# Designing & Testing a Kelvin-Probe Head

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Proposal for a 'Beyond the Frontiers' research Honours Project
– by Timo Bretten, May 13, 2013

## Curriculum Vitæ


Timo Bretten

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### Education

- German Abitur, 2006
  - Gymnasium Rjeinkamp, Europaschule Moers
  - Bilingual (English-German)
  - Graded 1.0 (745 points of 750 possible)
- Bachelor of Science
  - Radboud Universiteit Nijmegen
  - passed 2012

### Extra-curricular educational activities

- Radboud Honours Academy
  - A two year, 40 EC, program for 'excellent students'
  - First year consisted of project work on achieving a sustainable Huygens-building
  - Second year consisted of a project entitled 'Solar Cell Models' in which I worked out theoretical solar cell models and applied them to a specific solar-concentrator cell, the SunCycle-Syste,
  - Second year also comprises a semester of practical lab-work at the Applied Materials Science centre.
- Kupcinet-Getz International Summer School 2012 at Weizmann Institute of Science

  - Two month of lab-work at Materials & Interfaces on an inversion-type Si/PDOT:PSS solar-cell
  - Attended six multi-disciplinary lecture sessions
- Attended Huygens-lectures during my B.Sc. (a broad choice of scientific lectures on diverse topics such as 'Lambda Calculus', 'Evolution', 'Digital Security' and 'Particle Physics')
- Within our student-corporation, "Leonardo da Vinci", I organised lectures; trips to companies and research institutes

### Miscellanea: Languages, Jobs, Experiences

- Languages: German (native); English and Dutch (fluent, academic level); French (basic - intermediate)
- Foreign-Exchange experiences
  - Two weeks in Venlo, The Netherlands in 1999 (English spoken)
  - Two weeks in Flixecourt, France in 2001 (French spoken)
  - One week in Liverpool, Great Britain in 2002 (English spoken)
  - Half a year in Christchurch, New Zealand in 2003 (English spoken)
- Work experience and internships
  - Three weeks as a cheap work-force in a reptile-zoo in 2000 (voluntary)
  - Three weeks internship 'Research and Development' at Sachtleben Chemie in 2005 (compulsory but enjoyable)
  - Four weeks as a kids-summer camp supervisor in 2006 (voluntary)
  - Half a year nature-conservation in the National Park Waddensea, comprising supervising tourist activities as well as nature-conservation work such as counting birds (as part of the compulsory German 'Zivildienst')
  - Half a year nature-conservation in Düsseldorf, comprising of supervising kids-activities, gardening, arboriculture and counting birds
  - Lab-Assistent for the practical courses 'Inleidend Practicum'; 'Practicum Condensed Matter'; 'Panorama Energie' & 'Natuurkundig Practicum voor Natuurwetenschappers' at the Radboud University

## Introduction, Motivation to participate

Thanks to exceptional high-school teachers, I found out quite early – at age sixteen – that I wanted to study science and participate in the scientific endeavour. Since I was equally interested in Physics and Chemistry, I decided to study 'Natural Sciences' in Nijmegen. In the first year, I was part of my studies' top 25%, I was highly motivated and was invited to take part in the disciplinary Honours Program. Thanks to that Program, I found out that my initial interest in more theoretical, fundamental questions was not for me after all. I became interested in sustainability questions and, due to my work with solar-cells at

