Self-Assembled Monolayer Compatible with Metal Surface Acoustic Wave Devices on Lithium Niobate

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The formation of a siloxane self-assembled monolayer (SAM) film on a lithium niobate substrate was investigated for surface acoustic wave (SAW) sensor devices for the detection of hydrogen. The most widely used SAM coupling reagent, octadecyltrichlorosilane, etches aluminum metal features that are integral to sensor devices, due to the formation of high local concentrations of hydrochloric acid. An alternative coupling reagent, octadecyltrimethoxysilane (OTMS), does not show any etching of metal parts. OTMS and related molecules are compatible with conventional SAW device manufacturing techniques and other devices that contain metal features susceptible to etching by acid released in the SAM formation process.

1. Introduction

Self-assembly of molecular films from solution has been extensively employed to construct monolayer thin organic layers because a molecularly ordered structure can be prepared very easily with expensive and sophisticated equipment.1 The most widely studied SAMs are alkanethiols on gold2 and alkylsilanes on glass (SiO2).3 The diverse applications of molecular self-assembly range from simple adhesion control4,5 and polymer grafting6,7 to more complex integrated functionalities such as organic light emitting diodes,8,9 molecular electronics,10,11 and biosensors.12

SAM coatings have recently been used in hydrogen (H2) gas sensor applications.13 Palladium (Pd) is well-known to absorb H2, and this property has been used for H2 sensor applications.14 Xu et al. suggested that the response of the Pd-based sensor to H2 was enhanced when the glass substrate surface was modified by an octyldimethylchlorosilane SAM prior to the Pd deposition.15 In recent times, the growth of alkylsilane SAMs has been extended to various kinds of surfaces such as TiO2,16 chromium,16 indium tin oxide,17,18 indium nitride,19 and tantalum pentoxide,20 to our knowledge, siloxane SAMs have not been grown on lithium niobate (LiNbO3).

Surface acoustic wave (SAW) devices have been utilized for a wide range of applications such as mobile communication systems21,22 and chemical sensors in gas23 and liquid.24 An SAW device consists of microelectrodes, the so-called interdigital transducer, which transforms an applied ac bias to an acoustic wave on a piezoelectric substrate (and vice versa).25 These devices can be manufactured using a variety of piezoelectric substrates, including quartz, LiNbO3, or lithium tantalate (LiTaO3). LiNbO3 and LiTaO3 have been widely used as piezoelectric substrates due to their high electromechanical coupling coefficients.25 The electrodes are normally made from aluminum (Al) or an Al alloy.26 SAW-based sensors consist of acoustic wave devices incorporating sensing materials, such as indium oxide layers deposited on LiTaO3 with an SAW device made of Al electrodes27 and a polysiloxane layer grafted on quartz with a gold electrode.28,29

It is tempting to combine the small, wireless features of the SAW device with self-assembly techniques to control wettability of the device to achieve controlled deposition of a metal layer or achieve direct grafting of biopolymer- and polymer-sensing materials or even the design of more complex nanostructures. Since most SAW devices are fabricated on oxide substrates, one strategy is to form siloxane SAMs on the surface. Conventional SAW device manufacturing processes, including deposition and photolithographic definition of metal-interdigitated electrode and bus structures, preferably precede the SAM coating process. Under these conditions, it is important to examine the effect of...
SAM formation on SAW device features and properties, e.g., the possibility of corrosion in the wet chemical process.

In the present study, the formation of a siloxane SAM on a LiNbO$_3$ substrate with aluminum SAW devices was investigated. The most widely used coupling reagent, octadecyltrichlorosilane (OTS), etches Al metal features due to the formation of high local concentrations of hydrochloric acid. On the other hand, an alternative coupling reagent, octadecyltrimethoxysilane (OTMS), does not show any etching of metal parts. This SAM has characteristics that make it compatible with conventional SAW device manufacturing techniques.

