Optical nonlinearity of transparent conducting oxides - more metallic than realized

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Abstract

Transparent conducting oxides (TCOs) have recently been shown to have a remarkably strong nonlinear optical response. We show that the popular ascription of their nonlinearity to the temperature-dependence of the plasma frequency is only a partial description of their response to intense illumination. Specifically, we show that the increase of the electron collision rate upon illumination and consequent heating contributes to the permittivity in a manner quantitatively comparable and sometimes even

superior to the contribution of the temperature-dependent plasma frequency. This behavior makes the optical nonlinearity of TCOs more similar to that of noble metals than realized so far, and in some aspects, this behaviour is qualitatively opposite compared to that assumed so far.

Keywords: Transparent Conducting Oxides, epsilon-near Zero materials, nonlinear optics, intensity-dependent permittivity changes, thermo-optic nonlinearities

Introduction

Transparent conducting oxides (TCOs) are highly-doped semiconductors which are popular within the micro-electronics industry due to their CMOS-compatibility and their use as transparent electrodes; frequently studied materials include Indium Tin Oxide,[1] Aluminum-doped Zinc Oxide,[2] Cadmium oxide,[3] Copper sulfide[4] etc.. From the optical point of view, they are frequently thought of as low electron density Drude (LEDD) metals,[5–9] i.e., their permittivity is given by

$$\epsilon(\omega) \;=\; 1+\chi_{inter}(\omega)+\chi_{intra}(\omega), \qquad \chi_{intra}(\omega)=-\frac{\omega_p^2}{\omega^2+i\omega\eta}, \qquad \omega_p^2=\frac{e^2N_e}{m_e^*\epsilon_0}, \quad (1)$$

where the plasma frequency ω_p is typically found within the visible spectral range, rather than in the soft UV, as for noble metals. This numeclature stems from the much lower conduction band electron density N_e (typically, by 1-2 orders of magnitude) and the high frequency threshold for interband transitions in TCOs ($\approx$ 4.5 eV), which enables approximating $1+\chi_{inter}(\omega)$ by the constant ϵ_∞ for near-infrared (IR) frequencies.

A key feature in the optical response of TCOs / LEDD metals is the convenient spectral position of their epsilon-near-zero (ENZ) spectral regime, i.e., the frequency range at which the material switches between being plasmonic to dielectric; this occurs indeed in the near-IR at $\omega_p/\sqrt{\epsilon_\infty}\approx\omega_p/2$. The ENZ spectral regime attracted ample attention due to associated

unique opportunities to manipulate wave propagation, since phase distortions in this regime are minimal.[10–16]

More recently, TCOs/ LEDD metals emerged as promising nonlinear optical materials.[7,17–29] Initially, the strong optical nonlinearity they exhibited in experiments was also associated with operation in the near-IR ENZ frequency regime. This implies on a divergence of the *relative* permittivity change, which is the quantity that determines the strength of the nonlinear optical effects;[17,30–32] this explanation provided a *qualitative* match to the unprecedented observation of intensity-dependent permittivity changes of hundreds of percent.[17,18,20,22,26,28,29]

However, due to the electron collisions, represented by η, TCOs / LEDD metals are not truly transparent. Indeed, the imaginary part of their permittivity is small in the visible range, but in the ENZ spectral regime it does not vanish, with typical values not lower than $\epsilon'' \sim 0.3$.[33] Accordingly, the local field, hence nonlinear response, cannot diverge at the ENZ point, and instead, a resonance emerges, with moderate levels of local field enhancements.

In this context, a complementary explanation to the strong optical (near-IR, hence, intraband) nonlinearity ascribed it to the non-parabolicity of the conduction band.[1,6,34] This effect causes electrons excited to high momentum/energy states to experience a different band curvature, hence, a different effective mass, m_e^*. Under the assumption that the conduction band electron subsystem undergoes a particularly rapid thermalization, the nonlinear optical response associated with the non-parabolicity was described by an electron temperature - dependent plasma frequency, $\omega_p = \omega_p(T_e)$, where T_e is the electron temperature. More recently, this model was put in the general framework of a non-perturbative description of the nonlinearity,[35] where the optical response associated with the conduction band electrons was shown to gradually weaken upon illumination, i.e., to have a saturable-like response,[28,35] $\chi_{intra} \rightarrow \chi_{intra}/(1 + I/I_{sat})$. Remarkably, although this behaviour emerges from a system at thermal equilibrium, it is similar to that of a true saturable absorber, a system which is as far as possible from thermal equilibrium due to a maximal inversion of its electron population.

