RF magnetron sputtering of Bi$_{12}$TiO$_{20}$ thin films on various substrates

I Balchev*,1,6, T Nurgaliev1, I. Kostadinov2, L Lakov3, M Aleksandrova3, G Avdeev4, E Valcheva5, S Russev5, K Genkov5 and T Milenov1

1 Institute of Electronics, Bulgarian Academy of Sciences, 72 Tsarigradsko Chaussee Blvd., 1784 Sofia, Bulgaria
2 Institute of Solid State Physics, Bulgarian Academy of Sciences, 72 Tsarigradsko Chaussee Blvd., 1784 Sofia, Bulgaria
3 Institute of Metal Science, Equipment and Technologies with Hydro- and Aerodynamics Center, Bulgarian Academy of Sciences, 67 Shipchenski Prohod Blvd., 1574 Sofia, Bulgaria
4 Institute of Physical Chemistry, Bulgarian Academy of Sciences, Acad. G. Bonechev Str., bl. 11, 1113 Sofia, Bulgaria
5 Faculty of Physics, University of Sofia, 5 James Bourchier Blvd., 1164 Sofia, Bulgaria
6 Rezekne Academy of Technologies, 115 Atbrivosanas aleja, 4601 Rezekne, Latvia

E-mail: ivobalchev@gmail.com

Abstract. Using RF magnetron sputtering, we deposited Bi$_{12}$TiO$_{20}$ (BTO) thin films on various substrates (glass, quartz, stainless steel (SS304), (001) and (111) Si and sial-ceramics, Al and Cu foils). The films had a constant thickness of 1.3 µm. The as-deposited films were studied by Raman spectroscopy, scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDX), as well as by grazing incidence X-ray diffractometry (GIXRD). The GIXRD results reveal that the films are amorphous, while the Bi/Ti ratio varies between 9.5/1 and 11.8/1, as shown by the energy dispersive X-ray analysis (EDX). Further, the films deposited on glass and SS304 substrates were modified by laser irradiation (CuBr laser with a wavelength λ = 511 nm) to obtain an ordered cubic phase. The films deposited on quartz and on (001) and (111) Si substrates were thermally annealed at about 510 ºC for three hours in ambient atmosphere. The modified films were characterized by Raman spectroscopy, scanning electron microscopy (SEM), EDX and X-ray diffractometry.

1. Introduction

Last decade saw a trend of increasing interest in lead-free materials in view of replacing environmentally harmful substances. Such a role has been assigned to bismuth titanium oxide (Bi-Ti-O) and its related compounds, such as: Bi$_2$Ti$_2$O$_7$, Bi$_2$Ti$_4$O$_{11}$, Bi$_4$Ti$_3$O$_{12}$, Bi$_{12}$TiO$_{20}$. The latter crystal is part of a well-known group of the sillenite-type crystals Bi$_{12}$MO$_{20}$ (where M = Ti, Si and Ge, with the common abbreviation BTO, BSO and BGO, respectively) [1]. Their structure was first determined by Sillen [2] and later refined by neutron diffractometry by Radaev et al. [3].
Sillenite-type Bi$_{12}$MO$_{20}$ (where M can be Ti, Si or Ge) crystals have non-centrosymmetric, body-centered cubic structure belonging to the I23 space group [1-3]. Belonging to this space group, these crystals present a number of remarkable properties, such as piezoelectric, electro-optic, elastic-optic and photoconductive properties, which have potential applications in light modulators, acoustic delay lines, for hologram recording and phase conjugation [4, 5]. Among sillenite crystals, Bi$_{12}$TiO$_{20}$ (BTO) is the best known one due to its low dielectric losses and temperature-stable permittivity, $\varepsilon_r \sim 30 - 40$ near room temperature. This material attracts also a great deal of attention due to its relatively easy processability by different methods and its low sintering temperatures ($500 - 850 ^\circ C$), high photocatalytic activity, non-toxicity, small band gap and chemical compatibility with metallic (for example silver) electrodes.

Of particular importance are the specifics of preparing thin films of BTO, such films being attractive for different micro- and nanoelectronics applications. Thin films of Bi$_{12}$TiO$_{20}$ can be prepared by using standard chemical and physical procedures, such as sol-gel [6], laser ablation [7] and magnetron sputtering [8]. Unfortunately, not many detailed studies have been published focused on the synthesis of Bi$_{12}$TiO$_{20}$ thin films by magnetron sputtering and their characterization.

In this paper, we report results of studies on the deposition of BTO films by RF magnetron sputtering on some conventional and nonconventional substrates, their modification by visible laser radiation and their structural parameters.

