# Ferroelectric metamaterials: towards a refractive index control

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**Abstract**

Recently the fabrication of metamaterials with tunable refractive index has caught the attention of the scientific community. In a tunable metamaterial the wavelength at which the negative refractive index occurs can be changed by applying an external stimulus. Here we report on the use of lead zirconate titanate (PZT) - a well known electro-optic ceramic - to realize electrically tunability of fishnet metamaterials. Thin PZT films were deposited on ITO-coated soda-lime glass and the crystallographic, surface morphology and ferroelectric properties were investigated, as well as the electro-optical properties via spectroscopy ellipsometry. An example of "fish-net" nanostructured metamaterial comprising PZT is also reported.

## 1. Introduction

Recently, the fabrication and optimization of nano-hole arrays in noble metal layers has attracted much attention [1-2]. In particular nano-hole arrays in metal-dielectric-metal stacks, also known as "fish-net" type structures, are nowadays the best candidates to accomplish some suggestive physical phenomena like negative refractive index, super-lensing and invisibility cloaks in the visible optical range [3-4]. Electric tuneability of the negative refractive index wavelength is theoretically foreseen to be possible by use of dielectrics with electro-optical properties such as Lead Zirconate Titanate (PZT) The ferroelectric and dielectric properties of PZT bulk ceramics and micron thin films have been extensively studied, while there are really few reports on electro-optical properties of very thin PZT films [5]. Here we report our preliminary results on the preparation and characterization of ultrathin (down to ca 50 nm) PZT films as electro-optical material usable in the nanofabrication of "fish-net" type Au/PZT/Au meta-material stacks. Sol gel PZT thin films were deposited on ITO-coated soda-lime glass and the material properties were determined. Crystallographic phases, surface morphology and ferroelectric properties were investigated, as well as the electro-optical properties. An example of "fish-net" nanostructured metamaterial comprising PZT is also reported. Nano-hole arrays have been realized on Au(30 nm)-PZT(40nm)-Au(40nm)/ITO stacks by means of direct ion milling with FIB using a FEI Nova 600i instrument. Finite element method (FEM) simulations were used to design the structures and to foresee their optical behaviour. FEM simulations have been used to design the optimized system and the prepared samples have been analyzed by means of transmittance and reflectance measurements in order to verify the presence of the resonance.

## 2. PZT film deposition and material characterization

Sol-gel PZT thin films were prepared on ITO/Glass substrate by following a procedures previously described [6]. An example of XRD, hysteresis loops and SEM micrograph obtained is reported in figure 1. Figure 1D reports preliminary results on ellipsometric measurements on Au/PZT/ITO/Glass structure with an applied voltage. As can be observed a small variation of n is present , around $\Delta n$=0,002 on average.

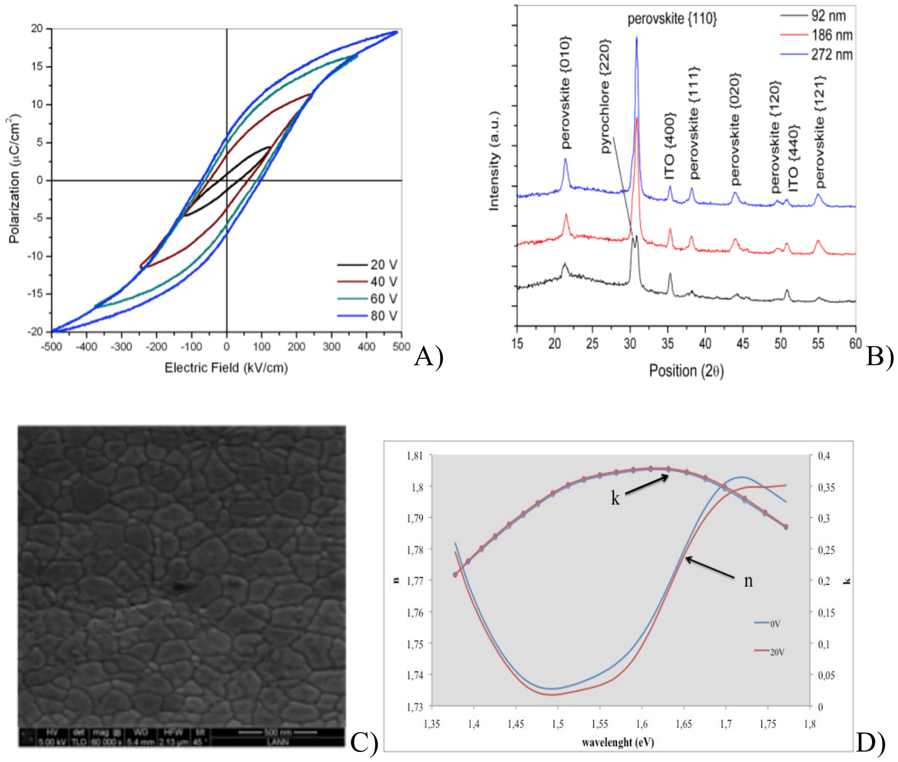


Figure 1. Example of PZT thin film characterization. A) Hysteresis loops at different polarization voltages; B) XRD spectrum of films with different thickness; C) SEM micrograph of PZT surface; D) ellipsometric measurements on Au/PZT/ITO/Glass structure on different applied voltage.

