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$BaTiO_3$ nanocrystalline thin films: synthesis, plasma treatment, and memristive effect

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Abstract. Here, experimental studies on barium titanate nanocrystalline thin films fabricated by pulsed laser deposition and the influence of the oxygen pressure on the morphological parameters are presented. The average grain size changes from (20.1±1.8) nm to (88.2±7.9) nm with increasing oxygen pressure from 1×10^{-5} Torr to 1×10^{-2} Torr. The effect of plasma treatment on the parameters of $BaTiO_3$ nanocrystalline thin films was studied. It was found that the formation of whisker-like structures is preferred for $BaTiO_3$ when the power of inductively coupled and capacitive plasma sources increases. The results can be applied to the design and development of technological processes for promising lead-free energy converters, eco-friendly energy devices and memristive structures developed based on pulsed laser deposition.

Keywords: barium titanate, thin films, pulsed laser deposition, plasma treatment, memristive effect

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Тонкие нанокристаллические пленки $BaTiO_3$: синтез, плазменная обработка, мемристивный эффект

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Аннотация. В работе представлены результаты экспериментальных исследований влияния давления кислорода при импульсном лазерном осаждении и режимов плазменной обработки на морфологические параметры нанокристаллических тонких пленок титаната бария. Полученные результаты могут быть использованы при проектировании и разработке технологических процессов для перспективных бессвинцовых преобразователей энергии и мемристивных структур, созданных на основе импульсного лазерного осаждения.

Ключевые слова: титанат бария, тонкие пленки, импульсное лазерное осаждение, плазменная обработка, мемристивный эффект

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Introduction

Ferroelectric materials attract attention for promising applications such as non-volatile memory devices [1], transducers and actuators [2], and energy harvesters [3]. Barium titanate ($BaTiO_3$) can be used in many applications due to ferroelectricity, high dielectric constant, and large electro-optic coefficients [4]. RF sputtering, molecular beam epitaxy, sol-gel, and pulsed laser deposition (PLD) can be used for $BaTiO_3$ thin film fabrication. Due to the ability to provide stoichiometric growth of multi-component oxide films in reactive environments PLD is one of the prospective techniques for $BaTiO_3$ thin film fabrication [5].

$BaTiO_3$ nanocrystalline films formed by pulsed laser deposition often have rough relief due to the presence of drop-shaped structures on the surface [6]. This issue is common to a wide range of ferroelectric materials and significantly limits the integration of ferroelectric films with silicon technology. Plasma treatment is one of the possible ways to control the modification of the thin film's surface topography [7]. However, the data on plasma treatment of $BaTiO_3$ is fragmentary. Therefore, understanding the processes involved in the micro- and nanofabrication of multicomponent oxide films requires additional research. Thus, the purpose of the experimental studies was to determine the regularities of the influence of capacitive and inductively coupled plasma sources power on the morphological parameters of nanocrystalline $BaTiO_3$ films.

Materials and Methods

$BaTiO_3/SiO_2$ structures fabricated by PLD technique in Pioneer 180 module (Neocera LCC, Beltsville, MD, USA) with a KrF excimer laser (λ = 248 nm) were used as experimental samples. $BaTiO_3$ target (Kurt J. Lesker) was in a vacuum chamber evacuated to 1×10^{-6} Torr. The films were formed in oxygen atmosphere in the pressure range from 1×10^{-5} Torr to 1×10^{-2} Torr. Substrate temperature, laser power density, and pulse repetition rate were 600 °C, 1.7 J/cm^2, and 10 Hz, respectively. The etching process was carried out by plasma-chemical processing of materials in a combined capacitive and inductive discharge plasma in STE ICPe68. The power values of the inductively coupled and capacitive plasma sources ranged from 200 W to 600 W and from 10 W to 40 W, respectively.

The morphology of the obtained films was studied by scanning electron microscopy (SEM) and atomic force microscopy (AFM) in the semicontact mode using a Nova Nanolab 600 scanning electron microscope (FEI.Co, Netherlands) and the Ntegra probe nanolab (NT-MDT-SI, Russia) [8]. In order to correctly determine the depth of etching, a protective plasma-resistant layer was applied to the samples. I-V measurements of the $Si/SiO_2/ITO/ZnO/Ti$ structure was carried out using Probe Nanolaboratory Ntegra (NT-MDT-Si, Russia) [9].

Results and Discussion

Fig. 1 shows AFM images of $BaTiO_3$ nanocrystalline films obtained under different oxygen pressures.

