Mass sensitivity of Langmuir-Blodgett monolayer film coated surface acoustic wave resonators to volatile organic solvents

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Abstract. Langmuir-Blodgett (LB) monolayer films deposited from a Dipalmytoyl Phosphatidyl Ethanolamine head labelled with Nitrobenzoxadiazole (DPPE-NBD), have been studied for their ability to be used as sensing layer for chemical gas sensors. DPPE-NBD molecules are known for their similarity to bio membrane molecules. Therefore, it is expected that they can serve as a matrix for immobilization of proteins, enzymes, aptamers, while preserving their function for selective reaction with organic analytes. In this study, LB monolayers of DPPE-NBD were deposited on Rayleigh Surface Acoustic Wave (RSAW) resonant devices working at 411 MHz and simultaneously on ultra-flat Si wafer substrates for Atomic Force Microscopy (AFM) inspection. Depositions were carried out both at a low surface pressure where the liquid-expanded phase dominates, and at a high surface pressure, where the liquid-condensed (solid) phase dominates. AFM topography reveals the liquid and solid phase coexistence as well as the formation of 3D pyramids of 3 to 30 nm height and 50 to 1000 nm in diameter. In a vapour sensing experiment, the RSAW devices were exposed subsequently to vapours of 6 volatile organic compounds (VOCs) and water. The most significant resonant frequency shift of 225 kHz which corresponds to 11.42 ng mass change was observed with chloroform vapours when the substrate with the solid phase LB monolayer was used as a sensing layer. Adsorption and desorption of the vapours was very fast (a few seconds) and completely reversible. The higher-pressure deposited LB film demonstrates higher sensitivity to all gases. Mechanisms of this behaviour are discussed.

1. Introduction

Volatile organic compounds (VOCs) belong to a class of reactive gases and vapors that are currently attracting increasing attention. These chemicals have a high vapor pressure and quickly evaporate at room temperature. VOCs are used in a variety of industrial applications and can be used as markers for explosives. When released in the atmosphere, they can impose a serious threat to the environment and human health. Their presence in human breath is used as an indicator for certain diseases. Sensing VOCs is challenging as they are in general nonreactive and have a limited affinity to solid surfaces. This makes it difficult to find materials that selectively bind to or adsorb them. High resolution molecular separation approaches such as gas chromatography and mass spectrometry offer high
sensitivity, but are difficult to implement in portable, real-time monitors, where approaches such as chemical sensors and biosensors are considered as an alternative. Gravimetric transduction methods, in which the mass of an adsorbed vapor is directly measured, have several potential advantages over other techniques [1, 2]. Among these devices are Surface Acoustic Wave (SAW) resonators, as used in this paper. Compared to the classical quartz crystal microbalance, they offer orders of magnitude higher sensitivity, extremely low limits of detection and much higher dynamic range [3]. In addition, SAW devices are readily available, occupy a small surface area and easily integrate with CMOS structures [1]. In mass sensitive sensor systems they are typically coated with sensing layers responsible for interactions with different types and forms of analytes, in which the layers change their mass and cause a measurable mass proportional shift of the device center frequency. Materials used as VOC detection layers in SAW devices are typically: pristine polymers; self-assembled layers; supramolecular structures; molecularly imprinted polymers; carbon nanotubes and hybrids; metal oxide nanostructures, etc. [4]. Thick layers (e.g. polymer coatings) offer high selectivity and dynamic range but as they rely on in-depth penetration of the analyte molecules they have slow reaction times. Alternatively, thin layers obtained by e.g. self-assembly [5] can offer faster reaction times in the seconds range. An alternative method for nano scale thin-film deposition of high quality organic layers is the Langmuir-Blodgett (LB) method [6]. The high surface area to volume ratio of LB films causes fast surface adsorption and desorption effects which dominate over slow bulk diffusion processes. A mixture of two-component LB film on a SAW device has been used for detection of methanol and ethanol [7]. Polypyrrole 29 layer LB film has been used as a sensing layer for NH3 on a SAW device with excellent sensitivity and good selectivity to other interfering gases [8]. The problem of gas selectivity, which depends not only on the gas mixture but also on the concentration of the different gases, can be solved with the concept of the electronic nose (e-nose) [9]. In this concept an array of sensors with different selective coatings are used and their responses are analyzed to determine the compound sensed. A “fingerprint” measurement for the different gas combination and concentrations is performed. The method of self-assembled monolayers, which is similar to the LB method used here, showed that molecules with long hydrophobic tales (with a number of CH2 groups) have strongest adsorption to a number of tested gases including methanol, ethanol and acetone [10]. In this study we use a fluorescently labelled phospholipid molecule which has two such tales so high gas adsorption is expected. Additionally, for this molecule, 3 new effects were described [6] which can additionally improve sensor performance.

