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Chemical-dynamic polishing of semiconductor materials based on Bi and Sb chalcogenides by using HNO_3–HCl solutions

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Abstract. The chemical etching of Bi_2Te_3 and *n*-$(Bi_2Te_3)_{0.9}(Sb_2Te_3)_{0.05}(Sb_2Se_3)_{0.05}$ and *p*-$(Bi_2Te_3)_{0.25}(Sb_2Te_3)_{0.72}(Sb_2Se_3)_{0.03}$ crystals of solid solutions with HNO_3–HCl etchant compositions was investigated. The dependences of dissolution rate of these semiconductors on etchant composition, stirring, temperature and their shelf-time storage have been studied. It was shown that the process of dissolution of the investigated materials in the polishing solutions HNO_3–HCl is limited by the diffusion stages.

Keywords: chemical etching, etchant, solid solutions, bismuth telluride, etching rate, chemical-dynamic polishing.

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1. Introduction

Solid solutions based on Bi and Sb chalcogenides are highly efficient thermoelectric materials for low-temperature zone ($T < 220$ K) [1]. Currently, these materials have no alternative both in thermoeffectivity in this temperature range and in terms of their practical use for production of thermoelectric energy converters. In making the devices based on semiconductor materials the problem of getting high quality of surface at the final stage of chemical treatment remains one of the topical ones in the modern semiconductor materials science [2]. In practice, to prepare surface with a needed quality, usually used is chemical-dynamic polishing (CDP) in specially selected etching compositions [3].

Thus, for the chemical treatment of Bi_2Te_3, the authors [4] used I_2 solution in methanol, as the result they got triangular etching pits on the surface, which density was 10^6 cm^{-2}. For etchant preparation, they have mixed iodine with HCl and heated to 60 ºC, cooled to room temperature and then added other components of etchant. After etching, the samples were washed in HCl, water and dried up in air flow. Rinsing in HCl helps to eliminate from the sample surfaces bismuth compounds and I_2, insoluble in water, which can precipitate on crystals. Then samples were washed with ethanol (at finish rinsing, we can also use methanol, because it is a good solvent of residual iodine). For the chemical treatment of Bi_2Te_3, authors [5] have used solutions of ($2HNO_3$ + 1HCl + $6H_2O$) or (10 ml HNO_3 + 10 ml HCl + 40 ml H_2O + 1 g I_2) for 1-2 min. After etching in the first solution, the samples were washed with water and in the second one by ethanol and dried by filter paper. As a result, in both cases hexagonal etching pits were formed on the surface. When etching Bi_2Te_3 with 30% HNO_3, hexagonal etching pits were obtained on the surface of wafers, and in [6], for chemical polishing Bi_2Te_3, hot solution of dilute "aqua regia" has been used.

The object of this work is investigation of chemical etching the Bi_2Te_3 crystals as well as *n*-$(Bi_2Te_3)_{0.9}(Sb_2Te_3)_{0.05}(Sb_2Se_3)_{0.05}$ and *p*-$(Bi_2Te_3)_{0.25}(Sb_2Te_3)_{0.72}(Sb_2Se_3)_{0.03}$ solid solutions with HNO_3–HCl etching compositions, determination of concentration limits for polishing solutions, ascertaining the influence of aging processes in etchants on the etching rate and quality of polishing, optimization of etching compositions and chemical treatment modes to use them in producing materials for making operation elements of devices.

