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# 열전 박막 $Bi_{0.5}Sb_{1.5}Te_3/Bi_2Te_{2.4}Se_{0.6}$ p/n 접합에서의 확산 장벽에 관한 연구

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# A Study on the Diffusion Barrier at the p/n Junctions of $Bi_{0.5}Sb_{1.5}Te_3/Bi_2Te_{2.4}Se_{0.6}$ Thermoelectric Thin Films

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***Abstract*** In the fabrication processes of thin film thermoelectrics, a subsequent annealing treatment is inevitable to reduce the defects and residual stresses introduced during the film growth, and to make the uniform carrier concentration of the film. However, the diffusion-induced atomic redistribution and the broadening of p/n junction region are expected to affect the thermoelectric properties of thin film modules. The present study intends to investigate the diffusion at the p/n junctions of thermoelectric thin films and to relate it to the property changes. The film junctions of p-type($Bi_{0.5}Sb_{1.5}Te_3$) and n-type($Bi_2Te_{2.4}Se_{0.6}$) were prepared by the flash evaporation method. Aluminum thin layer was employed as a diffusion barrier between p- and n-type films of the junction. This was found to be an effective barrier by showing a negligible diffusion into both type films. After annealing treatment, the thermoelectric properties of p/n couples with aluminum barrier layer were accordingly retained their properties without any deterioration.

## 1. INTRODUCTION

Efforts for making small and highly-integrated thermoelectric modules have employed the new techniques for the preparation of $Bi_2Te_3$-[1~8], PbTe-[9~11], and $FeSi_2$-based[13,14] thin films : i.e. sputter deposition, molecular beam epitaxy, co-evaporation, solid state reaction, electrochemical deposition, vacuum evaporation, etc. Flash evaporation, which is a modified vacuum evaporation method for better compositional control, has been successfully applied to fabricate a thin film thermoelectrics of good quality[15~19].

As-deposited films of $Bi_2Te_3$-based thermoelectric materials show very poor thermoelectric properties, even if the overall compositions can be controlled as precisely as stoichiometry for p- and n-type components. This is due to the structural defects(mainly antistructure defects), residual stresses, and local inhomo-geneity in composition. Therefore, adequate subsequent heat treatments are inevitable to reduce the defects and to improve the thermoelectric properties. For $Bi_2Te_3$-based thermoelectrics, it is necessary to anneal the thin films at 200~250℃ for several hours to acquire their thermoelectric properties compared to those of bulk materials[6,18]. In the fabrication of thermoelectric modules, p- and n-type thin films have to be connected to make the junctions, and then these junctions are subject to be annealed for the improvement of properties as mentioned above. This gives rise to the inter-diffusion of component elements through the p/n junctions. Therefore, the variation of composi-

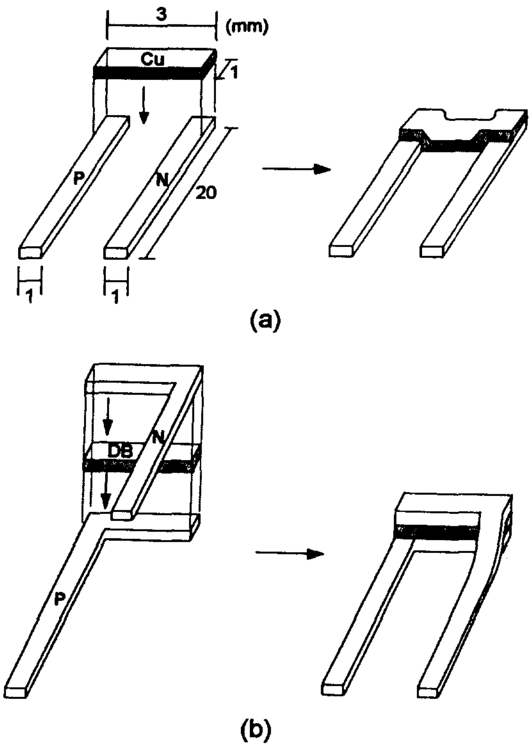

Fig. 1. Shape and dimension of p/n couples(film thickness of 1㎛ was exaggerated).
(a) bridge type (b) over-layer type
P : p-type film, N : n-type film, DB : diffusion barrier.