If we combine the gravimetric transduction method with the electrical transduction method it is possible to increase the selectivity and sensitivity of a sensor. For example some molecules can adsorb identical mass on the gravimetric device but also change its electrical conductivity. In this way both methods can be differentiated. This is the case of methanol and ethanol which adsorb almost identical mass but methanol decreases electrical impedance around 1000 times compared to ethanol at low frequencies [11]. We have applied a sophisticated electrical transduction method called electrochemical impedance spectroscopy (EIS) in a wide frequency scan range from 0.1 Hz to 3 MHz to the same SAW devices to measure their conductivity when probing with different gases [11].

2. Materials and Methods
The Dipalmitoyl Phosphatidyl Ethanolamine head labelled with NitroBenzaDiazole (DPPE-NBD) of 99% purity was purchased in chloroform solution from Avanti Polar Lipids (USA). This substance was used as a material for the LB film depositions. Ultra-pure deionized water was used in the experiments as a subphase and air purification in the laboratory was performed with a HEPA filter system. The Langmuir film was compressed very slowly, (measurement of a DPPE-NBD isotherm takes over 2 hours), to avoid kinetic effects and prior to deposition the film was allowed to stabilize for at least 10 minutes at constant surface pressure. The LB film deposition was carried on a symmetrical barrier system (Advanced Technologies Ltd., Bulgaria) on an upstroke at a slow deposition speed of 0.01 mm/s. For the deposition on the two SAW resonators used, two surface pressures (Π) were applied: resonator G2 – Π = 3.8 mN/m, mean area per molecule
A = 0.593 nm²/molec.; and resonator G3 - Π = 35 mN/m; A = 0.371 nm²/molec. Simultaneously deposition was carried out on ultra-flat Si wafer (Nanoandmore, Germany) substrates with roughness in the 0.2-0.3 nm range for Atomic Force Microscopy (AFM) studies by MFP-3D Infinity AFM (Oxford Instruments Asylum Research, USA). To test the mass sensitivity of quartz based SAW sensors to VOC vapors we used 411 MHz two-port Rayleigh SAW (RSAW) devices very similar to the ones described in [12]. The only difference to those devices is in the dimension of the spacer between the two interdigital transducers (IDT) which was modified in such manner that the resonant device forms a two-pole coupled resonator filter (CRF) response as shown in figure 2. This technique is typically used to double the phase slope of the acoustic device which provides better stability in RSAW resonant sensors operating with an oscillator interface [13]. For the vapor probing experiments the LB film coated SAW devices were placed above a Petri dish with the corresponding liquid solvent or water and covered with another dish. The vapor concentration was not measured but was estimated at about 40% for all compounds we used for probing. Spectral measurements were taken every 50 ms until no change of signal was observed.

3. Results and Discussion
The isotherm of the DPPE-NBD molecule, along with surface potential and Brewster angle microscopy measurement, was described in earlier work [14]. The liquid-expanded and liquid-condensed phase coexistence region starts at around 6.5 mN/m at a temperature of 22°C. In the phase coexistence region, circular domains of the solid phase coexist with the liquid phase and the height difference between the two, as observed from the AFM data in figure 1, is around 1.1 nm. Simultaneously, multilayer cylinders are formed (see figure 1) which significantly increase the surface-to-volume ratio of the sensing layer. This, in turn, should increases sensor sensitivity.

![Figure 1. 3D view of an AFM of an LB monolayer from DPPE-NBD on a Si wafer deposited simultaneously on resonator G2.](image-url)
device frequency down by 182 kHz in the case of sample G3, which results in a DPPE-NBD monolayer absolute mass of 9.2 ng. Taking into account the active sensing area calculated as 0.7 mm² for this device, we calculate the monolayer’s mass per unity area as 13.2 ng/mm². From the measurement in figure 2 we conclude that RSAW based resonant devices on quartz tolerate LB deposited monolayers from DPPE-NBD in an excellent manner which makes these monolayers the perfect choice as chemo sensitive layers in such mass sensitive devices. Peculiarities of the LB film deposition of DPPE-NBD molecule will be discussed in more detail elsewhere.

Figure 2. Frequency response of the RSAWLB sensor a) before and b) after LB monolayer coating.

