ABSTRACT

PhD dissertations for PhD
specialty 6D071000 - Materials Science and Technology of New Materials

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"Structure and electronic properties of modified GeSbTe films"

General description of work. The dissertation paper presents the results of an experimental study of the structure and electronic properties of thin films of a chalcogenide glassy semiconductor of the Ge-Sb-Te system of $Ge_2Sb_2Te_5$ composition modified with bismuth impurity.

Relevance of the topic.

Physics and technology of non-crystalline materials are one of the dynamically developing areas of condensed matter physics, materials science and nanotechnology. In a large variety of materials with a non-crystalline structure, a special place is occupied by the class of chalcogenide glassy semiconductors (CSC), which have a number of unique properties and phenomena, such as switching and memory effects, photostructural transformations, and a weak effect of impurity on electronic properties that have no analogues in crystalline materials. These properties of CGSs are due to the peculiarities of their atomic structure, the presence of lone pairs of electrons in atoms, and the high density of localized electronic states, which are based on the intrinsic charged structure defects that fix the Fermi level in the middle of the forbidden band.

The switching effect is observed in thin CGS films and is associated with a reversible stepwise decrease in the resistance of CGS in strong electric fields. If, after a switching effect, a restructuring of the local structure occurs, leading to its crystallization, and a state with low resistance is maintained even in the absence of an external electric field, then this effect is called a memory effect.

Based on the glass-crystal phase transition effect, a separate class of storage media has been formed for PCM (Phase Change Memory) memory devices with high performance and reliability. PCM devices use CGS complex Ge-Sb-Te system compositions with a labile structure. Of these, the most promising for use in PCM devices today is the composition of $Ge_2Sb_2Te_5$, lying on the line of the GeTe-Sb_2Te_3 quasi-binary section.

The ability to control the electronic properties and structure of materials based on Ge-Sb-Te in the amorphous and crystalline state will significantly expand their field of application and is an important scientific and practical task.

To change the physicochemical properties of CGS, two approaches are used, based on structural and impurity modifications [1]. Both of these approaches for producing CGS films allow one to implement the method of ion-plasma high-frequency sputtering. On the one hand, it was shown in [2] that CGS films obtained by ion-

plasma spraying differ in their structure and electronic parameters from films obtained by thermal evaporation in vacuum, which is associated with significantly different conditions of vaporization and condensation of atoms. On the other hand, the method of ion-plasma co-sputtering of CGS and metal makes it possible to obtain amorphous films with a high impurity concentration, avoiding crystallization, and significantly change their electronic properties [3]. This method of controlling the electronic properties of CGS has received in literature the name of the method of "cold" doping or modifying (chemical modification) [4]. In addition, it is important to note that the method of ion-plasma sputtering to produce films of complex and multicomponent compositions, such as the composition of $Ge_2Sb_2Te_5$, has several advantages over the widely used method of thermal evaporation, as it allows to obtain films of uniform composition with a given ratio of components.

In our studies, bismuth was used as a modifying impurity for $Ge_2Sb_2Te_5$ films. This is due to the fact that Bi can be a isovalent and isomorphic impurity for one of the main components of the composition $Ge_2Sb_2Te_5$ and will allow doping by the substitution mechanism [5, 6]. In addition, bismuth atoms can fill existing vacancies in the $Ge_2Sb_2Te_5$ structure, the concentration of which according to [7–9] can reach up to 20%. It is significant that the modification of Ge-Sb-Te compositions by bismuth leads to a decrease in the time of their crystallization by 30% [10,11] and to a change in the type of conductivity from p-type to n-type [12, 13]. However, in these few works, a comprehensive study of the influence of Bi impurity on the structure, optical and electrical properties of $Ge_2Sb_2Te_5$ films was not carried out, and the effect of switching and memory was practically not studied.

Thus, to determine the efficiency of controlling the electronic properties of the non-crystalline semiconductor material $Ge_2Sb_2Te_5$ by impurity modification with bismuth, it is necessary to conduct a comprehensive study of the structure and electronic properties of the material $Ge_2Sb_2Te_5$ <Bi>.

