Thermoelectric and optoelectronic devices
Claire Gmachl\textsuperscript{1} and Alain André Quivy\textsuperscript{2}

\textsuperscript{1}Department of Electrical Engineering, Princeton University, Princeton, NJ 08544, USA
\textsuperscript{2}Instituto de Física, Universidade de São Paulo, São Paulo, SP 05508-900, Brazil

Overview

This proposal aims to build up new ties between Princeton University (PU) and the University of São Paulo (USP) in order to explore innovative semiconductor devices. The focus of the project is to create an interaction between the groups in the development of new semiconductor devices. The collaborative research will be based in the growth and characterization of thermoelectric materials and of high-performance optoelectronic devices based on III-V nanostructures such as quantum cascade lasers (QCLs), quantum cascade detectors (QCDs), quantum well infrared photodetectors (QWIPs), and quantum dot infrared photodetectors (QDIPs). These devices can be used in infrared cameras and gas sensing systems that have many practical applications related to agriculture, engineering, public health, energy management, environmental conservation, defense, etc.

One branch of the proposal lies on the development of new semiconductor heterostructures in order to study the heat and electrical propagation in the pursuit of a more efficient thermal energy harvester. The innovation envisioned is on the use of self-assembled quantum dots to create a restraint in the phonon propagation, diminishing the conduction of high frequency phonons and creating an approach to treat heat propagation as waves. The treatment of heat transport as waves, instead of diffusive, allows the realization of completely new devices, i.e., heat waveguides, diodes for heat, heat lenses and thermal cloaking.

Another branch is focused on the development and improvement of infrared solid-state lasers and photodetectors that are the main research topics at Princeton and São Paulo, respectively. The group at Princeton is known worldwide for its research about QCLs, and would like to gain experience in the growth of quantum dots. The group at São Paulo has a extensive experience with quantum dots, quantum wells and related infrared detectors, and would like to take advantage of Princeton’s experience to start producing QCLs and integrated QCL-QCD devices.

It is the first time that both groups will interact, but it is obvious from their background that this partnership will tremendously improve their respective expertise by sharing their complementary know-how on these topics. Dr. Germano Penello, who was recently granted a post-doctoral fellowship in Princeton’s group, is familiar with both groups, and therefore will be the initial bridge between both. Several faculty members and students are expected to travel and visit the partner group every year and will receive full support to develop their activities on both sides. Short-, medium- and long-term programmatic goals have been established in order to provide a way to check the evolution of the project and evaluate the benefits it will have after its completion in 2017. Among the long-term goals, we can mention the formation of technicians, students and post-docs with high technological skills for the Brazilian and US markets, the interaction with local companies and industries to develop devices and systems with commercial use, and the seed of new interactions involving other groups from both universities. The two group leaders at Princeton (Prof. Gmachl) and São Paulo (Prof. Quivy) are very active in their respective field and have several
grants that can already be considered as a counterpart to the present proposal. In addition, new and joint proposals will also be submitted on both sides to local funding foundations in order to support and even extend the activities included in the present scientific project.

**Detailed layout and objectives**

Since William Herschel’s experiment in 1800, the scientific community realized that visible light (to the human eye) is only a tiny part of the electromagnetic spectrum and that, in order to have access to the rest of it, it was necessary to have special detectors sensitive to other wavelengths. The infrared radiation (0.76 μm to 1 mm) can usually be detected by two types of devices: thermal detectors and photon detectors. In a thermal detector, the incident radiation heats up the detector for which property being monitored (electric polarization, electrical conductivity, etc.) varies as a function of the temperature. A thermal detector has the great advantage to operate at room temperature, but it is not very sensitive, cannot distinguish different wavelengths, does not have a good spatial resolution, and generally has a slow response. Photon detectors (or photodetectors) are much faster, are selective (in terms of wavelength), are much more sensitive and provide an excellent spatial resolution thanks to the great maturity of the semiconductor industry and its ability to pattern focal plane arrays, but usually need cryogenic temperatures in order to operate in good conditions.

