0.1 Thin-Film Physics Group

Head
PD Dr. H. Zogg
Academic Staff
Prof. Dr. A. N. Tiwari
Dr. D. Gttler
Dr. S. Nishiwaki
Dr. Y. Romanyuk
D. Brmaud
S. Bcheler
A. Chirila
F. Felder
M. Fill
J. Perrenoud
M. Rahim
S. Seyrling
R. Verma
D. Corica
Technical Staff
J. Dscher, O. Meier

0.1.1 Epitaxial IV-VI narrow-gap semiconductor layers and mid-IR devices

F. Felder, M. Fill, M. Rahim, D. Boye, A. Fognini, A. Khiar and H. Zogg, *www.tfp.ethz.ch*

Epitaxial narrow gap lead chalcogenide (IV-VI) layers like PbX, $Pb_{1-y}Sn_yX$, $Pb_{1-y}Eu_yX$ and $Pb_{1-y}Sr_yX$ (X = Te, Se) are investigated for applications and basic research. The band gaps of the active infrared layers range from < 0.1 to 0.4 eV (corresponding to wavelengths in the mid-IR range). Larger band gaps are realised with larger y values for the cladding $Pb_{1-y}Eu_yX$ and $Pb_{1-y}Sr_yX$ layers. All layers are grown by solid source molecular beam epitaxy (MBE) onto Si(111)-substrates by employing a CaF_2 buffer layer, or onto BaF_2(111) substrates. The layers are heavily lattice- and (for Si-substrates) thermal-expansion mismatched. Lead-chalcogenides are fault tolerant, and allow to realize high quality mid-infrared optoelectronic devices even with such mismatched layers.
In addition, epitaxial Bragg mirrors with very high reflectivity over a broad spectral range are easily obtained with a few quarter wavelength layers with alternating high and low refractive indices.

Vertical External Cavity Surface Emitting Laser (VECSEL)

VECSELs for the visible and near-infrared range are popular due to their easy fabrication, scalability, and good beam quality. We realized the first VECSELs emitting above 3 μm wavelength. The devices were grown on BaF_2 or Si substrates, optically pumped with a commercial 1.55 μm wavelength laser diode, and operated up to 175 K. The active layer was PbTe with emission wavelength around 5 μm. Recently, we built the first mid-IR VECSEL operating up to above room temperature. A resonant design was chosen: The active part consists of a single 850 nm thick epitaxial PbSe gain layer. It is followed by a 2.5 pair $Pb_{1-y}Eu_yTe/BaF_2$ Bragg mirror and an Al heat spreader layer. No microstructural processing is needed. The device operates up to 45°C with 100 ns pulses and delivers 6 mW output power at 27°C heat-sink temperature. Compared to edge-emitting mid-IR lasers like type-W or quantum cascade lasers (QCL), the structure is remarkably simple, easily wavelength tunable and emission is into a narrow output beam cone only.

