Near-infrared transparent electrodes for precision Teng–Man electro-optic measurements: In$_2$O$_3$ thin-film electrodes with tunable near-infrared transparency

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Highly near-infrared (NIR) transparent In$_2$O$_3$ thin films have been grown by ion-assisted deposition at room temperature, and the optical and electrical properties characterized. NIR transparency and the plasma edge frequency can be engineered by control of the film deposition conditions. As-deposited In$_2$O$_3$ thin films were employed as transparent electrodes for direct thin film electro-optic (EO) characterization measurements via the Teng–Man technique. Using LiNbO$_3$ as the standard, the relationship between electrode NIR transparency and Teng–Man EO measurement accuracy was evaluated. It is found that In$_2$O$_3$ electrodes can be tailored to be highly NIR transparent, thus providing far more accurate Teng–Man EO coefficient quantification than tin-doped indium oxide. In addition, the EO coefficients of stibazolium-based self-assembled superlattice thin films were directly determined for the first time using an optimized In$_2$O$_3$ electrode. EO coefficients $r_{33}$ of 42.2, 13.1, and 6.4 pm/V are obtained at 633, 1064, and 1310 nm, respectively. © 2005 American Institute of Physics. [DOI: 10.1063/1.2089184]

To date, the simple reflection technique developed by Teng and Man, is extensively used in characterization of the electro-optic (EO) properties of nonlinear optical (NLO) thin-film materials. Here an EO-active film is sandwiched between a top transparent conducting electrode and a bottom metal electrode. This technique is extremely simple, convenient, in principle accurate, requires no waveguiding or cladding material, and is thus the preferred method for determining the EO coefficients (e.g., $r_{33}$) of NLO materials. Since the EO coefficient is typically wavelength dependent, direct EO coefficient measurement is at different wavelengths, especially at telecommunication wavelengths (1310 and 1550 nm), is of great importance.

A primary assumption of the Teng–Man technique is that the laser beam passes through the EO film only twice—before and after reflection by the metal electrode. This requires high transmittance of the transparent electrode at the working wavelengths, otherwise the top electrode and metal electrode behave as a Fabry–Pérot resonator, giving rise to a systematic error in the measured EO coefficient. Transparent conducting oxide (TCO) thin films are usually used as top electrodes in Teng–Man measurements because they can be both optically transparent and electrically conductive. The most popular electrode material at present is tin-doped indium oxide (ITO). ITO is a degenerate semiconductor with a carrier concentration of $\sim 10^{21}$ cm$^{-3}$. The optical transmittance of conventional (commercial) ITO exhibits a sharp plasma edge starting at wavelengths $\approx 900$ nm due to free carrier scattering. ITO electrodes therefore function well as top electrodes in the visible region, but are limited for measurements in the near-infrared (NIR) region. Recently, Michelotti et al. reported that, compared to ITO, Al-doped ZnO exhibits improved Teng–Man accuracy at 1550 nm. However, to our knowledge, this particular material is far from optimum and introduces significant systematic error ($\sim 10\%$) arising from its limited NIR transparency.

Ion-assisted deposition (IAD) is a unique thin-film growth technique which employs two ion beams to simultaneously effect film deposition, oxidation, and crystallization, resulting in smooth, adherent, and dense oxide thin films on various substrates at room temperature. One important advantage of this technique is that In$_2$O$_3$ thin film microstructural, electrical, and optical properties can be finely tuned by the growth system O$_2$ partial pressure and ion beam energy during film growth. Moreover, IAD is capable of depositing high-quality TCO thin films on organic substrates at room temperature.

In this letter, a series of highly NIR transparent In$_2$O$_3$ thin films is grown on glass substrates and single-crystal LiNbO$_3$, and evaluated as transparent electrodes for the Teng–Man technique. Here, LiNbO$_3$ with an accurately known $r_{33}$ is used as a standard, and the relationship between TCO electrode carrier concentration, NIR-transparency, and EO coefficient measurement accuracy is systematically investigated. The measurement accuracy is found to be strongly dependent on the degree of the NIR transparency. It is shown that In$_2$O$_3$ thin films with carrier concentrations in the range $10^{18} - 10^{19}$ cm$^{-3}$ exhibit excellent NIR transparency ($\sim 90\%$), and provide far more accurate Teng–Man measurements than conventional ITO electrodes. In$_2$O$_3$ thin films were also successfully grown on organic self-assembled super-lattice (SAS) thin films for Teng–Man...
measurements. The EO coefficients are quantified at 633, 1064, and 1310 nm for the first time.

