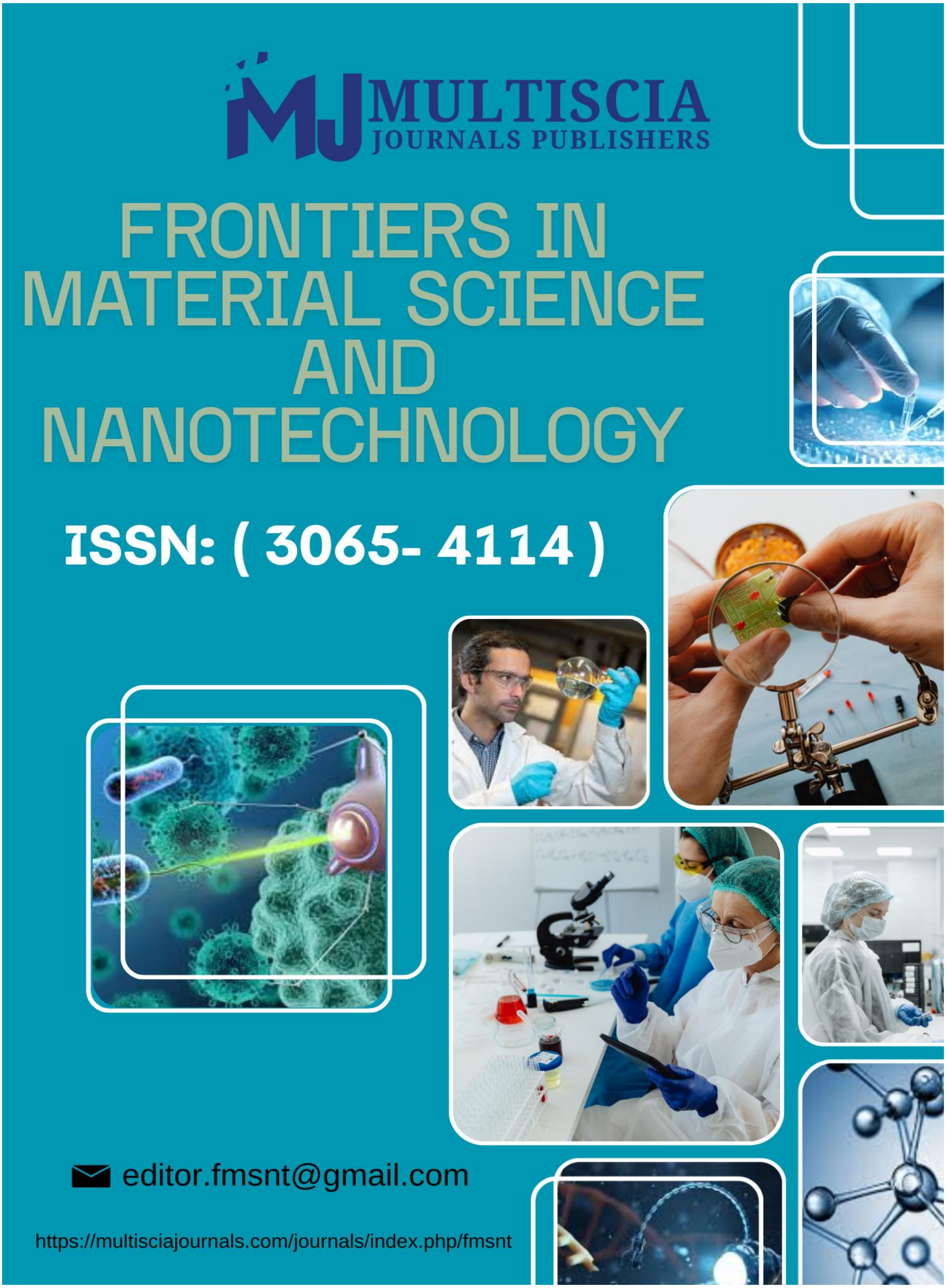

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# Effect of a Water Layer on a Surface of a Self-Assembled Monolayer That Is Both Hydrophobic and Hydrophilic

