UDC 539.234:539.216.2

T. V. Kruzina, S. O. Popov*, Yu. M. Potapovych, V. M. Sidak, A. M. Kyrylov

Oles Honchar Dnipropetrovsk National University, Dnipropetrovsk, Ukraine
**e-mail: spopov@meta.ua*

SYNTHESIS TECHNOLOGY OF THE MAGNETRON TARGETS FOR DEPOSITION OF $Na_{0.5}Bi_{0.5}TiO_3$ FILMS

Sodium bismuth titanate $Na_{0.5}Bi_{0.5}TiO_3$ ceramics were produced to use as the target in high-frequency magnetron sputtering technology. Solid-state reaction technique with a two-step sintering process was used to prepare the $Na_{0.5}Bi_{0.5}TiO_3$ ceramics. A powder of raw Bi_2O_3, TiO_2 and Na_2CO_3 were mixed, pressed and then a heat treatment was carried out at T = 800 °C for 15 hours in the air. The X-Ray diffraction results showed that the sintered ceramics were a mixture of $Na_{0.5}Bi_{0.5}TiO_3$ perovskite structure and additional pyrochlore phase, most probably $Bi_2Ti_2O_7$. The sintered ceramics were ground and then pressed into target-disks of 43 mm in diameter and 4 mm in thickness and a heat treatment was carried out at T = 1100 °C for 1 hour in the air. The X-Ray diffraction pattern of the target-disks showed only pure structure of $Na_{0.5}Bi_{0.5}TiO_3$. Thus the mechanically strong targets with homogeneous structure were obtained for using in technology of films deposition which is based on magnetron sputtering method. It is proposed to coat non-working surface of targets with a layer of metal to improve cooling conditions during the sputtering process.

Keywords: thin films, magnetron sputtering, bismuth sodium titanate.

Кераміка натрій вісмутовий титанату $Na_{0.5}Bi_{0.5}TiO_3$ виготовлена для використання в якості мішені в технології високочастотного магнетронного розпилення. Кераміка $Na_{0.5}Bi_{0.5}TiO_3$ отримана за методом твердофазної реакції шляхом двостадійного спікання. Первинні матеріали Bi_2O_3, TiO_2 та Na_2CO_3 змішувались, пресувались і потім відпалювались при T = 800 °C протягом 15 годин у повітрі. Результати рентгенівської дифракції показали, що синтезована кераміка виявляє структуру перовськіту $Na_{0.5}Bi_{0.5}TiO_3$ та містить залишки додаткової пірохлорної фази, найбільш ймовірно $Bi_2Ti_2O_7$. Попередньо подрібнена синтезована кераміка пресувалась в мішені-диски діаметром 43 мм і товщиною 4 мм та спікалася при T = 1100 °C протягом 1 години на повітрі. На рентгенівських дифрактограмах мішеней-дисків виявлено тільки чисту структуру $Na_{0.5}Bi_{0.5}TiO_3$. Таким чином механічно міцні мішені з однорідною структурою були отримані для використання у технологіях осадження плівок за методом магнетронного розпилення. Пропонується покривати неробочу поверхню мішеней шаром металу для поліпшення умов охолодження в процесі розпилення.

Ключові слова: тонкі плівки, магнетронне напилення, натрій-вісмутовий титанат.

Керамика натрий висмутового титаната $Na_{0.5}Bi_{0.5}TiO_3$ была изготовлена для использования в качестве мишени в технологии высокочастотного магнетронного распыления. Керамика $Na_{0.5}Bi_{0.5}TiO_3$ получена методом твердофазной реакции путем двухстадийного спекания. Исходные материалы Bi_2O_3, TiO_2 и Na_2CO_3 смешивались, прессовались и затем синтезировались при T = 800 °C в течение 15 часов на воздухе. Результаты рентгеновской дифракции показали, что синтезированная керамика проявляет структуру перовскита $Na_{0.5}Bi_{0.5}TiO_3$ и содержит остатки дополнительной фазы пирохлора, наиболее вероятно $Bi_2Ti_2O_7$. После предварительного измельчения синтезированная керамика прессовалась в мишени-диски диаметром 43 мм и толщиною 4 мм и спекалась при T = 1100 °C в течение 1 часа на воздухе. На рентгеновских дифрактограммах мишеней-дисков обнаружена только чистая структура $Na_{0.5}Bi_{0.5}TiO_3$. Таким образом, механически прочные мишени с однородной структурой были получены для применения в технологиях осаждения пленок методом магнетронного распыления. Предлагается покрывать нерабочую поверхность мишени слоем металла для улучшения условий охлаждения во время процесса распыления.

Ключевые слова: тонкие пленки, магнетронное напыление, натрий-висмутовый титанат.

1. Introduction

Extremely high level of components integration on a silicon substrate for integrated electronics requires reckoning with a number of physical restrictions. It means that it is necessary to search for new principles of construction of integrated microelectronics. Migration to functional electronics is one of possible solutions. New active materials which can be used to integrate different physical effects in one medium are necessary for development of functional electronic devices.

