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The dielectric constant of PZT nanofiber at visible and NIR wavelengths

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ABSTRACT

Dielectric constant measurements of PZT nanofiber were performed at visible and near infrared wavelengths using ellipsometry. The nanofibers, formed by electro-spinning with diameters ranging from 10 to 100 nm were collected on Si wafers for the measurement. A nominal 150 nm PZT thin film was also fabricated on Si and measured in parallel for comparison. Several models were developed to fit the ellipsometry measurements and the results show consistent values of dielectric constant in the range of -1 to 6 over the frequency range for both the fiber and the film. The complex dielectric properties are useful for matching optical impedances as well as analyzing the material for potential applications including combining with other materials to form metamaterials. At certain wavelengths negative permittivity and epsilon-near-zero characteristics are identified.

1. Introduction

Lead Zirconate Titanate (PZT) $PbZr_xTi_{(1-x)}O_3$ is a ceramic perovskite material that is widely used at low frequency for sensors, transducers and actuators [1–4] because of its high piezoelectric coefficient and high dielectric constant. It also exhibits ferroelectric [5] and pyroelectric [6] effects. More recently, optical properties of perovskites like PZT are being investigated [7–10]. In this research, the dielectric properties of PZT at visible and near infrared optical frequencies in the form of nanofibers and thin films are explored with ellipsometry. The spectrum from 0.3 to 1.75 μm wavelength is covered which includes the entire visible spectrum and most of the Near Infrared (NIR) as well as a small sliver of the Ultraviolet (UV) spectrum. The peak of the sun's radiation is in the visible spectrum as it can be considered a black body radiator at 5778 °K. Consequently, materials research is ongoing in the visible spectrum for solar energy applications [11,12]. With increasing wavelength into the infrared, the peak emission of objects occurs at lower temperature. This ties into many other applications including spectroscopy, astronomy, detection, imaging, medical treatments [13–18] and more.

Plasmonics is one the most intense relatively new research areas in the field of optics and nanotechnology today and is based on collective charge oscillations as opposed to excitonics for individual charges. Plasmonic[1] structures can support various bulk and surface propagating modes and can act as constituent subwavelength inclusions in a larger metamaterial. There are several ways to optically couple/match light (photons) with plasmons, which have different momentums. This includes using gratings [19] or via the evanescence of a totally internally reflected wave residing in the reflective medium [20].

Researchers [21–23] have found that optical impedance matching between mediums can be accomplished by utilizing various types of optical resonances including plasmons. There are many

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[1] Similar phenomena have been observed with phonons which are the direct result of collective lattice oscillations rather than charge oscillations. A polariton is a consequence of light–matter interaction where photons couple with other excitations like plasmon and phonon resonances.

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other applications for plasmonics in the visible and NIR spectrum [24–27]. As one example, Sotiriou [28] has successfully developed nanoparticles that heat up when they absorb NIR light, enabling them to kill tumor tissue. These nanoparticles have a strong and tunable surface plasmon resonance absorption in the NIR and are aggregated into nanostructures whose precisely defined distances between particles transform them into a configuration that absorbs NIR light and thus generates heat.

Although metals are commonly exploited as metamaterial elements for their negative permittivity [29,30], dielectrics have been found to be applicable as well [31,32]. It is ultimately a materials' permittivity (both real and imaginary) that determines whether and how well it can support a plasmonic or phononic mode. Zhong [33] modeled plasmonic and phononic modes with a Drude–Lorentz model and a phenomenological model respectively. A general rule followed, where the real part of the plasmonic materials' permittivity must be negative below the resonant frequency and the imaginary part must be small. The phononic material also exhibits negative permittivity, however, only across a narrow range of frequencies as determined by its' crystalline structure. Notably, the perovskite strontium titinate ($SrTiO_3$) was found to be phononic at some mid-infrared wavelengths. In the same manner that single electron waves can be quantized by confinement in a nanostructure [34] due to size, plasmons are also affected by the boundary conditions in a thin film or nanoparticle. Subwavelength optical modes can be engineered to a surrounding medium with certain choices of dielectric constant, nanosize features and plasmonic material [35].

Silveirinha [36] has shown that Epsilon Near Zero (ENZ) materials have vanishingly small dielectric permittivity over some range of wavelengths, typically near a transition from positive to negative permittivity. Javani [37] shows that their remarkable optical properties include total light reflection at all angles, a phase velocity of light tending toward infinity and consequently carrying light waves at almost constant phase. A waveguide formed inside an ENZ material is expected to confine light at deep subwavelength dimensions, preventing reflections even at sharp bands and be tolerant of the unavoidable roughness of waveguide walls.

