Realizing remarkable tunability in optical properties without sacrificing speed is critical to obtain all optical ultrafast devices. In this work, we investigate the ultrafast temporal behavior of optically tunable epsilon-near-zero (ENZ) metamaterials, operating in the visible spectral range. To perform this the ultrafast dynamics of the hot electrons is acquired by femtosecond pump-probe spectroscopy and studied based on two-temperature model (2TM). We show that pumping with femtosecond pulses changes the effective permittivity of the metamaterial more than 400%. This significant modulation is more pronounced in ENZ region and we confirm this by the 2TM. The realized ultrafast modulation in effective permittivity, along with the ultrashort relaxation time of 3.3 ps, opens a new avenue towards ultrafast photonic applications.

Hot Electron Dynamics in Ultrafast Multilayer Epsilon-Near-Zero Metamaterials

Alireza R. Rashed,¹ Bilge Can Yildiz,¹ Surya R. Ayyagari,¹ and Humeyra Caglayan¹∗

¹Faculty of Engineering and Natural Sciences, Photonics, Tampere University, 33720 Tampere, Finland
(Dated: March 11, 2020)

Research on optical metamaterials has seen an impressive progress during the past decade. They have created not only a better understanding of the light-matter interaction, but also a broad range of applications [1–3]. Among those, ENZ (epsilon-near-zero) metamaterials have become a topic of interest, because the interaction of the electromagnetic fields with such media generates particular optical properties [4–6]. The unique and fascinating features of ENZ structures enable the realization of advanced optical applications such as directional light enhancement [7,8], coherent perfect absorption [9], radiation pattern tailoring [10], nonlinear fast optical switching [11], and index of refraction sensing [12].

The ability to tune the electromagnetic properties is crucial to develop advanced ultrafast photonic devices. The electrically tunable optical properties of transparent conducting oxide (TCO) based structures are well studied in several works [13–17]. Furthermore, recent studies show that optical pumping can change drastically the optical properties of TCOs close to their ENZ wavelengths, in NIR (near-infrared) spectral range [18–21]. The large optically induced modification in the dielectric constant, in combination with the ultrashort response time makes TCOs a promising candidate to realize high speed tunable devices, operating near the telecommunication wavelength. To bring the advantages and broad range of applications from NIR spectral range to visible, Papadakis et al. have proposed a TCO based metamaterial to modify the effective optical parameters [22]. However, the performance of this device, which works by field-effect gating, is hindered due to the design complexity and low modulation speed for visible range applications.

On the other hand, vanishing permittivity of hyperbolic metamaterials, with metal and dielectric multilayers at particular wavelengths of visible and infrared spectral ranges, make them a promising alternative to realize ENZ metamaterials [23–25]. By changing the material composition of such metamaterials, it is possible to modify the hyperbolic dispersion and consequently the ENZ wavelength [26–27]. In a recent study, laser-induced tunability in the optical properties of a layered hyperbolic metamaterial is investigated in the NIR range [28]. However, realizing a full optical tunable ENZ metamaterial with a simple design and ultrafast response for visible range applications has remained challenging.

To control efficiently the optical ultrafast tuning of an ENZ metamaterial, it is critical to identify the temporal electron dynamics. The temporal electron dynamics and the nonlinear femtosecond response of metallic nanocrystals and metal thin films have been investigated using femtosecond pump-probe spectroscopy [29–32]. The temporal nonlinear response of excited systems with free electron distributions can be studied by two-temperature model (2TM) [32–34]. The adoption of this model to ENZ systems helps to reveal the hidden aspects of the observed modulation in effective permittivity of the excited system. In a recent work, free electron dynamics of a 310 nm thick indium-tin oxide (ITO) film pumped at $\lambda_{ENZ} = 1240$ nm, is studied using the 2TM [19]. The nonlinear behavior in the laser-induced structure is attributed to the thermalization of the conduction-band electrons. However, the temporal nonlinear dynamics related to the relaxation of hot electrons in an optically excited multilayer ENZ metamaterial has remained unrevealed so far, which is one of the focuses of this study.

Here, we present a tunable ENZ metamaterial based on a simple design of multilayer metal-dielectric nanos-structure. The proper composition of gold (Au) and Titanium dioxide (TiO$_2$) thin films provides an ENZ response in the visible spectral range. We investigate the modulation of the effective permittivity of the laser-induced ENZ metamaterial based on the hot electron generation effect. We quantitatively analyze for the first time the ultrafast temporal behavior of electron and lattice temperatures of multilayer ENZ metamaterials by 2TM. We show that the ultrafast relaxation of the excited metamaterial is determined by the electron-phonon interactions. The observed maximum change in the permittivity is confirmed by the 2TM. Our investigations reveals the potential of the metamaterials for ultrafast tunable optical devices in

*humeyra.caglayan@tuni.fi
A multilayer metamaterial structure composed of 16 nm of Au and 32 nm of TiO$_2$ is fabricated on a fused silica (SiO$_2$) substrate (Fig. 1(a)). Four pairs of metal-dielectric stack is alternatively deposited using electron-beam evaporator. The SEM image presented in Fig. 1(b) shows the cross-section view of the fabricated sample.

