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Co-P Diffusion Barrier for p-Bi_2Te_3 Thermoelectric Material

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$(Bi_{0.25}Te_{0.75})_2Te_3$ (p-Bi_2Te_3) is thermoelectric material that can harvest waste heat into useful electric power. A severe reaction between p-Bi_2Te_3 and Sn-based solder decreases the reliability of thermoelectric modules. Sn/p-Bi_2Te_3 and Sn3.0Ag0.5Cu (SAC305)/p-Bi_2Te_3 with and without electroless Co-P at the interfaces were investigated in this study. Without a Co-P layer, brittle SnTe, Sn_3Sb_2, and Bi precipitates formed at the interface. A thin layer of SnTe after reflow results in growth of a layer-type Sn_3Sb_2 instead of a strip-like Sn_3Sb_2. The addition of a Co-P layer to both systems successfully inhibited the formation of brittle intermetallic compounds. Shear test results confirmed that the Co-P diffusion barrier also effectively increased the joint strength.

Key words: Thermoelectric materials, electroless Co-P, diffusion barrier, interfacial reaction, shear strength

INTRODUCTION

Thermoelectric module is a device that harvests waste heat and converts it into useful electric power.[1–3] It can also be utilized as a cooler.[4] Bi_2Te_3 is a well-known thermoelectric material that offers high conversion efficiency at low-temperature. The conversion efficiency could be evaluated with a figure of merit, zT, given by $zT = (S^2\sigma T)/K$, where S is the Seebeck coefficient of thermoelectric materials, σ is the conductivity, T is the temperature, and K is the thermal conductivity.[5] zT value is affected by the properties of the thermoelectric material. The performance of the thermoelectric module relies significantly on its reliability.

Soldering process is an important step in assembling thermoelectric materials into a useful thermoelectric module. Sn is one of the most common elements used in solder, and Sn3.0Ag0.5Cu (SAC305) is the most widely adopted Sn-based solder alloy for assembly. It is important to understand the reaction between Sn-based solder and thermoelectric substrates. It was reported that Sn reacts rapidly with Te to form a thick and porous SnTe intermetallic compound (IMC).[6] The porous structure can decrease the mechanical strength of solder joints. Thus, fast growth of SnTe should be inhibited. In consumer electrical products, a Ni–P layer has been widely adopted as an effective diffusion barrier for electronic packaging. The diffusion barrier is applied between the solder and thermoelectric substrates.[7,8] It was reported that the addition of a Ni–P barrier in a thermoelectric module enhanced the mechanical strength of the joints.[9] However, the Ni–P layer further reacted with the Bi_2Te_3 thermoelectric substrates and formed a Ni-Te IMC at the interface.[10] Upon further annealing, Kirkendall voids formed in the Ni-Te layer.[11] Since the zT value is related to the composition of thermoelectric materials,[12] the formation of a Ni-Te IMC would deplete Te and could affect the performance of thermoelectric devices. Therefore, an alternative diffusion barrier is proposed in this study to overcome this problem. Co was found to effectively inhibit diffusion between Sn and Te. Furthermore, it was suggested that it is more difficult to form a Co-Te than a Ni-Te IMC.[13] Moreover, Chao et al. reported that thermoelectric materials with Co coatings exhibited higher Seebeck coefficients than those with Ni coatings.[14]

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These results indicated that Co might be suitable for forming an alternative diffusion barrier.

Electroless plating is commonly used for electronic packaging. Electroless plated Ni–P on various substrates has been widely investigated.[7–13] However, electroless plated Co-P on thermoelectric substrates and the resulting interfacial reactions are rarely reported. This study investigated the interfacial reactions between solder and p-Bi_2Te_3 with/without Co-P coatings. An electroless Co-P layer with a thickness of 5 ± 0.5 μm containing about 10 at.% P was deposited on the p-Bi_2Te_3 substrates. In Sn/p-Bi_2Te_3 and SAC305/p-Bi_2Te_3 systems, SnTe, Sn_3Sb_2, and Bi precipitates formed at the interfaces. In Sn/Co-P/p-Bi_2Te_3 and SAC305/Co-P/p-Bi_2Te_3 systems, Co-Sn, Cu-Sn, and Co-Sn-P layers were observed without formation of Co-Te IMC. A ball shear test was performed to investigate the mechanical strength of the joints. The results show that Co-P diffusion barrier can successfully inhibit the formation of SnTe and Co-Te IMCs and improve the shear strength of solder joints.