It was found that the samples obtained at an oxygen pressure of 1×10^{-5} Torr have a fine-grained structure compared to the films obtained at higher oxygen pressures. The average grain size changes from (20.1±1.8) nm to (88.2±7.9) nm with increasing oxygen pressure from 1×10^{-5} Torr to 1×10^{-2} Torr (Fig. 2).

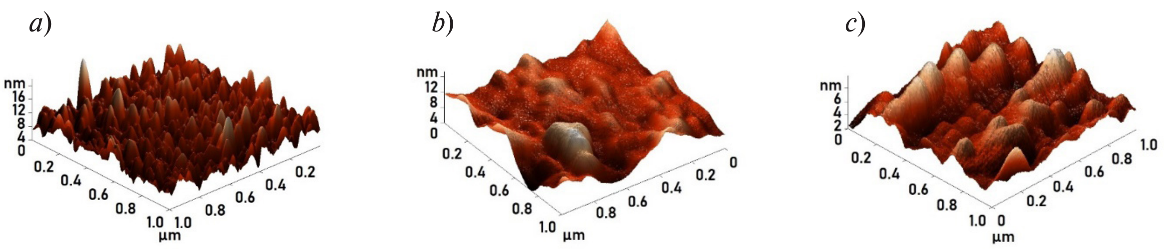

Fig. 1. AFM images of $BaTiO_3$ nanocrystalline films fabricated under different oxygen pressure: 1×10^{-4} Torr (*a*), 1×10^{-3} Torr (*b*), and 1×10^{-2} Torr (*c*)

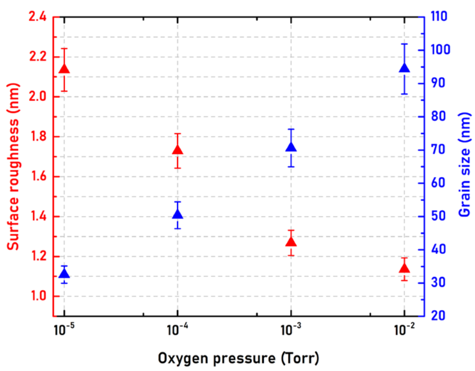

Fig. 2. AFM studies of $BaTiO_3$ nanocrystalline films obtained at different oxygen pressures: surface roughness (red) and grain size (blue)

Thus, at lower oxygen pressures, there is an increase in nucleation density, which leads to the formation of small size grains (Fig. 1), and the reason for the increase in grain size (with increasing oxygen pressure) may be phase separation (formation of clusters on the surface of the film) [10]. In addition, changes in the morphological parameters of the films may be associated with the combined effect of mismatch deformation, the appearance is caused by a mismatch of the crystal lattices of the film and substrate materials and is an indicator of island growth at the initial stage of $BaTiO_3$ film formation [11]. All $BaTiO_3$ films obtained in the pressure range under consideration have a homogeneous structure and no cracks. The surface of $BaTiO_3$ films obtained at an oxygen pressure of 1×10^{-5} Torr is smooth except for small particles, the appearance of which is probably caused by the effect of redeposition of the material from the surface of a heated substrate. As oxygen pressure increases, cluster aggregation is observed due to a decrease in the surface roughness of the films (Fig. 1). In this case, the grain size increases with increasing oxygen pressure since the evaporated particles do not have enough energy to migrate across the substrate surface due to decreased kinetic energy and free path length.

Fig. 3 shows the dependence of the etching depth of $BaTiO_3$ films on the power of inductively coupled and capacitive plasma sources.

a) *b*)

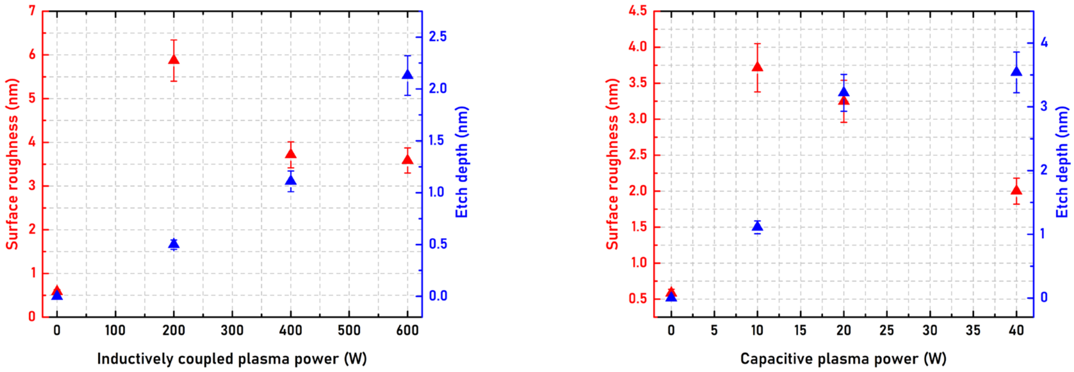

Fig. 3. Dependencies of etch depth (blue) and surface roughness (red) of $BaTiO_3$ nanocrystalline films on power of inductively coupled (*a*) and capacitive (*b*) plasmas

