Indium-Tin-Oxide for High-performance Electro-optic Modulation

Zhizhen Ma, Zhuoran Li, Ke Liu, Chenran Ye, and Volker J. Sorger*

Abstract: Advances in opto-electronics are often led by discovery and development of materials featuring unique properties. Recently, the material class of transparent conductive oxides (TCO) has attracted attention for active photonic devices on-chip. In particular, indium tin oxide (ITO) is found to have refractive index changes on the order of unity. This property makes it possible to achieve electro-optic modulation of sub-wavelength device scales, when thin ITO films are interfaced with optical light confinement techniques such as found in plasmonics; optical modes are compressed to nanometer scale to create strong light-matter interactions. Here we review efforts towards utilizing this novel material for high performance and ultra-compact modulation. While high performance metrics are achieved experimentally, there are open questions pertaining to the permittivity modulation mechanism of ITO. Finally, we review a variety of optical and electrical properties of ITO for different processing conditions, and show that ITO-based plasmonic electro-optic modulators have the potential to significantly outperform diffraction-limited devices.

1 Introduction

A potential viable way of fulfilling both size and power requirement for future photonic integrated circuit (PIC)

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The unique electro-optic properties of indium tin oxide (ITO) such as unity refractive index modulation and epsilon-near-zero (ENZ) behavior allow for new functionality of active photonic devices on-chip. However, processing conditions and physical non-concurrences in recent work have led to question in the field. Here we review recent advanced of ITO processing and devices specifically for electro-optic modulation; we highlight promising results and point to open research directions.

technology lies in down-scaling opto-electronic devices beyond the diffraction limit of light [1–4]. The advantage of such sub-diffraction limited photonics is two-fold; reduced optical power requirements and physical device size. To elaborate on this, while being physically compact, the optical mode confinement of such components can strongly enhance light matter interactions (LMI) [5, 6], which can reduce required drive power to obtain the desired effect, for example, signal modulation, optical non-linearities [7, 8]. In order to address these demands, photonic components and even circuits based on surface plasmon polaritons (SPPs), collective oscillations of electrons at metal-dielectric interfaces are thought of a solution for nanoscale PICs [9]. However, while SPP-based schemes have been explored before, many do not offer both sub-wavelength confinement beyond the diffraction limit and long enough interaction lengths making these designs often unsuitable towards nanoscale photonic integration [10, 11]. As a result, the use of plasmonics for photonic on-chip solutions, in particular for optical interconnects remained uncertain until recently. However, emerg-
ing materials such as the recently explored transparent conductive oxides (TCOs) show promise to deliver greatly enhanced functionality and performance.

One possible path for future photonic technology is to decouple passive light routing from active light manipulation leading to hybrid integration strategies [8]. To this end, a low-loss platform would build the backend data link, for example, silicon-on-insulator (SOI) based waveguides [12], while SPP-based components offer compact and efficient light manipulation [5, 6, 13–16]. Therefore, these components are required to fulfil two design criteria; strong mode confinement and a sufficiently long propagation length to utilize the mode towards light manipulating effect or signal [17, 18]. Both criteria combined can be used to form a figure-of-merit (FOM) suitable for comparing design concepts towards highly scaled integrated nanophotonic building blocks as will be discussed below. A remaining challenge, however, is then given by the need to reduce the optical coupling loss arising from the optical mode size mismatch between the diffraction limited and sub-diffraction limited modes in the passive and active regions of the PIC, respectively [19]. In addition to the LMI enhancements, the choice of the optical active material is critical; towards enhancing the device performance for on-chip photonic building blocks, a variety of novel materials are emerging in recent years. These materials inhibit unique properties for nanoscale optoelectronics such as high carrier density for a tunable permittivity. Here, we discuss a particular material indium-tin-oxide (ITO), which belongs to the family class of TCOs. By reviewing material fundamentals and recent work in nanophotonics, we show that using ITO and nanophotonic field enhancement techniques produce the aforementioned high FOM devices as exemplified by the first \( \lambda \)-scale electro-optic modulators (EOM) [20].

2 Transparent Conductive Oxides Used in Photonics

TCOs are widely used for their optically transparent yet electrically conductive properties. As such, TCO’s found increasing interest in optoelectronic technologies such as for displays (i.e. flat panel displays) and energy conversion (i.e. photovoltaics, architectural and window glass). The discovery of TCOs dates back about one century, where Badeker found the resistivity of CdO to be as low as \( 1.2 \times 10^{-3} \) \( \Omega \)-cm. Note, this is about one order of magnitude higher than that of ITO films – the widely used TCO material today [21]. Tin dioxide (SnO\(_2\)) made technological progress when scientists applied it as a transparent heating layer in the airplane cockpit windows [22]. The broad industrial utilization of TCO materials occurred at the end of the 1960s, when infrared light filters composed of Tin or In\(_2\)O\(_3\) were used on low-pressure sodium discharge lamps for increasing the lamp efficiency by reducing heat losses [23, 24]. Afterward, with the advent of flat-panel display technology around 1970, ITO became the most commonly used TCO material for transparent electrodes [25]. Until now, ITO is the TCO material having with the lowest resistivity (i.e. order of \( 1\times 10^{-4} \) \( \Omega \)-cm), which is widely utilized as the transparent electrodes in flat-panel displays [28, 29].

