

Research and First Experiments on Self Assembled Monolayers (SAM) for Area-Selective Atomic Layer Deposition

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Abstract— This work gives the theoretical background which is needed to understand what self-assembling monolayers are, how they work, how and for what they can be used. A closer look is taken on the possibility to create an area selective atomic layer deposition process. In a practical experiment the foundation for this process is laid. Therefore a silicon wafer is coated with gold using an evaporation process. The gold samples are exposed to the SAMs solution to grow them. Contact angle measurements as well as Fourier transform Infrared spectroscopy are used to check the existence of SAMs on the gold samples. Also there is investigated if different exposure times make any differences.

I. INTRODUCTION

Self-assembling monolayers (SAMs) are monolayers of a specific substance consisting of hydrocarbon chains and are characterized by head and end groups. The monolayer builds itself on a substrate which is covered with a solution the SAMs are dissolved in. The self-organization of adsorbates on surfaces is known since 1946 when Zisman et al. reported about the formation of monolayers from hydrocarbons on surfaces [1]. Although the possibilities of the self-assembling monolayers were not seen at this point. Until in 1978 Polymeropoulos and Sagiv predicted the possible use to measure the resistance between two metallic surfaces [2]. The first article about defined monolayers on Silicon-dioxide was in 1980 [3]. Self-assembling monolayers build themselves spontaneously on different surfaces. The best known adsorbate/surface combinations are alkyl silanes on oxide surfaces and sulfur containing molecules on Gold surfaces [3]. The SAMs on Gold became more famous, probably because they are easy to produce. Nevertheless have the alkyl silane monolayers a few advantages like outstanding stability because they form a covalent bond to the surface. Furthermore, they are compatible with the processes in the silicon technology. Since the 1980's the number of published reports about self-assembling monolayers exploded. The SAMs are no longer just a possibility to passivate a surface today they are even used in the bottom-up Nanofabrication.

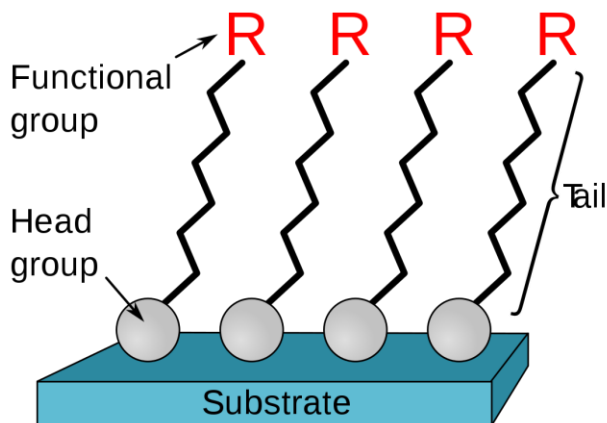


Figure 1: Structure of SAMs [8]

Self-assembling monolayers consist of three main groups. Figure 1 shows that the SAMs consist of a head group, a tail group and a functional group. The head group is needed for the SAMs to bond to the substrate. The tail group builds the connection between the head and the functional group, and is needed for the self-organization of the SAMs. The functional group is then the most important group for the function and the desired use case of the SAMs.

SAMs are for example used for designing catalysts [4]. Dong et al. used them to selectively coat vertical surfaces of nanopillars [5]. SAMs can also be used to achieve area selective atomic layer deposition. Eun K. Seo et al. used two types of SAMs, one to activate and one to passivate the surface during ALD[6].

The possibility to design an area selective atomic layer deposition process is very promising. Our research group decided to take a closer look at the steps needed to use SAMs for area selective ALD. The project was about getting a self-assembled monolayer on silicon wafers coated with gold. To prove the SAMs grew on the substrates different measurements were performed.

II. MATERIALS AND METHODS

A. Fourier transform Infrared spectroscopy

Fourier transform Infrared spectroscopy (FTIR) is a non-destructive way to characterize materials. The FTIR is a special version of the infrared spectroscopy which calculates a spectrum with an interferometer. The radiation in the infrared sector gets partially adsorbed and partially reflected. The adsorbed wavelengths stimulate the molecules to swing. The not interacting wavelengths are detected by the FTIR. The infrared spectrum is like a fingerprint for molecules, with this it is possible to identify molecules.

