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Structural and electrophysical properties of barium titanate epitaxial films

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Abstract. One of the rapidly developing areas of nanophotonics is the creation of integrated optical circuits for the operation of ultrafast, energy-efficient devices. Electro-optical modulators are the integral part of such systems. The possibility of optical modulation is provided by the electro-optical effect occurring in the waveguide structure and providing the opportunity to manage the optical properties of waveguide materials under the influence of electric fields. Barium titanate $BaTiO_3$ (BTO) exhibits one of the largest known electro-optical coefficients, which makes it an ideal candidate for use in photonic integrated circuit modulators. This work is dedicated to the fabrication of BTO/MgO(001) epitaxial heterostructures and to characterization of their structural and electrophysical properties. The substrate material was chosen based on the difference in the refractive indices of BTO and MgO. The growth was carried out by pulsed laser deposition (PLD). The crystal structure and epitaxial relations in the grown heterostructures were monitored in situ during growth using high-energy electron diffraction. To study the dependence of the BTO layer polarization on the external electric field, test samples with a buffer conducting layer of $SrRuO_3$ and gold contacts deposited on top were grown. Measurements of the electrophysical properties were performed using a two-probe mode.

Keywords: electro-optical modulators, waveguides, barium titanate, Pockels effect

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Исследование структурных и электрофизических свойств эпитаксиальных пленок титаната бария

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Аннотация. Одним из активно развивающихся направлений нанофотоники сегодня является создание интегральных оптических схем для работы сверхбыстрых, энергоэффективных устройств. Электрооптические модуляторы являются неотъемлемой частью таких систем. Возможность оптической модуляции обеспечивается электрооптическим эффектом, возникающим в волноводной структуре и позволяющим получать необходимое изменение оптических свойств материалов волновода при воздействии электрических полей. Титанат бария $BaTiO_3$ (BTO) демонстрирует один из самых больших известных электрооптических коэффициентов, что делает его идеальным кандидатом для применения в модуляторах фотонных интегральных схем. Настоящая работа посвящена получению эпитаксиальных гетероструктур BTO/MgO (001), а также характеризации их структурных и электрофизических свойств. Материал подложки выбирался, исходя из разницы показателей преломления BTO и MgO. Рост осуществлялся методом импульсного лазерного осаждения (PLD). Кристаллическая структура и эпитаксиальные соотношения выращенных пленок контролировались in-situ во время роста с помощью дифракции быстрых электронов (RHEED). Для исследования зависимости поляризации слоев BTO от внешнего электрического поля были выращены тестовые образцы с буферным проводящим слоем $SrRuO_3$ и нанесенными сверху золотыми контактами. Измерения электрофизических свойств производились по двух-зондовой методике.

Ключевые слова: электрооптические модуляторы, волноводы, титанат бария, эффект Поккельса

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Introduction

Integrated waveguide optics is a rapidly developing scientific direction. Electro-optical modulation methods are widely used in optoelectronic systems for various purposes (information processing and transmission systems, fiber-optic communication systems, laser resonator Q-modulators, various measuring sensors, etc.) and electro-optical modulators are an integral part of such systems. Integral waveguide modulators are used in optoelectronic devices allowing to operate the amplitude of the light signal passing through the waveguide. The possibility of optical modulation is provided by the electro-optical effect being present in waveguide structures and allowing to obtain the necessary change in the optical properties of the waveguide materials under the influence of electric field [1].

It is well known that ferroelectric materials can be used for voltage control of waves propagating in different media. For example, solid solution of $Ba_xSr_{1-x}TiO_3$ was employed for manipulation of spin waves propagating in magnetic film waveguides [2]. Lithium niobate modulators [3] are used widely for phase and intensity modulation of optical radiation in optical information systems. Barium titanate $BaTiO_3$ (BTO) is another promising material for photonics applications [4]. Among other ferroelectric materials, BTO is well-known to exhibit large effective Pockels coefficient [5] which makes it a perfect candidate for the manufacture of electro-optic modulators. In cubic BTO, titanium atoms are in the Oh coordination of oxygen. Ferroelectrical properties of tetragonal BTO are due to the average relative displacement along the c-axis of titanium from its centrosymmetric position in the unit cell and consequently the creation of a permanent electric dipole [6]. The present study was dedicated to technological peculiarities relevant for nucleation and further epitaxial growth of tetragonal BTO thin film and investigation of the films structural and electrophysical properties.

