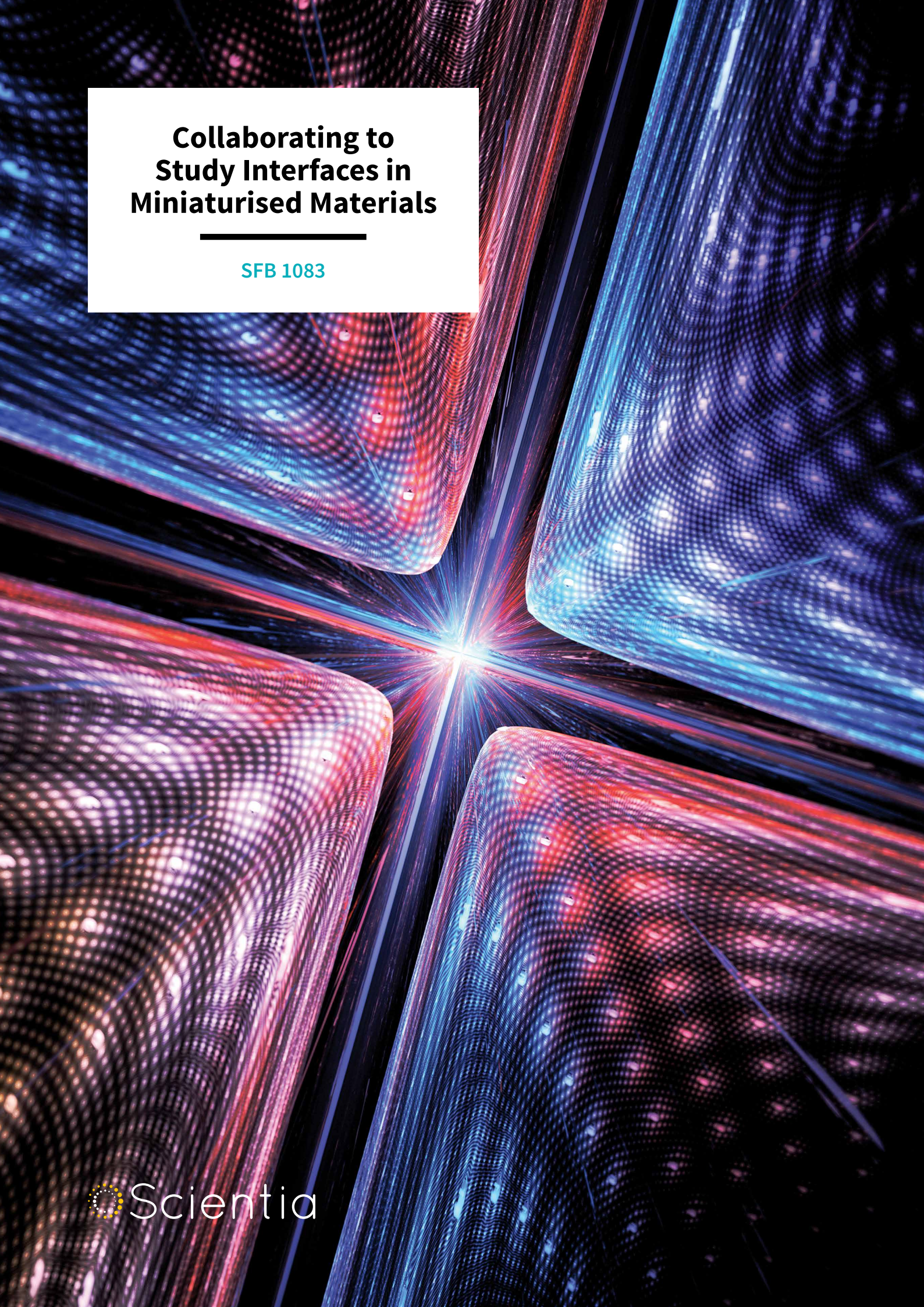


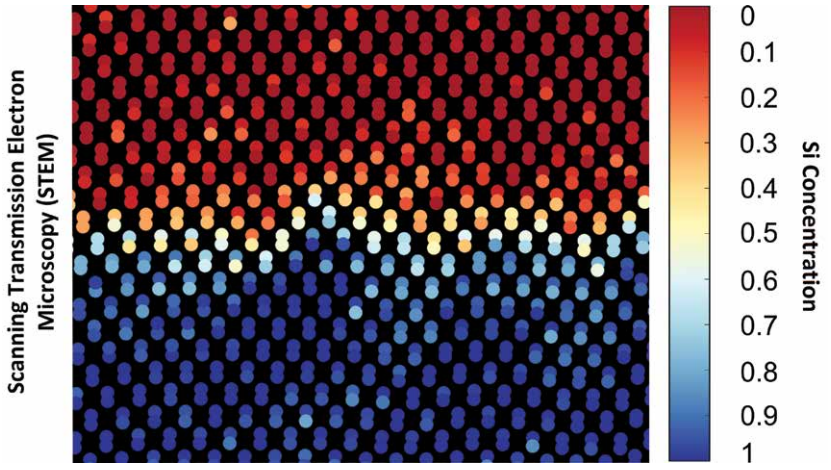
Collaborating to Study Interfaces in Miniaturised Materials

SFB 1083

Scientia

COLLABORATING TO STUDY INTERFACES IN MINIATURISED MATERIALS

Creating technologies from multiple materials with different physical properties can be hugely beneficial, but the process doesn't come without its challenges. As we fabricate new devices, an understanding of the physics occurring at the interfaces where different miniaturised materials meet is now crucial, but seriously lacking. Based at Philipps-Universität Marburg, the Collaborative Research Centre