Project No. 02311 / Grant No. JPMXP0723833151

Report form of Joint Research Project at ZAIKEN (FY2023)

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)		
New proposal			
Name of Main Applicant	Steven M. Durbin		
Institution	University of Hawaii at Manoa (originally granted with PI at Western Michigan University)	**title**	Associate Dean

Aim of the research project

The traditional route to tuning specific application-specific properties in new candidate materials is alloying, and in the context of compounds, either mixing cations, anions, or both. While a time-tested and industry-adopted approach, including within the semiconductor arena for electronic devices, the method has significant limitations, especially as not all alloy compositions are easily realized. One alternative is to exploit the direct numerical relationship between some property values and quantitative metrics of disorder such as the Bragg-Williams order parameter ("S"). In the context of semiconductors, two of the project investigators, R. Makin and S. Durbin, have recently demonstrated that band gap energy exhibits a precise linear relationship with cation disorder when measured by techniques such as x-ray diffraction, reflection high-energy electron diffraction, and Raman spectroscopy. They have subsequently demonstrated that electron microscopy is an equally viable, and more accessible, route for measuring S. Identifying how crystal growth process parameters determine S for a specific material and synthesis technique allows disorder tuning and achieving the desired property value (e.g., an ideal band gap energy of 1.4 eV for a terrestrial solar cell).

The goals of the project are to investigate in detail the relationship between process parameters used during synthesis of semiconductors such as binary nitrides as well as the prototype mixed cation compounds including $ZnSnN_2$ and $AgGaTe_2$, measured values of the order parameter characterizing each sample, and the corresponding sample energy band gap as measured using optical transmission. $AgGaTe_2$ samples were to be synthesized using closed-space sublimation, characterized by optical transmission at the University of Canterbury to determine the experimental value of the band gap energy, and characterized using analysis of electron microscopy images at Waseda University by the Western Michigan University group.

Contents and results of the research

Samples of $AgGaTe_2$ were synthesized by the Kobayashi research group and sent to Western Michigan University, who further divided samples to enable parallel analysis. The full set was analyzed using photoluminescence by collaborator Prof. Roger Reeves (University of Canterbury, New Zealand) between 4 and 130 K, excited by a 450 nm laser diode with spectra acquired by an InGaN detector (**Fig. 1**). At cryogenic temperatures, some peak shift of the feature near 950 nm was in evident; further detector calibration is planned to improve signal-to-noise ratio and enable more reliable peak fitting. This will be compared to planned S^2 measurements using scanning electron microscopy and compositional measurements with ion beam analysis (Rutherford backscattering spectrometry). Both are scheduled for this spring (2024); equipment downtime delayed the originally scheduled measurements. The goal here is to relate the order parameter (measured as S^2) to the optically-measured band gap energy, in tandem with compositional information, to ascertain the full range of achievable band gap energy in this material.

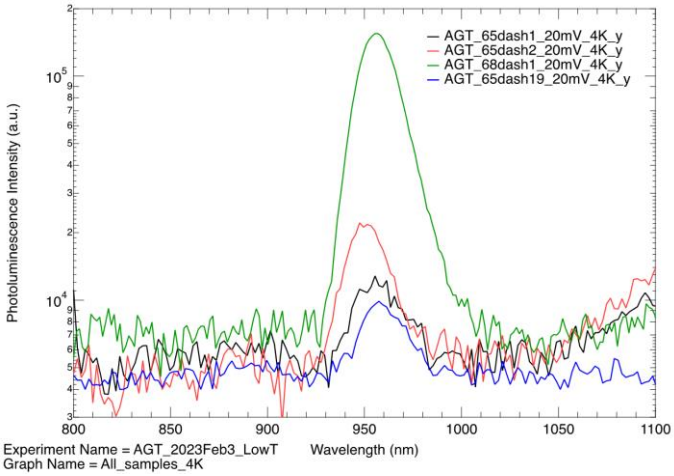

Figure 1. Cryogenic photoluminescence spectra of a series of $AgGaTe_2$ samples.

In January 2024, the PI (Durbin) travelled to Waseda University to meet with Prof. Masakazu Kobayashi and discuss the preliminary findings. He also participated in measuring two nitride electronic material samples using the 200 kV JEOL transmission electron microscope (TEM). High-resolution sample images were acquired after a detailed survey of each sample. Composition (stoichiometry) was measured for each sample using energy dispersive x-ray (EDX) analysis, and will be compared to upcoming ion beam analysis (which does not have the spatial resolution of the JEOL instrument but can confirm a sample average). Most importantly, several transmission electron diffraction patterns were captured from each sample. These images will be analyzed in a fashion similar to what we have done previously in the case of reflection high-energy electron diffraction (see **Fig. 2** for first analysis). The goal is two different measures, acquired nearly simultaneously on each sample, that can provide quantitative information regarding disorder in the sample layer – including any spatial variation that might exist. With these benchmark measurements, additional crystal growth experiments will be designed with the goal of explicitly altering key material properties including band gap energy. A paper is planned on the preliminary measurements conducted to date, once the electron microscopy image and diffraction pattern data can be processed. WE should note that this will represent our first quantitative disorder measurement using transmission electron diffraction, providing another technique to obtain this parameter. We have also recently improved our image-based disorder measurement, and are planning on applying it to the electron microscopy images already acquired. Objectives have been achieved to 75% at this stage, and should be at 100% by May 31, 2024 once all measurements are completed, analysis can be performed, and the results evaluated.

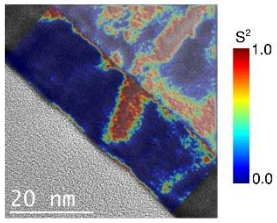

Figure 2. First pass S^2 order parameter analysis (color) overlaid on TEM image acquired at Waseda University in January 2024. Image shows substrate influence (top) on film (middle layer).

Outputs of the project (publications, presentations, patents)

1. A publication is in preparation (viewing MRS Advances journal).

2. R.A. Makin (collaborator) provided an online presentation at ZAIKEN on 1 March 2024.