A series of In$_2$O$_3$ thin films with tunable NIR transparency was grown on Corning 1737F glass substrates using a Veeco horizontal dual-gun IAD system at room temperature. The O$_2$ partial pressure was maintained between 1.2 x 10$^{-4}$ –2.0 x 10$^{-4}$ Torr during film deposition. ITO was also deposited for comparison. In$_2$O$_3$ (99.99%) and ITO targets (In$_2$O$_3$ : SnO$_2$ = 9:1) were purchased from Williams Advanced Materials and Sputtering Materials, Inc., respectively. In$_2$O$_3$ thin film growth rates were from 3–5 nm/min, depending on the conditions. Film thickness was measured with a Tencor P-10 step profilometer after etching a step in the film. Single-crystal LiNbO$_3$ slides (MTI Corp., Z cut, optical grade) were top coated with 140 nm In$_2$O$_3$ or ITO by electron beam evaporation. The device structure Au/LiNbO$_3$/In$_2$O$_3$ or ITO is shown in Fig. 1(A). For organic SAS film samples, a 140 nm In$_2$O$_3$ electrode was deposited on the SAS films, which in turn were grown on a SiO$_2$/Au/GaAs substrate using layer-by-layer self-assembly techniques. Details concerning SAS film growth are reported elsewhere. The structure of the In$_2$O$_3$/SAS/SiO$_2$/Au/GaAs specimen is shown in Fig. 1(B).

A 633 nm He–Ne laser and 1064 and 1310 nm diode lasers were the laser sources. The frequency of the driving voltage applied to the samples was 1 KHz, and the amplitude ranged from 1 to 10 V.

The electrical properties of IAD-derived In$_2$O$_3$ thin films were characterized as a function of O$_2$ partial pressure ($P_{O_2}$) and primary ion beam energy (Table I). By increasing $P_{O_2}$ and diminishing the primary ion beam energy, carrier In$_2$O$_3$ film concentrations can be incrementally reduced from 2.2 x 10$^{20}$ to 4.3 x 10$^{18}$ cm$^{-3}$, with conductivity dropping from 845 to 21 S/cm. It is known that In$_2$O$_3$ thin-film conductivity originates from oxygen vacancies or In$^{3+}$ interstitials. With increasing $P_{O_2}$, more oxygen vacancies are compensated, leading to lower carrier concentrations and conductivities. Note that the decreased conductivity is caused by reduction in carrier concentration, not in mobility, which remains within a small range. Thus, the carrier concentrations and conductivities of In$_2$O$_3$ thin films are engineered by the IAD deposition conditions. ITO films with a conductivity of 1520 S/cm and a carrier concentration of 5.0 x 10$^{20}$ cm$^{-3}$ were obtained as reported previously.

The optical transmittance spectra of In$_2$O$_3$ films as a function of carrier concentration are shown in Fig. 2. Note that the NIR transparency of the In$_2$O$_3$ thin films is a strong function of carrier concentration. The plasma edge progressively red-shifts as the film carrier concentration is decreased. When the concentration is <1.4 x 10$^{19}$ cm$^{-3}$, the transmittance of In$_2$O$_3$ films with thickness ~450 nm is ~90% at 1310 nm and ~97% at 1550 nm, and there is no significant difference in transparency from the visible to NIR, indicating that free carrier scattering is not a dominant factor in NIR transparency. In contrast to the In$_2$O$_3$ films, the transmittance spectrum of ITO films, with a typical carrier concentration of 5 x 10$^{20}$ cm$^{-3}$ (Ref. 5), evidences a sharp plasma edge beginning at ~900 nm. The poor NIR transmittance is undoubtedly due to free carrier scattering at such high carrier concentrations, rendering ITO nonideal for NIR-sensitive measurements.

