

Gold-particle-mediated detection of ferroelectric domains on the nanometer scale

Thomas Härtling^{a)} and Lukas M. Eng

Institute of Applied Physics/Photophysics, University of Technology Dresden, 01062 Dresden, Germany

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We report on an unique optical method which facilitates detection of ferroelectric (FE) domain orientation on the subwavelength scale. The FE material of interest is decorated with Au nanoparticles of 100 nm diameter and then completely covered with a thin film of birefringent liquid-crystal (LC) molecules. The latter align to the FE surface in accordance to the domain-specific electric stray field, which causes a characteristic spatial orientation of the dielectric tensor $\hat{\epsilon}_m$ of the LC layer. As their spectral response strongly depends on the dielectric constant of the surrounding medium, the embedded Au particles are used as nanoscale optical antennas revealing either an intensity, a polarization, or a spectral contrast. This technique provides an ultrafast optical read-out mechanism for detecting antiparallel oriented FE domains with subwavelength resolution. © 2005 American Institute of Physics. [DOI: 10.1063/1.2048825]

As is known from many examples based on scanning force microscopy, it is possible today to remanently write and switch time-stable ferroelectric (FE) domains down to some 10 nm in diameter.¹ Therefore, ferroelectric crystals and thin films are prospective materials for memory device applications that encode information in the FE domain orientation. Furthermore, as optical methods of data processing advance, the challenge arises to both read and write such memories fully optically.

Here, we introduce a novel method which allows one to optically distinguish the antiparallel orientation of FE c^+ and c^- domains on the subwavelength scale.² Small gold nanoparticles of 100 nm diameter are used as optical antennas spread on the surface of the FE material. The dependence of the optical properties of such particles on the dielectric constant of the embedding medium is used as the subwavelength contrast mechanism for antiparallel domain reading.

When small metal particles are illuminated with visible light, collective electron oscillations, so-called surface plasmon polaritons (SPPs) are excited. For most metals, the simple Drude model is accurate enough in providing the fundamental understanding of such electron oscillations and the resulting optical properties of the nanoparticle.³ In such a description, the resonance frequency ω_{res} of the dominant dipolar electron oscillation becomes⁴:

$$\omega_{\text{res}}^2 = \frac{\omega_p^2}{2\epsilon_m^i + 1}, \quad (1)$$

where ω_p is the plasma frequency given as

$$\omega_p^2 = \frac{Ne^2}{m_e \epsilon_0}. \quad (2)$$

Here, N is the number of electrons per unit volume in the sphere, e is the elementary charge, m_e is the free-electron mass, ϵ_0 the vacuum permittivity, and ϵ_m^i the dielectric constant of an isotropic embedding medium. Typically, the resonance of 100 nm Au particles in such an isotropic medium of

$n \sim 1.5$ is found at ~ 600 nm.⁵ Note that both the quantitative and spectral response of the SPP depends on the size and material chosen for the nanoscale optical metal antenna.

Equations (1) and (2) directly reflect that the SPP resonance frequency ω_{res} primarily depends on the electronic charge density in the nanoparticle and the dielectric properties of the embedding medium. Hence, changing either parameter results in a sensitive signature read by the resonance frequency. Achieving an image contrast by changing the charge density on the metal nanoparticle turns out to be very demanding.^{6,7} In contrast, it is much easier to control the embedding medium and its dielectric constant.^{8,9} Hence, we use the latter possibility in order to achieve a subwavelength optical contrast mechanism for antiparallel domain reading in FEs. The orientation of the electron dipole oscillation in the particle depends on the polarization of the incident light beam. Conversely, if the embedding material has tensorial dielectric properties ($\hat{\epsilon}_m$) as is the case here, ω_{res} dramatically depends on the dipole oscillation direction.

In our experiment, we use the uniaxially oriented triglycine sulfate (TGS) single crystals cleaved to 1 mm thick slices perpendicular to the b axes as the ferroelectric system. The slices were heated above the Curie temperature $T_c \sim 49^\circ\text{C}$ for approximately 10 min and kept at room temperature for the next 4 h of cooling down. This treatment enables a stable and dense ferroelectric domain distribution as shown in Figs. 1(a) and 1(b). Presented are two polarization microscopy images taken at 0° and 45° analyzer orientation of the TGS sample that was decorated with a thin film of a nematic liquid crystal (LC) (MERCK ZLI 2583-100) using a brush. The reversed contrast for c^+ and c^- domains is clearly visible. Prior to LC decoration, an aqueous dispersion of gold nanoparticles having a 100 nm diameter (BBInternational EM.GC100) was spin coated on every single TGS slice. Hence, the Au nanoparticles are completely embedded within the LC film.¹⁰ Figure 1(d) shows two such Au nanoparticles. They are situated on antiparallel oriented ferroelectric domains separated by a 180° domain wall (DW) as proven by piezoresponse force microscopy (PFM) [Fig. 1(c)]. Note that no topographic change or any surface step was observed at the DW boundary.¹¹

