

## EFFECT OF Pd-P LAYER ON THE BONDING STRENGTH OF Bi-Te THERMOELECTRIC ELEMENTS

In this study, the effect of electroless Pd-P plating on the bonding strength of the Bi-Te thermoelectric elements was investigated. The bonding strength was approximately doubled by electroless Pd-P plating. Brittle Sn-Te intermetallic compounds were formed on the bonding interface of the thermoelectric elements without electroless Pd-P plating, and the fracture of the bond originated from these intermetallic compounds. A Pd-Sn solder reaction layer with a thickness of approximately 20  $\mu\text{m}$  was formed under the Pd-P plating layer in the case of the electroless Pd-P plating, and prevented the diffusion of Bi and Te. In addition, the fracture did not occur on the bonding interface but in the thermoelectric elements for the electroless Pd-P plating because the bonding strength of the Pd-Sn reaction layer was higher than the shear strength of the thermoelectric elements.

*Keywords:* Bismuth-Telluride, Thermoelectric module, Electroless Pd-P plating, Bonding strength

### 1. Introduction

Bi-Te thermoelectric elements are thermoelectric materials showing the thermoelectric performance at the relatively low temperature range of 200°C or less and are widely used as materials for direct conversion of thermal to electric energy, and vice versa [1-5]. The thermoelectric module has a structure in which multiple n- and p-type thermoelectric elements are electrically connected to each other in series on a copper electrode formed on a ceramic substrate. The number of thermoelectric element bonds should be greater than ten for commercial thermoelectric modules in a thermoelectric cooling system using the Peltier effect or a thermoelectric power generation system using the Seebeck effect. Therefore, a single defective thermoelectric element bond can affect the thermoelectric performance of the entire module. For bonding of thermoelectric elements and copper electrodes, a soldering method using a Sn-Ag-Cu solder with a melting temperature of approximately 220°C is most commonly used. However, Sn, the main component of the solder, and Te, a component of thermoelectric elements, are known to form brittle intermetallic compounds at a temperature of approximately 250°C, and it has been reported that Sn-Te intermetallic compounds formed by this process lower the overall bonding strength of the thermoelectric module [6-7].

A Ni layer is commonly used as a diffusion barrier layer for suppressing the formation of Sn-Te intermetallic compounds [8-9]. Electroplating, electroless plating, physical vapor deposition (PVD), and the spraying method have been suggested as effective methods for forming this Ni layer. Although the Ni

layer formed using these methods is effective as a diffusion barrier layer, it has been reported as the starting point of cracking [10-11]. This is due to the formation of Ni-Te intermetallic compounds through the reaction with Te in the thermoelectric elements [12-13].

Therefore, in this study, we formed a Pd-P plating layer on the surface of Bi-Te thermoelectric elements by electroless plating to suppress the formation of Sn-Te and Ni-Te intermetallic compounds. Then, we investigated the effect of the Pd-P layer on the bonding strength of the Bi-Te thermoelectric elements by measuring the bonding strength of the thermoelectric module formed with the Pd-P layer. In addition, we investigated factors improving the bonding strength of the thermoelectric module by electroless Pd-P plating through the analysis of the bonding and fractured interfaces of the thermoelectric module, and through evaluation of the solder spreadability.

### 2. Experimental

A commercially available n-type ( $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ ) and p-type ( $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ ) Bi-Te ingot (Daeyang Co. Ltd., Korea) was pulverized, and thermoelectric powders with a particle size of approximately 75  $\mu\text{m}$  or less were prepared and used in this study. They were sintered using the spark plasma sintering (SPS) method with a 22 mm diameter graphite mold at 350°C and 50 MPa. The sintered thermoelectric body was cut into a disk shape with a thickness of 3 mm by electric discharge machining. The surface of the sintered disk was roughened by spraying alumina

\* KYUNGPPOOK NATIONAL UNIVERSITY, DEPARTMENT OF MATERIALS SCIENCE AND METALLURGICAL ENGINEERING DAEGU 41566, REPUBLIC OF KOREA

