First-principles study of defect formation in photovoltaic semiconductor Cu₂GeS₃

H. Nishihara, T. Maeda, A. Shigemi and T. Wada

Department of Materials Chemistry, Ryukoku University Seta, Otsu 520-2194, Japan Phone: +81-77-543-7686, E-mail: nishihara@rins.ryukoku.ac.jp

Abstract

Formation energies of Cu, Ge and S vacancies in monoclinic Cu₂GeS₃ were calculated with first-principles pseudo-potential calculations using plane-wave basis functions. The calculations were performed in typical points in a schematic ternary phase diagram of a Cu-Ge-S system. The results are qualitatively similar to the case in Cu₂SnS₃, suggesting Cu₂GeS₃ is also a preferable lightabsorbing material for thin-film solar cells.

1. Introduction

A ternary copper chalcogenide Cu₂GeS₃ (CGS) has attracted considerable interest recently as a light absorbing material for thin-film solar cells as well as Cu₂SnS₃ (CTS) and Cu₂ZnSnS₄ (CZTS), since they are synthesized from earth-abundant materials [1]. CGS was first synthesized by Hahn et al [2]. The crystal structure of CGS has been reported to be monoclinic [3, 4]. The monoclinic structure with the space group Cc shown in Fig.1 is most probable as the ground state structure, which contains two inequivalent Cu sites (Cu₁ and Cu₂), one Ge site and three inequivalent S sites $(S_1, S_2 \text{ and } S_3)$, confirmed with first-principles calculations [5]. The efficiency of fabricated CGS solar cells is 1.70% [1] and they are smaller than those observed for CZTSSe (12.6%) [6] or Cu(InGa)Se₂ (21.7%) [7]. However, the solid solution thin-film solar cell of Cu₂SnS₃ and Cu₂GeS₃, Cu₂Sn_{0.83}Ge_{0.17}S₃, showed an efficiency of 6.0% [8], which is higher than Cu₂SnS₃ solar cells [9].

In this study, we report here theoretically calculated formation energies of neutral vacancies of Cu, Ge and S atoms in CGS by first-principles pseudopotential calculations and compare with those in CTS, CZTS and CuInSe₂ to see if there is a pronounced difference that may affect the efficiency of the solar cell.

2. Computational procedures

First-principles calculations were performed based on a density functional theory with the generalized gradient approximation (GGA) and the parametrization procedure by Perdew, Burke and Ernzerhof (PBE) using a plane-wave pseudopotential method. The code used is the Cambridge Serial Total Energy Package (CASTEP) ver. 7.02. Ultrasoft pseudopotentials were applied with a plane-wave cutoff energy of 500 eV. A specific 10*10*10 k-point mesh was generated for a conventional CGS cell by the Monkhorst-Pack scheme for numerical integrations over the Brillouin zone.

Self-consistent total energies were obtained by the densitymixing scheme in connection with the conjugate gradient technique. Atomic positions were optimized by the quasi-Newton method with the Broyden-Fletcher-Goldfarb-Shanno scheme. The formation energy of point defect was calculated from the difference of total energy between imperfect crystal and perfect crystal. Calculations for the imperfect crystal were performed using a supercell with 96 atoms. The lattice constants were fixed at values optimized for the perfect crystal. Atomic arrangements around a vacancy were optimized allowing relaxation of the first and second nearest neighbor atoms.



Fig. 1 Crystal structure of monoclinic Cu₂GeS₃.

3. Results and discussion

The formation energy of a neutral vacancy in a compound depends on the atomic chemical potential μ in the system. The formation energy of Cu vacancy in CGS is expressed as