SFB 1083 is a wide collaboration of researchers at institutions across Germany, who are tackling the diverse range of problems involved with these interfaces.



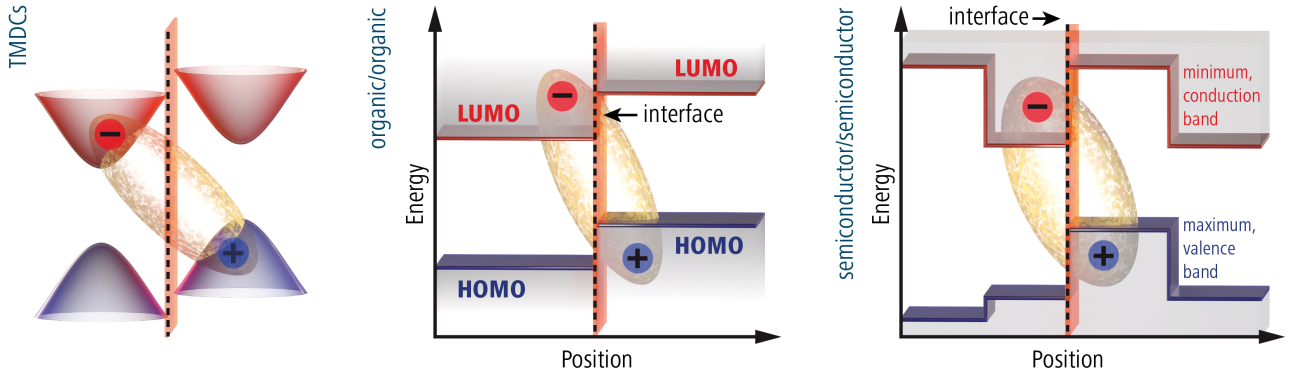
As modern technologies rapidly improve, the materials they are made from must become more and more complex. To keep up with new advances, scientists can often create useful properties in materials by bringing two or more solids into contact with each other in intricate, innovative ways. This might sound fairly simple, but in fact, the physics involved in building materials from multiple solids quickly becomes complicated.