\*\* KOREA INSTITUTE OF MATERIALS SCIENCE, POWDER & CERAMIC MATERIALS DIVISION, GYEONGNAM 51508, REPUBLIC OF KOREA

<sup>#</sup> Corresponding authors: ijson@knu.ac.kr, ktkim@kims.re.kr

powder using the sand-blasting technique. The surface of the sintered disk treated with sand-blasting was cleaned by ultrasonic degreasing at 25°C for 1 min in acetone and for 1 min in a 2.5 M NaOH solution. Palladium nuclei were formed on the surface of the thermoelectric elements by immersion in a commercially available Pd catalyst solution (Atotech, Adhemax Activator SF, Germany) at 25°C for 60 s. After, it was immersed in a commercially available electroless Pd-P plating solution (YoungIn Plachem Co., Ltd., PNF, Korea) at 45°C for 30 min to form a Pd-P plating layer with a thickness of approximately 1.5  $\mu\text{m}$ . The thickness of the plating layer was measured using a fluorescent X-ray measuring instrument (XAN 250, Helmut Fisher, Germany).

The sintered disk completed by Pd-P electroless plating was wire-cut and processed into a 3 mm  $\times$  3 mm  $\times$  3 mm cubic block. This block was solder-jointed using hot air at 270°C for 10 min after coating a Cu electrode formed on alumina with a thickness of approximately 0.18 mm with a lead-free solder paste (Sn-3%Ag-0.5%Cu) by screen printing. The shear load acting on the thermoelectric module was converted into bonding strength from the measurements using a ball-shear tester (Nordson, Dage 4000, USA) until the bond was fractured. The bonding strength was measured 10 times for the thermoelectric modules built under identical conditions. The averages of these values are shown in the graphs presented herein. Component analysis of the bonding interface between the thermoelectric elements and the solder was performed using a field emission electron probe micro-analyzer (FE-EPMA, JEOL, JXA8530F, Japan). A solder ball with a diameter of 0.76 mm was placed on the flux and heated on a hot plate at 270°C for 90 s to compare the solder spreadability of the surface of each sintered disk. The solder spreadability (%) was calculated by measuring the height of solder balls before and after soldering. A total of 16 solder balls were used each measurement, and the average value is reported.

### 3. Results and discussion

Figure 1 shows the effect of the Pd-P plating layer on the bonding strength of the Bi-Te thermoelectric elements. The average value of the bonding strength of the n- and p-type thermoelectric elements without electroless Pd-P plating were 4.78 and 6.11 MPa, respectively. The average bonding strength of the thermoelectric elements after electroless Pd-P plating was significantly increased to 10.12 and 11.59 MPa, respectively. The bonding strength was approximately doubled in both the n- and p-type thermoelectric elements by electroless Pd-P plating. Therefore, it can be concluded that electroless Pd-P plating is effective in improving the bonding strength between the Bi-Te thermoelectric elements and the Cu electrode.

Figure 2 shows the results of the SEM observations of the surface of the n-type Bi-Te thermoelectric elements. The surface of the thermoelectric elements without the electroless Pd-P plating (a) was irregularly formed by the sanding treatment with the

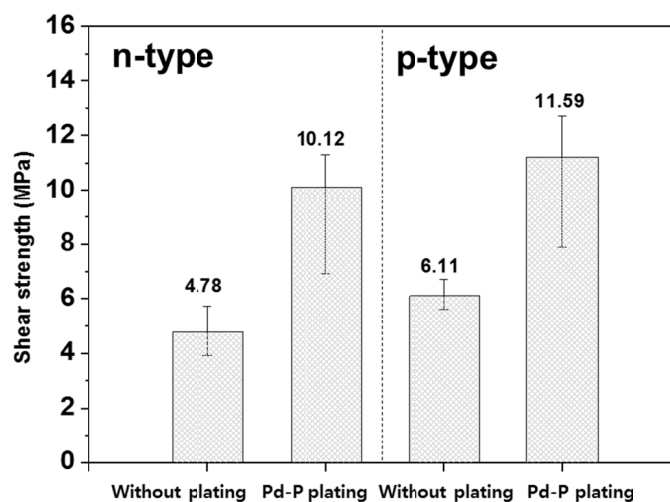


Fig. 1. Effect of the Pd-P layer on bonding strength of the Bi-Te thermoelectric elements