It was found that when the power of the inductively coupled plasma source is increased from 200 W to 600 W, the etching depth of $BaTiO_3$ films increases from (0.52±0.04) nm to (2.14±0.27) nm. When the capacitive plasma power was changed from 10 W to 40 W, the etching depth of $BaTiO_3$ nanocrystalline films increased from (1.1±0.1) nm to (3.5±0.3) nm. The increase in the etching depth can be attributed to the strong influence of the physical component in the etching process when the power of the capacitive plasma source increases.

It was found that the formation of whisker-like structures is a preferred for $BaTiO_3$ films when the power of inductively coupled (from 0 W to 200 W) and capacitive (from 0 W to 10 W) plasma sources increases (Fig. 4), which leads to a sharp increase in surface roughness of $BaTiO_3$ nanocrystalline films from (0.60±0.15) nm to (5.9±0.5) nm when using inductively coupled plasma and to (3.7±0.3) nm when using capacitive plasma.

a) *b*) *c*)

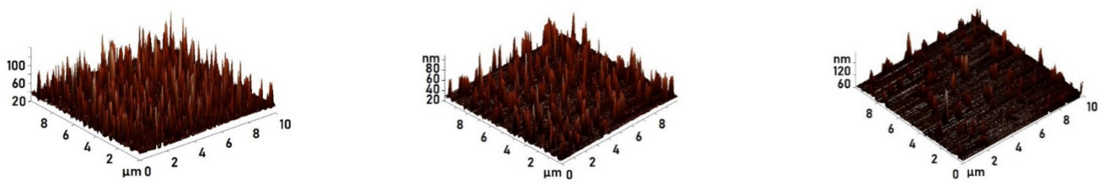

Fig. 4. AFM images of $BaTiO_3$ nanocrystalline films after plasma treatment in inductevely coupled plasma: 200 W (*a*), 400 W (*b*), and 600 W (*c*)

With further increase of plasma source power up to 600 W for inductively coupled plasma and 40 W for capacitive plasma, respectively, a gradual decrease in the surface roughness of $BaTiO_3$ films is observed, which is associated with a decrease in the height and density of nanostructures on the surface of the obtained films.

The I-V sweep in Fig. 5 show bipolar switching characteristic in $BaTiO_3$ nanocrystalline film.

It was found that the obtained $BaTiO_3$ films have a memristive effect. R_{HRS}/R_{LRS} ratio for $BaTiO_3$ films fabricated under 1×10^{-2} Torr was 22, with the low resistance state $R_{LRS} = (0.28\pm0.04)\times10^9$ Ω and high resistance state $R_{HRS} = (6.25\pm0.52)\times10^9$ Ω.

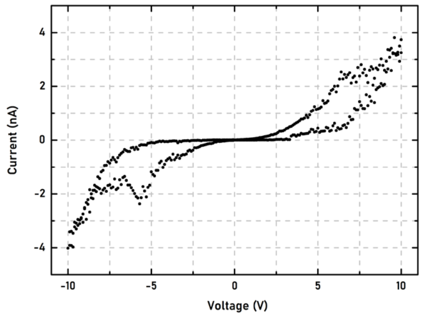

Fig. 5. Current-voltage characteristic of $BaTiO_3$ nanocrystalline film

Conclusion

It was established that increasing oxygen pressure from 1×10^{-5} Torr to 1×10^{-2} Torr results in an increase in average grain size in the range from (20.1±1.8) nm to (88.2±7.9) nm, and cluster aggregation is observed due to a decrease in the surface roughness of the films. $BaTiO_3$ nanocrystalline thin films have a whisker-like structure after plasma treatment. With the increase in plasma source power up to 600 W for inductively coupled plasma and 40 W for capacitive plasma, a gradual decrease in the surface roughness of $BaTiO_3$ films is observed. The current-voltage characteristic showed a bipolar resistive switching with $R_{LRS} = (0.28\pm0.04)\times10^9$ Ω and $R_{HRS} = (6.25\pm0.52)\times10^9$ Ω. The results can be applied to the design and development of technological processes for promising lead-free energy converters, eco-friendly energy devices, and memristive structure manufacturing based on pulsed laser deposition.

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