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FERROELECTRICS IN ACOUSTOELECTRONICS

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Abstract: *Acoustoelectronics is one of the areas of acoustics, associated with the use of mechanical resonance effects and the piezoelectric effect, as well as the effect based on the interaction of electric fields with waves of acoustic stresses in a piezoelectric material. The main materials used in acoustoelectronics are ferroelectrics, which are mainly complex oxide materials. This article discusses the possibility of increasing the purity and homogeneity of ferroelectric materials, as well as softening the regimes of their synthesis using the solution extraction-pyrolytic method. It is shown that the synthesis temperatures of $BaTiO_3$, $SrTiO_3$, and $Pb(Zr)TiO_3$ ferroelectric films are reduced to 550-600°C, and the synthesis time is down to 5-10 minutes. The dielectric constant and Curie temperature values correspond to the maximum characteristics for these materials. Thus, using the extraction-pyrolytic method we obtained suitable for use in acoustoelectronic technology ferroelectric films.*

Keywords: *acoustoelectronics, ferroelectrics, solution extraction-pyrolytic synthesis*

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1. INTRODUCTION

High and sometimes contradictory requirements for devices for converting, processing and recording radio signals (speed, high sensitivity, frequency tuning and selectivity) for acoustic devices can only be satisfied using a variety of physical and chemical phenomena. The purely radiotechnical methods of receiving and processing signals are being replaced by new methods based on optical or acoustic conversion of radio signals [1].

At the middle of 20th century, at the intersection of research in physical acoustics of a solid, semiconductor physics and radiophysics the acoustoelectronics emerged as a boundary region between acoustics and electronics. Its main task was to develop principles for constructing ultrasonic devices for converting, processing and recording radio signals. In the first period of the acoustoelectronics development the signal conversion devices used volumetric acoustic waves, which were excited and detected using piezoelectric transducers. Then it was discovered and investigated the photosensitive excitation of high-frequency elastic waves at the frequency of the exciting electric field in the crystals with a large dielectric constant ($SrTiO_3$ and $KTaO_3$). Reflection and refraction of waves on an acoustically induced periodic domain structure are found [2].

Piezoceramics are used to make small-sized microphones, telephones, high-frequency loudspeakers, hearing aids, detonators for weapons, various devices for ignition in gas systems. Piezoceramic elements can be used as sensors for pressure, deformation, acceleration and vibration. The double conversion of energy (electrical to mechanical and vice versa) is the basis for the operation of piezoresonance filters, delay lines and piezotransformers [3].

Nonlinear acoustoelectronic devices for analog signal processing are based on the nonlinear interaction of acoustic waves with each other and with free electrons in conducting media (semiconductors). A layered structure of piezoelectric semiconductor is usually used to observe the effects of nonlinear interaction of acoustic waves.

The observed anomalies in the velocity and damping of elastic waves in the phase transition region are associated with the onset of disordering of the anionic sublattice of the crystal. Phase transitions in ferroelectrics are excited by strong anomalies in physical characteristics (heat capacity, conductivity, velocity and attenuation of ultrasound, etc.). In theoretical terms, such phase transitions can be described on the basis of Landau's phenomenological theory [4].

The growing interest in the problems of the practical use of ferroelectric domain structures in acoustoelectronic devices is due to the successful combination of the properties of some ferroelectrics.

2. FERROELECTRICS IN ACOUSTOELECTRONICS

Ferroelectrics, for the most part, are complex oxides, and the brightest representatives of ferroelectrics are titanates of barium, strontium and lead [5]. Ferroelectric materials have specific properties, such as high dielectric constant dependent on an external electric field, reversible polarization, direct and reverse piezoelectric effect, pyroelectric effect.

Ferroelectrics are characterized by a domain structure. The external electric field changes the direction of the domains, which creates a strong polarization effect. Domain polarization is accompanied by the nucleation of new domains and displacement of domain walls. The spontaneous polarization disappears at the heating to the Curie point, and the dielectric constant reaches its maximum value. The domains are reoriented upon reverse cooling. The presence of a domain structure is one of the main properties of ferroelectrics. Periodic domain structures (PDSs) based on ferroelectrics began to be used to convert optical radiation, and then to generate ultrasonic waves [6]. The promise of the PDS usage in various acoustic signal conversion systems is obvious.

Until the mid-1980s, single-domain ferroelectric and piezoelectric bulk crystals were mainly used in acoustoelectronic devices for signal conversion. Then they were made in the form of thin plates up to frequencies of 10 Hz, and in the form of thin films for higher frequencies. The conversion efficiency in periodic domain structures significantly exceeded the efficiency of single-domain converters.

There is a class of oxygen-octahedral ferroelectrics, a number of which ($PbZrTiO_3$, $BaTiO_3$, $BaSrTiO_3$ and some others) fully satisfy the requirements for high values of electro-optical and piezoelectric coefficients. Their conductivity can increase tens of times under the action of optical irradiation.