alumina powder, and Bi, Te, and Se, the components of n-type thermoelectric elements, were detected by EDS (c). When the electroless Pd-P plating layer with a thickness of approximately 1.5  $\mu\text{m}$  was formed, the plating layer covered the irregular surface morphology generated before plating (b). In addition, Pd and P, the components of the electroless plating layer, were found in the component analysis of the surface of the plating layer (d). Because the chemical bonding through interdiffusion is weak between the thermoelectric elements mainly composed of Bi and Te and the Pd-P plating layer, the adhesion of the Pd-P plating layer can be enhanced by physical surface roughness (i.e. the anchor effect). The Pd-P plating layer with excellent adhesion can be formed by sanding treatment using alumina powder before performing the electroless Pd-P plating to ensure roughness of the surface of the thermoelectric elements.

Figure 3 shows the results of the cross-section and component analysis of the bonding interface without electroless Pd-P plating using FE-EPMA. The SEM image (a) shows that the thermoelectric elements and the Sn-Ag-Cu solder are bonded, but there are some pore-like interface defects at the interface. The pores on the bonding interface are likely formed due to the low spreadability between the surface of the thermoelectric elements and the molten solder. It is also thought that the stress applied to the thermoelectric module during the measurement of the bonding strength concentrates on these defects and fractures the materials at a low shear stress. Since the Sn in image (b) and Te in image (d) are distributed in almost the same location at the bonding interface, it is reasonable to assume Sn diffuses mutually with Te in the thermoelectric elements to form intermetallic compounds. The Sn-Te intermetallic compounds are known to show brittleness [8-9], and it is expected that cracking will propagate from the Sn-Te intermetallic compounds to fracture the thermoelectric materials.

Figure 4 shows the results of the FE-EPMA analysis of the bonding interface of the thermoelectric module with electroless Pd-P plating. It was found that a Pd layer with a thickness of approximately 20  $\mu\text{m}$  was formed at the bonding interface between

