# Ultracompact Electro-Absorption Modulators Based On Novel Materials

**“Epsilon-Near-Zero Material and Electro-Absorption Modulation Based on Indium-Tin-Oxide”**

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Ultracompact Electro-Absorption Modulators Based On Novel Materials(I):
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## 6. AUTHORS
Zhaolin Lu

## 7. PERFORMING ORGANIZATION NAMES AND ADDRESSES
Rochester Institute of Technology
141 Lomb Memorial Drive
Rochester, NY 14623 -5603

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The views, opinions and/or findings contained in this report are those of the author(s) and should not contrued as an official Department of the Army position, policy or decision, unless so designated by other documentation.

## 14. ABSTRACT
Indium-tin-oxide (ITO) is widely used as transparent electrode in solar cells and displays. Recent work showed that ITO and other transparent conducting oxides can work as novel metamaterials supporting highly confined surface plasmons. In this project, based on ITO we demonstrated a novel optical material with refractive index significantly smaller than unit, namely epsilon-near-zero (ENZ), which may find numerous applications. We also investigated the applications of ITO for electro-optic modulation. When applying gate voltage through electrolyte gel on an

## 15. SUBJECT TERMS

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a. REPORT
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## 17. LIMITATION OF ABSTRACT
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Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

Received

Paper

TOTAL:

Number of Papers published in peer-reviewed journals:

(b) Papers published in non-peer-reviewed journals (N/A for none)

Received

Paper

TOTAL:

Number of Papers published in non peer-reviewed journals:

(c) Presentations

Number of Presentations:  5.00

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Number of Manuscripts:

Books

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TOTAL:

Patents Submitted

Patents Awarded

Awards

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FTE Equivalent: 1.00

Total Number: 4

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Total Number: 1

Names of Under Graduate students supported
### Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

- The number of undergraduates funded by this agreement who graduated during this period: **0.00**
- The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields: **0.00**
- The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields: **0.00**
- Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale): **0.00**
- Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering: **0.00**
- The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense: **0.00**
- The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields: **0.00**

### Names of Personnel receiving masters degrees

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<tr>
<td>Mohammed Kaleem</td>
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### Names of personnel receiving PHDs

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### Names of other research staff

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Sub Contractors (DD882)
Inventions (DD882)

Scientific Progress

See the attached PDF file.

Technology Transfer
Ultracompact Electro-Absorption Modulators Based On Novel Materials (I):
“Epsilon-Near-Zero Material and Electro-Absorption Modulation Based on Indium-Tin-Oxide”

Sponsor: United States Army
(Grant No. W911NF-12-1-0451)

Final Project Report
October, 2012 - May, 2013

Zhaolin Lu
Microsystems Engineering, Kate Gleason College of Engineering
Rochester Institute of Technology
168 Lomb Memorial Drive, Rochester, NY 14623
Phone: 585-475-2106; Fax: 585-475-6879

Abstract

Indium-tin-oxide (ITO) is widely used as transparent electrode in solar cells and displays. Recent work showed that ITO and other transparent conducting oxides can work as novel metamaterials supporting highly confined surface plasmons. In this project, based on ITO we demonstrated a novel optical material with refractive index significantly smaller than unit, namely epsilon-near-zero (ENZ), which may find numerous applications. We also investigated the applications of ITO for electro-optic modulation. When applying gate voltage through electrolyte gel on an ITO-based structure, electric double layers are formed at the interfaces of ITO and electrolyte gel, which can significantly alter the optical properties of ITO. Two different structures are investigated, and modulation depth up to 38.8% has been achieved in the attenuated total reflection configuration. Preliminary result is presented for the real time response of an ITO/electrolyte gel/doped Si modulator.
This report covers the work done in support of the United States Army (Grant No. W911NF-12-1-0451). Contributors to this effort include Prof. Zhaolin Lu, graduate students Wangshi Zhao, Amanpreet Kaur, Kaifeng Shi, Riaz Haque, Runchen Zhao, Bingyin Zhao, Mohammed Kaleem, and Saptarshi Banerjee. PhD student Wangshi Zhao has graduated and taken positions in industry in US.

Most of the research results will be published in journal or conference papers. Accordingly, this report only contains milestone data of research. In brief summary, we have passed the following milestones during this year.