2. Experimental

To investigate semiconductor dissolution, ascertain the character of corresponding reactions and determine limiting stages of the process, we have used the method of rotating disk and appropriate device for its practical implementation – installation for CDP [7]. The crystals of Bi_2Te_3 as well as *n*-$(Bi_2Te_3)_{0.9}(Sb_2Te_3)_{0.05}(Sb_2Se_3)_{0.05}$ and *p*-$(Bi_2Te_3)_{0.25}(Sb_2Te_3)_{0.72}(Sb_2Se_3)_{0.03}$ solid solutions were grown using vertical growth zone melting of the components. For the investigation, we cut from the ingots the wafers with dimensions (~5×7×1.5 cm), which were abraded by aqueous suspension of M10, M5 and M1 abrasive powder one after another. After each stage of wafer treatment – cutting, abrading, mechanical and chemical-mechanical polishing interoperable cleaning was performed to eliminate various contaminations from the surface. Physical or mechanical contaminations

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(mote, abrasive, metallic materials, fibers and semiconductor particles that are crumbled into small pieces) were eliminated with warm water with addition of surfactants. The final stage of treatment included washing in distilled water, degreasing by ethanol or acetone, then samples were dried up in air flow.

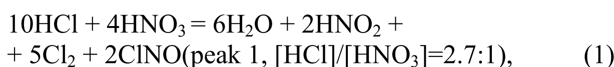
Mechanically polished surface of crystalline samples are stable in time, but it is not structurally perfect, and therefore, before researching, the layer with a thickness of 80-100 μm was eliminated from it with etchant of the same composition, in which the process of chemical treatment was subsequently performed. Samples were stuck by their operation surface to glass substrates by using picein and placed on the disk of CDP installation. The dissolution rate of crystals was measured by the difference in the sample thickness before and after the etching process by using the watch indicator 1MIGP to within ±0.5 μm. Etching time was chosen so that the process was shot by one of at least 10-15 μm of material.

To prepare etching compounds, we used 70% HNO_3 and 36.6% HCl. Etching compositions were prepared directly before use, then they were hold up for 80-120 min. After completion of etching process, the samples were quickly bereaved from etching composition and immediately washed several times with deionized water and in ultrasonic bath for 5 min at 20 °C for surface cleaning from etchant residues, then dried up in air flow.

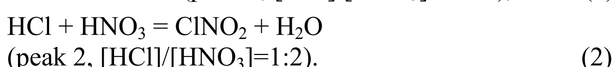
The surface microstructures obtained after etching were photographed using the universal stage microscope ZEISS JENATECH INSPECTION with a digital camcorder possessing magnifications between 25× to 1600×.

3. Results and discussions

Investigation of chemical dissolution Bi_2Te_3, n-$(Bi_2Te_3)_{0.9}(Sb_2Te_3)_{0.05}(Sb_2Se_3)_{0.05}$ and p-$(Bi_2Te_3)_{0.25}(Sb_2Te_3)_{0.72}(Sb_2Se_3)_{0.03}$ were performed within the concentration range 10-100 vol.% HNO_3 to HCl at $T = 293$ K and the disk rotation speed $\gamma = 86\,\text{min}^{-1}$. Concentration dependences of the etching rate (v_{etch}) of these crystals in the HNO_3–HCl solutions are shown in Fig. 1. As seen from the figure, with increasing the amount of HNO_3 in HCl the dissolution rate of Bi_2Te_3 increases from 1.7 to 23 μm/min, for n-type material – from 1 to 88 μm/min and for p-type material – from 0.3 to 71 μm/min, while the corresponding curve is characterized by two peaks at different ratio etching components. Depending on the volume ratio of components $[HNO_3]$:[HCl], we can assume the following course of these reactions in the etching solution:



$10HCl + 4HNO_3 = 6H_2O + 2HNO_2 +$
$+ 5Cl_2 + 2ClNO$(peak 1, $[HCl]/[HNO_3]=2.7:1$), (1)



$HCl + HNO_3 = ClNO_2 + H_2O$
(peak 2, $[HCl]/[HNO_3]=1:2$). (2)