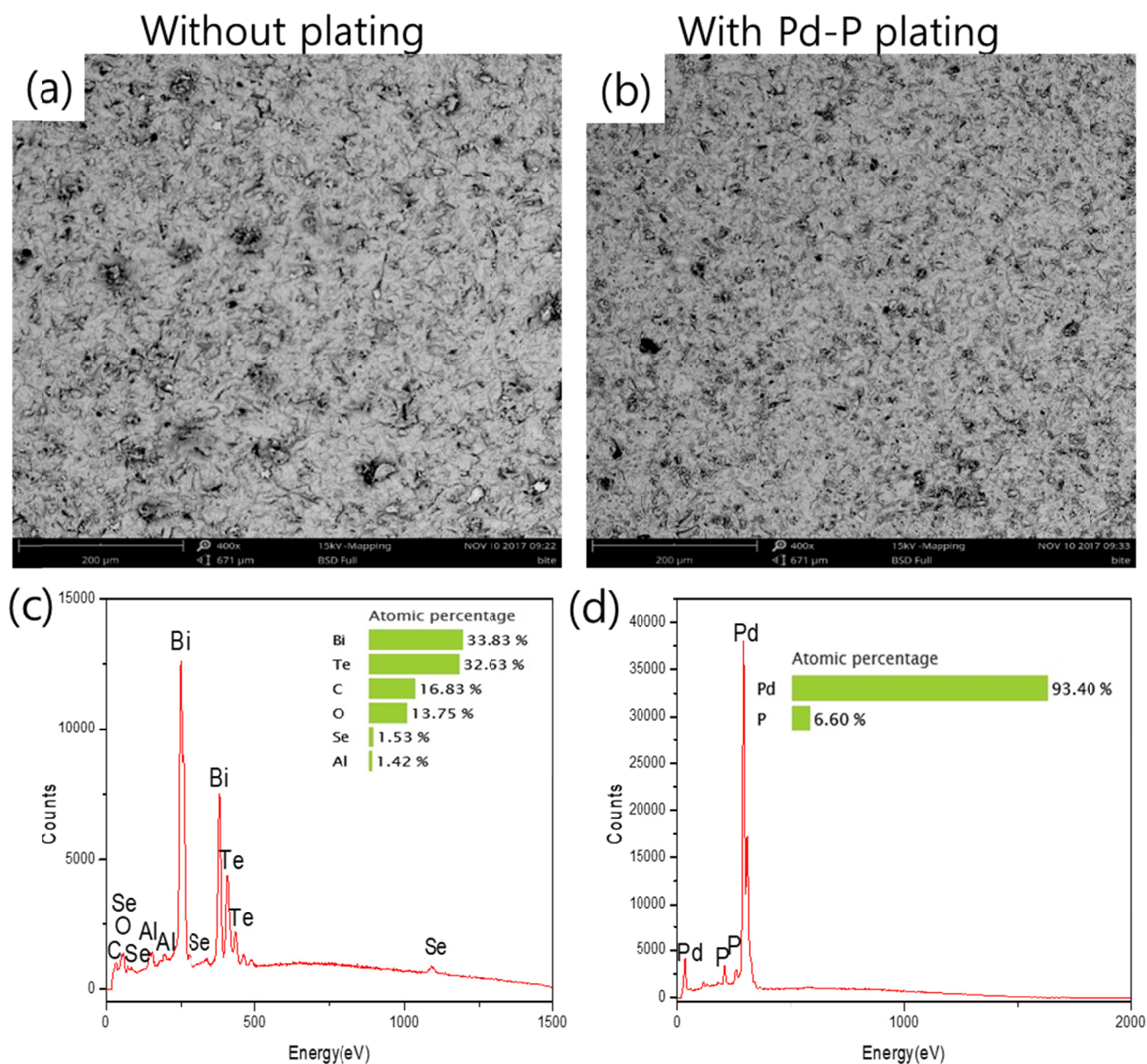


Fig. 2. Scanning electron microscopy (SEM) observation of the thermoelectric elements [(a), (b)] and energy dispersive spectrometry (EDS) component analysis [(c), (d)]

the thermoelectric elements and the solder. Since Bi (b) and Te (c) do not extensively diffuse under the solder reaction layer, it can be seen that the Pd-P plating layer serves as a diffusion barrier, preventing the mutual diffusion of the thermoelectric elements and the solder. The Pd of the electroless Pd-P plating layer rapidly and uniformly diffuses into the solder layer to form a reaction layer with the solder, with Pd (d) and Sn (e) present in the reaction layer. Thus, it is likely that the electroless Pd-P plating layer serves as a diffusion barrier layer preventing the diffusion of the thermoelectric elements and the solder, and forms a relatively thick Pd-Sn layer beneath the Pd-P plating layer due to rapid diffusion into the solder layer.

Figure 5 shows the results of the fractured cross-section of the n-type thermoelectric elements after the bonding strength test. Sn, Cu and Ag, the main components of the solder, were found on the surface [(a), (c)] of the fractured thermoelectric

module without electroless Pd-P plating. In other words, Sn in the solder and Te in the thermoelectric elements mutually diffuse to form brittle intermetallic compounds (Fig. 3), and fracture of the thermoelectric elements occurs mainly on the bonding interface. Conversely, the grayish white region, considered to be the fractured surface of the thermoelectric elements, was observed for electroless Pd-P plating [(b), (d)]. It is not the bonding layer interface but the thermoelectric elements that are considered to be fractured given that only the Bi, Te, and Se components of the n-type thermoelectric elements are present in the grayish white fracture region. This is because the shear strength of the bond is higher than the shear strength of the thermoelectric elements, making it reasonable to assume that the thermoelectric elements are the fracture sites.