2. Experimental Section

All glassware was cleaned by piranha solution (3:1 (v/v) concentrated sulfuric acid/30% hydrogen peroxide) (caution: piranha solution is extremely corrosive and can react violently with organic compounds) and dried by a stream of hot air prior to use. ST-cut quartz (Sawyer) and Y-cut LiNbO$_3$ (Crystal Technology, Inc.) substrates were O$_2$ plasma treated (100 mW rf power, 400 mTorr of O$_2$, 5 min). O$_2$ plasma treatment does not degrade Al devices but maximizes the number of hydroxyl groups on the substrates as indicated by the wettability. The rms roughness of the LiNbO$_3$ wafer, evaluated for regions of $\sim$2 $\mu m \times 2 \mu m$, was measured by AFM after cross section and found to be $\sim$0.2 nm for the polished front surface and $\sim$75 nm for the unpolished backside. The rms roughness of the quartz wafer was found to be $\sim$0.3 and $\sim$40 nm for the polished and unpolished surfaces, respectively. OTS (Gelest Inc.) and OTMS (Gelest Inc., >95%) were used without further purification. The OTS SAM was made by immersing a clean substrate into a 0.1% (2.5 mM) OTS solution in a mixture (4:1) of hexadecane (Sigma, >99%) and chloroform (Sigma-Aldrich, 99.8%) at room temperature (ca. 22 °C) in an ambient atmosphere (typical RH $\approx$ 40%) for 20 min.$^{28,29}$ The OTS sample was rinsed with chloroform and methanol.

The OTMS SAM was made by immersing a clean substrate into a 1% (24 mM) OTMS solution in hexanes (Malinckrodt, ACS grade) or anhydrous ethanol (Pharmco-AAPER, ACS/UPS grade) at room temperature in an ambient atmosphere for 4 h unless otherwise indicated. The OTMS sample was rinsed with hexanes and methanol (Pharmco-AAPER, ACS/UPS grade). Ultrasonic cleaning, which is often used to remove excess physiosorbed polymeric layers,$^{30}$ was avoided since ultrasonic cleaning sometimes breaks LiNbO$_3$ substrates. After being dried with a stream of N$_2$, the SAM-coated sample was stored in a Petri dish. The quality of the SAMs on quartz and LiNbO$_3$ surfaces was characterized by FTIR and water contact angle measurement. FTIR spectra were measured using a Bruker Optics TENSOR 27 spectrometer equipped with a DTGS detector in transmission geometry at a normal incidence.$^{31}$ All the FTIR spectra were background corrected by subtraction of a spectrum of the clean, bare (i.e., SAM-free) substrate. All of the spectra were recorded by integrating 200 scans with a resolution of 4 cm$^{-1}$. Degradation of Al circuits on the LiNbO$_3$ substrate was visually examined by an optical microscope using various magnifications of up to 400x. Electrical testing was performed on wafer-level OTS- and OTMS-coated SAW device samples using an rf probe station connected to an HP-8753 network analyzer to measure the reflected response ($S_{11}$) over a 100 MHz frequency range centered at 250 MHz.

3. Results and Discussion

The quartz and LiNbO$_3$ substrates coated with an OTS SAM showed water contact angles around 105° at the polished surface and 120° at the unpolished backside surface, indicating that OTS SAMs were constructed on both quartz and LiNbO$_3$ substrates. FTIR spectra of the OTS SAM on quartz (dashed line) and LiNbO$_3$ (solid line) surfaces in the CH stretching region (Figure 1) show the two major peaks associated with the symmetric and asymmetric stretching modes of the methylene groups. For OTS on quartz these appear at 2850 and 2918 cm$^{-1}$, respectively. These frequencies indicate that the alkyl chains are in a crystalline-

![Figure 1. FTIR spectra of an OTS SAM on quartz (dashed line) and LiNbO$_3$ (solid line) in the CH stretching region. Distortion of the spectral shape in the dashed line was caused by an incomplete compensation of background subtraction.](image)

![Figure 2. Typical optical microscope images of an Al device on a LiNbO$_3$ substrate (a) before and (b) after OTS treatment. The Al lines are nominally 3.5 $\mu$m wide.](image)
like structure rather than the liquid phase. The peak absorbance of ~3 mOD suggests the formation of a monolayer of octadecyl groups on the substrate. The larger absorbance for LiNbO₃ (~5 mOD) is probably associated with either some multilayer formation or the larger surface area due to the larger surface roughness of the unpolished backside. Interestingly, when a quartz surface was cleaned by piranha solution, the asymmetric stretching mode was observed at 2917 cm⁻¹ with a peak absorbance of ~3 mOD for OTS on quartz. The two major peaks were observed at 2850 and 2921 cm⁻¹ for OTS on LiNbO₃, which indicates a relatively disordered alky1 layer. Thus, we conclude that it is possible to form a hydrophobic OTS SAM on a LiNbO₃ surface pretreated with O₂ plasma but with a slightly disordered monolayer structure compared to an OTS SAM on a quartz surface.