Ferroelectric materials have parameters that allow them to be a good candidate for such new medium. In these materials, along with such specific physical phenomenon as switching of spontaneous polarization, there are other important features like high dielectric permeability, dielectric nonlinearity, pyro- and piezo- activity, linear and square-law electro optical effects, etc.

Until recent time one of the limiting factors that prevented wide use of a ferroelectric material in integrated and functional microelectronics was the impossibility to create heterostructures on their basis. During the last 10-15 years there was a set of research works concerning ferroelectric materials use in thin-film technologies. Heterostructures of nanoscale ferroelectric oxides films are very perspective for applications in micromechanical systems, high-speed optical modulators, high density non-volatile memories etc.

Ferroelectric $Na_{0.5}Bi_{0.5}TiO_3$ (NBT) is one of the most perspective materials for use in functional microelectronics. It has high values of both the dielectric permeability and the piezoelectric coefficients and is transparent in a visible range of wavelengths (band-gap 3.03 eV). Due to absence of lead in the material structure, NBT is ecologically safe.

2. Experimental setup

It is reported that $Na_{0.5}Bi_{0.5}TiO_3$ thin films can be prepared either by chemical solution decomposition [1], pulse laser deposition [2] or radio frequency (RF) magnetron sputtering [3] methods.

In our opinion, the high-frequency magnetron sputtering method is the most technological and perspective for obtaining of nanoscale ferroelectric films. The method involves target material surface bombardment by ions of working gas (active oxygen or inert argon) in plasma and thus sputtering of target material. Typical for such method relatively high speed of sputtering is achieved by means of increasing ion current density due to the localization of the plasma near the target surface in the strong transverse (relative to electric field) magnetic field. The method leads to deposition of films with a chemical composition similar to the composition of the target material [4]. Therefore deposition of NBT film composition requires that the stoichiometric proportion for the target material must comply with the stoichiometric proportion of NBT material.

The advantages of the magnetron scattering can be achieved if the target meets the following requirements:

1) the target diameter should correspond to the diameter of the magnetron cathode;
2) the target thickness should not exceed the size of the “dark space” of the glow discharge, to avoid plasma deformations and thus decreasing of sputtering efficiency;
3) the target material should have high thermal conduction for effective cooling;
4) the target should be mechanically strong, without cracks on entire working surface;
5) the relation of elements of target composition must comply with required stoichiometric proportion, but the technology of target preparation should provide the possibility to vary the stoichiometric relation in some relatively small limits;

6) the working surface of the target should be flat and smooth to prevent formation of ion current channels which may lead to a local excessive heating of the target.

3. Experimental results

Assuming usage of VUP-5M vacuum unit for deposition of NBT films, the following four-stage procedure to prepare magnetron targets is developed and suggested.

At the first stage the raw materials (Bi_2O_3, TiO_2, and Na_2CO_3) were prepared according to stoichiometric ratio, mixed and milled in a ball mill within 12 hours. Then the mix of components was dried up at T=200 ºC for 24 hours. Then the mixture was uniaxially pressed into a 43 mm diameter tablet (target-disk) with 10 MPa pressure within 1 hour and then, the tablet was annealed at 800 ºC during 15 hours in the air. The purpose of the first stage is to remove moisture, to purify the substance from volatile impurity, to carry out initial synthesis of the material. The X-Ray diffraction patterns of the tablet (Fig.1) showed that at the given temperature the substance with NBT structure was synthesized. It means that easily violating Bi did not evaporate yet and there was no stoichiometry violation. The additional reflexes at 28.3º and 31.2º can be attributed to the traces of pyrochlore phase, most probably of $Bi_2Ti_2O_7$ [4] or $Bi_{12}TiO_{20}$ [5].

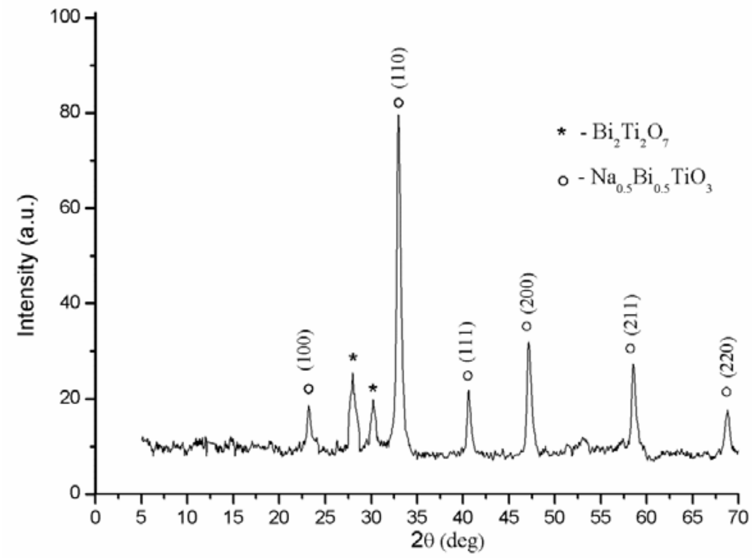

Fig. 1. X-Ray diffraction patterns of the NBT target annealed at T=800 ºC during 15 h in the air.

