

EUROPEAN ORGANIZATION FOR NUCLEAR RESEARCH
Proposal to the ISOLDE and Neutron Time-of-Flight Committee

Local structural studies on CIGS thin-film solar cells

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Abstract: Cu(In,Ga)Se₂ (CIGS) thin film solar cells are an extremely promising candidate, where the ZSW¹ is holding the world record of 21.7% conversion efficiency. The complex composed layer of CIGS and addition materials rise questions of diffusion processes of different ions and structural changes due to doping. Buffer layers of ZnS, CdS or In₂S₃ between p-type CIGS absorber and n-type ZnO:Al front contact enhance the performance significantly, but a detailed understanding of the diffusion processes is missing. It is the major goal of this project to use ISOLDE solid state physics such as perturbed angular correlation (PAC), ASPIC with its ultra high vacuum system to produce clean surface sample, radioactive PL at ISOLDE's solid state physics laboratories to study this phenomena by use of radioactive isotopes.

Requested shifts: 8 shifts, split into 2 runs over 2 years

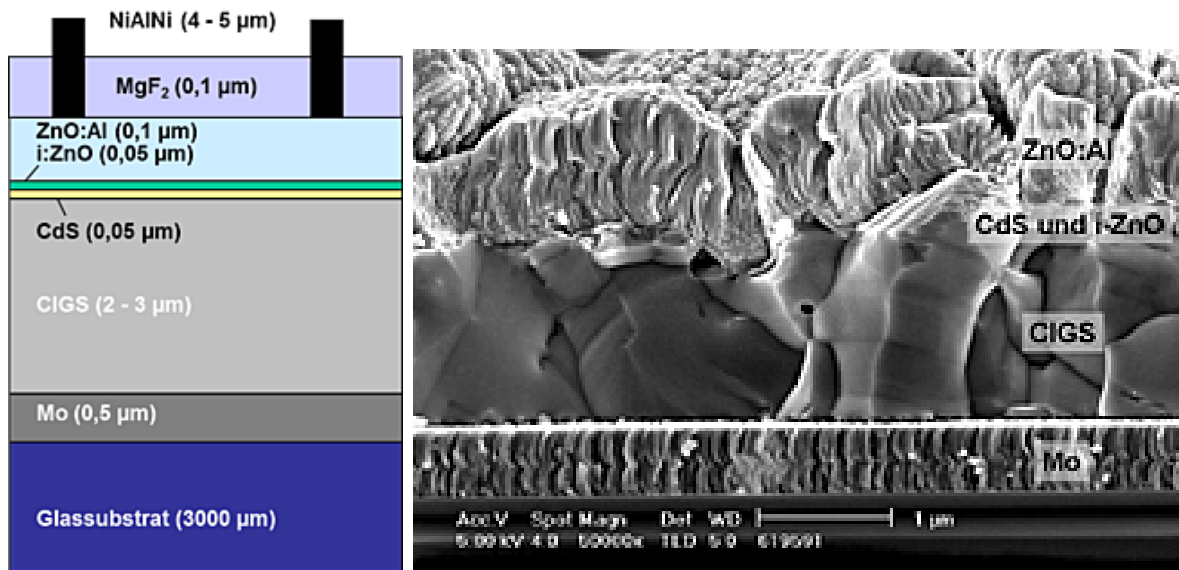


Figure 1: CIGS solar cell: left: structural model, right: SEM picture

1 Introduction

Thin film solar technology holds one of the key features of reduced material needs in manufacturing that economizes resources on large scale productions. In addition, the possibility to use flexible substrates is another big plus. Yet, thin film solar modules have in generally an efficiency that is significantly less than that can be achieved by single crystal silicon solar cells. CIGS thin film solar cells of the material system $\text{Cu}(\text{In,Ga,Al})(\text{Se,S})_2$ is an extremely promising candidate where the ZSW is holding the world record of 21.7% conversion efficiency [1]. This rises the thin film solar technology into serious concurrence to silicon solar cells, especially also regarding the lower production costs of CIGS solar cells. The complex layer structure is illustrated in Figure 1, where on a glass substrate a molybdenum layer holds the back electrical contact and the light absorbing CIGS is deposited above it. Two thin layers of cadmium sulfide and zinc oxide follow and are finalized with two layers of aluminum doped zinc oxide and magnesium fluoride.