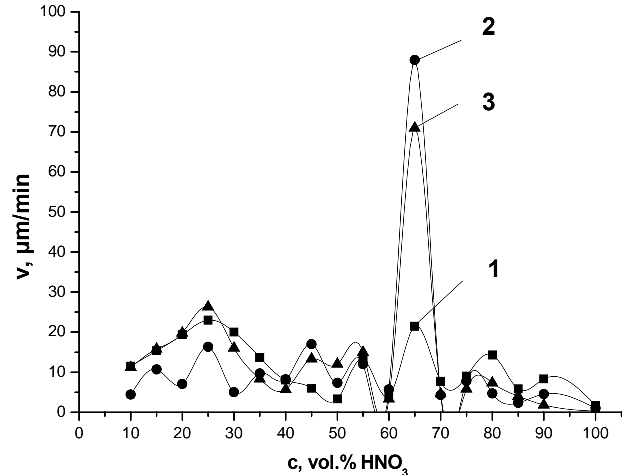


Fig. 1. Concentration dependences of the etching rate for Bi_2Te_3 (1), n-$(Bi_2Te_3)_{0.9}(Sb_2Te_3)_{0.05}(Sb_2Se_3)_{0.05}$ (2) and p-$(Bi_2Te_3)_{0.25}(Sb_2Te_3)_{0.72}(Sb_2Se_3)_{0.03}$ (3) in the solutions of the HNO_3–HCl system ($T = 293$ K, $\gamma = 86\,\text{min}^{-1}$).

The results of metallographic analysis of the samples surface obtained by etching Bi_2Te_3, n- and p-type conductivity semiconductors designed by polishing etchants, showed the possibility to use them for CDP of thermoelectric materials surface.

In order to study the processes that occur by dissolution of the investigated semiconductor materials in etching compositions of HNO_3–HCl system, we performed kinetic research and plotted the dependences of the dissolution rate (v) in the coordinates $v^{-1} - \gamma^{-1/2}$ ($36 < \gamma < 120\,\text{min}^{-1}$) at $T = 293$ K as well as of the etchant temperature in the coordinates $\ln v - 1/T$ in polishing solution of 55 vol. % HNO_3 in HCl. As seen from Fig. 2a, for all the investigated materials the suitable lines can be extrapolated to the origin, which indicates a diffusion mechanism of dissolution inherent to these materials. Investigation of temperature dependences of the dissolution rate of the mentioned above materials in the same etching solution (Fig. 2b) revealed that the apparent activation energy did not exceed $E_a = 30$ kJ/mol in all the cases [8]. This confirms the conclusion that the limiting stage of the process of dissolution of these materials is diffusion.

For technological purposes, it is important information about the stability of etching solutions, which means the influence of the storage duration on such basic things as the etching rate, polishing ability and others. To establish this influence, we carried out the research of etching rate changes observed for Bi_2Te_3 and solid solutions based on it in the etching composition of 55 vol.% HNO_3–HCl, which were aged for 2, 24, 48, 72 and 96 hours at room temperature. As seen from Fig. 3, with increasing duration of etchant aging, the dissolution rates of investigated materials have been hardly changed. It should be also noted that aging this etchant of HNO_3–HCl system for five days has no effect on the polishing properties, so, these etchants can be used for chemical

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polishing for a long time after their preparation, which is another advantage of them. This should be considered in practical use of the proposed etching compositions.

