Investigation of Optical Loss Mechanisms in Oxide Thin Films

A. F. Chow and A. I. Kingon
North Carolina State University
Raleigh, North Carolina

O. Auciello
MCNC
Electronics Technology Division
RTP, North Carolina

D. B. Poker
Oak Ridge National Laboratory
Oak Ridge, Tennessee

"The submitted manuscript has been authored by a contractor of the U.S. Government under contract No. DE-AC05-84OR21400. Accordingly, the U.S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so, for U.S. Government purposes."

Prepared by the
Oak Ridge National Laboratory
Oak Ridge, Tennessee 37831
managed by
MARTIN MARIETTA ENERGY SYSTEMS, INC.
for the
U.S. DEPARTMENT OF ENERGY
under contract DE-AC05-84OR21400

May 1995

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED
DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.
INVESTIGATION OF OPTICAL LOSS MECHANISMS IN OXIDE THIN FILMS

ALICE F. CHOW, ORLANDO AUCIELLO*, DAVID B. POKER**, AND ANGUS I. KINGON
North Carolina State University, Raleigh, NC 27695
*Also MCNC, Electronics Technology Division, RTP, NC 27709-2889
**Oak Ridge National Laboratory, Oak Ridge, TN 37831

Abstract KNbO3, K(Ta,Nb)O3, KTaO3, and Ta2O5 thin films have been grown by ion-beam sputter deposition. KNbO3 has excellent nonlinear properties for second harmonic generation; however, high optical losses are still characteristic of these films. Several loss mechanisms, such as, high angle grain boundaries, twin domains, interface and surface scattering, and oxygen vacancies can all contribute to the high losses. In order to isolate the various mechanisms, amorphous Ta2O5 films, epitaxial cubic KTaO3 and tetragonal K(Ta,Nb)O3 films were grown on MgO and Al2O3 substrates subjected to post-deposition annealing treatments and various oxygen pressure conditions. The optical losses and refractive indices were observed to differ depending on the substrate surface and annealing treatments. Resonant scattering experiments were performed to analyze the oxygen composition. The optical properties of these oxide thin film systems are reported and the breakdown of the loss mechanisms is addressed.

INTRODUCTION

The demand for increasing present optical recording densities can be met by blue or green lasers. One of the most promising methods of generating the high frequency is by second harmonic generation (SHG) where an IR laser can frequency double into the blue or green via a nonlinear material. Potassium niobate (KNbO3) is an excellent candidate for SHG due to its high nonlinear coefficients, large birefringence, noncritical
phase-matching, high damage threshold, and transparency in the appropriate wavelengths. Moreover, higher power densities can be achieved in a thin film waveguide configuration due to beam confinement, and direct integration with present semiconductor materials is possible.²

Although SHG has been demonstrated recently in KNbO₃ thin films,³ the high losses present in most film-waveguides are problematic and must be overcome for practical device applications. The research focused on the breakdown of loss mechanisms is at a nascent stage; several groups have generated valuable models.⁴ We approach the problem of the high KNbO₃ losses by studying oxide systems with simpler structures where specific loss mechanisms are eliminated and isolated in order to understand their contribution to losses.

The microstructural and optical properties of the KNbO₃ films are summarized as reported by previous work.⁵ Basic loss theory is addressed where the relevant mechanisms are noted. Tetragonal potassium tantalum niobate (K(Ta,Nb)O₃), cubic potassium tantalate (KTaO₃), and amorphous tantalum oxide (Ta₂O₅) films were deposited by ion-beam sputtering and their properties and pertinence to the loss study are discussed. The characterization techniques used include prism-coupling to measure the refractive index, an optical fiber loss method to quantify the optical scattering losses, atomic force microscopy (AFM) to probe surface roughness, and elastic resonant scattering to analyze oxygen composition.

**KNbO₃ FILMS**

Ion-beam sputter deposition was used to deposit all the oxide films. For KNbO₃ film deposition, two potassium superoxide (KO₂) targets and one niobium target were sequentially sputtered. The details of the deposition process can be found in another paper.⁵ The films were grown on MgO, MgAl₂O₄, and KTaO₃ substrates. X-ray diffraction (XRD) revealed the films to be orthorhombic (110) single orientation. XRD rocking curves, Rutherford backscattering spectrometry (RBS) channeling, and transmission electron microscopy diffraction analyses showed the films to possess a high degree of epitaxy. Small grain sizes (1000 to 5000 Å) were detected and the film surface roughnesses were low with root mean square (rms) values between 9 and 37 Å by AFM. The refractive indices approach bulk values indicating dense films. These results are summarized in Table I.
TABLE I  Summary of KNbO$_3$ thin film microstructural and optical properties on KTaO$_3$, MgAl$_2$O$_4$, and MgO substrates.

