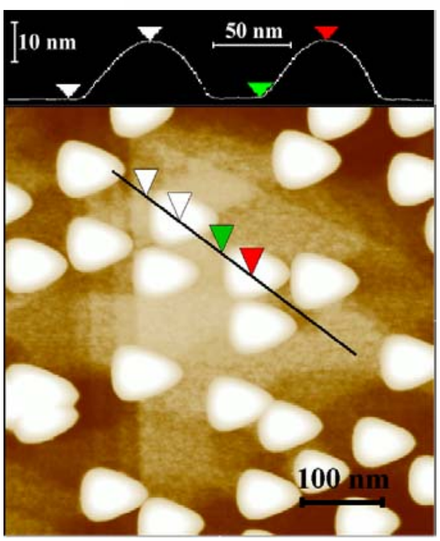
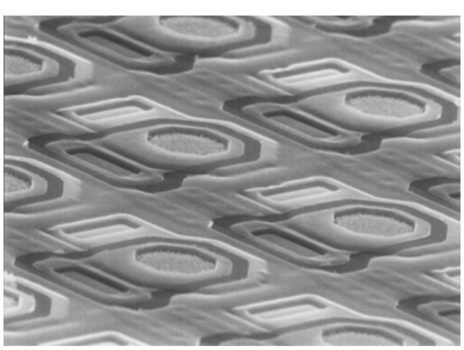
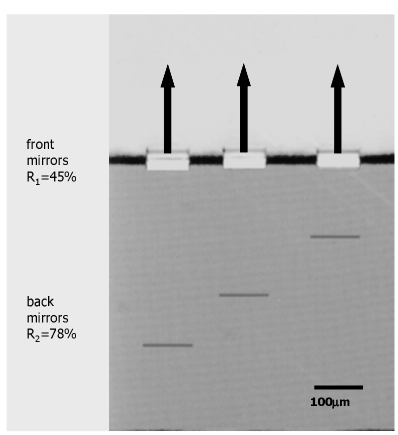
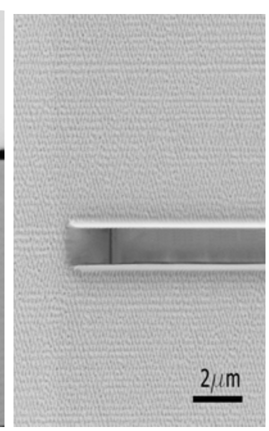
Thin Film Physics Group at ETH Zurich









Cover page:

Top: Flexible $Cu(In,Ga)Se_2$ solar cell on a polyimide sheet. Total thickness of the cells and substrate is 15 μm. Record efficiencies of 12.8% and 11.0% have been achieved for flexible $Cu(In,Ga)Se_2$ and CdTe solar cells, respectively.

Middle: Self assembled PbSe quantum dots of nearly equal sizes.

Bottom: Partial view of a monolithic staring photovoltaic PbTe-on-Si infrared focal plane array (IR-FPA) with 5.5 μm cut-off wavelength (left); etched mirrors for optically pumped lead-chalcogenide QW lasers on Si(111) (right).

CONTENT

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GENERAL

The thin film physics group is with the Laboratory for Solid State Physics ETHZ (Head: Prof. Dr. H.-R. Ott) since Oct. 2000.

Before, the group was with the Institute of Quantum Electronics ETHZ (head: Prof. Dr. H. Melchior, retired in Oct 2000), and before 1997, the group was part of the organisation AFIF (Arbeitsgemeinschaft für industrielle Forschung) located at ETHZ until 1997.

The group is financed exclusively by projects ("Drittmittel").

SPONSORS

ETH
European Space Agency
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Swiss National Science Foundation
Swiss Federal Office for Education and Science (BBW, for EU-projects)
Swiss Commission for Technology and Innovation (KTI)
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Institute of Semiconductor Physics, Mins, Belarus
Central Solar Energy Laboratory, Sofia, Bulgaria
EMPA Dübendorf
INSAMET, San Sebastian, Spain

Science and technology of compound semiconductors:

- Growth of molecular beam epitaxial (MBE) and polycrystalline layers of II-VI, IV-VI, I-III-VI_2, and III-V binary and multinary compounds. Applications for optoelectronic devices. Growth kinetics of heterostructures, superlattices and nano-structures (quantum dots). Phase formation and their identification.
- Structural properties of thin films, surfaces and interfaces. Crystallographic and microstructural defects. Lattice vibrational properties of semiconductors. Measurement and modelling of strain relaxation in thin films. Kinetics of dislocation-glide and -reactions in IV-VI-on-Si epitaxial layers. Recrystallization in semiconductors.
- Optical and electrical properties of thin films and heterostructures. In- and ex-situ doping in semiconductors, electronic defects and transport properties.
- Growth, properties and applications of transparent conducting oxides (ZnO, ITO, FTO).
- Growth and properties of permeation barrier layers ("flexible glass" on plastics).
- Thin film growth processes like molecular beam epitaxy, e-beam evaporation, d.c. and r.f. sputtering, chemical bath deposition, electro-deposition, etc.

Infrared sensors and emitters on silicon substrates:

- MBE growth of narrow gap IV-VI layers (lead chalcogenides) on Si-substrates.
- Fabrication of 1-d and 2-d IR sensor arrays; the Si-substrate may contain integrated read-out circuits.
- Development of microlithographic patterning techniques. Applications include thermal imaging and IR-spectrometry.
- Optically pumped edge emitting IV-VI lasers with 3-5 µm emission wavelength, with cleaved or etched cavity mirrors.
- Optically pumped microcavity wavelength converter from 870 nm to 3-5 µm

Compound semiconductor thin film solar cells:

- Solar cells based on Cu(In,Ga)Se_2 and CdTe (these materials yield stable and very high efficiency solar cells for economical production of solar electricity). Development of material technologies, fabrication processes, novel materials and processes for improved performance, and advanced tandem devices. Interface and transport properties of heterojunctions.
- Studies of basic material properties and heterostructures for large area and industrial production. Stability and reliability of devices. Terrestrial and space applications of lightweight and flexible thin film solar cells.

Some highlights:

- Development of 1- and 2-dimensional infrared sensor arrays for thermal imaging in epitaxial PbTe on Si-substrates which contain active circuits
- Development of optically pumped IV-VI lasers on Si-substrates with cleaved or etched cavity mirrors
- Development of optically pumped IV-VI microcavity wavelength converters on Si-substrates
- Flexible CdTe solar cells on polymers have been developed for the first time, and a record efficiency (11%) is achieved
- Long term stable and low resistance quasi-ohmic contacts on CdTe that yield 11% efficiency solar cells
- Lightweight and flexible $Cu(In,Ga)Se_2$ solar cells on polymer with a world record efficiency of 12.8%
- Electronic and structural comparison of $Cu(In,Ga)Se_2$ substrate and superstrate solar cells, 11% efficient superstrate solar cells have been obtained
- A low temperature deposition process for $Cu(In,Ga)Se_2$ solar cells; cells with 14% efficiency were achieved
- Highly transparent and conducting ZnO:Al layers with high deposition rates by RF magnetron sputtering

AWARDS

- D. Baetzner, shared with G. Agostinelli, "Young Scientist Award of Symposium B", E-MRS Spring Meeting, Strasbourg, June 18-21, 2002
- D. Baetzner, G. Agostinelli, "Best poster presentation", 29th IEEE Photovoltaic Specialists Conference, New Orleans, May 20-24, 2002

EQUIPMENT

4 MBE-chambers with solid sources for CaF_2, (Pb,Sn)Se, Cu(In,Ga)Se, and CdTe
6 PVD for sample sizes up to 20 x 20 cm^2, thermal and e-beam evaporation
3 sputtering systems, DC and RF (substrate size up tp 30x30 cm^2)
Complete photolithographic processing equipment
Bonder
Profilometer
Light microscopy, SEM, XRD
Electrooptic characterization for infrared sensors/emitters and solar cells

Self assembled PbSe quantum dots on PbTe/Si(111) with near equal sizes

K. Alchalabi, D. Zimin, H. Zogg

Self assembled PbSe quantum dots (QD) were grown on a few µm thick PbTe(111) layers on Si(111). The QD form as pyramids with three (100) side faces and (111) base, i.e. with a very high aspect ratio. After overgrowth with 4 ML, about 100 dots μm^{-2} form with heights of about 16nm. The heigths of a large number of dots were determined with AFM. Since all dots exhibit the same shape, their volumes are determined by one parameter (e.g. the heights) only.The observed distribution of these heights (and therefore the volumes of the dots) is extremely narrow: The standard deviation of the heights as measured by AFM can be as low as 2%. This seems to be the narrowest distributions ever observed for self assembled quantum dots.

Similar PbSe quantum dots with pyramidal shapes have first been described by Pinczolits et al. (Applied Phys. Lett. 73, 1998, p. 250). These authors used cleaved BaF_2 as a substrate. They observed two types of dots and with somewhat larger size distributions, however.