Figure 6 shows the effect of the electroless Pd-P plating layer on the solder spreadability. It can be seen with higher solder

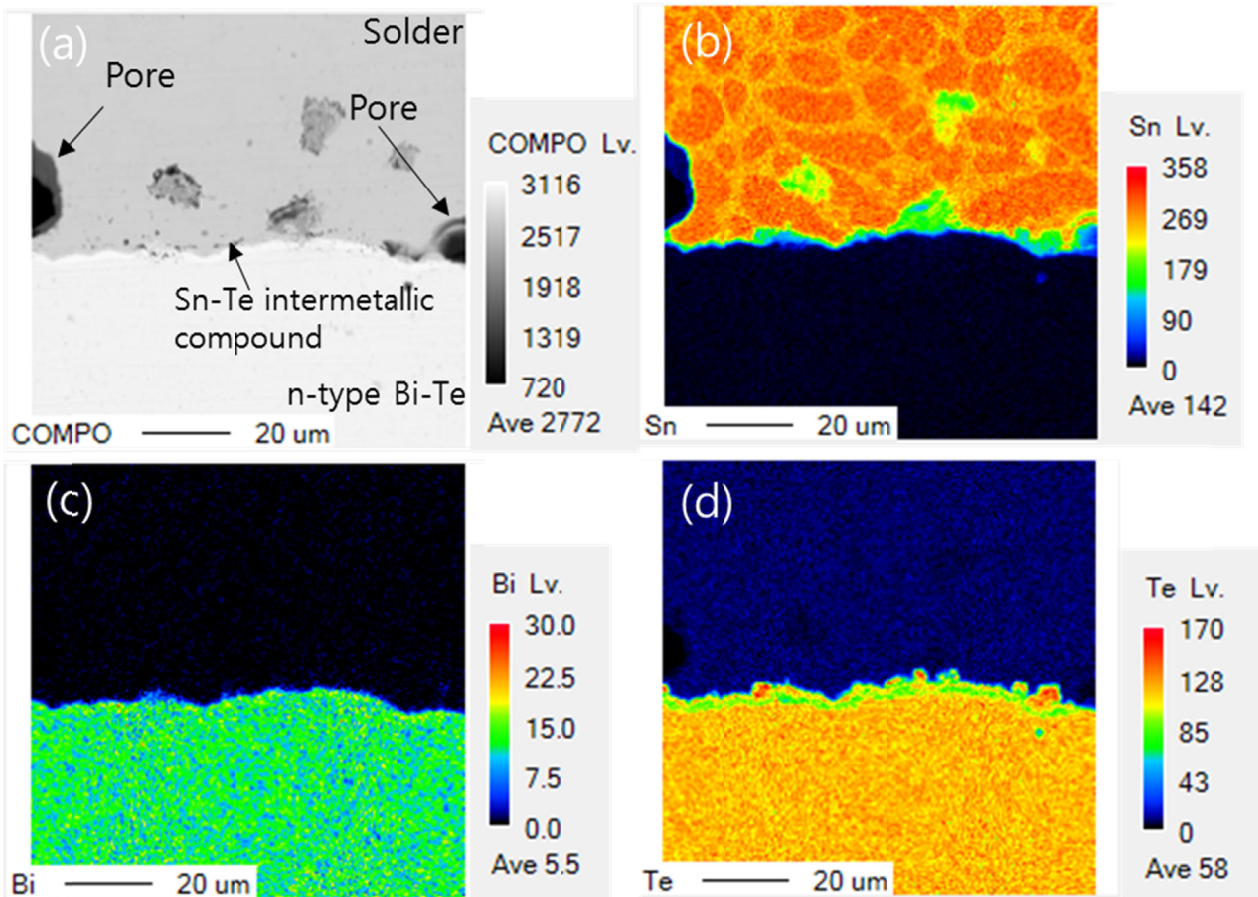


Fig. 3. Analysis of the bonding interface of the thermoelectric module without electroless Pd-P plating using FE-EPMA

