CECAM/Psik Workshop Scientific Report

Workshop: **Reliable and quantitative prediction of defect properties in Ga-based semiconductors**

Organizers: *Klaus Irmscher (IKZ Berlin, Germany)*
Susanne Siebentritt, (University Luxembourg)
Joel B. Varley (LLNL, US)
Peter Deák (University of Bremen, Germany)
Thomas Frauenheim (University of Bremen, Germany)

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I. State-of-the-Art Summary

Defect engineering in micro/optoelectronics and in photovoltaics has immensely profited from electronic structure calculations. In the past two decades, local and semi-local approximations of density functional theory were the workhorses of theoretical studies but, by now, it has become clear that they do not allow a sufficiently accurate and reliable prediction of defect properties in wide band gap materials. While *ab initio* energy methods for calculating the total energy are struggling with the system sizes necessary for defect modeling, semi-empirical methods using various corrections or hybrid functionals are being applied for the purpose. While the theoretical background of these methods and their relation to each other is by now more or less understood, the transferability of the semi-empirical parameters and the overall predictive power is still unclear. Progress requires further systematic testing and comparison of the various methods, as well as validation against experiments. For that, accurate measurement data on defects are needed on a set of materials, which are structurally or compositionally related. Gallium based semiconductors, like GaN, Ga_2O_3 and $CuIn_xGa_{1-x}Se(S)_2$ chalcogenides (CIGS) offer a good possibility for testing theory and are interesting also experimentally due to their versatile applications. While there are still open defect-related questions in the much studied blue LED-material GaN, very few defects could be positively identified as yet in CIGS solar cell materials, while the research on the potential power semiconductor and UV transparent electrode Ga_2O_3 has barely started. Following the successful workshops on Gallium Oxide and Related Materials, held in Kyoto (Japan) in 2015, and in Parma (Italy) in 2017, as well as several workshops on chalcogenide photovoltaic materials, e.g., Symposium V at the E-MRS Spring meeting 2016, the CECAM-workshop in Bremen 2018 has focused on bringing together experimentalist interested in gallium oxide and Ga-based semiconductors with theorists who are active in the field. A friendly and stimulating environment has facilitated discussions, adding impetus to both the development of practically applicable theoretical methods and to progress in the defect engineering of these materials.

The workshop in Bremen has become a forum to discuss experimental and computational progress, and to generate a unified understanding of defect related properties in Ga-based semiconductors. We have been successful to achieve the following key objectives:

- Bringing together researchers from experiment and theory working on defect characterization and electronic structure simulations related to optoelectronic and photovoltaic properties, in order to highlight recent progress, and to discuss challenges and opportunities in applying beyond-standard DFT methods to predict properties of defects in these materials.
- Foster the exchange of methodological expertise and new developments between scientists working on different theoretical approaches for application to defects in Ga-based bulk semiconductors.
- Discussing possibilities for optimizing the materials properties and to carry out highly accurate defect spectroscopy on well defined samples.
- Provide opportunity to form new worldwide interdisciplinary collaborations on spectroscopic defect characterization for the mutual benefit of theoretical, experimental and applied researchers.

The program consisted of 28 invited talks of 40 minutes (30+10) each and one poster session presenting 18 posters. In addition, social events (reception and conference dinner) were held to allow for informal exchange. The invited talks were given by well-established scientists from the different theoretical and experimental communities, which acted as platform for interesting cross-/interdisciplinary discussions. The invited talks were followed by a poster session where young participants showed their scientific work/progress and exchanged ideas in a broad field of computational chemistry, solid state physics and computational materials science. The organization was very compact with the scientists accommodated in the same hotel, fostering exchange and discussion between the participants also outside the meeting room.

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II. Scientific content, main outcome of key presentations, selected discussions

The workshop has brought together theoretical and experimental physicists interested in three areas of materials science, related to power electronics, optoelectronics and photovoltaics. All three areas apply Ga-based semiconductors: GaN for power devices and light emission, $CuGa(In)Se(S)_2$, for short CIGS, for photovoltaics, and Ga_2O_3 for power devices or as transparent conductor in light emitting or photovoltaic devices. These materials are all based on Ga but, due to their different structure and composition, span a band gap range from 1.7 eV to 4.9 eV. This makes it necessary to treat them with different techniques both experimentally and theoretically. Therefore, general talks were also invited, bringing in earlier experience, e.g., on band structure engineering and doping control (S.H. Wei, Beijing CSRC, PRC; S. Lany NREL, USA), or the effect of amorphisation (J. Cottom, Univ.Collge London, GBR). Methodical issues were also discussed in CV and DLTS measurements (J. Lauwaert, Ghent Univ., B; M. Igalson, Warsaw U. Techn., P), and in the application of TD-DFT (S.B. Zhang, RPI, USA), many-body theory (M. Feneberg, O.v.Guericke U. Magdeburg D), and computer-assisted search for new material combinations (C.A. Sutton, MPI_F.Haber.Inst, D).

