 Superior gamma-detection and IR imaging via ALD-passivated germanium nanostructures (SUGER)

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ABSTRACT

The SUGER is based on several innovative approaches that are implemented in photodiode manufacturing to reach record-high device performance in near-infrared and gamma-ray detection. The approaches mitigate electrical and optical losses and are fully CMOS compatible. The obtained results include external quantum efficiency >130 % in UV, surface recombination velocity <5 cm/s and absorbance >99 % in UV-NIR. In ATTRACT Phase 2, we plan to partner with experts from different parts of the detector value chain to scale up our technology to industrial system-level prototypes and even to commercial products.

Keywords: near-infrared, gamma radiation, defect passivation, high absorption, high sensitivity

1. INTRODUCTION

Near-infrared (NIR, wavelength 750–3000 nm) and gamma-ray sensors have a vital role in several application areas that are critical for our everyday life, including medical diagnostics, telecommunications and security. However, the current sensors have limited performance in terms of sensitivity, wavelength range and cost. There is hence an urgent need to develop sensor technologies that overcome these shortcomings.

In the SUGER project, we have three innovative ideas for reaching ground-breaking sensor characteristics. First, instead of using externally doped pn-junctions that are expensive to fabricate and result in severe electrical losses, we propose a concept where the charge collection is realised via a dopant-free inversion layer. This kind of junction enables collection of the signal with very little electrical losses resulting in superior sensitivity. Furthermore, such concept brings a great asset for gamma-ray sensors that currently require complex multi-sided ion implantation for junction formation. Second, to address the major recombination losses present at the surface and interfaces of the state-of-the-art detectors, our idea is to control the presence of charge-carriers at the surfaces using charged dielectrics and take advantage of the properties of atomic layer deposition (ALD). Third, instead of depositing a separate antireflection coating that is only working for a single wavelength, our idea is to fabricate a graded refractive-index interface that is based on surface nanostructures. This should result in fully absorbing surface at wide range of wavelengths and acceptance angles as well as provide efficient light trapping paths inside the substrate.

In this project we have applied the above ideas to CMOS compatible semiconductor substrates (Ge and Si). As a result, we have achieved record high (>99 %) absorbance in the whole UV-VIS-NIR spectrum up to 1600 nm wavelength using industrially up-scalable methods. Secondly, we have demonstrated that our novel idea of dopant-free junction is feasible and have achieved high performance induced junctions both in Ge and Si. Thirdly, we have succeeded in reducing the recombination losses drastically at the detector surfaces using ALD technology and as a result reached surface recombination velocities (SRV) below 1 cm/s and 5 cm/s in Si and Ge, respectively. Finally, after applying all these ideas into the final device, we achieved >130 % external quantum efficiency in deep UV, which is the highest performance ever achieved with a single photodiode.

2. STATE OF THE ART

State of the art (s-o-t-a) NIR sensors are typically made of InGaAs. However, their fabrication is expensive, they have limited wavelength range and the material is not CMOS compatible. Hence, InGaAs has very limited potential to enable ground-breaking solutions for the
detector industry. Germanium (Ge), instead, has a lot of breakthrough potential due to its CMOS compatibility and low cost [1]. However, the sensitivity of Ge-based sensors has yet remained modest due to several issues that are listed below.

One of the largest factors limiting the performance of NIR Ge detectors is the highly reflecting detector surface. Reflectance of a bare Ge surface is higher than 40%, which means that at the maximum only 60% of the incoming NIR radiation can be absorbed and detected. In s-o-t-a devices, the reflectance losses are mostly addressed by depositing a thick antireflection (AR) coating on the flat surface. However, this solution works efficiently only for a single wavelength and for a single incident angle for which it has been optimized.

Another important problem consists of electrical losses, which are mainly caused by various forms of charge carrier recombination. First, the dopant atoms needed to form a signal-collecting junction are known to activate both Auger and Shockley-Read-Hall (SRH) recombination. The former is caused by the dopants themselves, while the latter results from the crystal defects introduced during the junction formation, conventionally realised with ion implantation technology (or in specific applications e.g. by Li+ diffusion). These recombination losses kill the signal leading to a so-called “dead-layer”. Further recombination losses are encountered at the surfaces of the devices as the passivation of Ge surfaces is known to be very difficult due to the high reactivity of Ge with common processing chemicals and environment.

In addition to the above losses, formation of the pn-junction and activation of the dopants is challenging in Ge. This is an issue already at wafer level, but especially challenging and expensive in cylindrical 3D structures that are used in s-o-t-a gamma-ray detectors.

3. BREAKTHROUGH CHARACTER OF THE PROJECT

When successful, SUGER technology will enable reasonably priced sensors that can see in the dark, detect much smaller cancer tumors and revolutionize the detection limits of scientific equipment, which have so far been only a subject of imagination. We believe that such breakthroughs in sensor technology can be achieved using three unconventional approaches that we implement in photodiode manufacturing. First, instead of conventional pn-junction formation by ion implantation, our idea is to form the junction by applying a highly charged conformal thin film on the sensor surface using ALD. The pn-junction induced by the fixed charges is completely free of recombination, and the detector fabrication process becomes much simpler and less expensive as there is no need for ion implantation. Since ALD films by nature grow on all exposed surfaces during single deposition, the benefit is expected to be ground-breaking especially in 3-dimensional coaxial gamma-ray detectors that are currently relying on complex ion implantation and annealing procedures.