Although there are many applications for individual detectors, the market today is increasingly interested in infrared cameras operating with an FPA (Focal Plane Array). This is a hybrid device consisting of a two-dimensional network of small detectors processed on the sample and interconnected to an electronic multiplexer (ROIC, Read-Out Integrated Circuit) made of silicon that allows to read the information from each detector. It is therefore the equivalent of a CCD chip (Charge-Coupled Device) from a common digital camera, except that the FPA is more complex and can operate in any region of the electromagnetic spectrum (depending on the type of detectors from which it is manufactured), while the CCD chip operates mainly in the visible and near infrared (limited by the band gap of silicon). This type of device has numerous applications, and its research is currently funded by many agencies around the world as it also allows the generation of one of the human senses (such as the electronic nose and tongue) and its extension to other regions of the electromagnetic spectrum. Each pixel of a FPA is actually a small photodetector, with a size of a few tens of μm, which transforms the incident photons into an electrical signal. Therefore, in order to achieve high-performance FPAs, one must first of all get high-quality individual photodetectors, which is one of the main objectives of this project. The general idea is to improve existing structures by optimizing their growth parameters, but also to investigate more challenging structures like Quantum Cascade Detectors (QCDs) that should provide a much lower dark current due to their photovoltaic nature, and sub-monolayer QDs whose size should be much easier to control than usual self-assembled QDs and thus should provide QDIPs with better tunability.

The second objective of the present proposal is very similar to the first one but uses exactly the opposite principle: instead of designing a device that detects specific radiation and generates an electrical output, the idea is to build a solid-state laser that converts an electrical signal into a concentrated beam of radiation (visible or infrared)
with a specific wavelength. There are many ways to obtain the inversion of population that is necessary to produce a laser, but one of the most practical ways is to use a p-n junction of two semiconductors which can be made of the same materials that are generally used for some types of photodetectors. A more sophisticated way (which is necessary in order to get a good tunability) involves the repetition of an asymmetric structure containing a sequence of semiconductor quantum wells with different energy levels forming a cascade (hence their name Quantum Cascade Lasers, QCLs). In general, these semiconductor lasers can be made very small (mm and even μm scale) and therefore can be integrated in order to provide coupling to a beam of optical fibers or other optoelectronic devices. Since Princeton’s group is worldwide known for its QCLs and São Paulo’s group is one of the few groups in Brazil able to fully design, grow, process and test high-performance infrared photodetectors, one of the long-term goals of this project is to integrate both devices monolithically (on the same substrate and using the same materials) in order to produce compact systems capable of exciting and detecting at the same wavelength that will serve as fully independent sensors for bio and gas sensing applications.

The research involving thermoelectric (TE) materials and devices is a new topic in Princeton’s Group (starting with the arrival of Dr. Penello) and has its target directed to the optimization of the production of renewable energy. Since the 1960’s, with the development of thermoelectric materials based on BiTe alloys, researchers are trying to develop materials with high TE performance. Semiconductors are known to be the best materials for tuning the energy conversion, but it is only in 1993 that semiconductor heterostructures became a fertile ground for the development of new TE devices. A recent theory shows that, in semiconductors with embedded nanoparticles, the heat conduction can be analyzed as wave propagation with the possibility of creating destructive or constructive interferences of heat. We intend to investigate new semiconductor heterostructures in order to experimentally study the heat and electrical propagation in the pursuit of a more efficient thermal energy harvester. The innovation here will be related to the use of self-assembled quantum dots to create an approach to treat heat propagation as waves. The treatment of heat transport as waves, instead of diffusive, allows the realization of completely new devices as heat diodes, heat lenses, heat waveguides, thermal cloaking and could lead to better TE devices. Since Princeton’s group has no experience with quantum dots, the unique experience of São Paulo’s group in the field of self-assembled InAs quantum dots grown by molecular beam epitaxy (MBE) will be of great value to start this new research.

Both groups have MBE systems dedicated to III-V compounds but use them for different purposes. In Princeton, most growths are related to the production of high-quality QCLs that are based on the periodic repetition of a specific sequence of thin quantum wells. In São Paulo, the MBE system provides a great variety of heterostructures to most Brazilian groups working in the field, as well as specific quantum-well and quantum-dot structures used in infrared photodetectors. Both groups have good infrastructure for processing devices in a cleanroom, yet their testing facilities are different but complementary: lasers are the main research focus at Princeton, while in São Paulo most equipment are dedicated to infrared detectors. Therefore, the interest and infrastructures are complementary and both groups have much to gain with this new partnership. At Princeton, the new research line about thermoelectric materials, headed by Dr. Penello needs samples containing quantum dots and requiring a detailed study of their growth conditions. The group at São Paulo
has an experience of more than 15 years with the growth of self-assembled quantum dots and would be very pleased to share its knowledge. On the other hand, the Brazilian laboratory would like to learn as much as possible about the growth, processing and testing of QCLs at Princeton, in order to be able in the future to develop its own lasers and to integrate them monolithically with the infrared detectors that are already fabricated there.