 $E_F(V_{Cu}) = E_t(Cu_{31}Ge_{16}S_{48}) - E_t(Cu_{32}Ge_{16}S_{48}) + \mu_{Cu}$, where E_t is total energy of the supercell with or without a defect, and μ_{Cu} is the chemical potential of Cu. The chemical potential changes depending on the chemical environment of the system. As was reported in the literatures [10, 11], calculations of the formation energy of a Cu vacancy have been done for five points around the phase of CGS in a schematic ternary phase diagram of the Cu-Ge-S system shown in Fig.2. The five points shown in Fig.2 correspond to the vertices of the three-phase regions. For example, at point 1, CGS is in equilibrium with Cu₂₉S₁₆ and Cu metal. At point 3, CGS is in equilibrium with GeS₂ and S. Points 1 and 5 correspond to Cu-rich conditions and the point 3 corresponds to Cu-poor condition. Chemical potentials for the bulk samples were obtained as total energies per formula by separate calculations. Calculated vacancy formation energies for inequivalent sites of Cu₁, Cu₂, Ge, S₁, S₂ and S₃ are plotted in Fig.3 for the five points in Fig. 2. The formation energy of Cu1 vacancy, which is nearly the same as that of Cu_2 vacancy, takes the minimum value of 0.08 eV at point 3, which is in Cu-poor condition. The formation energy of Ge vacancy takes the minimum of 0.62 eV at point 2 which is in Ge-poor condition. Similarly, the formation energies of S₁, S_2 and S_3 vacancies take the minimums at point 5 which is in S-poor condition. The minimum formation energy of Cu vacancy is smaller than that of S or Ge, showing easy creation of Cu vacancies in CGS compared with S or Ge vacancies. These features are similar to the case of Cu₂SnS₃ which has similar crystal structure as Cu2GeS3 and Ge atom is replaced with Sn atom. The intrinsic p-type conductivity is attributable to the Cu vacancy in these compounds. In this respect, Cu₂GeS₃ has the appropriate character of a light-absorbing material for thin-film solar cells as are the cases with CTS, CZTS and CuInSe₂.

Displacements of near-neighbor atoms around a vacancy of Cu, Ge or S are also studied. Relative changes of the distances between a Cu1 vacancy and the four nearestneighbor S atoms of S₁, and another S₁, S₂ and S₃ from the original arrangement without the vacancy were calculated to be -3.61%, -3.04%, -2.91% and -0.41%, respectively, in Cu_2GeS_3 , which are to be compared with -0.81%, -0.33%, -0.88% and +0.17%, respectively, in Cu₂SnS₃. The magnitudes of the displacements are found to be larger in the case of Cu₂GeS₃ than in Cu₂SnS₃. The positive change in Cu₂SnS₃ corresponds to the case of S3, which is bonded by two Sn and two Cu atoms. The behavior has been interpreted to be due to the stronger bonding of Sn-S bonds than those of Cu-S. The smaller displacement in magnitude of -0.41% for S₃ in Cu₂GeS₃, although it has negative sign, could be interpreted to be due to the stronger bonding of Ge-S bonds than those of Cu-S. Calculated relative changes of the bond lengths between the S atoms with Cu1 vacancy and their nearest-neighbor Ge atoms range from -2.03% to -2.31% which are also larger in magnitude compared with those of S-Cu bonds ranging from -0.47% to -0.93% in accordance with the case of Cu₂SnS₃.

In summary, formation energies of Cu, Ge and S vacancies in monoclinic Cu₂GeS₃ were calculated in typical points in a schematic ternary phase diagram. The results are qualitatively similar to the case in Cu₂SnS₃ which has a similar behavior as CZTS and CuInSe₂. Cu₂GeS₃ is concluded to be also a preferable light-absorbing material for thin-film solar cells.

Acknowledgements

This work was supported in part by a grant based on the Core Research for Evolutional Science and Technology (CREST) from the Japan Science and Technology Agency (JST) under the Ministry of Education, Culture, Sports, Science and Technology of Japan.



Fig. 2 Schematic ternary phase diagram of Cu-Ge-S system.



Fig. 3 Calculated vacancy formation energies of inequivalent Cu₁, Cu₂, Ge, S₁, S₂ and S₃ sites in Cu₂GeS₃ plotted at five points in Fig.2.

References

- [1] H. Araki et al., J. J. Appl. Phys. 53 (2014) 05FW10 and references therein.
- [2] H. Hahn et al., Naturwissenschaften 53 (1966) 18.
- [3] M. Khanafer et al., Bull. Soc. Chim. Fr. 3 (1973) 859.
- [4] L.M.de Chalbaud et al., Mater. Res. Bull 32 (1997) 1371.
- [5] A. Shigemi et al., Phys. Status Solidi B 252 (2015) 1230.
- [6] W. Wang et al., Adv. Energy Mater. 4 (2014)1301465.
- [7] P. Jackson, et al., Phys. Status Solidi RRL 9 (2015) 28.
- [8] M. Umehara et al., Appl. Phys. Express 6 (2013) 045501.
- [9] M. Nakashima et al., Appl. Phys. Express 8 (2015) 042303.
- [10] H. Nishihara et al., J. J. Appl. Phys. 55 (2016) 04ES08.
- [11] T. Maeda et al., Thin Solid Films 519 (2011) 7513 and references therein.