

Near-infrared transparent electrodes for precision Teng–Man electro-optic measurements: In_2O_3 thin-film electrodes with tunable near-infrared transparency

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(Received 1 April 2005; accepted 15 August 2005; published online 13 October 2005)

Highly near-infrared (NIR) transparent In_2O_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_2O_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_2O_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 stilbazolium-based self-assembled superlattice thin films were directly determined for the first time using an optimized In_2O_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.¹ 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 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).^{2–4} ITO is a degenerate semiconductor with a carrier concentration of $\sim 10^{21} \text{ cm}^{-3}$. The optical transmittance of conventional (commercial) ITO exhibits a sharp plasma edge starting at wavelengths $\geq 900 \text{ nm}$ due to free carrier scattering.⁵ ITO electrodes therefore function well as top electrodes in the visible region, but are limited

for measurements in the near-infrared (NIR) region.^{4,6} 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.⁴

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.⁷ One important advantage of this technique is that In_2O_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.⁷

In this letter, a series of highly NIR transparent In_2O_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} ,⁸ 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_2O_3 thin films with carrier concentrations in the range $10^{18} - 10^{19} \text{ cm}^{-3}$ exhibit excellent NIR transparency ($> 90\%$), and provide far more accurate Teng–Man measurements than conventional ITO electrodes. In_2O_3 thin films were also successfully grown on organic self-assembled super-lattice (SAS) thin films for Teng–Man

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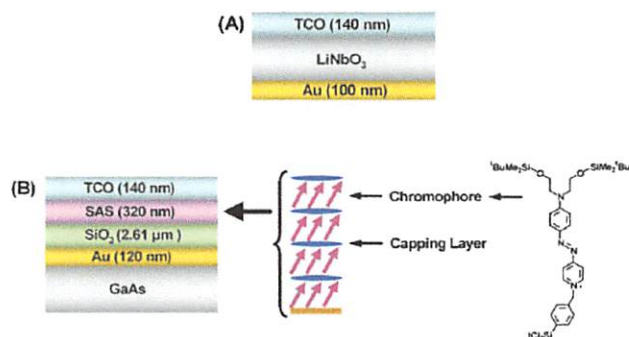


FIG. 1. (Color online) (A). Cross-sectional structure of a sandwiched LiNbO₃ Teng–Man sample. (B) Cross-sectional view of a SAS-based Teng–Man structure.

measurements.⁹ The EO coefficients are quantified at 633, 1064, and 1310 nm for the first time.

A series of In₂O₃ 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 O₂ partial pressure was maintained between 1.2×10^{-4} – 2.0×10^{-4} Torr during film deposition. ITO was also deposited for comparison. In₂O₃ (99.99%) and ITO targets (In₂O₃:SnO₂=9:1) were purchased from Williams Advanced Materials and Sputtering Materials, Inc., respectively. In₂O₃ 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 LiNbO₃ slides (MTI Corp., Z cut, optical grade) were top coated with 140 nm In₂O₃ or ITO by room temperature IAD, and bottom coated with 100 nm gold by electron beam evaporation. The device structure Au/LiNbO₃/In₂O₃ or ITO is shown in Fig. 1(A). For organic SAS film samples, a 140 nm In₂O₃ electrode was deposited on the SAS films, which in turn were grown on a SiO₂/Au/GaAs substrate using layer-by-layer self-assembly techniques. Details concerning SAS film growth are reported elsewhere.^{9,10} The structure of the In₂O₃/SAS/SiO₂/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 In₂O₃ thin films were characterized as a function of O₂ 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 In₂O₃

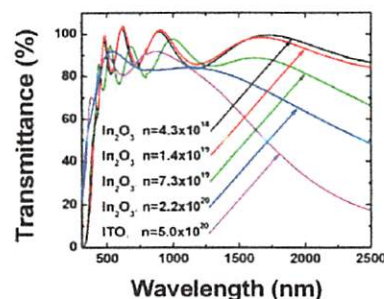


FIG. 2. (Color online) Transmission optical spectra and carrier concentrations of IAD-derived In₂O₃ and ITO thin films grown on 1737F glass substrates. The carrier concentrations and the thicknesses correspond to those for the samples in Table I.

film concentrations can be incrementally reduced from 2.2×10^{20} to 4.3×10^{18} cm⁻³, with conductivity dropping from 845 to 21 S/cm. It is known that In₂O₃ thin-film conductivity originates from oxygen vacancies or In³⁺ 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 In₂O₃ thin films are engineered by the IAD deposition conditions. ITO films with a conductivity of 1520 S/cm and a carrier concentration of 5.0×10^{20} cm⁻³ were obtained as reported previously.⁷

The optical transmittance spectra of In₂O₃ films as a function of carrier concentration are shown in Fig. 2. Note that the NIR transparency of the In₂O₃ 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 $\leq 1.4 \times 10^{19}$ cm⁻³, the transmittance of In₂O₃ films with thickness ~ 450 nm is $\sim 90\%$ at 1310 nm and $\sim 97\%$ 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 In₂O₃ films, the transmittance spectrum of ITO films, with a typical carrier concentration of 5×10^{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 In₂O₃ and ITO as transparent electrodes for Teng–Man measurements, and to investigate the relationship

TABLE I. Physical and electrical properties of IAD-derived In₂O₃ and ITO thin films.

