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Melt growth of bulk Bi_2Te_3 crystals with a natural p–n junction

K. A. Kokh,*[abc] S. V. Makarenko,[b] V. A. Golyashov,[b] O. A. Shegai[d] and O. E. Tereshchenko[bcd]

Single crystals of Bi_2Te_3 were grown from Bi–Te melts using the modified Bridgman method. It was shown for the first time that solidification of 61 and 62 mol.% Te melts provides a built-in p–n junction on the cleaved plane of as grown crystals without any post growth treatment. The formation of a p–n junction along the growth crystal was explained by Te segregation. Both p- and n-parts of the ingot have shown high carrier concentrations $n \approx p \approx 1 \times 10^{19}$ cm^{-3} and high carrier mobility ~10^4 cm^2 V s^{-1} at 4 K. In the transition p–n region, Hall carrier concentration is decreased by two orders of magnitude as a result of intrinsic compensation of carriers.

Introduction

Bismuth telluride based compounds are considered to be among the best thermoelectric materials operating near room temperature.[1] During the last 5 decades, a large amount of research has focused on the study of the Seebeck coefficient in doped Bi_2Te_3 in order to increase the performance of thermoelectric devices. Another issue was to check the type of conductivity provided by a given impurity since it is necessary to have separate blocks of n- and p-type elements.

Satterthwaite and Ure Jr.[2] provided the details on the phase diagram of the Bi–Te binary system close to the melting point of Bi_2Te_3. The data show that the composition with congruent melting is not a stoichiometric compound but is shifted to the Bi-rich side. That implies that the equilibrium melt for electrically neutral stoichiometric Bi_2Te_3 should be enriched with tellurium. Fig. 1a shows a part of the phase diagram of the Bi–Te system. The "boundary" melt composition, which separates primary crystallization of p- and n-type regions of Bi_2Te_3, was reported to be ~63 mol% Te + 37 mol% Bi.[2] Later, it was shown that polycrystalline buffer material may be used for changing the composition of bulk Bi_2Te_3 by annealing.[3] Incorporation of foreign atoms into the structure of Bi_2Te_3 may also result in the inversion of conductivity. For instance, in ref. 4, it was shown that annealing of bulk p-type Bi_2Te_3 crystals in selenium vapor transforms the surface layers of the samples to the n-type $Bi_2Te_{3-x}Se_x$. In that way, a p–n junction between outer n-layers and the internal Se free part of the sample was formed. The same effect was shown for sulfur which leads to the formation of a Bi_2Te_3–$Bi_2Te_{3-x}S_x$ ($x \geq 0.12$) p–n junction by using heat treatment.[5] Partial substitution of cation by indium also produces the n-type material. This phenomenon was demonstrated for the melt grown $Bi_{2-x}In_xTe_3$ ($x \geq 0.1$) material in ref. 6.

In recent years, a great deal of attention has been paid to the properties of the tetradymite mineral group showing a novel property of three-dimensional topological insulators.[7,8] Bismuth telluride is among the compounds of this class; theoretically, its surface state consists of a single nondegenerate Dirac cone, while the bulk state remains insulating.[9] However, due to their nonstoichiometry, all as grown Bi_2Te_3 crystals are of p- or n-type and therefore exhibit metallic behavior in the bulk. And the resulting intrinsic carriers hamper the study and application of the specific surface states.

Sidestepping of this problem may be carried out by using previous data on transformation of conductivity type in Bi_2Te_3 since the p–n transition should result in the compensation of intrinsic carriers. For instance, the electrical properties can be tuned through a slight increase of Te content in the as grown p-type Bi_2Te_3 crystal by Te-vapor annealing.[10] Another example is the growth of $Bi_2(Te,Se)_3$ mixed crystals. It was shown that Bridgman solidified $Bi_2Te_2Se_{0.995}$ melt may provide the samples with a positive to negative transition of the Hall coefficient with temperature.[11] The same effects as well as domains with different carrier types were found in the crystal grown from the Bi_2Te_2Se melt.[12]

Although the adjustment of tellurium pressure is very promising for the growth of stoichiometric Bi_2Te_3 thin

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[a] Sobolev Institute of Geology and Mineralogy, SB RAS, 3, Koptyuga Ave., Novosibirsk 630090, Russia. E-mail: k.a.kokh@gmail.com; Fax: +7 383 33066392

[b] Novosibirsk State University, 2, Pirogov Str., Novosibirsk 630090, Russia. E-mail: k.a.kokh@gmail.com; Fax: +7 383 33066392

[c] Tomsk State University, 36, Lenina Ave., Tomsk, 634050, Russia. E-mail: k.a.kokh@gmail.com; Fax: +7 3822 529585; Tel: +7 3822 529852

[d] Rzhanov Institute of Semiconductor Physics, SB RAS, 13, Koptyuga Ave., Novosibirsk 630090, Russia. E-mail: teresh@isp.nsc.ru; Fax: +7 383 3304475