Contrary to our expectation, no acoustic response was observed upon electrical testing of these SAW devices. To identify the impact of the OTS SAM formation procedure on performance, optical microscope images were acquired (a) before and (b) after OTS treatment as shown in Figure 2. These images clearly show that OTS treatment causes significant degradation of the Al metal features, which are critical for the device operation. This is probably because during SAM formation, the OTS releases HCl near the surface of the wafer when it hydrolyzes (see the reaction in Scheme 1a), and HCl etches the delicate Al device elements, which are approximately 150 nm thick and nominally 3.5 μm wide. OTS in solvent at first hydrolyzes with a trace amount of water adsorbed on the substrate, releasing three molecules of HCl per OTS molecule hydrolyzed near the surface (reaction 1, Scheme 1). Then the condensation reaction takes place, releasing H₂O back to solution in the near-surface region (reaction 2, Scheme 1). The cycles of reactions 1 and 2 may result in a low effective surface pH. Clearly, OTS is not an appropriate reagent to form a SAM on the substrate with Al devices. A similar etching effect has been reported for chlorosilanes on stainless steel, suggesting that the chloride ion is the source of the corrosion.

A silane coupling agent without chloride such as a trialkoxysilane has been suggested to be an appropriate alternative for coating of corrosion-susceptible materials. As shown in Scheme 1b, OTMS releases only methanol during hydrolysis. In contrast to monolayer formation from chlorosilane precursors, methoxysilane SAMs have been studied less extensively. Some groups have reported OTMS SAM formation in nonpolar solvents such as toluene and bicyclohexane, while other groups used polar solvents such as 2-propanol solutions for OTMS and ethanol for N-[3-(trimethoxysilyl)propyl]ethylenediamine. To justify these protocols, we examined hexanes and ethanol as solvents for OTMS SAM formation. The SAM coating was carried out by immersing LiNbO₃ substrates into 24 mM OTMS (i.e., 1%) solution in hexanes (Figure 3a) and anhydrous ethanol (Figure 3b) for various times. The relatively high concentration of the OTMS solution was chosen to form a good monolayer without using an acid/base catalyst. Many research groups have used acids or bases as catalysts to promote hydrolysis of methoxide, methanol, and water.

without catalyst in 48 h. Good monolayers were not obtained from 0.1 M OTMS in bicyclohexyl oxysilane. However, it was also reported that good monolayers in hexanes forms densely packed SAMs on LiNbO$_3$. The peak absorbance (ca. 10 mOD) for samples immersed more than 14 h showed a monolayer formation. Since we have on occasion seen larger defects. Comparing the 4 h immersion sample with the 20 h saturation occurs at a longer time (20 h). Thus, the faster growth time for the OTMS SAM to grow on piranha-cleaned quartz. The fact that OTMS did not show any etching effect supports our hypothesis that the release of HCl is the cause of Al device degradation upon OTS treatment. The expected acoustic response was also observed upon electrical testing of these devices, indicating that the OTMS SAM layer also did not interfere with the acoustic wave generation and propagation.

4. Conclusion

This work demonstrated that OTS forms densely packed SAMs on both LiNbO$_3$ and quartz. The formation process of OTS SAMs degrades Al devices significantly, while that of OTMS SAMs does not. OTMS SAMs were constructed on LiNbO$_3$ substrates with good reproducibility from hexane solutions, while OTMS did not form reproducible SAMs on LiNbO$_3$ or quartz from ethanol solutions. OTMS SAM formation is potentially useful as one step in a procedure that can be used to manufacture SAW-