Table 1 summarizes the most promising mechanisms of modulation and its corresponding materials. In 2010, the Atwater group found the characteristic of unity order refractive index change for TCO materials, and gave ways to utilize TCO films as an active material in EOM, which could lead to a new generation of fast, on-chip, nanoscale devices with unique capabilities. The mechanism for TCO films as an active material in EOMs resembles the electrostatics found in metal-oxide-semiconductor (MOS) capacitors, a bias voltage can change the carrier concentration in an accumulation (or inversion) layer of a modulator device. This carrier change has been found to result in a refractive index change, therefore an intensity modulation could be achieved. This modulation mechanism of carrier concentration has been deployed in semiconductor modulators for many years. As an example, carrier-effect based silicon optical modulators (e.g. carrier-depletion) may reach a modulation speed of over 50 Gbps [30]. However, these devices still suffer a weak LMI (i.e. refractive index change of \( 2 \times 10^{-3} \) at a wavelength of 1.55 \( \mu \)m with \( 10^{18} \) carriers/cm\(^3\) [31]) and then a larger device footprint. The behavior of phase transition (i.e. a semiconductor to metal phase transition) is observed in some smart materials, presenting a noticeable permittivity change between the two phases. For example, vanadium dioxide (VO\(_2\)) has been studied extensively in the last decade because of its large, reversible change in its electrical, optical, and magnetic properties at a temperature close to room temperature. At room temperature VO\(_2\) behaves as a semiconductor with a band gap of ~1 eV. At temperatures higher than 68\( ^\circ \)C VO\(_2\) passes through an abrupt transition to a metallic state. This process is reversible when lowering the temperature below 65\( ^\circ \)C (VO\(_2\) becomes semiconductor again). Taking advantage of the phenomenon, a compact VO\(_2\)-based absorption modulator at 1550 nm wavelength on a SOI platform can be realized through the stimuli of substrate heating [32]. The thermo-optic effect results from a temperature dependent refractive index of a material,
Table 1: Comparisons of a variety of active EO materials [36]. TCO’s allow for strong optical modulation due to their ability to modulate the carrier density over several orders of magnitude electrically. However, typically, optical losses are high.

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<thead>
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<th>Mechanism</th>
<th>Active material</th>
<th>Advantage</th>
<th>Challenge</th>
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<tr>
<td>Carrier change</td>
<td>Si, III-V</td>
<td>Fast, low loss</td>
<td>Weak</td>
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<td></td>
<td>Graphene</td>
<td>Fast, significant</td>
<td>Lossy</td>
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<td></td>
<td>TCO (ITO, GZO, AZO)</td>
<td>Fast, significant</td>
<td>Lossy</td>
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<td>Phase transition</td>
<td>VO$_2$, Ga, BiFeO$_3$, BaTiO$_3$, etc.</td>
<td>Significant response</td>
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such as in tuning the refractive index of silicon via resistive heating (i.e. $\sim1.8 \times 10^{-4}/K$ of thermo-optic coefficient of Silicon) [33]. Another widely used thermo-optic effect material is polymer, which has the advantages of low density and refractive index, less dispersion, cheap manufacturing cost, easy to make complex shapes, and good electrical insulation. However, these types of materials suffer shortcomings such as limited temperature usability, degraded time dependence of properties (e.g. electro-optic polymers), and fatigue and solvent sensitivity. Although polymer-based thermo-optic modulators (and switches) have several drawbacks such as significant power consumption, slow transition time (usually $>1\mu s$), the mechanism shows operational devices and sub-systems on-chip [34, 35]. Phase transition and thermal-optic effect based modulators can provide significant response, however the time frame is high and allows for an operation speed on the order of MHz [36].

TCOs such as ITO, GZO (ZnO: Al), and AZO (ZnO: Ga) have very similar properties and allow for an efficient change of carrier concentration. As an outstanding representative of TCO materials used for EOMs, ITO exhibits its unique advantages, such as epsilon-near-zero (ENZ) in the near infrared regime and electrically tunable permittivity [37, 38]. A recently explored example of MOS-based EOM is an ITO-SiO$_2$-Au stack in a SOI waveguide [20]. The effective index of ITO changes from being a dielectric to a quasi-metallic state when a voltage bias is applied. Such a modulator exhibits a low insertion loss of $\sim1$ dB for the 5 µm long device, a sub-wavelength compact size of 0.78 λ, and the broadband operation of $>500$ nm with a non-resonant MOS mode [39]. Though TCO materials have a strong electro-optical response compared to the aforementioned materials (Table 1). A large index change (real part) is also accompanied by a significant extinction coefficient change (imaginary part of index) making TCOs often rather lossy due to the Kramers–Kronig relations. However, since the carrier concentration of TCOs may be selectively controlled in a post-processing, local resistivity tuning step. This allows separating the optically active material from the passive electronic, and may be realized by a plasma treatment process to optimize the resistivity of TCO layer as discussed in detail below. In the remaining sections, we specifically focus on material, processing and electro-optic modulation details for the material ITO.

