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Characterization of PZT nanostructures by infrared spectroscopy

V. Železný [a,*], D. Chvostová [a], I. Szafraniak [b,c], M. Alexe [d], D. Hesse [d]

[a] *Institute of Physics ASCR, 182 21 Prague 8, Czech Republic*
[b] *Poznan University of Technology 60965 Poznan, Poland*
[c] *Institute of Molecular Physics, Polish Academy of Sciences, M. Smoluchowskiego 17, 60-179 Poznań, Poland*
[d] *Max-Planck-Institute Mikrostrukturphysik, Weinberg 2, D-06120 Halle, Germany*

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Abstract

PZT (40/60) nanocrystals were prepared by chemical solution deposition on (0 0 1) MgO substrates. The method allows to prepare uniform and good quality structures of 15–20 nm high and about 100 nm lateral size. We measured the infrared reflectance of PZT nanocrystals on MgO substrates in the far and mid infrared range from 30 to 4000 cm^{-1} and we found spectral features in the spectrum, which can be related to infrared active phonons of PZT. The features occur in the spectrum as three groups corresponding to cubic perovskite modes. The phonon peaks could be fitted by the model of damped harmonic oscillators. The island-like nature of PZT could be described by a dielectric function in effective medium approximation, which could be used for qualitative evaluation of the spectra.
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1. Introduction and background

The problem of a critical size for ferroelectricity has long existed, and has been still remained as an open question irrespective of the shape including small crystal sizes, thin films and polycrystalline ceramics. The finite size effect results in structural instability (ferroelectricity vanishing below a critical size), imposing size modifications of ferroelectricity mostly by modifying the coercive field and the bulk phase transition temperature. The mean-field theory predicts the existence of a critical size equal to the ferroelectric correlation length. It can be interpreted as bulk ferroelectricity suppressed by surface depolarization energies and imply that the bulk transition has a minimum critical size. The other approach is based on the surface energy, connected with the truncation of the crystal and it predicts different estimates for the dielectric properties. These considerations have been used to calculate a critical size, which is about 25 Å for small spherical particles of lead zirconate-titanate (PZT).[1]

However, little is known about the microscopic mechanism which is responsible for this effect. As PZT is a displacive ferroelectric, the main contribution to the dielectric permittivity arises from polar phonon modes. It can be seen from LST relationship that, as the frequency of one of the transverse optical modes anomalously decreases—the soft mode, the static dielectric permittivity increases. It is, therefore, of considerable interest to know how the transverse optic mode frequency is influenced by the size effect. The lattice dynamical study provides important information for understanding the mechanism of these phenomena. A special role plays here infrared spectroscopy as a very useful tool for study of polar phonons.

2. Experimental

The epitaxial $Pb(Zr_{0.4}Ti_{0.6})O_3$ (PZT) nanoislands were deposited on cubic MgO (0 0 1) substrates. Details on the growth of the nanoislands by chemical solution deposition (CSD) were reported separately[2,3]; advanced knowledge in CSD preparation of nanostructured ferroelectrics can be found in Ref. 4.

In order to fabricate uniform, single-crystal nanosize ferroelectric structures we have applied a self-patterning method based on the instability of ultrathin films during high-temperature treatment. It was previously observed that the preparation of ultrathin epitaxial films by chemical solution deposition (CSD) is hindered by a microstructural instability, i.e., thin films with a thickness below a critical value break up into islands with a narrow size distribution after a high-temperature annealing.[2,3] This fact was intentionally

* Corresponding author. Tel.: +420 266052957.
E-mail address: zelezny@fzu.cz (V. Železný).

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exploited for nanoisland fabrication.[4,5] The preparation details have been described elsewhere.[5,6] Briefly, PZT ultra-thin films were obtained by spin-coating at 6000 rpm a metallorganic solution with nominal composition $Pb(Zr_{0.4}Ti_{0.6})O_3$. (0 0 1)-oriented MgO single crystals (Crystal GmbH, Berlin) were used as substrates. The initial film thickness was set by dilution of the raw precursor in xylene. The obtained gel film was dried on a hot plate at 80 °C for 5 min, pyrolyzed at 300 °C for 5 min, and finally crystallized at 800 °C for 1 h in a lead oxide atmosphere.

The obtained nanostructures were studied by atomic force microscopy (AFM) (Dimension 5000, Digital Instruments). PZT islands on MgO substrate have the height of about 25 nm and the lateral size up to few hundred nanometers (see Fig. 1). The distance between close neighbors is relatively large resulting in a low density of the islands.