We explained the results on the basis of nucleation and growth theories (see Phys. Rev. Lett. 90, 2, Jan. 2003, 26104

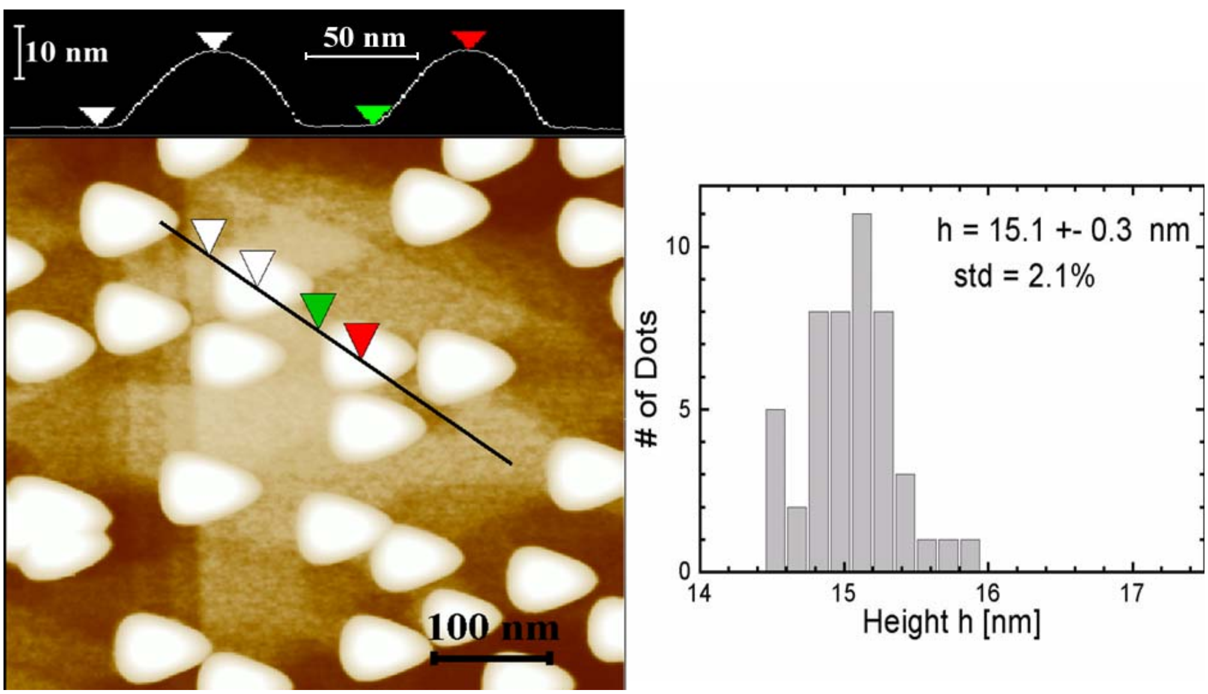


Figure: AFM micrograph and size distributions of pyramidal qutum dots with 15 nm heigths and size nonuniformities as low as 2%.

Sponsor: Swiss National Science Foundation

Monolithic heteroepitaxial PbTe-on-Si infrared focal plane array with 96 x 128 pixels

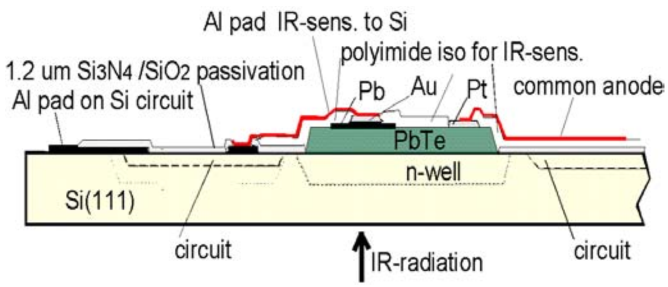
K. Alchalabi, D. Zimin, M. Arnold, H. Zogg

A two-dimensional infrared focal plane array in a heteroepitaxial narrow gap semiconductor layer has been realized for the first time on a Si substrate containing the read-out electronics, and thermal images are demonstrated.

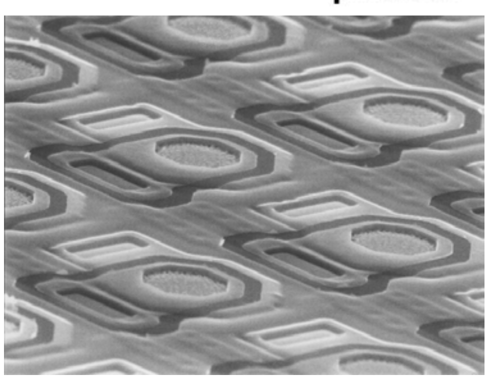
CMOS technology was used to fabricate the circuitries in the Si-substrate. Pitch is 75 µm, each pixel contains a bare Si-area where epitaxial growth of the narrow gap layer occurs, and an access transistor. Addressing is performed line-by-line with a shift-register integrated on the chip.

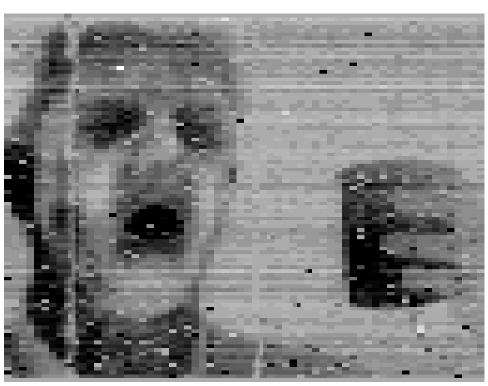
The infrared-sensitive layer (PbTe for the 3-5 µm wavelength range) is grown by molecular beam epitaxy at temperatures below 450°C, allowing fully processed and tested Si chips to be employed. Individual pixels are obtained by mesa-etching, and photovoltaic sensors are fabricated with standard photolithographic techniques.

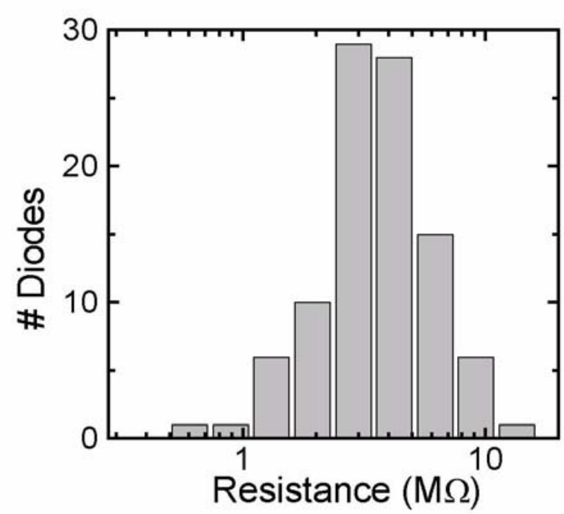
Within the >97% operational pixels, high quantum efficiencies and differential resistances at zero bias with 4 MΩ mean value at 95K are observed. These values are much above the background noise limit for room temperature radiation.



Figures. Schematic cross section (left), part of the 2-d array (middle), demonstrational thermal image at 95K of the 96 x 128 PbTe-on-Si array with 5 µm cut-off wavelength (bottom) and differential resistances (sensitivities) of the sensor (below).







Sponsor: GR, KTI

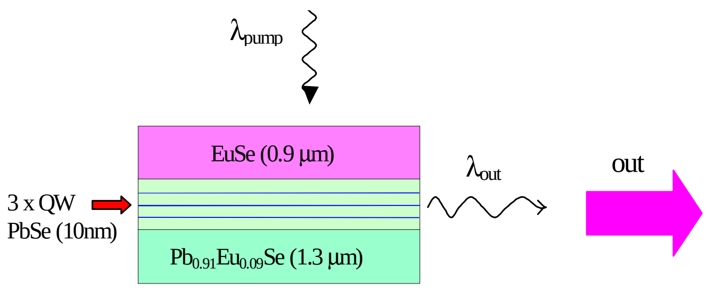
Optically pumped IV-VI edge emitting IR-lasers

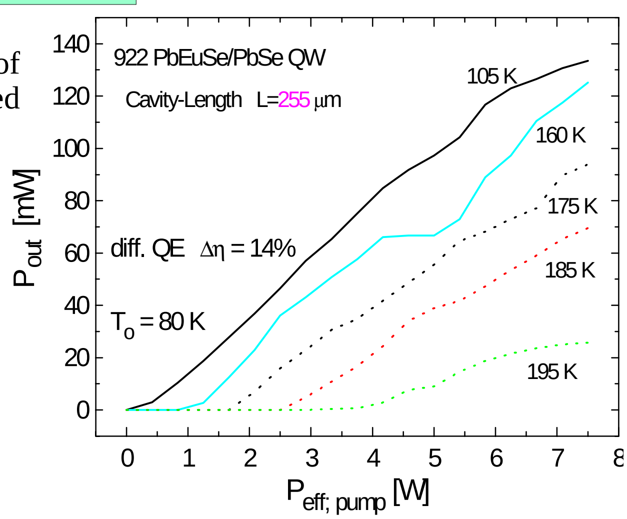
K. Kellermann, D. Zimin, K. Alchalabi, H. Zogg

With the advent of compact high-power laser diodes with around 900 nm or 1500 nm emission wavelength, low-cost optically pumped lead chalcogenide IR-emitters for wavelengths above 3 µm become attractive. In addition, the low Auger recombination of the lead chalcogenides is highly advantagous

DH (double heterostructure) and QW (quantum well) structures are grown by MBE on Si substrates. The structures typically consist of a bottom $Pb_{1-x}Eu_xZ$ (Z = Se or Te) cladding layer, the active $Pb_{1-y}Eu_yZ$ layer containing PbSe QWs, and a top EuZ cladding layer which is transparent to the incoming 870 nm laser beam. If grown on (100) oriented Si-substrates, the about 2-3 µm thick layers are lifted-off from the substrate by dissolving a previously grown BaF_2 buffer layer, cleaved into pieces of e.g. 2000 x 300 µm size and clamped between a heat-conducting substrate and a glass cover. When grown on Si(111)-substrates, edge mirrors are etched (see figure on cover) using dry processing.

