PRELIMINARY STUDY ON GeTe-SbTe AND Sm-B TOPOLOGICAL INSULATORS

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Abstract: *The process of developing the field of materials science is often driven by the discovery of new advanced materials. Especially, the material characteristics and uniformity of quantum mechanics are considered the most important. Of which, the topological insulator material with electrical insulation in the bulk but high conductivity on the surface has been extensively investigated as a new research direction in recent years due to its interesting properties that can be applied in spintronic applications. In this work, we investigate structural and electrical property of topological insulator materials of $[(GeTe)_2(Sb_2Te_3)_1]_n$ (GTST) multilayers which were fabricated on the Si wafers using a helicon-wave sputtering system and SmB_6 single crystals grown by the Aluminum-flux method;*

Keywords: *Topological insulator, chalcogenide alloys, GeTe-Sb_2Te multilayers, SmB_6 single crystal.*

1. Introduction

The material class of topological insulators (TIs) has been discovered a few years ago and displays amazing properties. Inside its bulk exhibits a finite electronic bandgap (Figure 1a) and is, therefore, insulating. On the other hand, its surface states are gapless and metallic. These unusual properties are attributed to the intrinsic spin-orbit coupling which causes the quantum Hall effect and modifies the electronic structure significantly (Figure 1b).

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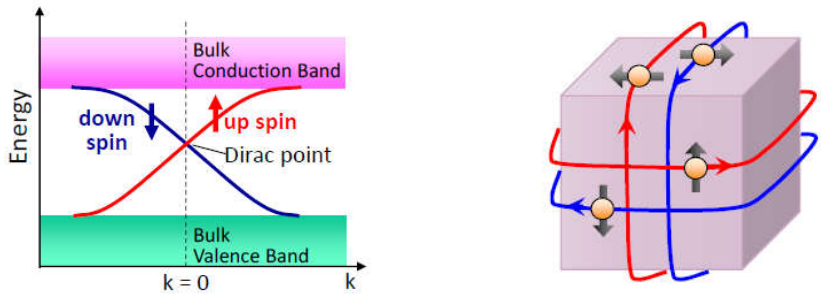

Figure 1. *(a) Schematic bulk and surface band structures; (b) Schematic real-space picture the 2D helica surface state of a TI*

In ordinary materials, backscattering, in which electrons take collisions with crystal defects, effectively degrades the current flow and increases the resistance. However, on the surface of TIs, such backscattering processes are completely suppressed, so charge transport is in dissipation less or low dissipation states. In 2008, the first TI material as experimentally identified was $Bi_{1-x}Sb_x$ with the Sb concentration range of 0.09 to 0.23 [1]. However, it was found out that this material is not very suitable for detailed studies of the topological surface state due to its complicated surface-state-structure [2,3]. Then several theoretical band calculations to elucidate the parity eigenvalues were done [4,5] and came up with a prediction that Bi_2Se_3, Bi_2Te_3, and Sb_2Te_3 would have a simple surface band structure (Figure 2).

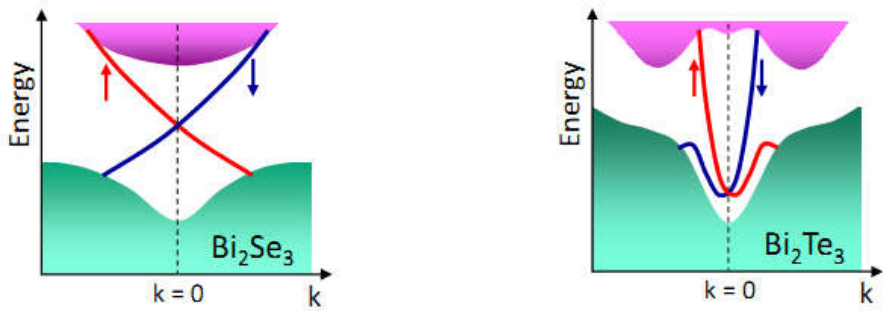

Figure 2. *Schematic bulk and surface structures of (a) Bi_2Se_3 and (b) Bi_2Te_3*