tions induced by atomic redistribution could be responsible for the unwanted physical property changes, in spite of the defect reduction. This problem becomes more significant if the relative area of p/n junctions compared with that of p/n legs increased considerably, as the modules become smaller and thinner[19]. It was found that thermoelectric properties were deteriorated with the increase of the relative junction area : therefore, diffusion barrier at p/n junctions is a necessary and important measure to solve the above problem if the smaller moduless are intended to be fabricated.

In the pressent study, p/n junctions of $Bi_{0.5}Sb_{1.5}Te_3/Bi_2Te_{2.4}Se_{0.6}$ thin films were prepared on the single crystal silicon wafers by the flash evaporation technique. The annealing treatments for thin film p/n junctions were carried out under several conditions : 200~300℃ for 1~10 hours. The effects of diffusion barriers (nickel or aluminum layer) on the p/n junction were also investigated in conjunction with property changes.

## 2. EXPERIMENT

Thin films of ≈1㎛ thick for each type material were deposited onto Si(111) single crystal wafers. The detailed method and procedure for thin film deposition were described elsewhere[18]. Configurations and dimensions of p/n couples were shown in Figure 1 with the fabrication process. The bridge type p/n couple(Figure 1-

Table 1. Physical properties of thermoelectric materials and several metals used in this experiment.

| | Bi | Sb | Te | Se | $Bi_{0.5}Sb_{1.5}Te_3$ | $Bi_2Te_{2.4}Se_{0.6}$ | Cu | Ni | Al |
|---|---|---|---|---|---|---|---|---|---|
| Seebeck coefficient ($\mu$V/K) | -80 | 35 | 400 | 1000 | 225[20]<br>160[18] | -230[20]<br>-200[18] | 2.9 | -18 | -0.6 |
| Electrical conductivity ($\Omega^{-1}m^{-1}$) | 84 | 230 | 0.04 | 800 | 7.8[20]<br>6.1[18] | 8.7[20]<br>5.1[18] | 5790 | 1400 | 3660 |
| Thermal conductivity (W/m·k) | 1.19 | 2.11 | 1.53 | 0.90 | 1.37[20] | 1.66[20] | 3.43 | 4.50 | 4.28 |
| Electro-negativity | 2.02 | 2.05 | 2.10 | 2.55 | | | 1.90 | 1.91 | 1.61 |
| Atomic radius(pm) | 154.7 | 159.0 | 143.2 | 140.0 | | | 127.8 | 124.6 | 143.1 |
| Melting point(K) | 544.6 | 903.9 | 722.7 | 494 | 813 | 853 | 1358 | 1728 | 933.5 |
| Atomic mass | 208.98 | 121.75 | 127.60 | 78.96 | | | 63.546 | 58.70 | 26.98 |
| Crystal structure | rhomb. | rhomb. | hcp | hcp | rhomb. | rhomb. | fcc | fcc | fcc |