The light of the 870 nm laser diode (typically up to 10W pulsed) is focused onto the structure and the lasing characteristics are determined. Up to now, we observed lasing up to about 250K with this limited power and without a lateral confinement. These lasers exhibit high characteristic temperatures T_o up to 125K. This despite dislocation densities are as high as 10^8 cm^{-2}. We expect room-temperature operation if higher quality layers are used.





Figures: Structure of an optically pumped edge emitting IV-VI IR-laser (top), the light-in - light-out characteristics (bottom) and a typical spectrum (right).

Sponsor: GRS , ETH

Vertical emitting optically pumped IV-VI IR-microcavity

K. Kellermann, D. Zimin, K. Alchalabi, H. Zogg

A "wavelength transformer" downconverting part of the incoming 870 nm light to about 4 µm wavelength was realized. It has a similar structure as a VCSEL (vertical cavity surface emitting laser), but with much lower reflectivity top and bottom mirrors: A λ/2 PbEuSe active layer containing PbSe QW (quantum wells) at the antinodes of the wave pattern is sandwiched between the two Bragg mirrors and illuminated from the top with a 870 nm III-V laser diode. The top Bragg mirror consists of e.g. 2 pairs of EuSe/BaF2 which are transparent to the incoming light, the bottom mirror of e.g. 1 pair PbEuSe/BaF_2. Reflectivities are between 85% and 95%. The device works at RT in the subthreshold region. Its line width is given by the resonator design, about 6% for the present application for low-cost gas sensing of gases like CO_2, CO, CH_4. The layers are grown by MBE on Si(111) or BaF_2(111) substrates, the substrates are transparent to the output beam and also act as a mechanical protection.

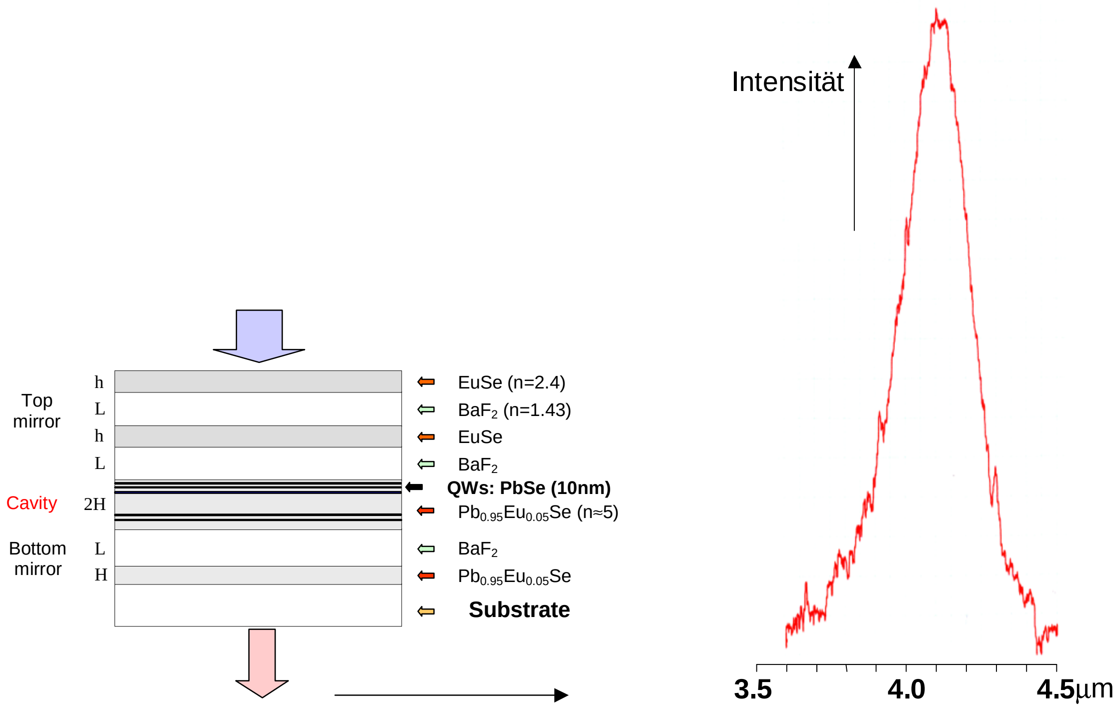


Fig. Schematic structure of an optically pumped microcavity mid-IR-source and emission characteristics.

Sponsor: GRS

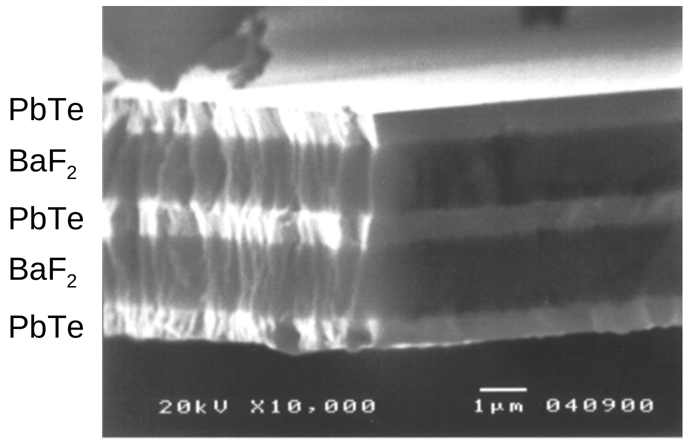
Broad-band high reflectivity Bragg mirror for the mid-infrared range

K. Kellermann, D. Zimin, K. Alchalabi, H. Zogg

We fabricated high reflectivity Bragg-mirrors using alternating layers with high and low refractive index arranged in a quarter wavelength stack. BaF_2 (n=1.4) served as low index and PbTe (n=5.5) as high index material. This large index difference leads to a high reflectance with already few layers (calculated maximal reflectivity is 99.8%), and the spectral response is extremely broadband.

The layers are grown by molecular beam epitaxy onto Si(111) substrates using solid sources. Fig. 1 shows an image of the stack. The measured reflectivity is shown in fig. 2, together with the calculated curve. The reflectivity is above 98% (Measurement uncertainties 2%) from about 9 µm to 16 µm wavelength.

The mid-IR range is extremely suited for trace gas analysis. The mirror will be applied for one analysis method, cavity ringdown (see report of Prof. M.W. Sigrist, Lab. for Laser Spectroscopy and Environmental Sensing). As a side result of this method, the absolute reflectance at selected wavelengths is obtained with much higher accuracy, as needed for the calibration.



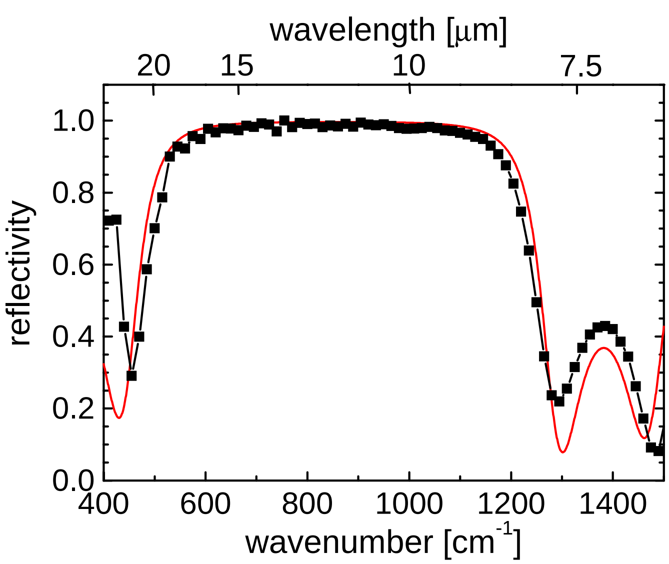


Fig. 1 (top)
BaF_2/PbTe five layer Bragg-mirror structure for the mid-IR range.

Fig. 2 (bottom)
Measured (squares) and calculated (full line) reflectance of the BaF_2/PbTe Bragg mirror.

Sponsor: GRS

Development and electrical characterisation of $Cu(In,Ga)Se_2$ superstrate solar cells

F.-J. Haug, D. Rudmann, H. Zogg, A. N. Tiwari

For thin film solar cells two configurations are distinguished: the substrate and the superstrate solar cell. Solar cells with $Cu(In,Ga)Se_2$ absorber layers are usually prepared in the substrate configuration. Efficiencies of up to 18.8% are obtained with a CdS buffer layer which requires a wet chemical process. All dry processed substrate solar cells reach efficiences of up to 16.2%.