At the second stage the NBT tablet was crushed and secondary milled in a ball mill. After drying the mix was pressed in a tablet of 43 mm in diameter and 4 mm in thickness with the pressure of 15 MPa within two hours. Secondary annealing was carried out at T=1100 ºC within two hours in the air. Fig. 2 shows that more high annealing temperature on this stage led to absence of pyrochlore phase in the tablet substance and its structure became a single-phase, strictly corresponding to NBT [4].

The following stage was a machining of the target: diameter reduction to 40 mm (diameter of the VUP-5M magnetron cathode), thickness reduction to 3 mm and polishing of surfaces. The ceramic target had very dense and homogeneous structure.

As far as during sputtering process the target is strongly heated up the main purpose of the last stage was to improve a thermal contact between the target and the magnetron cathode. The thermal evaporation method was used to coat the non-working surface of the target with 0.1 mm copper layer to improve the thermal contact.

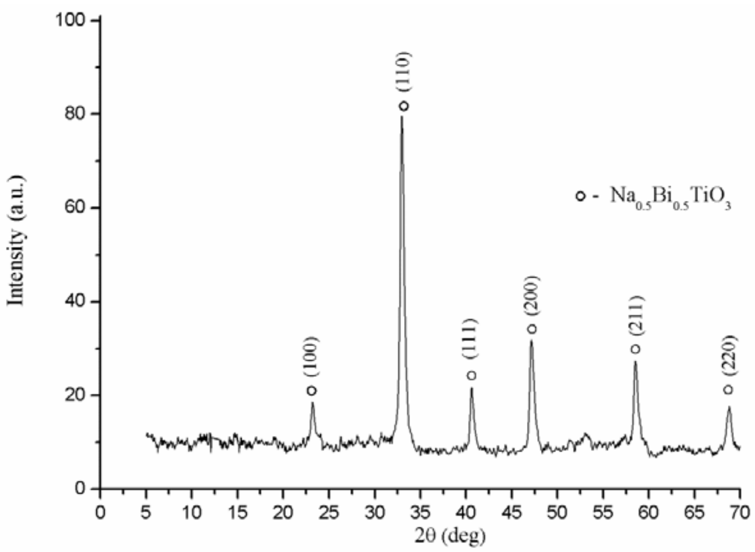

Fig. 2. X-Ray diffraction patterns of the NBT target annealed at T=1100 ºC within 2 h in the air

4. Conclusions

Technology for the production of high-quality magnetron targets was developed. The targets were used for deposition of thin NBT films by the method of high-frequency magnetron sputtering. Two stages of synthesis at temperatures T=800 ºC and T=1100 ºC allowed to exclude presence of pores in structure of the target material and to produce homogeneous, mechanically strong targets. Technological parameters of synthesis provided formation of the single-phase NBT structure target.

Acknowledgments

The authors would like to thank Prof. Trubitsyn M.P. for fruitful discussions and Dr. Golovko V.O. for help in X-ray phase analysis.

References

1. **Yang, C.H.** Properties of $Na_{0.5}Bi_{0.5}TiO_3$ ferroelectric films prepared by chemical solution decomposition, [Text] / **C**.H. Yang, Z. Wang and Q.X. Li // J.Cryst.Growth. 2005. – No. 284. – P. 136 – 141.

2. **Duclere, J.R.** Lead-free $Na_{0.5}Bi_{0.5}TiO_3$ ferroelectric thin films grown by Pulsed Laser Deposition on epitaxial platinum bottom electrodes, [Text] / J.R. Duclere, C. Cibert and A. Boulle // Thin Solid Films. 2008. – No. 517. – P. 592 – 597.

3. **Zhou, Z.H.** Leakage current and charge carriers in $(Na_{0.5}Bi_{0.5})TiO_3$ thin film, [Text] / Z.H. Zhou, J.M. Xue, W.Z. Li, J. Wang, H. Zhu and J.M. Miao // J.Phys.D. Appl.Phys. 2005. – No. 38. – P. 642 – 648.

4. **Zhou, Z.H.** Ferroelectric and electrical behavior of $(Na_{0.5}Bi_{0.5})TiO_3$ thin film, [Text] / Z.H. Zhou, J.M. Xue, W.Z. Li and J. Wang // Applied Physics Letters 2004. – Vol. 85, No. 5. – P. 804 – 806.

5. **Gusakova L. G.** Physical and chemical transformations in $(Na_{0.5}Bi_{0.5})TiO_3$ based solid solutions in solid solution synthesis process, [Text] / L. G. Gusakova, V. M., Ishchuk, N. G. Kisel, D. V. Kuzenko // Functional Materials 2011. – Vol. 18, No. 3. – P. 375 – 378.

Received 15.05.2015