Sample	Thickness (nm)	Sheet resistance (Ω/\square)	Conductivity (S/cm)	Mobility (cm ² /V s)	Carrier concentration (cm ⁻³)
1. In ₂ O ₃	140	85	845	24	2.2×10^{20}
2. In ₂ O ₃	150	108	631	28	1.4×10^{20}
3. In ₂ O ₃	520	62	311	27	7.3×10^{19}
4. In ₂ O ₃	450	342	65	29	1.4×10^{19}
5. In ₂ O ₃	500	629	32	24	8.2×10^{18}
6. In ₂ O ₃	450	1080	21	30	4.3×10^{18}
7. ITO	250	28	1520	19	5.0×10^{20}

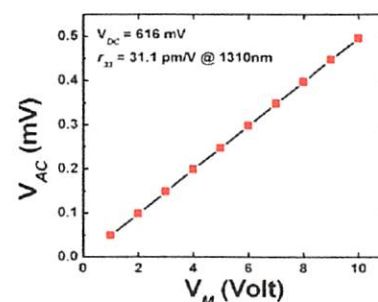


FIG. 3. (Color online) Modulated-beam signal V_{ac} vs applied voltage V_M recorded on an In₂O₃-coated LiNbO₃ Teng–Man specimen. This electrode corresponds to sample 1 in Table I.

TABLE II. Experimental r_{33} results for LiNbO₃ using 140 nm In₂O₃ and ITO electrodes in direct Teng–Man EO measurements at 1310 nm.

Sample	r_{33} (pm/V)	Relative deviation (%)	Electrode conductivity (S/cm)	Electrode carrier concentration (cm ⁻³)
Standard value	30.8 ^a			
1. In ₂ O ₃	31.1	0.97	18	4.0 × 10 ¹⁸
2. In ₂ O ₃	29.5	-4.2	58	1.3 × 10 ¹⁹
3. ITO	42.2	37.0	1400	4.5 × 10 ²⁰

^aStandard value independently measured by the vendor, MTI Crystal Corporation.

between NIR transparency and Teng–Man measurement accuracy, Z-cut single-crystal LiNbO₃ was employed as a standard. The Au/LiNbO₃/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

$$r_{33} = \frac{3\sqrt{2}\lambda}{4} \frac{1}{\pi V_M V_{dc}} \left[\frac{n_o n_e \sin^2 \theta}{\sqrt{n_e^2 - \sin^2 \theta}} + 0.279 \left(\frac{n_o^3}{n_e^2} \sqrt{n_e^2 - \sin^2 \theta} - \frac{n_o^4}{\sqrt{n_e^2 - \sin^2 \theta}} \right) \right], \quad (1)$$

where V_{dc} is the working voltage, V_{ac} is the modulated signal, V_M is the modulation voltage applied to the sample, θ is the incident angle of the laser beam (fixed at 45°), and n_o and n_e are the ordinary and extraordinary refractive indices of LiNbO₃, respectively. Experimental r_{33} determination results using In₂O₃ 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 In₂O₃ 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 In₂O₃ 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.^{1,4} To maintain good experimental accuracy in the NIR region, the NIR 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 In₂O₃ films provide excellent experimental accuracy. Considering the consistency in excellent transparency over the NIR region (Fig. 2), the present In₂O₃ 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 In₂O₃ electrodes. SAS thin films have been used for fabrication of EO

phase modulators.¹⁰ Direct EO measurements on SAS films were carried as for LiNbO₃ films, with a 140 nm high-quality In₂O₃ film deposited by IAD on the SAS films at room temperature. The In₂O₃ thin-film conductivity and carrier concentration were 24 S/cm and 4.2 × 10¹⁸ cm⁻³, respectively. Assuming $r_{33} = 3r_{13}$ and using the approximation $n_o \approx n_e \approx n$, Eq. (1) simplifies to Eq. (2) for SAS thin films

$$r_{33} = \frac{3\sqrt{2}\lambda}{4} \frac{1}{\pi V_M V_{dc}} \frac{V_{ac}}{n_{SAS}^2 \sin^2 \theta} \sqrt{n_{SAS}^2 - \sin^2 \theta}. \quad (2)$$

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 In₂O₃ electrodes for direct EO measurements.

In summary, highly NIR transparent In₂O₃ thin films grown on glass substrates, single-crystal Z-cut LiNbO₃, 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-In₂O₃ electrodes was further demonstrated by characterizing the EO properties of organic SAS thin films. Importantly, highly NIR transparent In₂O₃ films should have many other applications in NIR-sensitive optoelectronic devices and measurements.

The authors thank DARPA/ONR (N00014-04-1-0093/P0001) and the NSF-MRSEC program through the Northwestern Materials Research Center (DMR-0076097) for support of this research.

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