ESRF

ESRF	**Experiment title: Diffraction study of defects and Diffusion in the Photovoltaic Material CuInSe2**	**Experiment number**: HS-966
ID 11	**Date of experiment**: from: 27.10.1999 to: 02.11.1999	**Date of report**: 28.08.2000
Shifts: 15	**Local contact(s)**: Ake Kvick	*Received at ESRF:*

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Report:

Introduction. CuInSe2 is studied and developed as the absorber material in photovoltaic cells. Besides that, CuInSe2 is of fundamental interest because it is a semionic semiconductor. Semionic semiconductors possess at least one type of the electrically active defects which can be mobile under conditions of extrinsic superconductivity. Thus, subjecting CuInSe2 crystals to a stong electical (E) field can type-convert the material and yield transistor formation. Radioactive tracer experiments confirmed this to be due to thermally assisted electromigration. Cu electromigration was invoked also to explain the outstanding stability of solar cells made with the material. However, the mechanism of electromigration is not at all clear. Using sort wavelength (0.24 Ang) synchrotron radiation to minimize absorption (μ=3.7mm^{-1}) ultra-high resolution x-ray structure determination coud be performed to elucidate electromigration mechanism.

We prepared all CuInSe2 single crystals by the traveling heater method (THM). This method gives crystals of very high quality and prevent twinning along the (112) plane. Three types of samples were prepared from one large crystal: -n-type as-grown; p-type converted samples (by annealing in Se).

General remarks. Careful analysis of our 5/98 (CH-316) sets of synchrotron diffraction data shows that we have poor statistics at low (due to overloads) and high (due to inherent weakness of data) resolution ranges.

We have tried to improve this in 11/99 (HS-966) sets of data, but failed to reach this goal. High resolution data can be relatively easily improved by scanning longer time. Lower resolution data can be easily improved by using shorter exposure time and/or absorbers of the direct beam. All this lead to the solution very well known to the crystallographers: data should be collected in two (or more) experiments and later should be merged together using adequate software. Unfortunately, commercial software, which is in use on ID 11 station have been developed for use with the commercial laboratory x-ray sources many orders of magnitude weaker than synchrotron and careful data merging is out of the scope this software. We were not able to merge data properly using this software. Very large dynamic range of the data in CuInSe2 crystals together with very high resolution of the data and natural necessity to support high resolution data statistics by longer exposures produce a problem which presently is the bottleneck of the project.

HS-966 session. During allocated 15 shifts we were able to collect 10 data sets: three data sets from n-type as-grown crystals, four data sets from crystals treated by E-filed (to different crystals E-filed was applied 1.5 years, 2 month and one week prior to the experiment), one p-type (Se annealed). Additional two data sets were collected form n-type as grown crystals (one already collected at λ=0.24 Ang.) using λ=0.44 Ang. to maximize anomalous signal of In. Unfortunately we were not able to get an anomalous signal probably to the fact that we were on the absorption edge during the experiment. During HS-966 session we were not able to solve the dynamic range problem of our data, nor we were able to produce wavelength dependent data.

Results. Results obtained using synchrotron x-ray diffraction data[1] provide clear experimental indication (in addition to radioactive tracer studies for the thermally-assisted elecctromigration mechanism that has been proposed for E-field induced transistor formation. They provide important experimental support for the model of ion migration-mediated self-

stabilization of CuInSe2-based solar cells. Further experiments, such as temperature dependent diffraction to help map diffusion paths and wave-length-specific diffraction, using the wavelength tunability of the synchrotron source to find Cu and In-specific effects in addition with the attempts to solve computational problems related to data merging are in progress.

References.

1. Synchrotron X-ray diffraction Evidence for Native Defects in the Photovoltaic Semiconductors CuInSe2. Kaplan L., Leitus G., Lyakhovitskaya V., **Frolow F.**, Hallak H., Kvick A., Cahen D. *Adv. Mater*. 12 (5), 2000, pp. (366-370).