3 ITO Material Science and Processing Fundamentals

ITO sputtering targets typically consist of 10% SnO$_2$ to 90% In$_2$O$_3$ by weight. ITO has been widely adopted by the solar industry as a transparent electrode due to both its high optical transmittance yet high electrical conductivity. In addition to the photovoltaic applications, new possibilities for ITO are emerging for electro-optic modulation. However, ITO has been found to be a difficult material to work with due to its processing invariances. In this review, we first focus on ITO’s fundamental properties, and in a second step relate them to the device details of high-performance EOM.
Figure 1: Indium oxide structure. (a) Eight oxygen atoms are situated within a compressed octahedron (b site) and have six equidistant oxygen atom neighbors at 2.18 Å. (b), Eight indium atoms are situated at the corners of a highly distorted octahedron (d site). For these indium atoms, there are three possible cation-oxygen distances: 2.13, 2.19 and 2.23 Å [41]. As Fig. 1a & 1b, indium atoms, on both b and d sites, reside at the center of a distorted cube with the six corners occupied by oxygen atoms, while the remaining two corners are empty. In the case of the b sites, oxygen vacancies are located along the body diagonal; for the d site they are located along a face diagonal [41, 42]. Figure 1c shows tin (Sn) doping sites in an indium oxide lattice, where the Sn atom occupies an interstitial site and contributes an electron (i.e., a donor), making the doped indium oxide into indium tin oxide.

3.1 Indium Oxide and Tin doped Indium Oxide Structure

The atomistic structure of a unit-cell of ITO resembles that of indium oxide (In$_2$O$_3$), with the latter being an ionically bound semiconducting oxide, which crystallizes in a cubic bixbyite-type structure with a space group Ia3 and a lattice constant of 10.118 nm [40]. The unit cell of ITO contains 80 atoms, and the indium cations are located in two different six-fold-coordinated sites. One-fourth of the cations are located in trigonally compressed octahedral, referred as b sites (In-O distance: 2.18 Å), while the remaining three-quarters are located on highly distorted octahedral d sites (set of three In-O distances: 2.13, 2.19 and 2.23 Å) [41].

3.2 Indium Oxide and ITO Band Structure

The actual material properties of ITO have been found to be highly sensitive to the processing conditions [43]. While the detailed insights of band structure, as a function of processing parameters is desirable, the band structure is a function of the complex unit cell lattice and respective electronic interactions. Therefore, the properties are usually discussed in terms of an assumed band diagram consisting of an isotropic parabolic conduction band [41, 44]. A first attempt for its description was made by Fan and Goodenough [45] who proposed the schematic energy band model for indium oxide and ITO, which allows for a qualitative explanation of the observed high optical transparency and electrical conductivity in ITO (Fig. 1d). In Fan’s band model, indium oxide exhibits a wide direct band gap (3.5 eV) prohibiting interband transitions in the visible range and hence making it transparent within this frequency range, which is still the reference model used today for ITO. The conduction band was proposed to arise mainly from the indium 5s orbitals and the valence band from oxygen 2p electrons. The Fermi energy $E_F$ is found a few eV’s below the conduction band due to n-type doping of the Tin impurities [41]. The bands are slightly different; for low doping density donor states are formed just below the conduction band, and the Fermi energy lies between the donor level and the conduction band minimum (Fig. 1d). However, for very high doping, the donor density increases. Note that the donor states merge with the conduction band at a certain "critical" density, $n_c$, known as the Mott density defined by $n_c^{1/3} = 0.25$ for ITO, where the effective Bohr radius $a_0^* = 1.3$ nm for In$_2$O$_3$ resulting in $n_c$ (ITO) = $3.43 \times 10^{-19}$ cm$^{-3}$ [41]. Above the critical Mott density, the impurities and the associated electrons occupy the bottom of the conduction band forming a degenerate electron gas, and the electron gas in-
creases the ionized-impurity scattering and reduces the mobility [46, 47].

3.3 Optical and Electrical Properties of ITO

In order to utilize ITO for nanophotonic devices, a detailed knowledge and parameter interdependencies relating to the optical and electrical properties must be known. In general, the optical properties were previously modeled by a Drude–Lorentz model, due to the high carrier concentration as we discuss further below [49]. Focusing here on the electrical properties, the carrier concentration and mobility of ITO have been found to vary widely with process conditions for the deposition method such as sputtering power, oxygen flow, and annealing temperature. We therefore limit the discussion to a few key observations based on ITO’s resistivity ($\rho = \frac{1}{ne\mu}$, where $n$ is the carrier concentration, $\mu$ is the mobility and $e$ is the free electron charge). For ITO, electrons are the majority carriers originating mainly from the doping donor Sn and oxygen vacancies. Therefore the carrier concentration of ITO films depends on the oxygen vacancy concentration, and the Sn doping levels. The latter is important since substituting an indium atom frees an electron increasing the carrier density. However, doubly-charged oxygen vacancies and singly-charged Sn on an indium site reduce the mobility of charge carriers due to ionized-impurity scattering [41]. Based on this understanding of ITO’s doping interplay, the resistivity for ITO films can be tuned, either to a minimum such as for photovoltaic applications, or to a high-resistivity level. The latter is significant for electro-optic modulation as is discussed in section 4 in more detail.