The main material for the manufacture of piezoceramic elements is $PbZrO_3$-$PbTiO_3$ solid solutions. This ceramic is used to create powerful ultrasonic emitters in a wide frequency range for the purposes of hydroacoustics, flaw detection, and mechanical processing of materials. Films $PbTiO_3$, $LiNbO_3$, $LiTaO_3$, $KTaO_3$ and $Bi_4Ti_3O_{12}$ can be used in acoustic devices, electronic devices. $ZrTiPbO_3$ films are applicable in microelectromechanical systems as acoustic sensors, vibration monitors, molecular biosensors, positioners, micropumps, and stepper motors [7].

3. FERROELECTRIC MATERIALS OBTAINTD BY THE EXTRACTION-PYROLYTIC METHOD

The production of complex oxides of refractory metals by the solid-phase method is characterized by a high process temperature (1100 - 1300 °C), for example, the crystalline phase of $BaTiO_3$ is formed from oxides at 1460 °C with process duration of 24 hours. At the same time, differences in the melting temperatures of metal oxides such as Ba, Ti and Pb create significant difficulties in obtaining homogeneous materials by conventional solid-phase synthesis. A complicating factor in the process of high-temperature synthesis of lead zirconate-titanate films is the high volatility of PbO vapors, which in some cases changes the crystal structure of the films and leads to the formation of oxygen vacancies.

To obtain high-quality ferroelectrics with improved properties, it is important to develop methods for the synthesis of materials that are homogeneous in composition and in homogeneous morphology, which is possible using the extraction-pyrolytic method. It was shown that ferroelectric materials with a uniform grain size possessed the maximum pyroelectric coefficient [8]. Therefore, it is important to develop methods for obtaining materials that are homogeneous in composition and homogeneous in morphology.

Solution methods for the synthesis of complex oxide materials make it possible not only to homogenize the composition of ferroelectrics, but also to reduce the temperature and time of synthesis of these materials [9]. We have developed an extraction-pyrolytic (EP) method for the synthesis of complex oxide ferroelectric films of the composition $BaTiO_3$, $SrTiO_3$, as well as $PbZr_{0.5}Ti_{0.5}O_3$, $ZrTiO_3$.

A feature of this method is the usage of extraction processes to obtain organometallic precursors, in which not only the transfer of the metal ion to the organic phase from aqueous solutions of salts of this metal is carried out, but also the purification from impurities. We used a mixture of carboxylic acids (RCOOH) as an extractant. The resulting extracts (metal carboxylates) can be mixed in solution in the required stoichiometric ratios. Organic ectracts also have high wetting and film-forming ability. After applying the wetting film to the substrate, thermal decomposition of the organic phase takes place, which is carried out in a narrow temperature range 400-500°C (Fig. 1)

Fig. 1 shows the curves of thermal decomposition of lead carboxylate and zirconium carboxylate.

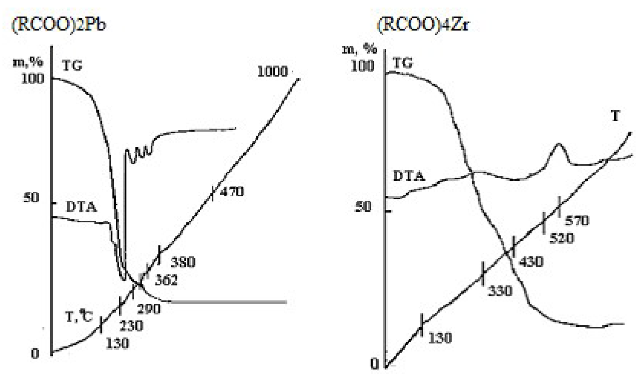

Fig. 1: Derivatogram of lead and zirconium carboxylate

After removal of chemically bound water (130°C) and the remainder of the free extractant (250°C), the process of thermal decomposition of Pb carboxylate begins at 290°C, then the reaction rate increases and ends at 380°C. The decomposition process is superimposed on endothermic reactions of evaporation of decomposition products, which causes fluctuations in the reaction rate, characterized by the DTA curve. The curves of thermal decomposition of various metals carboxylates are similar and almost all metal carboxylates completely decompose with the formation of oxides at temperature range of 400-500°C. Lowering the crystallization temperature can be achieved by forming the metal complexes or coordination compounds, which have the same arrangement of metal and oxygen ions as in the final crystalline state already in the solution, and/or by increasing the homogeneity of the solution.

During thermal decomposition of a carboxylates mixture the mutual influence of elements on the rate and temperature of the processes leads to the fact that carboxylates decompose together in a narrow temperature range [10].

Ferroelectric films were obtained by immersion and centrifugation methods. Dielectric substrates made of sitall, quartz, and polycor were used. The wet films were deposited on a cold substrate from a heated solution and, after drying at 100-120°C, the substrate with the film was placed in an oven heated to an annealing temperature of 450-500°C. The deposition and pyrolysis processes were alternated 10–15 times to obtain a film with a thickness of 0.3–0.8 μm.

