Project No. 02502

Report form of Joint Research Project at ZAIKEN (FY2025)

Title of Project	Engineering Cation Disorder in Novel Compound Semiconductors		
Priority Area	**III: Energy Saving & Processes/ & Structures/ &Properties**		
~~**New proposal**~~ ~~**or**~~ **Continuation of**			
Name of Main Applicant	**Steven M. Durbin**		
Institution	**University of Hawaii at Manoa**	**title**	**Associate Dean**
Name of partner applicants (if any)	**Dr. Robert Makin, Western Michigan University, USA** **Prof. Roger Reeves, University of Canterbury, New Zealand**		
Name of the host faculty at Waseda	**Prof. Masakazu Kobayashi**		

Aim of the research project

The aim of the research project is to determine the extent which controlled introduction of cation disorder in the candidate photovoltaic material $AgGaTe_2$ can be exploited to engineer specific properties relevant to electronic devices, including the band gap energy.

The project has its basis in the pioneering work of Bragg and Williams from the 1930s, who employed x-ray diffraction to quantitatively measure the amount of disorder present in metal alloys [1]. Subsequently, Loveluck and Sokolov [2] demonstrated a Raman spectroscopy-based alternative to determining what is now referred to as the Bragg-Williams order parameter (S), and two of us (Durbin and Makin) developed a method based on analysis of electron microscopy images [3]. The same framework can be made to apply to crystalline semiconductors, and an Ising model approach coupled with cluster expansion theory allows for a direct relationship to be established between S^2 and specific properties, such as the band gap energy.

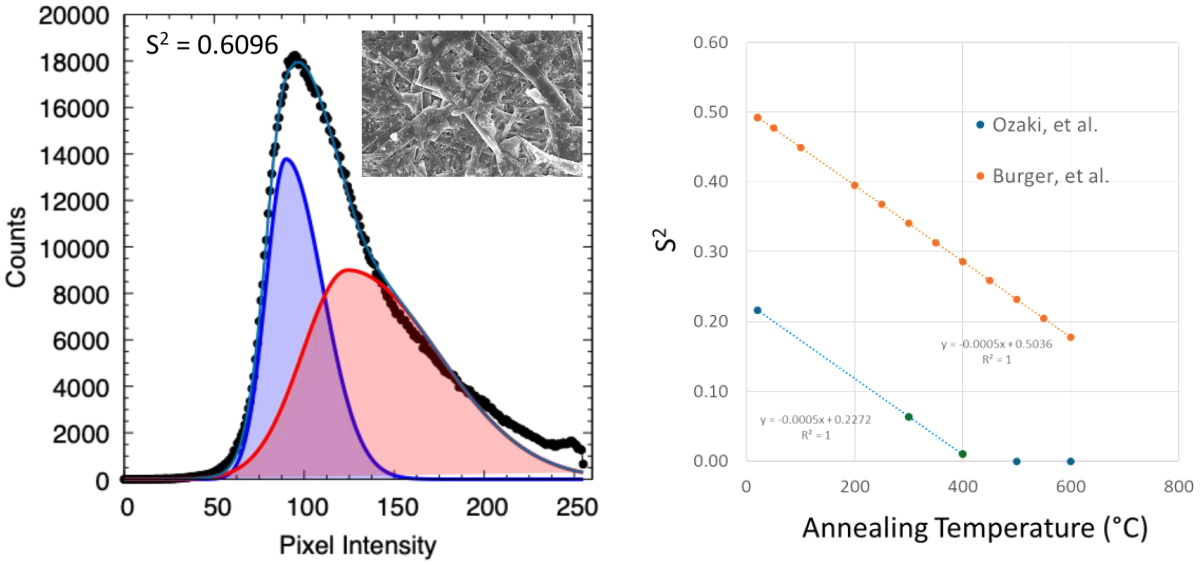
Typically, the value of S^2 is determined during synthesis, through adjustment of specific process parameters. In the case of $AgGaTe_2$ synthesized using the two-step radio-frequency magnetron sputtering process employed for this study, suitable energetics should be available, although we are also interested in the potential adjustment available through ex-situ ion bombardment.

[1] W.L. Bragg and E.J. Williams, Proc. Royal Soc. London. Series A. 145 (1934) 699-730.
[2] J.M. Loveluck and J.. Sokoloff, J. Phys. Chem. Solids 34 (1973) 869-884.
[3] R.A. Makin, et al., Phys. Rev. Lett. 122 (2019) 256403.

Contents and results of the research

We have measured the Bragg-Williams parameter for the first series of $AgGaTe_2$ samples synthesized at Waseda University employing our methodology based on analysis of scanning electron microscopy images (Fig. 1a). However, concerns regarding the incomplete substrate layer coverage for some samples is an indication that an additional analysis step is likely needed, where a heat map is generated to ascertain the range of S^2 values across the sample. We also plan to measure the stoichiometry of the samples, as preliminary comparison with samples reported in the literature (Fig. 1b) – which show good linear behavior of S^2 with temperature, consistent with a viable measure of a continuous order-disorder transition – suggest a sufficiently different composition to impact the band gap energy.

Detailed analysis indicates that it is straightforward to achieve the ideal single junction band gap energy of 1.3 – 1.5 eV in this material by tuning cation disorder to a moderate value (approximately 0.02 to 0.35 for nominally stoichiometry material, with the same value achievable with either Ag or Ga excess at different values of S^2). We would like to extend the study to include a new series of $AgGaTe_2$ where process parameters are adjusted, with the goal of employing transfer learning within an artificial intelligence model to assist with mapping the achievable values of S^2 (and through that, achievable values of band gap energy).



(a) (b)

Figure 1 (a) Example histogram analysis of a scanning electron microscopy (SEM) image of a magnetron-sputtering deposited $AgGaTe_2$ sample, with a measured value of $S^2 = 0.6096$. (b) Plot of S^2 as function of sample annealing temperature from two $AgGaTe_2$ studies in the literature (refs. [4,5]).

[4] S. Ozaki and T. Ogura, Jpn. J. Appl. Phys. 53 (2014) 44-49.
[5] A. Burger, et al., J. Crystal Growth 225 (2001) 505-511.

Outputs of the project (publications, presentations, patents)

A paper is currently in development, pending ion beam analysis (Rutherford Backscattering Spectrometry) followed by ion beam bombardment, which has been difficult to schedule (experiments anticipated by May 2026). The results of the study have been presented annually at the ZAIKEN program reporting sessions (online).