Matrin et al. provided a useful, yet qualitative, overview linking the apparent as-deposited color of ITO films to the films resistivity, and the $O_2/\text{Sn}$ doping concentration (Fig. 2a) [48]. The observed resistivity minimum (i.e. ‘well’) depending on both the $O_2$ and Sn doping levels, does explain the empirically observed challenge to tune ITO’s resistivity; that is, the resistivity is high for low doping concentrations due to low carrier concentration, and low for high doping due to scattering from oxygen vacancies which reduce the mobility. Moreover, the observed apparent film illustrates that the higher doping could induce a particular state “extinguishing” Sn, but the high oxygen flow could not be well related to the color on the right side [41].

Interestingly, another group found the other resistivity-well trend as a function of sputtering power density (Fig. 2b) [50]. Increasing the power density creates ionized impurity centers, which induce scattering of the free electron carriers and then reduce the mobility. The gradual increase in the carrier concentration between a power density of 1 and 3 W/cm$^2$ is closely associated with the increased number of substituted Sn ions in the lattice. Increasing the sputtering power density further results in a flat carrier concentration due to a cancellation effect, which is from the increased level of Sn ion substitution and the decreased number of oxygen vacancies from the increased ITO film crystallinity. Many groups reported strong resistivity decreases with higher annealing temperatures; note that the annealing temperature leads to the related physical behavior as for the power density, as shown by the similar curve trends (compare Fig. 2b & 2c). However, the outlier data point (i.e. last data point for carrier concentration in Fig. 2c) actually drops instead of keeping constant, which may possibly be caused by the different oxygen flows used. Lastly, tuning with the oxygen flow the resistivity-well effect is present as well (Fig. 2d). Higher carrier densities are expected with comparatively low oxygen content and vice versa, and high mobility with increasing oxygen content, because of the enhanced crystallization. Since both mechanisms cause the opposite effects, the specific resistivity shows a minimum in the oxygen flow level. In summary, these results show explainable trends for the resistivity, and color of ITO films as a function of doping, oxygen flow, deposition power, and substrate temperature. However, it seems the error bars are still rather large, while the more quantitative data and processing details are needed towards guaranteeing a to-spec engineered ITO film electrical property.

3.4 Typical Deposition Methods

This section highlights a variety of typically deployed methods for the deposition of ITO films. The different deposition conditions for each method significantly change the optical and electrical properties of ITO film.

3.4.1 Sputtering

Sputtering is one of the most widely used techniques for the deposition of TCO films. Within sputtering, a variety of techniques have been adopted, including conventional direct current (DC), radio frequency (RF), and magnetron reactive sputtering of a metal alloy target in the presence of oxygen, as well as RF and ion beam sputtering of a pressed oxide powder target [41]. Among these options, DC and RF magnetron sputtering are the most attractive techniques.
for industrial development because both allow for high deposition rates, good reproducibility, and the possibility of using commercially available large area sputtering systems [53]. Typically, magnetron sputtering processes are performed at high substrate temperatures (≥ 200°C), as these allow the best results in terms of layer transparency and conductivity to be obtained. However, several applications, for example, solar cells and devices on plastics, require a low deposition temperature, as higher temperatures would damage the underlying either electronic device structures or substrate itself. This challenging task has been investigated by several workers where the RF technique was mostly adopted [54, 55]. The main difficulty of RF deposition at room temperature is due to insufficient recrystallization of ITO at low temperatures leading to the poor structural and electrical properties [56]. Furthermore, DC magnetron sputtering at room temperature is also challenging since the formed ITO layers are usually amorphous with a high electrical resistivity [57]. High temperature ITO sputtering can be done in DC and RF discharge plasma modes which allow layers with obtainable similar transparency/conductivity properties. Depending on the plasma mode (DC or RF), an essential difference of optimum sputtering conditions (i.e. discharge power density, pressure, oxygen concentration, etc.) was observed, as well as a difference in the crystalline structure and morphology of the formed layers [53]. In general, sputtering allows for a relatively wide range of film tunability due to the various process conditions involved in the process. However, the very process flexibility also requires precise control of all parameters.

3.4.2 Evaporation

For evaporation methods such as electron beam evaporation and direct thermal evaporation, typical powders of metallic Sn and In are commonly used. Regarding the latter, indium will be preferentially vaporized, causing a change in the composition of the tin and indium liquid alloy with time due to the significantly higher vapor pressure of In relative to Sn [58]. That being the case, an electron beam can be a more reproducible method for low resistivity and high transparency films. Furthermore, low resistivity ITO films processed at low temperature have been reported using reactive electron beam evaporation onto
heated glass substrates (300°C and an oxygen pressure above 0.5 mT) [59]. Under optimum conditions, the resistivity is $3 \times 10^{-3}$ Ω·cm with an average mean transmittance of about 84% in the visible range [41].