2. Experimental

Bi$_{12}$TiO$_{20}$ (BTO) thin films were prepared by RF off-axis magnetron using sputtering equipment operating at 13.6 MHz and RF magnetron power of ~60 W. The sputtering gas mixture was Ar:O$_2$ = 1:1 at a total working gas pressure of ~6 Pa. The deposition was performed from a stoichiometric polycrystalline target of Bi$_{12}$TiO$_{20}$ onto dielectric Si (100 or 111) and quartz substrates at room temperature. Thin films of BTO were also sputtered on conductive stainless steel (SS304) and Al and Cu foil substrates, which could be used as electrodes after characterization of the films.

The samples were treated further by irradiation with the 511-nm wavelength emitted by a MOPA CuBr laser system. The output laser power was 6 W, with a pulse repetition rate of 5 kHz and a pulse duration of 30 ns. A 30-cm focusing lens was used to focus the laser beam on the thin films surface. In order to avoid ablation, we defocused the laser beam by 10 – 12 mm above the focal spot (from about 0.8 mm to 1 mm) and also varied the scanning speed (from 100 mm/s to 200 mm/s). The parameters (laser power, defocus and scanning speed) used in the different experiments were as follows: I experiment – aBTO deposited on a glass substrate, 6 W, 10 mm, 200 mm/s; II experiment – aBTO deposited on a glass substrate, 6 W, 12 mm, 200 mm/s; III experiment – aBTO deposited on SS304 substrate, 6 W, 10 mm, 100 mm/s.

Additionally, two specimens (aBTO films deposited on (001) and (111) Si substrates) were annealed at 510 °C for three hours in ambient atmosphere. Both specimens were cooled from 510 °C to room temperature by freezing, i.e., for about 45 minutes.

We used a LYRA TESCAN scanning electron microscope at 5 – 10 kV accelerating voltage for the SEM studies without deposition of any conducting amorphous film on the specimens studied. Images were obtained in secondary electron image (SEI) and in backscattered electron image (BEI) modes. The composition was determined by energy dispersive X-ray analysis (EDX).

The grazing incidence X-ray powder diffraction (GIXRD) measurements were performed using a PANalytical Empyrean apparatus; $\omega$-20 scans were conducted at $\omega = 0.5^\circ$ with Cu K$_\alpha$ radiation. The Raman measurements were performed on a HORIBA Jobin Yvon Labram HR 800 micro-Raman spectrometer with a He-Ne laser (633 nm, 0.5 mW power). The laser beam was focused on a spot of about 1 µm in diameter on the studied surfaces. The spectral resolution was 1 cm$^{-1}$ or better.

3. Results and discussion

The SEM observations show that the thickness of all studied samples is 1.3 µm as seen in the images of the films cross-section – figure 1. The surface is rough (figure 1) and second phases were not observed.
in the BEI images. Also, second phases were not observed in-depth of flakes of the thin films scratched from the specimens.

![Figure 1. BEI of the surface morphology of aBTO film deposited on Al-substrate. Inset – BEI of the cross-section of a flake scratched from the substrate – the film’s thickness is 1.3 μm.](image)

The average composition determined from areas of 50×50μm² varies significantly with the molecular ratio of Bi₂O₃/TiO₂ varying in the range 11.9/1 (BTO on Si, quartz, stainless steel and Cu) to 9/1 (BTO on Al) for different samples. The local composition measured at a point with a diameter of 1 μm varies in the same range for different areas of all specimens. It should be remarked that the phase homogeneity area of Bi₁₂TiO₂₀ lies in the range from 11.5/1 up to 13.85/1 Ti/Bi [1]; therefore the above results could be referred as a potential indication for the absence of a long-range (more that several interatomic distances) ordered sillenite phase.

The GIXRD observations of the as deposited and of the laser-treated aBTO films do not reveal any ordered phase. The additionally performed φ scans (φ = (0 – 360°)) with reference to d(001) of silicon at 2θ = 69.13° (ICSD-29287) reflection does not reveal any ordered phases. According to these measurements, these films should be referred to as amorphous.

The GIXRD pattern of an annealed specimen (aBTO film deposited on (001) Si substrates) (figure 2) reveals crystallization of four phases: Bi₁₂SiO₂₀ (ICDD 98-018-0370), TiO₂ – rutile (ICDD 98-007-5179), Bi₄Ti₃O₁₂ (ICDD 98-015-9929) and Bi₂O₂.₃ (ICDD 98-003-7366), denoted in figure 2 as BSOs, T, BTOe and BO, respectively. It is worth noting that the second annealed specimen (aBTO film deposited on (111)) has an identical GIXRD pattern.
Figure 2. GIXRD pattern taken from an annealed aBTO film deposited on (001) Si substrate.