MBE is an evaporation technique where solid materials of high purity are heated in an ultra-high-vacuum chamber and deposited on a hot crystalline substrate in order to get a film with the best possible crystalline quality. When the substrate and the alloy deposited on top of it have the same lattice parameter (or very close), the growth occurs epitaxially (with the same crystalline structure and lateral lattice parameter as the substrate) and the quantum wells formed are of excellent quality. However, when a semiconductor material is deposited on top of another semiconductor having different lattice parameters, the film grows epitaxially under stress until it reaches a critical thickness which mainly depends on the lattice mismatch between both materials\textsuperscript{vi}. When the deposited material has a lattice parameter significantly larger than the substrate, there is another mechanism that allows a partial strain relief before the introduction of structural defects in the film: the system tends to form a high density of small islands of crystalline material (quantum dots) that provide a reduction of the total energy by relaxing the stress at the edge of these three-dimensional structures. The major advantage of quantum dots (QDs) on the other low-dimensional systems (like quantum wells and quantum wires) is that, due to their very small size, the carriers are confined in all three spatial directions, yielding a discrete density of states (like in atoms).

Photodetectors based on QDs (QDIPs, Quantum-Dot Infrared Photodetectors) have recently been investigated, as they have, theoretically, numerous advantages\textsuperscript{vii,viii} over quantum-well infrared photodetectors (QWIPs), such as a longer lifetime of photogenerated carriers, a higher photoconductive gain\textsuperscript{x}, better temperature stability\textsuperscript{v}, a lower dark current and noise\textsuperscript{xii}, as well as an improved sensitivity\textsuperscript{xii} (in addition to a good detection for normal incidence). Therefore, QDIPs are seen as extremely promising for the production of high quality FPAs at near room temperature. Very recently, some work also showed that the insertion of quantum dots into the active region of a QCL could somehow improve its performance\textsuperscript{xiii}. Therefore, both groups have a lot to gain by sharing their respective knowledge.

**Programmatic goals and international aspirations**

The main objective of this mutual collaboration is to promote the exchange of faculty members, postdocs and students between both groups in order to transfer experience and knowledge, at short and medium term, and eventually to interact with other groups at longer term. This kind of exchange program provides a more diverse academic formation that would not be possible within a single university environment. The person that travels abroad will be immersed in a new culture, facing different challenges that allow him/her enhanced professional and personal growth. The benefits are not only for the person that moves to a different and new place but also for the people receiving that person. Postdocs and faculty will additionally create an easier route of communication with other students, and will have many possibilities to expand their professional contacts. Every year, the Brazilian group intends to send 2 faculty members (Profs. Quivy and da Silva) that will stay 2 weeks
at Princeton, as well as 2 PhD students (one of them might be substituted by a postdoc) for 30 days. The faculty members will be responsible for the knowledge transfer between groups (about QD growth and their theoretical calculation on one side, and about QCL growth, processing and testing on the other side), while the students will have to take care of the experience transfer (experimental setups, computer programs, etc.) that might be of interest for their own project or for their host group. This part by itself already represents around ¾ of the full funding for 3 years.

Another important goal is the establishment of a broader research field in both groups, both theoretically and experimentally. This will be accomplished by enhancing the knowledge of the groups in the optoelectronic area and starting a new thermoelectric research line. Again, the interchange of personal will be valuable: by sharing the complementary know-how of each group, both research centers will develop better laboratories with increased capabilities, improving their facilities and the knowledge in their research areas. On the Brazilian side, the first year will be dedicated to learn how to design, grow, process and test QCLs, and to write a parallel proposal that will be submitted to a local funding foundation in order to buy everything that will be necessary to test the QCLs in Brazil (the growth and processing infrastructures are already present). The second year will be dedicated to the importation of the equipments and to the installation of the full experimental setup at USP. In parallel, QCL samples will be grown and processed in Brazil, and then tested in Princeton during the visits to the US group. The third year will be used to optimize the growth, processing and testing of the lasers and photodetectors in order to get Brazilian devices as good at their US counterpart.

The Brazilian group is part of a national effort to develop high-performance infrared photodetectors (INCT-DISSE) in collaboration with local companies and universities. Some of them (Orbital, Optovac, iVision) already showed a clear interest in using their samples to develop devices, FPAs and infrared cameras for the Brazilian market. The idea to fabricate a compact monolithic device containing a small QCL and an infrared photodetector on the same chip will certainly increase their interest. Both kinds of devices are however longer-term goals.