At the heart of the issue are the elusive properties of internal interfaces – the planar surfaces where solids come into contact with each other, hidden from outside-view. Perhaps one of the most relevant examples of internal interfaces in technology today is seen in miniaturised semiconductors.

Because of their composition, semiconductors have the remarkable ability to switch between being conductors and insulators. If the temperature of the material changes, or a voltage is applied across it in a certain direction, its conductive properties can be easily changed. These effects have made semiconductors vital components of the modern electronic devices we use every day, including transistors and diodes in computers, radios and mobile phones.

Increasingly, hybrid miniaturised semiconductors made from multiple solids are being used to allow these electronic systems to become increasingly intricate and sophisticated, and the interfaces between these solids determine many of their useful optical and electronic properties. However, miniaturisation of these hybrid semiconductors introduces a wide range of challenges, stemming from the greatly increased influence of the interface between the different solids compared with previous materials.

Typically, when scientists probe large (non-miniaturised) hybrid materials to measure their properties, the resulting signals they observe are dominated by those originating from atoms in the interiors of solids, which comprise almost their entire volume. Comparatively, far fewer atoms are found in the edges of solids, meaning the interfaces between solids have virtually no effect on the properties of the overall material.



For miniaturised materials, however, these interface atoms have a far greater influence, as the ratio between interface atoms and those within the interior is far greater. In semiconductors composed of graphene and metallic monolayers, for example, every atom is in contact with an atom in another material, making an understanding of the interfaces involved fundamental to understanding the properties of the overall material. Previously, our knowledge of what is happening at interfaces at a microscopic level has not kept up with improving technologies, making it increasingly difficult to engineer more desirable miniaturised semiconductors. Now, a new research collaboration known as 'SFB 1083' aims to address this problem in detail.

To solve the wide variety of issues arising from internal interfaces, SFB 1083 has brought together groups of researchers throughout Germany in fields including chemical synthesis, semiconductor physics, structure analysis, and laser spectroscopy. Using their combined expertise, the researchers use experiments with specially prepared model systems, with internal interfaces that are precisely engineered to allow their optical and electronic properties to be intricately analysed on an atomic level. In the last few years, the collaboration has followed four important lines of research, each focusing on different issues.

Analysing the Structure of Gallium Phosphide/Silicon Interfaces

Although internal interfaces represent definite boundaries between solids, they don't always appear as distinctive lines. For materials connected at their interfaces, the atoms on the edge of each solid appear to intermix with each other, making the interface appear blurred and unpredictable. This apparent intermixing presents difficulties to interface models that assume abrupt boundaries between solids with little mixing.