3.4.3 Chemical Vapor Deposition

Chemical vapor deposition (CVD) is a process in which a chemical reaction involving gaseous reacting species takes place on, or in the vicinity of, a heated substrate surface. This technique has the advantage of being cost-effective with respect to the apparatus, and enables the production of coatings with good properties without the use of high vacuum even on substrates with complicated shapes. The deposition of ITO films by the CVD method generally faces difficulties due to a lack of volatile and thermally stable source materials [41]. Under certain conditions, an ITO film with a resistivity as low as $2.9 \times 10^{-5}$ Ω·cm is obtained at a reaction temperature of 400°C [41]; however, more research is needed in this field.

4 ITO for Electro-optic Modulation

ITO has recently sparked the interest for active photonic components on-chip. In particular, the research by the Atwater, Leuthold, and Sorger group had raised the interest for electro-optic (EO) modulation utilizing ITO as an active switching material [60, 61]. For instance, Sorger et al. demonstrated a 3-A compact EO modulator using ITO inside a plasmonic hybrid mode [20]. In this section, we summarize these effects along with some original content on ITO processing for high-efficient EO modulation. Furthermore, we review biasing options for ITO to produce ENZ characteristics for EO modulation, and close this section by critically reviewing some outstanding questions in the field of ITO for EO modulation that shall guide the future research.

4.1 Drude Model and Refractive Index Ellipsometry

The aim for strong EO modulation is to alter the effective modal index of an optical mode traveling inside the device. Note, in this discussion we exclude localized modulation effects, that is, non-propagating modes towards maximizing the index change of the active material, $\Delta n_{\text{active}}$, while minimizing the utilized voltage bias. Since the latter is related to the electrostatics inside the EOM, this discussion is postponed to the section 5, where a variety of experimental demonstrations of ITO for next generation EO modulation are highlighted and discussed. In what follows now, we discuss the possible strength of ITO-based EO modulation, which connects ITO’s index to the carrier concentration via a Drude–Lorentz model. This model has been previously used for TCOs such as ITO [62, 63], and allows us to write the complex permittivity as

$$\varepsilon(\omega) = \varepsilon_{\infty} - \frac{\omega_p^2}{\omega(\omega + i\gamma)}; \quad \omega_p = \frac{n_c e^2}{\varepsilon_0 m^*} \quad (1)$$

where $\gamma$ is the electron scattering rate, $\omega$ is the angular momentum in rad/s, $\varepsilon_0$ and $\varepsilon_{\infty} = 1 + \chi = 3.9$ [35] are the free space and long-angular-momentum-limit permittivities, respectively, $\omega_p$ is the plasma frequency, $m^*$ is the reduced mass of ITO equating to 0.35$m_0$, with $m_0$ being the rest mass of the electron, $n_c$ is the voltage-modulated carrier density for the ITO film, and $\varepsilon$ is the elementary electron charge. Using Eqn. 1 and sweeping the free parameter, $n_c$, versus the device operating frequency, the general function for the permittivity and index are obtained (Fig. 3). The Drude–Lorentz model assumes the physical EO modulation origin to be the free carrier modulation. Thus, if the carrier concentration in a waveguide-type device design can be electrically altered, then EO modulation can be expected. However, only meaningfully strong modulation can be achieved if the ITO’s index change may influence the effective mode index of the device, and not just the material films index. This therefore requires the mode field enhancement techniques such as observed in plasmonics, slot-waveguides, or optical cavities. The underlying physical mechanism is to enhance the non-linear polarization of the active material leading to a permittivity and hence index change as a function of applied voltage bias. This can be done by confining the mode into sub-diffraction limited fields, which increases the field strength at the active material, and thus leads to higher modulation efficiency (i.e. extinction-ratio/Vb). It is remarkable to notice that if the carrier concentration of ITO can be changed from $-10^{19}$ to $-10^{21}$ cm$^{-3}$, the index changes dramatically; the real part by unity, and the extinction coefficient by about 2-orders of magnitude (Fig. 3). Since the electrostatics of a device limits the achievable change of the carrier concentration, $\Delta n_{\text{ITO}}$, it is imperative to process ITO in such a way that the as-deposited film pertains to carrier concentration as low as possible. This is important, because a given finite voltage bias will increases the carrier density by only a finite amount dictated by the electrostatics in an accumulation layer formed in an MOS capacitor. For instance the experimental results of Ref. [20] indicate an about 70 times
carrier density increase for ITO when being sandwiched in a plasmonic MOS design. Note, that the optimization goal of processing ITO to exhibit a high-resistivity for the as-deposited films is opposite to the material goals of the photovoltaic industry, which utilizes ITO as a transparent electrode, where the aim is to decrease resistivity. However, EOM devices face a double-sided challenge when it comes to ITO’s resistivity; when high-speed modulation is desired requiring low RC-delays, the contact resistance to ITO should be minimized. Thus, the carrier density seems to be a trade-off of the device performance, thus balancing signal extinction ratio (ER) and low energy consumption (i.e. energy/bit) on one side, and modulation speed on the other. However, this dilemma can be bypassed via spatially selective ITO plasma treatments which n-dopes ITO in a selected region at the electrical contact (i.e. assumed ITO is being electrically contacted serving as the active material). The latter case is discussed in more detail below.