the Department of Applied Materials Science, I very quickly found out that my strength lies in applied, hands-on lab work. For this reason, I also enjoy my position as a teaching-assistant for practical lab-courses.
About three years ago, during a study-trip to Israel, I made first contact with the highly prestigious Weizmann Institute of Science (WIS) and fell in love instantly. Scientists and students working there are all highly motivated, come from all over the globe & the work they do is truly multidisciplinary. I wanted to come back.
Two-and a half years later, I was lucky enough to be one of the select group [1] of international students who could participate in the Kupcinet-Getz Summer School. For two months, during the regular summer holiday, I worked at WIS, as a member of Professor Doctor David Cahen's Materials & Interfaces (M & I) group. My project there was hands-on lab work again, working on silicone based inversion-type solar-cells.
While there, I got to know a new site of myself. Never before had I been so motivated, so bursting with energy, so fully immersed in scientific work. The work mentality is not 'nine-till-five', but 'stay till it's done'. Upon asking, Professor Cahen did not hesitate to admit me back into his research group for another, extended stay.
Thus, independently from the Honours Program, I organised an 11-months stay at WIS starting this September. My reason to go back is to relive what I experienced during the summer: fulfilling work that keeps me busy all day. As such, combining my stay abroad with the extra challenge of the Honours Program seemed like a natural idea. The Honours Program offers a reasonable possibility to see how far I can push myself in the right environment, to go beyond my Master's study and to prove to myself that I am cut out for the demanding work-life of a scientific-researcher at an institute of higher learning.
The project I have in mind is very practical in nature, experimentally useful to my intended Masters' project and some of the knowledge I would gain would be applicable to other, future projects. Thus, it is completely in line with my interests and my preferred method of work.

# Letters of Recommendation, List of grades

Please confer to the Appendices for letters of recommendation and a list of grades.

# Research Proposal

## Project description

In Israel, I will be finishing my Masters studies with a project on gallium-arsenide surface passivation. I will not go into detail [2], but this solar-cell related project is heavily dependent on being able to do experiments in an oxygen-free environment and to, subsequently, measure surface properties, again without contamination by oxygen. For these reasons, I will carry out virtually all experiments in a glove-box.

[1] 30 admissions out of more than 150 applicants
[2] See the Appendices for the corresponding project proposal

An established, precise and above all non-invasive method for the detailed study of surfaces is the Kelvin Method. Currently, there is no Kelvin Probe available for use in a glove box. Mr. Nir Klein-Kedem, a Ph.D. student at M & I is tasked with assembling such a probe.
For this Honours Project, I would like to design a reliable Kelvin Probe-head and help Mr. Klein-Kedem with the assembly and testing of the full system.

**Contact Potential Difference Measurements, the Kelvin Method** The work function (w.f.) of a conductor is the change in free energy when an electron is removed far from the conductor to vacuum. The change in free energy is the change in electrochemical potential of the conductor plus the change in electrostatic potential of the electron removed. When two conductors with different Fermi-levels, i.e. different electrochemical potentials, are brought into electrical contact, charge will flow from one to the other until the difference in Fermi-levels is evened out. This will result in a buildup of charge and an accompanying potential between the conductors, the so called contact-potential-difference (c.p.d.).
Of the available methods to measure the w.f. of conductors, the Kelvin Method is applicable over the widest range of temperatures and pressures and is compatible with the most different kinds of materials. Since it does not rest upon ejection of electrons from the material, the w.f. obtained by the Kelvin Method is the arithmetic mean of the surface under study even when that surface is inhomogeneous. Methods that do rely on ejection are biased towards lower values, because ejection will preferably take place where it is easiest, i.e. where the w.f. is lowest.
The Kelvin Method measures the c.p.d between two conductors that form the electrodes of a capacitor $C$, connected by an electrical resistance $R$. When charge flows from one electrode to the other, a drop in voltage across $R$, $\Delta V_R$, can be measured. By varying the capacitance [3] a known amount of charge will flow, resulting in a known $\Delta V_R$, a series connected direct current backing voltage $V_B$ will result in $\Delta V_R = 0$, if $V_B$ is equal to the potential difference between the electrodes of the capacitor, i.e. the c.p.d of the conductors. If the w.f. of one of the electrodes is known, the w.f. of the other can be deduced from the c.p.d.

## Final Result

First and foremost, this Honours Project will result in a physical artifact: a working Kelvin-Probe that I could use in conjunction with the experimental work I plan to do for my Masters' project. Furthermore, I plan to write a detailed report about the design, assembly, testing and resulting precision of the Kelvin Probe. This report should be detailed enough for researchers given permission to access to assemble a corresponding system themselves. The report would also comprise an analysis of the precision of the probe and its benefits to my Masters project.

[3] for example by varying the distance between the electrodes

## Approach, plan of work

My stay in Israel will be for eleven months. During this time, as a student at WIS, I will be entitled to 14 free days apart from Jewish religious holidays. This gives me time enough to finish a 60 EC Masters' project as well as a 15 EC Honours Project, especially when one considers the 'stay-till-it's-done' work mentality at WIS. Since the whole proposed Honours Project relies on cooperation with other scientist and working-schedules of WIS's metal-workers, the following work-time estimation has some inherent uncertainties.