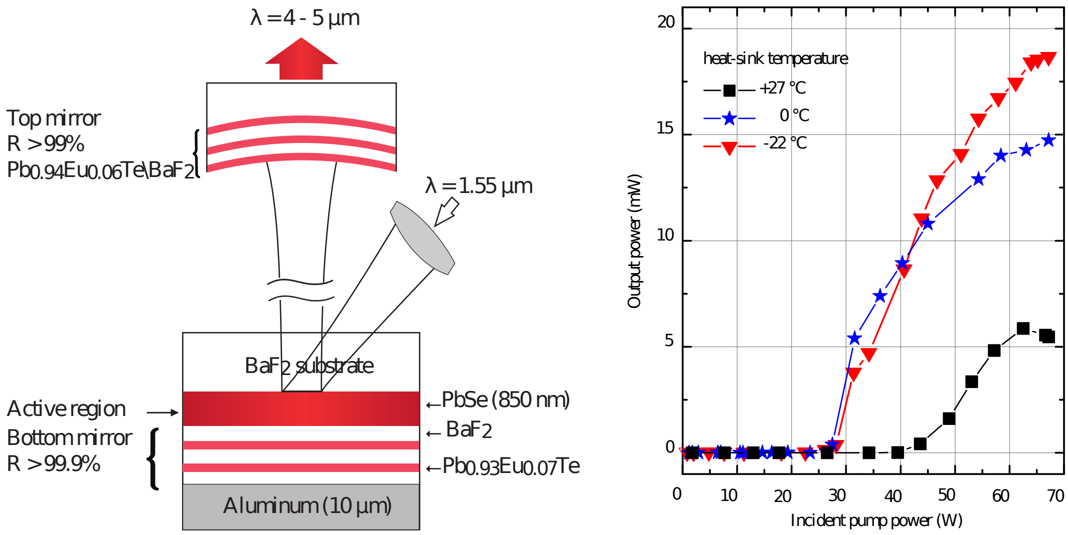

Figure 1: (left) Schematic representation of a PbSe-based IV-VI VECSEL. The curved Bragg mirror is used as output coupler. (right) Light-in/light-out characteristics at different temperatures.

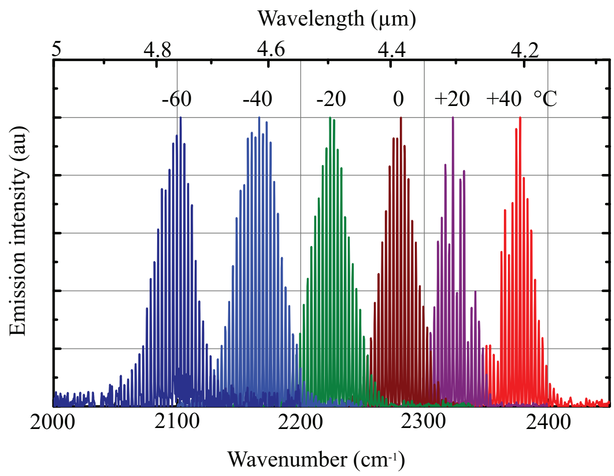

Figure 2: Normalized PbSe based VECSEL lasing spectra at different heat sink temperatures.

Resonant Cavity Enhanced Detector (RCED)

A resonant cavity enhanced detector (RCED) is an embedded absorber layer within a Fabry-Perot cavity. It is sensitive mainly at the resonance wavelengths, where it exhibits a high quantum efficiency. By changing the cavity length, wavelength tuning is possible. We realized a RCED with movable MEMS micromirrors. Due to alloying the bandgap of the $Pb_{0.98}Sr_{0.02}Te$ absorber layer is blue-shifted. The total tunable range is 0.5 μm wide.

PbTe quantum dots in a CdTe-layer on Si(111)

Quantum dot infrared photodetectors (QDIP) have high sensitivity limits and are especially suited to be employed in RCEDs. PbTe QDs are promising IV-VI candidates for this purpose. They may be embedded in a CdTe matrix. PbTe is nearly lattice matched with CdTe but has a different crystal structure: The lattice is rocksalt for PbTe, while it is zinkblende for CdTe. Coherent PbTe precipitates form since intermixing is avoided. PbTe QD in a CdTe matrix were studied on different substrates, for example on GaAs(100). Here

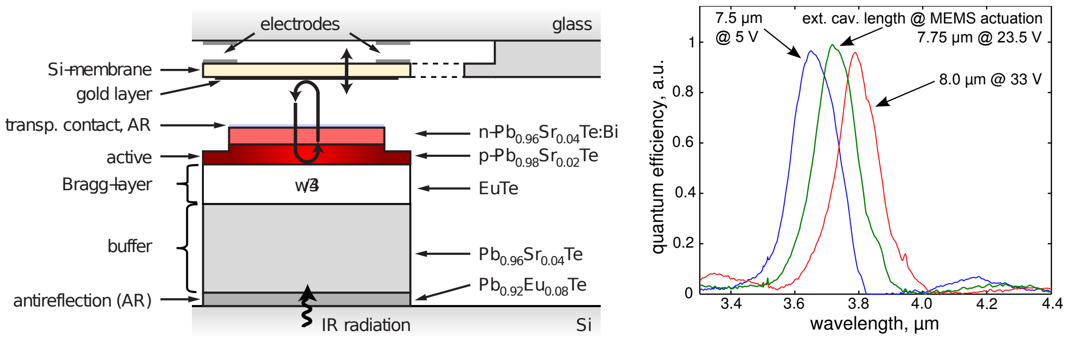

Figure 3: Schematics of a RCED and measured spectra for different MEMS actuation voltages.

we present the formation of self assembled PbTe QD in a CdTe matrix on Si(111). Fig. 2 shows the PL spectra of an ensemble of PbTe QD showing a blueshift with regard to bulk PbTe as well as the calculated energies for a specific QD size.