Materials and Methods

The BTO epitaxial films were grown on MgO (001) substrates by means of pulsed laser deposition (PLD) from a stoichiometric $BaTiO_3$ target ablated with KrF excimer laser (λ = 248 nm, Coherent, COMPex Pro). The growth was performed in the PLD setup produced by SURFACE (Germany). The choice of MgO substrate was motivated by several reasons: firstly, the lattice parameters of MgO ($a = b = c$ = 4.21 Å) match reasonably to those of tetragonal BTO ($a = b$ = 3.99 Å, c = 4.03 E), secondly, the refractive index of MgO (n = 1.7 at 0.6 μm) is much lower than that of BTO (n = 2.4 at 0.6 μm), which facilitates the fabrication of waveguides based on such structures [7]. During BTO deposition, the substrate was clamped to a stainless-steel sample holder that was heated from the backside with a platinum filament, the temperature of the sample holder was measured with a type-K thermocouple. The growth was performed in an oxygen atmosphere (p = 0.05 mbar) and with the substrate temperature of 800 °C. The growth rate was measured by means of Inficon quartz thickness monitor and was about 0.5 Å/s. Crystal structure and epitaxial relations of the grown films were monitored *in-situ* during the growth by reflection high energy electron diffraction (RHEED). The RHEED system was equipped with an RDEC (Japan) 30 kV electron gun and a custom Rheed Capture acquisition software. The RHEED pattern processing and modeling was carried out with a custom Rec Space reciprocal space mapping software [8]. To investigate ferroelectric properties of epitaxial BTO films, a 30 nm thick $SrRuO_3$ (SRO) conducting layer was deposited on the MgO substrate before the growth of 200 nm-thick BTO layer. Having a similar crystal structure and lattice constants close to BTO, the SRO layer did not prevent the following epitaxial growth of BTO. To provide electrical contact from the upper side, round shape gold electrodes with a diameter of 60 μm were deposited on the surface of the BTO film.

X-ray diffraction (XRD) measurements were carried out using a 4-circle Bruker diffractometer (with a fixed photon energy corresponding to the Cu Kα emission) and 2D CCD X-ray detector. Both specular and off-specular reflection measurements enabled identification of the film crystal lattice.

Medium Energy Ion Scattering (MEIS) spectrometry made it possible to evaluate thickness, crystalline quality and element composition of the films under investigation. Two backscattering ion registration channels were used: low-resolution semiconductor spectrometric detector (SCD) with the backscattering angle of 170 °, able to "see" the depths of several hundred nanometers, and high-resolution spherical electrostatic analyzer (ESA) for the study of extremely thin films and near-surface layers up to tens of nm. ESA has the backscattering angle of 120 °. Protons with initial energy of 227 keV were used as probe ions. The measurements were carried out in the two modes: aligned with the direction of probe beam close to the low-index crystal axis (normal to the surface), and off-axis with the angle between the beam and the axis of several (6–8°) degrees. Aligned/off-axis ratio characterizes the crystalline quality; the computer simulation fitted to experimental values of off-axis spectrum makes it possible to evaluate the element composition.

Electrophysical measurements were carried out using a two-probe technique. Voltage was applied between the two upper gold electrodes by precisely placing conductive gold-plated needles on top of them. The resulting electrical circuit consisted of two capacitors connected in series with a common lower plate formed by the SRO layer. The resistance of the lower plate was low enough to be neglected. With a sufficiently large contact area the capacitance of the wires could also be neglected. The current flowing in the system was measured with a sinusoidally changing voltage. The current response of a conventional capacitor is calculated as $i = C \cdot dU/dt$ (where C is the capacitance and dU/dt is the time derivative of voltage) and, with a sinusoidal voltage, looks like a horizontal ellipse. In the presence of leaks, the ellipse becomes slightly tilted. In a conventional paraelectric the polarization at reasonable voltages increases slowly, linearly, and reversibly with the applied field (small voltage-independent capacitance). In contrast to this, the polarization of a ferroelectric increases much faster with the applied field and reaches quasi-saturation at already small fields (voltages). In addition, this dependence exhibits hysteresis.

