Explosive crystallization of PZT microstructures by femtosecond infrared radiation

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Abstract. The features of microstructure crystallization into perovskite phase in lead zirconate titanate film by femtosecond laser radiation of near-infrared range were discussed. In-situ crystallization kinetics by method of second harmonic generation (SHG) was studied. The presence of several types of crystallization was shown, including ultra-fast (explosive) crystallization occurring immediately after the start of exposure, and slow (self-sustaining) crystallization, occurring after termination of exposure. The advantage of the second-harmonic generation microscopy for the study of annealed microstructures was shown. The morphology of microstructures was investigated by transmission electron microscopy (TEM).

1. Introduction

Thin-film ferroelectric structures form the basis for a new generation of micro- and nanoelectronic devices [1, 2]. For obtaining the ferroelectric phase from the amorphous film it is annealed. Thermal annealing furnace is used in the vast majority of technologies [3].

Laser annealing is used for local crystallization of amorphous films into the ferroelectric phase in order to minimize surrounding functional area elements heating. Upon annealing by excimer laser with photon energies much higher than the band gap, absorption, and hence the annealing occurs in a thin surface layer [4]. In addition, the mode structure of excimer laser spot does not allow localizing crystallization in the submicron region.

In paper [5] we proposed to use for annealing of ferroelectric film on platinized substrate single-mode femtosecond laser with a wavelength that falls in the transparency of the PZT film and consequently absorbs by platinum layer. This method makes it possible to solve three problems simultaneously. Firstly, the annealing conditions are close to the thermal annealing furnace, as the heating of the film is carried out by the platinum. Second, the heating is carried out locally with a Gaussian distribution of temperature along the radius of the laser spot. Third, the use of femtosecond laser allows diagnosing the formation of the ferroelectric phase during the process of annealing. The basis of this diagnosis is the method of optical second harmonic generation (SHG), which is an effective method for studying phase transitions, including the crystallization of perovskite phase. We also show the advantage of the SHG technique for ex-situ visualization of the annealed regions compared with linear-optical imaging.
2. Experimental setup

Film of a solid solution of lead zirconate titanate (PZT) with thickness 700 nm, with a 10 percent excess lead oxide (Pb(Zr0.54Ti0.46)O3+10%PbO) was deposited on platinized silicon substrate by RF magnetron sputtering (without annealing) [6].

Femtosecond Ti: sapphire laser («Avesta-Project») was used as the laser source with a wavelength of 800 nm, pulse duration of 100 fs, a repetition frequency of 100 MHz. Duration of annealing exposure was 1 s - 30 s. Confocal microscope Alpha-300 (Witek) was used for beam focusing during annealing, diagnosing and scanning after all. Focusing lens x40 (numerical aperture NA = 0.65) were used and the size of the laser spot on the surface of the film, measured as the width of the constriction was 1 μm. There was no scanning of the laser spot on the sample during annealing and in-situ monitoring. We used a double-beam scheme in reflection geometry with two mixed coinciding beams – for annealing and diagnosing both focused at the same place. The power density of the annealing beam took the value W_A = 1,0 MW/cm², diagnosing – W_D = 0.2 MW/cm². Annealing and its registration were performed as follows: on the way of the annealing beam (before mixing with the other one) was set shutter which opens only during annealing (for a time $t_A$), diagnosing beam exposed the sample throughout the experiment, thereby second harmonic generation is also registered for the entire duration of the experiment. The moment of opening the shutter was set as zero point of time $t = 0$, that is the beginning of annealing. Thus, when $t < 0$ SHG signal was detected from the non-annealed film at a laser power $W_D$, when $0 < t < t_A$ SHG signal was detected during annealing at the total power of annealing and probing beam ($W_A + W_D$), and when $t > t_A$, after closing the shutter, SHG signal was detected during cooling / crystallization at laser power $W_D$. Since the intensity of the SHG is proportional to the square of the incident power, to compare the results of diagnosing for all areas SHG signal was normalized by the square of the corresponding power in each of the intervals $t < 0$, $0 < t < t_A$, $t > t_A$.