1. Epsilon-Near-Zero Material Based on Transparent Conducting Oxide

Research on metamaterials has shown that the dielectric constant of materials can be engineered to be almost any arbitrary value (positive, zero, or negative). One example is epsilon-near-zero (ENZ) (or low-index, index-near-zero in literature) materials, which have attracted significant interest and found applications in squeezing electromagnetic energy through very narrow channels, reflectionless sharp bends, design of matched zero-index materials, zero-index resonators, enhancing optical nonlinear effect, as well as shaping the radiation pattern. Recent works on the optical and electro-optic (EO) properties of transparent conducting oxides (TCOs) in the near infrared regime (NIR) provide a new insight into the fabrication of ENZ materials. The dielectric constant of a TCO is determined by its free carrier concentration. With a suitable doping and a fabrication process, the dielectric constant of a TCO can be engineered very close to zero.

The effect of free carriers on an optical material can be approximated by the Drude model, 
\[ \varepsilon = \varepsilon_{\infty} - \frac{\omega_p^2}{\omega(\omega + \Gamma)} \]
where \( \varepsilon_{\infty} \) is the high frequency dielectric constant, \( \omega_p \) is the plasma frequency, and \( \Gamma \) is the electron damping factor. Thus, the ENZ effect can be seen in many materials at \( \omega \approx \omega_p / \sqrt{\varepsilon_{\infty}} \). For example, tungsten at \( \lambda_0=48.4 \) nm with \( |\varepsilon(W)| =0.483 \), and aluminum at \( \lambda_0=83 \) nm with \( |\varepsilon(Al)| =0.035 \). The magnitude of their dielectric constant can be significantly smaller than 1, i.e. “epsilon-near-zero”. However, the plasma frequencies of most metals are located in the ultraviolet regime due to their high carrier concentration. To make ENZ located in the near infrared (NIR) regime, the carrier concentration should reduce to \( 10^{20} \sim 10^{22}/cm^3 \), which coincides that of TCOs. In this project, we were able to, for the first time, experimentally verify the feasibility of fabrication of TCOs as ENZ materials.

Because TCOs are non-stoichiometric compounds, their optical properties largely depend on the growth/deposition processes and annealing conditions, including the temperature and ambient gasses. To explore the TCOs for ENZ applications, we have done two experiments based on the attenuated total reflectance (ATR) method (Kretschmann configuration) as shown in Fig. 1(a).
The ITO film to be tested was sputtered on a float glass slide and pressed against an N-BK7 glass cylindrical lens (functioning as a coupling “prism”). Index matching liquid is filled between the sample and lens. The light polarization can be either TE or TM. We found that TM-light is more sensitive to the index change. Thus, all tests were performed based on TM polarization. The complex dielectric constant of the thin film at a given wavelength can be measured by curve-fitting of $R-\theta$ relation as illustrated in Fig. 1(b). The Drude dispersion relation can be established after the film is measured at different wavelengths, from 1260nm to 1620nm in our case.

We found that the carrier concentration and hence optical properties of ITO films are very sensitive to substrate temperature during RF magnetron sputtering. With different fabrication temperature values, the cross-over wavelength can shift in a large range. In particular, we investigated the dielectric constant of ITO sputtered at 350°C. The following table shows the measured complex dielectric constant at different working wavelengths. As can be seen, the minimum achieved dielectric constant is $\min\{|\varepsilon|\}=0.12$ at $\lambda=1260$nm. Note 60% of power is absorbed at $\theta=46°$ within the 25-nm ITO sample. This measurement illustrates that ENZ can really be realized by TCOs. Optimization of the processes may further reduce the magnitude of the dielectric constant at ENZ.

### Table 1. The measured dielectric constant as a function of working wavelength.

| $\lambda$ (nm) | $\text{Re}\{\varepsilon\}$ | $\text{Im}\{\varepsilon\}$ | $|\varepsilon|$ |
|----------------|-----------------|-----------------|----------------|
| 1260           | 0.0617          | 0.0998          | 0.12           |
| 1350           | -0.1004         | 0.1203          | 0.16           |
| 1440           | -0.4352         | 0.2106          | 0.48           |
| 1520           | -0.8764         | 0.1909          | 0.90           |
| 1620           | -1.6136         | 0.1936          | 1.63           |

2. ITO-based Multilayer Electro-Optical Modulation
The high carrier concentration enables guiding surface mode at the interface of ITO and dielectric materials, for example air, which has a great potential in the applications of electro-optic (EO) modulators. In a previous work done by Feigenbaum and co-works, they have experimentally showed that unity-order index change in ITO can be achieved in a metal-oxide-semiconductor (MOS) structure by a thin layer (~5nm) of voltage-induced accumulation charge formed at the interface of the ITO and SiO$_2$.