Cd and Zn can diffuse into CIGS absorbers during the CdS or ZnS buffer growth from the solution at typical temperatures of 60 - 90°C. A stronger diffusion of these elements is expected at substrate temperatures of up to 200°C during the sputtering of the ZnO:Al window layers. Often CIGS cells with ZnS buffer layers can be improved by a post-annealing step of the whole cell stack at temperatures around 200°C for several minutes. Na diffuses during the CIGS deposition process at elevated temperatures around 500 - 600°C from the soda-lime glass substrate through the Mo back contact into the CIGS layer and accumulates at the grain boundaries.

This complex structure of layers of different materials rise questions of interactions and diffusion of ions from one to the other layer. Especially, why is there an increase of the performance using a ZnS, CdS or In_2S_3 buffer layer and a specific annealing procedure? It is the major goal of this proposal to provide a more fundamental understanding of the

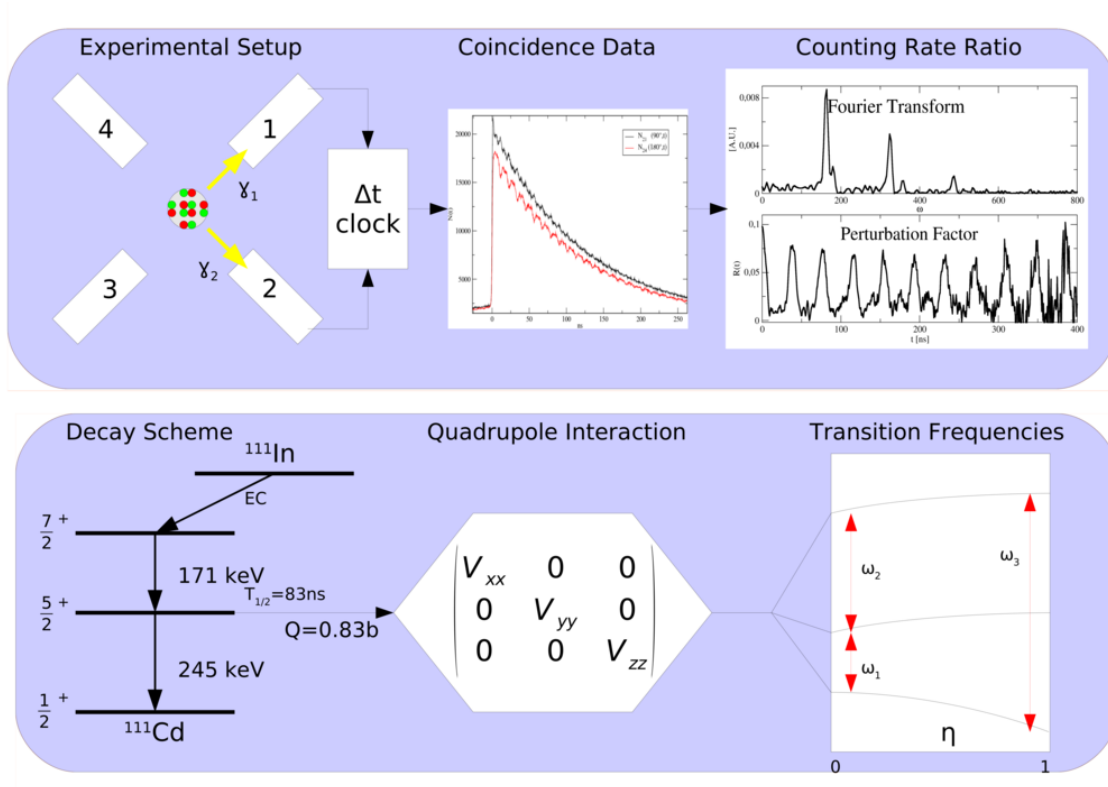


Figure 2: PAC Schema for example $^{111}\text{In}/^{111}\text{Cd}$.

performance enhancing procedure that would allow to choose directly optimal parameters or other materials.

ISOLDE's local probe techniques of the solid state physics equipment can contribute to these problems significantly due to the high sensitivity and very low concentrations in the range of ppb using radioactive probe methods.

In order to understand results using local probes, systematic studies that characterise the material are required, like:

1. basic frequencies of well crystallized CIGS versus high performing CIGS
2. the optimal annealing temperatures for the studies
3. the significant differences between clean surfaces prepared in ASPIC and atmospheric exposed samples?
4. the difference in PAC data with or without the ZnS, CdS or In_2S_3 buffering layers compared with the unbuffered CIGS
5. diffusion coefficients of radioactive probes ^{111m}Cd , ^{111}In and ^{24}Na and their diffusion type by use of tracer diffusion, to understand the location of probes when interpretic local probe data, such as PAC
6. the optical properties studied by PL, especially regarding impurities?

