**Interface Reactions in LiNbO₃ Based Optoelectronics Devices**

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**ABSTRACT**

We present secondary ion mass spectrometry (SIMS) study results on interfaces of LiNbO₃ based optoelectronic devices, which have been performed in order to examine the cause of device failures. The devices are widely used in current high-speed optical fiber communication systems, and such investigation from a materials-viewpoint is important to improve the device quality. Especially, the device long-term stability is strongly affected by alkali-contaminants diffused into the SiO₂ buffer layer of device, and here we confirmed that an adoption of common Si₃N₄ passivation is effective in preventing the process-induced contamination without any influence to device performance.

**INTRODUCTION**

Since LiNbO₃ based optical waveguide modulators are widely used in global fiber communication systems, their long-term reliability has been carefully investigated from the viewpoint of stability of device performance, such as drift phenomena. The latest Telcordia GR-468-CORE standard comments on reliability and quality requirements for LiNbO₃ modulators in addition to conventional laser devices [1]. However, to our knowledge, reports on problems in device quality due to the LiNbO₃ modulator fabrication processes are limited, although a demand for LiNbO₃ modulators is rapidly increasing. For instance, the magnitude of the dc drift in modulator optical output is largely enhanced by alkali-contaminants injected into a SiO₂ buffer layer covering the LiNbO₃ substrate [2]. Because the dc drift is a main cause of device wear-out failures, the drift must be suppressed [3]. We found previously that the alkali-contamination was caused by wet-processes for exposed SiO₂ layer, such as photolithography, wet-etching, etc. In this report, applicability of a Si₃N₄ passivation layer, common material in Si device processes, to LiNbO₃ modulators is shown. The Si₃N₄ layer works not only as the passivation layer but also as the glue layer, for Au/Ti electrodes formed on modulator surface.

**STRUCTURE OF LiNbO₃ MODULATORS**

Figure 1 shows a schematic cross-section of the LiNbO₃ optical intensity modulators, mainly consisting of an LiNbO₃ substrate with the buried optical waveguides, the SiO₂ buffer layer covering the LiNbO₃ surface, and the thick gold electrodes. The optical waveguides were formed by a thermal diffusion of metallic Ti lines at approx. 1000°C. After the waveguide formation, the SiO₂ layer was deposited by a vacuum evaporation method and annealed at 600°C in an oxygen atmosphere. On the SiO₂ surface, the Au/Ti binary film was
deposited by a sequential vacuum evaporation of Ti and Au, as a glue layer for the thick Au electrodes prepared by all electro-plating method. The role of the Ti layer is to increase the bonding strength of Au layer to the SiO₂. The Au electrodes were grown between photoresist walls. Which had been patterned on the Au/Ti binary layer. and these photoresists were chemically removed. In the last process, the Au/Ti binary layer left between the Au electrodes was chemically etched to expose the SiO₂ surface as shown in Fig. 1.

Fig. 1 Cross-sectional illustration of LiNbO₃ optical intensity modulator.

In the above mentioned fabrication process of LiNbO₃ devices, some chemicals for wet-processes may contaminate the device constituent materials, especially a LiNbO₃ wafer surface and a SiO₂ buffer layer. For instance, an inorganic-based photoresist-developer, including sodium silicates, diffuses alkali-contaminants into the SiO₂ buffer layer as shown in SIMS analysis results of Fig. 2. In this sample, the SiO₂ layer was found to be contaminated by Na and K, although thin Au/Ti layers covered the layer. The Li detected through SiO₂ layer is considered to come from the LiNbO₃ substrate. Figure 3 shows another example of the SiO₂ layer contamination due to chemical treatment of the wafer. Before the electrodes plating process, the Au/Ti surface is slightly etched using commercial chemicals in order to increase the bonding strength of electro-deposited Au layer. With the chemicals containing fluorides, F-residue was found in the Au/Ti layer. Further, the F ions seemed to diffuse into the SiO₂ layers.

Fig. 2 SIMS results on SiO₂ layer of defective modulator.
SILICON NITRIDE PASSIVATION

Because the contaminated SiO₂ buffer layer deteriorates modulator performance and shortens a device lifetime, the deposition of silicon nitride passivation layer on the SiO₂ is thought to be effective. The 100-150 nm thick silicon nitride film was synthesized by reactive RF-sputtering of the pure Si target with an Ar/N₂ mixture. The substrate was not intentionally heated during the sputtering deposition. The obtained film was confirmed to be in Si₃N₄ composition by an X-ray photoelectron spectrometer. On the Si₃N₄-passivated SiO₂ layer, the patterned Au-electrodes were prepared by an electro-plating method after a deposition of the thin Au/Ti binary layer on the Si₃N₄ passivation film. The Au/Ti layer left between a pair of electrodes was chemically removed and the Si₃N₄ film exposed.

The x-cut LiNbO₃ modulator samples with Si₃N₄ passivation were designed to work in 10 Gb/s optical transmission systems, and here we examined whether the silicon nitride passivated modulators could perform expected E/O characteristics or not. Table 1 is a list of E/O parameters measured on four modulators from three different wafers (wafer #101, #102, #103). The first line of Table 1 denotes our expected specifications for this modulator design. If an electrical conducting layer exists between the electrodes, there is a possibility of an increase in $V_\pi$ and dc drift performances. However, concerning E/O parameters, we conclude that the silicon nitride passivated x-cut LiNbO₃ modulators can exhibit the performances meeting 10 Gb/s systems without any significant problems.