Results and Discussion

RHEED measurements demonstrated high crystalline quality of the grown BTO films. Fig. 1 shows cuts of the reciprocal space map obtained during the azimuthal rotation of the sample: the in-plane (Fig. 1, *a*) and out-of-plane (Fig. 1, *b*) reciprocal space cuts. The film grows with BTO [001] and BTO [010] axes parallel to MgO [001] and MgO [010] axes respectively.

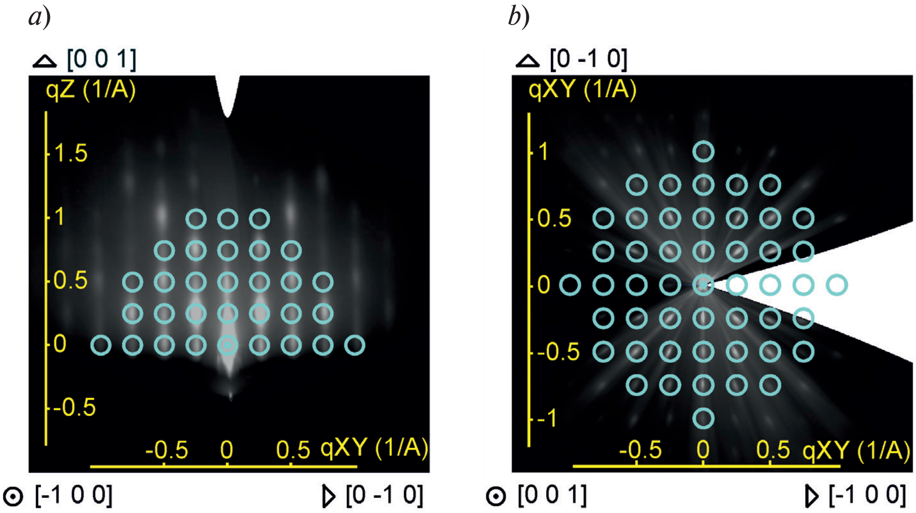

Fig. 1. Reciprocal space structure of BTO film: the in-plane (*a*) and out-of-plane (*b*) reciprocal space cuts. The circles indicate the modeled positions of reciprocal space nods

As the c lattice parameter is only a few percent different from the a and b lattice parameters in BTO, it was not possible to distinguish the cubic and the tetragonal crystal structure by means of RHEED. Post-growth XRD measurements showed that the actual lattice constants of the grown BTO films are: $a = b = 4.02$ Å, $c = 4.09$ Å, which confirms that the grown BTO films possess a tetragonal crystal structure.

The SCD MEIS spectra of the BTO film are shown in Fig. 2 (main panel) together with the results of the off-axis spectrum simulation. The value of aligned/off-axis ratio of ~4.5% (high energy region, right vertical axis) corresponds to the crystalline quality of almost an ideal single crystal. The inset shows the ESA off-axis spectrum and its simulation. As a result, the Ba/Ti composition is estimated as 0.95/1.05, i.e., close to the stoichiometric BTO.