EXPERIMENTAL PROCEDURES

A zone-melting $(Bi_{0.25}Te_{0.75})_2Te_3$ (p-Bi_2Te_3) ingot was produced by the Industrial Technology Research Institute (ITRI) in Taiwan. Samples were cut into 2 mm thick columns with an automatic metallographic cutting machine. Surface oxidation and roughness were then removed from p-Bi_2Te_3 substrates by grinding and polishing. Acetone, isopropyl alcohol, and deionized water were used to clean the samples. Before electroless deposition, the p-Bi_2Te_3 substrates were etched with HNO_3 solution for 8 min to roughen the sample surfaces to enhance adhesion. The substrates were immersed in sensitization and activation solutions. The composition of each pretreatment solution can be seen in a previous publication.[15] An electroless Co-P diffusion barrier was deposited on the p-Bi_2Te_3 at 85 ± 3°C. The pH value of the plating bath was adjusted to 8.0 with NaOH, and the plating parameters of the Co-P layer can be found in Ref. 15.

Solder balls (0.02 g) were reflowed on bare and Co-P coated p-Bi_2Te_3 substrates. Two types of solder were used in this study: Sn with 99.999 wt.% purity (Alfa Aesar, USA) and Sn3.0Ag0.5Cu (SAC305; Accurus Scientific, Taiwan). Both multiple reflow and aging tests were conducted, and soldering was performed at 260°C for 5 s. In multiple reflow tests, specimens were subjected to the same soldering conditions in each cycle for 1, 3, and 5 times reflow. In aging tests, samples underwent one reflow before annealing at 150°C for 1 days, 5 days, 10 days, and 15 days. After thermal aging, specimens were removed from the furnace and cooled in air. All specimens were embedded in epoxy and subjected to further grinding and polishing.

Shear test was applied to determine the mechanical strength of the joints. First, substrates with/without a Co-P layer were coated with S1813 photoresist and photolithography was used to produce circular openings with a 300 μm diameter. Sn and SAC305 solder balls (450 μm diameter) were employed to reflow on the defined pattern at 260°C for 5 s. After soldering, the specimens were aged at 150°C for 15 days. A bond tester (Dage 4000) was used to measure the shear stress. The shear height was set at 45 μm and the shear speed was 50 μm/s.

Scanning electron microscopy (SEM, Hitachi S-4700) was used to observe the interfacial morphology. Field-emission electron probe microanalysis (FE-EPMA, JEOL JXA-8500F) was used to analyze the compositions and elemental distribution of the IMCs. The phases of the IMC layers were characterized by x-ray diffraction at beamline 17B1 of the National Synchrotron Radiation Research Center. The spot size was approximately 500 × 700 μm^2 (V × H), and the energy resolution was 10^{-4} at 10 keV photon energy.

RESULTS AND DISCUSSION

Interfacial Reaction of Sn/p-Bi_2Te_3 and SAC/p-Bi_2Te_3

To compare systems with/without Co-P diffusion barrier, Sn/p-Bi_2Te_3 and SAC/p-Bi_2Te_3 were investigated as baselines. Figure 1 shows SEM images of samples aged at 150°C for different times. Two different IMC layers could be observed between solder and substrate. As the aging time increased, the thickness of the IMCs increased from 5.62 μm to 226.15 μm and from 5.42 μm to 133.13 μm in the Sn/p-Bi_2Te_3 and SAC/p-Bi_2Te_3, respectively. FE-EPMA results indicated that the IMC layers were Sn_3Sb_2 (Sn-2.8 at.% Bi-34.0 at.% Sb-0.09 at.% Te) and SnTe (Sn-3.3 at.% Bi-2.8 at.% Sb-41.5 at.% Te). Figure 2 shows the x-ray diffraction pattern for these two phases. Furthermore, Bi precipitate was formed on the solder side and near the solder/Sn_3Sb_2 interfaces. Although Sn_3Sb_2 is reported in the literature, the morphology of the IMC in this study was significantly different from these results.[16,17] Chen et al. reflowed pure Sn on a homogenized p-Bi_2Te_3 substrate and found that SnTe and Sn_3Sb_2 appeared in alternating layers at the interface.[16] They speculated the fast diffusion of Sn resulted in Sb supersaturation, leading to the formation of strip-like Sn_3Sb_2 in the SnTe. Ye et al. reflowed Sn on both zone-melting and homogenized p-Bi_2Te_3 substrates.[17] They surmised that the growth direction of strip-like Sn_3Sb_2 depended on the orientation of the substrate. However, only layer-type Sn_3Sb_2 was found in our study. EPMA color mapping of Sn/p-Bi_2Te_3 samples aged for 1 day, shown in Fig. 3, indicated that Sn_3Sb_2 indeed formed a layer-like structure after aging.

