Solid State Communications 224 (2015) 5–9

Contents lists available at ScienceDirect

Solid State Communications

journal homepage: www.elsevier.com/locate/ssc

Reverse-directional explosive crystallization of microstructures in transparent film on absorbing substrate by a multipulse femtosecond radiation

A.S. Elshin [a,*], I.P. Pronin [c], O.M. Zhigalina [d], M.Yu. Presniakov [e], D.N. Khmelenin [d], E.D. Mishina [a], V.I. Emel'yanov [b]

[a] Moscow State University of Information Technologies, Radioengineering and Electronics (MIREA), Vernadsky Ave. 78, 119454 Moscow, Russia
[b] M.V. Lomonosov Moscow State University, Leninsky Gory, 119899 Moscow, Russia
[c] Ioffe institute RAS, 26 Politekhnicheskaya, St. Petersburg 194021, Russia
[d] Shubnikov Institute of Crystallography RAS, Leninsky ave. 59, 119333 Moscow, Russia
[e] NRC "Kurchatov Institute" Academician Kurchatov sq. 1, 123182 Moscow, Russia

ARTICLE INFO

Article history:
Received 25 August 2015
Received in revised form
30 September 2015
Accepted 2 October 2015
Available online 13 October 2015

Keywords:
Laser annealing
Explosive crystallization
Ferroelectric thin films
Second harmonic

ABSTRACT

The crystallization in a transparent precursor of a perovskite ferroelectric film deposited on an absorbing platinized silicon substrate initiated by multipulse femtosecond sharply focused laser beam of near-infrared spectral range is studied by transmission electron microscopy. Time dependences of the shapes of crystallized areas point to initiation of explosive crystallization with a seed on the opposite side of a heat source localized in a platinum interface layer. The radius of the crystalized semispheres varies from 150 to 900 nm, with maximal crystallization velocity up to 1.2 cm/s. Reverse direction of the spherical wave front propagation regarding to a heat source is explained in terms of the developed model based on thermal stress-induced modification of the activation energy.

1. Introduction

The kinetics of transitions between thermodynamically stable phases of matter is a subject of intense interest in a broad spectrum of research fields ranging from condensed matter physics to chemistry [1–3]. Conventionally, such transitions are triggered by a change of ambient conditions, such as temperature, pressure, and magnetic or electric fields. Controlling a phase of matter by an ultrashort (100 fs or less) optical excitation is both a new, rapidly developing research area and a counterintuitive phenomenon in which subtle excitations are able to lead to dramatic changes in crystallographic, electric, or magnetic properties of media [4–9]. Separating materials with different functionalities in space and observing propagation of the front of phase transition is an elegant approach to understand the kinetics of the photo-induced phase transitions. Therefore, investigation of photo-induced phase transition in heterostructures offers a rich playground for understanding these phenomena and attract an intense research interest [10].

Explosive crystallization (EC) is a process in which an amorphous material crystallizes, with a significant part of the crystallization activation energy being provided by the latent heat which was released when previous material crystallized [11]. Once initiated the release of latent heat can be sufficient to drive a self-sustaining (autocatalytic) crystallization front which propagates through the material at a high (explosive) velocity. Explosive crystallization of amorphous films has been extensively studied in the end of 20th century both theoretically [11–15] and experimentally [16,17]. A lot of investigations were focused at silicon due to obvious technological applications [18], although other semiconductors as well as metals and glasses have been considered. Renewed interest to EC is called fundamentally by general importance of heterogeneous and fast phase transitions [9] and also by possibility to use the EC for controlled fabrication of crystal micro- and nanostructures [19–21].

EC can be initiated by thermal annealing [22], laser annealing [23], electron beam treatment [24] and pressure [25] (including AFM tip induced). In the case of laser annealing, location of the heat source depends on an absorption coefficient of an annealing material. Mostly the so far used wavelength fall into absorption band of the annealed material (excimer or CO_2 lasers), then the heat source is localized at the surface. In transparent amorphous material high energy laser pulses give rise to ionization due to multiphoton absorption which initiates filamentation, optical breakdown and melting with further crystallization as well. The power density which initiates such processes falls in the range of

* Corresponding author.
E-mail address: elshin_andrew@mail.ru (A.S. Elshin).

http://dx.doi.org/10.1016/j.ssc.2015.10.001
0038-1098/

tenths of TW/cm^2 [26,27]. Is it possible to crystallize transparent material by much lower pulse laser power?

Recently, [28] we suggested to use metallized substrate absorbing light which propagated in a transparent film as a heat source for crystallization initiated by near IR femtosecond radiation. We showed that multipulse radiation is required in order the crystallization takes place. However, the use of ultrashort pulses is an indispensable condition for initiating the process, because it provides locality of the process seeding while the surrounding areas are kept almost unperturbed even if ablation of material occurs [29].

Here we report about experimental and theoretical studies of the process of multipulse femtosecond laser crystallization of amorphous ferroelectric precursor film on a platinized silicon substrate. Cross-sectional transmission electron microscopy (TEM) images obtained for different crystallization times allow us to consider the crystallization propagation within the film. Although the femtosecond pulses are practically not absorbed by the film and result in an ultrafast laser-induced heating of Pt-layer, the crystallization is seeded at the surface of the film and propagates to the heat source at the film/Pt interface. The suggested theoretical model can fully explain the observed phenomenon with no fit parameters by taking into account thermal stress-induced modification of the activation energy.