The actual Kelvin Probe apparatus itself is, of course, more complicated than the relatively simple theory explained above would suggest. Stray-capacitances, 1/f-noise, electrical-shielding & apparatus-vibrations complicate the measurement and even 'just' determining the w.f. of the reference-electrode all pose serious experimental difficulties. To address these issues, I estimate I would need 60 to 80 hours of time for literature research and discussions with Mr. Klein-Kedem & Dr. Ayelet Vilan, who assembled M & I's non-glove-box Kelvin-Probe.
The next phase would be the design of the actual probe-head itself. I would use CAD [4]-software to define the shapes of the probe-head's pieces. Through personal interest, I am already familiar with one example of CAD-software, have worked with another one during my current Masters project and am generally quick to pick up new ways of working with the the computer. The cutting & welding of the metal-pieces would be done by the institute's metal-workers. Fine-assembly of the head-pieces would again be my task, as would be testing the working of the probe-head. We would cycle this until satisfactory results can be obtained with the new apparatus. I expect to spend 200 to 240 hours on this main phase of the project.
The final stage of my proposed Honours Project would be writing a report about the assembly of the Kelvin Probe. With good documentation during the experimental phase, a draft of the report could be done 30 hours, but finalising the report in cooperation with Mr. Klein-Kedem and Dr. Cahen will take time again. In total, I would expect to spend 40 to 60 hours on writing the report.
Confer to Table 1 for a summary of the phases and accompanying work-times.

Table 1: Summary of the workload estimation.

| Project Phase | Estimated workload (hours) |
|---|---|
| Literature research | 60-80 |
| Building & Testing | 200-240 |
| Report | 40-60 |
| total | 300-380 |

[4] Computer-Aided-Design

## Estimation of costs

Since my stay abroad will be outside of Europe, the question if the exchange-rate arises. The currency in use in Israel is the 'New Israeli Shekel', NIS. The exchange rate 'Euro to Shekel' fluctuates a little, but is always close to ∼1:5.
I have arranged for accommodation in a student-house close to the Weizmann Institute. The room is 2000 NIS a month, or about 400 Euro. This is a regular price for a $10m^2$ room in Rehovot.
A return-flight from either Liège or Cologne to Israel can be bought for ∼ 300 Euro, transportation to the airport is negligible compared to other expenses.
I will sign-up for an Israeli health-insurance but will cancel my regular health insurance for the period of my stay, so this item will not result in additional cost, at 350 NIS/month, the price for insurance is comparable to what I pay in the Netherlands. See Table 2 for a detailed summary of the estimation of cost.

Table 2: Detailed estimation of reimbursable costs.

| Type of expense | estimated cost (Euro) |
|---|---|
| Return flight | 300 |
| Accommodation | 4400 |
| total | 4700 |

## References


[1] W. Thomson (Lord Kelvin), Philosophical Magazine 46, p.82 ( 1898).

[2] N.A. Surplice & R.J.D. Arcy, Journal of Physics E: Scientific Instruments 3, p.477 (1970).

[3] A. Zisman, Review of Scientific Instruments, 3, p.367 (1932)

[4] J. Bonet et al., Le Vide (Suppl.) 201, 1129 (1981).

[5] Baikie et al., Review of Scientific Instruments, 62, p.1326 (1991).

[6] I.D. Baikie, E. Venderbosch, J.A. Meyer and P.J.Z. Estrup, Review of Scientific Instruments,, 62, 725 (1991).


## Appendices

The appendices are independently added pdf-documents and will appear starting on the next page.
The list of grades will be followed by a letter of recommendation from Dr. Ing. John Schermer of the Radboud University, followed by a letter from Prof. Dr. David Cahen from the Weizmann Institute of Science. The last appendix is the research proposal for my Masters' project at the Weizmann Institute.