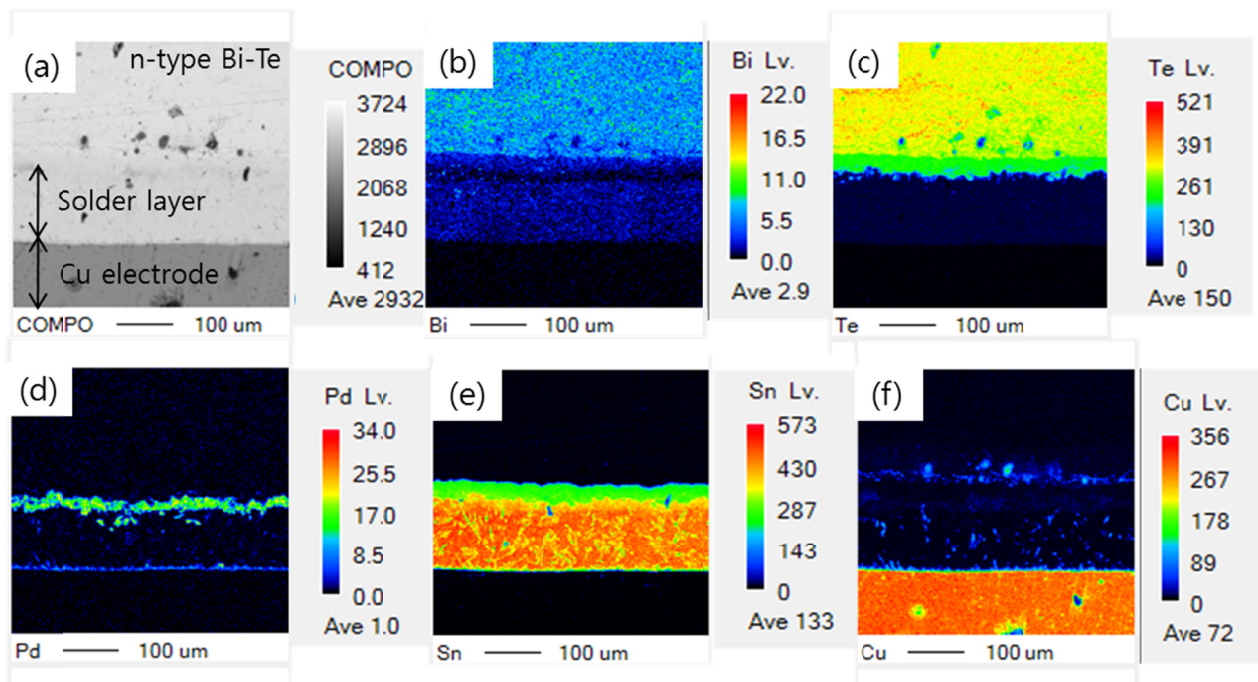


Fig. 4. Analysis of bonding interface of the thermoelectric module with electroless Pd-P plating using FE-EPMA

spreadability, faster mutual diffusion of surficial thermoelectric elements and the molten solder occurs. The solder spreadability of the thermoelectric elements without electroless plating is

25.0% on average, which is very low, but is increased to 65.8% with Pd-P plating. The diffusion speed of Pd into the molten solder layer is expected to be faster than that of Te, thus, the