The major reason for the different morphologies might be the thickness of SnTe. The reflow time was above 15 min in the study by Chen et al., while it was 60 s in that by Ye et al. In our research, the reflow

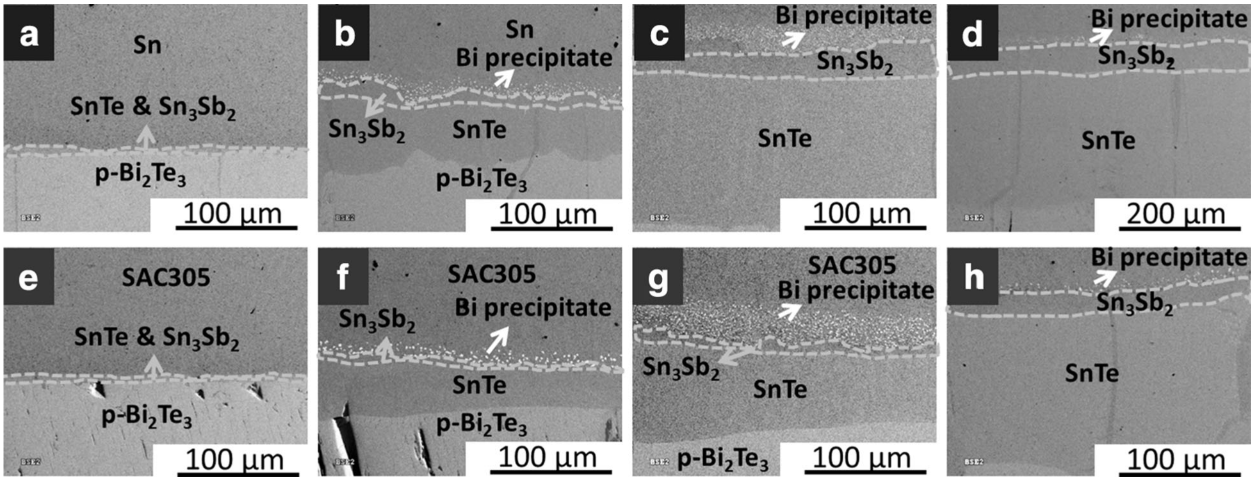

Fig. 1. Cross-section images of Sn/p-Bi_2Te_3 (a-d) and SAC/p-Bi_2Te_3 (e-h) aged at 15$\bar{0}$C for 1 day, 5 days, 10 days, and 15 days.

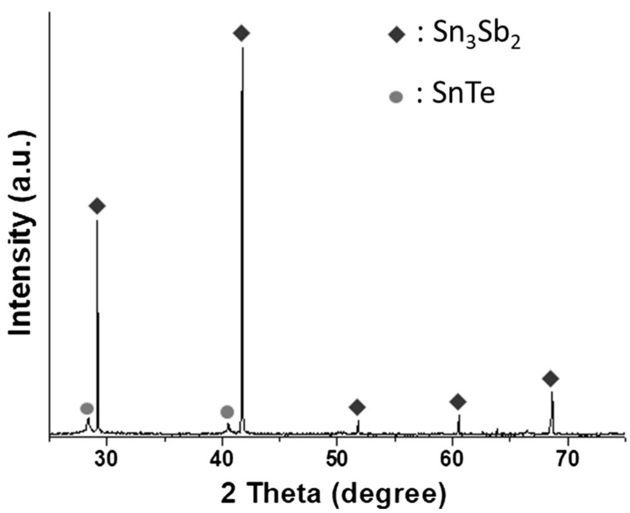

Fig. 2. X-ray diffraction pattern of Sn/p-Bi_2Te_3 aged at 150°C for 15 days.