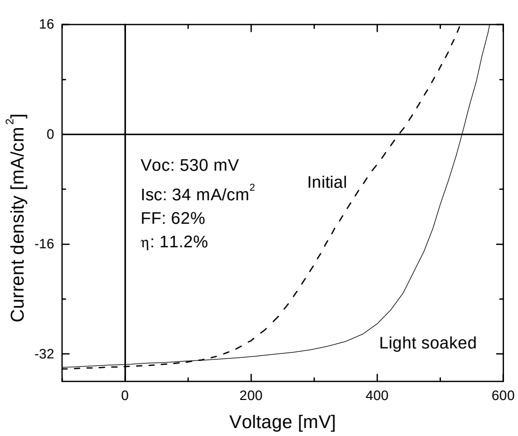
$Cu(In,Ga)Se_2$ solar cells in superstrate configuration exhibit lower efficiencies, however, this configuration is advantageous because it involves only dry process steps and it offers easier encapsulation, therefore giving rise to lower manufacturing costs. Superstrate solar cells show metastable illumination effects, the j-V characteristics considerably improve upon illumination (see below). We have achieved superstrate solar cells with efficiencies of up to 11.2% after light soaking.

For further improvements it would be desirable to know if the performace is limited by bulk or interface properties. A method to study the transport mechanism is the analysis of the saturation current j_0 at different temperatures:

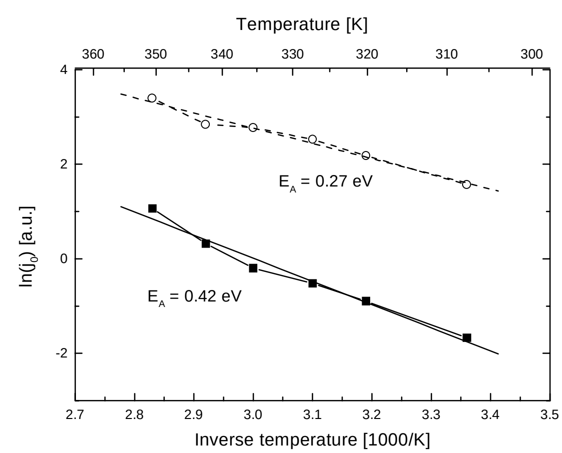
$$j(V) = j_0 e^{\frac{qV}{AkT}} = j_{00} e^{\frac{qV - E_A}{AkT}}$$

The absolute temperature is denoted by T, k is the Boltzmann konstant, j_{00} is the saturation current density prefactor. After correction with the diode quality factor A the activation energy E_A corresponds to the bandgap in case of bulk dominated recombination processes or to the barrier at the interface in case of interface recombination processes.

The diode quality factors before and after light soaking are about 2.4 and 1.6, respectively. Thus, the corrected activation energies of the Arrhenius plots yield approximately the same value of 650 mV. With a bandgap of 1.2 eV this suggests predominant interface recombination. Future developments should therefore aim at improvements of the interface.



Current voltage characteristics before and after light soaking.



Arrhenius plot of the saturation current density before and after light soaking.

Sponsor: GRS

A novel method to improve the efficiency of CIGS solar cells

D. Rudmann, A.F. da Cunha, M. Kaelin, F. Kurdesau, A.N. Tiwari

A certain amount of Na in Cu(In,Ga)Se_2 (CIGS) is essential for the development of high efficiency CIGS solar cells. Most often, Na is introduced during CIGS growth by diffusion either from the soda-lime glass substrate or from a thin Na-containing precursor layer deposited prior to the CIGS growth. These methods are not reliable for controlled incorporation of Na in CIGS. Moreover, the CIGS layers on flexible substrates like metal and polyimide foils need externally added Na in a controlled manner. The processing temperature for CIGS on polyimide should not exceed 450 °C.

The effects of Na on the structural properties of CIGS layers are controversial and depend on the methods of Na incorporation and its concentration. The beneficial effects of Na on the electronic properties of CIGS layers and solar cells are commonly observed. We have investigated different methods of Na incorporation in CIGS and compared the growth kinetics and structural properties. Finally, we have developed a method (patented) for a controlled incorporation of Na in CIGS to improve the efficiency of solar cells. In this method, a thin layer of NaF is deposited onto the CIGS and subsequently annealed under Se ambient. This passivates the donor states at the grain boundaries and increases the net acceptor density in the CIGS layers. As a result of the post deposition Na incorporation the solar cell efficiency increased (fig. 1) from 10.4% to 14.4% for the CIGS layers grown at 450°C.

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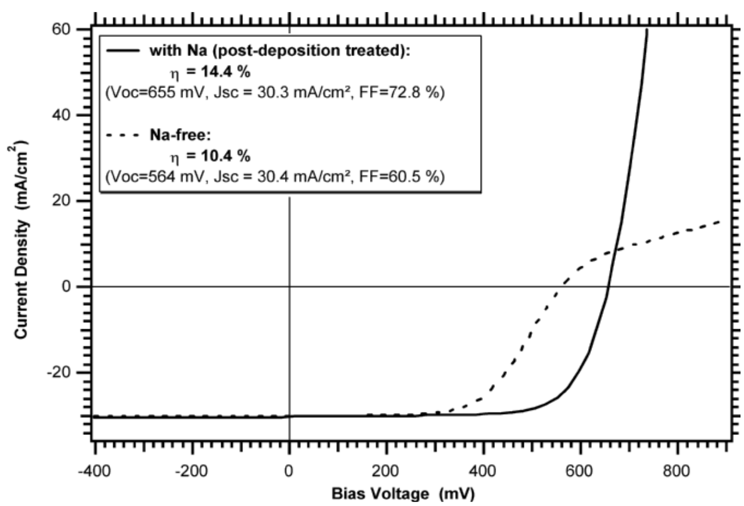


Figure 1 I-V characteristics showing efficiency improvement from 10.4% to 14.4% due to Na incorporation in CIGS.

Sponsor: BBW (EU projects), Swiss National Science Foundation

Flexible CIGS cells on polyimide and metal foils

D. Rudmann, F. Kurdesau, M. Kaelin, T. Kämpfer, K. Kessler, A.N. Tiwari

Flexible $Cu(In,Ga)Se_2$ (CIGS) solar cells and modules are interesting for terrestrial applications, especially when the rigidity or weight of modules encapsulated with glass plates causes problems for installation. Also for space use, flexible CIGS solar cells are very attractive due to the savings in the weight of the deployable power generators and due to an excellent tolerance against proton and electron irradiation. Polyimides and metal foils have been used as a substrate in CIGS flexible solar cells. In general, these foils do not contain sodium which is known to have some beneficial electronic influences on CIGS solar cells. Therefore, we have investigated alternative methods of Na incorporation into CIGS for flexible solar cells. Employing those methods, solar cells of more than 12% efficiency have been developed. The solar cells have been processed on 5 x 5 cm^2 substrates (figure 1). Currently, we are scaling up the deposition processes for 30 x 30 cm^2 substrate size.

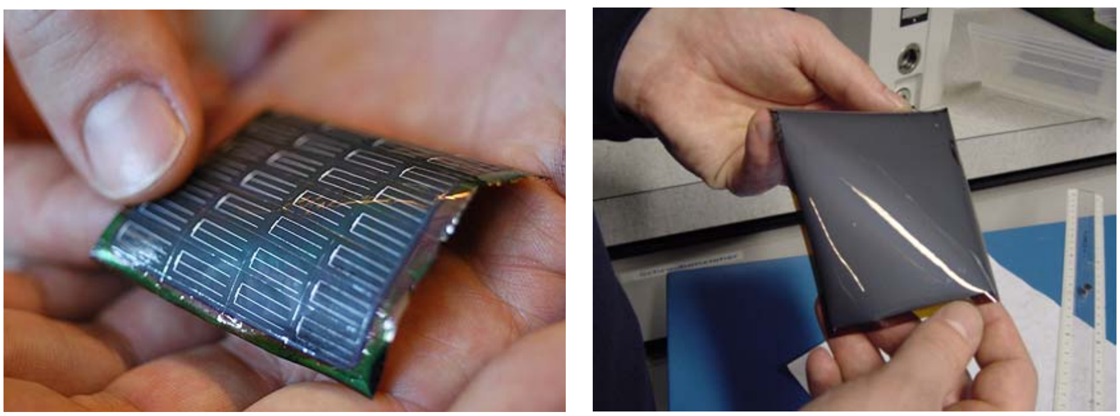


Figure 1: Flexible CIGS solar cells on 5 x 5 cm^2 foils and ZnO:Al/CdS/CIGS/Mo layers on 15 x 15 cm^2 polyimide foils.

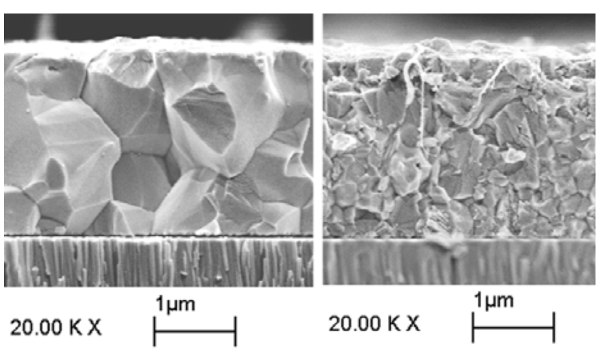
Sponsor: BBW (EU project), GRS

Effects of Na on structural properties of $Cu(In,Ga)Se_2$ thin films

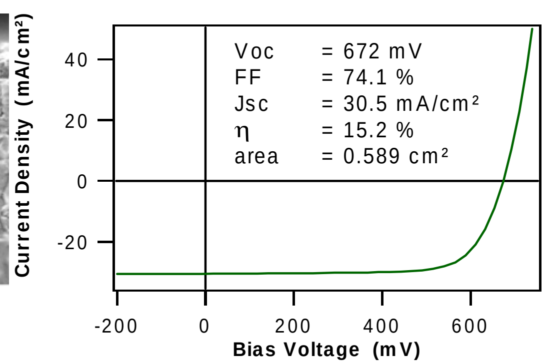
D. Rudmann, M. Kaelin, F.-J. Haug, F. Kurdesau, P.K. Srivastava, H. Zogg, A.N. Tiwari

Flexible $Cu(In,Ga)Se_2$ (CIGS) solar cells and modules are interesting for terrestrial applications, especially when the rigidity or weight of modules encapsulated with glass plates causes problems for installation. Also for space use flexible CIGS solar cells are very attractive due to the savings in weight of deployment constructions and due to excellent resistance of CIGS solar cells against proton and electron irradiation. As substrates for flexible solar cells primarily polyimides and metal foils can be used. In general, none of them contain sodium. Na is known to have beneficial electronic influences on CIGS solar cells, therefore, we have investigated alternative methods of Na incorporation into CIGS and examined structural effects on the material.