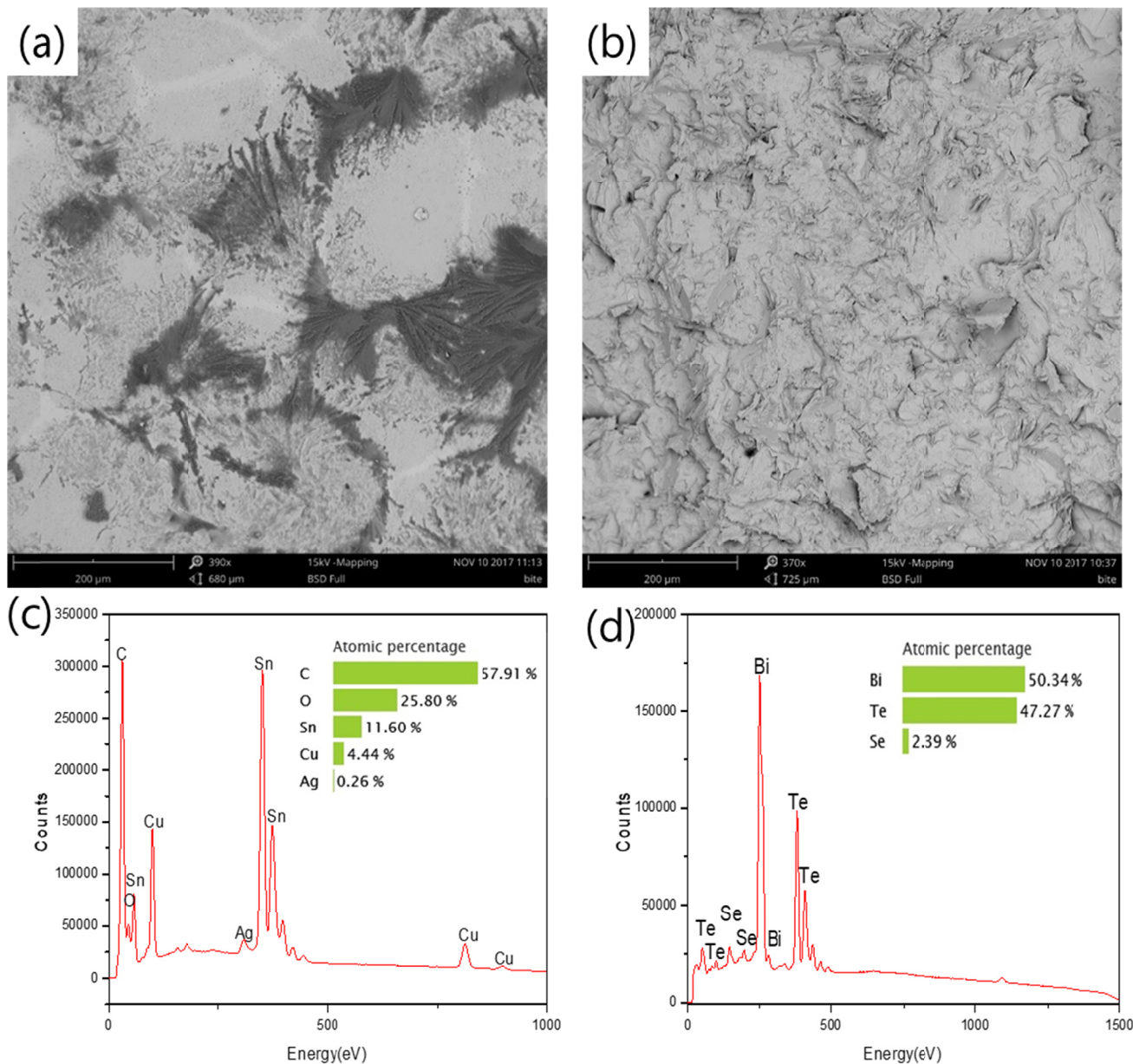


Fig. 5. SEM observation and EDS analysis of the fractured cross-section of the n-type thermoelectric elements after the bonding strength test [(a), (c): without plating, (b), (d): with Pd-P plating]

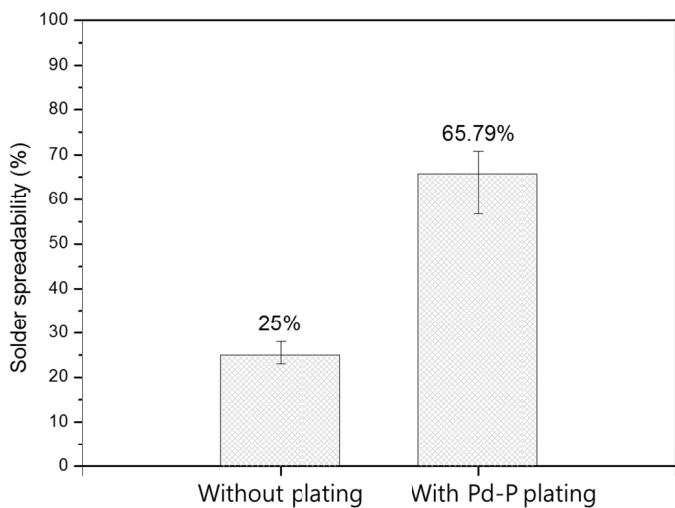


Fig. 6. Effect of electroless Pd-P plating on solder spreadability

electroless Pd-P plating significantly improves the solder spread rate. It is also expected that a higher the solder spreadability will result in thicker diffusion layer, increasing the bonding strength.