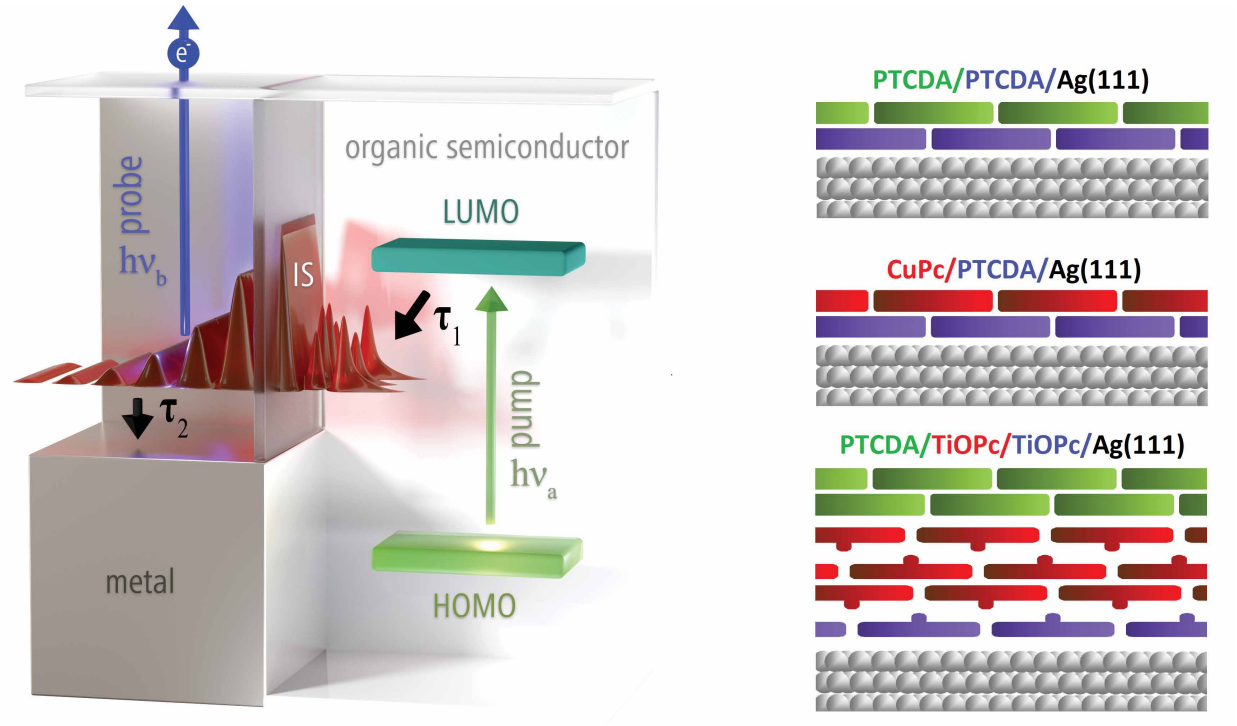
However, in one special case analysed by SFB 1083 collaborators, intermixing between two particular solids is far easier to observe. When the SFB 1083 researchers deposited the semiconducting material gallium phosphide (GaP) onto silicon (Si), they noticed that characteristic pyramids of atoms formed across the silicon surface, translating into predictable limits to the smoothness of the interface. For scientists wishing to study the behaviour of internal interfaces, this is remarkably useful.

An important step to image the imperfections in a GaP/Si surface was taken in a 2013 study, led by Kerstin Volz at Philipps-Universität Marburg. In the study, the team analysed how the performance of semiconductors grown on silicon surfaces is affected by defects on the silicon, in turn affecting the distribution of electric charge at the interface. Using a highly sensitive imaging technique called scanning transmission electron microscopy, the researchers imaged the defects to reveal their atomic structures for the first time. Where the GaP/Si border previously seemed intermixed, images of the interface revealed a scale small enough to show abrupt boundaries between the solids. The team discovered that the defects introduced local regions of electric charge, ultimately determining the performance of the overall semiconductor.

After this study, the researchers' attention turned to how GaP/Si semiconductors could be built and fine-tuned on atomic scales. As semiconductor volume decreases, the contribution of internal interfaces becomes increasingly important, making a detailed understanding of their molecular properties all the more crucial.

In a 2016 study, the team zoomed out from the atomic scale studied in their previous work, to reveal characteristic molecular-scale structures at the GaP/Si interface. They discovered that what appeared to be intermixing between the solids were, in fact, distinctive pyramids on the silicon surface, which formed to minimise the mechanical stresses that arise when GaP is deposited. With knowledge of this structure, descriptions of how miniaturised semiconductors could be engineered to optimise their optical and electronic properties, taking the molecular roughness of their interfaces into full account, could be made for the first time.

One particularly useful application of the research was the improvement of a new type of laser, in which electrical



charges are transferred across internal interfaces. Lasers that operate using single-solid semiconductors are difficult to create, since they must operate at low frequencies of light – created in a process in which electrons are ejected from their atoms, changing the fundamental properties of the material.