Different amounts of co-evaporated NaF have been used during different stages of CIGS growth and using different methods. The results show that the Na concentration in CIGS can be varied with NaF coevaporation, while F cannot be detected in the films. An influence of Na on the reaction kinetics is observed. The texture of CIGS has not been found to be influenced by Na, except when NaF precursors have been used. A further effect of Na observed is that the CIGS grain size becomes smaller with increasing Na concentration (see figure). This phenomenon is independent of the Na incorporation method used. A large grain size would be preferable since grain boundaries are potential recombination centres in an absorber. On the other hand, Na seems to passivate defects at grain boundaries, which leads to a strong enhancement in the electronic properties of CIGS. Cell performance indicates that the electronic benefits induced by Na are more important than a large CIGS grain size. Solar cells with an efficiency exceeding 15 % (η = 15.2 %, V_{OC} = 672 mV, FF = 74.1 %, J_{SC} = 30.5 mA/cm², area = 0.589 cm², no antireflection coating) have been obtained with Na containing CIGS absorber layers (see figure).



Cross-section SEM micrographs of CIGS layers without (left) and with (right) Na.



I-V characteristics of a 15 % CIGS solar cell.

Acknowledgements

The authors would like to thank P. Wägli for SEM pictures.

Sponsor: BBW (EU Project), Swiss National Science Foundation

Transmission electron microscopy of interfaces in $Cu(In,Ga)Se_2$ based solar cells

D. Abou-Ras, M. Kälin, A. Romeo, D. Rudmann, A.N. Tiwari

We have investigated the crystallographic, microstructural and chemical properties of the interfaces in $Cu(In,Ga)Se_2$ (CIGS) based solar cells. The CIGS based solar cells are produced by deposition of thin films and consist of a substrate (e.g. soda lime glass), a back contact (e.g. Mo), the CIGS absorber, a buffer layer (e.g. CdS or ZnS or In_2S_3) and a transparent conducting window layer (e.g. ZnO:Al). The interface properties of CIGS-Mo and CIGS-buffer influence the photovoltaic properties of the solar cells. Investigations are performed using SEM, HRTEM, EFTEM, EDX, EELS, and RBS.

The formation kinetics of the $MoSe_2$ interface layer between Mo and CIGS is investigated with RBS. The selenization of Mo produces a $MoSe_2$ surface layer but the growth of CIGS on Mo can inhibit the formation of the $MoSe_2$ interface layer.

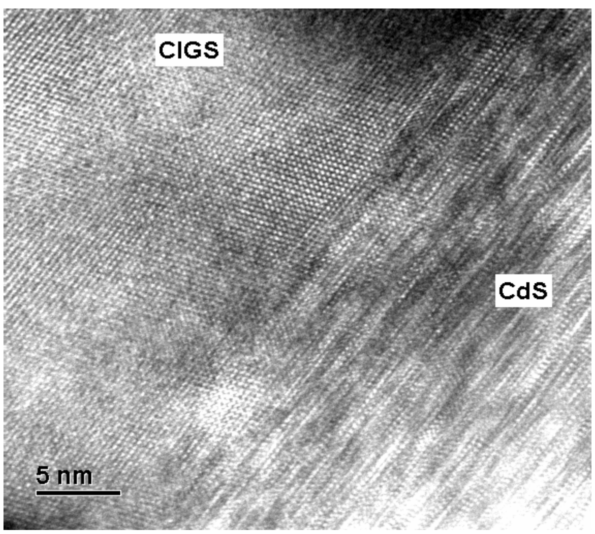


Figure 1: HRTEM image of the CIGS-CdS interface. Clear orientation relation of the layers, high density of lattice defects inside the CdS.

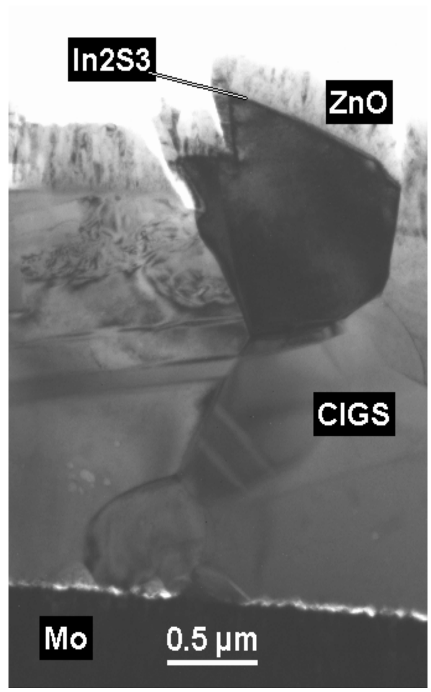


Figure 2: BF-TEM image of a CIGS based solar cell with In_2S_3 buffer layer (grown at Stuttgart University) shows uniform coverage of the CIGS layer.

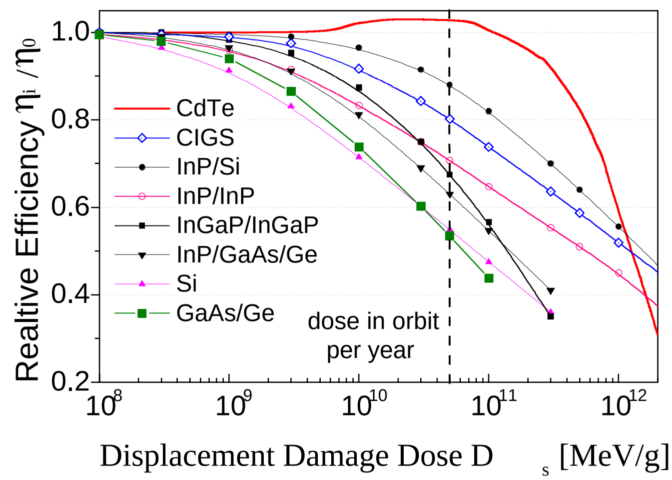
In cooperation with the group of Prof. G. Kostorz, Institute for Applied Physics (IAP), ETH Zurich and Dr. M. Döbeli, PSI/ETH Zürich.

Sponsor: BBW (EU projects), Swiss National Science Foundation

Stability of CdTe solar cells for terrestrial and space applications

D.L. Bätzner, A. Romeo, A. N. Tiwari, H. Zogg

CdTe/CdS solar cells have a promising potential for space application due to their high specific power (kW/kg) on thin and flexible substrates and excellent radiation hardness. We investigated the radiation tolerance of CdTe/CdS cells developed in our laboratory, by irradiation with protons (at the TANDEM accelerator of PSI/ EHTZ) and electrons (at the DYNAMITRON electron accelerator of the University of Stuttgart). The cells were irradiated with very high fluences of the particles of different energies in the MeV range, equivalent to the exposures of decades in space. The displacement damage dose formulation was applied to determine one single degradation characteristics as a function of damage dose, that contains the data of all particles, energies, and fluences.With this formulation it was possible to compare the CdTe solar cell technology in terms of radiation hardness to other technologies (see figure). Comparison of solar cell efficiency degradation curves clearly shows that CdTe is the most radiation tolerant solar cell. While the efficiency of high efficiency Si and III-V solar cells drops to ~50% of the initial value, CdTe cells remain stable for a realistic dose in space (~10^{11}MeV/g). The CdTe cells also recover fast from any damage, which implies that for operation in space no performance degradation due to radiation damage is expected.



The stability of CdTe solar cells is still an issue and depends crucially on the impurities in the devices. SIMS measurements indicate impurity diffusion from the back contact material into the CdTe bulk and the CdS with accumulation in the CdS layer or near the CdTe/CdS interface. To correlate these observations of changed chemistry in the cell with the photovoltaic properties, i.e. generally degradation, the technique of voltage dependent quantum efficiency measurement (referred to as Apparent Quantum Efficiency, AQE) was developed and applied to thermally stressed cells. In order to understand and interpret the AQE measurements a novel model was developed. The measurements indicate diffusion of Cu and Au into the CdTe cell resulting in degradation, whereas Sb and Mo may diffuse only in much smaller quantities and degrade the PV properties much less. Stable CdTe cells with Sb/Mo and Sb_2Te_3/Mo back contacts have been demonstrated.

