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Synthesis and structural properties of predominantly oriented $(Sr,Ba)Nb_2O_6$ films on alumina substrate

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The influence of the composition and pressure of the working gas on the structural properties of strontium-barium niobate films obtained by high-frequency magnetron sputtering on polycrystalline aluminum oxide substrates was studied. The pressure and ratio of oxygen and argon in the working gas at which a film with a predominant orientation (00*l*) is formed on alumina were determined. This is the first successful attempt to form predominantly oriented strontium-barium niobate films of high structural quality on polycrystalline aluminum oxide substrates.

Keywords: strontium-barium niobate, oriented growth, alumina substrate, microwave applications.

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Ferroelectric (FE) films are of interest in the development of electrically controlled capacitive elements of microwave electronics, such as variable capacitors, phase shifters, delay lines, etc. [1]. The design of these elements is made feasible by the high dielectric nonlinearity of FE materials and relatively low microwave losses. The search for FE materials with the optimum electrophysical properties for microwave applications has been ongoing for a long while [2]. Strontium-barium niobates ($Sr_xBa_{1-x}Nb_2O_6$, SBN) with a tetragonal tungsten bronze structure with 5/6 cation sites occupied are regarded as promising FE materials. SBN crystals are characterized by a disordered arrangement of Ba and Sr ions. On the one hand, this allows one to adjust the permittivity, piezoelectric parameters, the phase transition temperature, and relaxor characteristics of SBN solid solutions within a wide range by varying their composition. On the other hand, it leads to the emergence of volumetric compositional fluctuations and various types of secondary crystalline phases [3]. SBN single crystals are used successfully in optoelectronics, photorefractive optics, and nonlinear optics [4]. In the form of thin films, the material has been studied to a lesser extent; certain questions regarding the mechanisms responsible for ferroelectric polarization [5] and the formation of dielectric (in particular, relaxor) properties [6] still remain unanswered. It is important to note that the structural quality of strontium barium niobate films has a strong influence on their electrophysical characteristics, which distinguishes them from, e.g., the well-studied barium strontium titanate (BST) films. This is attributable to the fact that strontium barium niobate is, unlike ferroelectrics with a perovskite-type structure, a uniaxial material, and the FE polarization in SBN is oriented exclusively along the (00*l*) direction. Thus, polycrystalline films of BST and other perovskites may still have fine nonlinear properties [7], whereas SBN films need to be (00*l*)-oriented. This makes it significantly harder to grow them on structurally mismatched substrates.

Oriented SBN films have already been obtained on dielectric substrates of magnesium oxide [3,6,8] and $SrTiO_3$ [3], as well as on silicon substrates with a platinum sublayer [9]. The hygroscopicity of MgO, the high permittivity of strontium titanate, and significant dielectric losses of silicon at microwave frequencies make all these substrates suboptimal for microwave applications. The results of synthesis of predominantly (00*l*)-oriented SBN films on single-crystal aluminum oxide (sapphire) have been reported relatively recently in [10,11]. This substrate material has excellent dielectric characteristics, but is also expensive. The growth of oriented SBN films on substrates made of much cheaper polycrystalline Al_2O_3 (alumina) has not been implemented yet. This material is also of interest for microwave applications, since its microwave characteristics and cost are comparable to those of sapphire. Only the data on production of polycrystalline films have been published to date [12]. In this regard, the aim of the present study is to investigate the possibility of oriented growth of SBN films on alumina and characterize their structural properties as functions of the technological process conditions in the context of application of these films in controlled microwave devices.

Thin films of strontium barium niobate were deposited onto polycrystalline alumina substrates by RF magnetron sputtering. A $Sr_{0.75}Ba_{0.25}Nb_2O_6$ (SBN 75) powder was prepared by solid-phase synthesis from high-purity $SrCO_3$, $BaCO_3$, and Nb_2O_5 (taken in a stoichiometric ratio) at the Prokhorov General Physics Institute (Moscow, Russia). This SBN 75 powder had a tetragonal structure with lattice parameters $a = b = 12.45$ Åand $c = 3.94$ Å. A ceramic target with a diameter of 76 mm and a thickness of 5 mm was fabricated from the obtained powder at the Ferrite-Domen Scientific Research Institute (St. Petersburg, Russia). The