2. Material and methods

For the study we used films of lead zirconate titanate (PZT) with the thickness of 700 nm deposited on a platinized silicon substrate (Pt (80 nm)/SiO_2(300 nm)/Si(300μm)) by RF magnetron sputtering [30]. For annealing we employed femtosecond laser pulses generated by Ti: sapphire laser («Avesta-Project»). Wavelength of the laser radiation was set at 800 nm. The laser pulses have duration of 100 fs, and the repetition rate of 80 MHz. To anneal the ferroelectric film the latter was exposed to the laser radiation for the period τ_A from 0.1 s to 12 s, the samples are denoted as PZT-τ_A. The beam was focused by a confocal microscope (WITec alpha300) onto a spot with the diameter of 1 μm. The power density at the annealed spot ranges from 1.0 to 2.0 MW/cm^2, which corresponds to the pulse power energy from 0.1 to 0.2 J/cm^2.

To monitor crystallization to perovskite structure in all three dimensions, transmission (TEM) electron microscopy studies were performed. Cross-sections for TEM were prepared by focused ion beam (FIB) in a FEI Helios. TEM investigations were carried out in a Tecnai G230 ST equipped by a high annular dark field detector (HAADF) for STEM (scanning TEM) mode and a EDX (energy-dispersive X-ray) detector at accelerating voltage of 300 kV.

3. Experimental results

General TEM views of the cross-sectional selected annealed microstructures are shown in Fig. 1. The marked areas are semicircles with the center at the surface of the film. Non-annealed (as-grown) areas reveal columnar structure which is typical for films obtained by magnetron sputtering. In the annealed areas the structure is changed to a granulated one. The size of grains varies from 10 to 200 nm. The size of the pores, which are seen as white areas, also varies from a few nanometers (as in Fig. 1b) to tens of nanometers (see Fig. 1c).

The most unexpected peculiarity of these images is the semi-spherical shape of crystallized areas. Although the heat source is located at the bottom PZT/Pt interface, the center of semi-spheres is located at the top interface (surface) of the PZT film. For small annealing time (τ_A=0.1 s), semi-sphere itself is located near the top interface (Fig. 2a) with the radius of R_A=150 nm. For τ_A=4 s, semi-sphere touches the bottom interface, its radius equals to the film thickness R_A=700 nm=h_{PZT}. For τ_A=11 s, the semisphere is truncated, and its radius exceeds the film thickness $R_A \cong 900\ \text{nm} > h_{PZT}$.

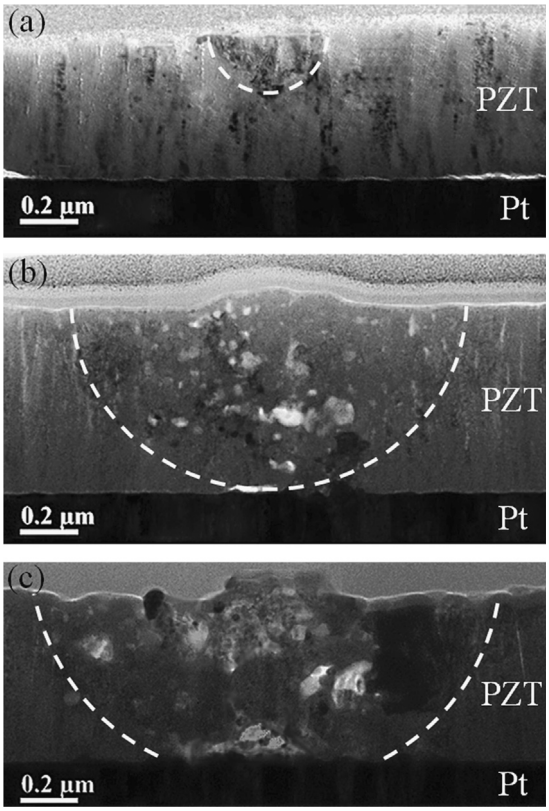

Fig. 1. Cross-sectional TEM images of PZT microstructures annealed for 0.1 s, PZT-0.1 (a), 4 s, PZT-4 (b) and 11 s, PZT-11 (c): general view. The annealed areas are marked by white dashed lines.

Enlarged images and selected area diffraction (SAED) patterns of the structures with annealing time of 0.1 s and 11 s are shown in Fig. 2. The annealed area in the PZT-0.1 sample reveals perovskite (Pe) nanocrystals (areas with a dark contrast, Fig. 2a). The intensities of Pe and Py reflexes in the diffraction pattern are very high (Fig. 2b) although amorphous halo is also visible.

In the case of the PZT film annealed during 11 s, the diffraction pattern from the central region of the annealed area indicates the presence of the perovskite grains only. The size of the grain is relatively small-about 50 nm (Fig. 2c,d). A large grain of the perovskite phase with [010] zone axis and the length of about 0.5 μm is seen in the peripheral region of the laser annealed area (Fig. 2a). The area grows from the surface of the PZT film. Calculations of the interplanar distances showed that the perovskite in this area has an increased tetragonality (1.35 ± 0.05) compared to the tabulated value of 1.02 [31].

The observed remarkable and largely counterintuitive spatio-temporal scenarios can be understood from a simple thermodynamical considerations.

The source of the heat is localized at the bottom interface. However, the heat propagates very fast and the temperature of both the top and the bottom interfaces are almost equal due to a very small thickness of the layer. At the same time, the film at the bottom interface undergoes high strain due to the difference in thermal expansion of Pt and PZT layers. The strain increase results in an increase of activation energy which suppresses crystallization at the bottom interface. As a result, crystallization starts from the top interface i.e. the surface of the film.

4. Theoretical calculations

Taking all necessary parameters from the experiments and neglecting the pulsed nature of the excitation, we could demonstrate