ISSN 1062-8738, Bulletin of the Russian Academy of Sciences: Physics, 2020, Vol. 84, No. 9, pp. 1100–1103. © Allerton Press, Inc., 2020.
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Effect of Heat Treatment on the Stability of Nanosized $(Co_{40}Fe_{40}B_{20})_{34}(SiO_2)_{66}/ZnO/In_2O_3$ Multilayers

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Received March 12, 2020; revised April 15, 2020; accepted May 27, 2020

Abstract—An investigation is performed of the thermal stability and phase transformations of thin-film heterogeneous $[(Co_{40}Fe_{40}B_{20})_{34}(SiO_2)_{66}/ZnO/In_2O_3]_{85}$ multilayers obtained via ion beam sputtering. The system contains 85 layers, each consisting of a $(Co_{40}Fe_{40}B_{20})_{34}(SiO_2)_{66}$ composite layer and ZnO and In_2O_3 semiconductor spacers. The sample structure in the initial state and after heat treatment is studied by means of X-ray diffraction. It is shown that the samples are stable at temperatures of up to 500°C. Zn_2SiO_4, $InBO_3$, CoFe, and In_2O_3 phases form during annealing.

DOI: 10.3103/S1062873820090051

INTRODUCTION

Wide-gap oxide semiconductors are the main functional materials of transparent electronics. It is therefore important to study the solid-state reactions that occur between semiconductor, dielectric, and metal phases in such electronic devices [1–4]. A multilayer film with nanometer thick layers is a model object for observing the formation of compounds at the points of contact between wide-gap oxide semiconductors and metal and dielectric compounds.

Earlier studies on solid-phase chemical transformations in the $[(Co_{40}Fe_{40}B_{20})_{34}(SiO_2)_{66}/ZnO]_{112}$, $[(Co_{40}Fe_{40}B_{20})_{34}(SiO_2)_{66}/SnO_2]_{32}$, and $[(Co_{40}Fe_{40}B_{20})_{34}(SiO_2)_{66}/In_2O_3]_{92}$ films showed that the products of reaction depend on the composition and the ratio between the thicknesses of the metal oxide layers and spacers in the composite [5]. On the other hand, different semiconductor compounds can come into contact with metal and dielectric layers in the functional elements of transparent electronics. A $Co_{40}Fe_{40}B_{20}$ alloy nanograin in our case simultaneously has a common interface with ZnO and In_2O_3, which can lead to competing transformations during solid-phase chemical reactions. This situation cannot be studied on bilayers.

In view of the above, the aim of this work was to establish patterns of the variation in the structure and phase composition of $[(Co_{40}Fe_{40}B_{20})_{34}(SiO_2)_{66}/ZnO/In_2O_3]_{85}$ films containing spacers of several semiconductor compounds in their initial state and after heat treatment in the temperature range of 200 to 650°C.

EXPERIMENTAL

$[(Co_{40}Fe_{40}B_{20})_{34}(SiO_2)_{66}/ZnO/In_2O_3]_{85}$ multilayer films were obtained via the ion beam sputtering of three targets with layer-by-layer deposition onto the surface of a Si(100) substrate mounted on a rotating carousel, according to the procedure described in [6]. ZnO, In_2O_3, and $Co_{40}Fe_{40}B_{20}$ alloy ceramic plates ($280 \times 80 \times 15$ mm^3 in size) with 13 quartz (SiO_2) weights ($80 \times 10 \times 2$ mm^3 in size) were used as targets. The parameters of the investigated films are given in Table 1.

The elemental composition of the $(Co_{40}Fe_{40}B_{20})_{34}(SiO_2)_{66}$ films was analyzed on an Oxford INCA Energy 250 energy dispersive X-ray spectrometer. The structural investigations were performed on a Bruker D2 Phaser X-ray diffractometer

Table 1. Film and spacer thicknesses in a $[(Co_{40}Fe_{40}B_{20})_{34}(SiO_2)_{66}/ZnO/In_2O_3]_{85}$ multilayer

	Layers, nm		
Sample thickness, nm	CoFeB–SiO_2	ZnO	In_2O_3
385	3.0	0.9	0.7
428	3.0	0.9	1.2

