

Peculiarities of BaTiO₃ in electronic and X-Ray analysis

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Abstract. We have studied the most promising material of semiconductor nanotechnology BaTiO₃. Barium titanate, a compound of barium and titanate oxides, was studied in three dimensional varieties: in the form of powder with a diameter of 1÷1.5 mm, solid BaTiO₃ target with a diameter of 76 mm and thin films obtained by ion-plasma sputtering with a thickness $d \approx 10 \div 50$ nm, on the Si (III) surface. The spectra were recorded at room temperature on an XRD-6100 powder X-ray diffractometer, and spectra were taken from room temperature to 673 K, and the amorphous and crystalline phases of this substance were determined based on the obtained X-ray diffraction spectrograms. The peaks of the spectrogram based on the Miller indices and interplanar distances d_{hkl} show complex compounds that are newly formed on the basis of barium titanate.

1 Introduction

Obtaining high quality thin; films of metals, semiconductors, and dielectric films is one of the urgent problems in the technology of manufacturing various elements of microelectronics. On the other hand, they are important for practical applications and are already widely used in modern nanoelectronics, optoelectronics, photovoltaics and other fields. The creation of new devices based on thin nanoscale films requires a detailed knowledge of the mechanism of their growth, especially at the initial stages [1,2]. In the second half of the 20th century, thin films were obtained mainly by the thermal vacuum method, which evaporates the atoms of a substance in a high vacuum and condenses on the surface of the samples. The method is characterized by rather simplicity and high deposition rates, but does not provide sufficient reproducibility of film properties, especially when deposition of substances of complex composition.

The current thin film deposition methods using low-temperature plasma and ion beam make it possible to obtain films of various materials (including refractory and multicomponent compositions), which are practically impossible to obtain by the thermal vacuum method.

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In the processes of ion-plasma deposition, the material deposited on the substrate is obtained by sputtering a solid target with energy ions.

One of the most important differences between ion-plasma deposition and thermal vacuum deposition is the high energy of sputtered particles (4÷5 eV) compared to evaporated (0.15 eV at $T_{ucn} \approx 2000\text{ K}$), which allows the deposited particles to partially penetrate into the substrate, providing high adhesion of the film to the substrate. We used to obtain thin films $BaTiO_3$ standard magnetron sputtering, which is a kind of diode cathode sputtering. This method of film deposition is a further development of ion-plasma deposition [3.4].

At present, it is impossible to imagine electronics without semiconductor heterostructures. Such structures are widely used to create light-emitting diodes, short-wavelength photodetectors, semiconductor lasers, solar cells, and other products of modern optoelectronics. Important conditions for the widespread use of such devices are low cost, as well as their resistance to high temperatures and other critical conditions. A promising material for creating various optoelectronic devices on its basis is barium titanate. Barium titanate - a compound of oxides barium and titanium $BaTiO_3$. Crystal modification of barium titanate with perovskite structure is a ferroelectric, possessing photorefractive and the piezoelectric effect. Barium titanate is characterized by high values of dielectric constant (up to 104 ; 1400 ± 250 at n.o.); on its basis, several types of ferroelectric ceramics have been developed, used to create capacitors, piezoelectric sensors, and posistors [5-15].

2 Experiment technique

The work investigated barium titanate, a compound of barium oxides and titanate. In experiment $BaTiO_3$ were used in the form of a powder with a diameter of 1÷1.5 mm. Besides the target is made of one-piece compounds $BaTiO_3$ with a diameter of 76 mm.

Obtained in a magnetron sputtering system in a high vacuum $BaTiO_3$ on the surface of single crystals Si (111). The deposition rate of barium titanate was 0.5 \AA/s and the maximum coverage was 100 \AA . If necessary, a sample with a sputtered film $BaTiO_3$ subjected to 30-minute annealing at a temperature of 4000 C. For the study of electronic and optical properties of barium titanate.

Powder X-ray diffraction is a method for studying the structural characteristics of a material using X-ray diffraction (X-ray diffraction analysis) on a powder or polycrystalline sample of the material under study. The result of the study is the dependence of the scattered radiation intensity on the scattering angle. The corresponding instrument is called a powder diffractometer. The advantage of the method is that the Debyeagram for each substance is unique and allows you to determine the substance even when its structure is not known. X-ray phase analysis method was used to study the structure, composition, properties of raw materials and annealing products. It was used to study the mineralogical and phase compositions [6]. A monochromatic X-ray beam is directed to a sample of the test material, ground into powder. On a photographic film rolled into a cylinder around a sample, the image (Debyeagram) is obtained in the form of rings. The distance between the lines of the same ring on the debyeagram makes it possible to find the Bragg reflection angles. Then, using the Bragg-Wulf formula, $2d \cdot \sin\theta = n \cdot \lambda$ you can get the ratio of the $\frac{d}{n}$ -distance between the reflecting planes to the order of reflection.