So, a fundamentally new solid-state laser was engineered by the theoretical physicists of the SFB and afterwards built, utilising the interfaces in a stack of gallium-based semiconductors. With 'W-lasers', named for the shape of the arrangements of electron energy levels in the material, transitions between solids across internal interfaces can create high frequencies, which are not strongly diminished. Using the insights gained by the collaborators, the roughness of interfaces could be carefully designed, allowing for the controlled operation of powerful lasers at high, optical frequencies. In addition, knowledge of miniaturised semiconductor interfaces could be crucial when improving miniaturised computer technology.

Transferring Charges Across Interfaces

The process of charge transfer itself is an important area of SFB 1083's research, as negatively-charged electrons do not always cross internal interfaces directly; rather, the process often occurs through charge-transfer (CT) 'excitons'. In regular materials, excitons form when a charge is excited to a higher energy level, leaving behind a 'hole', which represents where the particle would be if it moved back into its original energy level. Each exciton consists of an excited particle and its respective hole. In CT excitons, the particle and its hole form between particles on either side of the interface, ultimately allowing the two solids to interact with each other.

In theory, when excited electrons move back into their respective holes, they transfer across the interface while emitting photons of light that determine the optical and electronic properties of the overall semiconductor. However, for semiconductors made from solids of different compositions, exploiting this process becomes difficult in practice. To truly understand what is happening as electrons separate and recombine, a knowledge of CT excitons is fundamentally important.

SFB 1083 researchers have now explored these issues in detail. In their study, the groups of experimental physicists Gregor Witte, Sangam Chatterjee, Martin Koch and Wolfram Heimbrodt teamed up with the groups of theoreticians Stefan Koch and Mackillo Kira. Through their work, it became possible to manipulate CT excitons selectively for the first time, using pulses of terahertz radiation (THz) and light. The investigation allowed the team to directly measure how the formation and decay of CT excitons progress over time.

For miniaturised semiconductors used in technological applications, it is important that users can carefully control the charges that are transferred by CT excitons. In a 2015 study, the team of theoreticians outlined new techniques to selectively control which charges are transferred between two solids. To understand the control mechanisms they needed to develop, the researchers first analysed the properties of CT excitons, and the relationships between pairs of particles across internal interfaces. Their calculations allowed them to develop a sequence of THz pulses, which can induce particular charges to transfer while leaving others unaffected.

The researchers conducted an experiment using a theoretical model that was more precise than any previous description, and which unexpectedly revealed a fascinating additional characteristic of interfaces. The model showed directly how quantum mechanical information can be transferred between particles without the need for charge or energy transfer. This type of information transfer had never been observed before.

In addition to the need for selective charge transfer, the compositions of the solids themselves can pose significant challenges to ensuring transfers that induce useful optical and electronic properties. In many cases, the structures of the two solids can make it difficult for CT excitons to form across interfaces, meaning the materials used to build semiconductors must be carefully selected.

In 2017, the experimentalists carried out the first detailed study into how exciton formation is affected by the various different ways in which arrangements of molecules in different solids align with each other across interfaces. For the materials they used, the researchers quantified how the strength of the emitted photons of light, created when excited charges move into their respective holes and transfer across the interface, is affected by this alignment.

The insights they have gathered could be an important step in the right direction – potentially allowing engineers to choose molecular alignments that will ensure the optical and electronic properties they require.

Charge Transport at Metal-Organic Contacts

In addition to the general problems arising from the process of charges travelling across interfaces, one specific transfer case has its own important set of issues. In modern technology, miniaturised semiconductors made from combinations of metal and carbon-based (organic) materials, are becoming increasingly important, particularly for connecting organic semiconductor devices to power supplies. Devices that currently use this technology include organic solar cells and LEDs.

Metals and organic materials are remarkably useful when used together, as their combined properties are far more diverse than simply using combinations of similar materials. However, the properties of charge transfer across the interface between the materials throw up a variety of further, more specific questions.