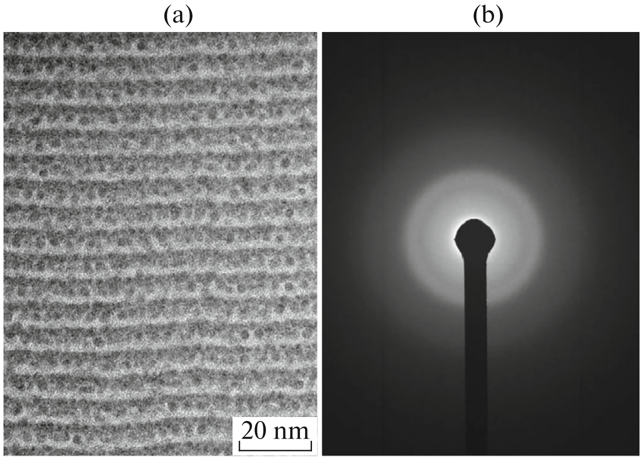

Fig. 1. (a) Cross-sectional TEM microphotograph and (b) electron diffraction pattern of a $[(Co_{40}Fe_{40}B_{20})_{34}(SiO_2)_{66}/ZnO/In_2O_3]_{85}$ multilayer.

(Cu$K_{\alpha1}$ radiation, $\lambda = 1.5406$ Å). Crystal phases were identified using the DIFFRAC.EVA 3.0 software with the ICDD PDF 2012 database. The multilayer cross section was examined on a Hitachi HT7700 transmission electron microscope (TEM). The heat treatment of the films was done in a vacuum chamber under a residual pressure of 5×10^{-2} Torr. On one hand, this residual pressure suppressed oxidation of the investigated structures during annealing; on the other, it prevented the reduction of the metal oxides during solid-state chemical reactions.

RESULTS AND DISCUSSION

Our small (1°–7°) Bragg angle X-ray diffraction study confirmed the multilayer structure of the films [7, 8]. Period d of the $[(Co_{40}Fe_{40}B_{20})_{34}(SiO_2)_{66}/ZnO/In_2O_3]_{85}$ film structure was calculated using the angular positions of the diffraction peaks. The d values calculated for the investigated films are consistent with the data obtained using the technological parameters of the deposition and the layer thicknesses measured during deposition (see Table 1).

In addition, we obtained cross-sectional TEM images of the initial $[(Co_{40}Fe_{40}B_{20})_{34}(SiO_2)_{66}/ZnO/In_2O_3]_{85}$ compound. Analysis of these images confirmed the periodic arrangement of the layers. In our investigated sample, the layer thicknesses were 3 nm for $(Co_{40}Fe_{40}B_{20})_{34}(SiO_2)_{66}$, 1.5 nm for the ZnO layer, and 1 nm for the In_2O_3 layer. The composite layer of this thickness was single-grain and consisted of spherical metal grains separated by dielectric SiO_2 layers. The composite layers were separated by a double layer of indium and zinc oxides. In the presented photographs, the In_2O_3 layers have considerable dark contrast, while the ZnO layers are indistinguishable in their phase contrast from the SiO_2 spacer in the composite.

In the electron diffraction pattern (Fig. 1b), we can see the halo typical of amorphous films, which (as we will see below) is consistent with the X-ray diffraction data. It should be noted that ZnO and In_2O_3 single-layer films obtained in a similar way were crystalline [9]. We may assume that the amorphous structure of the $(Co_{40}Fe_{40}B_{20})_{34}(SiO_2)_{66}$ composite results in morphization of the semiconductor layers.

Two samples with different spacer and film thicknesses were chosen to study the phase composition of the films. X-ray diffraction of the initial $[(Co_{40}Fe_{40}B_{20})_{34}(SiO_2)_{66}/ZnO/In_2O_3]_{85}$ films revealed the X-ray amorphous structure of the samples (Fig. 2).

A series of 30-min annealings at temperatures of 200–645°C with a step of 50°C was performed to study the thermal stability of the samples. An X-ray diffrac-