These materials were also experimentally confirmed and reported in references [6-10]. Furthermore, the bulk gap of Bi_2Se_3 is relatively large (0.3 eV), and thus one can see the technological relevance that topological properties can be exploited at room temperature. However, its chemistry is always degenerately doped due to naturally occurring crystalline defects, which cause its transport properties to be dominated by bulk carriers. In this respect, TI material having tetradymite structure is promised and it was first reported for Bi_2Te_2Se and Sb_2Te_2Se [10-12]. An important theme in the research of TIs is to reduce unintentionally-doped bulk carrier that hinders observations of surface transport properties by using suitably

doped elements [13-15]. In fact, another useful approach to reducing bulk carriers is to reduce the size of samples by making thin ribbons, films and nanowires [16-18]. Another candidate topological zero-gap semimetals are Heusler or half-Heusler compounds (LnAuPb, LnPtBi…). Several experimental evidences of this have been reported so far [19-21]. Moreover, the rare earth containing crystal SmB_6 is also predicted to be a TI due to strongly correlated heavy fermion material to exhibit topological surface states [22]. Recently, our collaborating research group in Japan has succeeded in fabricating high quality crystalline $[(GeTe)_2(Sb_2Te_3)_1]_n$ (GTST) topological superlattices, which lead to as much as a 95% reduction in the switching energy of electrical non-volatile phase-change random-access memory [23]. In this study, we investigated the effect of annealing process on the crystalline structures and electrical properties of the GTST multilayers, and influence of fabrication conditions on structure of SmB_6 bulk samples prepared by the Aluminum-flux method.

2. Experiment

Most of the confirmed TI materials are chalcogenides. Since the chalcogen atoms are volatile, the syntheses of the TI materials can be done by using Bridgman method for bulk samples, molecular beam epitaxy (MBE) or sputtering system for thin films and chemical vapor transport for ribbon and nanowires samples. To avoid unexpected contaminations, the grown crystalline should be done in the vacuum or in Ar/I_2 gas.

The $[(GeTe)_2(Sb_2Te_3)_1]_n$ topological superlattices were fabricated at different substrate temperatures of 150 to 210 ºC on Si wafers using a helicon-wave sputtering system that has GeTe and Sb_2Te_3 composite targets (2-inch) and automated control shutters at pressures less than 0.5 Pa Ar. Thicknesses of each GeTe and Sb_2Te_3 sublayers were 0.85 nm and 1.0 nm, respectively. A 3 nm-thick Sb_2Te_3 layer was firstly deposited to ensure the strong crystalline orientation. Finally, a 20 nm-thick $ZnS\text{-}SiO_2$ layer was deposited as a capping layer to protect the GTST multilayers from oxidation [24]. We then investigated the effect of annealing process on the crystalline structures and electrical properties of the GTST multilayers by using X-ray diffraction (XRD) and resistivity measurements, respectively.

By reviewing several fabrication methods of topological insulator materials, we realized that Bridgman and Aluminum-flux methods can be realized on the research facilities in Vietnam. In addition, most components of TI materials contain toxic elements such as Pb, Bi, Sb, and Se. Therefore, the selection of investigational compounds would be selected to limit the effect on human and environment. In this work, SmB_6 compound was chosen to synthesize by the aluminum-flux method with the starting materials of samarium ingot, boron powder and aluminum granules. Sm, B, and Al were weighted in an atomic ratio of 1:4:200. The mixture was placed in an alumina crucible and heated to 1150ºC in the vacuum. During the reaction, the crucible was covered with an alumina lid to reduce Al evaporation. After maintaining at 1150ºC for 2 hours, the furnace was slowly cooled to 25ºC in 10 hours. The aluminum - flux was dissolved by a concentrated NaOH solution in a fume hood, and shiny single crystals of SmB_6 of millimeter-size were picked out.

Scanning/Transmission Electron Microscopy (SEM/TEM) and X-ray diffraction (XRD) measurements were used to study the structure of the SmB_6 samples.