Near normal reflectance measurements in frequency range from 30 to 4000 cm^{-1} (1–100 THz) were carried out using a Bruker IFS 113v Fourier transform spectrometer. At low temperature, the reflectance was measured in a reduced spectral range 30–650 cm^{-1}, because this is the transparency region of the windows in our cryostat. Pyroelectric DTGS detectors were used for room temperature measurements and a helium cooled Si bolometer for the measurements with the cryostat.

The data were analyzed by modeling the reflectivity in two steps. First, the geometrical model consisting of two layers was constructed: the bottom layer for MgO substrate and the top one for PZT nanoislands. The dielectric properties of the latter one were calculated in effective medium approximation (EMA). The layer thickness was taken to be equal to the height of the nanoislands (35 nm). The concentration of the islands and air in the layer, which must be substituted into the EMA formula, was determined as a fraction (0.33) of the surface area occupied and unoccupied by PZT nanoislands. The software used for fitting provides varying of many parameters including depolarization field whereby it enables to estimate the shape of nanoislands.

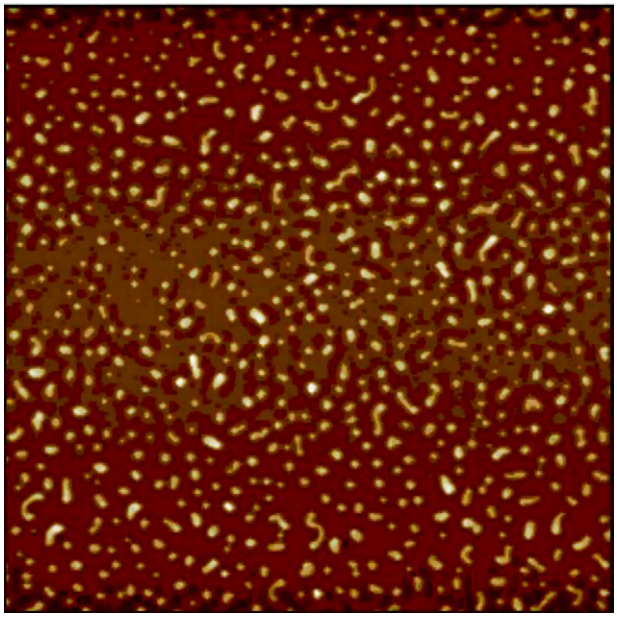

Fig. 1. The 5 μm × 5 μm image of PZT islands on (0 0 1) MgO substrate (the *z*-axis ranges 0–40 nm).

3. Results and discussion

For the PZT composition Zr/Ti = 40/60, the material has a tetragonal structure (*P4mm*) at room temperature. In this phase, three triply degenerate polar F_{1u} modes of the parent cubic structure (*Pm3m*) split into $3A_1 + 3E$ modes. Moreover, a silent F_{2u} mode splits into A_2 and E modes, the latter being also infrared active. Therefore, the total number of the infrared active modes is 7. Their symmetry can be easily assigned by comparing our reflectivity measurements with those[7] on ceramic samples. The parameters of the Lorentz model for PZT have been studied and their variation with composition Zr/Ti is well known.[8]

The most commonly used fit for dielectric dispersion in ordinary crystals is the Lorentz model, where the dielectric function is modeled by the sum for independent damped harmonic oscillators:

$$\hat{\varepsilon}(\omega) = \varepsilon_\infty + \sum_{j=1}^{n} \Delta\varepsilon_j \frac{\omega_{\mathrm{TO}j}^2}{\omega_{\mathrm{TO}j}^2 - \omega^2 + i\omega\gamma_{\mathrm{TO}j}}$$

where ε_∞ is the high-frequency (electronic) dielectric constant, $\Delta\varepsilon_j$ the oscillator strength of the *j*th transverse vibrational mode, $\omega_{\mathrm{TO}j}$ its frequency, and $\gamma_{\mathrm{TO}j}$ its damping coefficient. The infrared reflectivity can be obtained from complex dielectric response $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$:

$$R(\omega) = \left| \frac{\sqrt{\varepsilon(\omega)} - 1}{\sqrt{\varepsilon(\omega)} + 1} \right|^2$$