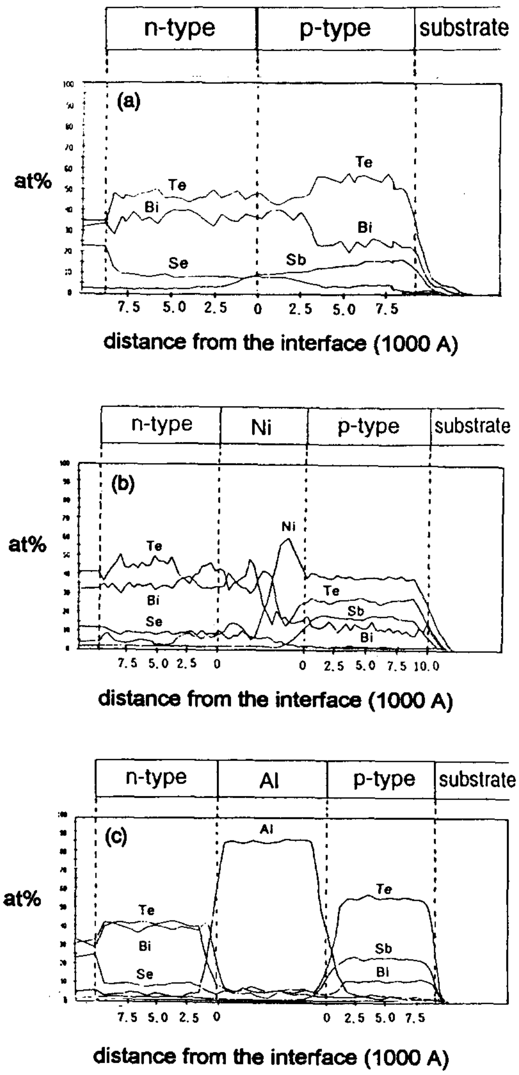

Fig. 2. AES depth profiles of the p/n junction. (a) annealed at 200℃ for 10 hours without diffusion barrier (b) anneled at 200℃ for 1 hour with Ni-barrier (c) anneled at 200℃ for 1 hour with Al-barrier

(a)) was prepared for the investigation of annealing effect without any existence of interdiffusion at the p/n junction. After deposition of p- and n-type film, vacuum annealing was employed with p- and n-legs unconnected, and then copper film as a connector was deposited. Figure 1-(b) shows the over-layer type p/n couple, which was used for the study on diffusion barrier effects at the junctions. Diffusion barrier layer of 1~1.5㎛ thick pure nickel or aluminum was interlaminated between p- and n-type films, and then p/n couple was annealed in a vacuum atmosphere.

Atomic redistrbution at the p/n junction region due to the diffusion was analyzed by Auger Electron Spectroscopy(AES) depth profiling. Phases were identified using X-Ray Diffactometer(XRD). Scanning Electron Microscopy(SEM) was employed to observe the cross-section of p/n junction. Seebeck coefficent and electrical conductivity of p/n couples were measured and analyzed in conjuncton with the changes caused by diffusion.

## 3. RESULTS AND DISCUSSION

Physical properties of metal elements used as a connector and a diffusion barrier, and thermoelectrics used in these experiments were listed in Table 1. Low Seebeck coefficient and high electrical conductivity might indicate copper, gold, and silver as appropriate barrier materials, but these elements were reported showing high diffusion behavior into $Bi_2Te_3$-based thermoelectrics even at room temperature[21,22]. It is also customary to perform nickel plating onto thermoelements prior to making copper link in the bulk module formation process, in order to prevent the diffusion of copper into thermoelectrics. Since nickel is ferromagnetic, it is not suitable for the application of diffusion barrier in the presence of a magnetic field, particularly when the effects such as galvanomagnetic and thermomagnetic are required.

It has been reported that aluminum hardly diffuses into $Bi_2Te_3$-based thermoelectrics[21] so that little harmful side effects such as contamination and defect formation would be explected. The reason for this has not been clear yet, but aluminum with low Seebeck coefficient, high electrical conductivity and nonmagnetic property was chosen as a diffusion barrier material.

Figure 2 shows the AES depth profile data for the annealed over-layer type p/n junctions. Vertical dotted lines indicate the original inter-