3. Results and discussion

The XRD patterns of the as-deposited GTST multilayers are shown in Figure 3a. For the higher depositing temperature of 210ºC multilayer has a better crystalline structure. Especially, the intensity of the (001) crystalline direction gradually increases when the depositing temperature increases from 150 to 210ºC. These results can be explained by the self-organized van der Waals epitaxy model due to the reactive selectivity of the surface [25]. It has been reported that Te forms a compound with Si, while Sb does not. On the other hand, both the Sb and Te react with O which will form a mixed position of Sb and Te on the first Sb_2Te_3 sublayer. Therefore, it is expected that the surface oxide would be effectively removed at higher temperatures, resulting in a reactive selectivity and the surface would be covered with a monolayer of Tb preferentially. Then the second monolayer would be Sb as the layer by layer structure of Te and Sb atomics.

The 150ºC as-deposited multilayer was annealed at 210ºC for 1 hour and its XRD patterns was measured again as shown in Figure 3b. It is clearly seen that the crystalline structure was significantly improved after the annealing process due to reconstruction at higher temperatures.

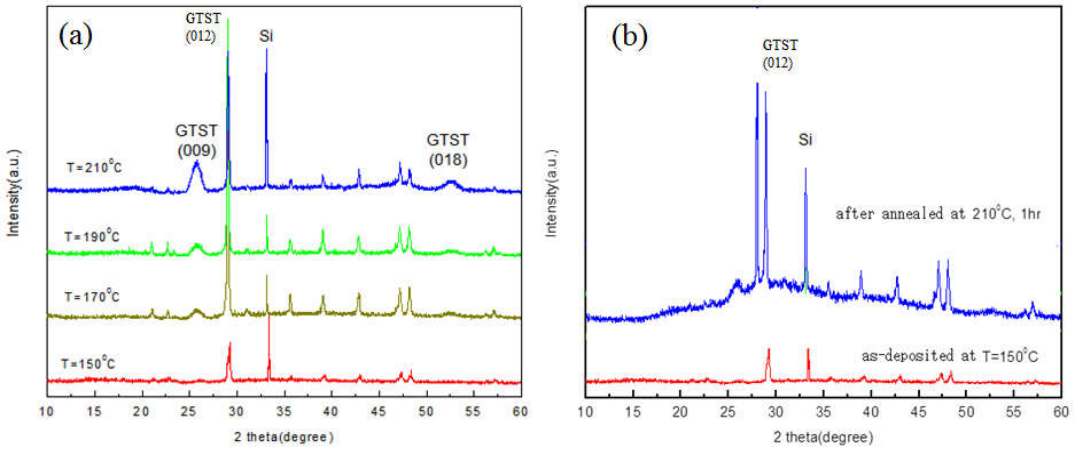

Figure 3. *X-ray diffraction patterns of (a) 150, 170, 190, and 210 ºC as-deposited GTST multilayers and (b) the 150ºC as-deposited multilayer was annealed at 210ºC for 1 hour*

The magnetic field dependences of the resistivity measured at room temperature for the 150, 210ºC as-deposited and 210ºC annealed GTST multilayers are shown in figure 4. For the 150ºC as-deposited sample, its resistivity is one order higher than those of the other ones. This high resistivity is comparable with that of the GeSbTe alloy. It means that the main part of the 150ºC as-deposited sample is not in well crystalline structures as shown in the XRD patterns (figure 3) but in alloy compounds of GeTe and SbTe which have semiconductor behaviors at

room temperature. On the other hand, the resistivity of the 210ºC as-deposited and 210ºC annealed GTST multilayers is as low as that of a good GeTe-SbTe superlatice. It suggested that the annealing process at high temperatures can improve the crystalline structure as well as the electrical property of the low temperature deposited GTST films due to the reconstruction of atoms.