Table 1. Summary of FTIR, Contact Angle (CA) Measurements, and Rms Roughness of the Substrate: Peak Absorbance, Peak Frequency (freq), and Full Width at Half-Maximum (fwhm) of the CH$_2$ Asymmetric Mode$^a$

<table>
<thead>
<tr>
<th>sample</th>
<th>abs (mOD)</th>
<th>freq (cm$^{-1}$)</th>
<th>fwhm (cm$^{-1}$)</th>
<th>CA (deg) (polished)</th>
<th>CA (deg) (unpolished)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Q/OTS</td>
<td>5.0</td>
<td>2917.9</td>
<td>15.3</td>
<td>105</td>
<td>115</td>
</tr>
<tr>
<td>LNB/OTS</td>
<td>5.0</td>
<td>2920.9</td>
<td>20.4</td>
<td>105</td>
<td>120</td>
</tr>
<tr>
<td>Q/OTMS(4)</td>
<td>3.0</td>
<td>2918.5</td>
<td>16.7</td>
<td>100</td>
<td>120</td>
</tr>
<tr>
<td>Q'/OTMS(4)</td>
<td>2.4</td>
<td>2919.5</td>
<td>19.0</td>
<td>105</td>
<td>115</td>
</tr>
<tr>
<td>LNB/OTMS (4)</td>
<td>6.1</td>
<td>2918.7</td>
<td>19.0</td>
<td>105</td>
<td>120</td>
</tr>
<tr>
<td>LNB/OTMS (4)'</td>
<td>6.4</td>
<td>2918.3</td>
<td>17.9</td>
<td>105</td>
<td>120</td>
</tr>
<tr>
<td>Q/OTMS (20)</td>
<td>3.0</td>
<td>2918.0</td>
<td>15.6</td>
<td>100</td>
<td>120</td>
</tr>
<tr>
<td>Q'/OTMS (20)</td>
<td>3.4</td>
<td>2919.1</td>
<td>18.3</td>
<td>105</td>
<td>117</td>
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<tr>
<td>LNB/OTMS(20)</td>
<td>6.2</td>
<td>2918.5</td>
<td>18.3</td>
<td>105</td>
<td>120</td>
</tr>
</tbody>
</table>

$^a$ Key: Q, quartz; LNB, LiNbO$_3$; (4), 4 h of immersion; (20), 20 h of immersion; Q', quartz cleaned by piranha solution. The uncertainty of the CA measurements was ca. ±5°. The uncertainty of frequencies in FTIR measurements was <±0.2 cm$^{-1}$. LNB/OTMS (4)' is a duplicate experiment.

When the SAM coating was carried out in an ethanol solution of 24 mM OTMS, the band intensity of the FTIR spectrum was quite variable and irreproducible. Furthermore, the time evolution of the OTMS immersion was nonmonotonic and never showed saturation. Typically, an absorbance of a few mOD was observed for a relatively short immersion time (30 min), but with continued immersion the absorbance decreased to almost zero (2 h) and then increased to 0.5 mOD (4 h). Further immersion in ethanol solution up to 15 h did not improve the SAM formation. Since the same trend was observed for OTMS on quartz surfaces, ethanol was considered to be the cause of the poor SAM formation. This is probably because ethanol hydrogen bonds with surface silanol more strongly than hexanes, preventing OTMS molecules from reacting with the surface silanol. Although ethanol has been used as a solvent for reactions of aminomethoxysilane due to its good solubility, the present results indicate that using a non-hydrogen-bonding solvent seems to improve the coverage and reproducibility of the methoxysilane SAM.

As we expected, there was no etching effect of OTMS on the Al device on the LiNbO$_3$ substrate (Figure 4), demonstrating the compatibility of OTMS formation with delicate metallic devices. The fact that OTMS did not show any etching effect supports our hypothesis that the release of HCl is the cause of Al device degradation upon OTS treatment. The expected acoustic response was also observed upon electrical testing of these devices, indicating that the OTMS SAM layer also did not interfere with the acoustic wave generation and propagation.

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based hydrogen sensors or the coating of any device whose metal parts are susceptible to corrosion. These findings suggest that although alkyltrichlorosilane SAMs have been widely used and investigated, alkyltrimethoxysilanes may be of more practical importance when self-assembly is required on surfaces with delicate metal components.

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