A confocal microscope in combination with a CCD spectrometer, operating in visible spectral range, is used for acquiring the linear reflectance ($R_{lin}$) and transmittance ($T_{lin}$) of the fabricated sample. In addition to the measurements, these parameters are calculated by using transfer matrix method (TMM), and simulated by Numerical FDTD Solutions. In these calculations, Drude-Lorentz model is used for Au layer refractive index and the dispersion values for TiO$_2$ is adopted from reference [35]. The experimental and simulation results show an excellent agreement (Fig. 1(c)). Figure 1(d) depicts the calculated effective real and imaginary parts of the parallel complex permittivity.

In order to investigate the optical tunability of the designed metamaterial, we have measured the reactivity, $\Delta R/R_{lin}$, and transmittivity, $\Delta T/T_{lin}$, by pump-probe spectroscopy. Here, $\Delta R = R_{pump} - R_{lin}$ and $\Delta T = T_{pump} - T_{lin}$, where $R_{lin}$ and $T_{lin}$ are the reflectance and transmittance in the presence of weak probe pulses (i.e., linear response), while $T_{pump}$ and $T_{pump}$ are the reflectance and transmittance in the presence of intense pump pulses. The pump signal is fixed at a single wavelength with a pulse duration of 120 fs, while the broadband probe beam (500 nm to 750 nm) is varied temporally with respect to the pump beam by using a precise delay line. We have gradually increased the pump signal wavelength from 420 nm to 500 nm with the step size of 10 nm at a constant power in order to identify the maximum modification in the transmitted ($\Delta T/T_{lin}$) and reflected ($\Delta R/R_{lin}$) probe signals. The maximum change in optical constants is observed at $\lambda_{pump}=470$ nm. As seen in Fig. 1(c), this wavelength corresponds to the maximum absorbance of the multilayer nanostructure, in which both transmittance and reflectance reach to their minimum values below the ENZ wavelength.

Furthermore, the probe pulses are delayed with respect to the pump pulses to investigate the ultrafast temporal dynamics of the designed system. Figure 2(a) and (b) show the change in the reflectance and transmittance of the metamaterial, pumped at fluence of $F=1.45$ mJ/cm$^2$, with respect to the time delay. The modification in the optical response reaches to a maximum few hundred femtoseconds after the pump pulse. Figure 2(c) and (d) show the spectra of reflectivity and transmittivity as function of probe wavelength at four different fluence values of 0.54 mJ/cm$^2$, 1.45 mJ/cm$^2$, 1.83 mJ/cm$^2$ and 2.47 mJ/cm$^2$. The intensity of the probe beam changes gradually, as the pump fluence increases. At sufficient intensities of the pump beam, a significant modification in both reflectivity and transmittivity is observed. In Fig. 2(c) (2(d)), the negative sign of reflectivity (transmittivity) corresponds to transient absorption, whereas a positive sign corresponds to transient bleach. At the wavelengths below $\sim 660$ nm, as a consequence of simultaneous optically
induced reduction in reflectivity and transmittivity, the absorbance of the metamaterial increases. However, for the spectral range beyond 660 nm, ΔT/T_{lin} goes above zero, while ΔR/R_{lin} remains at negative values. Considering that for the bleach region of the transmissivity, the linear transmittance is almost zero, further reduction of this parameter is not allowed. Consequently, the negative values of reflectivity results reduction in the absorbance.

The pump-induced complex ε_{eff} of the designed metamaterial can be extracted by applying inverse TMM over the experimentally acquired reflectivity and transmissivity, and the R_{lin} and T_{lin}. Although the modification of the complex permittivity is observed for a broad spectral range of the probe beam, as shown later, this modification is much more pronounced in the ENZ region, as the occurred nonlinear effects are stronger in that region. Figure 3(a) shows the modification of the ENZ wavelength as a function of the incident pump fluence. We observe that the pump pulse can induce 10 nm of red-shift in the ENZ wavelength, with respect to the linear case (605 nm). The reduction in the pump-induced plasma frequency around ENZ wavelength is resulted from the increase in the free-electrons of the metamaterial. In Fig. 3(b), we extract the real and imaginary parts of the pump-induced permittivity at 610 nm, as the transition from dielectric to metallic regime is pronounced around this wavelength. The total increase of Δε_{eff,real} ≈ 0.16 (420 % change) is evident in Fig. 3(b), compared to linear regime.

FIG. 3. (a) The tuning of the ENZ wavelength as a function of pump power. (b) Modulation of the real and imaginary parts of the pump-induced permittivity around ENZ wavelength. λ_{pump} and λ_{probe} are considered as 470 nm and 610 nm, respectively.