The outstanding aim for an ITO-based EOM optimization is therefore to achieve low carrier concentrations of ITO during processing for the device region.

We performed a variety of experimental ITO processing tests for EO modulation, choosing the physical vapor deposition (PVD) method of sputtering to investigate effects of (a) O$_2$ concentration, (b) RF power, (c) bias effect such as DC vs. AC, and (d) the effect of a wafer substrate. Regarding the results, we report on two selected parameters affecting the ITO’s refractive index most strongly: the oxygen flow and the RF bias, whose effect can be visually seen by the optical appearance of the as-deposited ITO film (Fig. 4a), and by ellipsometry refractive index data (Fig. 4c). At a wavelength of 1550 nm, an increase in the

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**Figure 3:** ITO optical film parameters. (a)&(b) ITO permittivity dispersion for various carrier concentrations. (c)&(d) Index dispersion of the active materials ITO based on the Drude–Lorentz model for various carrier concentrations [64]. Arrows indicate switching range for ON (arrow start) and OFF (arrow tip), respectively [65]. $\lambda = 1310$ nm vertical dashed line.
O_{2} chamber concentration clearly increase the refractive index, which correspond to a lower carrier concentration. It is consistent with the result of section 3, where a higher oxygen flow prohibits the existence of oxygen vacancies. However, altering the RF bias voltage induces a minor carrier concentration decrease. Note, that similar ITO film properties were observed between electron-beam evaporated films and sputtered films without oxygen flow, which can be explained by the lack of O_{2} in both cases.

It is worthwhile to report our procedure and details of the performed ellipsometry tests. Variable angle spectroscopic ellipsometry (VASE) is a rather complex procedure and many physically non-meaningful results can be generated. For ITO the procedure is specifically challenging for several reasons due to (a) low signal-to-noise ratio owing to optical absorption, (b) strong dispersion (i.e. for broadband ellipsometry), and (c) vertical index variations since ITO grows commonly in graded microstructures. Following Ref. [66] we are able to provide the reliable ITO results following a 2-step procedure; ITO films are first fit with a Cauchy model over a smaller and typically less optical lossy wavelength range (i.e. 300–600 nm) to determine the film thickness. In a second step the Lorentz–Drude model is used to obtain the broadband index information using the film thickness as an input parameter. Depending on the film thickness and application a graded index profile for ITO can be assumed for more accurate results. This relates to a gradually changed index profile with the film thickness due to the formation of an accumulation layer in the EOM devices. However, even following this procedure blindly is not advised, but a second control mechanism is needed for accurate results. That is, both angular functions Psi & Delta are fitted by both a material and a layer-composition model returning a residual mean error (RME) value (Fig. 4b). We found that the RME values above 10 are to be discarded, with our results reported here having RME < 5. If higher accuracy is desired the fitting procedure should be repeated until an RME minimum is found. We also tested the Tauc-Lorentz model for the step-1 fit, which provided the relatively stable results. As for the data presented here, an increase in oxygen flow shifts ITO to drop its loss, in accordance to the Kramers-Kronig (KK) relations, increase its refractive index (real part). A higher sputtering RF bias voltage has a similar effect, however with less severity than oxygen.

Of particular interest for EOMs is a material’s ability to change its refractive index as a function of voltage bias. Early tests by Feigenbaum et al. performing ellipsometry on metal-oxide-ITO-metal heterostructures left the field with open questions [60]; the group argued that a capacitive accumulation layer is formed at the ITO-SiO_{2} interface leading to the ITOs index modulation (Fig. 8 below). However, these data showed a decreasing loss with increasing carrier concentration, which appears non-physical or at least, unlike trends found in semiconductors. Moreover, as the loss decreases with bias, the real part was found to decrease simultaneously which seemingly violates the KK
relations. It is for these non-congruent findings, that we repeated the biased ITO VASE experiments following the above-described methodology. In addition these measurements are extended into the telecommunication frequency range. Unlike Ref. [60] we find an increase of the ITO’s loss with a bias voltage, which denotes an increase in optical loss due to carrier accumulation at the ITO-oxide interface (Fig. 5). Noteworthy is the sudden index jump with voltage and range; we note an increase from about 0.006 – 0.14 for the top 5 nm of a graded ITO film. Critical point for low RME is that the top metal acting as an electrode is semitransparent. For the top metal contact a skin-depth thickness is selected for a wavelength in the NIR.