<table>
<thead>
<tr>
<th>KNbO$_3$ on Substrate</th>
<th>KTaO$_3$ (001)</th>
<th>MgAl$_2$O$_4$ (001)</th>
<th>MgO (001)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FWHM rocking XRD</td>
<td>0.25°</td>
<td>0.30°</td>
<td>0.84°</td>
</tr>
<tr>
<td>RBS/channeling</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\chi_{\text{Nb}}, \chi_{\text{K}}$</td>
<td>7%</td>
<td>9%, 15%</td>
<td>18%, 49%</td>
</tr>
<tr>
<td>Grain size</td>
<td>~3-5000 Å</td>
<td>~1000 Å</td>
<td>~1200 Å</td>
</tr>
<tr>
<td>Grain tilt from TEM</td>
<td>2 to 3°</td>
<td>2 to 3°</td>
<td>10°</td>
</tr>
<tr>
<td>Film refractive index, TE, TM</td>
<td>2.27, —</td>
<td>2.28, 2.21</td>
<td>2.28, 2.21</td>
</tr>
<tr>
<td>Surface roughness, rms</td>
<td>21 Å</td>
<td>9-19 Å</td>
<td>18-37 Å</td>
</tr>
</tbody>
</table>

The optical losses were measured by an optical fiber method. An optical fiber scans the length of the light streak and measures the scattering intensity where the signal is fed into a photodiode and nanovoltmeter. A longer scattered light streak reflects a lower loss for the waveguide. For the KNbO$_3$ films, longer streaks were observed for thinner films as shown in Figure 1.

![Figure 1](image)

**Figure 1**  Streak length of KNbO$_3$ waveguide versus film thickness.
According to loss mechanism theory, this would support a volume scattering mechanism rather than a surface scattering mechanism. If the majority of losses took place in the bulk of the film, higher losses would be observed as films became thicker. On the other hand, if interface and film surface scattering were dominating, then thicker films would possess lower losses since there are fewer reflections at the boundaries in the waveguide for an arbitrary distance in thicker films.

Several volume scattering mechanisms could be contributing to the losses in the KnbO3 films. These include twin domains that form in the orthorhombic structure, grain boundary scattering and grain size, and oxygen vacancies. In addition, there is always a surface scattering component that is affected by the interface and film roughness. In order to isolate these various mechanisms, other oxide systems of simpler structures were grown and analyzed where the range of bulk scattering mechanisms gradually narrow as seen in Table II. In the case of amorphous Ta2O5 films, the loss due to surface scattering can be focused in the absence of oxygen vacancies which would be significant in determining the minimum surface scattering contribution to losses under optimum conditions (devoid of bulk scattering).

**TABLE II** Thin film oxide systems and the possible volume scattering sources.

<table>
<thead>
<tr>
<th>Thin film oxide</th>
<th>Volume scattering source</th>
</tr>
</thead>
<tbody>
<tr>
<td>orthorhombic KnbO3</td>
<td>twin domains, grain boundaries, oxygen vacancies</td>
</tr>
<tr>
<td>tetragonal K(Ta,Nb)O3</td>
<td>twin domains? grain boundaries, oxygen vacancies</td>
</tr>
<tr>
<td>cubic KTaO3</td>
<td>grain boundaries, oxygen vacancies</td>
</tr>
<tr>
<td>amorphous Ta2O5</td>
<td>oxygen vacancies</td>
</tr>
</tbody>
</table>

**AMORPHOUS Ta2O5 FILMS**

Ta2O5 films were deposited by ion beam sputter deposition of a tantalum metal target in an oxygen environment. Initial films showed no light streaks and refractive indices higher than the bulk value of 2.206. Oxygen deficiency in the films was suspected and therefore, a film was annealed at 560°C for 20 minutes in oxygen. The post-deposition anneal lowered the refractive index close to that of bulk and a long light streak extending the length of the sample (> 8mm) was observed. Next, the oxygen flow during
deposition was increased to similarly improve the film quality but without post-deposition annealing. Figure 2 shows a plot of the refractive index versus deposition rate. With increasing oxygen flow, both the refractive index and deposition rate decreased as expected.

![Graph showing refractive index versus deposition rate with increasing oxygen flow.]

Figure 2 Ta₂O₅ refractive index and deposition rate for increasing oxygen flow during deposition.

![Graph showing resonant scattering spectrum for a Ta₂O₅ film on MgO.]

Figure 3 Resonant scattering spectrum for a Ta₂O₅ film on MgO.