Experimental reflectance spectra of both bare MgO substrate and system of substrate with PZT nanoisland on its top are shown in Fig. 2(a). The spectrum of MgO consists of a broad restrahlen band corresponding to a infrared active phonon. Small deviations from an ideal shape are caused by multiphonon processes. The spectrum of MgO with PZT nanoislands is very similar to the spectrum of the bare MgO with the distinction that three groups of absorption features can be found there. The two peaks of the first group point upwards and are added to the slope of MgO absorption, as the MgO is transparent in this region. The two peaks of the second group point downwards and look like notches in the MgO reststrahlen band. This is a typical behavior of extra absorption features in a reststrahlen band. The last group of at least three peaks point again downwards and behaves similarly to the second one. These effects are much more pronounced in Fig. 2(b), which displays substraction ($R_{\mathrm{syst}} - R_{\mathrm{sub}}$) and ratio ($R_{\mathrm{syst}}/R_{\mathrm{sub}}$) reflectance of MgO and system (PZT + MgO), respectively. The small peaks represent the infrared absorption in the PZT film. The three groups of the peaks correspond to three F_{1u} phonons of cubic perovskite phase, which are split into A_1 and E due to the tetragonal symmetry of the room temperature phase.

Quite consistent with this scenario, suggesting that the absorption features correspond to regular phonons, is their temperature dependence. Our preliminary measurements show that only the frequency of the sharpest mode at 431 cm^{-1} slightly

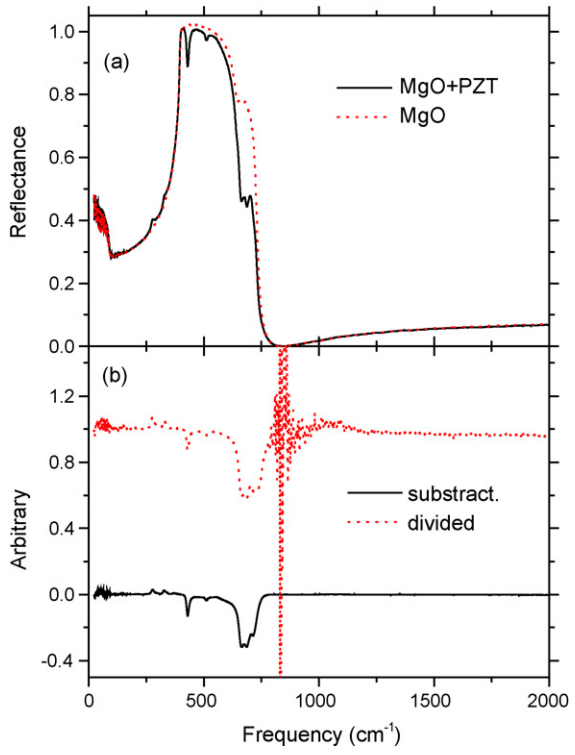

Fig. 2. Panel (a) shows reflectance spectra of bare MgO and MgO with PZT islands on its top. Panel (b) presents divided and subtracted reflectance of both samples.

increases on cooling. This completely regular behavior is due to normal temperature contraction. No anomalous variation of phonon frequency, which could be ascribed to a soft phonon, was observed.

We also could fit the experimental spectra with the model described above. First, we fitted the bare MgO then we fixed its parameters and we varied only the parameters of PZT nanoislands. To obtain good agreement between experimental and calculated curves, we had to introduce eight oscillators with following frequencies: the first group 279, 330, the second group 431, 512 and the third group 583, 664, 688 and 721 cm^{-1}. Their number is by one larger than that predicted by group theory including the activation of silent mode. Comparing them with those for bulk of the same composition material,[8] we can clearly see a shift to higher frequencies, i.e., stiffening phonon modes. The bulk frequencies of the E-modes obtained from the literature[8] are about 64, 220 and 550 cm^{-1} and for the A_1-modes 130, 360 and 640 cm^{-1}. An extremely large shift is seen in the position of the first mode denoted as the soft mode, whose frequency increases at least about 200 cm^{-1}. This indicates that the PZT nanoislands are forced into the tetragonal phase much more than a bulk material. This can be caused by the size effect itself or due to mechanical strain arising on the interface, which comes from crystalline misfit of the substrate and islands.

4. Conclusion

We observed two doublets and one more complicated group of absorption features in the infrared spectra of PZT nanoislands, which can be interpreted as polar phonons. Their frequencies are shifted upwards in respect to their bulk values.

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