A band diagram analysis shows the band bending of the ITO layer at the ITO-SiO$_2$ interface (Fig. 5c). Note, ITO conduction band drops below the Fermi level, resulting in an accumulation of electrons for positive voltage bias at the top-metal contact. Note, this is consistent with the measurements from Ref. [20], where no modulation effect was observed for a negative voltage bias. Furthermore, the electrostatic of the MOS capacitor is primarily governed by the ‘gate’ oxide layer (i.e. thickness and dielectric constant). Naturally, a stronger (weaker) electrostatics on the ITO layer, that is, thinner (thicker) $t_{\text{gate-ox}}$, leads to an earlier (delayed) turn-on of the optical loss and hence OFF-state of an electro-absorption modulator. On the other hand a thinner $t_{\text{gate-ox}}$ also leads to a larger EOM device capacitance slowing down the 3-dB bandwidth. It is therefore interesting to note, that $t_{\text{gate-ox}}$ is a trade-off EOM device parameter that should be optimized for a specific EOM performance (i.e. low power, or high speed).

### 4.2 ITO Selective Contacts

Above we argued that in order to achieve a high modulation depth (i.e. extinction ratio) for EOMs, ITO should be deposited for a low-loss state (i.e. ON-state in EOM terminology), because raising the carrier density via a voltage bias increases optical loss shifting the EOM into the absorption (OFF) state. However, if ITO is to be electrically contacted, this poses a dilemma since ITO’s low-loss state comes with low carrier concentration, and hence high resistivity specifically for thin films below 50 nm thickness. The latter makes high-modulation speeds challenging due to the limited RC delay time of the high resistive contacts. A potential solution explored here is to deposit ITO in a low-loss state at the device area, but then selectively treat ITO at the contact area. Since micrometer-scale local annealing is challenging, we explored selective plasma treatment. This method exposes ITO to an O$_2$ plasma thus dop-

**Figure 5:** Dynamic VASE on ITO MOS structures to determine the optical loss change as a function of voltage bias. (a) Setup schematic. Note, no significant change in the results were recorded when ITO or the doped silicon substrate was contacted. Oxide = SiO$_2$ (ALD), metal = Gold. ITO and Au were sputtered. (b) ITO film extinction coefficient vs. bias voltage shows a strong modulation. Graded ITO film, results for top 5 nm. (c) Band diagram of the ITO-MOS design identifying the ITO-SiO$_2$ interface for the charge accumulation region.
ing the contact. Figure 6 summarizes 4-probe resistivity results for the various process conditions. The EOM optimized deposition method yields the expected high resistivity, but annealing and more importantly an exposure to O₂ plasma reduces the resistivity by several orders of magnitude. While these results are encouraging, a more in-depth study should be carried out to map-out this effect in detail, and we invite readers to perform this study.

4.3 Epsilon Near Zero ITO for Modulation

Recently, the field of ultra-compact EO modulation has turned some attention to the concept of ENZ materials, where the real part of permittivity is electrically tuned based on the Drude model [37]. Using free carrier density tuning can lead to a regime where the real part of index approaches zero, which in turn results in a dramatic change in the optical property of the material. Figure 3a above showed the carrier concentration condition where the ENZ effect occurs in ITO, which happens around a carrier concentration of about \(10^{21}\) cm\(^{-3}\) around a telecom frequency. It is interesting to note, that the experimental results of Ref. [20] where very close to this bias point, and hence are the first experimental evidence of this effect (even though the authors did not label it as an ENZ effect). The detailed picture is that ENZ materials impose a unique boundary condition onto electric fields (i.e. of nearby waveguides). This is a direct consequence of the continuity condition of the normal component of the electric field displacement, and leads in turn to large field enhancements inside the ENZ material relative to the adjacent layer. It is

![Figure 7](image-url)
Indium-Tin-Oxide for High-performance Electro-optic Modulation

Figure 8: (a) MOS structure with (dashed red) and without (solid green) charge accumulation [60]. From top to bottom are the structure schematics, band diagram, carrier concentration, permittivity and refractive index, respectively. (b) The complex refractive index \( n \) for the real part and \( \kappa \) for the imaginary part) in a 5 nm accumulation layer, extracted from the ellipsometry data.

5 EOM Devices based on ITO

Based on the potential for active EO modulation using ITO discussed above, this section reviews some initial experimental work demonstrating EOMs. In 2010, the Atwater group reported a method for obtaining unity-order refractive index changes in the accumulation layer of a MOS heterostructure with ITO as the active material [60]. This pioneering work demonstrated a local \( \Delta n_{\text{index}} \) of 1.5 in the ITO film using plasmonic mode confinement as shown in Fig. 8a. Under an applied field, the structure forms an accumulation layer at the dielectric-conducting oxide interface. This increased carrier concentration in the ITO lowers the permittivity due to the Drude model. Furthermore, ellipsometry was performed on the entire heterostructure, until self-consistency was achieved between the complex indices in the heterostructure and the respective permittivity for each individual material. The measurements indicated a large change in the refractive index between 25–75%, at the visible wavelengths in a 5 nm layer (Fig. 8b). For 2.5 V, at 500 nm wavelength the index change is \( \Delta n_{\text{index}} \approx 0.41 \) and at a wavelength of 800 nm the index change is \( \Delta n_{\text{index}} \approx 1.39 \) [60]. However, the work left some open and unanswered questions such as why were the Kramers–Kronig relations violated, and the physical picture of increasing optical loss with increasing carrier density (see above). Although this work did not fabricate an actual EOM, their pioneer work pointed out that modulation of the local refractive index within these structures, com-
combined with the high mode confinement achievable in plasmonic waveguides, could produce large changes in the effective index of propagating plasmonic modes, which gave ways to the future SPP EOM study as we will discuss next.