Since all the oxide films were deposited on oxide substrates, the oxygen content of the films cannot be quantified by RBS because the oxygen film peak is obscured by the substrate peak. Elastic resonant scattering is one technique that enhances the scattering of the oxygen peak, and thus, oxygen composition of different films can be compared. Resonant scattering experiments were performed with a 3.09 MeV helium
ion beam energy and a scattering angle of 160.27°. A typical resonant scattering spectrum of a Ta₂O₅ film on a MgO substrate is seen in Figure 3. The normalized oxygen content versus deposition rate of the various Ta₂O₅ films with increasing oxygen flow during deposition is shown in Figure 4. (The oxygen counts were normalized to the film with the highest oxygen flow.) This graph suggests that the original films were indeed oxygen deficient and the films showed long light streaks and lower losses only upon increasing the oxygen flow. A loss of 13 dB/cm was attainable.

![Graph showing the normalized oxygen content of Ta₂O₅ films with increasing deposition rate and oxygen flow.]

**Figure 4** Normalized oxygen content of Ta₂O₅ films with increasing deposition rate and oxygen flow.

In order to further lower the losses and also to evaluate the effect of substrate roughness on losses, an extensive AFM study on various substrates was performed. First, MgO substrates from various vendors were analyzed. The substrate surface roughness seemed to vary depending on the vendor as seen in Table III.

<table>
<thead>
<tr>
<th>MgO substrate vendor</th>
<th>Rms (Å)</th>
<th>Maximum feature height (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Advanced Composite Materials</td>
<td>23</td>
<td>196</td>
</tr>
<tr>
<td>ESPI</td>
<td>19</td>
<td>218</td>
</tr>
<tr>
<td>Commercial Crystal Lab (C.C.L.)</td>
<td>48</td>
<td>507</td>
</tr>
<tr>
<td>Marketech</td>
<td>94</td>
<td>765</td>
</tr>
</tbody>
</table>
One reason for the deviation is the susceptibility to hydroxide growth of the MgO surface. To eliminate the surface hydroxides, the substrates were subjected to a high temperature anneal at 1150°C for 14 hours in oxygen. However, it was important to use the annealed substrate within a few days, otherwise hydroxide growth begins to occur as shown in Table IV.

TABLE IV  AFM results of an annealed MgO substrate over 14 days.

<table>
<thead>
<tr>
<th>MgO substrate</th>
<th>Rms (Å)</th>
<th>Maximum feature height (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Day one of anneal</td>
<td>13</td>
<td>127</td>
</tr>
<tr>
<td>Day four after anneal</td>
<td>12</td>
<td>107</td>
</tr>
<tr>
<td>Day seven after anneal</td>
<td>32</td>
<td>833</td>
</tr>
<tr>
<td>Day ten after anneal</td>
<td>53</td>
<td>1133</td>
</tr>
<tr>
<td>Day fourteen after anneal</td>
<td>48</td>
<td>2733</td>
</tr>
</tbody>
</table>

Table V compares the AFM results of other substrates that were analyzed. A sapphire substrate with a novel superpolish was obtained from Crystal Systems that exhibited an rms of only 3.2 Å by AFM. When an amorphous Ta₂O₅ film was deposited on that substrate with the increased oxygen flow conditions, the lowest loss streak was observed as compared to the other Ta₂O₅ films. In fact with our present optical fiber setup, a loss was not measurable due to the low signal to background ratio. A loss of < 5 dB/cm is probable for that film. This result asserts the necessity of a low substrate roughness in obtaining low losses.

TABLE V  Surface roughness of various substrates.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Rms (Å)</th>
<th>Maximum feature height (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO (C.C.L.)</td>
<td>20</td>
<td>184</td>
</tr>
<tr>
<td>MgO annealed (C.C.L.)</td>
<td>13</td>
<td>96</td>
</tr>
<tr>
<td>quartz</td>
<td>11</td>
<td>643</td>
</tr>
<tr>
<td>sapphire (C.C.L.)</td>
<td>12</td>
<td>198</td>
</tr>
<tr>
<td>sapphire super polish</td>
<td>3.2</td>
<td>234</td>
</tr>
<tr>
<td>(Crystal Systems)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
TETRAGONAL K(Ta,Nb)O₃ FILMS

K(Ta,Nb)O₃ (KTN) is a solid solution of KTaO₃ and KNbO₃. Its curie temperature can be controlled by altering the Ta to Nb concentration and excellent nonlinear properties are observed for particular compositions. KTa₀.₅₅Nb₀.₄₅O₃ is an interesting composition to analyze due to its tetragonal structure which can be grown devoid of twin domains.