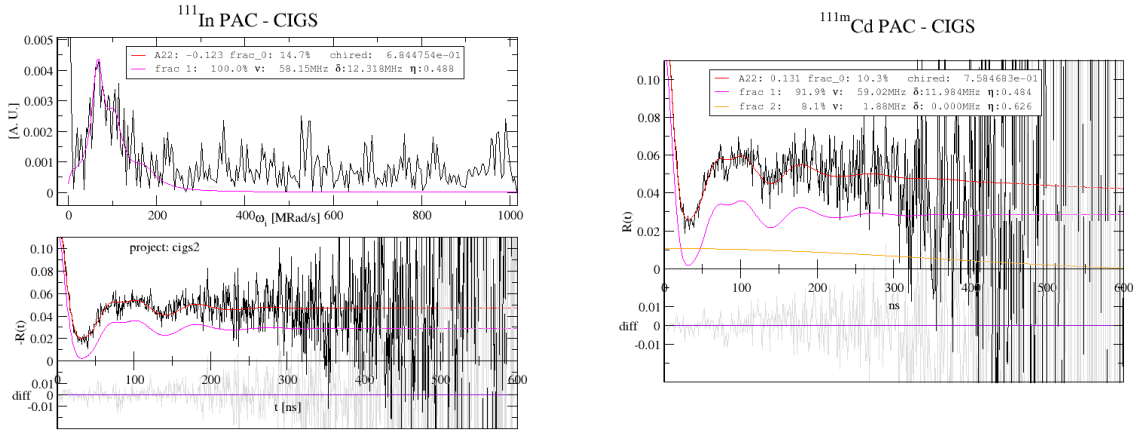


Figure 3: CIGS solar cell: left: CIGS with implanted ^{111}In , right: with implanted ^{111m}Cd . Annealed at about 500°C and measured at room temperature.

Diffusion properties have been studied by a series of other authors already mainly by secondary ion mass spectroscopy (SIMS) [3, 4, 5, 6], which will provide a sufficient base for optimizing experimental conditions. Self-diffusion experiments using tracer diffusion will complete important material characteristics.

Local structure techniques like perturbed angular correlation (PAC), optical properties using radioactive photo luminescence (PL) and tracer diffusion may contribute with different insights into material properties to deeper understanding, why and how certain mixtures of layer compositions show a gain in performance. PAC as a hyperfine technique is well known at ISOLDE and shortly as major method introduced in Figure 2.

First PAC studies on a high performing CIGS have been tried by using ^{111m}Cd and ^{111}In mother isotopes with on the first with implantation and the second as liquid and drying with addition diffusion, shown in Figures 3, and choosing temperatures for diffusion that were used in the production process. To our surprise, the results show in each case a wide frequency distribution, rather than a clear frequency as known from related chalcopyrites. From the first experiments we cannot differentiate whether the broad frequency distribution is from the bulk or a grain boundaries or otherwise from poly-selenide oxides or optionally different oxy-selenide anions due to the atmospheric exposure, which is also part of the production process as well as an aqueous treatment. Another consideration is the Ga/In ratio causing a highly distorted structure. Additional phases could also be introduced during the annealing procedure.

A series of related chalcopyrites, e.g. CdSnP_2 or CuInS_2 have been studied in the past by various groups [7, 8, 9, 10, 11, 12, 13, 21, 22, 23], which provide data for comparison. From here we could expect less damped data. A series of measurements with different preparations and temperature dependent will provide more clear information also with much better statistics than in the first data. Especially ASPIC may provide interesting differences in ultra high vacuum conditions.

In order to gain a deeper understanding of these interesting results, a series of systematic experiments, varying implantation depth, temperature treatments, surface cleaning methods, and compare these results with experiments in ultra high vacuum and clean

surfaces using ASPIC are required. They will be complementary completed with tracer diffusion using the diffusion chamber to study thin films and radioactive PL. We are in the hope, that ASPIC will be back online during the time slice of this proposal.