To evaluate In$_2$O$_3$ and ITO as transparent electrodes for Teng–Man measurements, and to investigate the relationship

![FIG. 2. (Color online) Transmission optical spectra and carrier concentrations of IAD-derived In$_2$O$_3$ and ITO thin films grown on 1737F glass substrates. The carrier concentrations and the thicknesses correspond to those for the samples in Table I.](image-url)

![FIG. 3. (Color online) Modulated-beam signal $V_m$ vs applied voltage $V_m$ recorded on an In$_2$O$_3$-coated LiNbO$_3$ Teng–Man specimen. This electrode corresponds to sample 1 in Table II.](image-url)

### Table I. Physical and electrical properties of IAD-derived In$_2$O$_3$ and ITO thin films.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Thickness (nm)</th>
<th>Sheet resistance ($\Omega$ /sq)</th>
<th>Conductivity (S/cm)</th>
<th>Mobility (cm$^2$/V s)</th>
<th>Carrier concentration (cm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. In$_2$O$_3$</td>
<td>140</td>
<td>85</td>
<td>845</td>
<td>24</td>
<td>2.2 x 10$^{20}$</td>
</tr>
<tr>
<td>2. In$_2$O$_3$</td>
<td>150</td>
<td>108</td>
<td>631</td>
<td>28</td>
<td>1.4 x 10$^{20}$</td>
</tr>
<tr>
<td>3. In$_2$O$_3$</td>
<td>520</td>
<td>62</td>
<td>311</td>
<td>27</td>
<td>7.3 x 10$^{19}$</td>
</tr>
<tr>
<td>4. In$_2$O$_3$</td>
<td>450</td>
<td>342</td>
<td>65</td>
<td>29</td>
<td>1.4 x 10$^{19}$</td>
</tr>
<tr>
<td>5. In$_2$O$_3$</td>
<td>500</td>
<td>629</td>
<td>32</td>
<td>24</td>
<td>8.2 x 10$^{18}$</td>
</tr>
<tr>
<td>6. In$_2$O$_3$</td>
<td>450</td>
<td>1080</td>
<td>21</td>
<td>30</td>
<td>4.3 x 10$^{18}$</td>
</tr>
<tr>
<td>7. ITO</td>
<td>250</td>
<td>28</td>
<td>1520</td>
<td>19</td>
<td>5.0 x 10$^{20}$</td>
</tr>
</tbody>
</table>
TABLE II. Experimental results for LiNbO$_3$ using 140 nm In$_2$O$_3$ and ITO electrodes in direct Teng–Man EO measurements at 1310 nm.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$r_{33}$ (pm/V)</th>
<th>Relative deviation (%)</th>
<th>Electrode conductivity (S/cm$^{-1}$)</th>
<th>Electrode carrier concentration (cm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard</td>
<td>30.8$^a$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1. In$_2$O$_3$</td>
<td>31.1</td>
<td>0.97</td>
<td>18</td>
<td>4.0 $\times$ 10$^{18}$</td>
</tr>
<tr>
<td>2. In$_2$O$_3$</td>
<td>29.5</td>
<td>-4.2</td>
<td>58</td>
<td>1.3 $\times$ 10$^{19}$</td>
</tr>
<tr>
<td>3. ITO</td>
<td>42.2</td>
<td>37.0</td>
<td>1400</td>
<td>4.5 $\times$ 10$^{20}$</td>
</tr>
</tbody>
</table>

$^a$Standard value independently measured by the vendor, MTI Crystal Corporation.

between NIR transparency and Teng–Man measurement accuracy. Z-cut single-crystal LiNbO$_3$ was employed as a standard. The Au/LiNbO$_3$/TCO structure [Fig. 1(a)] was used in this simple reflection configuration to evaluate the EO coefficient accuracy obtained with the different transparent electrodes. Here $r_{33}$ is derived from Eq. (1)$^2$

$$
r_{33} = \frac{3\sqrt{2}}{4} \frac{V_{ac}}{\pi V_{M} V_{dc}} \left[ \frac{n_e n_n \sin^2 \theta}{n_e^2 - \sin^2 \theta} + \frac{0.279}{n_n^3} \left( \frac{n_e^3}{n_n^3} \frac{n_e^2 - \sin^2 \theta}{n_n^2 - \sin^2 \theta} \right) \right],
$$