**Table 1** Electro-Optic performances of x-cut LiNbO₃ modulators with Si₃N₄ passivation.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>N₂ Flow Rate [sccm]</th>
<th>DC $V_{π}$ @ 1 kHz [V]</th>
<th>AC $V_{π}$ @ 5.33 GHz [V]</th>
<th>Electrode B.W. [GHz]</th>
<th>Phase Modulator AC $V_{π}$ @ 10.66 GHz [V]</th>
<th>Electrode B.W. [GHz]</th>
<th>On/Off Extinction Ratio [%]</th>
<th>Design</th>
</tr>
</thead>
<tbody>
<tr>
<td>#101-1</td>
<td>4.1</td>
<td>5.0</td>
<td>6.5</td>
<td>5.7</td>
<td>9.8</td>
<td>5.7</td>
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<td>-</td>
</tr>
<tr>
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<td>4.1</td>
<td>4.9</td>
<td>5.5</td>
<td>6.2</td>
<td>9.2</td>
<td>5.5</td>
<td>34.1</td>
<td>-</td>
</tr>
<tr>
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<td>4.8</td>
<td>6.3</td>
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<td>9.2</td>
<td>4.9</td>
<td>27.4</td>
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</tr>
<tr>
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<td>5.3</td>
<td>9.6</td>
<td>5.3</td>
<td>21.5</td>
<td>-</td>
</tr>
</tbody>
</table>
Figure 4 exhibits the dc drift measurement results on x-cut LiNbO$_3$ modulators, with the Si$_3$N$_4$ passivation layer (solid curve) and without any passivation (dashed curve). The measurement was carried out at 85 °C in order to accelerate the dc drift phenomenon. The vertical axis denotes the dc bias voltage that is applied to adjust the state of optical output signal. If the bias voltage drifts fast, as the dashed curve, driver-circuits get to no longer control the modulator (failure). The cause of such defective drift performance was found to be alkali-contamination of the SiO$_2$ buffer layer as shown in Fig. 5 (SIMS results of failed modulator surface) [2-4]. The alkali-contaminants were considered to diffuse into the exposed SiO$_2$ layer during wet processing of wafers. On the other hand, when the Si$_3$N$_4$ passivation layer was inserted between SiO$_2$ and electrodes, the diffusion of alkali-contaminants was suppressed as shown in Fig. 6.

![Typical Dc Drift Measurement Results](image)

**Fig. 4** Example of dc drift performance of modulators.

![SIMS results of the failed modulator without Si$_3$N$_4$ Passivation.](image)

**Fig. 5** SIMS results of the failed modulator without Si$_3$N$_4$ Passivation.
In addition to the passivation effect, the insertion of Si₃N₄ layer was found to improve bonding strength of the electrode layer. In order to increase the bonding strength of Au-electrodes to SiO₂ buffer layer, a thin Ti film is usually inserted in-between. However, when the Ti layer is excessively oxidized due to a fluctuation of SiO₂ processes and/or H₂O contaminants in the SiO₂ layer, the bonding strength of the electrode is largely decreased [5]. Such defective electrodes were found to peel-off easily at the boundary between SiO₂ and Ti. The Si₃N₄ layer inserted between SiO₂ and Ti layers was expected to strongly prevent the excess oxidization of the Ti, bonding the electrode layer. Here in order to check the electrode bonding performance qualitatively, the electrodes of silicon nitride passivated wafers were intentionally peeled-off, and a debonding of the SiO₂/LiNbO₃ boundary was observed (not at the Ti/Si₃N₄ interface). The result suggests that use of the silicon nitride passivation film in LiNbO₃ modulators is advantageous also in the mechanical performance.

Li-DIFFUSION INTO SiO₂ LAYER FROM LiNbO₃ SUBSTRATE

In fabrication processes of LiNbO₃ modulators, a diffusion of Li⁺ ions into the SiO₂ buffer layer from the substrate itself seems to be an inevitable problem as shown in the above SIMS results. Fortunately, we have not found any significant deterioration in modulator performance possibly due to the Li-diffusion. However, an investigation on Li-diffusion is necessary to improve the modulator quality and process repeatability.

Figure 7 reveals SIMS results on Al-thin-film polarizer installed directly on x-cut Ti:LiNbO₃ waveguides, which can cut selectively the TM-mode light. In order to achieve higher polarization extinction ratio and chemical stability of the Al layer [6], we designed the polarizer to have a layer-structure of "SiO₂/Al/SiO₂/LiNbO₃-substrate". The thickness of the SiO₂ inserted between Al (and LiNbO₃) must be 10 nm to obtain the most effective interaction of light between waveguide and Al layer. All films were prepared by a multi-target RF-sputtering technique in the same deposition chamber. A notable fact found in Fig. 7 is that the Li ions diffuse through the metallic Al layer toward the thick SiO₂ layer. A higher affinity of Li to SiO₂ [7] may be a cause of the phenomenon. Although the fabricated polarizers are working without failures, because there is a possibility that condensation of alkali-ions at the interface deteriorates the bonding strength, further investigation on the phenomena from a long-term viewpoint is needed.
CONCLUSION

Typical SIMS measurement results on LiNbO₃ optical modulator devices were presented. The process originated alkali-contaminants in the SiO₂ buffer layer deteriorated device performances, and was confirmed to be able to be suppressed by the insertion of a Si₃N₄ passivation layer between SiO₂ and surface-electrode layer. The diffusion of Li⁺ ions from LiNbO₃ itself into the SiO₂ film was also found, although its effect to device performances and mechanical reliability is not known at this time.

REFERENCES