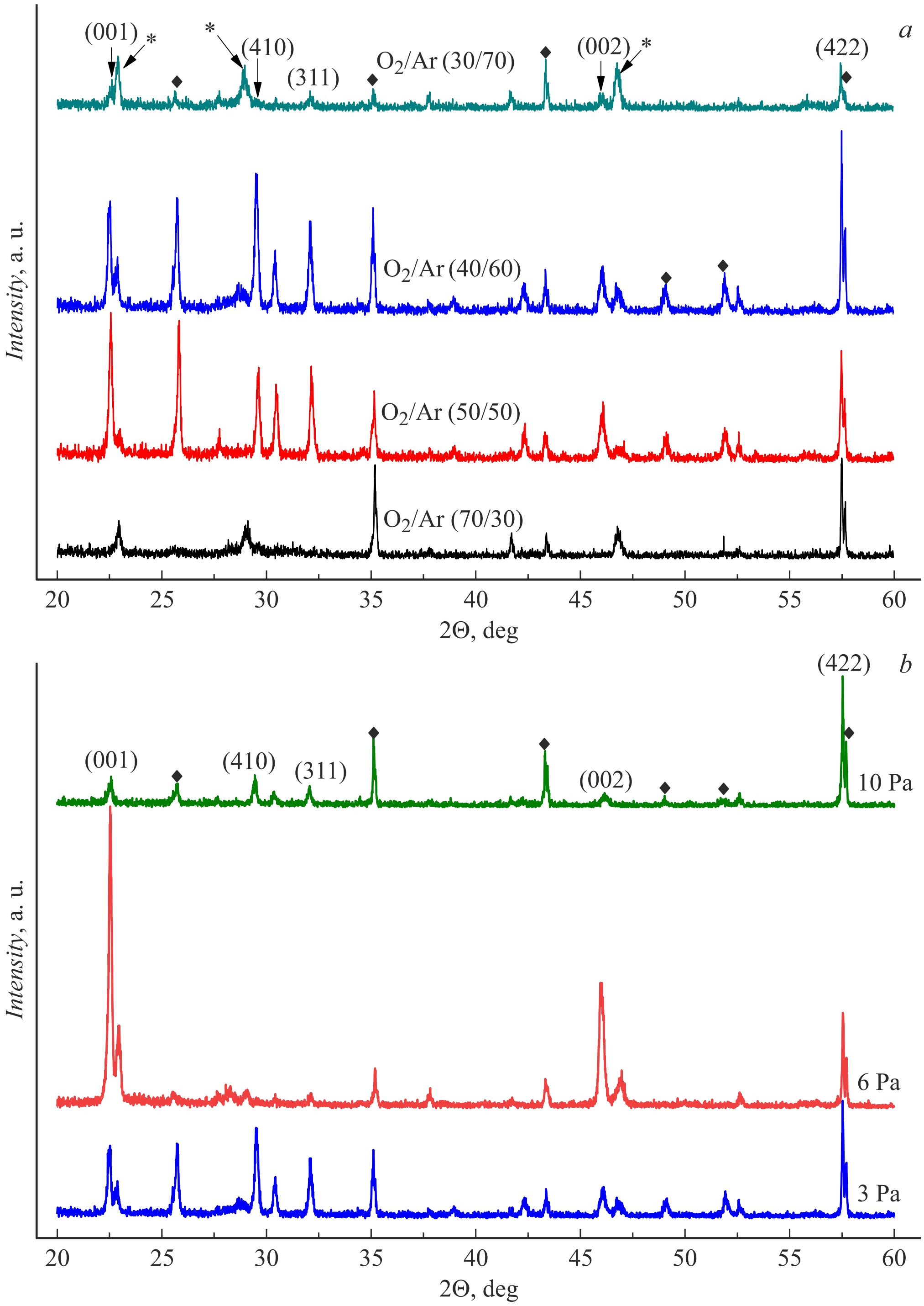

Figure 1. Diffraction patterns of films obtained at a pressure of 3 Pa and different gas compositions (*a*) and films obtained at a gas composition of 40/60 and different pressures (*b*).

substrate for film growth was 10 × 10 mm in size and had a thickness of 0.5 mm. Prior to film deposition, the vacuum chamber was evacuated to a residual pressure of 10^{-3} Pa. Films were synthesized at a substrate temperature of 900 °C. The temperature of film deposition onto alumina substrates was chosen based on the results of earlier studies [12], where the formation of a solid SBN solution on alumina was found to proceed at temperatures above 850 °C. A mixture of O_2 and Ar in different proportions was used as the working gas; its pressure was varied within the 3–10 Pa range that was chosen with account for the discharge stability and the maximum sputtering rate of the SBN target. The deposition time of continuous films was varied from 120 to 240 min (depending on the working gas