**Bhattachari D***

**Department of Material Science and Nanotechnology**

## Article Info

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## Abstract

For self-assembled monolayers to form tightly packed, the water layer next to the hydrophobic and hydrophilic moieties on the surface is crucial. The quality of the self-assembled monolayer of thiols depends on the re-structuring of the surrounding water molecules, according to a research based on atomic force microscopy and Fourier transforms INRS.

**Keywords:** Self-assembled monolayers; Hydrophobicity; Clustering

## Introduction

The term "self-assembly" refers to the spontaneous yet structured arrangement of constituent parts [1]. As the steps progress, the constituent parts come together to create a limited structure resembling self-assembled monolayers (SAMs) [2]. The formation of such a basic building block arrangement adsorbed on solid surfaces, where intermolecular interactions are crucial, may occur spontaneously from a solution. The primary hydrophobic chain, a designated terminal group, and a head group make up the building block. Every substrate type undergoes self-assembly due to the head group, which covalently bonds the hydrocarbon chain to the surface of the semiconductor or metal [3,4]. The structure is stabilized and the monolayers are packed compactly thanks to the interactions of hydrophobic and van der Waals forces among the hydrocarbon chains and the solvent environment [5-8]. One of the most common combinations of chemisorbed ordered monolayers is n-alkanethiols adsorbed on semiconductor or metal surfaces [9]. The spontaneous adsorption from ethanol solutions is the usual method for depositing these monolayers. This research detailed the steps necessary to create tightly packed SAMs of 16-Mercaptohexadecanoic acid (MHDA) thiol, including the importance for water.

## Materials and Methods

### Monolayer Preparation

The research included the preparation of self-assembling monolayers of 16-Mercaptohexadecanoic acid (MHDA) thiol [10] that were acquired from Sigma-Aldrich. SAMs made on flat surfaces, such as thin gold sheets mounted on silicon wafers. Using the physical vapor deposition (PVD) technique to create these substrates is a breeze. The next step is to submerge the finished substrate in a 2mM MHDA solution. On this substrate, SAMs were synthesized using a 2-minute self-assembly time.

### Fourier transform infrared (FT-IR) spectroscopy (TENSOR II FT-IR Spectrometer with HYPERION 3000 FT-IR Microscope) measurement

To investigate the effect of water on SAMs, samples were prepared in both ethanol and ethanol-water mixture in a ratio of 7:3, 3:2 and 1:1 respectively and was used in FTIR measurements under nitrogen ($N_2$) with low signal attenuation.

### Fourier transform infrared (FT-IR) mapping measurement (TENSOR II FT-IR Spectrometer with HYPERION 3000 FT-IR Microscope)

The FTIR mapping, samples were kept in microscope chamber under nitrogen ($N_2$) with low signal attenuation. The estimated surface area probed with the IR beam was 30 μM during the experiment.

### Atomic force microscopy (AFM) based study

The measurements were carried out with Nano Scope III AFM in the taping mode. AFM scans were performed in air and ethanol. Silicon nitride cantilevers with nominal spring constants of 0.38 and 0.12 N/m were used. The system was allowed to equilibrate prior to taking measurements. All images shown in this work correspond to unprocessed data obtained in the height mode.