3. Investigations of laser annealing

3.1. In-situ investigation

Before annealing irradiation is turned on, SHG signal from the amorphous PZT film is absent. After the annealing beam is turned on (moment $t = 0$ on Fig.1 a), in a short time of the order 0.1 second, PZT film is heated to a temperature of 700 K, due to the optical absorption in Pt layer. These values were estimated in COMSOL Multiphysics software. At these times superfast crystallization of the film material occurs with a transition to noncentrosymmetric-perovskite phase, which is accompanied by a sharp rise in the SHG signal. This ultra-fast crystallization apparently does not occur by the classical mechanism of nucleation and growth of nuclei, which works in a conventional (slow) furnace annealing [7], but by the mechanism of superfast explosive crystallization of PZT or transition of "order-disorder" [8].
Then the growth and the intensity of SHG is saturated and during the entire time of irradiation ($\tau_{A1} = 1$ s), SHG signal remains approximately constant. The inhibition of PZT crystallization due to a sharp increase of the activation energy of crystallization can cause SHG saturation. The large tensile stresses in the amorphous regions surrounding the crystallized areas can be a reason of increasing of activation energy [9]. Such stresses occur due to increased density of the crystallized material [10]. Increasing the annealing time to $\tau_{A2}$ (fig. 1 b) lead to a decrease of the SH signal. Reduction of the SHG signal may be connected with the fact that the center of the spot where the temperature is highest may be "overheated" with the formation of defects. After the annealing radiation is turned off sharp (in times of the order or less than 0.1 s) cooling (to room temperature) of the film including the perovskite PZT phase and a Pt layer occurs. Corresponding sharp decrease in their volume take place. Due to the higher thermal expansion coefficient, Pt layer compresses more, so that the PZT film suffers shock compressive stress. We can assume that this shock decrease in activation energy launches slow wave of explosive crystallization, extending from the perovskite phase. Estimates show that the critical temperature of ignition and propagation of a wave may be lower than room temperature [11], due to the huge value of the latent heat of crystallization of PZT, including the elastic interactions energy [12,13], and due to the strain-induced reduction of the activation energy. The described effect is very distinct in the case of short-time annealing $\tau_{A1}$ and much weaker with prolonged annealing time. It can be assumed that "overheating" causes defects formation which damps crystallization wave propagation.

3.2. Ex-situ monitoring

To monitor the results of annealing ex-situ confocal optical and nonlinear optical microscopy was used. For imaging the sample was scanned by diagnosing beam with a wavelength of 800 nm with a power density $W_D = 0.2$ MW/cm$^2$, wherein a linear microscopy detected emission had wavelength 800 nm, and microscopy SHG - at wavelength 400 nm.
The presence of a defective area in the case of large annealing times is confirmed by SHG microscopy (Fig. 2). For $\tau_{A1}$ annealing region is a bright perfect circle, and the cross section is approximated by a Gaussian function with a full width at half maximum FWHM = 1.5 $\mu$m, which corresponds to the estimated size of the annealed region. For $\tau_{A2}$ annealing region is a circular structure with a dark spot in the center. The decrease in the SH signal in the center of the annealed region indicates a disturbance of the perovskite structure. Line images (Fig. 2 c, d) have the same slightly distorted circular form with a strong blurring of the edge area. Cross sections of line images drawn through the diameter of the spots are approximated by Gaussian functions and differ only by the value FWHM, which is 2 $\mu$m and 3 $\mu$m for $\tau_{A1}$ and $\tau_{A2}$, respectively.

Figure 2. Top images (a, b, e) – nonlinear-optical images of annealed areas (incident wavelength 800 nm and power density WD = 0.2 MW/cm², detecting wavelength - 400 nm) and their cross-sections. Bottom images (c, d, f) – linear-optical images of annealed areas (incident and detecting wavelength – 800 nm) and their cross-sections; annealing time: a, c – 1 s; b, d – 10 s.

3.3. Transmission electron microscopy

Incisions of obtained microstructures for detailed analysis were made by focused ion beam. These incisions were investigated by scanning electron microscopy (Fig. 3). The film was coated with the layer of platinum to prevent damage to the film by an ion beam during cutting.

The delamination of the film from the lower layer of platinum at some distance on either side of the field of laser annealing was found. This shows the stresses and thermal expansion of the film.
Figure 3. Brightfield TEM image of microstructure incision (left) and corresponding diffraction images of different areas: perovskite polycrystal (bottom), monocrystal [010] (top). Highlights in PZT layer correspond to the pores.

TEM showed that the crystallization region is a hemispherical region centered on the film surface. Big (500 nm) and small (50 nm) perovskite crystals are presented. Some microstructures have pyrochlore and platinum inclusions in PZT layer.

4. Conclusions

Thus, we have proposed a method for the local crystallization of perovskite microstructures in amorphous PZT film by femtosecond laser radiation with monitoring of crystallization kinetics by optical second harmonic intensity. SHG technique helped to identify features of crystallization: its explosive nature in the initial stage of crystallization, as well as a transition to a self-sustaining mode at the termination of the annealing. It is confirmed that for obtaining microstructures with smooth spatial profile of the perovskite phase in addition to the previously detected narrow band power density [14], annealing times range is also narrow. Increasing of the annealing time leads to the formation of ring structures with defective perovskite center, which is easily detected using SHG microscopy. The proposed technique significantly increases the controllability of the process of laser annealing and can be used not only for ferroelectrics, but also for a wide range of materials that crystallizes into noncentrosymmetric phase. This work was supported by the Ministry of Education and Science of Russian Federation (project № 11.144.2014)

5. References

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