The Raman spectra (figure 3) are taken from different specimens: as-deposited aBTO film on a glass substrate; aBTO film deposited on a glass substrate laser-treated in experiment I; aBTO film deposited on a glass substrate laser-treated in experiment II; aBTO film deposited on a stainless steel (SS 304) substrate laser-treated in experiment III; and an annealed aBTO film deposited on a (001) Si substrate. The spectra of all as-deposited samples are very similar: the Bi-O vibrations arise in the region up to 600 cm\(^{-1}\) [9] (figure 3). Variations in the Raman spectrum occur in different areas of the samples due to the different laser treatment used. The most prominent one in the spectrum taken from the sample treated in experiment I can be ascribed to $\beta$-Bi$_2$O$_3$ (B4 peak in figure 3) [10], and may be related to an initial structural transformation that began in the film due to the laser treatment. The thermal annealing results in crystallization of the aBTO films. Several different Bi-O based phases crystallize due to the non-stoichiometric composition of the films: Bi$_4$Ti$_3$O$_{12}$ with eulytine structure; Bi$_2$O$_{3-x}$ and Bi$_{12}$SiO$_{20}$ with sillenite structure. Additionally, TiO$_2$ with a rutile structure also crystallizes. The Bi-O groups, which are common for the former compounds, exhibit vibrations in the regions 100 – 400 cm\(^{-1}\) and, therefore, B1-B3 and B5 peaks can be ascribed to Bi-compounds; for example, the B5 peak (figure 3) could be related to a superposition of features from the Si substrate or to $\delta$-Bi$_2$O$_3$ [10]. The two peaks designated as R1 and R2 (at about 440 cm\(^{-1}\) and 612 cm\(^{-1}\), respectively) should be ascribed to the $E_g$ and $A_g$ modes of rutile (a high-temperature modification of TiO$_2$) [11]. The modes of the highest frequencies (at about 820 cm\(^{-1}\) and 850 cm\(^{-1}\)) can be attributed to vibrations of tetrahedral Si-O (of sillenite type Bi$_{12}$SiO$_{20}$) [1], the peak at about 820 cm\(^{-1}\) to $\delta$-Bi$_2$O$_3$ [10], and the shoulder at about 840 cm\(^{-1}\), to eulytine type Bi$_4$Ti$_3$O$_{12}$ [12].
4. Conclusions
The results presented lead to the conclusion that the Bi-Ti-O films deposited by RF-sputtering are amorphous. According to the SEM/EDX study, the local chemical composition of the films varies significantly without formations of different phases, which indicates the absence of a short-range order. This conclusion is confirmed by the Raman spectrum of the as-deposited films. The absence of long-range order is further confirmed by the GIXRD results. The laser modification most probably initiates ablation of Bi$_2$O$_{3-x}$ ensembles, which violates additionally the chemical composition and hinders the formation of stable phases. The thermal annealing leads to crystallization of different Bi-O based phases and of rutile. The crystallization of the sillenite Bi$_{12}$SiO$_{20}$ phase should be ascribed to the oxidized silicon on the surface of the substrate reacting with the Bi$_2$O$_{3-x}$ in the aBTO film.

Acknowledgements
The authors acknowledge the financial support by the European Regional Development Fund, postdoctoral research assistance No. 1.1.1.2/16/I/001, research application "Analysis of the parameters of the process of laser marking of new industrial materials for high-tech applications, No. 1.1.1.2/VIAA/3/19/474".

References
[1] Kargin Yu F, Burkov V I, Mar’in A A and Egorysheva A V 2005 Bi$_{12}$M$_x$O$_{20+\delta}$ Crystals with a Sillenite Structure: Synthesis, Structure, Properties Azbuka, Moscow
[2] Sillén L G 1940 Inaugural Dissertation, Degree-Granting University, Stockholm, Sweden
[3] Radaev S, Simonov V, Kargin Y and Skorikov V 1992 Eur. J. Solid State Inorg. Chem. 29 383
[4] Rafailov M, Todorov R, Marinova V, Dimitrov Z, Gospodinov M 2019 Bul. Chem. Comm. 51 217–221
[5] Nogueiraa A, Longob E, Leitea E and Camargoa E 2015 Ceramics Int. 41 12073–1208
[6] Wei J, Huang B, Wang P, Wang Z, X Qin, Zhang X, Jing X, Liu H and Yu J 2012 *Int. J. of Photoenergy* **2012** 8

[7] Gorupa F et al. 2019 *Ceramics Int.* **45** 3510–3517

[8] Alfonso J E, Olaya J J, Bedoya-Hincapié C M, Toudert J and Serna R 2014 *Materials* **7** 3427–3434

[9] Egorysheva A, Volodin V, Milenov T, Rafailov P, Skorikov V and Dudkina T 2010 *Russ. J. of Inorg. Chem.* **55** 1810–1817

[10] Mazza T, Barborini E, Piseri P, Milani P, Cattaneo D, Li Bassi A., Bottani C and Ducati C 2007 *Phys. Rev. B* **75** 045416

[11] Hardcastle F and Wachs I 1992 *J. Sol. St. Chem.* **97** 319–331

[12] Dua Y, Chen G and Zhang M 2004 *Solid State Comm.* **132** 175–179