T.E. Bretten
Professor Bromstraat 104 -11
6525 BH NIJMEGEN



**Subject:** **File statement** **0800023**

**Date:** 13 May 2013

| Degree programme | Exami-nation | Fulltime/ Parttime | Specialisation | Exams | |
|---|---|---|---|---|---|
| Honoursopleiding Bachelor FNWI | - | P | | EB 30-08-2011 | passed |
| B Natural Sciences | - | F | | PB 31-08-2010<br>BA 31-08-2012 | passed bene meritum<br>passed |
| M Natural Sciences (research) | MA | F | | | |

**propedeuse bachelor results**

European Credits

| Course module | Title | Date | Result | Credits | Category |
|---|---|---|---|---|---|
| NWI-NP001B | Mechanics 1B | 31-10-2008 | 8,0 | 3,0 | |
| NWI-NP002B | Mechanics 2B | 23-01-2009 | 7,0 | 3,0 | |
| NWI-NP019B | Electricity and Magnetism 1B | 09-04-2009 | ND | | |
| NWI-SP001B | Structure&Reactivity Molec. 1 | 10-10-2008 | 10 | 3,0 | |
| NWI-SP003B | Structure&Reactivity Molec. 3 | 09-03-2009 | 7,5 | 2,0 | |
| NWI-SP004B | Function. Molec.&Materials 1 | 28-01-2009 | 8,0 | 3,0 | |
| NWI-SP005B | Function. Molec.&Materials 2 | 15-04-2009 | 6,0 | 3,0 | |
| NWI-SP006B | Function. Molec.&Materials 3 | 17-04-2009 | 6,0 | 1,0 | |
| NWI-SP007B | Function. Molec.&Materials 4 | 24-08-2010 | 8,5 | 3,0 | |
| NWI-SP008B | Meth.: Spectroscopy & Analysis | 30-01-2009 | 9,5 | 3,0 | |
| NWI-SP014B | Mathematics 1 | 05-11-2008 | 7,5 | 4,0 | |
| NWI-SP015B | Mathematics 2 | 26-01-2009 | 9,0 | 4,0 | |
| NWI-SP017B | Electricity and Magnetism 1A | 21-08-2009 | 9,0 | 3,0 | |
| NWI-SP024B | Project Biochemical Functional | 30-01-2009 | 7,5 | 2,0 | |
| NWI-SP025B | Mathematics 3 | 08-04-2009 | 8,0 | 3,0 | |
| NWI-SP027B | Physical Project Fuel Cells | 06-07-2009 | 8,5 | 3,0 | |
| NWI-SP028B | FGT | 18-06-2009 | 6,0 | 3,0 | |
| NWI-SP030B | Electricity and Magnetism 2A | 27-08-2009 | 9,0 | 3,0 | |
| NWI-SP033B | Oriëntation&Project Present. | 09-07-2009 | V | 1,0 | |
| NWI-SP034B | Project Synthesis | 17-04-2009 | 8,0 | 3,0 | |
| NWI-SP035B | Structure React. Molecules 2 | 07-11-2008 | 7,0 | 2,0 | |
| NWI-SP036B | Introductory Pract. Exercises | 07-11-2008 | 7,5 | 2,0 | |

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**Subject:** **File statement** **0800023**

**Date:** 13 May 2013

**propedeuse bachelor results**
European Credits

| Course module | Title | Date | Result | Credits | Category |
|---|---|---|---|---|---|
| NWI-SP039B | Mathematics 4 | 07-07-2009 | 8,5 | 3,0 | |
| **Total credits** | | | | 60,0 | |

**pre-master results**
European Credits

| Course module | Title | Date | Result | Credits | Category |
|---|---|---|---|---|---|
| NWI-TTM | Admission to Master courses | 15-12-2012 | V | 0,0 | |
| **Total credits** | | | | 0,0 | |