ITO has been implemented in a metal–insulator–metal (MIM) waveguide structure to demonstrate a subwavelength plasmonic modulator (Fig. 9a), for which a five percent change in the average carrier density (from $9.25 \times 10^{20}$ to $9.7 \times 10^{20}$ cm$^{-3}$) is observed [61]. The structure supports loosely bound SPP at a telecommunication wavelength of 1.55 µm owing to a MIM waveguide mode. A similar structure (Fig. 9b) based on a silicon-waveguide-integrated multilayer stack was fabricated and characterized. The logarithmic extinction ratio regarding to power up to 0.02 dB was achieved, which is much smaller than their prediction that 1 dB extinction ratio on 0.5 µm length. Moreover, there is always a trade-off between modulation depth and transmittance due to the high confinement achievable in the MIM waveguide and the high losses associated with both metal and ITO layers. However, the group showed the first AC modulation of ITO EOMs into the MHz range.

In 2012, a record-high extinction ratio of 1 dB/µm was demonstrated for a plasmonic modulator utilizing a metal-oxide-ITO stack on top of a silicon photonic waveguide (Fig. 10) [20]. Under an applied bias, the carrier concentration is changed from $1 \times 10^{19}$ cm$^{-3}$ to $6.8 \times 10^{20}$ cm$^{-3}$, and the propagation length is varied from 1.3 to 43 µm. Also, the total insertion loss comprising of both the SOI-to-MOS coupling ($-0.25$ dB/coupler) and plasmonic MOS mode propagation ($-0.14$ dB/µm) were fairly low, which could achieve a total insertion loss as low as only about $-1$ dB for a 5 µm long modulator due to the good impedance match between the SOI and MOS mode and low ohmic losses from the plasmonic MOS mode [20, 67–69].

Recently, another characteristic of the SPP EOM deploying ITO as an active material was demonstrated by the Leuthold’s team (2014); the hysteresis of the gate current and the optical transmission displays characteristics of a resistive random access memory (RRAM) (Fig. 10a) [70]. Note, the design is similar to that of Sorger’s work (2012), and hence the observed ER of 1.2 dB/µm is expected [20]. However, by gradually altering the voltage an IV hysteresis is observed which indicates the memory effect of the switch, and the authors’ claim arises from the metal pillars forming from the top metal through the gate oxide. The device demonstrates repeatability as indicated by a series of 50 consecutive measurements (Fig. 10b). Although the physical nature of the resistive switching mechanism is not fully understood, this work shows a new direction to utilize ITO as an active material.

6 Outlook and Conclusion

In addition to the experimental demonstrations briefly discussed above, there are a variety of theoretical proposals for TCO and/or ITO-based EOMs [37–39, 67]. Common to most of them is the usage of plasmonics to enhance the LMIs, resulting in small footprint and high-performance electro-optic properties.

In the context of PICs, TCO-based λ-size EOMs might be a logical next technological platform for hybrid networks on-chip. However, a variety of open questions are still outstanding in the field; (1) foremost, the debate of the nature of the index modulation of ITO is unsettled, and consists of two different viewpoints; one favours the carrier-based dispersion shift of ITO described by the Drude mode, whereas the second allocates the formation of metallic pillars that growth from the metal (typically Gold) contact through the electrical gate oxide [70]. Interestingly, the latter was reported in the supplementary in-
formation of the Feigenbaum’s original work already. In this regard, a detailed study correlating the device performance, with modelling and cross-sectional SEM images would be needed to solve this outstanding question on the modulation mechanism. (2) Based on our own ellipsometry work, we must conclude that this technique is very sensitive to the model type chosen and the fitting procedure. Thus, in order to make results comparable, detailed procedures to minimize the fitting errors should be followed. (3) The localized and selective doping ITO in a post-deposition process step to lower the contact resistance should be studied in more detail for future work.

In conclusion, TCOs, and particularly ITO, have been found to be intriguing candidates for strong refractive index modulation. The physical effect seems to point towards a strong carrier modulation of the TCO when biased near the ENZ point of ITO’s permittivity. Early studies have demonstrated electro-optic modulation devices that utilize plasmonic field confinement and these TCOs. While this research field is still ongoing, those early demonstrations have shown the potential to deliver λ-size, ultralow capacitance devices for future photonic integrated circuitry.

Acknowledgement: We acknowledge support from the Air Force Office of Scientific Research (AFOSR) under the award number FA9559-14-1-0215 and FA9559-14-1-0378.

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