The aim of the thesis is to study the structure and electronic properties of amorphous and crystalline thin films of CGS composition $Ge_2Sb_2Te_5$, modified with Bi impurity, obtained by ion-plasma high-frequency co-sputtering.

To achieve this goal, the following tasks were set:

- to work out the technology for producing thin amorphous films of composition $Ge_2Sb_2Te_5$ by the method of ion-plasma high-frequency sputtering in an argon atmosphere with a ratio of components corresponding to the composition of the initial CGS;
- to work out the technology of obtaining modified amorphous $Ge_2Sb_2Te_5$ <Bi> films by ion-plasma high-frequency sputtering of a combined target chalcogenide semiconductor - metal;
- to study the composition and structure of $Ge_2Sb_2Te_5$ and $Ge_2Sb_2Te_5$ <Bi> films in amorphous and crystalline states;

- to study the effect of Bi impurity on the optical and electrical properties of amorphous and crystalline thin films $Ge_2Sb_2Te_5$ <Bi>, to determine the optical contrast of the films and their main semiconductor parameters;
- to study the effect of Bi impurity on the parameters of the switching and memory effect in thin $Ge_2Sb_2Te_5$ <Bi> films.

Object of study. Amorphous and crystalline thin films of composition $Ge_2Sb_2Te_5$ and $Ge_2Sb_2Te_5$ <Bi>, obtained by the method of ion-plasma sputtering.

Subject of study. The structure and electronic properties of amorphous and crystalline thin films of CGS composition $Ge_2Sb_2Te_5$, modified with bismuth impurity, and the parameters of the switching effect.

Experimental and theoretical methods. The composition and structure of the films were studied by the method of energy dispersive analysis and the methods of scanning electron microscopy, Raman spectroscopy; X-ray photoelectron spectroscopy; used methods for the study of electrical, optical and photoelectric properties, as well as the method of studying the process of switching and memory effect.

Reliability and validity. The experiments were conducted on modern equipment with the use of proven research methods and innovative approaches. The discussion of the results was carried out at each stage of implementation at the scientific seminars of the department, at international and national conferences, symposia with the participation of leading experts in this field. The results obtained were tested for accuracy and validity when reviewing publications in periodical international scientific journals and reports of international conferences that are part of the Thompson Reuters and Scopus databases. Also, the results of the study were tested in the patent office of the Republic of Kazakhstan, on the basis of which the author obtained a patent.

Scientific novelty of the work

- The results of a comprehensive study of the structure and electronic properties of thin amorphous and crystalline $Ge_2Sb_2Te_5$ <Bi> films with a Bi concentration up to 15.9 at.% Obtained by ion-plasma high-frequency co-sputtering. It has been established that bismuth clusters are not present in the structure of the films, and the main semiconductor parameters of amorphous and crystalline films substantially depend on the impurity concentration.
- For the first time using the XPS method, it was shown that in amorphous and crystalline films $Ge_2Sb_2Te_5$ <Bi> bismuth atoms form various chemical compounds with matrix components, and at a concentration of ~ 6.3 at.%, Bismuth interacts only with Te atoms, forming compounds Bi_2Te_3.
- The spectral distribution of optical contrast (OC) in $Ge_2Sb_2Te_5$ <Bi> films was studied. It has been established that in the visible light range, the OC value for $Ge_2Sb_2Te_5$ <Bi> films is significantly larger than that for films without admixture. It is shown for the first time that $Ge_2Sb_2Te_5$ <Bi 6.3 at.%> Films are characterized

by the largest OC in the spectral range from 630 to 800 nm, and $Ge_2Sb_2Te_5$ <Bi films to 15.9 at.%> In the range from 360 to 600 nm.

- The effect of bismuth impurity on the parameters of the switching and memory effect in thin films $Ge_2Sb_2Te_5$ <Bi> was studied. It is shown for the first time that films with a Bi concentration of ~ 6.3 at.% Are characterized by optimal effect parameters.