**bachelor results**
European Credits

| Course module | Title | Date | Result | Credits | Category |
|---|---|---|---|---|---|
| FTR-FIBO10 | Philosophy of Science | 06-04-2011 | 8,5 | 4,0 | |
| NWI-FCEM01B | Introduction course CEM | 26-01-2011 | 9,0 | 3,0 | |
| NWI-FCEM02B | CEM: writing skill | 03-11-2010 | 8,5 | 3,0 | |
| NWI-FFIL100 | Philosophy & Ethics of Science | 09-07-2010 | 7,5 | 3,0 | |
| NWI-FFIL202A | Evolution and the Mind | 04-11-2011 | 9,0 | 3,0 | |
| NWI-HC001 | Reflection | 02-11-2009 | 9,0 | 3,0 | |
| NWI-HC003 | The Universe | 25-01-2010 | 4,0 | | |
| NWI-HC004 | Intro Elementary Particles | 12-04-2010 | 7,0 | 3,0 | |
| NWI-HC007 | Self-Assembly in Materials and Life | 11-04-2011 | V | 3,0 | |
| NWI-HC009 | Evolution | 05-07-2010 | 10 | 3,0 | |
| NWI-HC010 | New Number Systems | 01-11-2010 | 6,5 | 3,0 | |
| NWI-HC012 | Climate, Energy and Sustainable Dev. | 04-07-2011 | 6,0 | 3,0 | |
| NWI-MOL027 | DNA-Technology | 05-11-2009 | 6,5 | 3,0 | |
| NWI-MOL028 | Statistics | 03-11-2009 | 7,0 | 3,0 | |
| NWI-MOL029 | Bioinformatics | 23-10-2009 | 7,5 | 3,0 | |
| NWI-MOL030 | Coordination Chemistry | 21-10-2009 | 7,0 | 3,0 | |

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Radboud Universiteit Nijmegen

**Subject:** **File statement** **0800023**

**Date:** 13 May 2013

**bachelor results**
European Credits

| Course module | Title | Date | Result | Credits | Category |
|---|---|---|---|---|---|
| NWI-MOL032 | Crystal Structure | 28-01-2010 | 6,0 | 3,0 | |
| NWI-MOL033 | Programming in Matlab | 21-01-2010 | 7,5 | 3,0 | |
| NWI-MOL034 | Condensed Matter Laboratory | 08-07-2011 | 8,0 | 3,0 | |
| NWI-MOL036 | General Physiology | 19-08-2011 | 7,5 | 3,0 | |
| NWI-MOL039 | Physics Laboratory | 16-04-2010 | 7,5 | 6,0 | |
| NWI-MOL040 | Thermodynamics 2 | 12-04-2010 | 6,0 | 3,0 | |
| NWI-MOL041 | Quantum mechanics 1 | 15-04-2010 | 7,5 | 3,0 | |
| NWI-MOL046 | Quantum mechanics 2 | 04-07-2011 | 8,0 | 3,0 | |
| NWI-MOL047 | Synthesis of Biomolecules | 25-08-2010 | ND | | |
| NWI-MOL050 | Condensed Matter | 02-07-2010 | 7,5 | 3,0 | |
| NWI-MOL051 | Spectroscopy Project | 09-07-2010 | 7,5 | 3,0 | |
| NWI-MOL056 | Chemical Bonding | 27-10-2010 | 6,0 | 3,0 | |
| NWI-MOL061 | Electromagnetism A | 29-08-2012 | 7,5 | 3,0 | |
| NWI-MOL062 | Quantum chemistry | 26-08-2011 | 7,0 | 3,0 | |
| NWI-MOL064 | Spectr.Atoms&Molecules | 25-01-2011 | 6,0 | 3,0 | |
| NWI-MOL068 | Electromagnetism B | 23-08-2012 | 6,0 | 3,0 | |
| NWI-MOL071 | Crystal Growth | 11-03-2011 | 6,5 | 3,0 | |
| NWI-MOL077 | Energymetabolism | 14-04-2010 | 8,0 | 3,0 | |
| NWI-MOL084 | Study tour Natural Science | 01-07-2010 | V | 3,0 | |
| NWI-NB001B | Analytical Mechanics | 18-01-2010 | 6,0 | 3,0 | |
| NWI-NB006B | Vibrations and Waves | 16-02-2010 | 7,0 | 3,0 | |
| NWI-NB021C | Programming | 02-05-2011 | 7,5 | 3,0 | |
| NWI-NB027B | Introduction to Biophysics | 15-07-2010 | 6,0 | 3,0 | |
| NWI-NB067B | Solid State Physics | 19-08-2010 | 6,0 | 3,0 | |
| NWI-RHA001 | Multidisciplinary Project | 01-06-2010 | V | 10,0 | |
| NWI-SB206 | Molecular Materials | 01-05-2012 | 7,0 | 12,0 | |
| NWI-SB252 | Bach.Pract.Appl.Mat.Science | 31-08-2011 | EXNV | | |