Brittle Sn-Te intermetallic compounds were formed on the bonding interface of the thermoelectric elements in the absence of electroless Pd-P plating, and the fracture originated from these brittle Sn-Te intermetallic compounds. The bonding strength of the thermoelectric module was approximately doubled by electroless Pd-P plating on the surface of the thermoelectric elements (Fig. 1). It was found that the electroless Pd-P plating layer functions as a diffusion barrier layer, suppressing the formation of brittle Sn-Te intermetallic compounds by mutual diffusion of the thermoelectric and solder elements. In addition, the Pd-Sn diffusion layer was formed in the solder layer under the Pd-P plating layer due to the rapid diffusion of Pd (Fig. 4). It is likely that the formation of the Pd-Sn layer improved the

bonding strength by strengthening the bonding with the solder layer through improved spreadability with the solder and the formation of a thick solder reaction layer.

#### 4. Conclusions

In this study, the effect of Pd-P plating on the bonding strength of the Bi-Te thermoelectric module was investigated. The bonding strength was approximately doubled by electroless Pd-P plating on the surface of the thermoelectric elements. Brittle Sn-Te intermetallic compounds were formed on the bonding interface of the thermoelectric elements without electroless plating, and the fracture of the bond originated from these intermetallic compounds. The electroless Pd-P plating layer effectively functioned as a diffusion barrier layer, suppressing the formation of brittle Sn-Te intermetallic compounds through mutual diffusion of the thermoelectric and solder elements. This is because the Pd-P plating improves the solder spreadability due to the rapid diffusion of Pd into the solder layer and the thick Pd-Sn reaction layer that is formed at the interface under the Pd-P plating layer.

#### Acknowledgments

This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government (MOE) (NRF-2017R1D-1A1B03030792).

#### REFERENCES

- [1] R.J. Mehta, Y. Zhang, C. Karthik, B. Singh, R.W. Siegel, T. Borca-Tascuic G. Ramanath, *Nature Mater.* **11**, 233 (2012).
- [2] K.T. Kim, S.Y. Choi, E.H. Shin, K.S. Moon, H.Y. Koo, G.G. Lee, G.H. Ha, *Carbon* **52**, 541 (2013).
- [3] K.T. Kim, I.J. Son, G.H. Ha, *J. Kor. Powd. Met. Inst.* **20** (5), 345 (2013).
- [4] M.S. Park, H.Y. Koo, G.H. Ha, Y.H. Park, *J. Kor. Powd. Met. Inst.* **22** (4), 254 (2015).
- [5] D.Y. Chung, T. Hogan, P. Brazis, M. Rocci-Lane, C. Kannewurf, M. Bastea, C. Uher, M. G. Kanatzidis, *Science* **287**, 1024 (2000).
- [6] T.Y. Lin, C.N. Liao, Albert T. Wu, *J. Electron. Mater.* **41** (1), 153-158 (2012).
- [7] S.W. Chen, C.N. Chiu, *Scripta Mater.* **56**, 97-99 (2007).
- [8] H. Wada, K. Takahashi, T. Nishizaka, *J. Mater. Sci. Lett.* **9**, 810 (1990).
- [9] D. Vasilevskiy, F. Roy, E. Renaud, R.A. Masut, S. Turenne, *Proc. 25th Int. Conf. on Thermoelectrics, Vienna, Austria*, 666 (2006).
- [10] O.D. Lyore, T.H. Lee, R.P. Gupta, J.B. White, H.N. Alsharreef, M.J. Kim, B.E. Gnade, *Surf. Interface Anal.* **41**, 440 (2009).
- [11] Y.C. Lan, D.Z. Wang, G. Chen, Z.F. Ren, *Appl. Phys. Lett.* **92**, 101910 (2008).
- [12] W.P. Lin, D.E. Wesolowski, C.C. Lee, *J. Mater. Sci.: Mater. Electron.* **22**, 1313 (2011).
- [13] W.H. Chao, Y.R. Chen, S.C. Tseng, P.H. Yang, R.J. Wu, J.Y. Hwang, *Thin Solid Films* **570**, 172 (2014).