Sputtered Tellurite Glass Thin Films for Planar Optical Devices

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ABSTRACT
Tellurium oxide is a promising optical material, conjugating transparency in the infrared with high refractive index, low chromatic dispersion with strong nonlinear response, elevated acousto-optic figure of merit and rare earth doping capability. Reactive sputtering is a suitable technique to obtain thin films of pure TeO\(_2\) glass, with tunable stoichiometry, without the need for added components to help vitrification. We report on the growth of tellurite thin films, on the linear and non-linear optical characterization and on the process technology to implement high-contrast planar optics.

Keywords: tellurite glasses, tellurium oxide films, reactive sputtering, reactive ion etching, planar lightwave circuits.

1. INTRODUCTION
Amorphous oxides of chalcogen element Tellurium (TeO\(_x\) \(\approx 2\) ) have been extensively studied in recent years, as promising and versatile optical materials \cite{1-3}. In view of applications to optical communications, optical fibers from tellurite glass preforms have been developed since early 1990s, featuring the combination of good transparency in the visible and near-infrared optical range, low chromatic dispersion and high refractive index values. Broadband rare-earth based fiber optical amplifiers operating at \(\lambda = 1.5 \mu m\) and \(\lambda = 1.3 \mu m\) have also been realized \cite{4,5}.

A fundamental step to full technological exploitation of tellurium oxide and its functionalities is the availability of tellurite-based integrated optical devices; in particular, the material in its amorphous phase is expected to minimize waveguide birefringence. Actually, some work in this direction has already been reported in the literature, by starting from bulk tellurite glass from the melt \cite{6-9}. Technological solutions are either based on the direct laser writing of buried channel waveguides into tellurite multi-component bulk glass substrates, or they involve an ion-exchange method. In all cases, core-cladding index contrasts lower than 5\% are obtained and a non negligible level of surface damaging is induced by the processes of creation of the waveguide. Both drawbacks can be both overcome by a different technological approach, based on the growth of thin tellurite films onto suitable substrates and the development of lithographic and etching processes for the definition of waveguiding geometries.

In the present work, a technological process for the realization of high-contrast Tellurium oxide-based optical structures is presented. Amorphous films of adequate thickness have been grown on silicon substrates by radiofrequency reactive sputtering, as described in the next Section. The optical quality of the film has been assessed and third-order optical nonlinear response of the tellurite glass films has also been evaluated. In Section 3, the applicability of a standard industrial lithographic process to the definition of optical structures onto TeO\(_x\) films is discussed. In particular, a recipe for the dry etching of tellurite glass has been developed, as complementary to the optical lithography process. The experimental results are described and discussed in view of effective applications.

2. GROWTH OF TELLURITE THIN FILMS

2.1 Sputtering deposition
Pure TeO\(_2\) glass films have been grown by reactive sputtering, either from Te targets or from sintered TeO\(_2\) targets. In particular, sputtering is effective in tuning the oxygen molar fraction \(x\) in the oxide TeO\(_x\), from sub-stoichiometric O/Te ratio to oxygen-enriched films, by controlling the operating conditions and the amount of the oxygen gas in the sputtering chamber. In turn, the tuning of oxide stoichiometry is a degree of freedom in the definition of optical properties like refractive index and absorption coefficient, as described in Refs \cite{10,11}. In case of growth from metallic targets, process conditions as reported in ref. \cite{11}. In case of oxide target (purity 99,999\%), film deposition parameters are summarized in Table 1. By growing at room temperature, in a reactive Ar-O\(_2\) atmosphere (purity 99,999\%), amorphous films are obtained \cite{10,11}. Both Ar and O\(_2\) flows were introduced in the deposition chamber through MKS mass flow controllers. The Ar flow was set at Ar = 50 sccm and the oxygen flow was calibrated in order to compensate for O\(_2\) loss and tune oxide composition. In view of integrated optics applications, quasi-stoichiometric TeO\(_x\) (\(x \approx 2\)) is required, to keep low absorption coefficient in the near infrared spectrum, conjugated to elevated refractive index and nonlinear response, as explained in \cite{10}.
Table 1. Sputtering process parameters.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
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<tbody>
<tr>
<td>Target</td>
<td>TeO$_x$ diameter 4”, thickness 6 mm</td>
</tr>
<tr>
<td>Gas composition</td>
<td>Ar:O$_2$ atmosphere, Ar 50 sccm, O$_2$ 8-12-16-18-20 sccm</td>
</tr>
<tr>
<td>RF Power</td>
<td>300 W</td>
</tr>
<tr>
<td>Sputtering pressure</td>
<td>$1.1 \times 10^{-2}$ mbar – $1.3 \times 10^{-2}$ mbar</td>
</tr>
<tr>
<td>Target-Substrate distance</td>
<td>5.5 cm</td>
</tr>
<tr>
<td>Substrate Temperature</td>
<td>23°C</td>
</tr>
<tr>
<td>Deposition rate</td>
<td>10.5 nm/min</td>
</tr>
</tbody>
</table>

Oxide stoichiometry and film homogeneity in depth were performed by Rutherford Back Scattering. TeO$_x$ films grown on both Si and silica show good adhesion to the substrate and good quality of the film-substrate interface. All samples show a densely packed fine grain structure, without the formation of columnar grains. An example of film grown onto Si wafer is shown in Fig. 1.

![Figure 1. SEM image of amorphous TeO$_x$ film growth on Si substrate.](image)

2.2 Optical characterization

Linear refractive index $n$ and absorption coefficient $k$ have been characterized for the sputtered film samples at different compositions by variable angle spectroscopic ellipsometry, in the 260 nm – 1700 nm spectral window. The dispersion of $n$ and $k$ can be obtained by fitting experimental data with a suitable model for the optical function and for the film structure.