Princeton intends to send undergrad summer students to USP, who in turn continue on to senior thesyses and independent work at Princeton. Dr. Penello at Princeton will be a key team member facilitating the exchange.

This kind of partnership will also have several positive consequences that can be considered as long-term goals. Two major achievements will be to strengthen the international recognition of both groups (and institutions) and to create a fertile ground for new discoveries and devices. Both groups are leading groups in their respective institutions and countries, and sharing their complementary expertise is perhaps the best way to grow faster. This increase of expertise will also improve the formation of the students, postdocs and technicians that will be better prepared for their future career plans.

**Envisaged innovations**

The first and most relevant innovation for both groups will be related to the increase of knowledge generated by the transfer of complementary experience during the exchange of faculty and students. The group of Prof. Gmachl produces QCLs of the highest quality but needs to learn how to grow good quantum dots in order to start
a new research about thermoelectric materials. The group of Prof. Quivy has long standing experience with the growth of quantum dot and would like to learn how to fabricate QCLs. Since both groups are excellent in their respective fields, this partnership will be the fastest way to generate new knowledge and skills on both sides.

Our collaborative research also seeks to investigate and understand new phenomena in optoelectronics and thermoelectrics. By exploring fundamental processes in semiconductor devices, we expect to develop better infrared emitters (quantum cascade lasers), infrared sensors (quantum well and quantum dot photodetectors), and thermoelectric materials. All these topics have in common the use of high-quality semiconductor nanostructures (quantum wells and dots) that can only be obtained by a sophisticated deposition technique like MBE. The innovation relies on the fact that the performance of such devices and materials can be improved by using different combinations of nanostructures that will tune or change fundamentally their properties. Among them, quantum dots are a strong candidate due to their discrete density of states that results from their extremely small volume which allows the confinement of carriers in the 3 directions of space.

Quantum cascade lasers are compact devices that emit an intense beam of radiation (visible or infrared) in a very narrow part of the electromagnetic spectrum. The pursuit of a higher output power and single mode lasers is an area under intense research, and the use of quantum-dot cascade lasers is very promising in order to suppress optical losses and non-radiative recombination. The growth of such heterostructures is a major step to overcome, but with the combined knowledge of both groups we envision the possibility to develop completely new devices in this area.

The research in the photodetector area consists of two parts: the improvement of individual photodetectors in order to get better figures of merit, and the development of focal plane arrays (FPAs) to produce infrared cameras as a final product. The photodetectors used nowadays still require cryogenic temperatures to operate in good conditions, in order to achieve a low dark current which is mostly from thermal origin. A reduction of the dark current is expected by using superlattices, coupled quantum wells or quantum dots. However, it is the quantum cascade detectors (QCDs) that show the most promising advantage over the common quantum well photodetectors, because they operate without any external bias voltage (photovoltaic devices) and therefore show always an extremely low dark current, even in the presence of thermal excitations. An even more exciting heterostructure to be explored would be a quantum-dot cascade photodetector, because the introduction of quantum dots in the structure of a usual QCD might reduce the dark current even further. Self-assembled quantum dots are rather easy to grow but suffer from a lack of control resulting from their spontaneous formation process which can only take place in the presence stress. To solve this problem, sub-monolayer quantum dots will be investigated. Their growth is much more difficult, but they can have a broader range of sizes and can be grown without any wetting layer. The research about FPAs is a longer term project, because it involves two-dimensional arrays of up to $10^6$ photodetectors and more sophisticated equipments like a flip-chip bonder and a specific setup with high-speed components for testing the full FPAs that will require a separate proposal and a larger funding (around $700,000). However, since good photodetectors are already available in the Brazilian group, the FPA research is
expected to start during the third year of the PU-USP partnership and will continue well after its end (although the groups will surely continue to interact together).

The use of semiconductors heterostructures for the development of thermoelectric materials started at the beginning of the 90’s. A recent paper explored the use of embedded nanoparticles to control heat as a wave, allowing a new way of treating heat propagation. This theory foresees innovative devices with a better TE performance. Using the long experience of USP about the growth of quantum dots, the group at PU would like to investigate new thermoelectric materials using self-assembled InAs quantum dots embedded in a GaAs matrix in order to study their influence on the thermal and electrical properties of TE devices. Eventually, submonolayer quantum dots will also be investigated since they might behave very differently on a thermal point of view due to the absence of the thin InAs wetting layer that connects all the quantum dots of the same layer.