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**Subject:** **File statement** **0800023**

**Date:** 13 May 2013

**bachelor results**
European Credits

| Course module | Title | Date | Result | Credits | Category |
|---|---|---|---|---|---|
| **Total credits** | | | | 140,0 | |

EXAMENBUREAU
FACULTEIT DER NATUURWETENSCHAPPEN, WISKUNDE EN INFORMATICA
Radboud Universiteit Nijmegen

May 13th 2013

Dear Madam, Sir,

With this letter I wish to recommend Timo Bretten for a internship in your organisation. During his Bachelor studies Science at the Radboud University Nijmegen Timo was granted access to the honours program indicating that he was among the best students of his year.

During his previous extended Bachelor and current Master thesis projects in my group I learned to know Timo as a very enthusiastic and cleaver student with a very broad interest ranging from theoretical modelling of cell performance to experimental research on the optics of solar concentrator systems. Parallel to his own study Timo has been one of my assistants in a number of practical courses in Materials Science and Optics. During these courses he proved to be a dedicated guide to the students during execution of the experiments and provided valuable feed-back on the student reports.

Given his broad interest and previous performance I am confident that Timo is able to perform well in any challenging research project.

Kind regards,

Dr. ir. J. Schermer
Head Solar Energy Research
Institute for Molecules and Materials
Radboud University Nijmegen

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***David Cahen*** **דוד כאהן**
*Rowland and Sylvia Schaefer Professor in Energy Research*
Dept. of Materials & Interfaces *מחלקה לחומרים ופני שטח*
*Scientific Director,*
Campus-wide Alternative sustainable Energy Research Initiative (AERI)

March 28, 2013

To whom it may concern

From: David Cahen 

Re: Recommendation letter for Mr. Timo Bretten

Mr. Bretten has contacted me for performing his M.Sc. research in my group.

Mr. Bretten spent last summer in my lab in the framework of the Weizmann Institute's Kupcinet summer undergraduate program. He made a good impression, being very curious, eager to learn and enthusiastic and diligent. His work for this very short period of 2 months yielded interesting results on Si surface treatments for solar cells. He also fit in well socially with the group and I am glad that the period here kindled sufficient interest (or, at least did not diminish) in him to pursue his graduate studies in science.

His proposed research topic of "Towards chemically stable anti-oxidation/electrical passivation layers on gallium-arsenide surfaces" was initiated commonly - it has been and is within my scientific interests for a long time, but until recently I lacked the dedicated glove boxes to carry it out at the level of sophistication that we use now (in contrast to our path-breaking 2000 Vilan et al. paper).
Mr. Bretten is familiar with GaAs from his former work as under-grad. And this certainly helps him to understand the scope and the challenges in the proposed research. In view of this I trust that he is capable of accomplishing this task successfully and , therefore, will gladly welcome his in my group.

# Towards chemically stable anti-oxidation/electrical passivation layers on gallium-arsenide surfaces.

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A proposal for a one-year Masters graduation, visiting-student research project at the Weizmann Institute of Science