Second, we replace commonly used plasma-enhanced chemical vapour deposited (PECVD) dielectric layers with advanced thin film structures, which eliminate surface recombination and provide excellent interface quality with record-low surface recombination velocity (SRV).

Third, instead of the traditional approach to use a thick AR coating on a flat surface, our idea is to eliminate the reflectance from the detector surface by the application of a specific nanotexturing process to Ge surfaces. Such nanostructures eliminate the need for a separate AR coating and thus provide superior optical properties both in a large incident angles and over a wide spectral range.

By combining all these three ideas into a single device we come up with a novel sensor concept with unprecedented performance. The breakthrough potential of the proposed SUGER technology is benchmarked against the state-of-the-art technologies in Table 1.

Tab. 1. Breakthrough character of SUGER technology as compared to s-o-t-a technologies.

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Existing technology</th>
<th>SUGER technology</th>
</tr>
</thead>
<tbody>
<tr>
<td>Optical properties</td>
<td>Reflectance &gt; 40 %, Absorbance &lt; 60 %</td>
<td>Reflectance ~0 %, Absorbance &gt; 99 %</td>
</tr>
<tr>
<td>Electrical surface properties</td>
<td>SRV &gt; 100 cm/s</td>
<td>SRV &lt; 5 cm/s</td>
</tr>
<tr>
<td>Complexity of junction formation</td>
<td>Complicated (ion implantation / Li+ diffusion)</td>
<td>Simple (no doping needed)</td>
</tr>
<tr>
<td>Charge collection probability</td>
<td>Medium (recombination losses)</td>
<td>High (no electrical losses)</td>
</tr>
<tr>
<td>CMOS compatibility</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>Cost</td>
<td>High</td>
<td>Low</td>
</tr>
<tr>
<td>Efficiency (EQE)</td>
<td>&lt; 70 %</td>
<td>&gt; 100 %</td>
</tr>
</tbody>
</table>

4. PROJECT RESULTS

Superior optical properties

We have developed a special dry-etching process for Ge surfaces which has resulted in record-high absorbance >99% and extremely low surface reflectance of 0.85% in the whole UV-VIS-NIR spectrum up to 1600 nm wavelength (Fig. 1). Hence, the developed process provides ideal optical properties not only for NIR sensors but also for broadband detectors. Another important result is that the absorbance remains high also at large
incidence angles, which provides significant benefit in applications, where electromagnetic radiation needs to be detected from a low angle.

We developed also an alternative wet chemical process that consumes only a small amount of Ge and is thus applicable also to thin Ge layers. In this case optical performance was also superior (~50% higher absorbance) as compared to the state of the art. Both processes are capable of producing uniform absorbance over the full 100-mm-diameter substrate area as well as wafers with etch mask openings of different sizes and shapes, which demonstrates the process applicability to CMOS sensor manufacturing. The results have been published in prestigious scientific journals [2-4].

**Superior electrical properties**

Fig. 2 demonstrates that we were successful in fabricating a dopant free pn-junction that introduces similar band bending and thus charge collection than a conventional pn-junction. This simplifies the detector fabrication process as there is no need for complicated and expensive ion implantation. Furthermore, in the absence of dopant atoms, Auger and SRH recombination should be eliminated thus reducing the electrical losses in the junction.

In order to characterize the electrical quality of the junction further, we use the so-called minority charge carrier recombination lifetime that measures recombination losses both in the junction and at the surface. Fig. 3 demonstrates that we have achieved a drastic improvement in the electrical quality of the junction as the carrier lifetime increases from below 20 μs to more than 1.5 ms. The result also indicates that the SUGER technology provides excellent surface

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**Fig. 1.** Absorbance of Ge wafers with SUGER technology developed in the project and with a conventional flat surface.

**Fig. 2.** Band bending ($V_{FB}$) at Ge surface realised by a highly charged thin film as a function of added charge ($Q_c$) for alpha and beta development versions. The beta version is already equally good with conventional externally doped pn-junctions.

**Fig. 3.** Minority charge carrier recombination lifetime in Ge substrates with SUGER and conventional technology.

**Fig. 4.** External (EQE) and internal (IQE) quantum efficiency of photodiodes combining the breakthrough technologies.
passivation, which is an important milestone for achieving our ultimate goals.

**Superior sensitivity**

We combined the above breakthrough technologies in a single photodiode and achieved a remarkable (>130 %) external quantum efficiency (EQE, Fig. 4) in UV and visible wavelength regions. This is the highest sensitivity that has ever been reported by a single photovoltaic device. The result has been published in highly distinguished journal *Physical Review Letters* [5]. We are currently fabricating and analysing similar devices optimized for NIR and gamma-rays.