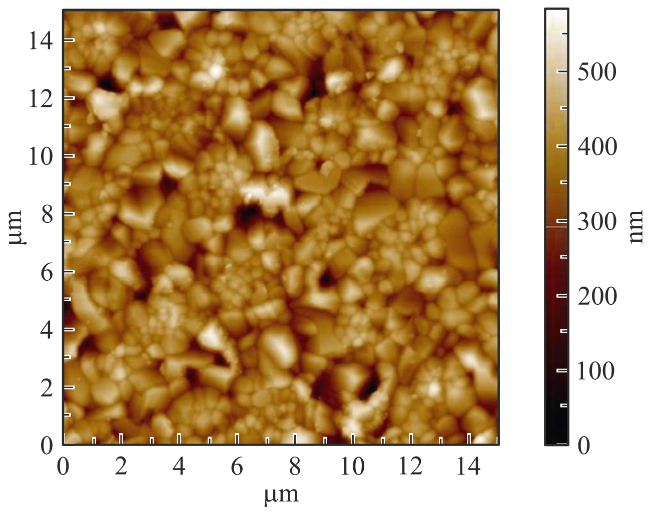

Figure 2. SPM image of microrelief of the SBN film synthesized at a pressure of 6 Pa.

Chemical composition of SBN films obtained at a pressure of 6 Pa

Element	Line type	Composition	
		wt.%	at.%
O	*K*-series	26.35 ± 0.06	66.47
Al	*K*-series	1.97 ± 0.05	2.94 ± 0.04
Sr	*L*-series	16.32 ± 0.02	7.52 ± 0.07
Nb	*L*-series	48.29 ± 0.08	20.98 ± 0.12
Ba	*L*-series	7.07 ± 0.05	2.08 ± 0.06
Total		100.00	100.00

pressure) in order to obtain films with a thickness of 500 nm. Following deposition, the films were cooled in the working gas atmosphere at a rate of 2−3 °C/min.

Their surface morphology was studied by scanning probe microscopy (SPM) using an Ntegra Prima NT-MDT probe station in intermittent contact mode with NS-35 cantilever probes with a characteristic free resonance frequency of 300 kHz and a stiffness of 16 N/m. The elemental composition of the samples was studied by electron microscopy (EM) in low vacuum with an SM-32 Melytec scanning microscope fitted with an Oxford Instruments energy-dispersive X-ray spectrometer. The crystal structure and phase composition of films were monitored by X-ray diffraction analysis (XDA) using a DRON-6 diffractometer with Cu$K_{\alpha 1}$ radiation ($\lambda = 1.54$ Å). Measurements were carried out within the angular diffraction range $2\Theta = 20$–$60°$ at a scanning rate of 2°/min in the continuous mode.

Figure 1, *a* shows the diffraction patterns of SBN films deposited onto alumina with different oxygen concentrations in the O_2/Ar gas mixture. Diamonds indicate the substrate reflections. These diffraction patterns suggest that both a deficiency and an excess of oxygen in the gas mixture leads to the suppression of growth of the SBN phase and to the formation of secondary phases (reflections at 23, 29, and 46.9° marked with asterisks). These phases are hard to identify due to the large number of oxide compounds of barium and niobium and to the fact that their reflections are superimposed onto the peaks of the main SBN phase. The most pronounced (00*l*) reflections with a minimum content of secondary phases are demonstrated by films deposited in a gas mixture with an oxygen content of 40%.

Figure 1, *b* shows the diffraction patterns of SBN films deposited in the O_2/Ar (40/60) gas mixture at different working gas pressures. It is evident that the film grown at a pressure of 6 Pa has a predominant (00*l*) orientation with a minimum amount of grains of other orientations and secondary phases. Films synthesized at higher and lower pressures are polycrystalline, which should have a negative effect on their nonlinear properties due to the suppression of polarization under the influence of an external field compared to (00*l*)-oriented films.

The dependence of the crystalline structure and texture of SBN films on the working gas pressure is due to energy processes involving sputtered atoms in the space between the sputtered target and the substrate and processes on the substrate surface. In the present case, the mean free path of RF-sputtered atoms in the ceramic target−substrate space is on the order of 2 cm at $P \approx 3$ Pa and close to 5 mm at $P \approx 10$ Pa [13]. Therefore, at high pressure, each sputtered atom undergoes several collisions with atoms of the working gas in the gap between the target and the substrate (2 cm), which leads to energy losses. The migration of adatoms on the substrate surface is hindered as a result, which promotes random formation of small-sized nuclei and the growth of a polycrystalline film [14]. At a low pressure, the transit of atoms becomes virtually collisionless, which leads, on the one hand, to an increase in activity of adatoms on the surface of the substrate and, on the other hand, to a change in elemental composition of the film (due to the differences in nature of transport of atoms of different masses through the gas medium that are governed by their thermalization lengths [15]). Violation of stoichiometry on the substrate surface hinders the formation of a solid solution and, on the contrary, promotes the crystallization of secondary phases of simple oxides and polyniobates [16]. Thus, in terms of formation of (00*l*)-oriented SBN films on alumina, the working gas pressure level optimum for our experiments is $P = 6$ Pa. At this pressure, the energy of adatoms incident on the substrate is sufficient to form an oriented film, and the deviation from the stoichiometric composition is insignificant. These films were subjected to further analysis of their surface morphology and elemental composition.