where $V_{dc}$ is the working voltage, $V_{ac}$ is the modulated signal, $V_M$ is the modulation voltage applied to the sample, $\theta$ is the incident angle of the laser beam (fixed at 45$^\circ$), and $n_e$ and $n_n$ are the ordinary and extraordinary refractive indices of LiNbO$_3$, respectively. Experimental $r_{33}$ determination results using In$_2$O$_3$ and ITO electrodes and electrical properties of the transparent electrodes, are summarized in Table II. The excellent linear relationship between modulated-beam signal $V_{ac}$ and applied voltage $V_{M}$ is displayed in Fig. 3. At 633 nm, both In$_2$O$_3$ and ITO electrodes exhibit good transparency and yield very close values of $r_{33}$ vs the standard $r_{33}$ value (30.8 pm/V). Likewise, $r_{33}$ values measured using two different In$_2$O$_3$ electrodes are also in good agreement with the standard value, and their relative deviations being 0.97% and -4.2%, respectively (Table I). In contrast, $r_{33}$ measured with the ITO electrode shows a very large deviation of +37.0% (Table I). Clearly, the accuracy of the derived $r_{33}$ is strongly dependent on TCO electrode NIR transparency. The large deviation of the ITO-electrode derived $r_{33}$ value presumably originates from reflection that leads to interference effects and Fabry–Pérot resonance, and hence introduces far greater error.$^{12}$ To maintain good experimental accuracy in the NIR region, the transparency of the electrodes should be considered, and Teng–Man EO measurements may incur substantial inaccuracies using conventional ITO as the NIR transparent electrode, and the present In$_2$O$_3$ films provide excellent experimental accuracy. Considering the consistency in excellent transparency over the NIR region (Fig. 2), the present In$_2$O$_3$ electrodes should provide high accuracy at 1550 nm or further into the NIR.

Teng–Man measurements were next carried out on intrinsically polar SAS thin films using optimized In$_2$O$_3$ electrodes. SAS thin films have been used for fabrication of EO phase modulators.$^{10}$ Direct EO measurements on SAS films were carried as for LiNbO$_3$ films, with a 140 nm high-quality In$_2$O$_3$ film deposited by IAD on the SAS films at room temperature. The In$_2$O$_3$ thin-film conductivity and carrier concentration were 24 S/cm and 4.2 $\times$ 10$^{18}$ cm$^{-3}$, respectively. Assuming $r_{33} = 3r_{13}$ and using the approximation $n_e = n_n$, Eq. (1) simplifies to Eq. (2) for SAS thin films

$$
r_{33} = \frac{3\sqrt{2}}{4} \frac{V_{ac}}{V_{M} V_{dc}} \sqrt{n_{SAS}^2 - \sin^2 \theta}.
$$

The highest $r_{33}$ determined is 42.2 pm/V at 633 nm. At 1064 nm, $r_{33}$ becomes 13.1 pm/V agreeing well with waveguiding EO modulator measurements.$^{10}$ An $r_{33}$ of 6.4 pm/V is obtained at 1310 nm, indicating that the EO response of SAS thin films exhibits a pronounced dispersion with wavelength.$^{11–13}$ These SAS results further demonstrate the effectiveness of In$_2$O$_3$ electrodes for direct EO measurements.

In summary, highly NIR transparent In$_2$O$_3$ thin films grown on glass substrates, single-crystal Z-cut LiNbO$_3$, and organic SAS thin films by room temperature IAD, can be employed as transparent electrodes for precision Teng–Man EO measurements. Tunable NIR transparency can be achieved by controlling the carrier concentration. It is found that Teng–Man measurement accuracy strongly depends on the NIR transparency of the TCO electrodes. In addition, the suitability of IAD-In$_2$O$_3$ electrodes was further demonstrated by characterizing the EO properties of organic SAS thin films. Importantly, highly NIR transparent In$_2$O$_3$ films should have many other applications in NIR-sensitive optoelectronic devices and measurements.

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8. The standard value is independently measured by MTI Crystal Corporation.