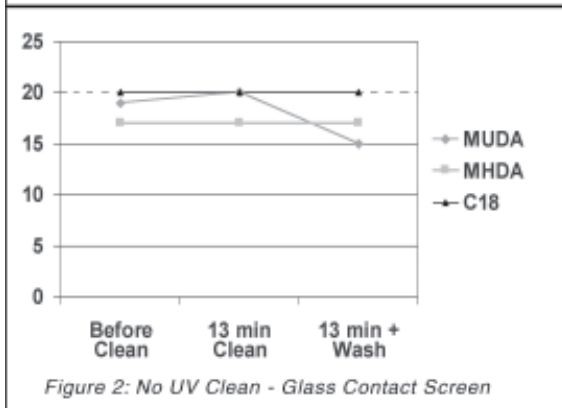


Figure 2: No UV Clean - Glass Contact Screen

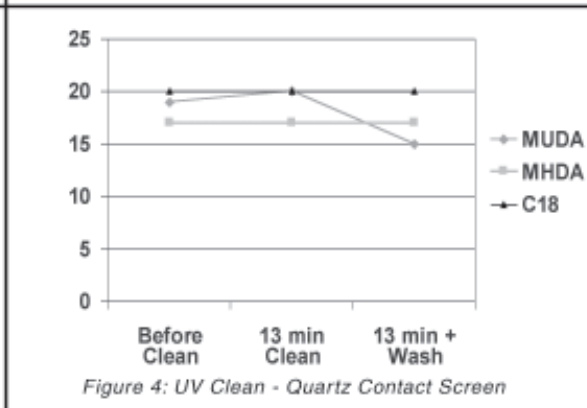


Figure 4: UV Clean - Quartz Contact Screen