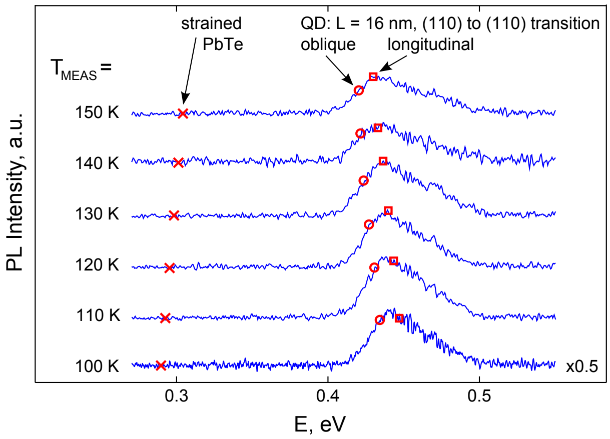

Figure 4: PL spectra of an annealed PbTe QD in CdTe sample strained PbTe, the calculated interband transitions for a QD size of 16 nm are shown.

0.1.2 Thin-film Cu(In,Ga)Se2 and CdTe compound semiconductors solar cells

D. Bremaud*, S. Bcheler*, A. Chirila*, S. Seyrling*, R. Verma*, A.N.Tiwari* and H. Zogg

* Now at EMPA, Dbendorf, *www.empa.ch/tfpv*

Thin film solar cells based on $Cu(In,Ga)Se_2$ (CIGS) and CdTe have potential to provide cost effective solar electricity. Flexible and lightweight solar cells are interesting for a variety of terrestrial and space applications as they offer potentially lower production cost and new application possibilities where lightweight, rollability, portability and high specific power (kW/kg, ratio of output electrical power to the weight of the solar module) are desired.

Alternative buffer layers and deposition

State of the art high efficiency CIGS solar cells contain a thin cadmium sulphide buffer layer between cell absorber and front contact. This buffer layer deposited by chemical bath deposition has limitations due to optical absorption loses below 2.4 eV and is not ideal for continuous in-line manufacturability. Therefore alternative materials and deposition processes are investigated and the properties of layers, heterojunctions,

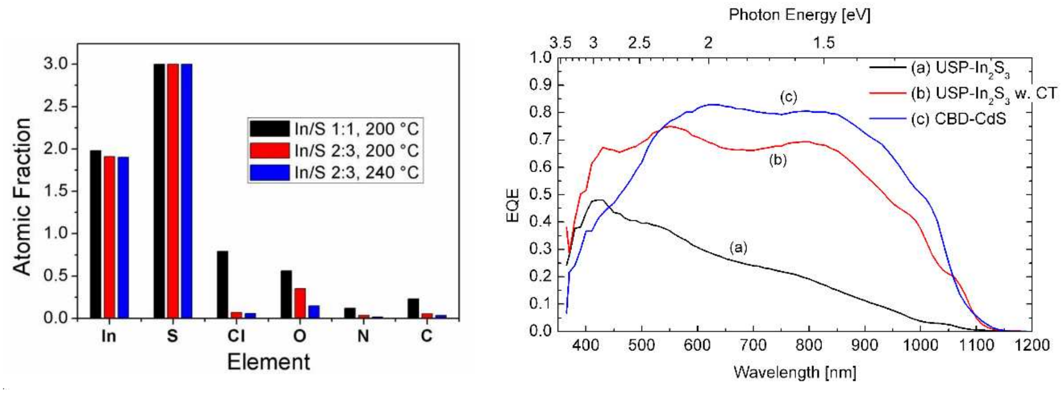

Figure 5: (left) Composition of layers on (111)-Si substrate deposited at different surface temperatures using solution of different In:S ratios as derived from ERDA measurements. (right) External quantum efficiency (EQE) of $Cu(In,Ga)Se_2$ based solar cells with different buffer layer: (a) sprayed In_2S_3, (b) sprayed In_2S_3 with 2 min chemical treatment (CT), and (c) CBD-CdS buffer reference cell.