The pump pulse creates energetic non-equilibrium electrons in the conduction band, which then thermalize in few hundred femtoseconds adopting a new Fermi-Dirac distribution with a well-defined temperature [39]. Pump-induced changes in the permittivity are attributed to these modifications in the energy distribution, also known as hot electron generation [38, 39]. The ultrafast relaxation of the thermalized electrons occurs at a rate determined dominantly by the electron-phonon coupling over a timescale of a few picoseconds. To understand the observed ultrafast temporal behavior of the permittivity modulation, we model the ENZ metamaterial using a phenomenological 2TM [40]. We define distinct temperatu-
in the permittivity. Therefore one can parametrize experimental $\Delta \varepsilon_{\text{eff,real}}$ with the electron and lattice temperatures, i.e., $\Delta \varepsilon(T_e, T_l) = \Delta \varepsilon(T_e) + \Delta \varepsilon(T_l)$. As shown in Fig. 4(a), the permittivity of the metamaterial experiences a rapid increase, reaching its maximum almost simultaneously with the pump. We correlate this maximum $\Delta \varepsilon_{\text{eff,real}}$ with the theoretical $T_e$ maximum, assuming $T_l$ is unperturbed at this particular time delay. This is a legitimate assumption, as the change in the lattice temperature is at least two orders of magnitude less than the change in the electron temperature. Similarly, one can correlate the steady-state temperature of the lattice with the experimental $\Delta \varepsilon_{\text{eff,real}}$ when the fast transient component has decayed away (i.e., after 6-8 ps). More specifically, we solve the 2TM equations for a guessed $G$ to find maxima of $T_e$ and steady-state values of $T_l$, and match them with the experimental maxima and steady-state values of $\Delta \varepsilon_{\text{eff,real}}$ at each fluence. This matching allows us to obtain the parametrized effective permittivity change as a function of $T_e$ and $T_l$, as follows,

$$\Delta \varepsilon(T_e, T_l) = A_0 + A_1 T_e + A_2 T_e^2 + B_0 + B_1 T_l$$  \hspace{1cm} (4)$$

where the coefficients, $A_i$ and $B_i$ are determined from the fit functions of the correlated $\Delta \varepsilon_{\text{eff,real}}$ and temperatures. We are now able to compare the experimental and parameterized $\Delta \varepsilon_{\text{eff,real}}$ with different guessed $G$ values. We start with the electron-phonon coupling constant of Au, $G = 3 \times 10^{16}$ W/(m$^2$K) \cite{1} and change it step-wisely to estimate the one for the studied metamaterial. Figure 4(b) shows the comparison of the experimental $\Delta \varepsilon_{\text{eff,real}}$ (blue line) measured at $\lambda = 590$ nm, for the fluence, $F = 2.47$ mJ/cm$^2$, with the parametrized $\Delta \varepsilon_{\text{eff,real}}$ for different guessed $G$ values.

The solutions of 2TM can be used to obtain the time dependence of $T_l$ and $T_e$. The electron dynamics is governed mainly by electronelectron, electron-surface scatterings and electron-phonon interactions. Figure 5(a) shows the calculated exchange of temperature between the thermalized electrons and the lattice based on the estimated electron-phonon coupling constant. The process lasts for few picoseconds, until the hot electrons and cold lattice phonons reach to an equilibrium. Estimating the electron-phonon coupling constants for the metamaterial next, we apply 2TM in a specific spectral range. Figure 5(b) shows the maximum electron temperatures reached at different wavelengths for $F = 1.83$ mJ/cm$^2$. The spectral behaviour of the maximum electron temperature displays a peak in the ENZ region, due to the much more pronounced nonlinearity of the pumped metamaterial in this region. Thermalization and cooling down of the hot electrons are the two main processes which determine the nonlinear transient response of an excited material with femtosecond pulses. The temporal response of the system provides the information regarding the rise and the relaxation time of the excited system. Figure 5(c) shows the analyzed ultrafast temporal response of the multilayer ENZ metamaterial to femtosecond pulses for the fluence value of $F = 1.83$ mJ/cm$^2$, based on the modification of the effective permittivity at 610 nm. The acquired 250 fs rise time in combination with 3.3 ps relaxation time are evidences for the ultrafast performance of our tunable ENZ metamaterial.

![FIG. 5. (a) Calculated electron dynamics by 2TM. (b) The calculated maximum electron temperatures at different wavelengths for the pump fluence of $F = 1.83$ mJ/cm$^2$. (c) The ultrafast modification in the effective permittivity of the ENZ metamaterial. Two horizontal dashed lines show 10% and 90% of the maximum modification of the permittivity for calculating the rise time and relaxation (fall) time of the excited system.](image-url)
short rise and relaxation times allows the ultrafast functionality for the tunable system with the modulation speed of at least 0.25 THz. The reported results prove the possibility to realize full optical ultrafast signal processing in the visible spectral range this can pave the way for the development of practical and cost-effective optical devices.

ACKNOWLEDGMENTS

We acknowledge the financial support of the European Research Council (Starting Grant project aQUARiUM; Agreement No. 802986), Academy of Finland Flagship Programme, (PREIN), (320165). We thank Prof. Nikolai Tkachenko for his help to perform ultrafast pump-probe measurements.

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