Powder samples $BaTiO_3$ were studied by X-ray diffraction and elemental analysis. Samples were identified on the basis of diffraction patterns, which were taken on a computer-controlled XRD-6100 (Shimadzu, Japan) apparatus.

3 Results and discussion

Determination of the qualitative composition of the sample, semi-quantitative determination of the components of the sample, determination of the crystal structure of a substance, as well as precision determination of the unit cell parameters, determination of the arrangement of atoms in the unit cell (full profile analysis - the Rietveld method), determination of the crystallite size (coherent scattering region) of a polycrystalline sample. Study of texture in polycrystalline materials. In addition, the study of the phase composition of the substance and the study of state diagrams, the assessment of the size of the crystals in the sample, the accurate determination of the lattice constants, the thermal expansion coefficient, the analysis of minerals, used Cu-K α - radiation (β - filter, Ni, $\lambda = 1.54178 \text{ \AA}$, current mode and voltage of the tube 30 mA, 40 kV) and a constant detector rotation speed of 4 deg/min with a step of 0.05 deg. ($\frac{\omega}{2\theta}$ - coupling), and the scanning angle varied from 10 to 80o. The X-ray power was 2 kW. The results were analyzed using the database [7]. The penetration depth of Cu-K α radiation is about 1 mm (980 μm) for light elements (carbon) and a few μm for heavy elements (Ag, W). For most inorganic substances, simple compounds, Cu-K α - is tens of microns (μm). Figure 1 shows the spectral dependences $BaTiO_3$ obtained by the powder diffractometer method. In addition, the Miller indices are given, as well as the interplanar spacing d_{hkl} for these samples. We used the Rietveld method [6,14] to refine the structure from powder data obtained using X-rays. The principle of the method is to use independent measurements of the intensity at each point of the diffraction pattern, describing the line profile using analytical functions, instead of using the integral intensity of the reflections. Function parameters, including structural, device and other characteristics, are refined using the nonlinear least squares method. Using this refinement method, we determined the interplanar distance d_{hkl} and Miller indices (hkl). In addition, using this method, we were able to accurately determine and designate the interplanar distance d_{hkl} and Miller indices (hkl) as can be seen from Fig. 1. As mentioned above, powder X-ray diffractometry allows for quantitative elemental analysis. The elemental analysis we carried out using the "Search and Match" software [7] of the samples shows that the samples $BaTiO_3$ have the following composition (in weight percent):

As is known from the literature data [6,8-9], Miller indices are applicable in all syngonies. As the Miller index increases, the interplanar spacing decreases [7,10].

For samples $BaTiO_3$ measured by X-ray diffraction analysis using the "Search and Match" software [11,13], the degree of crystallinity and amorphism was assessed. For barium titanate, this is as follows: the amorphous phase for barium titanate is 71.35%, and the crystalline phase, respectively, is 28.65%. Indexing - determination of indices (khl) of each line of the diffraction pattern and grating type. Indexing was carried out to identify impurities in the sample by isolating reflections that do not belong to the main substance. In this work, we determined the presence of hydrogen impurities for $BaTiO_3$. Table 1 below shows the data obtained by powder X-ray diffraction $BaTiO_3$.

Table 1. The data obtained by powder X-ray diffraction $BaTiO_3$.

No.	hkl	hw	2theta	I _{calc}	I _{obs}	Sigma	d - hkl
1.	1 0 0	0.070886	22.195	221.8	222.9	3.378	4.001815
2.	1 1 0	0.076811	31.592	1324.3	1338.2	6.593	2.829710
3.	1 1 1	0.083821	38.949	372.9	378.8	4.238	2.310449
4.	2 0 0	0.091393	45.283	480.6	490.8	4.694	2.000907
5.	2 1 0	0.099364	50.986	152.9	157.0	3.605	1.789666
6.	2 1 1	0.107689	56.261	619.1	638.8	5.482	1.633734
7.	2 2 0	0.125451	65.971	333.7	347.9	4.717	1.414855
8.	2 2 1	0.134977	70.542	74.0	77.6	3.339	1.333938
9.	3 0 0	0.134977	74.542	13.2	13.9	0.597	1.333938

10.	3 1 0	0.145024	75.089	283.6	298.8	4.841	1.265485
11.	3 1 1	0.155679	79.344	122.6	129.8	4.039	1.206593