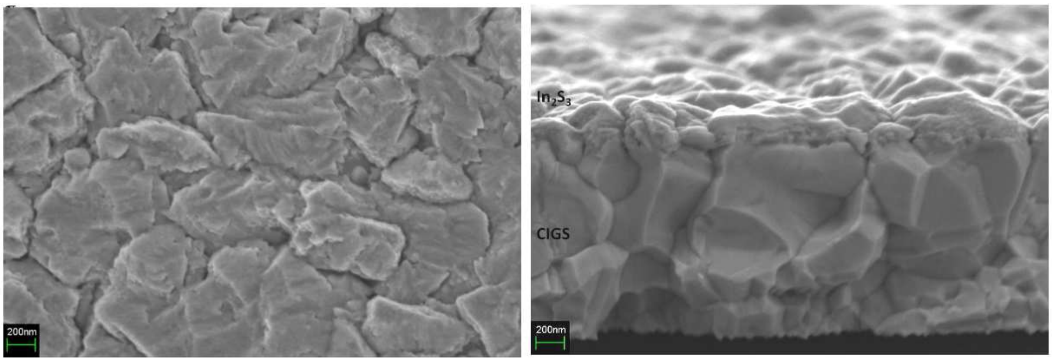

Figure 6: Surface morphology of the In_2S_3 film deposited on CIGS surface (a), and cross-section micrograph showing the presence of In_2S_3 buffer layer on CIGS film (b).

devices and meta-stabilities are studied with various analytical tools.
Non-vacuum deposited indium sulfide layers are a promising low-cost option as alternative buffer layers in CIGS thin film solar cells. The indium sulfide layers were grown by an ultrasonic spray pyrolysis method. Chemical analysis of the sprayed In_2S_3 films by RBS and ERDA revealed Cl, O, N, and C impurities; their concentration decreases with increasing substrate temperature and S excess in the solution. A chemical treatment of the as-deposited In_2S_3 buffer layer on CIGS for 2 min in a aqueous solution containing cadmium acetate, thiourea, and ammonia showed an improvement of the solar cell performance. Two distinct effects were observed: an increase of the Voc and FF for middle-high efficiency cells and for low efficiency cells additionally an increase in the Jsc. The external quantum efficiency (EQE) measurements suggest that collection of charge carriers is drastically improved if the buffer layer is chemically treated in Cd containing solution. The figure show the plan and cross-section of the polyimide/Mo/CIGS/(30nm) In_2S_3 stack. It was observed that the In_2S_3 film only non-uniformly covers the rough CIGS surface, which resulted in limited cell efficiencies. Furthermore the presence of intermediate residual Na(F) layer could be identified between the CIGS and buffer layers, which originates from the NaF post deposition treatment after CIGS growth. The presence of this residual layer is detrimental and a surface treatment method is needed to improve the interface properties of the hetetrojunction. A best cell efficiency of 10.1% was achieved for the flexible CIGS cell with indium sulfide buffer layer. This is 76% of the CdS reference cell, which yielded an efficiency of 13.2%.