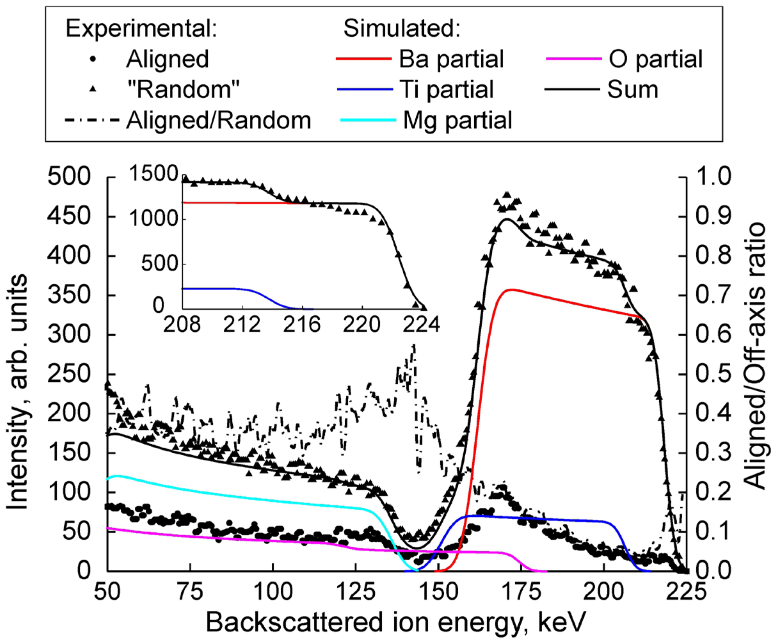

Fig. 2. SCD MEIS spectra measured for BTO/MgO structure

The schematic drawing of the BTO/SRO/MgO structure and the corresponding equivalent electrical circuit are shown in Fig. 3, *a* and Fig. 3, *b* respectively. In the grown BTO layers, a current–voltage characteristic in the form of a distorted ellipse at small amplitudes of the sinusoidal voltage below 2 V was observed. In such mode, a capacitor with a ferroelectric between the plates can be roughly described as having a large constant capacitance. As the voltage swing increases above 2 V the ferroelectric becomes saturated and the recharge current diminishes considerably. The current-voltage curve (showed characteristic current peaks at +2 V and −2 V where the derivative of polarization with respect to voltage dP/dU is maximal) is shown in Fig. 3, *c*. The reasonably looking $P(U)$ hysteresis loop is obtained by integration of the current-voltage curve over time (Fig. 3, *d*).

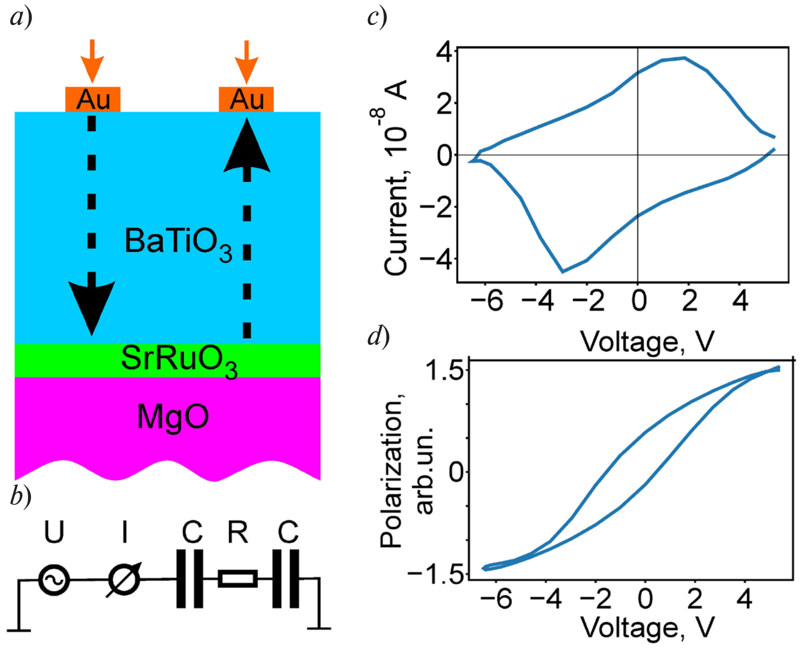

Fig. 3. Schematic drawing of BTO/SRO/MgO structure (*a*) and equivalent electrical circuit (*b*); current–voltage (*c*) and polarization–voltage (*d*) dependencies

Conclusion

Epitaxial quality barium titanate films were successfully grown by means of PLD in this study. The combination of multiple characterization techniques provided a comprehensive understanding of the structural and electrophysical properties of the films. The RHEED, XRD and MEIS studies showed that the obtained films possess high-quality tetragonal crystal structure with the composition close to the stoichiometric one. The electrophysical measurements showed that the grown films exhibit ferroelectric properties.

The obtained results are a good basis for further research aimed at development of technologies related to utilization of barium titanate in novel optical modulators.

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