The practical significance of the study

- It was shown that by ion-plasma high-frequency co-sputtering, it is possible to obtain $Ge_2Sb_2Te_5$ <Bi> films with a Bi concentration up to 15.9 at.% With an amorphous structure that does not contain metallic bismuth clusters.
- The possibility of effective control of the electronic properties of amorphous and crystalline thin films of composition $Ge_2Sb_2Te_5$, within wide limits by impurity modification with bismuth, is shown.
- $Ge_2Sb_2Te_5$ <Bi> films with a Bi concentration equal to 6.3 and 15.9 at.% Are a promising material for optical CD-RW, DVD, Blu-Ray discs.
- $Ge_2Sb_2Te_5$ <Bi 6.3 at.%> Films are promising for use in non-volatile cells for recording and storing information of a new generation.

Provisions for protection

- The structure of $Ge_2Sb_2Te_5$ films modified with Bi by ion-plasma high-frequency co-sputtering, with an impurity concentration of Bi up to 15.9 at.%, Is an amorphous matrix whose chemical composition is determined mainly by the compounds Bi_2Te_3, Sb_2Te_3, GeTe and Sb_2O_3, GeO_2 and elements of Ge, Sb, Te.
- The crystallization of amorphous $Ge_2Sb_2Te_5$ <Bi> films is accompanied by the formation of additional chemical compounds TeO_2, Bi_2O_3, $BiSbO_4$, $Bi_2Sb_2O_4$ and $Bi_2Ge_3O_9$, which are not observed in the amorphous phase.
- The magnitude and spectral distribution of the optical contrast in $Ge_2Sb_2Te_5$ <Bi> films can be effectively controlled by changing the concentration of the bismuth impurity.
- The optimal parameters of the switching and memory effect in $Ge_2Sb_2Te_5$ <Bi> thin films, observed at a bismuth concentration of 6.3 at.%, Are determined by the peculiarity of their structure, which consists in the fact that in the amorphous and crystalline state of the films, the bismuth atoms form a chemical compound only with tellurium atoms.

Approbation of work. The main results of the work were reported on:

- 13th Inter. Conf. “NON-CRYSTALLINE MATERIALS” (NCM-13). 24-29 Jul., Canada, Halifax. -2016.
- IEEE 36th International Conference on Electronics and Nanotechnology (ELNANO-2016) - 19-21 April, Kiev, Ukraine. - 2016
- International Conference Amorphous and Microcrystalline Semiconductors (AMS), July 4-7, St. Petersburg, Russia. -2016.
- XIII International Scientific Conference "Solid State Physics" (FTT), April 26-28, Astana, Kazakhstan. -2016.

- IV International Scientific Conference “Modern condensed matter condensed matter physics, nanotechnologies and nanomaterials”. 10-12 october, Almaty, Kazakhstan. -2016.
- 10th Intern. Conf. “Chaos and structures in nonlinear systems. Theory and experiment”. Almaty, Kazakstan, 2017

Communication of the thesis with research programs. The dissertational work was carried out within the framework of research under the program of grant funding for basic research of the Committee of Education and Science of the Ministry of Education and Science of the Republic of Kazakhstan on the priority “Fundamental research in the natural sciences” on topics No.GR 0215PK01347 (2015-2017) and No. GR 0118PK01188 (2018-2019)

Publications and personal contribution of the dissertation. According to the materials of the dissertation, 10 published works were published, including 1 article in the journal included in the Thomson Reuters and Scopus database (IF = 2.48; SJR = 0.72), 4 publications (including 1 patent) in publications recommended by the CCSON , 6 in materials of international conferences, 4 of them included in the database of Thompson Reuters.

The scope and structure of the thesis. The thesis work consists of introduction, three sections, conclusion and list of references. The work is presented on 102 pages of printed text, contains 83 figures, 12 tables and a list of references from 99 titles.