The charge transfer process within metals, semiconductors and organic materials is now well known, and the contact between metals and inorganic semiconductors has been subject to intense research in recent decades. Yet for metal-organic interfaces, the behaviour of electrons at the interface between both material classes has hitherto been little understood, making it more difficult to precisely engineer specific properties in miniaturised organic semiconductors. This is now one of SFB 1083's most active areas of research.

As the spokesperson of the collaboration, Professor Ulrich Höfer has played a leading role in several areas of research carried out by SFB 1083, but his interests in laser spectroscopy and ultrafast phenomena at surfaces and interfaces have made metal-organic contacts a particularly important area of his research. Currently, physicists are well aware that there are unique energetic states at the interface of metals and organic compounds, ultimately due to the preliminary work of scientists at Philipps-Universität Marburg. However, physicists have only just begun to describe these new states in detail, and it is still almost completely unknown how they might be utilised.

Carrying on from the preliminary work, SFB 1083 collaborators focussed on analysing the mechanisms in which specific energy levels of electrons form at metal-organic interfaces. The research team created model systems by depositing atom-thick films of flat lying organic molecules onto well-defined single crystals of silver.

By utilising a special kind of photoelectron spectroscopy named 'two-photon photoemission' (2PPE), the researchers investigated the properties of the so-called 'interface state', which is unique to a metal-organic interface and has no counterpart in pure organic material, metal or other types of interface. This state is spatially and energetically located between the electronic states of the metal and the organic material, so it is expected to contribute substantially to the energy and charge transfer at the boundary.

Typically, new electron energy levels will form on the surfaces of metals due to the abrupt boundaries between atoms inside the material, and on the outside. In stacked materials, the interface electrons behave in similar ways – quickly dispersing across the metal surface, and quickly decaying to lower energy levels. The researchers found that the electrons could transfer across the interface over remarkably short periods of time.

Continuing this line of research, in collaboration with theoreticians from the Donostia International Physics Centre, SFB 1083 researchers aimed to discover how the lifetime of the interface state can be determined, depending on the organic material used. The team calculated wave functions and band structures from scratch, using mathematical models that describe the energetic properties and the probability of states moving in the material. The model revealed how transfer rates of electrons across the interface can be affected by a number of mechanisms, including the properties of the binding mechanism and the temperature.

Using these insights, a new model for the fundamental properties of the interface state was introduced by developing a simple description of the

energetic potentials at the interface. The model was based on graphene, the simplest organic compound – consisting of atom-thick sheets of carbon. When its properties are modified slightly, graphene can be used to simulate more complex structures. The researchers discovered that the energy levels of interface electrons strongly depend on the lengths of the bonds between carbon atoms in the very first organic layer, and atoms in the metal. By experimenting with a wide range of metallic structures and carbon-metal bond lengths, the team gained an in-depth knowledge of the previously unknown interface structure that could become ubiquitous in new metal-organic contacts.

Chemo-Selective Reactions on Surfaces

Charge transfer has posed a great range of challenges to SFB 1083's researchers, but one further issue also arises from the actual process of fabricating miniaturised semiconductors from a special class of inorganic materials, which contain both organic and metal components.

Organic molecules possess 'functional groups' – sets of atoms attached to the molecule that will readily react with other molecules. However, many inorganic materials will not readily react with these groups, making it difficult to attach the materials across an interface. On the other hand, imperfections in materials such as silicon can be too reactive, making it difficult for engineers to carefully select which molecules will attach. In careful experimentation, SFB 1083's chemists adopted strategies from chemical biology by involving a particular molecule that can selectively react with silicon surfaces.

Important insights into these more selective reactions were gained in a collaboration between the research group of the chemist Ulrich Koert and the physicists Michael Dürr (Justus-Liebig-Universität Gießen) and Ulrich Höfer and colleagues at Philipps-Universität Marburg. As the building blocks for the reactions they wished to study, the researchers used a molecule named 'cyclooctyne' – consisting of a ring of eight carbon atoms, two of which are held together by three shared pairs of electrons, forming a triple bond. When cyclooctyne is adsorbed onto silicon, this triple bond will readily break down, forming a strong covalent bond with the silicon surface leaving a so-called 'dangling bond'. This highly reactive part can then be utilised to stack subsequent molecules that would typically not bind in a well-ordered structure.