time was only 5 s, which initially yielded an extremely thin SnTe. A thicker SnTe layer formed at the interface results in trapping more Sb in SnTe. As the rapidly diffusing Sn reacted with Sb, it forms strip-like Sn_3Sb_2. However, in our experiment, the SnTe was extremely thin after reflow. While Sn diffused rapidly, reacting with Te during aging and forming SnTe at the interface, Bi and Sb were relatively immobile. Bi did not react with Sn, and the supersaturated Bi formed precipitates. As the Sb concentration increased at the interface, it further reacted with sufficient Sn to form layer-like Sn_3Sb_2.

The results showed that SnTe, Sn_3Sb_2, and Bi precipitates rapidly formed at the interface. The severe reaction would affect the composition of the substrates and even degrade the performance of thermoelectric devices. It was reported that SnTe and Bi precipitates forming at the interface decreased the mechanical strength of the joints; thus, a diffusion barrier is necessary.[9,18]

Interfacial Reaction of Sn/Co-P/p-Bi_2Te_3 and SAC/Co-P/p-Bi_2Te_3

An electroless Co-P diffusion barrier was applied between the solder and the substrate. Figures 4 and 5 show SEM images with the addition of Co-P layer. It was observed that the Co-P diffusion barrier could successfully inhibit the formation of SnTe, Sn_3Sb_2, and Bi precipitates for all the samples that underwent multiple reflow (1, 3, and 5 times) or aging tests (150°C for 1 days, 5 days, 10 days, and 15 days). FE-EPMA showed that Co-Sn and Cu-Sn IMCs formed at the interface. In the Sn/Co-P/p-BST system, $CoSn_3$ (Sn-24.40 at.% Co-0.76 at.% Te-0.09 at.% P-0.04 at.% Bi) and Co-Sn-P (Sn-37.59 at.% Co-11.65 at.% P-0.66 at.% Te-0.03 at.% Bi) layers formed at the interface of the solder and Co-P layer. Sn initially reacted with the Co to form $CoSn_3$. As Co was consumed from the Co-P layer near the interface, the P content thus increased. The high-P Co-P layer further reacted with Sn and formed a Co-Sn-P layer between $CoSn_3$ and the Co-P layer. It is worth noting that no Co-Te IMC was formed at the interface. The IMCs formed in the SAC/Co-P/p-BST system were slightly different. The Co-Sn compound was identified as $(Co,Cu)Sn_3$ (Sn-23.1 at.% Co-3.7 at.% Cu), and this indicated that Co in the $CoSn_3$ phase was partially substituted by Cu. Moreover, as the aging time was prolonged, $(Cu,Co)_6Sn_5$ (Sn-3.4 at.% Co-46.9 at.% Cu-3.99 at.% Te) was found in the SAC/Co-P/p-BST system. Since $(Cu,Co)_6Sn_5$ was not observed in the multiple reflow samples, this might suggest that the formation of Cu_6Sn_5 was related to the heat treatment after soldering, which gave Cu enough time to react with Sn. A Co-P layer remaining at the interface after multiple reflow and aging tests suggested that the Co-P diffusion barrier could