Among the three materials, the workshop focused on, GaN appears to be the most established: not so much because of the level of understanding in defect behavior, but because this defect-tolerant material has allowed quick and wide-scale applications. Still the issues of p-type doping (with Mg the only shallow acceptor) and the effect of carbon (used to produce semi-insulating layers) continue to be of interest (A. Pasquarello, EPFL, Ch; M. Lorke, U. Bremen, D). CIGS materials have a great potential in photovoltaics but further increase in efficiency can only be achieved if defects can be identified and treated. As the talks on this subject have shown, the field is still far from consensus; progress in theoretical and experimental methods are required considerable progress has been made in identifying and attributing native defects and impurities (S. Siebentritt, U. Luxembourg, L; D. Lamoen, U. Antwerp, B., S. Schorr, HZ Berlin, D., HP Komsa, Aalto U, Espoo, FIN, Zh. Zeng, ISSP of the Chinese Acad. Sci, PRC). In particular, effects of metastable behavior of defects can dominate the response of the material (M. Igalson, U. Warsaw, P, D. Kuciauskas, NREL, USA). Ga_2O_3 is still a relatively new material. Several talks have summarized the achievements so far and pointed out the issues which still have to be investigated. The conference brought also new contributions in this field (see below).

Particular highlights of the conference were:

Experiment

Gallium sesquioxide, in particular its stable monoclinic phase β-Ga_2O_3, was in the focus of six experimental talks (M. Martin, RWTH Aachen, D; O. Bierwagen, PDI Berlin, D; H. J. v. Bardeleben, Sorbonne U. Paris, F; E. Nogales Diaz, Complutense U. Madrid, E; K. Irmscher, IKZ Berlin, D; M. Stavola, Lehigh U. Bethlehem, USA) thereby reflecting the present enormous interest in this material with great potential in power and optoelectronics. This issue was well supplemented by the discussion of growth and formation of metastable modifications of Ga_2O_3 with emphasis on the ε-phase (M. Eickhoff, U Bremen, D). All these talks showed that the interpretation of the experimental results benefits from theoretical predictions (see below), but also needs further iterative refinement of experiment and theory to be conclusive. As an example of defects in β-Ga_2O_3 of practical importance, the gallium vacancy and its complexes with hydrogen which counteract the intended n-type conductivity, an electron paramagnetic resonance study (H. J. v. Bardeleben, Sorbonne U. Paris) and a local vibrational mode investigation (M. Stavola, Lehigh U. Bethlehem, USA) elaborated these defects in much detail and certainty. It was shown that the experimental results can only be correctly interpreted with contributions from theory.

Progress in e**xper**imental characterisation of electronic defects in CIGS was presented, based on optical and electrical methods (S. Siebentritt, U. Luxembourg, L). The methodological limitations of electrical measurements were discussed in detail (J. Lauwaert, Ghent Univ., B). Of particular interest in these materials are metastable effects in the macroscopic behaviour of devices, which can be traced back to the metastable behaviour of individual defects. (M. Igalson, Warsaw U. Techn., P, D. Kuciauskas, NREL, USA). The programme was complemented by a discussion on structural methods to indentify native point defects (S. Schorr, HZB, D.)

Theory and computational studies

In the CIGS field, the most important theoretical progress shown was the successful treatment of extended defects (D. Lamoen, U. Antwerp, NL; K. Albe, TU Darmstadt,

D). New insights into the properties alkaline impurities and their role in secondary phase formation at grain boundaries were also provided (H.-P. Komsa, Aalto U., SF). These aspects illustrate the state-of-the-art theoretical models for understanding the remarkable properties of CIGS-based photovoltaics and the role of various processing steps (e.g. alkali post-deposition treatments) that have led to improved performance.

A majority of the theoretical contributions concentrated on the new semiconductor Ga_2O_3. After an excellent review on the subject (C.G. Van de Walle, UCSB, USA) significant progress was reported on defect complexes (J.B. Varley LLNL, USA) and on the luminescence properties (P. Deák, U. Bremen, D), as well as advanced theoretical phase diagrams for maximizing doping concentrations in language more understandable to experimentalists (S. Lany, NREL, USA). These studies, in conjunction with related experimental studies (K. Irmscher, IKZ, D; H. J. von Bardeleben, U. Sorbonne, FR; M. Martin, RWTH Aachen, D; and M. Stavola, Lehigh, USA) showed that theory and experiment are converging to understand the dopant and defect-related properties in Ga_2O_3, but that there is much work to be done in resolving the identities of observed and problematic point defects.