In this project, we employ a similar structure like MOS but using a new material called electrolyte gel to replace the sandwiched oxide material and form simple multilayer modulators based on ITO. Electrolyte has been used as gate insulators in organic field-effect transistors in 2005 by Nilsson et. al. The interface between a metal (or heavily-doped semiconductor) and electrolyte is of interest in most electrolyte applications, where two parallel layers of positive and negative charges called an electric double layer (EDL) are formed. Another advantage of using electrolyte as the gating material is, the device behavior can be conveniently controlled by varying the concentration of chemical compounds in the electrolyte. In our experiments, a commercially available electrolyte Redux® Gel is used to fabricate the ITO-based multilayer modulators. Sodium chloride (NaCl) is the main chemical compound in the electrolyte gel that makes it highly conductive.

![Figure 2. Illustration of proposed multilayer ITO modulators: (a) Heavily-doped Si/electrolyte gel/ITO/transparent substrate. (b) ITO/electrolyte gel/ITO. (c) Experimental setup for ATR measurement.](image)

The fabrication of the modulators starts from ITO film deposition on a transparent glass slide, by the method of physical vapor deposition (PVD) process using a (In$_2$O$_3$)$_{0.9}$(SnO$_2$)$_{0.1}$ weight percentage target at room temperature and 7.3mTorr pressure within the chamber. During deposition, argon is the only gas used. The thickness of ITO film is measured in the range of 22-25nm with a 12mins deposition time. Without the post-deposition annealing process, the sheet resistance of ITO film is measured around 3000~4000$\Omega$/$\square$. After applying a thin layer of electrolyte gel on the surface of ITO, a heavily doped (resistivity as low as 0.001-0.002$\Omega$·cm) silicon chip or another identical ITO sample with the ITO side facing the electrolyte gel is tightly pushed toward the substrate ITO to form the multilayer modulator, as shown in Fig. 2(a) and (b), respectively. In order to test the modulation performance of the two ITO-based modulators, we used an ATR setup in the Kretschmann configuration, as illustrated in Fig. 2(c).
During the experiment, the ITO-based modulators were mounted on the back of the hemicylindrical BK7 prism. To avoid a thin air gap between the prism and the modulator, a BK7 index matching liquid is applied between them. In all the experiments, the reflectance of the modulators was measured in a sequence of: (1) without externally applied voltage, (2) with an externally applied voltage $V_p$, and (3) with an externally applied voltage which has reversed polarity but the same magnitude. We firstly focused on a simple structure, as shown in Fig. 2(a), which includes only one active ITO layer. The measured reflectance of the modulator with different applied voltages, as a function of $\theta_1$ with a $p$-polarized incident light beam at $\lambda=1520$nm is shown in Fig. 3. With an applied voltage, an EDL is formed at the interface of the electrolyte gel and the ITO. Here we assumed there is a 5nm-thick depletion layer (with positive voltage $V_p=10V$, illustrated in Fig. 3), or accumulation layer (with negative voltage $V_p=-10V$) formed in ITO at the interface. The modulation depth, $M(\theta_1)$, as a function of angle $\theta_1$ at a given wavelength can be defined as:

$$M(\theta_1) = \left| \frac{R_{V_p} - R_{-V_p}}{R_0} \right|,$$

where $R_0$ is the experimentally measured reflectance without applied voltage, $|R_{V_p} - R_{-V_p}|$ is the magnitude of the difference of the two reflectance with applied voltages. From Fig. 3, the modulation depth at a specific angle of $\theta_1=70^\circ$ can be calculated as $M(70^\circ)=20.7\%$. We attribute the modulation to the change of the free carrier concentration in either the 5nm-thick depletion layer or accumulation layer in ITO at the interface, which is assisted by the redistribution of the ions in electrolyte gel induced by the applied voltage. The charge distribution at the interface and electric potential ($V$) at a stable status with the applied voltage is schematic illustrated in the inset of Fig. 3.

The measured reflectance of the ITO modulator is numerically fitted by calculating the reflectance through the multilayer structure based on the transfer matrix method (TMM). In this experiment, the film stack can be treated as BK7/ITO/electrolyte gel/heavily-doped Si. In order to simplify the fitting, we used the permittivity of the 5nm depletion layer or accumulation layer in ITO (both real and imaginary parts), and the thickness of the electrolyte gel as the variables to
model the measured reflectance data. The permittivity of the electrolyte gel is determined by a separate ATR measurement, which is \( \varepsilon_{\text{gel}} \approx 1.80 \) at \( \lambda = 1520 \text{nm} \). In the numerical fitting, the BK7 medium has a refractive index of \( n = 1.50 \) at \( \lambda = 1520 \text{nm} \). The result turns out that the dielectric constant of ITO film \( \varepsilon_{\text{ITO}} = 3.7 + j1.0 \) at \( \lambda = 1520 \text{nm} \) without applied voltage, and the thickness of the electrolyte gel \( t_{\text{gel}} \approx 5.22 \mu\text{m} \). With an applied voltage of \( V_p = 10 \text{V} \), the permittivity of the 5nm depletion layer of ITO is fitted as \( \varepsilon_{\text{ITO-dep}} = 4.23 + j0.5 \). When the polarity is reversed, the permittivity of the 5nm accumulation layer of ITO is \( \varepsilon_{\text{ITO-acc}} = -0.47 + j4.9 \). Combining Eq. (1) and (2), the carrier concentration in ITO can be estimated as: \( N(0 \text{V}) = 9.82 \times 10^{20} \text{cm}^{-3} \), \( N(10 \text{V}) = 5.34 \times 10^{20} \text{cm}^{-3} \) for the 5nm depletion layer, and \( N(-10 \text{V}) = 4.75 \times 10^{21} \text{cm}^{-3} \) for the 5nm accumulation layer, assuming \( \varepsilon_\infty = 4.55 \) for all the conditions.