– by Timo Bretten, February 12, 2013

## Introduction

The field of semiconductor physics has led to incredible technological advances, virtually all of today's consumer electronics is based on silicon (Si) semiconductor technology. Apart from that other useful devices, such as the light emitting diode (LED) and other opto-electronics are also based on semiconductors, but not necessarily on Si. As a key technology solar cells offer a possibility to overcome our increasing energy demand while being balanced from a sustainability point of view. Here, gallium based III-IV semiconductors promise great potential for many already existing but also for emerging technologies. When talking about solar cells, gallium-arsenide (GaAs) based cells are especially promising because their band-gap is nearly perfectly aligned to the sun's spectrum as received on earth and can even be further engineered by additional lattice atoms such as aluminium (Al), indium (In) or phosphorous (P). However, there are also drawbacks to using GaAs, to wit, its unstable surfaces which are prone to oxidation under ambient condition and a lack of understanding of the surface chemistry involved [1]. In contrast to silicon, gallium-arsenide's natural oxides do not form a natural passivation layer, neither with respect to electrical nor to chemical passivation. This results in unwanted recombination sites within the material's band gap and consequent energy loss as well as material degradation over time. For example it has recently been shown by Martin Green, that even today's best GaAs solar cell could reach a $\sim 40\,mV$ increase in open-circuit voltage ($V_{oc}$) if non-radiative recombination were suppressed [2]. Yet, due to the material's difficulties, no sufficiently chemically stable passivation layers could be achieved by wet-chemical methods and costly techniques such as molecular-beam-epitaxy have to be employed to passivate GaAs, not at least because GaAs surface chemistry is more diverse [1] and thus much more complicated than Si's. Thus, studying gallium-arsenide surface chemistry and surface passivation in particular is interesting for applied as well as fundamental research.

## Proposed Research

### Short summary – work so far

Substantial research into GaAs surface chemistry and passivation has been carried out at the Department of Materials and Interfaces of the Weizmann Institute of Science and elsewhere. So far, (di-)carboxylic, thiol, phosphate & phosphonate functional groups have been adsorbed to GaAs surfaces. [3], [4], [5]. Depending on the molecular 'tail', surface passivation against oxidation, i.e. *chemical passivation*, was demonstrated, whereas suppression of recombination sites within the band-gap, i.e. *electrical passivation*, depends more on the headgroup that makes the actual bond

[1] At least two instead of just one lattice atom with several oxidation states each

with the GaAs surface. It could be shown by systematic variation of tailor made molecules that surface physics can be varied with the dipole of the molecule adsorbed to the surface [6]. Alkanethiol passivating properties could be enhanced by post-processing with ammoniumsulfide [7] and in an unrelated study it is stated that phosphorous leads to more chemically stable passivation layers since its oxide is thermodynamically more stable than sulphur-oxide with respect to arsenic [8].
In a different approach – functionalising the GaAs surface with chlorine and subsequent nucleophilic Grignard reaction – surface alkylation by a direct Ga-C bond was demonstrated and shown to provide fair passivating characteristics, electrically as well as chemically [9]. An interesting and experimentally relatively simple mechanism for self-assembled monolayer (SAM) formation on hydrophilic surfaces has also been demonstrated [10]. Here, an amphiphile, octadecylphosphonic acid (OPA), is dissolved in a nonpolar solvent. Strongly dependent on the hydrophobicity of the solvent, OPA will either aggregate at the solid-solvent interface with its headgroups pointing towards the solid or form micelles within the solvent.

## Outlook – proposed work

I propose to adopt the mechanism demonstrated by Nie for silicon-oxide($SiO_2$) and mica to gallium arsenide surfaces and investigate post-processing possibilities to answer these questions:

- can the mechanism demonstrated by Nie for hydrophillic surfaces be applied to GaAs and if so
  - what are the reaction conditions needed for formation of high quality self assembled monolayers of different chemical species onto GaAs surfaces?
  - can a systematic relation between surface-molecule interaction strength, solvent polarity as indicated by their dielectric constant, $\epsilon$, and molecular polarity/amphiphilic character be extracted?
- can post-processing with ammoniumsulfide enhance surface passivation with chemical species other than alkanethiol?
- will phosphorous rather than sulphur atoms adsorbed to the surface lead to even more stable passivation layers?