Sponsor: BBW (EU-Project), European Space Agency

CIGS solar cells developed with evaporated II-VI buffer layers

A. Romeo, H. Zogg and A. N. Tiwari

High efficiency CIGS solar cells have been obtained with chemical bath deposited (CBD) buffer layers. However, for in-line production of modules vacuum deposition processes (PVD) are preferred for compatibility reasons and high throughput. We studied the possibility of obtaining high efficiency CIGS solar cells with all-dry processes. $Cu(In,Ga)Se_2$ absorbers were provided by IPE and ZSW in Stuttgart. Three different buffer layers were considered: CdS and as an alternative ZnS and ZnSe in order to reduce the optical absorption losses.

CdS was deposited by high vacuum evaporation at a substrate temperature of 50°C, chemical or thermal surface cleaning treatments were not applied.

Solar cells prepared with 80 nm thick PVD-CdS yield an efficiency of 10 to 12%, while for CBD-CdS 14.6% efficiency has been obtained (see figure1). ZnS and ZnSe buffer layers were applied as alternative to CdS. Layers of different thickness were grown by e-beam evaporation at different substrate temperatures (RT to 400 °C). ZnS shows a very high transparency superior to the conventional buffers ZnSe and CdS.

PV performance depends on the properties of buffer layers, post-deposition annealing and light soaking conditions. Thin buffer layers of ZnS grown at a temperature of 150°C and after annealing in vacuum at 300°C yield cells with V_{oc} exceeding 500 mV and FF of 63%.

It has been observed that diffusion of Zn into the CIGS is an important issue for high efficiency cells. If no post-deposition annealing of ZnS is applied than light soaking of the finished device improves the electrical properties, on the other hand a post deposition treatment gives the same results without applying light-soaking.

Up to now efficiencies of about 9% were obtained for cells made with ZnS buffer layers and 6% for ZnSe buffer layers (see figure 2).

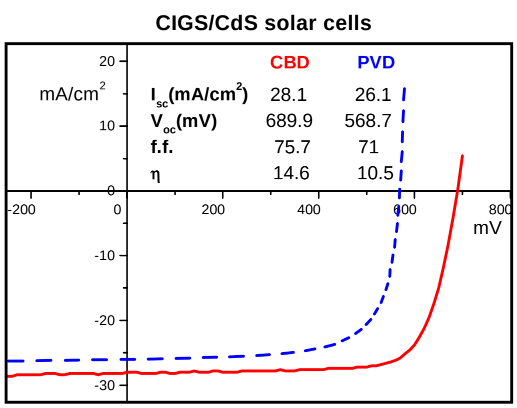


Fig. 1. Comparison of CIGS solar cells with CBD (full) and PVD (dashed) CdS

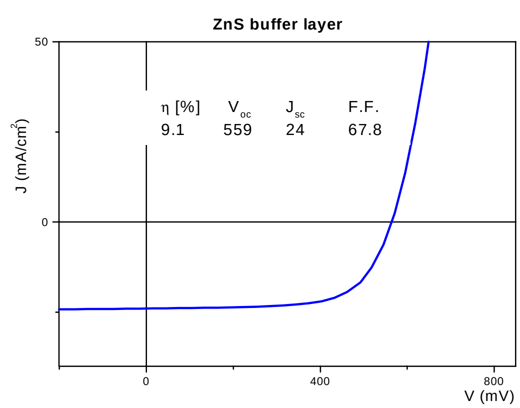


Figure 2. I-V of CIGS/ZnS solar cell.

Sponsor: BBW (EU-Project)

High efficiency flexible CdTe/CdS solar cells

A. Romeo, G. Khrypunov, D.L. Bätzner, H. Zogg, A.N. Tiwari.

Development of flexible and lightweight solar cells is interesting for many terrestrial and space applications that require a very high specific power (defined as the ratio of output electrical power to the solar module weight). We have presented a novel process for developing CdTe solar cells on polyimide film substrates in *super*strate configuration. The polyimide layer was spin coated on glass prior to the deposition of ZnO:Al, and the semiconducting layers are grown at low temperatures, around 400°C. Further development of the transparent conducting oxide (TCO) resulted in a record efficiency of 11% for CdTe flexible cell with V_{oc} = 842 mV, I_{sc} = 18.5 mA/cm^2, and FF = 70.9%. For space applications it is desirable to avoid polyimides because of their possible degradation under UV light.

A new process for preparing *sub*strate flexible CdTe solar cells has been developed to avoid these drawback. A layer of NaCl is deposited on glass prior to the deposition of TCO. Polyimide is spin coated on top of the layer so that it will still held the solar cell but it will not be exposed to radiation. After the deposition of the stacks, a lift-off process is applied. Solar cells of 7.3% efficiency with V_{oc} = 692 mV, I_{sc} = 21.5 mA/cm^2, and FF = 49% were obtained.

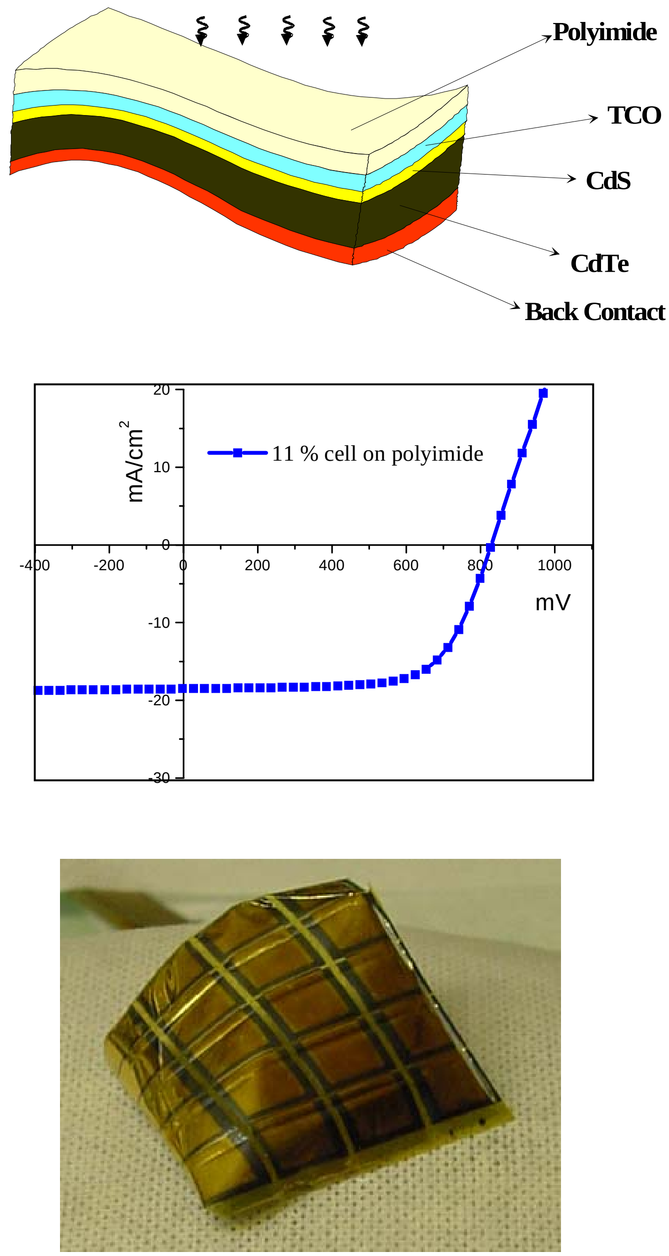


Figure1. Schematic cross-section of the flexible CdTe solar cell on polyimide in superstrate configuration (top), I-V characteristic of a 11% efficiency CdTe solar cell on polyimide (superstrate configuration) measured under AM 1.5 illumination (middle) and picture of a CdTe superstrate solar mini module on polyimide (bottom).

Sponsor: BBW (EU-Project), European Space Agency

Non-vacuum $Cu(In,Ga)Se_2$ layers from selenization of nanosized precursor materials

M. Kaelin, F. Kurdesau, D. Rudmann, A.N.Tiwari

In order to reduce process complexity and costs of solar cells simple and low cost deposition methods are required. A novel technology utilizing nano-sized precursors has been developed. By this technology solar cells with efficiencies up to 5% were fabricated without the use of expensive vacuum deposition systems.

Uniform deposition of thin compact layers is a key issue in this novel method. The precursor layers containing Cu, In and Ga in the desired stoichiometry were deposited on Mo coated glass substrates by the doctor blade method.

An annealing in a selenium containing atmosphere converts the precursor layer into the $CuInSe_2$ (CIS) and $Cu(In,Ga)Se_2$ (CIGS) compounds (fig. 3). Selenization is done typically at a temperature of 560°C for 20 minutes using a nitrogen flushed quarz container at low pressure (~10mbar).

Scanning electron microscopy (SEM) shows compact and crack-free layers with a grain size in the order of one micrometer (fig1). Such structures led to solar cells with efficiencies as high as 5% (fig. 2).

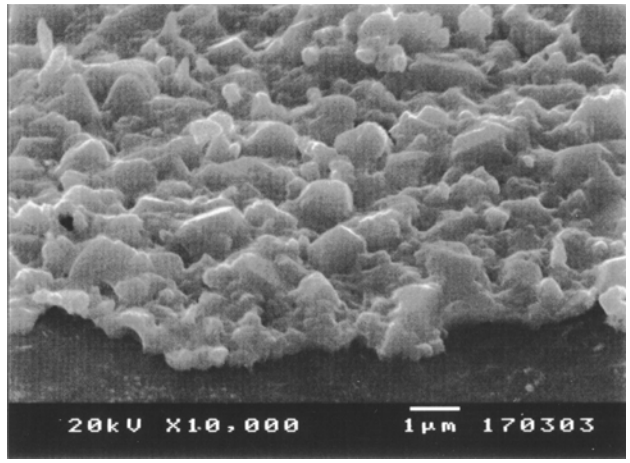


Figure 1: Cross Section of CIGS layer.

