Project No. 02402

Report form of Joint Research Project at ZAIKEN (FY2024)

Title of Project	Investigation of Engineered Cation Disorder as an Alternative to Alloying in New Materials Development		
Priority Area	III-A(Energy saving & Processes), III-B(Energy saving & Structure), III-C(Energy saving & Properties)		
Continuation of the project in FY2023			
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Aim of the research project

Traditionally, the band gap energy of semiconductors is tuned to the value needed for specific device applications through alloying. In the case of compound semiconductors, this can be achieved by mixing cations, anions, or both. There is an alternative approach, however, that avoids the complexity associated with introducing new constituents into an existing material system and with the associated need for carefully balancing their incorporation. Specifically, it has been demonstrated experimentally that controlled disorder can be used to engineer key semiconductor properties such as band gap energy and charge carrier mobility. The primary goal of the project is to investigate in detail the relationship between process parameters used during synthesis, and ex-situ ion bombardment post-synthesis, for example nitrogen and tellurium-based semiconductors, including mixed cation materials such as $ZnSnN_2$ (synthesized by Western Michigan University) and $AgGaTe_2$ (synthesized by Waseda University). This aligns closely with Energy Saving and Processes, providing potential pathways to utilizing a broader range of materials for energy conversion applications.

To provide reproducible values for material parameters of interest, it is critical to be able to measure disorder in a quantitatively meaningful way. We achieve this through a modification of the traditional Bragg-Williams approach of using x-ray diffraction, specifically a novel image-based methodology we have developed. Measurement of the band gap energy is accomplished through several means, with photoluminescence spectroscopy being one approach, but optical absorption being more general and hence preferred. If successful, a direct link to the measured Bragg-Williams order parameter and any material parameter is obtained, in parallel with a correlation between the order parameter and either in-situ or ex-situ process parameters which control disorder through energetic considerations.

Contents and results of the research

We have successfully tested a series of $AgGaTe_2$ films synthesized by the research group of Prof. Kobayashi. Films were characterized initially by scanning electron microscopy and photoluminescence spectroscopy. One film which has a visually opaque appearance and did not emit detectable light was also evaluated over the 180 - 1800 nm wavelength range using optical absorption, but the signal was ambiguous and further testing is necessary.

Initial results, however, are very promising. The Bragg-Williams order parameter ranges from zero (fully disordered, or in this case, random occupancy of the cation lattice site) to unity (perfectly ordered – no cation-related antisite defects). We anticipate a linear relationship between a material property dominated by pair-wise interactions (such as the band gap energy) and the squared value of the Bragg-Williams order parameter, S. In the case of the samples measured, we see a clear linear relationship, which takes the form $E_g(S) = 0.61S^2 + 1.28$ eV, as shown in Figure 1.

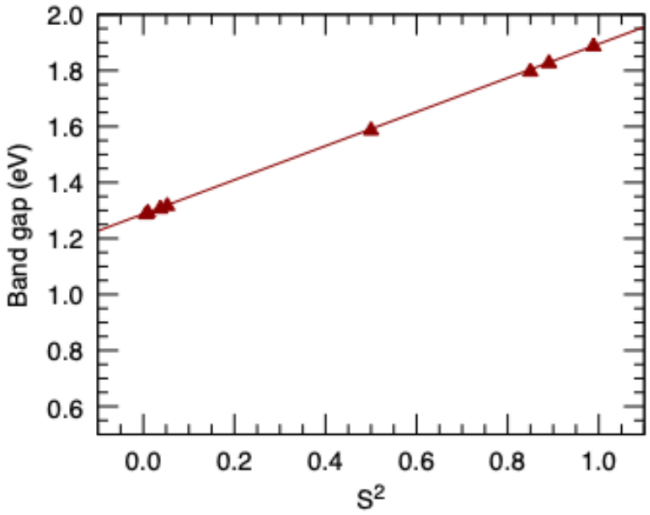

Figure 1 Optically measured band gap energy of a series of $AgGaTe_2$ films as a function of the Bragg-Williams order parameter S. Some points have been extracted from published values in the literature.

At a stoichiometric composition (equal amounts of Ag and Ga), increasing cation disorder is seen to result in a smaller band gap energy. The optimal value for terrestrial solar cells (under AM1.5g solar illumination conditions) is approximately 1.5 eV, corresponding to just below $S^2 = 05$. The impact of disorder on the band gap energy can be understood through the formation of unbalanced (either Ga- or Te-rich) tetrahedrally coordinated structures that comprise the lattice and which occur in greater numbers with increasing disorder.

Further optical measurements are currently underway, and a new series of samples is planned for the near future to better explore the full range of accessible band gap energy. This may include ex-situ ion bombardment to explore beyond the intrinsic energetic limitations of the closed-space sublimation technique used to synthesize samples at Waseda University. We will also be exploring other parameters such as charge carrier mobility.

Outputs of the project (publications, presentations, patents)

Presentation at Waseda University Kagami Memorial Institute for Materials Science and Engineering Collaborative Research Center for Environmentally Friendly Materials and Basic Technology
FY2024 Joint Research Results Reporting Session (R. Makin).

Paper in preparation.