For the VOC vapour probing experiments, the RSAW based LB sensors from figure 2 were mounted on a test board and connected to a scalar network analyser to evaluate the sensor performance and response to different VOC vapours and water in real time during probing. The sensor’s frequency response was recorded first before probing and then a few seconds later, after the active surface was exposed to the vapours. The results are shown in figure 3 for three of the compounds used in this experiment - acetone, hexane and water. We found that the sensor reacts to the vapour almost instantaneously and the downshifted frequency response reaches equilibrium and becomes stable just a couple of seconds after the active area is exposed to the vapours. As shown in figure 3 the CRF frequency response is not affected by the VOC vapours at all. The two resonance peaks stay in place. Just the overall frequency response shifts down by an amount proportional to the vapour mass adsorbed by the monolayer.

Figure 3. Typical frequency responses of the RSAWLB sensor to a) acetone, b) hexane and c) water.

The results from the vapour probing experiments are summarized in Table 1 for all 6 VOCs and water used in this study. It is evident that the RSAWLB sensor provides different sensor signals (frequency down shifts) to all 7 compounds but they do not seem to be directly related to their molecular weight, density or polarity. As we have only a monolayer with around 3.1 nm thickness of the sensing layer, surface adsorption would be the main adsorption mechanism compared to bulk
diffusion of the gases. The Langmuir adsorption model can be used in this case [15]. It assumes that gas molecules which attach to the surface of the sensing layer are held at specific sites that are expected to be identical with regard to the desorption energy required to remove the attached gas molecule which is the same for each of the sites. However to explain the result for the different gases, there are other mechanisms of interaction between the LB monolayer and the vapour molecules (e.g. polarity) that need further consideration and explanation and will be subject of a future work.

Table 1. VOC vapour frequency shifts and sorbed mass of the RSAWLB sensor to 7 different gases.

| VOC                  | Chemical formula | Molecular weight [g/mol] | Density [kg/m³] | Polarity         | G2 device | G3 device |
|----------------------|------------------|--------------------------|-----------------|-----------------|-----------|-----------|
| Chloroform           | CHCl₃            | 119.38                   | 1490            | 0.259           | 106       | 239       |
| Hexane               | C₆H₁₄            | 86.18                    | 655             | 0.009           | 34        | 83        |
| Petroleum ether      | C₆H₁₄            | 86.18                    | 655             | -0.01           | 34        | 78        |
| Acetone              | CH₂O             | 58.08                    | 784             | 0.355           | 68        | 166       |
| Ethanol              | CH₃OH            | 46.07                    | 789             | 0.654           | 34        | 63        |
| Methanol             | CH₂OH            | 32.04                    | 792             | 0.762           | 28        | 58        |
| Water                | H₂O              | 18.015                   | 997             | 1               | 44        | 107       |

Finally, we briefly investigated the dynamic behaviour of the RSAWLB sensor to chloroform - the heaviest VOC that we tested. It provides the largest response, accordingly. In this experiment, the scalar network analyser was operated in its accumulation mode in which it records a sweep trace once in every 50 ms. In this way it is possible to track the sensor response in real time in the process of sorption/desorption. The result from this experiment in which the sensor response was recorded between the moment the vapour came into action and the moment the response settled down after the vapour was removed, is shown in figure 4. We found that in this process the sensor is very well behaved and ideally returns to the baseline within 30 s after vapour removal. This is another indication that RSAW LB sensors using DPPE-NBD monolayers are very well suited for VOC vapour detection.

Figure 4. Open air dynamic behaviour of the RSAWLB sensor responding to chloroform vapours. Within 30 s. after removing the vapour effect, the sensor frequency response returns to the baseline within 5% of the sensor signal (see difference between the two vertical dotted lines in the centre of the data plot). No vapour residues remain in the monolayer after about two minutes after vapour removal, without flushing the active sensor area.

4. Conclusions
This study confirms our previous findings [16] that Langmuir-Blodgett films in the case of monolayer film deposition with a thickness around only 3 nm, are very well tolerated by RSW devices with negligible effect on the insertion loss and the Q factor. The frequency change due to adsorption of 7 different gases is in the range from 30 to 230 kHz which is readily measurable with a frequency counter if the RSW sensor is connected to an oscillator circuit. The mass sensitivity is high enough for a variety of practical applications. Reaction times are in the seconds range without flushing or heating needed. Sensor responses differ significantly from gas to gas. We believe that RSW resonant sensors using DPPE-NBD LB films for VOC detection may be quite competitive in future.
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