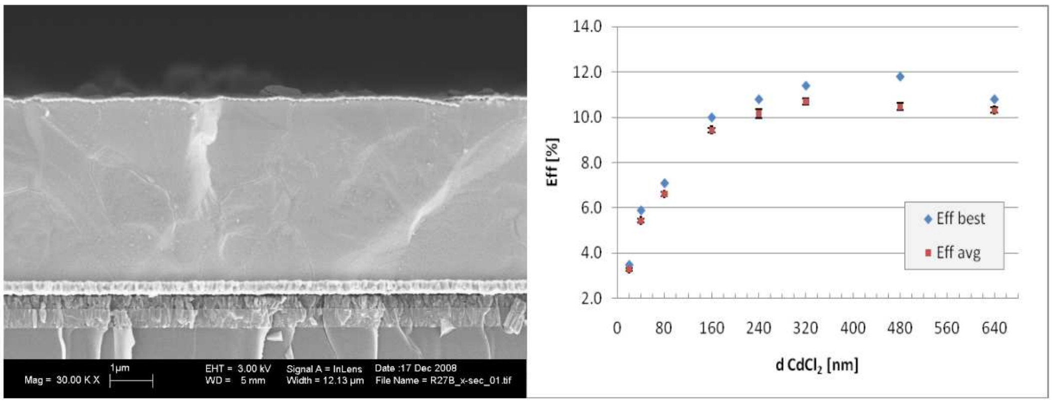

Figure 7: (left) SEM image of a CdTe thin film solar cell in superstrate configuration with highly resistive layer between the TCO and the CdS n-type junction partner. (right) Efficiency of CdTe solar cells versus the $CdCl_2$ layer thickness during the activation treatment.

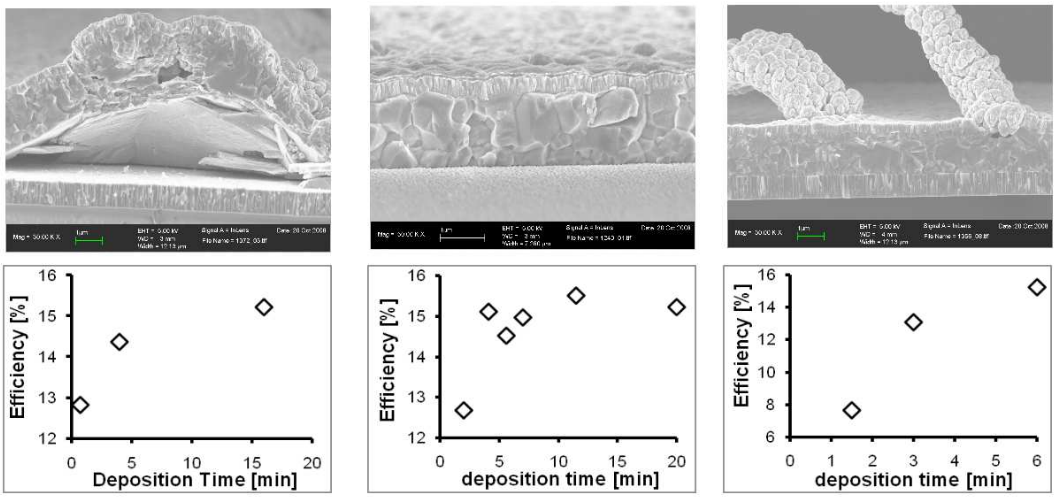

Figure 8: SEM micrographs (top) from CIGS films grown at high rates in the 1st stage (left), 2nd stage (middle) and 3rd stage (right) and solar efficiency dependence on the deposition time (bottom).

CdTe thin film solar cells by low-temperature deposition process

A highly resistive buffer layer between the front contact and the CdS layer in low temperature processed high vacuum evaporation (HVE)-CdTe/CdS thin film solar cells was implemented in order to reduce the optical absorption losses. An intrinsic ZnO layer, deposited by rf-magnetron sputtering, was used as high resistive transparent buffer layer. Substrate temperature as well as chamber pressure strongly influence grain structure, layer thickness and compactness. The growth rate of the layer increases with decreasing chamber pressure. X-ray diffraction revealed a preferred orientation in (002) direction with average grain size of 30 nm. The $CdCl_2$ layer thickness for the CdTe recrystallisation treatment was optimized to the new configuration. All solar cell parameters improved significantly with increasing $CdCl_2$ thickness and saturated with $CdCl_2$ thickness more than 400 nm. Best cell efficiency was 11.8%.