**Methodology**

To promote the interchange of undergraduate students, we expect to have students participating in summer internship. The internship will follow each institution calendar and the students will work on a research project developed with the agreement of both PIs. During their internship, a faculty and graduate students or postdocs will mentor the students, in order to increase their interaction with the host group. For graduate students going from USP to Princeton University, Princeton confers the status of Visiting Student Research Collaborator (VSRC). The number of VSRCs that the Electrical Engineering department can receive per semester is limited and imposes a detailed case-by-case plan depending on the time and the duration of staying however, so far the limit for ELE has never been reached. On the other hand, USP has no restriction on the number and time of visiting student.

During their visit, the students will be supervised by the host PI and will also have a mentor that will assist them in the new lab environment. The projects that the students will work on will be determined according to their thesis and to the feasibility of the research project in the host institution. If there are more students than the funding permits, a pre-selection will be realized by the PIs. Postdocs will receive funding similar to graduate students. Their project and CV will be analyzed by the PIs and the feasibility will be judged. Since postdocs can spend more time at the partner institution, their stay will be adjusted according to the project and will be designed as short-term (15 days to 1 months) and medium-term (1 to 3 months). Faculty members are in general only able to travel for short periods (1-3 weeks) but will do so at least annually to assure that the transfer of knowledge is complete between both groups.

All the visitors will have the same status and rights as their counterpart in the host institution, and will have a desk with a computer (unless they bring their own laptop), will have access to the internet and to usual scientific data bases, will be able to obtain books at the library, and will be allowed to use the USP's cafeteria. With respect to the lodging, the university might eventually have some student rooms during summer vacations (to be confirmed), but in principle the visitors will be responsible for their lodging. However, the host group will always do its best to help finding a student room for a short time or even a hotel or pension close to the university.

At this moment, two graduate students from USP, Marcel S. Claro and Ricardo A. Pereira, are willing to participate to the interchange both in the QCD and
QCL research. Marcel S. Claro is currently developing innovative QCD and sub monolayer quantum dots infrared photodetectors, while Ricardo A. Pereira is studying high efficiency quantum dots infrared photodetectors. From Princeton University we have a graduate student, Ching-Yu Chen, working on quantum cascade lasers design and characterization. Each student is working on a different subject and the interaction between them will be extremely fruitful for their education and careers. The interchange between São Paulo and Princeton will allow them to be more familiar with the infrastructure and equipments of another lab aimed for a different type but supplementary characterization.

Germano M. Penello is a postdoctoral research fellow at Princeton University pleased to participate in the collaboration. His research includes the study and improvement of quantum well infrared photodetectors by using coupled quantum wells. By narrowing the distance between the groups, the partnership will allow a deeper understanding of the phenomena observed in his recent results. Besides the improvement of photodetectors, the partnership will also allow him to expand his research knowledge about thermoelectric devices. This is a new and exciting subject that Dr. Penello is demonstrating interest in and is currently pursuing. He will carry on the research on thermoelectric devices developing new samples in collaboration with USP partners.

Both PIs are well known for their contribution to the optoelectronic field related to quantum well and quantum dots photodetectors, as well as quantum cascade lasers. With this partnership, the PIs will widen their research field and stimulate the studies of thermoelectric devices. This is a subject that will be primarily studied, but not limited to, by Dr. Penello. During the period of the partnership, new students will be encouraged to join both research groups in order to also study and stimulate the thermoelectrics research area. Prof. Euzi C. F. da Silva will also take part in the collaboration. Her theoretical and experimental knowledge on spectroscopy and optical properties of condensed matter will be valuable to the collaboration. As mentioned before, the close contact with faculty, postdocs, and students will allow an easier sharing of knowledge and a better improvement in the students’ skills.

The number of participating members is not limited to the names cited so far in this proposal. We also foresee the inclusion of new students, postdocs and faculty looking forward to participate in the partnership. As cited before, the project is three-year long and we will encourage and welcome new members to join the group and to collaborate in the enterprise.

In total, we desire to support the travel expenses and accommodations of nine undergrads and travel expenses and accommodations of six grad students, travel expenses and accommodations of two postdocs and also two faculty traveling and hosting expenses. As commented above, the projects will be carefully chosen to optimize the time and money spent on the visiting institution. Each project will be closely accompanied by both PIs to insure the quality of the work done during the visit. This will be accomplished by regular meetings with the host PI and with presentations during and at the end of the stay. The PI of the original university will also maintain contact with the student or postdoc via skype conferences and/or email to make sure that the work is running according to the original plan.