Ellipsometric research has been conducted on PZT thin films by others [38,39]. The researchers have found that excitonic modeling produced the best fit to their data. Their data also showed moding at NIR and visible wavelengths that diminished at UV wavelengths and was attributed to interference from a platinized substrate. The PZT film data from our research was baselined against PZT nanofiber to determine the dielectric characteristics in the NIR and visible spectrum that would otherwise be masked by similar moding.

Hence, the dielectric constant plays an important role in material selection as the visible and infrared spectrum are being exploited for new materials to more effectively couple and propagate light, even at subwavelength dimensions. To specifically explore the behavior of PZT $PbZr_xTi_{(1-x)}O_3$ with $x = 0.52$, we have prepared samples of both PZT film and PZT nanofiber and derived their dielectric constants using ellipsometric methods.

2. Materials and methods

2.1. Sample preparation

The Silicon (Si) substrate for each PZT sample consisted of a 4 inch diameter Si wafer with either a 10 nm or 300 nm thermal oxide layer formed on one side. A solution consisting of 1 ml PZT sol gel and 0.6 ml of acetic acid was added to a precursor of 0.1 g Polyvinylpyrrolidone (PVP) and 0.6 ml ethanol and drawn into a syringe after mixing thoroughly. Two different types of samples, namely PZT film samples and PZT nanofiber samples were formed from these same ingredients.

The PZT nanofiber samples were produced using an electrospinning process as shown in Fig. 1. A syringe pump was used at a flow rate of 5 μl/min to dispense the PZT solution to the tip of a 30 AWG needle. The needle was positioned 10 cm away from a metal base that the silicon wafer was temporarily attached to. The base was rotated at 1000 rpm about its vertical axis, which was parallel to the centerline of the needle. A DC voltage of 17 kV was applied between the needle and the rotating base (through a slip ring) in order to generate an electric field of 1.7 kV/cm.

The PZT film samples were fabricated by spin coating. The Si wafer was mounted to a spin coater using a vacuum chuck. The wafer was covered with the PZT solution and then the spin coater was ramped up to 3000 rpm and held at this speed for 2 min to produce a uniform coating.

Both the PZT nanofiber and film samples were baked on a hot plate at 300 °C for 30 min. Immediately afterwards, they were placed in a furnace that was preheated to 300 °C and then slowly ramped up to 650 °C to anneal for 30 min and then cooled down slowly to room temperature.

SEM and AFM images of the PZT nanofibers produced using this method for our experiments are also shown in Fig. 1. The topographical statistics measured from the AFM image were used as inputs to the model in Section 2.3

2.2. Ellipsometry measurements

Ellipsometry measurements were conducted using a J.A. Woollam M-2000 spectroscopic ellipsometer. At four specific angles of incidence, a full spectrum of light waves reflected off the sample are passed through a rotating compensator and dispersed across an InGaAs Charge-Coupled Device (CCD) array. Simultaneously across the spectrum, the changes in amplitude $\tan(\Psi)$ and polarization angle Δ of the reflected beam are measured and related to the incident beam by the complex reflection ratio:

$$\tilde{R} = \tan(\Psi)\, e^{j\Delta} \tag{1}$$

To provide a comparison of the thicknesses fit from ellipsometry, X-ray Reflectivity (XRR) measurements were performed on the PZT film samples using a Rigaku Ultima III Multipurpose Diffraction System that generates Copper $K\alpha_1$ X-rays having a wavelength of 0.154 nm. These rays reflect off of the sample and structural parameters including thickness, density and roughness of each layer are derived and presented in Section 3.1.

2.3. Models of samples used for data fitting

Only in very simple cases, (like for metals where all light energy that is not reflected by the surface is totally absorbed) can the measured Ψ and Δ be inverted directly to obtain "pseudo" optical constants. Otherwise, a model based regression analysis is required to estimate the Fresnel coefficients and derive the optical constants. A number of common methods to approach the data fitting are suggested by Woollam [40]. For our ellipsometry measurements, individual models were used for each type of sample.

To begin, bare wafers having various thermal oxide thicknesses were modeled. A previously established material model of a SiO_2 layer on top of a Si substrate was used as shown in Fig. 2 and also served as the common two base layers for the other two models. The optical material data for both the Si and SiO_2 layers was from Herzinger [41]. To establish a reference for comparison with nanofiber dielectric constant measurements, the PZT film on a Si Wafer with a 300 nm nominal oxide layer was modeled. As shown in Fig. 2, the model was comprised of an additional PZT film layer on top of the common model used for the oxide layer on Si

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