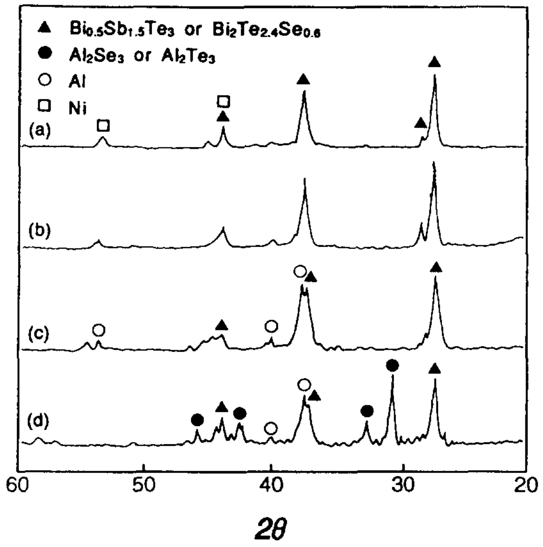

Fig. 3. XRD patterns of phases present in the region of p/n junction. (a) as-deposited p/n junction with Ni-barrier (b) annealed(200℃, 1hr) p/n junction with Ni-barrier (c) as-deposited p/n junction with Al-barrier (d) annealed(200℃, 1hr) p/n junction with Al-barrier

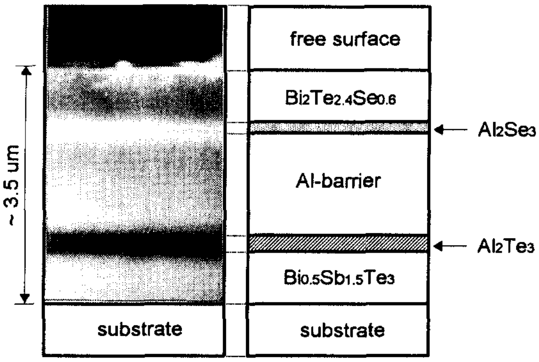

Photo 1. Scanning electron micrograph of cross-section of the p/n junction with Al-barrier annealed at 200℃ for 10 hours.

face. When the p/n junction without diffusion barrier was annealed at 200℃ for 1 hour, atoms of both sides interdiffused to form a diffused layer of ≈2000Å thick in the region of p/n junction[19]. The diffused layer expanded (≈6000Å thick) so intensively that the original junction area was nearly homogenized in composition as the annealing time increased upto 10 hours(Figure 2-(a)). It is natural to expect that themoelectric properties of the annealed p/n couples would be changed accordingly, possibly deteriorated.

In the junctions with Ni-barrier, nickel diffused much into both n- and p-type films, even when annealed at 200℃ for 1 hour(Figure 2-(b)). Especially, diffusion of nickel into p-type films was so pronounced that it could reach to the substrate. As shown in Figure 2-(c), however, Al-layer between p- and n-tupype thermoelectrics persisted sufficiently as a diffusion barrier by not allowing any interdiffusion of atoms. The Al-barrier layer remained almost unchanged even when heat-treated upto 300℃ for 10 hours[19].

To elucidate this marked diffusion barrier effect of aluminum compared with nickel, an analysis based on Zener's theory[15] was made under the assumptions for conventional metallic diffusion : however, the outcome of analysis was contradictory to our observation for Ni- and Al-Diffusion barrier. Thus it was clear that the understanding the effectiveness of aluminum would require more complex considerations of correlation factors for each component and of new phases formed at the interface region.

Variations of XRD patterns for p/n junction

Table 2. Formation free energy($\Delta G_f$) at 200℃.

| Compound | $\Delta G_f$(kcal/mole) | Compound | $\Delta G_f$(kcal/mole) |
|---|---|---|---|
| $Bi_2Te_3$ | -48.2 | AlSb | -19.4 |
| $Bi_2Se_3$ | -41.4 | NiSb | -16.4 |
| $Sb_2Te_3$ | -60.7 | NiTe | -17.6 |
| $Al_2Se_3$ | -146.7 | NiSb | -28.9 |
| $Al_2Te_3$ | -97.5 | NiBi | -11.9 |