B. Contact Angle Measurement

To measure the contact angle a single drop of a liquid is put on the measured surface which is a good way to measure the surface energy. The simplest way to perform a contact angle measurement is to measure the static contact angle. With this method the angle is measured when the drop on the surface is not moving. The angle is measured at the three-phase boundary. With the contact angle the surface free energy can be calculated. The contact angle measurement is a quick and easy way to see if the surface is either hydrophilic or hydrophobic.

C. Evaporation

The evaporation process is used for thin film deposition. In this process the substrate is mounted in a vacuum chamber. The evaporation source holds the desired thin film material. Once the vacuum is good enough, to ensure the mean free path of the molecules is long enough, the evaporation source gets heated. The material will melt and start to evaporate. The vapor hits the substrate, condenses back to the solid state and a thin film is build.

D. Octadecanethiol

The SAMs used in this project are named Octadecanethiol. The structural formula is $[\text{CH}_3(\text{CH}_2)_{17}\text{SH}]$. The head group $[\text{SH}]$ will form a sulfur bond with Gold. The tail group $[(\text{CH}_2)_{17}]$ is needed for the organization of the SAMs. The functional group $[\text{CH}_3]$ should prevent the growth in the atomic layer deposition (ALD) process by being unreactive toward the ALD chemistries.

E. Atomic Layer Deposition

The atomic layer deposition (ALD) is a modified chemical vapor deposition process. It is a process with cyclically repeated self-limiting surface reactions. The material to be deposited is available as precursor and is brought into the reaction chamber by means of a carrier gas. The simplest ALD process consists of two reactants. Then the process steps are:

- self-limited reaction of reactant A
- purge
- self-limited reaction of reactant B
- purge

In the first step the reactant A bonds to the substrate. In the second step the rest of reactant A which has not reacted and the reaction products are purged. Then the reactant B is let into the chamber and reacts with reactant A to the desired layer. The final step again removes the not reacted rest of reactant B and the reaction products. These four steps are repeated until the desired thickness is reached. The ALD process has advantages compared to the chemical vapor deposition. The layers are highly uniform and reproducible, have a high conformity even on complex structures and the layer thickness is outstandingly controllable.

III. EXPERIMENTATION

First the wafer has to be covered with gold. Therefore a 4-inch silicon wafer is used. The gold layer is deposited using the evaporation process. Firstly a 15 nm thick adhesion-layer of titanium is deposited. On top of this layer the 50 nm thick gold layer is deposited. Some parts of the wafer were covered with tape to prevent deposition in those areas. With this there is a possibility to characterize different materials at once in the to be followed ALD process. The finished wafer was cut into square pieces of approximately 2 cm length. Figure 2 shows the coated and cutted wafer.

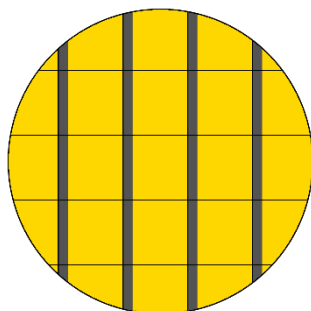


Figure 2: schematic representation of the gold wafer

For the second step the SAMs were dissolved in ethanol. The produced solution had a concentration of 2.87 mMol. To fully dissolve the SAMs the solution was put on a Hotplate with stirring at 40° C to 45° C which is slightly higher than the melting temperature of the SAMs which is at 30° C [7]. Once the SAMs were fully dissolved nine of the gold substrates were put into the solution and set aside at room temperature. The rest of the samples are used as reference samples. Three of the samples were exposed one hour to the solution. Three of the remaining samples were exposed two hours and the last three were exposed three hours. Figure 3 shows the samples in the solution.



Figure 3: Gold samples in the SAMs solution

IV. RESULTS

The contact angle measurements showed that the samples which are coated with SAMs are more hydrophobic. They show a higher contact angle with water than the uncoated samples. Figure 4 shows a waterdrop on a reference and a coated sample. The results are summarized in the following table.