The switching speed of the modulator is directly influenced by the relaxation of the ions in the electrolyte gel. For the modulator structure shown in Fig. 2(a), another experiment is carried out to test this relaxation effect, where two rectangular voltage pulses are excited by a DC power supply. The first pulse is 30s wide with a height of +20V applied on ITO, after 120s the second pulse is excited with the same width but an opposite polarity, as illustrated by the blue curve in Fig. 4. The incident light beam is at \( \lambda = 1310 \text{nm} \) with p-polarization.

The response of the ITO-based modulator to the applied voltage pulses as a function of time is measured at a specific angle \( \theta_1 = 65^\circ \) and the reflectance is shown in Fig. 4. When there is no applied voltage, the reflectance \( R \) is at its baseline level. When the voltage pulses are applied on the ITO (at time \( t_1 \) and \( t_2 \)), EDLs are immediately formed at the interface of the electrolyte gel/ITO. The induced change of the reflectance is similar as we observed in the first experiment shown in Fig. 3, and the modulation depth is around 12.4%. When both the rectangular pulses vanished, the reflectance of the modulator either decreases or increases toward its baseline level, respectively. However, it is clearly seen that for both the situations, the modulator needs a long time to recover to its baseline level. With the positive voltage pulse, the recovery time is even longer. The phenomenon could be caused by the different mobility of the major carriers in the 5nm region in ITO at the interface. The response of the ITO modulator under high-frequency
AC signals needs further investigation. Both the ions in electrolyte gel and the free carriers in ITO needed to form the electric double layer will probably limit its applications at high frequency.

Figure 5. Reflectance as a function of angle for the ITO/electrolyte gel/ITO modulator with different applied voltages. Inset: illustration of the modulator.

The modulation depth can be further enhanced when the electrolyte gel sandwiched between two identical ITO samples. To make the measurement result accurate, we used a glass deflector on the other side of the modulator, to avoid any light reflected back and collected by the detector. When applying a voltage to the double-ITO modulator, there will be an EDL formed at each electrolyte gel/ITO interface, as shown in Fig. 5. The double EDLs result a higher modulation depth, which is $M(70^\circ)=38.8\%$, at a specific angle of $\theta_1=70^\circ$ with s-polarized light at $\lambda=1520$nm. This result also shows that the ITO-based multilayer modulator is not sensitive to the polarization of the incident light beam.

To summarize, we have experimentally demonstrated (1) ENZ material based on ITO, and (2) modulation effect with easily fabricated multilayer modulators based on ITO. The modulation depth is around 21.7% with only one ITO active layer, and this result can be further enhanced to 38.8%, where there are two ITO active layers. The real time response of the ITO-based modulator needs further investigation, which is determined by the relaxation of the ions in electrolyte gel and the free carriers in ITO.

3. List of Education activities:

(1) Four PhD students and four master students have been supported by this program to some degree.

(2) The research results have been incorporated in two courses: Optoelectronics and Integrated Optics.

(3) Two lectures were given in the Introduction of Microsystems and Nanotechnology based on the results of this program.

4. Training and Development:
The students involved in this research have been exposed to an R&D environment and participate in technology development while learning advanced techniques. These include: Nanophotonic and Electromagnetic Device design and simulation, Nanofabrication, and Characterization of nanoplasmonic devices.

Two students have been sent to NSF Nanofabriation facilities at Cornell.

The experience the students obtained has helped their future work in job market.

5. List of Contributions:
(1) The first demonstration ITO as epsilon-near-zero materials for near-infrared applications.
(2) Demonstration of electro-optic modulation based on ITO-electrolyte structures.

6. List of Publications for this Effort

Journal Papers

Conference Papers/Presentations