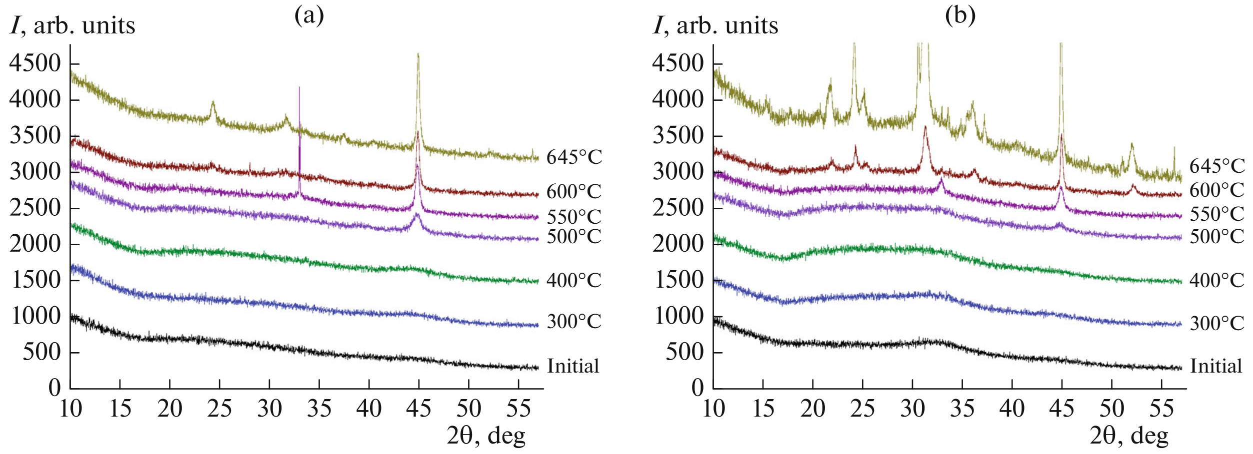

Fig. 2. Diffraction patterns of $[(Co_{40}Fe_{40}B_{20})_{34}(SiO_2)_{66}/ZnO/In_2O_3]_{85}$ thin films (a) 385 (b) 428 nm thick before and after heat treatment at 250–645°C.

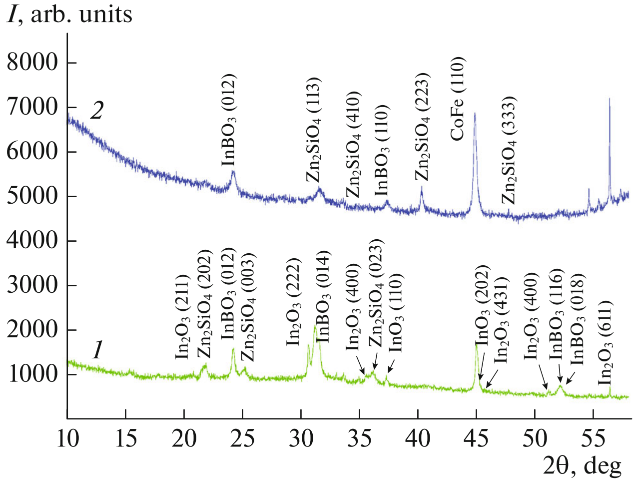

Fig. 3. Diffraction patterns of $[(Co_{40}Fe_{40}B_{20})_{34}(SiO_2)_{66}/ZnO/In_2O_3]_{85}$ thin films formed on a rotating substrate after heat treatment at 645°C. The sample were (*1*) 428 and (*2*) 385 nm thick.

tion study was performed after each annealing (see the data in Fig. 2). Based on the observed dependences, we may state that annealing at temperatures below 400°C does not lead to crystallization of the samples. The crystallization of individual phases begins above 450°C. The well-resolved high-intensity line in the diffraction patterns (Fig. 3) corresponds to the (110) reflection of the CoFe phase with a cubic lattice (sp. gr. *Pm*3*m*). The diffraction maxima of the $InBO_3$, Zn_2SiO_4, and In_2O_3 compounds appear and their intensity grows. We assume that the $InBO_3$ compounds form due to the interaction between oxides B_2O_3 and In_2O_3, since it is the only known compound in this system [10]. Boron oxidation can be judged according to thermodynamic characteristics: the standard Gibbs energy for B_2O_3 is $\Delta G = -1193$ kJ/mol [11], which is much lower than the Gibbs energy of other possible compounds in this system. The boron deficiency limits the total transition of indium oxide to the $InBO_3$ compound and, consequently, the existence of the separate In_2O_3 phase. The Zn_2SiO_4 compound could form via interaction between oxides ZnO and SiO_2, which is also energetically advantageous: $\Delta G = -954$ kJ/mol. Compounds CoFe and In_2O_3 formed from the phases contained in the multilayer and crystallized upon heat treatment.