In their research, the chemists synthesised several cyclooctyne-based molecules with different functional groups, which were then reacted with silicon. In every case, the team observed that the organic molecules immediately formed thin layers on the silicon surface without any need for intermediate processes – a feat that had never been achieved for organic molecules before. With this chemo-selective technique, the researchers now hope that new types of miniaturised semiconductors made from

organic and inorganic materials can be grown easily, layer by layer, without the complications previously involved.

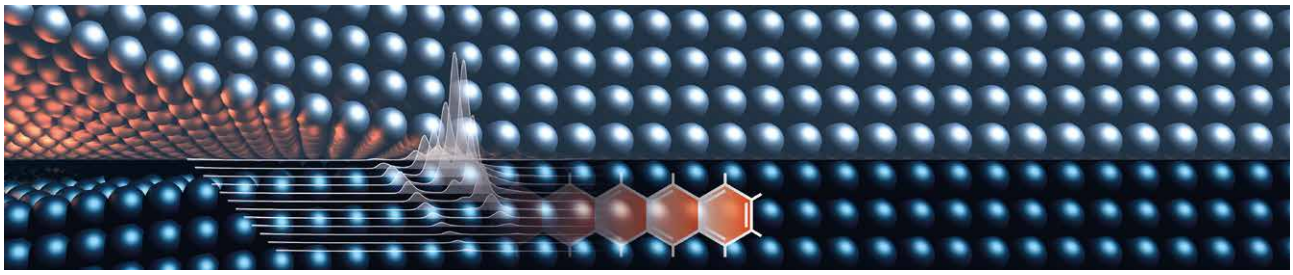
Broad Advances in Our Knowledge of Interfaces

In recent years, the SFB 1083 collaborators have made significant strides towards understanding the diverse properties of internal interfaces between different solids. Through analysing the atomic structures of the interface between gallium phosphide and silicon, they have gained a detailed knowledge of the properties that arise when materials are deposited on silicon, and how they can be accounted for in practical devices.

They have also studied the formation and decay of charge transfer excitons between different materials in detail, revealing new insights into how these transfers can be controlled through terahertz pulses, and engineered molecular alignments.

The team's examination of the interface state, forming specifically on a variety of organic molecules on metal surfaces, has also led to new insights into the electronic structure of electronic contacts. Specifically, their work revealed how electron energy levels form on metal surfaces and decay at rates that depend on the organic material composition and binding properties. The researchers implemented cyclooctyne as an anchor between functional molecules and silicon, demonstrating how organic materials can be easily and selectively reacted to silicon surfaces.

The work of SFB 1083's scientists has already contributed significantly to our fundamental understanding of the properties of internal interfaces. Their research could soon prove invaluable to the production of diverse miniaturised semiconductors, allowing the technologies we use to continue to improve.



About SFB 1083

Collaborative Research Centre (Sonderforschungsbereich)

Philipps-Universität Marburg

Germany

The Collaborative Research Centre, SFB 1083, is funded by the German Research Foundation (DFG), and was established at Philipps-Universität Marburg in 2013. SFB 1083 now hosts a collaboration of over 80 scientists, including 24 principal researchers, 15 postdoctoral researchers and more than 40 PhD students. With a combined expertise encompassing many fields across physics and chemistry, the researchers share the common goal of investigating the properties of internal interfaces between different solids, composed of both organic and inorganic materials. By experimenting with accurate model systems, the collaborators aim to achieve a detailed microscopic understanding of the chemical bonding, electronic coupling, and dynamics of energy transfer at interfaces – discovering how these properties vary when different types of material are used. As of 2017, SFB 1083 also includes research groups from the Universities of Gießen and Münster and the Jülich Research Centre.

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