III. Assessment of the results and impact on future direction of the field

While GaN will probably serve only as a test field for method development in the future, CIGS and Ga_2O_3 require a lot of progress in the knowledge of defects. The workshop has successfully brought together theorists and experimentalists in these fields, allowing a synthesis of the achievements so far. Ga_2O_3 is still in a data collection phase, requiring additional studies to systematically address extrinsic and complex defects, both theoretically and experimentally. The defect physics of CIGS seems to be slowed down by inaccuracies in theory and interpretation problems of experiment, requiring methodology improvements on both sides. For example, it became apparent that many comparisons between experimentally measured defect levels and the theoretical predictions are commonly flawed owing to misunderstanding of the reported theoretical levels (e.g. thermal versus optical transitions) and not comparing the relevant transition energies. By bringing the most recognized experts in both theory and experiment, the workshop helped to address these issues and shape the future direction of research.

IV. Infrastructure requirements to make advances in the field

As discussed above, the advancement of theories of the operation of semiconductor defects requires the development of novel theories and codes which can i) capture the inherent complexity of intersystem crossing processes and ii) contain sufficiently accurate description of physico-chemical processes, including photon-electron interactions, electron-hole coupling, electron-phonon coupling, etc. The development of such theories and the resulting computer software will benefit the broad community of theoretical researchers, but also have important impacts on experimental studies and industry. However, to achieve this, a continued investment is required, as method and code development usually occur on a longer time scale compared to the study of applications. This also requires the training of masters and PhD students not only in physics, materials science or biology, but also in computer programming (including parallelization of software) and use of high-performance computing resources.

V. *Impact to address the need of industry in driving economic growth*

The development of theoretical and experimental models to understand the role of point and extended defects in CIGS, as well as beneficial process steps (alkali treatments) are critical to optimizing the performance of commercial CIGS solar cells. Understanding which defects and additives are the most beneficial and/or problematic is a key step in designing process steps that could ultimately improve efficiencies and reduce costs in the manufacturing of these solar cells, which would increase the adoption of CIGS-based solar cells.

Community needs (minimum 1000, maximum 2000 characters)

Discuss the needs of the community in terms of computational infrastructure (e.g. existing codes, use of HPC resources), networking (e.g. outreach to other communities including experimentalists), event organization (e.g. should a series of CECAM workshops on this topic be considered and if so why?)

The discussions at the workshop made it evident that two significant research directions have started to emerge in the field of computational studies for single point defect applications. First, for complete quantitative understanding the physics of know point defects, the community needs to carry out highly accurate calculations of the electronic structure and numerous of derived magneto-optical quantities in realistic models of single point defects. For the electronic structure calculation, the workhorse method today is the HSE06 hybrid functional, which provides reasonably convergent electronic structure in supercell models as large as ~500 atom. For superb numerical accuracy one needs to apply either larger supercell, consisting of 1000-3000 atoms, or increasing the number of k-point for sampling the Brillouin-zone, e.g. to 2x2x2. For appropriate treatment of excited states, one need to apply high level approaches. Recent methodological developments made sophisticated calculations, such as GW+BSE and cRPA+CI, practically feasible on point defect supercell models. The second emerging direction is the identification of potential point defect for single defect applications. This direction requires a systematic search in the zoo of intrinsic and impurity related defect in 2D and 3D semiconductor hosts.

Funding (minimum 500, maximum 1000 characters)

Summarize typical funding channels and identify possible new sources in upcoming calls e.g. Horizon 2020, national funding schemes. Was the possibility of joint research proposals discussed during the meeting?

The EU has launched the FET Flagship on Quantum Technologies as a part of Horizon2020, and the consortia of the first round of calls are being established where the leading scientists participated at the conference. In addition, EU QuantERA initiative fosters cooperation between theoretical and experimental groups on solid state qubits in Europe where again the consortia have been formed and started to work together. Future calls are expected to appear in the Quantum Technology and QuantERA where the cooperation was discussed between the participants in the social events and breaks of the conference.

Furthermore, national quantum technological programmes support research and development in the field in the European countries, the USA, Japan, China, Australia.

Will these developments bring societal benefits? (minimum 1000, maximum 2000 characters)

Discuss potential societal benefits of the research topic of the workshop. For example, summarize economic benefits, through the use of our methods by industry; societal benefits such as sustainability; health benefits such as novel drug design. If possible reference funding opportunities related to these benefits.

October 20th 2018

The Organizers