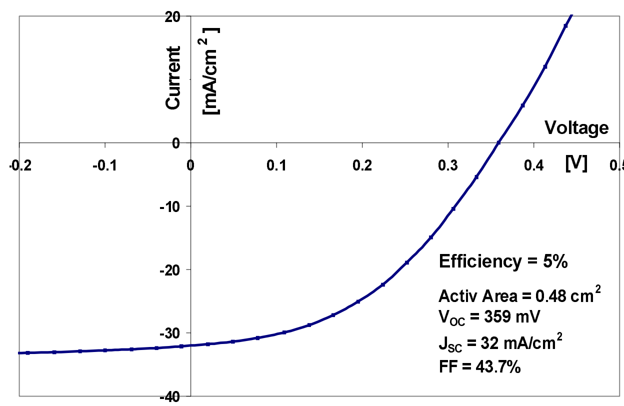


Figure 2: I-V curve of a 5 % efficient solar cell.

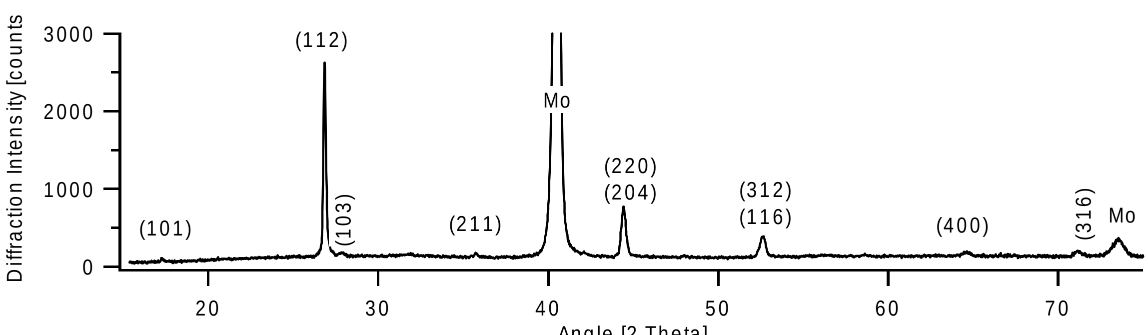


Figure 3: XRD pattern of selenized precursor film shwing the formation of single phase CIGS.

Sponsor: KTI (TOPNANO 21)

PUBLICATIONS

Ph.D. theses

Derk Leander Bätzner,
Performance and stability of CdTe/CdS Solar Cells for Terrestrial and Space Applications,
Diss ETH Nr. 14834, 2002,
Referent: Prof. Dr. L. Gaukler,
Korreferenten: PD Dr. H. Zogg, Dr. A.N. Tiwari

Mathias Terheggen
Microstructural changes in CdS/CdTe thin-film solar cells during annealing with chlorine
Diss. ETH 15214, 2003
Referent: Prof. Dr. G. Kostorz
Korreferenten: Prof. Dr. M. Rühle (Univ. Stuttgart), Dr. H. Heinrich, Prof. Dr. A.N. Tiwari
(Projekt: Institut für Angewandte Physik, ETHZ)

Book chapter

H. Zogg

"Lead Chalcogenide Infrared Detectors Grown on Silicon Substrates", in “Optoelectronic Properties of Semiconductors and Superlattices”, M.O. Manasreh, Series editor, Vol. 18, “Lead Chalcogenides: Physics and Applications”, D. Khokhlov ed., Taylor & Francis Books, Inc., New York and London, 2003, pp 587-616.

Journal Publications

216 K. Kellermann, D. Zimin, K. Alchalabi, Ph. Gasser, N.A. Pikhtin, H. Zogg
Optically pumped lead-chalcogenide mid-infrared lasers on Si-substrates, **J. Appl. Phys.**, to be published

215 K. Kellermann, D. Zimin, K. Alchalabi, Ph. Gasser, H. Zogg
Optically pumped lead-chalcogenide infrared emitters on Si-substrates,
Physica E, to be published (Proc. ngs11 conference, Buffalo, June 2003)

214 A.Romeo, M. Arnold, D.L. Bätzner, H.Zogg, A.Tiwari
Development of High Efficiency Flexible CdTe Solar Cells
Proc. conf. “PV in Europe from PV Technology to Energy Solutions”,Rome, Italy 7-11 Oct. 2002; pp 377-381.

213 D. Rudmann, G. Bilger, M. Kaelin, F. -J. Haug, H. Zogg, A. N. Tiwari
Effects of NaF coevaporation on structural properties of Cu(In,Ga)Se2 thin films,
Thin Solid Films 431-432 (2003) 37-40

212 M. Kaelin, D. Rudmann, F. Kurdesau, T. Meyer, H. Zogg, A. N. Tiwari
CIS and CIGS layers from selenized nanoparticle precursors,
Thin Solid Films 431-432 (2003) 58-62

211 D. L. Bätzner, G. Agostinelli, M. Campo, A. Romeo, J. Beier, H. Zogg, A. N. Tiwari
Study of spatially resolved impurity diffusion in CdTe solar cells using voltage dependent quantum efficiency,
Thin Solid Films 431-432 (2003) 421-425

210 F. -J. Haug, D. Rudmann, H. Zogg, A. N. Tiwari
Light soaking effects in Cu(In,Ga)Se2 superstrate solar cells,
Thin Solid Films 431-432 (2003) 431-435

208 D.L. Bätzner, A. Romeo, M. Döbeli, K. Weinert, H. Zogg, A.N. Tiwari,
High energy irradiation properties of CdTe/CdS Solar cells,
Proc. 29th IEEE Photovoltaic Specialist Conference, New Orleans (2002) 982-985

207 G. Agostinelli, D.L. Bätzner, M. Burgelman,
An alternative model for V, G and T dependence of CdTe solar cells IV characteristics,
Proc. 29th IEEE Photovoltaic Specialist Conference, New Orleans (2002) 744-747

206 F.-J. Haug, H. Zogg, A. N. Tiwari,
11% efficiency CIGS superstrate solar cells without sodium precursor,
Proc. 29th IEEE Photovoltaic Specialist Conference, 20-24 May 2002, New Orleans, USA, 728-731

205 O. Grimm, H. Anderhub, J.R. Bates, D. Bätzner, S. Baumgartner, A. Biland, C. Camps, M. Capell, V. Commichau, L. Djambazov, Y.-J. Fanchiang et al.,
Design and construction of the prototype synchrotron radiation detector,
Nuclear Instruments and Methods in Physics Research A491 (1-2) (2002) 98-112

204 H. Anderhub, D. Baetzner, S. Baumgartner, A. Biland, C. Camps, M. Capell, V. Commichau, L. Djambazov, Y.-J. Fanchiang, G. Fluegge et al.,
The Prototype Synchrotron Radiation Detector (PSRD),
Nuclear Instruments and Methods in Physics Research A478 1-2 (2002) 123-124

203 M. Terheggen, H. Heinrich, G. Kostorz, F.-J. Haug, H. Zogg, A.N. Tiwari,
Ga_2O_3 Segregation in Cu(In,Ga)Se_2/ZnO Superstrate Solar Cells and its Impact on their Photovoltaic Properties,
Thin Solid Films 403-404 (2002) 212-215

202 M. Kaelin, H.Zogg, A.N. Tiwari, O. Wilhelm, S.E. Pratsinis, T. Meyer, A. Meyer
Electrosprayed and selenized thin metal films
Thin Solid Films, to be published 2003

201 K. Alchalabi, D. Zimin, H.Zogg,
Self Assembled PbSe Quantum Dots with Almost Equal Sizes Grown by MBE on PbTe/Si(111),
Mat. Res. Soc. Symp. Proc. Vol. 737, 2003, E5.5.1-5.

200 K. Alchalabi, D. Zimin, G. Kostorz*, H. Zogg,
Self-Assembled Semiconductor Quantum Dots with Nearly Uniform Sizes,
Phys. Rev. Lett. 90, 2, Jan 2003, 026104, 4 pages *Institut für Angewandte Physik, ETH Zürich

199 K. Kellermann, D. Zimin, K. Alchalabi, N.A. Pikhtin[#], H. Zogg,
Optically pumped lead-chalcogenide IR-emitters,
IEE Proceedings - Optoelectronics, submitted (Proc. MIOMD-V, Sept. 2002, Annapolis MD) [#]Ioffe Physico-Technical Institute, Russia

198 H. Zogg, K. Alchalabi, D. Zimin, K. Kellermann,
Two-dimensional monolithic lead chalcogenide infrared sensor arrays on silicon read-out chips and noise mechanisms,
IEEE Trans. Electron Devices ED50, Jan 2003, pp. 209 - 214.

197 H. Zogg, K. Alchalabi, D.Zimin,
Two-dimensional monolithic lead-chalcogenide on active Si-substrate IR-FPA,
Proc. **SPIE 4820-47**, 2002, pp. 429-435.

