Robust p-type Behavior of Epitaxial $Mg_2Sn_{1-x}Ge_x$ Thermoelectric Thin Films

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Mg_2Sn and its derivatives Mg_2(Si, Sn, Ge) are potential low-cost thermoelectric (TE) materials for operation at temperatures between 400 K and 800 K[1]. In the previous study, Mg_2Sn epitaxial thin films alloyed with germanium have been successfully prepared using molecular beam epitaxy (MBE)[2], and the applicability of which to a TE device has been demonstrated[3]. Robust p-type behavior has been observed for the $Mg_2Sn_{1-x}Ge_x$ films across measuring temperatures, implying that intrinsic point defects are responsible for the p-type behavior. However, defect levels for the films have not been evaluated yet. In this study, we aim to systematically study the p-type behavior of MBE-grown $Mg_2Sn_{1-x}Ge_x$ films by elucidating intrinsic defects to possibly control them for achieving higher thermoelectric performance.

$Mg_2Sn_{1-x}Ge_x$ films were grown using an MBE system (Eiko, EV-500) under vacuum conditions of 10^{-6} – 10^{-7} Pa on sapphire (0001) substrates (Shinkosha)[4]. The growth temperature was maintained at 370℃. Elemental magnesium (>99.95%), tin (>99.999%) and germanium (>99.999%) metals were evaporated using conventional Knudsen cells at 380℃ for Mg, 1120-1180℃ for Sn and 1050-1150℃ for Ge. Crystalline quality was evaluated by X-ray diffraction measurements (Rigaku MiniFlex600). Thermoelectric transport properties were measured using ZEM3 under He gas environment. The nanostructure of the films was observed using a transmission electron microscope (TEM; JEM-ARM200F, JEOL) at 200kV acceleration voltage with magnification accuracy of ±3%. Vacancy-type defects in the films were probed using positron annihilation spectroscopy. Electronic band structure calculations were performed using density functional therory as implemented in Quantum ESPRESSO code.

Seebeck coefficient of pristine Mg_2Sn film exhibits weak p-type characteristics below 375K and strong p-type behaviors for $Mg_2Sn_{1-x}Ge_x$ films across the measured temperature range which is consistent with the previous study[2]. Electronic band structure calculations reveal the energy level shift of the valence band above the Fermi level indicating the p-type behavior occurs for structures with Mg vacancy (V_{Mg}), whereas alloying with Ge alone does not cause a similar energy level shift of the valence band. This is suggesting that V_{Mg} is responsible for p-type behavior of the films. The presence of edge dislocations and intrinsic point defects in $Mg_2Sn_{1-x}Ge_x$ films was confirmed in the TEM images as detected by parallel Moiré patterns. In addition, vacancy-type defects were recorded from all the measured films with the vacancy concentration possessing an upper limit approximately at ~5% Ge. This may be necessary to keep a stable crystal structure. The knowledge of the vacancy concentration in the grown films would make a great influence on the further improvement of the TE performance by the point defect engineering.

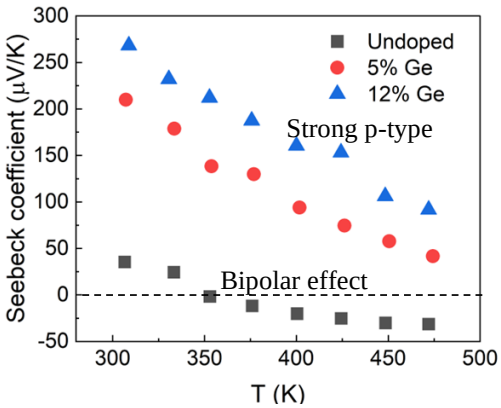

Figure 1 Seebeck curve of Mg_2Sn and $Mg_2Sn_{1-x}Ge_x$ films.

References

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