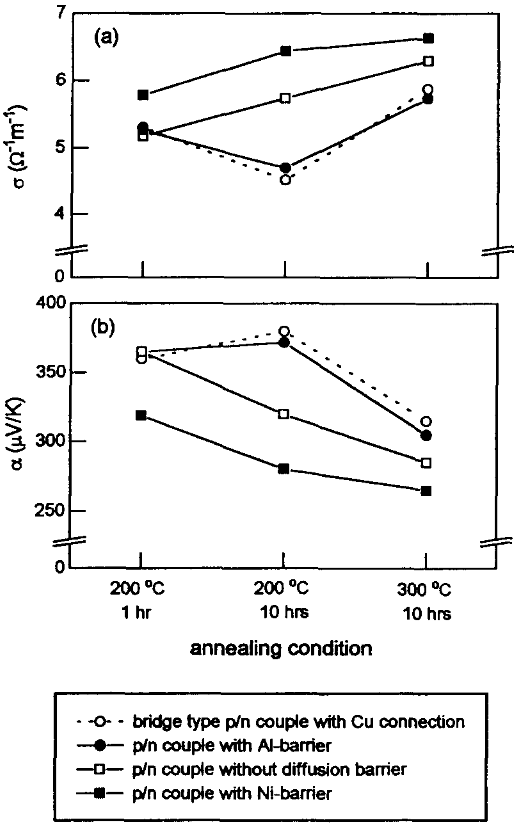

Fig. 4. Variation of thermoelectric properties of the p/n couples with annealing condition. (a) Electrical conductivity (b) Seebeck coefficient

regions with the annealing condition were presented in Figure 3. For the films containing Ni - barrier layer, no nickel compounds were traced after annealing(Figure 3-(b)). On the other hand, in the case of Al-barrier layer, various aluminum compounds were detected after annealing treatment(Figur 3-(d)).

It was believed that these compounds might be preferentially located at both interfaces between aluminum layer and p-type film, and between aluminum layer and n-type film. Intermediate layers were observed in the SEM picture(Photo. 1) of cross-sectional region of p/n junction containing Al-barrier. They could prevent the interdiffusion of matrix atoms across aluminum layer and the diffusion of aluminum atoms into both p- and n-type materials.

It was deduced from the XRD patterns and the data for free energy of formation ($\Delta G_f$) at 200℃ that these layers may be $Al_2Se_3$ and $Al_2Te_3$(see Table 2). Consequently, aluminum compounds formed at both sides of its own layer were believed to suppress the diffusion of aluminum itself and other elements across its layer.

Seebeck coefficient and electrical conductivity of p/n couples annealed at various conditions were measured to analyze the effects of diffusion on the thermoelectric properties(Figure 4). The result from the diffusion-inhibited bridge type couple were given for the comparison. Directly-contacted p/n couples without diffusion barrier layer showed the inferiority in thermoelectric properties to the couples containing proper diffusion barrier. This similar phenomenon was also observed for the p/n couple with Ni-barrier which was found to be an ineffective diffusion barrier. As shown in Figure 4, thermoelectric properties of p/n couple with Al-barrier were comparable with those of bridge type p/n couple.

## 4. CONCLUSIONS

The effects of diffusion barriers on the p/n junction were investigated for $Bi_{0.5}Sb_{1.5}Te_3/Bi_2Te_{2.4}Se_{0.6}$ thermoelectric thin films. The results obtained in these experiments were summarized as follows :

1)When annealed at 200℃ for 1 hour, diffused layer of about 2000Å thick was formed at the p/n junction in case of no diffusion barrier. As annealing time increased, more interdiffusion occurred across the p/n junction, and considerable changes in composition of the films were found. That, in turn, deteriorated the thermoelectric properties of the p/n couples.

2)Nickel layer used as a diffusion barrier was found to be ineffective. It diffused into both sides of p- and n-type films(much more into p-type thermoelectrics), and could not prevent interdiffusion of atoms across its layer properly.

3)Aluminum was a very efficient diffusion barrier for the p/n junction of $Bi_2Te_3$-based thermoelectrics. It hardly diffused into thermoelectric films and also maintained original layer even when it was annealed at 300℃ for 10 hours. It was believed that the aluminum compounds formed at both sides of the layer, which might be $Al_2Te_3$ and $Al_2Se_3$, suppressed the diffusion of aluminum itself and other elements across the junction.

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