Table 1: Results of the contact angle measurement

Sample	Contact Angle [°]
Gold-reference	76.83 ± 0.69
SAMs 1h	102.03 ± 0.64
SAMs 2h	100.21 ± 0.75
SAMs 3h	101.99 ± 1.10

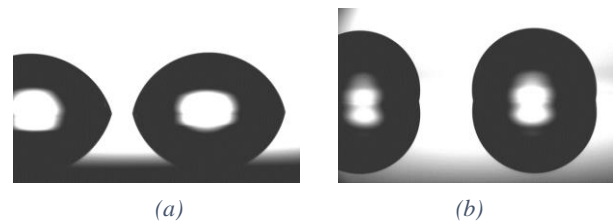


Figure 4: A waterdrop on the reference sample (a) and a waterdrop on a SAMs coated sample (b)

The FTIR measurements of the samples showed that the samples with SAMs are generally less reflective than the reference sample. Overall the spectrum of the reference sample is repeated with lower reflectivity. But the spikes which are also there in the reference sample are more intense in the

samples coated with SAMs.

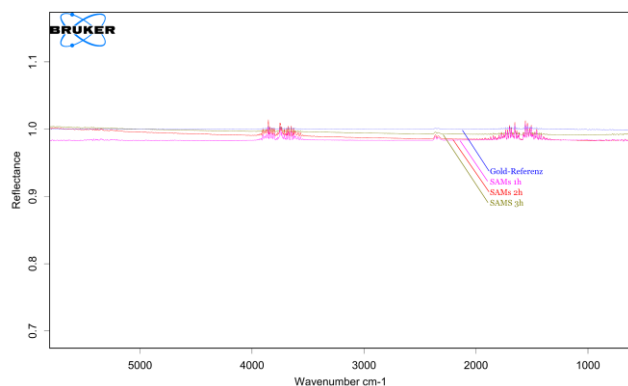


Figure 5: FTIR measurements of the samples

Figure 5 shows the different measured spectra. The measurement showed that the coated samples are less reflective but the time they were exposed to the SAMs solution also made a difference. For instance, is the sample with 1 hour duration less reflective than the sample which was exposed 3 hours.

V. DISCUSSION

The measurements showed that the SAMs grew successfully on the gold samples. The hydrophobicity can be explained by the functional group of the SAMs. The $[\text{CH}_3]$ methyl groups are hydrophobic and unresponsive elements which is the reason they should prevent film growth in the ALD process. Further investigations which are possible with the contact angle measurement were not made because the only goal was to prove the existence of the SAMs on the gold.

They FTIR measurements also proved that the chosen method for coating SAMs on gold worked. Interestingly the FTIR measurement showed differences with the samples which were exposed different durations to the SAMs solution. One possible reason for this is the process of self-organization. Firstly the SAMs bond to the surface but are not upright yet. Only when the surface is fully covered with SAMs they start to raise up. This could explain why the sample which was exposed 3 hours is the most reflective. Once the SAMs are upright the infrared light could possibly pass through better than when they are still laying down and therefore get reflected by the underlying Gold. That could be the reason why the sample of 3 hours is the most reflective out of the coated samples. This assumption needs further investigation. As well as with the contact angle measurement also the FTIR results were not analyzed more specific because the overall reflectiveness is a good indication to see if the SAMs grew on gold or not.

VI. CONCLUSION & OUTLOOK

In conclusion SAMs can give loads of new opportunities. They can also revolutionize and improve state of the art processes. For example they can bring the possibility of structuring a coating to the atomic layer deposition. So its possible to combine the advantages of atomic layer deposition with the versatility known from the lithography processes in microsystems technology.

The tested method to grow SAMs on gold substrates worked well. Future experiments must investigate whether the SAMs really prevent the growth of films in the ALD process. Furthermore it is possible to see, if the exposure of one hour to the SAMs solution is enough to prevent the growth or if the samples need to be exposed two or three hours in order to work as masking layer in the ALD. If the chosen SAMs are suitable as masking layer further experiments can investigate how the SAMs can be used to transfer structures to the gold samples. With this working there would be a possibility to create structures with the ALD and SAMs like with photoresist and evaporation for example.

VII. ACKNOWLEDGMENT

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