^{a)} Author to whom correspondence should be addressed; electronic mail: hertling@iapp.de

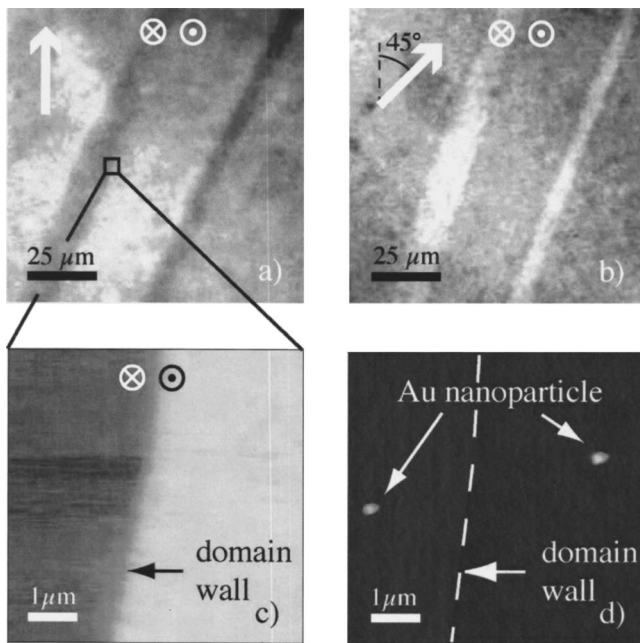


FIG. 1. (a) and (b): White-light polarization microscopy images of a TGS surface covered with LC molecules. White arrows in the upper left corner indicate the analyzer orientation. (c) Close-up PFM image showing the 180° ferroelectric domain wall in TGS. (d) Atomic force microscopy sample topography of the same area as in (c) revealing isolated 100 nm sized Au particles situated on up/down oriented TGS domains.

Decorating ferroelectric materials with a LC film is well known as a fast method for visualizing ferroelectric domains.¹² In the absence of an electric field, the LC molecules are arbitrarily oriented. Therefore, the material has an isotropic index of refraction, that is in our case: $n=1.55$. However, when the LC molecule agglomerates to the surface of a ferroelectric material, it is exposed to the electric stray field of the material's surface charges and thus becomes aligned. Triglycine sulfate cleaved in the described way exhibits c^+ and c^- domains only, which are aligned perpendicular to the cleavage plane.¹³ Since the surface charges on different domains are of opposite sign, the LC molecules are differently aligned ($\sim 45^\circ$ misorientation on TGS; see Fig. 3) leading to the birefringent character as shown in Fig. 1. Hence, two indices of refraction, $n_o=1.49$ and $n_e=1.62$, exist in two mutually perpendicular directions, both being oriented parallel to the FE sample surface. Note that n_o and n_e reflect two components of the anisotropic dielectric tensor $\hat{\epsilon}_m$.

In order to verify the birefringent behavior, the LC decorated TGS sample was investigated with linearly polarized white light using a conventional polarization microscope as described above. Figures 1(a) and 1(b) clearly show that bright areas turn dark and vice versa when rotating the analyzing polarization filter by the amount specified. This verifies that the LC molecular orientation is different on c^+ and c^- domains, e.g., the direction of the fast optical axis of the LC differs on adjacent domains. Moreover, the polar axes of the LC molecule in use are neither aligned perpendicular to the c^+ nor to the c^- domain surface, as was reported earlier for another type of LC molecules.¹⁴

The same polarization experiment was repeated at much higher precision using the setup shown in Fig. 2. The sample was mounted into an inverted confocal microscope (ZEISS AXIOVERT 200) and illuminated with polarized white light through a numerical aperture (NA)=1.3 objective. We scan

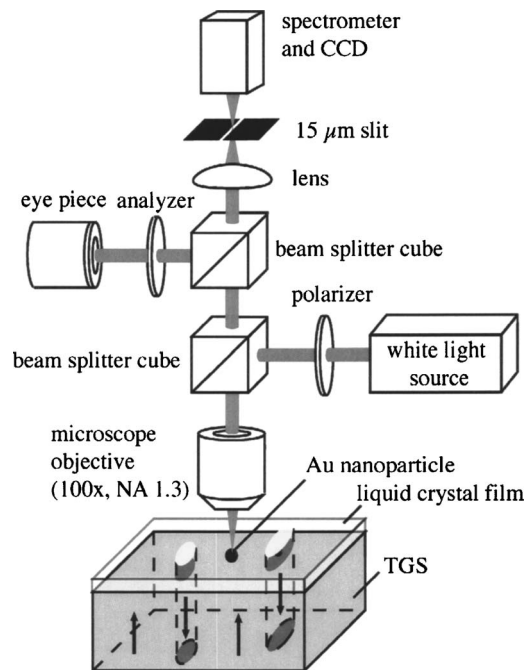


FIG. 2. Inverted confocal microscope setup for polarization microscopy and spectroscopy. Addressing single Au nanoparticles as well as identifying FE domains is possible by scanning the sample.