A typical SPM image of surface microrelief of the SBN film on alumina is shown in Fig. 2. A developed structure with grains of different sizes and their agglomerates is seen clearly. The average size of agglomerates is 500–1000 nm, and the grain size is 100–200 nm, which agrees with the XDA data. The average surface roughness of the studied films is on the order of 50 nm. This morphology of SBN films on alumna is indicative of a Volmer−Weber

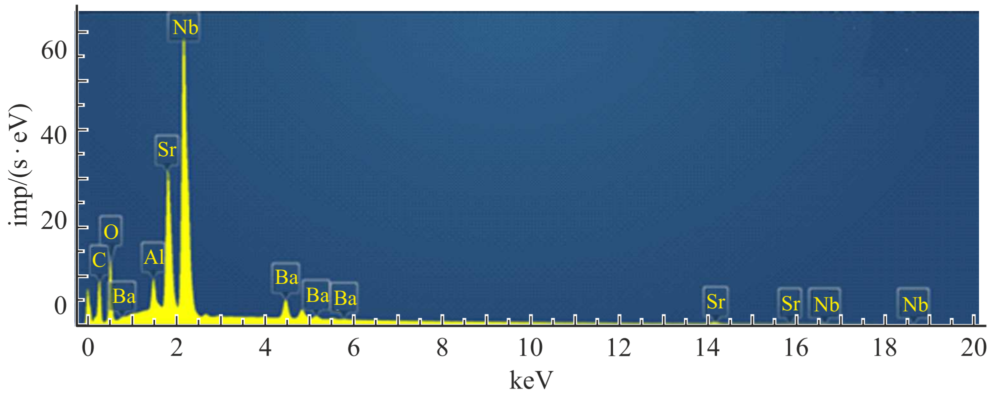

Figure 3. Elemental composition of SBN films obtained at a pressure of 6 Pa.

crystallization mechanism [12]. This mechanism is observed when the forming nuclei interact more strongly with each other than with the substrate surface, which is attributable to weak chemical bonding of the film and the substrate. Crystallites, which may vary significantly in size, are formed as a result.

The results of elemental analysis of films deposited at a working gas pressure of 6 Pa are presented in Fig. 3 and in the table. Compared to the target composition, the films are depleted slightly in barium and enriched in strontium $Sr_{0.78}Ba_{0.22}Nb_2O_6$). Deviations of the elemental composition of the deposited films from the target composition may be attributed to the influence of pressure of the gas environment on the trajectories of motion of sputtered atoms of different masses from the target to the substrate [15]. At low pressures, the thermalization length of heavy Ba atoms does, in contrast to the one of Sr atoms, exceed the target–substrate distance [15]. Therefore, barium atoms leaving the target move along a ballistic trajectory, while light strontium atoms propagate in the diffusion mode, which may lead to depletion of the solid solution in barium.

The influence of the composition and pressure of the working gas on the texture and microstructure of 500-nm-thick strontium-barium niobate films, which were obtained by RF magnetron sputtering on alumina substrates, was investigated. It was demonstrated that the optimum oxygen concentration in the gas mixture for synthesis of (00l)-oriented films is 40 %. A deficiency or excess of oxygen in the gas mixture leads to the suppression of growth of the SBN phase and the formation of secondary crystalline phases. At high working gas pressures, a polycrystalline SBN film forms on alumina due to the suppression of migration of adatoms on the substrate surface. At low pressures, the stoichiometry of sputtered atoms on the substrate surface may be violated, hampering the formation of a solid solution. Working gas pressure $P = 6$ Pa appears to be the optimum one in terms of formation of oriented (00l) SBN films on alumina.

The obtained results may be of interest in the context of formation of (00l)-oriented SBN films with high dielectric nonlinearity on alumina substrates for electrically controlled microwave devices.

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Conflict of interest

The authors declare that they have no conflict of interest.

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