The rapid thermalization which is at the heart of this model must stem from frequent electron-electron ($e-e$) collisions. Indeed, in Ref. [8,9], a microscopic *non-thermal* rigorous model for the conduction electron dynamics showed that the conduction electron subsystem in LEDD metals (specifically, in Indium Tin Oxide, ITO) thermalizes much faster than in noble metals. This fast electron collision rate is attributed to weaker screening effects arising from the low electron density and to the enhanced density of states resulting from the non-parabolic conduction band in LEDD metals.[8] Frequent collisions occur also with various phonons and impurities.[8,9] The sum of these collision rates (Matthiessen rule) can reach the level of a few femtoseconds (see Fig. 1(a)).

The microscopic rigorous model also provided the distribution and dynamics of the conduction electrons, and demonstrated that a thermal model of the permittivity is justified even for pulses as short as a few 10's of femtoseconds. It also showed that the electron temperature can reach extremely high values, even exceeding the Fermi temperature ($\sim 10,000$K). The predictions of the model of Ref. [8,9] were the first to reach qualitative *and quantitative* agreement with scattering measurements from an ITO layer.[17,26,28]

The goal of this Viewpoint is to highlight an implication of the success of the microscopic rigorous model which seems to have been overlooked so far: since all the different electron collision rates naturally increase upon heating, the temperature-dependence of the total collision rate, $\eta = \eta(T_e)$, yields a large contribution to the optical nonlinearity of LEDD metals. This effect was accounted for in Ref. [28,36] using a qualitatively similar yet simpler *thermal* model; however, both works predicted a rather weak temperature dependence of η, whereas our quantitatively successful model implies that the strong sensitivity of η to the temperature, and the extremely high temperatures that can be reached gives rise to a nonlinearity which can become as important as that of the nonlinearity so far associated with the temperature-dependence of the plasma frequency $\omega_p = \omega_p(T_e)$.

To demonstrate this point, we show an example in which in addition to the rapid $e-e$ collisions, there is also a high density of impurities (or equivalently, surface roughness). Fig. 1(b)

shows that the contribution to the real part of the permittivity (ϵ') by the temperature-dependent collision rate is qualitatively and quantitatively comparable to that of the strong temperature dependence of the plasma frequency. This happens because the relatively fast collision rate in ITO is only one order of magnitude smaller than the typical operating near-IR frequencies at room temperature, and because at elevated electron temperatures, it may even be comparable to it (see Fig. 1(a)). This contrasts the situation in noble metals where the collision rate is two orders of magnitude smaller than the operating frequency. The meaning of these results is that it is easy to confuse the contributions of ω_p and η to the nonlinearity in experimental data.

In addition, the plasma frequency and the (total) electron collision rate have opposing effects on the imaginary part of the permittivity, ϵ'', see Fig. 1(c). In particular, the strong increase in η can be the dominant effect at electron temperatures of up to a few thousands K, giving rise to a net increase of ϵ''. From the physics point of view, this behaviour makes the intensity-dependence of the imaginary part of the permittivity of TCOs/LEDD metals similar to that of the intraband thermal nonlinearity of noble metals.[32,37–39] This also means that under these conditions, the change of ϵ'' upon heating is the opposite to that predicted by the "saturation"-like model of Khurgin and Kinsey.[35,40] Nevertheless, for even higher temperatures, the decreasing plasma frequency may become the dominant effect on the change of ϵ'', which thus decreases upon further heating. Under these conditions, the permittivity follows qualitatively the "saturation" model of Khurgin and Kinsey.[34,35] Unfortunately, since the relative changes to the imaginary part of the permittivity are smaller than those of the real part, it is challenging to observe this behaviour in experimental data. Thus, our finding should motivate experimental efforts to isolate the absorption and its temperature-dependence (as in Ref. [18]), towards a resolution of the magnitude of the two contributions to the thermal nonlinearity.