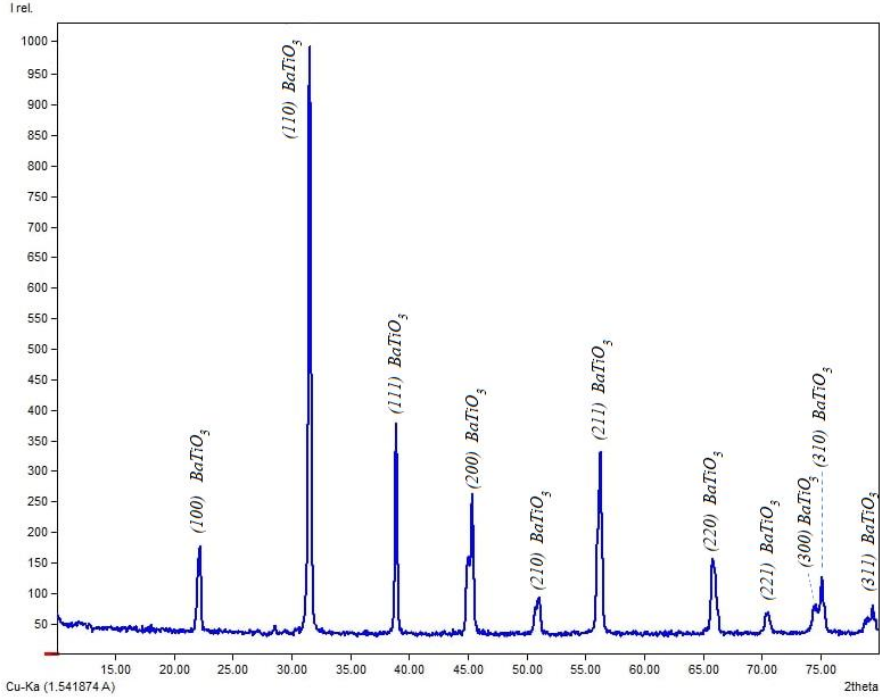


Fig. 1. Spectral dependence $BaTiO_3$ obtained by the powder diffractometer method. Miller indices are given.

Fig. 1 shows an x-ray pattern at room temperature and $BaTiO_3$ heated to 673K. X-ray phase analysis at room temperature shows that at several angles 22.19530, 31.59230, 38.49220, 45.28320, 50.98610, 56.26100, 56.26100, 65.97120, 70.54280, 74.54240, 75.08919, 79.34417 peaks of varying degrees are visible. The main ideal peak is seen at an angle of 31.59230degrees (101). When heated to 400 degrees, the angle of the peaks in the image does not change, but the intensity does. The release of some light volatile elements during heating and crystallization can be explained by the crystallization of the sample. In this X-ray phase analysis [15] in the literature, a sample heated to 850 degrees can be seen in X-ray phase analysis peaks appearing at certain angles, although the peaks are very small in intensity and contrast.

The analysis results measured at room temperature and 400 degrees Celsius show that the intensity of the peaks varied by a factor of 2.5. X-ray diffraction data were processed using the Fullprof program. The results of measurement and processing of X-ray diffraction data are shown in Fig.2 and Table 2.

Processing of X-ray diffraction data by the full – $BaTiO_3$ profile method showed that the sample has a cubic structure (sp.gr.Pm-3m) with the following lattice parameters: $a = 4.0018\text{\AA}$, $b = 4.0018\text{\AA}$, $c = 4.0018\text{\AA}$ and positions, coordinates of atoms in the unit cell (Table 2).

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No.	Atoms	Atomic coordinates			Thermal factor
		x / a	y/b	z/c	B
1	Ba	0.00000	0.00000	0.00000	0.15676
2	Ti	0.00000	0.00000	0.24696	0.16562
3	O ₃	0.00000	0.00000	0.37505	0.16383

The unit cell of the cubic $BaTiO_3$ structure is shown in Fig.2.

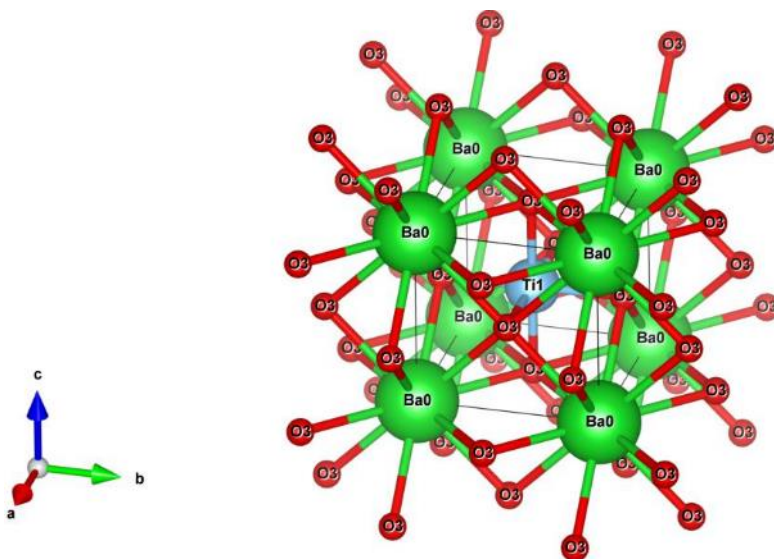


Fig. 2. Crystal structure $BaTiO_3$ (cubic structure sp.gr. Pm-3 m).