The diffraction patterns of the ternary multilayer systems were compared to the results of heat treatment of the previously obtained two-component samples of systems [5] annealed at 600°C. The presence of common compounds (Zn_2SiO_4, $InBO_3$, CoFe, In_2O_3), which form in both binary and ternary systems, was established. In contrast to the bilayer systems, no zinc or iron oxide phases were found in the $[(Co_{40}Fe_{40}B_{20})_{34}(SiO_2)_{66}/ZnO/In_2O_3]_{85}$ compound.

We may assume that the investigated samples contained several amorphous phases, including the composite (metal grains of the $Co_{40}Fe_{40}B_{20}$ alloy and the α-SiO_2 dielectric phase) and the individual semiconductor spacers, the structure of which was almost amorphous due to the thinness (1–3 nm) of the layers, all of which contributed to the resulting dependence.

The presence of the nanometer ZnO and In_2O_3 spacers should affect the chemical transformations and crystallization of the sample with the composite layers upon heating. If we assume that, e.g., indium oxide crystallites form in the In_2O_3 layer upon heating, their sizes in the direction perpendicular to the film's plane should not exceed the layer thickness ($h \sim 1$ nm). The size of a nanocrystal can grow, due to the atoms forming the composite spacer. Since the composite layers in the $[(Co_{40}Fe_{40}B_{20})_{34}(SiO_2)_{66}/ZnO/In_2O_3]_{85}$ films do not contain In and Zn atoms in their initial state, interlayer crystallization proceeds mainly with the formation of complex oxide compounds (Zn_2SiO_4 and $InBO_3$).

CONCLUSIONS

Films obtained via the layer-by-layer deposition of $(Co_{40}Fe_{40}B_{20})_{34}(SiO_2)_{66}$ composite, zinc oxide ZnO, and indium oxide In_2O_3 with layer thicknesses of ~1 nm have a multilayer structure. In the initial state, all spacers in the $[(Co_{40}Fe_{40}B_{20})_{34}(SiO_2)_{66}/ZnO/In_2O_3]_{85}$ film were amorphous. Upon annealing at temperatures above 500°C, structural phase transformations were observed that ended in the formation of compounds Zn_2SiO_4, $InBO_3$, CoFe, and In_2O_3, and the violation of layer periodicity.

ACKNOWLEDGMENTS

The authors thank the Krasnoyarsk Territorial Shared Resource Center, Krasnoyarsk Scientific Center, Russian Academy of Sciences, for allowing our electron microscope investigations.

FUNDING

This work was supported by the RF Ministry of Science and Higher Education as part of State Task no. FZGM-2020-0007.

REFERENCES

1. Li, M., Wang, Ya., Wang, Y., and Wei, X., *Ceram. Int.*, 2017, vol. 43, no. 17, p. 15442.
2. Yu, S., Liu, Y., Zheng, H., et al., *Opt. Lett.*, 2017, vol. 42, p. 3020.

3. Bykova, L.E., Myagkov, V.G., Tambasov, I.A., et al., *Phys. Solid State*, 2015, vol. 57, no. 2, p. 386.
4. Tambasov, I.A., Maygkov, V.G., Ivanenko, A.A., et al., *Zh. Sib. Fed. Univ., Ser. Mat. Fiz.*, 2017, vol. 10, no. 4, p. 399.
5. Kalinin, Yu.E., Sitnikov, A.V., Babkina, I.V. et al., *Bull. Russ. Acad. Sci.: Phys.*, 2019, vol. 83, no. 9, p. 1116.
6. Rylkov, V.V., Nikolaev, S.N., Chernoglazov, K.Yu., et al., *Phys. Rev. B*, 2017, vol. 95, 144202.
7. Andreev, A.V., *Sov. Phys. Usp.*, 1958, vol. 28, no. 1, p. 70.
8. Gudymenko, A.I., Krivoi, S.B., Stanchu, G.V., et al., *Metallofiz. Noveishie Tekhnol.*, 2015, vol. 37, no. 9, p. 1215.
9. Babkina, I.V., Gabriel's, K.S., Epryntseva, T.I., et al., *Bull. Russ. Acad. Sci.: Phys.*, 2016, vol. 80, no. 9, p. 1168.
10. Li, H.K., Caia, G.M., Fana, J.J., and Jin, Z.P., *J. Alloys Compd.*, 2012, vol. 516, p. 107.
11. Glushko, V.P., *Termicheskie konstanty veshchestv: Spravochnik* (Thermal Constants of Substances: A Handbook), Moscow: VINITI, 1981.

Translated by E. Bondareva