High growth rates for CIGS solar cells

We investigated the so-called three-stage vacuum evaporation process for the growth CIGS layers which yields the highest efficiencies up to date. In order to enhance the deposition rates the process steps were scaled down in time independently from each other. It was found that in each step very high deposition rates can lead to deterioration in solar cell performance. In the 1st stage the main problem is attributed to the selenium pressure which must be chosen appropriately high in order to avoid blisters forming due to stress relaxation. The 2nd stage posed was found to lead to degradation only at very high deposition rates. The 3rd stage proved to be crucial and we found that the selenium pressure needs to be extremely high in order to prevent the formation of copper whiskers which lead to shunts in the devices. The microstructures of CIGS absorbers grown at high deposition rates are shown in the figure. Depicted are the above described phenomena as the development of blisters and whiskers. Plots of cell efficiencies versus deposition time show, that the deposition speed can be increased by a factor of 3-4 without a significant efficiency loss if the modified three-stage process can be optimized further.

0.2 Publications

M. Rahim, F. Felder, M. Fill, H. Zogg
Optically Pumped 5 μm IV-VI VECSEL with Al-Heatspreader
Optics Letters 33, 24, pp. 3010-3012, 2008

M. Rahim, F. Felder, M. Fill, D. Boye, H. Zogg
Lead chalcogenide VECSEL on Si emitting at 5 μm
Electronic Letters 44, 25, pp. 1467-1469, 2008

H. Zogg, M. Arnold, F. Felder, M. Rahim, M. Fill, D. Boye
Epitaxial lead-chalcogenides on Si for mid-IR detectors and emitters including cavities
Proc. SPIE Vol. 7082, 70820H, 2008, 11 pages (invited)

N. Quack, S. Blunier, J. Dual, F. Felder, M. Arnold, H. Zogg
Mid-Infrared Tunable Resonant Cavity Enhanced Detectors
Sensors 2008, 8 (9), 2008, pp. 5466-5478

H. Zogg, M. Arnold, F. Felder, M. Rahim, C. Ebneter, I. Zasavitskiy, N. Quack, S. Blunier, J. Dual
Epitaxial lead-chalcogenides on Si for mid-IR detectors and emitters including cavities
Journal of Electronic Materials 37, 9, 2008, pp. 1497-1503

N. Quack, S. Blunier, J. Dual, M. Arnold, F. Felder, C. Ebneter, M. Rahim, H. Zogg
Vertically Moving Micromirror for Detectors in the Mid Infrared
Sensors and Actuators A: Physical, 2008, 5 pages

N. Quack, S. Blunier, J. Dual, M. Arnold, F. Felder, C. Ebneter, M. Rahim, H. Zogg
Tunable Resonant Cavity Enhanced Detectors using Vertical MEMS Mirrors
Journal of Opticts A: Pure and Applied Optics 10, 2008, 044015, 6 pages

D. Corica, S. Buecheler, D. Guettler, A. Chirila, S. Seyrling, R. Verma and A. N. Tiwari
Indium Sulfide Buffer Layer for Cu(In,Ga)Se2 Thin-Film Solar Cells Deposited by Ultrasonic Spray Pyrolysis
Proc. 23rd European Photovoltaic Solar Energy Conference and Exhibition, Valencia, Spain, Sept 1-5, 2008

S. Buecheler, D. Corica, D. Guettler, A. Chirila, R. Verma, U. Mller, T. P. Niesen, J. Palm and A. N. Tiwari
Ultrasonically Sprayed Indium Sulfide Buffer Layers for Cu(In,Ga)(S,Se)2 Thin-Film Solar Cells
Thin Solid Films (2008), doi:10. 1016/j. tsf. 2008. 10. 135

A. Romeo, S. Buecheler, M. Giarola, G. Mariotto, A. N. Tiwari, N. Romeo, A. Bosio, S. Mazzamuto
Study of CSS- and HVE-CdTe by different recrystallization processes Thin Solid Films (2008), doi:10. 1016/j. tsf. 2008. 10. 129

S. Calnan, H. M. Uphadhyaya, S. Buecheler, G. Khrypunov, A. Chirila, A. Romeo, R. Hashimoto, T. Nakada, A. N. Tiwari
Application of high mobility transparent conductors to enhance long wavelength transparency of the intermediate solar cell in multi-junction solar cells
Thin Solid Films (2008), doi:10. 1016/j. tsf. 2008. 11. 007