## Results and Discussion

According to the results of the Fourier transform infrared spectroscopy (FTIR) analysis, which can be shown in Figure 1, the band that is responsible for the asymmetric CH2 stretching vibration of SAMs always occurs between 2917 and 2922 cm-1, however its precise location differs among samples. The symmetrical stretching vibration of SAMs, which causes the adsorption band at 2850 cm-1, shows that the SAMs are ordered by their lateral interactions. The ordering of alkyl chains affects the band position. Figure 1 shows that when the monolayer is prepared in degassed ethanol, the peak is at 2921.4 cm-1. However, when the SAM is prepared in diluted degassed ethanol with degassed deionized (DI) water in a 7:3 (v/v), 3:2 (v/v), or 1:1 (v/v) ratio, the peak moves to 2919.5 cm-1, 2917.5 cm-1, and 2917.5 cm-1, respectively. Preparing SAM in a degassed ethanol-water combination results in a more intense absorbance measurement. When using ethanol alone as a solvent, the absorbance was lowest, however when using a 1:1 (v/v) ratio of ethanol to water, it was greatest. The asymmetric CH2 band's low-frequency shift suggests an improvement in monolayer order [11]. A multilayer structure is formed when several monolayers are stacked, as shown by the high frequency shift. Although the asymmetric band does expand, it is smaller for monolayers [11].

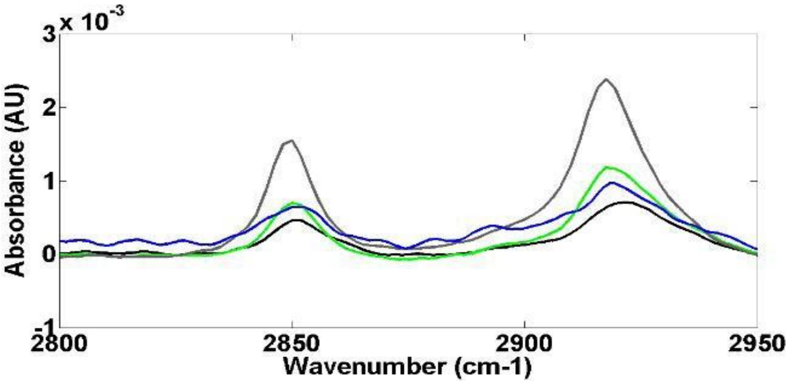

**Figure 1:**Transmission FTIR spectra of SAMs grown in ethanol (black) and ethanol diluted with degassed DI water in a ratio of 7:3 (blue), 3:2 (green) and 1:1 (violet)

An essential indication on uniform creation of SAMs is provided by the uniform blue pixel intensity reflected from FT-IR grid measurement. It has one layer in some places (Figure 2(b)), two layers in others (Figure 2(b)), or perhaps more than one layer (Figure 2(a)). What matters is how the surrounding water structure regulates the clustering of SAMs caused by various van der Waals forces of attraction (for details, see below). Thiol precipitation may be responsible for the enhanced absorbance intensity. An atomic force microscopy (AFM) investigation was conducted to rule out the likelihood of thiol precipitation. The roughness of the wafer rises during thiolation (as shown in Figure 3), reaches a peak at an ethanol to water ratio of 7:3, and then falls again when water is added up to a 1:1 ratio. It is confirmed that thiols precipitate with this very high water content by the extremely large rise in roughness with the 3:7 (v/v) ratio. Curiously, as can be seen from Figures 3 and 4, the roughness is similar with ethanol alone when using this specific ratio (1:1). Surface roughness is a more essential issue to consider when trying to understand the organization and quality of thin layer SAMs, because their dimensions are usually in the nanoscale range. This is due to the fact that roughness aids in both SAM quality control and precipitation, while thickness alone might reveal the problem. An intriguing reaction to SAM production with a 1:1 (v/v) ratio is seen. The hydrophobic molecule can engage in multiple van der Waals interactions with the water molecules because of their small size and flexibility in spatial arrangement, while thiols can arrange themselves around water without breaking hydrogen bonds or losing much energy.