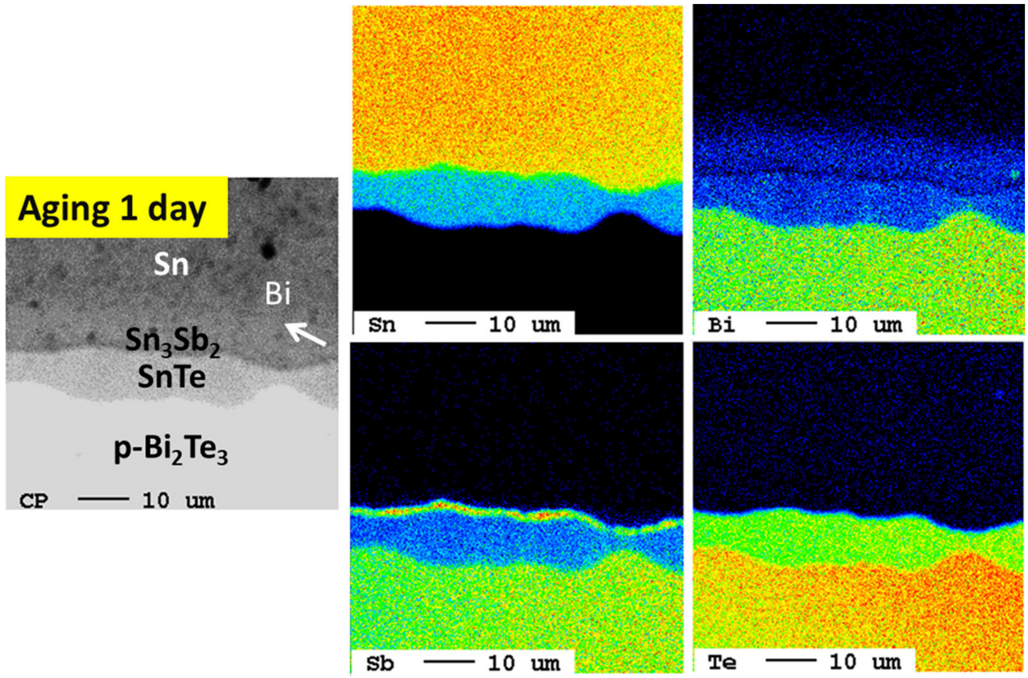

Fig. 3. Color mapping of $Sn/p\text{-}Bi_2Te_3$ aged at 150°C for 1 day.

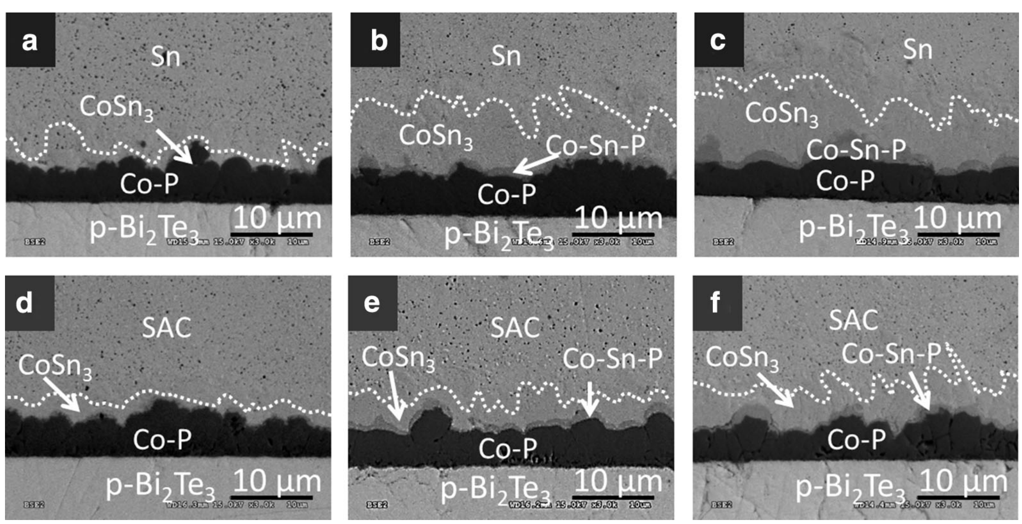

Fig. 4. SEM images of $Sn/Co\text{-}P/p\text{-}Bi_2Te_3$ (a-c) and $SAC/Co\text{-}P/p\text{-}Bi_2Te_3$ (d-f) after 1, 3, and 5 times reflow at 260°C.

be an efficient way to inhibit the severe reaction between Sn-based solder and p-Bi_2Te_3 substrates.

Shear test of p-Bi_2Te_3 with/without electroless Co-P layer

Mechanical shear testing is a reliability test for solder joints that can determine the influence of the Co-P layer on mechanical strength. Since thermoelectric devices are required to function with a heat source, samples were aged at 150°C for 15 days after soldering. Figure 6 shows the shear test results for p-Bi_2Te_3 with/without an electroless Co-P layer. It was observed that the shear strength of p-Bi_2Te_3 with the Co-P diffusion barrier was higher than that without it. Therefore, the Co-P layer indeed improved the mechanical strength of the joints after long-time aging.