CONFERENCE PRESENTATIONS:

invited:

H. Zogg, K. Kellermann, K. Alchalabi, D. Zimin
Optically pumped lead chalcogenide infrared emitters on Si-substrates
7th **AITA workshop** (7th Int. Workshop on Advanced Infrared Technology and Applications), Pisa, I, 9-11 Sept. 2003 (invited talk)

D.L. Bätzner, A. Romeo, D. Rudmann, M. Kälin, H. Zogg, A.N. Tiwari
CdTe/CdS and CIGS Thin Film Solar Cells
Keynote at **1. International Solar-Wind-Hydro Conference**, July 2003, Segovia, Spain

D.L. Bätzner, A. Romeo, M. Terheggen, M. Döbeli, H. Zogg, A. N. Tiwari
Stability aspects in CdTe/CdS solar cells
E-MRS Spring Meeting, Strasbourg, France, June 10-13, 2003

F.-J. Haug*, D. Rudmann, A. Romeo, H. Zogg, A. N. Tiwari
Electrical properties of the heterojunction in Cu(In,Ga)Se_2 superstrate solar cells
3rd World Conference on Photovoltaic Energy Conversion, **Osaka**, Jp., 12-16 May 2003.
*Present address: EMPA, Überlandstr. 129, CH-8600 Dübendorf, Switzerland

A.N. Tiwari, D. Rudmann, A.F. da Cunha*, M. Kaelin, F.-J. Haug**, H. Zogg
Effects of Na on the Growth of Cu(In,Ga) Se_2 Thin Films and Solar Cells
MRS spring meeting, San Francisco, 21-25 April 2003
*Permanent address: Departamento de Fisica, Universidade de Aveiro, 3810-193 Aveiro, Portugal
**Present address: EMPA, Ueberlandstr. 129, CH-8600 Dübendorf, Switzerland

contributed:

IR:

K. Kellermann, K. Alchalabi, D. Zimin, H. Zogg
Optically pumped mid-infrared lasers on Si-substrates
TDLS-2003, Tunable Diode Laser Spectroscopy conference, Zermatt, CH, 14-18 July 2003,

K. Kellermann, D. Zimin, K. Alchalabi, Ph. Gasser*, H. Zogg
Optically pumped lead chalcogenide infrared emitters on silicon substrates
NGS-11, 11th int. conf. on narrow gap semiconductors, Buffalo NY, USA, June 16-20 2003
*EMPA Dübendorf, CH

K. Kellermann, D. Zimin, K. Alchalabi, H. Zogg
Optisch gepumpte Bleichalkogenid Infrarotlaser auf Si-Substraten
33. IR-Kolloquium, Freiburg i. Br., D, 8-9 April 2003

K. Kellermann, K. Alchalabi, D. Zimin, H. Zogg
Optically pumped lead chalcogenide infrared emitters on Si-substrates
12th **Euro-MBE** workshop, Bad Hofgastein, A, 16-19 Feb. 2003

D. Zimin, K. Alchalabi, H. Zogg
“Self assembled PbSe quantum dots with nearly uniform sizes on PbTe/Si(111)”
12th Euro-MBE Workshop, Bad Hofgaststein, 16-19 Feb 2003

D. Zimin, K. Alchalabi, O. Anisimov*, A. Banshchikov*, N. Sokolov*, Sergey Suturin*, H. Zogg, “Self-assembled CaF2-on-Si(001) nanostructures”
12th Euro-MBE Workshop, Bad Hofgaststein, 16-19 Feb 2003
*Ioffe Institute, St. Petersburg, Russia

K. Alchalabi, D. Zimin, H.Zogg
Self Assembled PbSe Quantum Dots with Almost Equal Sizes Grown by MBE on PbTe/Si(111)
MRS Fall 2002, Materials Research Society Fall Meeting, Boston MA, Dec 1-6 2002.

K. Alchalabi, K. Kellermann, D. Zimin, H. Zogg
Optically pumped lead-chalcogenide IR-emitters
ISCS 2002, 29th International Symposium on Compound Semiconductors 2002, October 7-10, 2002, Lausanne, Switzerland

D. Zimin, K. Alchalabi, H.Zogg
Self assembled PbSe quantum dots with almost equal sizes on PbTe/Si(111)
ISCS 2002, 29th International Symposium on Compound Semiconductors 2002, October 7-10, 2002, Lausanne, Switzerland

D. Zimin, K. Alchalabi, H. Zogg
Self assemled semiconductor IV-VI quantum dots with extremely narrow size distribution
2002 Workshop on Nanoscience, September 30- October 4 2002, **Twannberg**, Switzerland.

K. Kellermann, D. Zimin, K. Alchalabi, N.A. Pikhtin#, H. Zogg
Optically pumped lead-chalcogenide IR-emitters
MIOMD-V, 5th Int Conf. on Mid-Infrared Optoelectronic Materials and Devices, Annapolis MD Sept 8-11, 2002
#Ioffe Physico-Technical Institute, Semiconductor Luminescence and Injection Emitters Lab., St. Petersburg 194021, Russia

K. Alchalabi, D. Zimin, K. Kellermann, H. Zogg
A 2-d Monolithic PbTe-on-Active-Si Infrared Focal Plane Array for Thermal Imaging
MIOMD-V, 5th Int Conf. on Mid-Infrared Optoelectronic Materials and Devices, Annapolis MD Sept 8-11, 2002

H. Zogg, K. Alchalabi, D. Zimin
Two-dimensional monolithic lead-chalcogenide on active Si-substrate IR-FPA
SPIE Int. Symp. Opt. Sci. & Techn., Infrared Technology and Applications XXVIII, **Seattle** WA, 7-11 July 2002

H. Zogg, K. Alchalabi, D. Zimin, K. Kellermann
Two-dimensional monolithic lead chalcogenide infrared sensor array on silicon read-out chip
New Developments in Radiation Detectors, **9th European Symposium on Semiconductor Detectors**, Schloss Elmau, Germany, June 23-27 2002

PV:

F. Kurdesau, V.B. Zalesski, V.F. Gremenok, V.I. Kovalevski, M. Kaelin
In-situ resistivity measurements during selenization process
E-MRS Spring Meeting, Strasbourg, June 10-13, 2003

D. Rudmann, M. Kaelin, F.-J. Haug, F. Kurdesau, H. Zogg and A.N. Tiwari
Impact of Na on structural properties and interdiffusion of $CuInSe_2$ and $CuGaSe_2$ Thin Films
3rd World Conference on Photovoltaic Energy Conversion, **Osaka**, Japan, 11-18 May 2003

M. Kaelin, F. Kurdesau, D. Rudmann, A.N. Tiwari, H. Zogg
Low cost Cu(In,Ga)Se2 absorber layers from selenization of precursor materials
3rd World Conference on Photovoltaic Energy Conversion, **Osaka**, Japan, 11-18 May 2003

A.Romeo, M. Arnold, D.L. Bätzner, H.Zogg, A.Tiwari
Development of High Efficiency Flexible CdTe Solar Cells
"**PV in Europe from PV Technology to Energy Solutions**"; Conference and Exhibition, Palazzo dei Congressi, Rome, Italy 7-11 October 2002

M. Kaelin
Nanopartikel für Solarzellen und optische Schichten
TopNano21 Third Annual Meeting, October 1st 2002, Kursaal Berne, **Veranstaltungsreihe Top Nano 21**, 2002

M. Kaelin, A. N. Tiwari, H. Zogg
Nanomaterials for high efficiency and low cost Cu(In,Ga)Se_2 thin film solar cells
2002 Workshop on Nanoscience, September 30- October 4 2002, **Twannberg**, Switzerland.

F. Kurdesau, M. Kaelin, D. Rudmann
Chemical bath deposited CdS nanolayers for Cu(In,Ga)Se2 solar cells
2002 Workshop on Nanoscience, September 30- October 4 2002, **Twannberg,** Switzerland.

D. L. Bätzner, G. Agostinelli, M. Campo, A. Romeo, J. Beier, H. Zogg, A. N. Tiwari
Study of spatially resolved impurity diffusion in CdTe solar cells using voltage dependent quantum efficiency, **E-MRS Spring Meeting**, Strasbourg, June 18-21, 2002

G. Agostinelli, D.L. Bätzner, M. Burgelman
A theoretical model for the front region of CdTe solar cells
E-MRS Spring Meeting, Strasbourg, June 18-21, 2002

M. Terheggen, H. Heinrich, G. Kostorz, A. Romeo, D. L. Bätzner, A. N. Tiwari
Transmission electron microscopy of diffusion induced strucdtural and chamical changes in CdTe solar cells, **E-MRS Spring Meeting**, Strasbourg, June 18-21, 2002

F.-J. Haug, D. Rudmann, H. Zogg, A. N. Tiwari
Light soaking effects in CIGS superstrate solar cells
E-MRS Spring Meeting, Strasbourg, June 18-21, 2002

M. Kaelin, T. Meyer*, D. Rudmann, A. N. Tiwari, H. Zogg
Cu(In,Ga)Se_2 layers from selenized nanoparticle precursors
E-MRS Spring Meeting, Strasbourg, June 18-21, 2002.
*Solaronix S. A., Rue de l'Ouriette 129, 1170 Aubonne

D. Rudmann, F.-J. Haug, M. Kaelin, H. Zogg, A. N. Tiwari
Effects of NaF Coevaporation on structural properties of Cu(In,Ga)Se_2 thin films
E-MRS Spring Meeting, Strasbourg, June 18-21, 2002