the sample in order to address smallest sample fractions by a diffraction limited spot and collect both the polarization dependent reflection signal and the spectral response at every position during the scan. Hence, this setup allows us to optically address individual Au nanoparticles on the TGS surface. At the same time, the underlying ferroelectric domain is analyzed giving a polarization contrast. Note that light scattered from a single Au nanoparticle reveals information from an area in the order of the nanoparticle diameter¹⁵ and thus is much smaller than the diffraction-limited spot size.

The polarization plane of the incident light beam was rotated in 20° increments. Consequently, the dipole on the Au nanoparticle gradually changes its spatial oscillation direction. For every polarizer position, the dipole is exposed to a different dielectric constant according to the tensorial components of $\hat{\epsilon}_m$. As described by Eq. (1), the resonance wavelength follows this shift. Figure 3 shows the varying light polarization ($0^\circ=s$ polarization) and the according resonance wavelength of a Au nanoparticle on an arbitrarily cho-

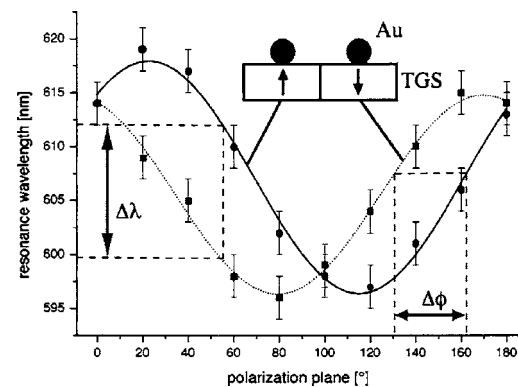


FIG. 3. Light polarization vs plasmon polariton resonance wavelength recorded for the two Au nanoparticles in Fig. 1(d) situated on antiparallel oriented TGS domains.

sen domain (dashed curve). Repeating the same experiment with a nanoparticle situated on an antiparallel oriented domain for which the optical axes of the LC molecule are markedly rotated, yields a shifted curve (solid curve in Fig. 3).

These experimental findings (Fig. 3) clearly verify the dependence of the resonance frequency on $\hat{\epsilon}_m$. The minimum resonance wavelength occurs when the dipole is excited along the ordinary (fast) optical axis of the LC molecule, which is shifted by $\sim 40^\circ$ with respect to the antiparallel domain. Consequently, the maximum resonance wavelength is found whenever the polarization plane of the incoming light beam meets the extraordinary (slow) optical axis. Minimum and maximum are separated by 90° (see Fig. 3) and the curves resemble a sine-behavior as shown by the fitting curves.

The most remarkable observation from Fig. 3 is the spectral dependence of the backscattered light. Note that no such behavior could be recorded in a reference experiment when using no Au nanoparticles at all. This clearly shows the medium-dependent ω_{res} behavior stated in Eq. (1).

Figure 3 clearly indicates that subwavelength optical polarization reading in a ferroelectric device can be carried out in three different ways. First, if we maintain a fixed analyzer position in our optical detection path, the recorded spectral shift $\Delta\lambda$ in Fig. 3 achieves values of up to 12–14 nm. On the other hand, operating the reading mechanism at fixed read-out wavelength λ reveals maximum intensity at different analyzer rotation angles ($\Delta\phi$ in Fig. 3). Finally, for a fixed wavelength as well as fixed position of the analyzer, the orientation of the ferroelectric polarization can be read through the optical intensity losses of up to 15% between antiparallel TGS domains, since the SSP resonance is shifted away from the read-out wavelength. Again, note that no such spectral effects were found when using a reference TGS sample carrying no Au nanoparticles.

In conclusion, we demonstrated that subwavelength optical domain orientation reading in FEs is possible when using an optical indicator for the sample polarization orientation, i.e., the LC molecule, and a nanosized antenna realized here through metal nanoparticles. We report that either a polarization, an intensity, or a resonance wavelength contrast results that is well explainable through the surface plasmon behavior in noble metal nanoparticles. By no means is the reported effect restricted to: (i) The wavelength regime, (ii) the size of the metal nanoparticle, or (iii) the type of LC used in this work.

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²In general, the method is able to differentiate between any FE polarization orientation. Due to the most common case in FE memories, though, we analyze here the c^+ , c^- case.

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