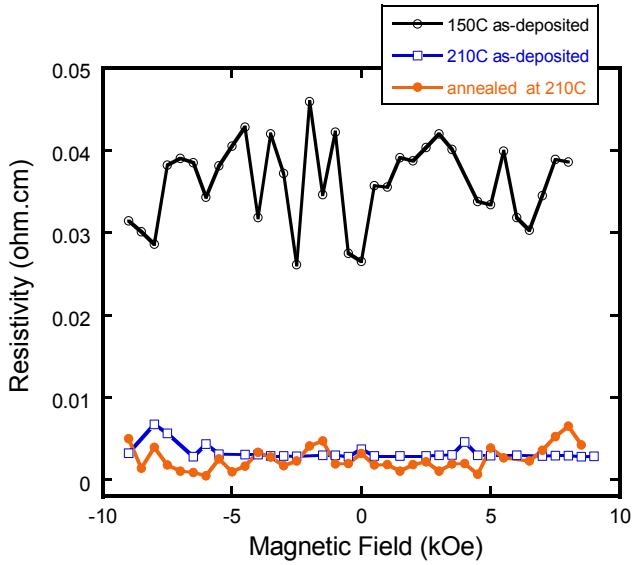

Figure 4. *Magnetic field dependences of resistivity for 150ºC as-deposited (opened circles) and 210ºC as-deposited (opened squares) GTST multilayers, and the 150ºC as-deposited multilayer was annealed at 210ºC for 1 hour (solid circles)*

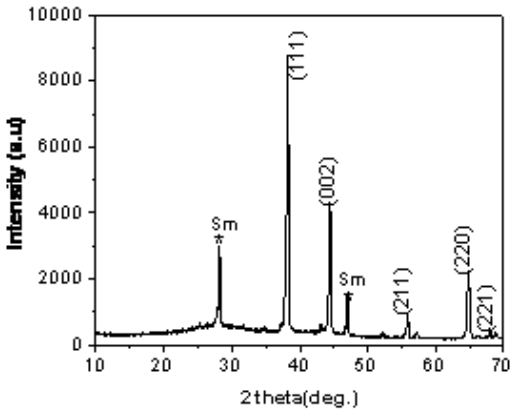

Figure 5. *XRD pattern of SmB_6 bulk sample synthesized at 1150^{0}C*

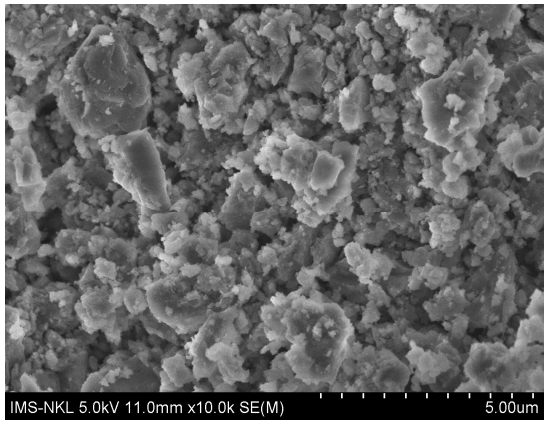

Figure 6. *SEM image of SmB6 bulk sample synthesized at 1150^{0}C*

As shown in [22], the single crystal structure of SmB_6 is cubic lattice with constant a = 4.1353Å. Figure 5 shows XRD pattern of SmB_6 prepared at 1150ºC using Sm, B, and Al as raw material. Aluminum here plays the role of reducing the melting temperature of elements in the component. It can be seen that all the diffraction peaks are not really the

SmB_6 single crystal structure. However, its XRD patterns are well indexed and assigned to the parallel crystal planes of (221), (220), (211), (002), (111) [26]. The impurity phases are identified to be Sm element.

The SEM image is shown in Figure 6. It can be seen that the SmB_6 bulk sample prepared at 1150^{o}C is mainly composed of a great deal of aggregated particles without any regular shapes, there are some large grains with non-cubic morphology mixing together. In the next steps, we will continue to synthesize samples at different temperatures to obtain the better SmB_6 single crystals.

4. Conclusion

We investigated the effect of annealing process on the crystalline structures and electrical properties of the GTST multilayers. It is found that the annealing process at high temperatures can improve the crystalline structure as well as the electrical property of the low temperature deposited GTST films due to the reconstruction of atoms. On the other hand, we also fabricated SmB_6 single crystals by the Aluminum-flux method and investigated their structure. The results showed that the SmB_6 bulk sample prepared at 1150^{o}C is mainly composed of a great deal of aggregated particles without regular shapes. There are some large grains with non-cubic morphology mixing together.

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