Fig. 2 shows X-ray diffraction patterns of $BaTiO_3$ films obtained in the course of pyrolysis at 500°C for 5 min. The reflections on the X-ray diffraction patterns correspond to the data for $BaTiO_3$. Similar studies were carried out for $SrTiO_3$ and $Pb(Zr)TiO_3$ films. The phase formation process in films is much faster than in bulk materials. According to the X-ray phase study of phase formation processes in films, the optimal pyrolysis temperature was 470°C, and the final annealing temperature was 550-650°C. The final annealing time is 5-10 minutes.

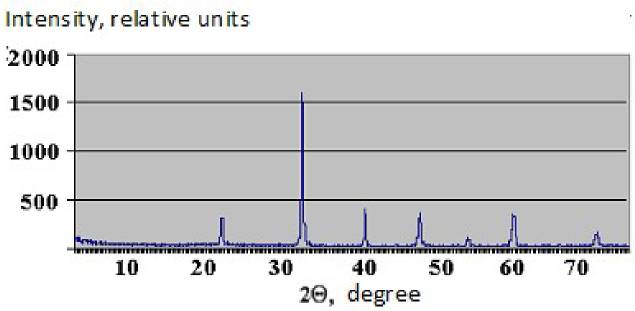

Fig. 2: X-ray diffraction pattern of a $BaTiO_3$ film on glass substrate, annealing at 550°C, 5 min.

Atomic force microscope studies have shown that 10-layer films of $BaTiO_3$, $SrTiO_3$, obtained by the extraction-pyrolytic method at a temperature of 550°C, consist of grains of uniform size and shape, 100-150 nm in size (Fig. 3).

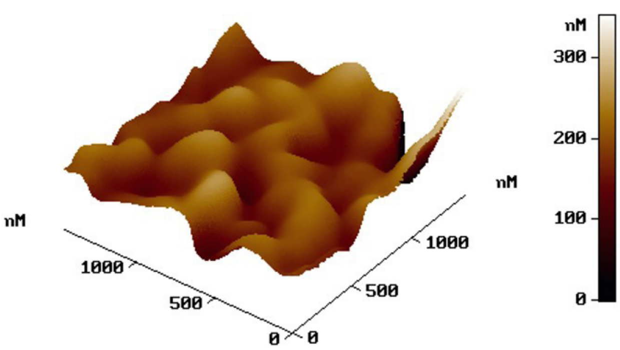

Fig. 3: Microstructure of $SrTiO_3$ film

The microstructure of the surface of a 10-layer $SrTiO_3$ film obtained by the extrusion-pyrolytic method at 550°C (Fig. 3) is represented by large round grains. Coarse grains are characteristic of complex oxides, the phase formation of which occurs at elevated temperatures.

Capacitor film structures were fabricated to measure the dielectric constant and polarization of ferroelectric films. The obtained values of spontaneous and residual polarization for films of various compositions presented in Tab. 1.

Ferroelectric thin films	Spontaneous polarization, μC / cm²	Residual polarization, μC / cm²	Dielectric constant, ™$_{max}$	Curie temperature
$BaTiO_3$	13,7	3,1	950	120
$SrTiO_3$	24,1	15,6	650	300
$PbTiO_3$	39,2	18,4	-	-
$PbZr_{0,5}Ti_{0,5}O_3$	338	251	1500	220

Tab.1: Characteristics of ferroelectric films obtained by the EP method

From Tab. 1 it can be seen that the introduction of bismuth into barium and strontium titanates noticeably decreases the polarization values of the films. It is also shown that the value of polarization and dielectric constant of $PbZr_{0.5}Ti_{0.5}O_3$ films is much higher than all others. This suggests that this material is promising.

4. CONCLUSION

On the basis of regular domain structures in ferroelectrics various acoustoelectronic devices have been implemented, such as controlled delay lines and resonators, filters of various types, energy concentrators, acoustic attenuators, deflectors and waveguides. With the help of acoustoelectronic devices it is possible to perform such operations on signals as transformation in time (signal delay, change in duration); frequency and phase transformations (phase shift, frequency multiplication); amplitude change, as well as more complex functional transformations (integration and differentiation, convolution, signal correction).

To obtain ferroelectric materials, it is advisable to use solution technologies that allow homogenizing the composition of complex oxides, reducing the temperature and time of their synthesis. The developed extraction-pyrolytic method for obtaining ferroelectric materials makes it possible to obtain a pure material with a uniform distribution of elements and crystallites of uniform size. It is shown that the synthesis temperatures of $BaTiO_3$, $SrTiO_3$, and $Pb(Zr)TiO_3$ ferroelectric films are reduced to 550-600°C, and the synthesis time is down to 5-10 minutes. The values of the dielectric constant, polarization, and Curie temperature of the obtained films correspond to the maximum characteristics of these materials.

Thus, using the extraction-pyrolytic method we obtained ferroelectric powders and films suitable for use in acoustoelectronic.

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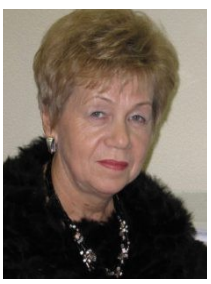

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