R. Verma, S. Buecheler, D. Corica, A. Chirila, S. Seyrling, J. Perrenoud, D. Guettler, C. J. Hibberd and A. N. Tiwari

Cu(In,Ga)Se2 Solar Cells with In2S3 Buffer Layers grown by Vacuum Evaporation and Chemical Spray Methods
Proc. 23rd European Photovoltaic Solar Energy Conference, Valencia, Spain, Sept. 1-5, 2008

0.3 Invited Talks

H. Zogg, M. Rahim, F. Felder, M. Fill, D. Boye
Lead-chalcogenide sensors and lasers for the mid-infrared range
10th Takanyanagi Kenjiro Memorial Symposium and 5th International Symposium on Nanovision Science: Nanospace Manipulation of Photons and Electrons for Nanovision Systems, Hamamatsu, Shizuoka University, Japan, Nov. 17-18, 2008

H. Zogg, M. Arnold, F. Felder, M. Rahim, M. Fill, D. Boye
Epitaxial lead-chalcogenides on Si for mid-IR detectors and emitters including cavities
SPIE Infrared Spaceborn Remote Sensing and Instrumentation XVI, San Diego , Aug. 10-14, 2008

Hans Zogg
Flexible Thin Film CdTe and CIGS Solar Cells
The 2008 Int. Symp. on Optoelectronic Materials and Devices, Chicago, IL, USA , Jul. 14-15, 2008

0.4 Talks

N. Quack, P. Rst, S. Blunier, J. Dual, F. Felder, M. Rahim, M. Fill, M. Arnold, H. Zogg
A Comb Drive Actuated Vertically Moving Micromirror for Mid-Infrared Resonant Cavity Enhanced Detectors
MNE 2008, 34rd International Conference on Micro- and Nano-Engineering, Athens, Greece, Sep. 15-18, 2008

F. Felder, M. Rahim, M. Fill, M. Arnold and H. Zogg, N. Quack, S. Blunier and J. Dual
Mid-Infrared Tunable Resonant Cavity Enhanced Detectors
MIOMD-IX, 9th International Conference on Mid-Infrared Optoelectronics: Materials and Devices, Freiburg, Germany, Sep. 8-11, 2008

M. Rahim, F. Felder, M. Fill, D. Boye, M. Arnold and H. Zogg
5 μm Vertical External Cavity Surface Emitting Lasers grown on BaF2 and Si substrates
MIOMD-IX, 9th International Conference on Mid-Infrared Optoelectronics: Materials and Devices, Freiburg, Germany, Sep. 8-11, 2008

R. Verma, S. Buecheler, D. Corica, A. Chirila, S. Seyrling, J. Perrenoud, D. Gttler, D. Brmaud, C. J. Hibberd, H. Zogg A. N. Tiwari
Cu(In,Ga)Se2 Solar Cells with In2S3 Buffer Layers grown by Vacuum Evaporation and Chemical Spray Methods
23rd European Photovoltaic Solar Energy Conference and Exhibition, Valencia, Spain, Sept 1-5, 2008

F. Felder, M. Rahim, M. Fill, M. Arnold, H. Zogg, N. Quack, S. Blunier, J. Dual
Durchstimmbare resonanzverstrkte Detektoren fr das mittlere Infrarot
DMBE WS08, Deutscher MBE-Workshop, Zrich, Switzerland, Sep. 1-2, 2008

M. Rahim, F. Felder, M. Fill, M. Arnold and H. Zogg
5 μm Vertical External Cavity Surface Emitting Lasers grown on BaF2 and Si substrates
DMBE WS08, Deutscher MBE-Workshop, Zrich, Switzerland, Sep. 1-2, 2008

A. Fognini, F. Felder, M. Rahim, M. Fill and H. Zogg
Wachstum und Charakterisierung von PbTe Quantendots in CdTe Matrix auf Si(111)
DMBE WS08, Deutscher MBE-Workshop, Zrich, Switzerland, Sep. 1-2, 2008

N. Quack, P. Rst, S. Blunier, J. Dual, M. Arnold, F. Felder, M. Rahim, M. Fill and H. Zogg
Mid-Infrared Tunable Resonant Cavity Enhanced Detectors Employing Vertically Moving Comb Drive Actuated MEMS Micromirrors