Fig.1 shows the crystal structure of $BaTiO_3$ barium titanate, the unit cell of the crystal lattice $BaTiO_3$ corresponds to a trigonal space group and consists of three chemical formulas: Ba, Ti, O.

4 Conclusion

Thus, the analysis of the X-ray diffraction spectra and electrophysical properties of barium titanate, in the form of powder and thin films with a thickness $d \approx 10 \div 50$ nm, to determine the structure from powder data using the Rietveld method [6,14]. A decrease in the interplanar distance with increasing Miller indices is determined. Indexing was used to identify impurities in the sample by isolating reflections that do not belong to the main substance. Elemental analysis was carried out in weight percent for $BaTiO_3$. For the first time, the degree of crystallinity and amorphism of the sample was determined $BaTiO_3$. The amorphous phase for barium titanate is 71.35%, and the crystalline phase, respectively, is 28.65%.

It is shown that after heating the sample to a ratio at room temperature, the intensity of X-ray peaks increases by a factor of 2.5.

References

1. M.V. Gomoyunova, G.S. Grebenyuk, I.I. Prozhin, B.V. Senkovskiy, D.V. Vyalykh, *FTT* **57(3)**, 609-615 (2015)
2. S.L. Zhang, M. Ostling, *Crit. Rev., Solid Meeter. Sci.* **28**, 1 (2003)
3. A.I. Kuzmichev, *Magnetron sputtering systems/Ki.1. Introduction to the physics and technology of magnetron sputtering* (K. Avers, 2008)
4. V.I. Grachev, V.I. Margolan, V.A. Dead, et.al., *RENSAT* **6(1)**, 18-29 (2014)
5. Sh.T. Khozhiev, I.O. Kosimov, B.B. Gaibnazarov, A.B. Bohodirzhonova, *Titanium oxide and its features manifested by powder x-ray diffractometry*, Novateur Publications, Pune, Maharashtra, India Journal NX- A Multidisciplinary Peer Reviewed Journal ISSN: 2581-4230, May 25th–26th 550 (2021)
6. Sh.T. Khozhiev, I.O. Kosimov, B.B. Gaibnazarov, *Problems solved with the help of powder diffractometry*. Collection of materials of the II International Scientific and Theoretical Conference "Actual Issues of Natural Sciences" May 19. Nux. 159 (2021)
7. B.V. Nekrasov, *Fundamentals of general xymia*. TI- Ed. 3rd, rev. I add. Moscow: Chemistry **146** (1973)
8. L. Smrcok, V. Langer, M. Halvarsson, S. Rупpi, *Zeitschrift fuer Kristallographie* **149**, 19 (2001)
9. H. Gnaser, B. Huber, Ch. Ziegler, *Encyclopedia of Nanoscience and Nanotechnology* **6.505** (2004)
10. Yun. Yuriev, *Properties of thin films of titanium oxide (TiO₂) and amorphous carbon (a-C) deposited using a dual magnetron distribution system: dissertation abstract for the search for the degree of candidate of technical sciences: spec. 04/01/07. Tomsk, (2016)*
11. T.G. Akhmetov, R.T. Porfiryeva, L.G. Gaisin, *I am a doctor. Chemical technology of neoorganic balances: in 2 books. Book 1. - Under red. Akhmetova, TG. (M.: Vishaya school, 2002)*
12. S. Pillet, M. Souhassou, C. Lecomte, K. Schwarz, et. al., *Acta Crystallograica* **57**, 209 (2001)
13. M. Gutierrez, A. Taga, B. Johansson, *Physical Review, Serie 3. B–Condensed Matter* **65** (2001)
14. M. Tashmetov, F.K. Khallokov, N.B. Ismatov, I.I. Yuldashova, I. Nuritdinov, S.Kh. Umarov, *Physica B: Condensed Matter* **613** (2021)
15. P.A. Kholov, N.V. Gaponenko, K.V. Sheidakova, V.I. Krymsky, et. al., *Reports of BSUIR* 18(1), 74-80 (2020)