![Figure 2. Linear optical properties of tellurite sputtered films, in dependence on stoichiometry: (a): Refractive index dispersion; (b): Absorption coefficient; (c): Refractive index values at $\lambda = 1550$ nm.](image)
Figures 2(a) and 2(b) show the dispersion of real and imaginary parts of the complex refractive index for the TeO\textsubscript{x} samples (1.9 < x < 2.15). The transparency range and absorption coefficient are practically unaffected by variation in stoichiometry in the range under test. Correspondingly, a variation of a few percent can be found in the values of refractive index. Results are in agreement with other experimental characterizations of chromatic dispersion of tellurium oxide films, as can be found in [10,11]. More specifically, Figure 2(c) plots the n values at $\lambda = 1550$ nm as a function of O/Te ratio. Substantial correspondence with results in Ref. 11 suggests that the nature of the target, whether metallic or oxide, has negligible impact on the optical properties of the deposited thin film, once the same final stoichiometry and structure are guaranteed by respective process steps. Nonlinear optical response has been assessed by a Maker Fringe method, as described in Ref 10. Values of $\chi^{(3)}$ in the range of $10^{-12}$ esu have actually been experimentally proven and reported in case of stoichiometric thin films, what can be exploited to all-optical processing of signals.

3. LITHOGRAPHY AND ETCHING OF TELLURITE THIN FILMS

Tellurium oxide, featuring a refractive index contrast over 48% with respect to SiO\textsubscript{2} and over 100% with respect to Air, can be selected as the core material in high-contrast geometries where either SiO\textsubscript{2} or Air are selected for the cladding. For this, lithography and etching of the tellurite films must be performed. In particular, tests were performed on 1100 nm thick quasi-stoichiometric TeO\textsubscript{x} films. Standard optical UV lithography has been chosen for the definition of the structures, involving the use of a broadband mask-aligner (MA6 Karl-Suss, working at 280 nm ÷ 450 nm), standard resists (AZ5214 and UV6) and alkaline development solutions. However, sputtered amorphous TeO\textsubscript{x} films have proven to be soluble both in acid and alkaline aqueous solutions, what therefore represents a critical issue. In order to protect tellurium oxide films during lithography, a 50 ÷ 100 nm thick SiO\textsubscript{2} cap-layer has been sputtered on top of the films and then masked by the photoresist. The SiO\textsubscript{2} films were eventually patterned by dry etching and used as hardmasks for the etching of tellurite films. The dry etching was performed in a traditional RIE system, designed for laboratory use and fed with Ar, O\textsubscript{2}, CF\textsubscript{4}/SF\textsubscript{6}, CHF\textsubscript{3}. The process steps therefore involve the etching of the SiO\textsubscript{2} cap-layer and subsequently of the tellurite glass. For the reactive etching of the patterned SiO\textsubscript{2} cap-layer, fluorine gases have been chosen. The same gas composition can in principle be used for the TeO\textsubscript{x} films, since volatile reaction products are expected. Fluorine-based etching of telluride has been experimentally tested, but elevated roughness is obtained, probably as a consequence of residual non volatile reaction products and some micromasking effects induced by them.

A way to overcome this effect is to keep the reactive process for the etching of the silica cap-layer and to perform a dry physical etching in Ar plasma of the TeO\textsubscript{x} film. The endpoints have been checked by SEM. In all cases, surface roughness is strongly reduced with respect to the reactive approach, as Ar plasma physically removes the tellurium oxide film, without risking the formation of not volatile species. Residual roughness is furtherly reduced by lowering the rf power and cathode temperature. The removal of the resist at the end of the overall process is an issue in itself, as neither the remover nor any other aggressive solution can be used, due to the solubility of TeO\textsubscript{x} films. A way to overcome this is to remove the resist after silica etching and to use the patterned silica as a hardmask for the etching of tellurite films. Results are shown in Figs.3-a and 3-b. Here, test structures are shown, made of tellurite films respectively grown directly on Si or on silica cladding layer. Fig. 3-a represents a tellurite film having been etched for all depth down to Si substrate and prior to resist removal, while Fig. 3-b is the cross-sectional view of a rib structure; in it the as-cleaved and not-polished surface distinguishes the partially etched tellurite layer from the lower silica cladding and the upper cap-layer. Residual resist tips, about 100 nm thick, are evident at the external corners of the silica cap-layer. In order to eliminate the whole resist film, its thickness can be calibrated so that it is fully consumed during the SiO\textsubscript{2} etching. The small amount of microtrenching can be a consequence of the not perfect verticality of the sidewalls of the mask.

![Figure 3. Results of physical dry etching test of TeO\textsubscript{2} film. (a): Complete etch of the film thickness; (b): Results of physical dry etching test of a rib structure after resist removal.](image-url)
4. CONCLUSIONS

In this work, the technological feasibility of high index contrast planar optical structures made of tellurite thin films has been addressed. To this aim, a process flow has been conceived and demonstrated, which starts from the sputtering of pure TeOx thin films of good optical performances onto Si wafers and ends with the realization of etched waveguide structures. Amorphous films of good optical quality and sub-nanometer surface roughness have been obtained, the residual surface roughness of patterned structures is estimated in the nanometer range. The technological issues related to the solubility of sputtered TeOx into aqueous solutions have been overcome by developing a physical dry etching step for the tellurite, while using a silica layer as a hardmask. Results here presented can be considered as a step in the direction of integrating tellurite-based optics onto silicon platforms for more complex optical subsystems.

REFERENCES