Optical MEMS and Nanophotonics 2008, Freiburg, Germany, Aug 11-14, 2008
F. Felder, M. Rahim, M. Fill, M. Arnold, H. Zogg
Durchstimmbare resonanzverstrkte Detektoren fr das mittlere Infrarot
38. IR-Kolloquium, Freiburg, Germany, Mar. 11-12, 2008
M. Rahim, F. Felder, M. Fill, M. Arnold, H. Zogg
Mid-Infrared Vertical External Cavity Surface Emitting Lasers for Spectroscopy
38. IR-Kolloquium, Freiburg, Germany, Mar. 11-12, 2008
A. Romeo, S. Buecheler, G. Mariotto, A. N. Tiwari, N. Romeo, A. Bosio, S. Mazzamuto
Study of CSS and PVD-CdTe by different recrystallisation processes
E-MRS Spring Meeting 2008, Strasbourg, France, May 26-30, 2008
S. Buecheler, D. Corica, D. Guettler, A. Chirila, R. Verma, U. Mller, T. P. Niesen, J. Palm, A. N. Tiwari
Ultrasonically Sprayed In2S3 Buffer Layer for Cu(In,Ga)(S,Se)2 Thin-Film Solar Cells
E-MRS Spring Meeting 2008, Strasbourg, France, May 26-30, 2008
S. Buecheler, D. Corica, A. N. Tiwari
Ultrasonically Sprayed Alternative Buffer Layers for CIGS Solar Cells
ATHLET general assembly, highlight session, Zurich, Switzerland, Jan 10-11, 2008
R. Verma, S. Buecheler, D. Corica, A. Chirila, S. Seyrling, J. Perrenoud, R. L. Sauaia, D. Gttler and A. N. Tiwari
Cd-free Buffer Layers for Cu(In,Ga)Se2 Thin-Film Solar Cells
A look inside solar cells, EMPA Workshop, Monte Verit, Ascona, Switzerland, 16-18 November 2008

0.5 Poster

S. Seyrling, S. Calnan, S. Buecheler, J. Hpkes, S. Wenger, D. Bremaud, H. Zogg, A. N. Tiwari
CuIn1-xGaxSe2 Photovoltaic Devices for Tandem Solar Cell Application
E-MRS Spring Meeting 2008, Strasbourg, France, May 26-30, 2008
R. Verma, D. Bremaud, S. Buecheler, A. Chirila, S. Seyrling, A. Zogg, A. N. Tiwari
Cu(In,Ga)Se2 Solar Cells with In2S3 Buffer Layer Deposited by Physical Vapor Deposition
E-MRS Spring Meeting 2008, Strasbourg, France, May 26-30, 2008
S. Calnan, H. M. Uphadhyaya, S. Buecheler, G. Khrypunov, A. Chirila, A. Romeo, R. Hashimoto, T. Nakada, A. N. Tiwari
Application of high mobility transparent conductors to enhance long wavelength transparency of the intermediate solar cell in multi-junction solar cells
E-MRS Spring Meeting 2008, Strasbourg, France, May 26-30, 2008
S. Buecheler, D. Corica, A. Chirila, S. Seyrling, D. Gttler, A. N. Tiwari
Indium Sulfide as Buffer Layer for Cu(In,Ga)Se2 Thin-Film Solar Cells Deposited by Ultrasonic Spray Pyrolysis
23rd European Photovoltaic Solar Energy Conference and Exhibition, Valencia, Spain, Sept 1-5, 2008
A. Fognini, F. Felder, M. Rahim, M. Fill and H. Zogg
Self assembled PbTe quantum dots in CdTe on Si(111)
MIOMD-IX, 9th International Conference on Mid-Infrared Optoelectronics: Materials and Devices, Freiburg, Germany, Sep. 8-11, 2008
S. Buecheler, J. Perrenoud and A. N. Tiwari
Development of Flexible and Stable CdTe Thin-Film Solar Cells
A look inside solar cells, Empa workshop, Monte Verit, Ascona, Switzerland, Nov 16-18, 2008