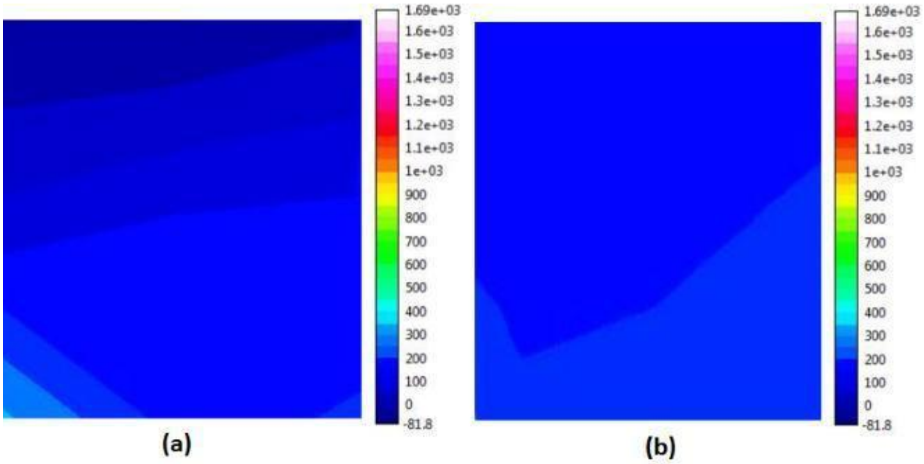

**Figure 2:** FTIR mapping of SAMs (a) blue color represents the SAMs and the cyan color is the region without SAMson Si wafer (b) FTIR mapping of SAMs fully covered on Si wafer

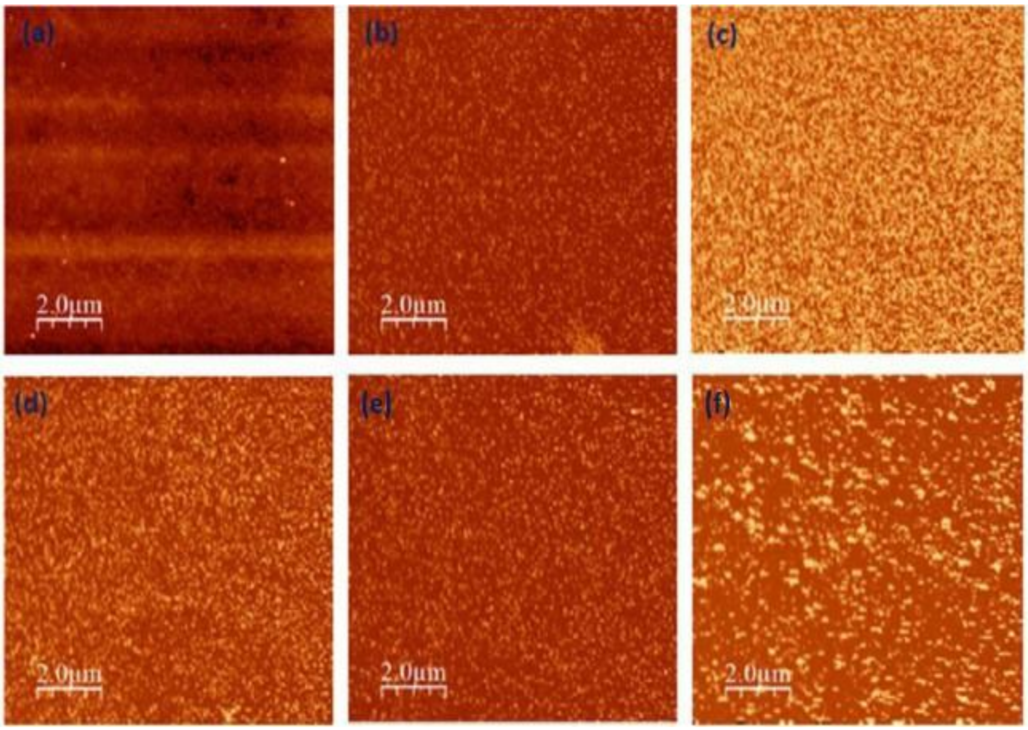

**Figure 3:** AFM images of (a) Si wafer without thiolation and after thiolation with (b) ethanol only, diluted ethanol with degassed water taken in ratio (c) 7:3, (d) 3:2, (e) 1:1 and (f) 3:7 (v/v) respectively