The most common means employed for generating luminescence in semiconductors is to use an optical pump (usually a laser) to produce electrons and holes in the semiconductor. When these carriers become bound at defects or impurities and recombine with holes or electrons respectively, photons are emitted of energies correlated to the energy level of the defect in the band gap. The spectrum of the recombination energies, the vibrational side bands, and temperature dependence of the intensities, etc. – contains a wealth of information on the defect or impurity. The term photoluminescence (PL) is used to denote such optically generated luminescence. PL is employed widely in all classes of semiconductor research and is recognized as one of the most important and powerful techniques available [15]. The principal advantage is, in addition to the usual advantages pertaining to spectroscopy, the potential for very high sensitivity. For semiconductors, the penetration depth of the laser radiation and the diffusion length of electrons and holes are generally of the order of 100 nm, often less. Depending on the recombination process, the detection limit can be as low as 10^{13} cm^{-3} in favorable cases, so that a total of 10^9 atoms can be sufficient to produce detectable PL signals. To get the full benefits from PL it is usually necessary to operate at liquid helium temperatures to freeze out all thermally excited charge carriers. At these temperatures even weakly bound electrons and holes remain bound at defects/impurities so that the optical transitions occur and vibrational (phononic) effects are minimized. One consequence of this high sensitivity is the capability of detecting trace contaminants in nominally intrinsic semiconductors. As has been described above, the role of Na is crucial to the high performance of CIGS solar cells. Previous investigations have shown that the Na presence of Na affects both the electrical and optical properties of CIGS cells [16, 17] but the precise nature of this influence is not fully understood.

The use of radiotracer PL to chemically identify optical features in semiconductors has long been demonstrated [18] and in more recent times has been used to reveal surprising behaviour in high purity Si and ZnO [20, 19]. In addition to systematic offline PL measurements, implantations with radioactive Na (^{24}Na) would offer the possibility to unravel some of the Na-related optical processes in clearer detail than is the case using more conventional methods. We propose to use one shift of ^{24}Na to investigate these Na-related processes using the on-site PL laboratory at ISOLDE.

2 Experiments

The main isotope of study will be ^{111m}Cd , which is an annual standard at ISOLDE for PAC and that fits best chemically to the system of studies. Complementary measurements from commercially available ^{111}In source will be a part of the experimental program. This will be especially useful to test and time optimize procedures such on ASPIC before starting with the short living probe ^{111m}Cd with about 48.5 minutes half-life. The chemical deposition in solution of an CdS or In_2S_3 layer is another example, where pretests in

accurate procedures with commercial ^{111}In , will be useful before trying on ^{111m}Cd . The proposed experiments are:

1. perform different annealing temperature measurements from 100 to 600°C in 100° steps for each 1 hour with ^{111m}Cd and ^{111}In
2. perform the same as above experiment using the industrial annealing temperature and the optimal annealing temperature from the above experiment but vary the annealing times in 5 to maximal 10 different steps.
3. use with ^{111m}Cd different implantation energies 50 kV and 30 kV (if 20 kV is possible as well) to study if surface related effects are influencing results such as poly-selenide oxides or different oxy-selenium ions
4. temperature dependent measurements of CIGS and its ternary compounds CuGaSe_2 and CuInSe_2 : 100, 200, 300, 400, 500, 600°C
5. using above experimentally optimized annealing temperatures and times, perform studies using ASPIC by applying ^{111}In and ^{111m}Cd on clean surfaces to test if humidity or poly-selenide oxides or different oxy-selenium ions play a major role.
6. study PL by identifying peaks with use of radio isotopes ^{111}In and ^{111m}Cd as well as ^{24}Na .

The strength of this program is the combination of testing procedures with a commercial ^{111}In source and apply the experiment then on a short living ^{111m}Cd source of 48.5 minutes, that will rise the success rate together will both well performing probes. Another strength is applying different methods available at ISOLDE's solid state laboratories to obtain complementary information, e.g., if diffusion is mainly of bulk or grain boundary nature to understand where the PAC probes are mainly expected and to study, how significant is the influence of poly-selenide oxides or oxy-selenium ions on surfaces. In addition of clear measurements in bulk, how broad distributed are electric field gradients in high performing CIGS and if there is a relation with the performance. PL measurements using radioactive isotopes will help to identify peaks in complex spectra for applications in standard PL.

Experiments will be mainly using the solid state equipment available at ISOLDE solid state physics laboratories and online devices like ASPIC and GLM chamber respectively. The experiments can be easily and partially integrated together with routinely solid state experiments as well as with short slices, e.g. during calibrations of other experiments, as implantation times are short for diffusion and PAC and measuring times significantly longer. Samples will be provided by the ZSW.

Summary of requested shifts: 8

beam	min. intensity (ions/s)	target	ion source	shifts
^{111m}Cd	$2 \cdot 10^8$	Sn	VADIS	7
^{24}Na	$2 \cdot 10^8$	UCx	Surface:Re,Ta,W	1

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Appendix

DESCRIPTION OF THE PROPOSED EXPERIMENT

The experimental setup comprises: Samples will be implanted in GLM chamber, transported to SSP laboratory building 508, annealed and measured in the PAC laboratory.