CONCLUSION

The interfacial reactions of Sn/p-Bi_2Te_3 and SAC/p-Bi_2Te_3 with and without a Co-P diffusion barrier were investigated. The phases formed in both systems without Co-P were Bi precipitates and layer-type IMCs, Sn_3Sb_2, and SnTe. The formation of layer-type Sn_3Sb_2 might be due to the initially thin SnTe layer in the as-reflowed samples. The Co-

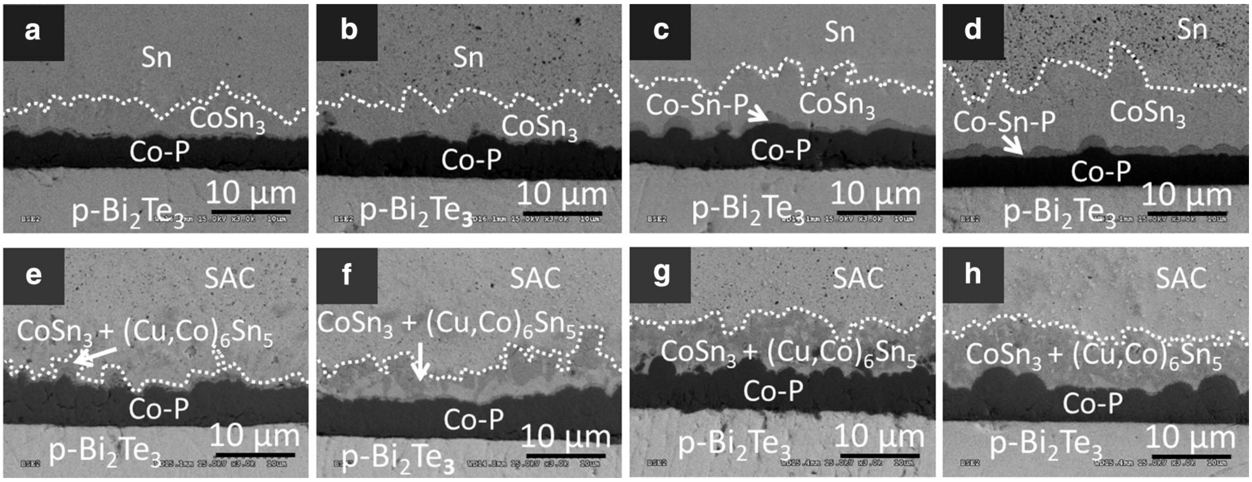

Fig. 5. SEM images of Sn/Co-P/p-Bi_2Te_3 (a-d) and SAC/Co-P/p-Bi_2Te_3 (e-h) aged at 150°C for 1 day, 5 days, 10 days, and 15 days.

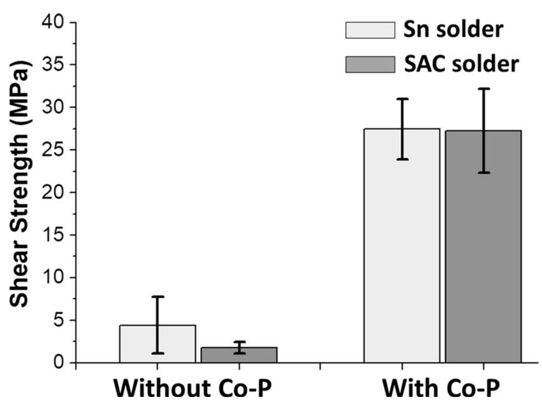

Fig. 6. Shear test of Sn/p-Bi_2Te_3, SAC/p-Bi_2Te_3, Sn/Co-P/p-Bi_2Te_3, and SAC/Co-P/p-Bi_2Te_3 aged at 150°C for 15 days.

P diffusion barrier successfully inhibited the formation of the above-mentioned brittle phases. The results of multiple reflow and aging tests showed that the Co-P layer could survive under these harsh test conditions. With the addition of Co-P diffusion barrier, Co-Sn and Cu-Sn compounds formed IMCs formed at the interface. Shear test results confirmed that Co-P coated p-Bi_2Te_3 exhibited better shear strength than that without the coating. These results indicated that the Co-P diffusion barrier could effectively prevent degradation of the reliability of a Bi_2Te_3 thermoelectric module.

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