## 3. Fish-net metamaterial fabrication

Here we report the fish-net structure fabricated in our laboratory. The substrate used is an ITO-coated (110 nm) soda-lime glass. Above the substrate the film stack comprises 30 nm of Gold, 50 nm of dielectric (PZT) and 30 nm of Gold. Patterning was carried out by focus-ion beam lithography. An array of 400x400 μm was prepared by using an accelerating voltage of 30 kV and a probe current of 28 pA. The period was fixed at 780 nm while two examples of holes with diameter of 300 and 480 nm were prepared. The total etched thickness was 150 nm and comprised the three layers stack and 40 nm of the ITO layer. SEM image of the nano-patterned sample is reported in Fig. 2. The realized structure has a theoretical resonance in the NIR spectral range. The characterization of its optical properties via spectroscopic ellipsometry, using a focusing probe, has been carried out and the simulation of the

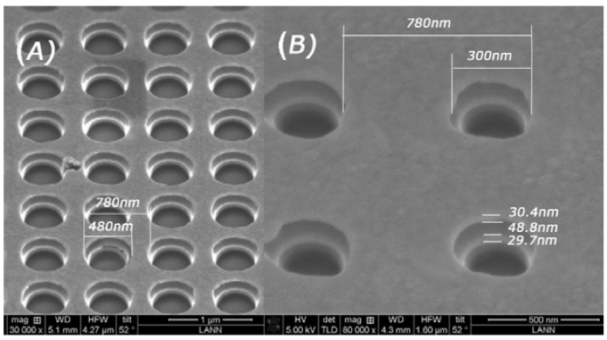


Fig. 2: SEM images of samples with hole diameter 480 nm (A) 300 nm (B).

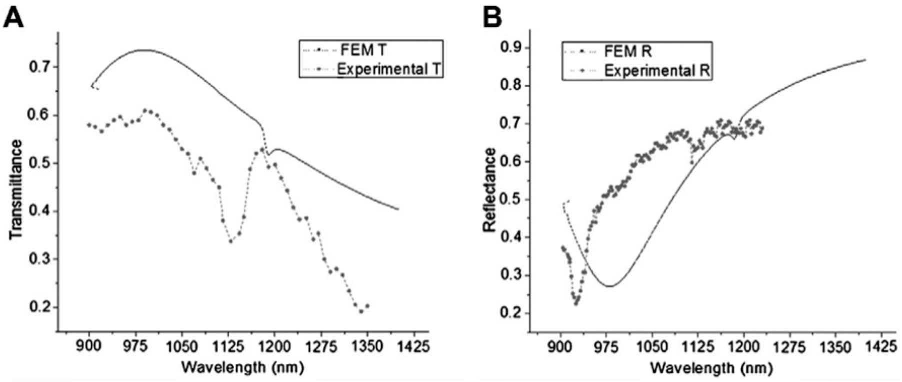


Fig. 3: Experimental and theoretical transmittance (A) and reflectance (B) data for the sample with hole diameter 480 nm.

refractive index has been performed using Finite Element Method (FEM) method. The transmittance measurement were performed at normal incidence (0°), while the minimum angle for the reflectance measurement is 15°. In Fig. 3 a comparison of the simulated and spectra data for reflectance and transmittance is reported. Numerical simulation of the reflectivity and transmittance are in good qualitative agreement with experimental optical measurements in a wide range of wavelengths although a shift in the position of the peak was observed. The shift to lower wavelngth of the resonant peaks in the transmission and reflectance spectra could be due to errors ,underestimation of e.g. effective hole diameter and/or film thicknesses and/or average PZT refractive index or possibly a combination of them.While a positive effective magnetic permeability was found - associated with a relatively weak magnetic resonance of the fabricated structure- the effective refractive index is negative at the resonance in the infrared at 1200 nm. In other words a wave-length band of single-negative operation is found where the sample exhibits NIM behavior

## 4. Conclusion

As a first step towards electrically tunable fishnet metamaterials ultrathin PZT films were deposited by sol-gel and the relevant material properties of the PZT was characterized. Trilayer stacks of Au/PZT/Au were deposited and patterned by FIB lithography. Spectroscopic ellipsometry was used to characterize the metamaterial, and its optical constants extracted by comparison with FEM simulations. A single negative refractive index band was found in the IR at ca 1200 nm.

## References

[1] U. K. Chettiar, A. V. Kildishev, H.-K. Yuan,Optics Letters, Vol. 32, Issue 12, pp. 1671-1673 (2007)
[2] J. Valentine, S. Zhang, T. Zentgraf1 nature Vol 455 18
[3] M. Kafesaki et al Physical Review B 75, 235114 2007
[4] F.J. Garcia-Vidal, H.J.Lezec, T.W. Ebbesen, L. Martin-Moreno, Phys. Rev. Lett., 90, no 21, 213901 (2003)
[5] M. Nakada,, K.Ohashi, J.Akedob, J. Cryst. Growth 275 (2005) e1275
[6] D. Garoli, M.Natali, V.Rigato, F.Romanato, submitted to Thin Solid Films (2011)