The “hydrophobic effect” of ethanol dissolved thiols in water is primarily a consequence of changes in the clustering in the surrounding water rather than water-solute interactions. This 1:1 (v/v) ratio provides the best close packed cluster structure due to 1:1 interaction. In all other ratio either hydrophobic or hydrophilic forces dominates but in this ration the clustering is stabilized by 1:1 water-solute interaction. The long alkyl chains associate via van der Waals and hydrophobic interactions in aqueous solutions that promote organization of the stable SAMs.

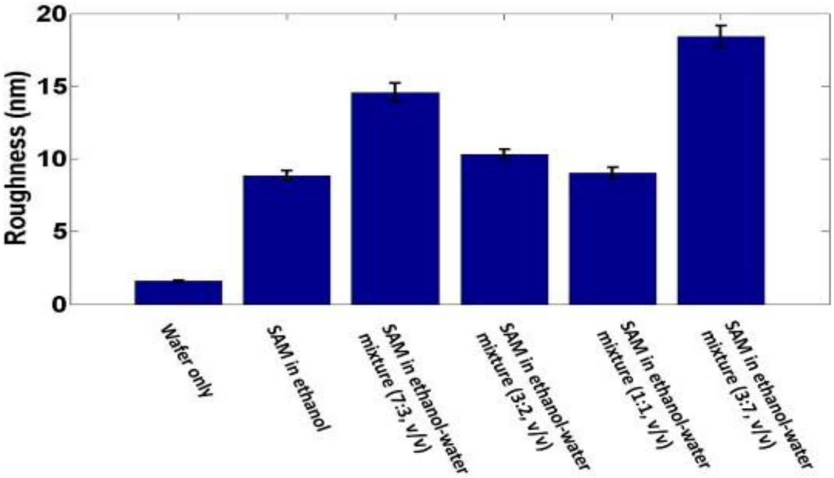

**Figure 4:** Roughness calculated from AFM images of wafer only without thiolation and after thiolation in degassed ethanol only and degassed ethanol-DI water taken in ratio (c) 7:3 (v/v), (d) 3:2 (v/v), (e) 1:1 (v/v) and (f) 3:7 (v/v) respectively

Initially when ethanol dissolved thiols are surrounded with water molecules the assembly of n-alkane thiols experience strong intermolecular forces between the alkane chains due to hydrophobic interaction as well as change the clustering in the surrounding water result ordering of SAMs. The increased absorbance in Figure 1 indicates the formation of densely packed monolayers. When the water content is less, the change in clustering of thiols in the surrounding water is less and moreover the randomness of the alkane chains are higher. It creates some local disorder result increase in roughness but when the water content is increases a bit the alkane chains are densely packed due to multiple van der Waals force of interaction. As a result the hydrophobic effect spatially rearrange the thiols to a densely packed cluster. So, the quality of self-assembled monolayer is strongly dependent on surrounded water structure.The roughness of the surface also decreases as it is reflected in Figure 3 and 4. But when water content is very high (i.e. ethanol to water ratio 3:7, v/v) the clustering effect collapses due to less solubility of thiols in the mixtures. A disorder is created due to precipitation of thiols. Therefore an abrupt increase in roughness (also the surface topology changes significantly) is observed and most interestingly, ethanol to water 1:1 (v/v) ratio performs the best for SAM formation.

## Conclusion

This finding lends credence to the idea that water's numerous van der Waals forces have a significant impact on SAM clustering. It turns out that the solvent's properties determine the clustering effect. The most effective method for rearranging thiols into a tightly packed cluster is a 1:1 (v/v) ratio of ethanol to water.

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