The observation highlighted in this Viewpoint is generic to TCOs / LEDD metals, yet, it is quantitatively sensitive to the exact values of the material parameters and to the details of

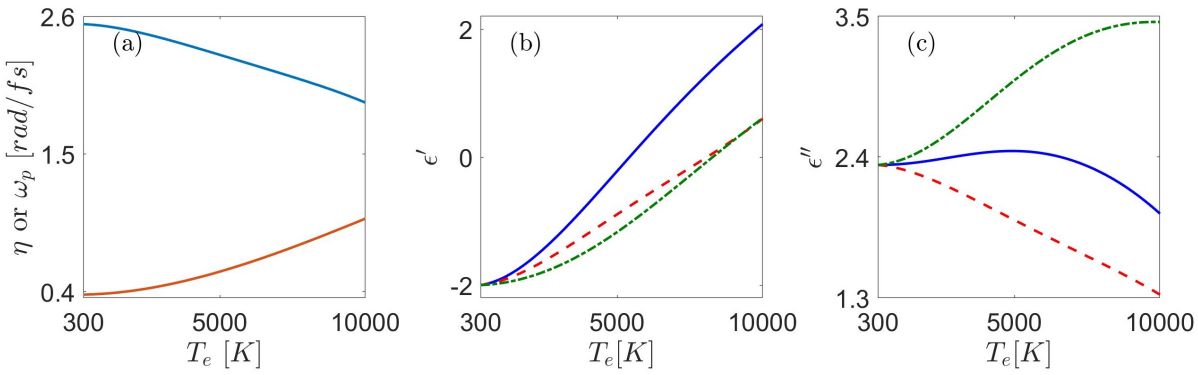

Figure 1: (a) Plasma frequency ω_p (blue) and damping rate η (red) as a function of the electron temperature. (b) Real and (c) imaginary parts of the permittivity as function of T_e at $\hbar\omega \approx 0.75$ eV. The complete model (where $\omega_p = \omega_p(T_e)$ and $\eta = \eta(T_e)$; blue solid line) is compared to the more popular model[35,40] ($\omega_p = \omega_p(T_e)$ and constant η; dashed red line), as well as to a model where only the collision rate is temperature-dependent (dash-dotted green line). Parameters are taken from Ref. [1].

the various collision mechanisms, which may vary significantly from one sample to another, as well as from one TCO to another. For example, for a stochiometric alloy, the effects of the impurities will be reduced, and the analysis of Ref. [34,35] will provide a better match to observations. Conversely, lattice heating (not accounted for here) would make the η growth stronger; a proper account for it requires a specification of a structure and a self-consistent solution of the electric field, permittivity and electron distribution, as in Ref. [9]. Further complexity is expected with variations in the non-parabolicity, effective mass etc..

Our analysis means that the quantitative claims on $\omega_p(T_e)$ obtained in previous work might need to be rescaled. It also serves as a basis for future quantitative modelling of TCO intensity-dependent nonlinearities and even for distorted scaling of harmonic generation induced by massive heating-induced permittivity changes.[23,41,42] Our analysis further emphasizes the importance of absorption to the ultrafast optical nonlinearity of TCOs/ LEDD metals, as well as its thermal nature - it is not a Kerr nor a saturable nonlinearity which are proportional to the instantaneous value of the electric field, but rather a delayed nonlinear response that is accumulated upon absorption (and also decays at a rate slower than that of the electric field), as pointed out already in Ref. [6]. In that sense, the similarity

to the intraband optical nonlinearity of noble metals[32,37–39] is further emphasized.

Finally, we note that the nonlinear optical response of TCOs to even shorter pulses, down to single cycle durations, may exhibit further complexity, which is the subject of ongoing investigations.[43,44] Resolution of these requires more detailed modelling of the interband contribution, and is the key to understanding the ability of TCOs/LEDD metals to withstand the high fluences associated with illumination levels required for realization of photonic time crystals.[45,46]

Acknowledgement

Views expressed in this Viewpoint are those of the author and not necessarily the views of the ACS. The authors thank M. Scalora, N. Kinsey and J. Khurgin for their careful reading and many useful comments.

Funding Sources

I.W.U. was funded by the Guangdong Natural Science Foundation (Grants No. 2024A1515011457). N.H. and Y.S. were partially funded by a Lower-Saxony - Israel collaboration grant no. 76251-99-7/20 (ZN 3637) as well as an Israel Science Foundation (ISF) grant (340/2020).

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