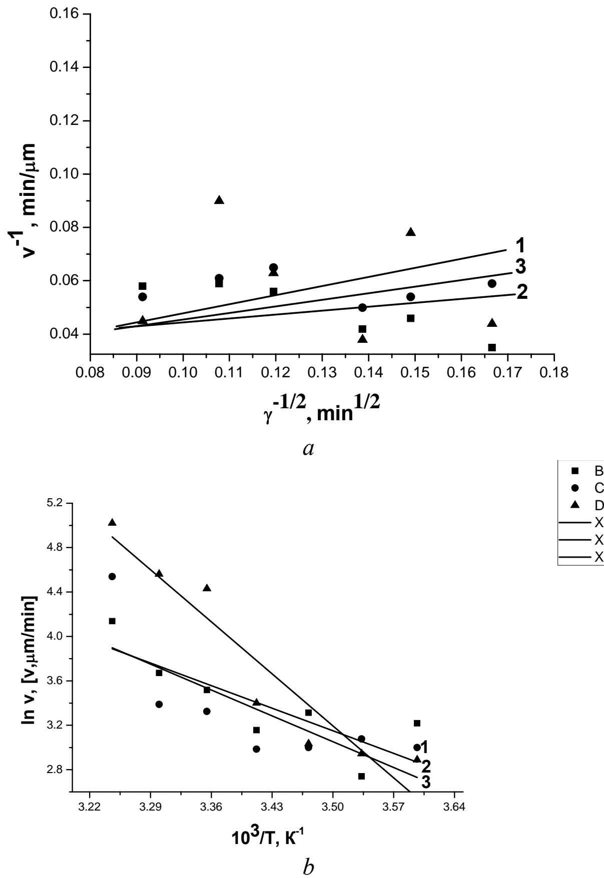

Fig. 2. Dependences of the etching rate for Bi_2Te_3 (1), n-$(Bi_2Te_3)_{0.9}(Sb_2Te_3)_{0.05}(Sb_2Se_3)_{0.05}$ (2) and p-$(Bi_2Te_3)_{0.25}(Sb_2Te_3)_{0.72}(Sb_2Se_3)_{0.03}$ (3) on the speed of disk rotation (T = 293 K) (a) and temperature (γ = 86 min^{-1}) (b) in the solution containing 55 vol. % HNO_3 to HCl.

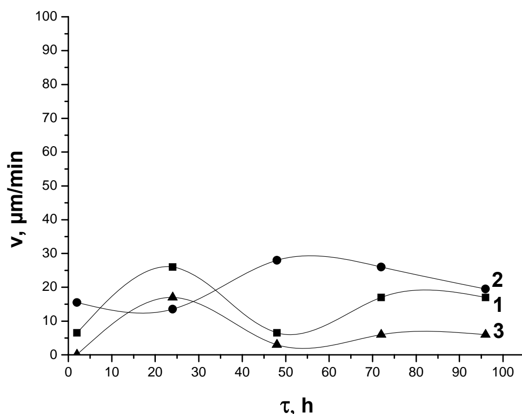

Fig. 3. Dependences of the etching rate of Bi_2Te_3 (1), n-$(Bi_2Te_3)_{0.9}(Sb_2Te_3)_{0.05}(Sb_2Se_3)_{0.05}$ (2) and p-$(Bi_2Te_3)_{0.25}(Sb_2Te_3)_{0.72}(Sb_2Se_3)_{0.03}$ (3) on the shelf-time of etchant containing 55 vol.% HNO_3 to HCl (T = 293 K, γ = 86 min^{-1}).

Thus, the results of the experiments revealed that all etchants HNO_3–HCl in the concentration range 10-100 % HNO_3 in HCl have a good polishing properties for surface of thermoelectric materials Bi_2Te_3, n-$(Bi_2Te_3)_{0.9}(Sb_2Te_3)_{0.05}(Sb_2Se_3)_{0.05}$ and p-$(Bi_2Te_3)_{0.25}(Sb_2Te_3)_{0.72}(Sb_2Se_3)_{0.03}$, characterized by a low etching rate and can be used for CDP of these materials.

4. Conclusions

We have investigated the dependences of the dissolution rate of Bi_2Te_3 crystals as well as solid solutions n-$(Bi_2Te_3)_{0.9}(Sb_2Te_3)_{0.05}(Sb_2Se_3)_{0.05}$ and p-$(Bi_2Te_3)_{0.25}(Sb_2Te_3)_{0.72}(Sb_2Se_3)_{0.03}$ on the composition of etchants HNO_3–HCl, their stirring, temperature and shelf-time storage. We showed that one can use solutions containing (10-60, 80) vol.% HNO_3 to HCl in chemical polishing the above semiconductors. We have found that the studied etchants are stable in time and keep their polishing properties for five days after preparation.

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