Both a Ta and a Nb metal target and one KO₂ target were ion-beam sputtered to deposit KTN films on MgO substrates. The film composition can be precisely controlled by altering the sputtering dwell times on each target as shown in Figure 5.

![Graph showing the relationship between Nb/Ta composition and Nb/Ta deposition setpoints.](image)

Figure 5 K(Ta,Nb)O₃ deposition setpoints versus composition.

The losses of KTa₀.₅₅Nb₀.₄₅O₃ films were analyzed and results similar to those of KNbO₃ films were detected. Thinner KTN films showed long light streaks indicative of a bulk scattering phenomenon. The thermal expansion coefficient of the MgO substrate is appreciably larger than that of KTN which would imply that the short axis of the KTN <100> lies in the film plane. This is the desired configuration since the unique or long axis must be perpendicular to the film surface to avoid twin domains. However, the tetragonality of this particular KTN composition is extremely small (difference between the a-axis and c-axis d-spacing is only 0.013 Å)\(^8\) that conventional XRD analysis cannot distinguish between the axes. Consequently, it is highly possible that these KTN films contain both a-axis and c-axis domains and twin domain scattering is present.
CUBIC $K_TaO_3$ FILMS

The cubic structure of $K_TaO_3$ films would assure a film without twin domains. $K_TaO_3$ films were deposited on MgO substrates by sputtering a Ta metal target and two KO$_2$ targets. At first, no light streaks and low refractive indices were observed. In light of the amorphous Ta$_2$O$_5$ results and the possibility of oxygen deficiency, different post-deposition annealing treatments were applied to the $K_TaO_3$ films. The first anneal took place at 560°C for 20 minutes in an oxygen environment alone. The film resulted in poor quality visually and light-coupling was not possible. Potassium volatility of the film surface was suspected to be the problem. Consequently, KNbO$_3$ powder placed in the crucible during annealing helped to preserve the original visually translucent film surface. Next, films were annealed at an increased temperature of 850°C for both 2 and 10 hours in O$_2$ and KNbO$_3$ powder. Again, high losses were present and in this case, the cause was attributed to the increased surface roughness after the high temperature anneal. Figure 6 displays the film roughness in terms of maximum feature height and rms as a function of increasing anneal temperature and time.

These results clearly show that there are critical limits of annealing conditions due to film roughening. Finally, a $K_TaO_3$ film was annealed at a compromised temperature of 650°C for 2 hours in O$_2$ and KNbO$_3$ powder. The refractive index increased slightly, from 2.178 to 2.185 (bulk value is 2.225) and a long light streak was observed (> 8mm). Therefore, a $K_TaO_3$ film was deposited with a higher oxygen pressure during deposition.
in order to provide adequate oxygenation and a low film roughness. As expected, the resultant film displayed a > 7mm light streak and the rms was only 16 Å.

In light of these results, preliminary resonant scattering experiments were performed on KNbO3 films with various oxygen flow conditions to explore the possibility of oxygen deficiency in those films. Increasing oxygen composition was observed for films deposited at higher oxygen pressures as seen in Figure 7.

![Figure 7](image)

Figure 7 Resonant scattering oxygen peaks of a bulk KNbO3 crystal and KNbO3 films deposited at increasing oxygen flows.

However, the original KNbO3 films appeared to possess near stoichiometric oxygen composition as normalized to a KNbO3 bulk crystal suggesting that oxygen vacancies is not a major factor in the volume losses. The high losses both in the KNbO3 and K(Ta,Nb)O3 films are most likely caused by the twin domains. The effect of grain boundaries and grain size on losses can also be significant and should be investigated.

**CONCLUSION**

High quality KNbO3, K(Ta,Nb)O3, KTaO3, and Ta2O5 films were deposited by ion-beam sputter deposition. The amorphous Ta2O5 films, in the absence of oxygen vacancies, offer a study where the sole loss mechanism is attributed to surface scattering. A Ta2O5 film was deposited on a super-polished sapphire substrate and the low loss achieved indicated that a low substrate roughness is mandatory for low overall losses. Post-deposition annealing treatments of both the Ta2O5 and KTaO3 films showed that the possibility of oxygen vacancies in oxide films should be considered since they can make significant contributions to volume losses. At the same time, post-deposition
anneals are limited due to the increased film roughness that also increases the surface scattering losses. Initial resonant scattering experiments suggest that the KNbO₃ films possess near stoichiometric oxygen composition and therefore, the main source for the high bulk scattering losses in these films is likely attributed to twin domains.

ACKNOWLEDGEMENT

This research was supported by the Office of Naval Research under Contract No. N0014-91-1307. The work at ORNL was sponsored by the Division of Materials Sciences, U.S. Department of Energy, under contract DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc.

REFERENCES


DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.