Part of the	Availability	Design and manufacturing
SSP-GLM chamber, SSP-GHM chamber, ASPIC	<input checked="" type="checkbox"/> Existing	<input checked="" type="checkbox"/> To be used without any modification
Implantation to GLM, (GHM)	<input checked="" type="checkbox"/> Existing	<input checked="" type="checkbox"/> To be used without any modification <input type="checkbox"/> To be modified
	<input type="checkbox"/> New	<input type="checkbox"/> Standard equipment supplied by a manufacturer <input type="checkbox"/> CERN/collaboration responsible for the design and/or manufacturing
ASPIC	<input checked="" type="checkbox"/> Existing	<input checked="" type="checkbox"/> To be used without any modification <input checked="" type="checkbox"/> when ASPIC is online again <input type="checkbox"/> To be modified
	<input type="checkbox"/> New	<input type="checkbox"/> Standard equipment supplied by a manufacturer <input type="checkbox"/> CERN/collaboration responsible for the design and/or manufacturing
SSP laboratory	<input checked="" type="checkbox"/> Existing	<input checked="" type="checkbox"/> To be used without any modification <input type="checkbox"/> To be modified
	<input type="checkbox"/> New	<input type="checkbox"/> Standard equipment supplied by a manufacturer <input type="checkbox"/> CERN/collaboration responsible for the design and/or manufacturing

HAZARDS GENERATED BY THE EXPERIMENT: SSP-GLM chamber, (SSP-GHM chamber), ASPIC installation: samples radioactive contaminated during and at the end of experiment.

Additional hazards:

Hazards	GLM	SSP Laboratory	ASPIC
Thermodynamic and fluidic			
Pressure	atmospheric pressure, chamber volume	atmospheric pressure, annealing in vacuum	UHV
Vacuum	yes	yes and no	yes
Temperature	RT	different annealing temperatures from 573K to max. 1173K, measuring RT	different annealing temperatures, measuring RT or lower
Heat transfer	no	radiation/conduction	radiation

Thermal properties of materials	melting point around 1273K	melting point around 1273K, protect from oxygen when heating	melting point 1273K
Cryogenic fluid	no	no	eventually liquid N ₂
Electrical and electromagnetic			
Electricity	no	PAC detectors 3kV but shielded	no
Static electricity			
Magnetic field	no	no	no
Batteries	<input type="checkbox"/>		
Capacitors	<input type="checkbox"/>		
Ionizing radiation			
Target material [material]			
Beam particle type (e, p, ions, etc)	ion		ion
Beam intensity	10 ⁸ to 10 ¹¹		10 ⁸ to 10 ¹¹
Beam energy	30,50keV		50keV
Cooling liquids	[liquid]		
Gases	[gas]		
Calibration sources:	<input type="checkbox"/>		
• Open source	<input checked="" type="checkbox"/>		
• Sealed source	<input type="checkbox"/> [ISO standard]		
• Isotope	^{111m} Cd, ²⁴ Na		^{111m} Cd
• Activity	70 MBq, 3.8 MBq		70 MBq
Use of activated material:			
• Description	<input type="checkbox"/>		
• Dose rate on contact and in 10 cm distance	[dose][mSV]		
• Isotope			
• Activity			
Non-ionizing radiation			
Laser			
UV light			
Microwaves (300MHz-30 GHz)			
Radiofrequency (1-300 MHz)			
Chemical			
Toxic	[chemical agent], [quantity]		
Harmful	[chem. agent], [quant.]		

CMR (carcinogens, mutagens and substances toxic to reproduction)	[chem. agent], [quant.]		
Corrosive	[chem. agent], [quant.]		
Irritant	[chem. agent], [quant.]		
Flammable	[chem. agent], [quant.]		
Oxidizing	[chem. agent], [quant.]		
Explosiveness	[chem. agent], [quant.]		
Asphyxiant	[chem. agent], [quant.]		
Dangerous for the environment	[chem. agent], [quant.]		
Mechanical			
Physical impact or mechanical energy (moving parts)	[location]		
Mechanical properties (Sharp, rough, slipperiness)	[location]		
Vibration	[location]		
Vehicles and Means of Transport	[location]		
Noise			
Frequency	[frequency],[Hz]		
Intensity			
Physical			
Confined spaces	[location]		
High workplaces	[location]		
Access to high workplaces	[location]		
Obstructions in passageways	[location]		
Manual handling	[location]		
Poor ergonomics	[location]		

Hazard identification:

Average electrical power requirements (excluding fixed ISOLDE-installation mentioned above): [make a rough estimate of the total power consumption of the additional equipment used in the experiment]