Since the mechanism intrinsically rests upon amphiphilic molecules being dissolved in a non-polar solvent, this route offers a water-free way to surface passivation and can thus be explored in the inert atmosphere of a glove box, hopefully allowing for virtually no oxygen contamination on the surface prior to passivation and after chemical etching. Nie studied octadeclyphosphonic acid initially and found that successful layer formation depends strongly on the dielectric constant of the solvent used to deliver the amphiphilic molecules compared to the polarity of the surface. By varying the amphiphilic character of the phosphonic acid to be delivered, i.e. by systematically changing the length of the hydrophobic 'tail', a reliable relation between solvent polarity, amphiphilic character and headgroup-surface interaction may possibly be extracted. Since oxide free GaAs' surfaces are hydrophobic rather than hydrophilic, it is reasonable to start with OPA and more hydrophobic solvents with an $\epsilon$ less than 4 , such as cyclohexane, toluene or o-xylene. Regarding the molecules to be used, it is too early to state definitively within which boundaries the tail-length should be varied. However, since GaAs is hydrophobic, I suspect molecules with shorter tails than OPA – decylphosphonic, octylphosphonic, hexylphosphonic acid... – to be more promising than longer ones. If the amphiphiles have too hydrophobic a tail they could develop a tendency to aggregate with their tails rather than their heads toward the surface. Once a relation as mentioned has been found, it may be possible to predict which solvents should be used to form high quality monolayers of amphiphilic molecules with suflonic and carboxylic headgroups, which are already known to bind

to GaAs and provide electrical passivation. Contrary to the probable requirements for the mechanism to work, to fulfil the ultimate goal of a high quality SAM with good electrical and especially chemical passivating properties, it is likely that 'long-tailed' molecules [2] will produce best results. The longer the tail, the stronger the stabilising intermolecular van der Waals interactions within the monolayer will be and the more of a barrier against oxygen the monolayer will constitute. Of course, if junction formation for solar-cell device fabrication is aimed at, it should also be considered that – at least at high forward bias – longer-tailed monolayers will result in more insulating layers, hindering current transport across the junction [11]. Finding the right balance between desirable chemical stability of the layer, chemical passivation against oxidation and its transport characteristics within the boundaries set by the mechanism may well be a research project of its own.

Once a stable SAM is achieved[3], post-processing possibilities may be explored, from this point on independently of the research into SAM formation chemistry. The dual approach offers a chance to obtain viable results even if experimental obstacles are encountered in one of the separate directives.

After preparation, both ellipsometry and contact-angle measurements provide a quick first characterisation of the monolayer: layer thickness [4] and surface coverage can be gauged. A peak shift in the $CH_2$ antisymmtric stretch of (fourier-transform) infrared spectra can reveal information about the monolayer's molecules's phase – liquid vs. solid-like – and thus also about their stability and adherence to the GaAs surface. Contact-Potential-Difference reveals how successful the surface was passivated electrically. Ascertaining a level of electrical passivation and observing its degradation over time, for example as a function of ambient oxygen or water-vapour concentration, would gain insight into the layer's chemical stability. At the same time, X-ray Photoelectron Spectroscopy (XPS) can reveal information about the oxidation state of the atoms involved and in what ratios the different oxidation states are present. It offers the possibility to check if all the oxygen present on the surface is due to the phosphonic, sulfonic or carboxylic groups or due to surface oxides, thus, XPS measurements, especially when done over time, possibly reveal a great deal of information about chemical passivation.

Junctions for study of current-voltage characteristics could be made either with Hg-drop or LOFO-Au deposition, both these approaches have already been shown to form non-destructive, non-shorting top-contacts on alkyl-tailed monolayers [6], [12]. The drawback of these two materials is their being opaque, thus only dark junction characteristics could be studied. Top-contacting via a conductive polymer, for example PDOT:PSS [13], or thinly evaporated lead [14] using evaporation-masks could also be explored and would allow for dark as well as light characterisation of the junction. It has been hinted that surface layer quality can be assessed from I-V measurements alone [3]. If this trend can be reproduced, it could save considerable time in analysing the GaAs surfaces. Generally, temperature dependent I-V would gain more detailed insight into the transport mechanisms across the junction – thermionic emission vs. tunneling vs. more involved mechanisms – and its dependence on the type of bond on the surface.

Substantial and promising research into surface chemistry & electrical transportation across molecular monolayers in general and into gallium-arsenide passivation in particular is being carried out at the Weizmann Institute of Science. Supported by the experimental facilities and expertise present in the group, I trust the proposed strategy to provide a fruitful step towards reproducible and reliable preparation of stable anti-oxidation/chemical passivation layers on gallium-arsenide.

[2] 10 carbon-atoms and more

[3] Either via the mechanism proposed by Nie or, if this proves to be inapplicable to GaAs, the one already demonstrated by Shpaisman [3]

[4] and thus the angle the molecules make with the GaAs surface

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