5. FUTURE PROJECT VISION

5.1. Technology Scaling

Within ATTRACT Phase 1 we have experimentally demonstrated a laboratory scale proof of concept for the SUGER technology, i.e., (i) dopant and recombination free pn-junctions, (ii) superior surface passivation and (iii) structure to eliminate optical losses in UV-NIR. The current TRL in the NIR sensors is hence between 3 and 4. All process steps are fully compatible to CMOS manufacturing lines, therefore, it should be relatively straightforward to scale up the chip technology even for large semiconductor foundries. However, before proceeding to large-scale mass-production in a CMOS foundry, we have a possibility for making an intermediate step in a smaller, yet high-tech, clean room facility called Micronova. The facility access enables us to demonstrate the technology in TRL 6, to fabricate the first chip-level prototypes in industrially relevant environment (TRL7) and to start even small-scale commercial production.

A larger share of the value chain would increase the value of the products, however, implementing the SUGER technology in system-level needs more development work, since the requirements for end-user systems are heavily application dependent. This work requires collaboration with industrial partners, who have expertise on complete detector circuits and systems, which will be discussed in the next section.

The most straightforward way to validate and demonstrate the SUGER technology in gamma ray detectors in industrially relevant environment (TRL 5-7) is to implement them in the commercial products of Baltic Scientific Instruments (BSI), who has been a partner in the consortium already in Phase 1. This work has already been started.

5.2. Project Synergies and Outreach

We have agreed tentatively on collaboration with several organizations at different parts of the sensor value chain for the Phase 2 (Fig. 5). The leading Ge wafer manufacturer, Umicore N.V., has expressed their interest in joining our consortium. They would provide us the wafers, assist us on material-related matters and possibly even develop the substrate material properties for the selected applications. Also a start-up company, ElFys, Inc., which spun off from our research group to commercialize nanostructured silicon photosensor technology, would like to join our team and support us in the application of Ge nanostructures to commercial IR photodiodes and modules. Furthermore, we have been actively planning joint experiments with the team at Open University (UK) (ATTRACT project #277: “Single Photon Visible Light Image Sensors for Science and Technology”) since the kick-off meeting of Phase 1. Open University has vast experience in the design of detector circuits, CCD and CMOS image sensors and their front-end, such as readout electronics, which would perfectly complement our expertise on chip-level technologies. We have also been in contact with a CMOS manufacturer, who would be willing to demonstrate the technology and the first prototypes in their industrial CMOS manufacturing lines, providing a straightforward path to TRL 7 and even mass production. We have also started initial collaboration with a French partner that has long experience in manufacturing of Ge/SiGe/GeSn thin film devices. Their contribution helps us to extend the application range of SUGER technology beyond the traditional bulk photodiode technologies. The only partner missing from our consortia is a system-level specialist who would help us to promote the technology towards end-user systems.

Regarding dissemination of our results, we will continue to publish our research and achievements actively in different medias, including scientific publications, scientific and professional conferences, various social media channels and press releases. We will keep the

![Fig. 5. Value chain of nanostructured sensors and planned consortium partners.](image-url)
5.3. Technology application and demonstration cases

Since our SUGER innovation is in the beginning of the value chain, it can have an impact on all the three areas: Scientific Research, Industry and Societal Challenges. Indeed, radiation sensors operating in UV, visible and NIR regions find numerous applications within various industry fields, including medical diagnostics, scientific instruments and security. As a concrete example, improved detector sensitivity makes it easier to detect smaller cancer tumors and improves the chances to find the disease early enough. As a second example, the enhanced sensitivity enables scientists to see beyond their current detection limits and make even completely new discoveries. Hence, large research infrastructures, such as CERN, are potential end users of our technology. Another example enabled by sensitive NIR imagers is night-time vision which improves security in the society during the dark hours. Improved sensor performance also allows to reduce energy consumption of hand-held devices, meaning longer battery life in mobile phones or activity tracking bracelets. In Phase 2, the consortia will select a few specific focus areas in order to make the project feasible within a reasonable time line.

5.4. Technology commercialization

We see a start-up company as the most potential pathway to commercialize the ground-breaking innovation. A start-up can first start small-scale production and simultaneously licence the technology to large industrial partners, while aiming to eventually become a large manufacturer itself. Our team has expertise on founding start-ups, and ElFys, Inc., which spun off from our research group, is one potential candidate to buy or license the SUGER technology. We are thus currently looking for investors and experienced members for the Board of Directors. We would like to get assistance from the ATTRACT consortium for commercialization of the technology and finding potential investors.

5.5. Envisioned risks

One potential risk is how to make the business profitable in the beginning. Our device performance is outstanding, but without mass production it may be challenging to compete in price. This could be mitigated by licensing the technology to ensure revenues that can be used to increase own production.

Another potential risk is related to entering mass production, since it may be challenging for a start-up company to access a semiconductor foundry. Nevertheless, industrial partners with such an access could open the door to CMOS manufacturing lines.

5.6. Liaison with Student Teams and Socio-Economic Study

We are looking forward to the out-of-the-box ideas that the students may come up with on how to utilize our technology to provide concrete solutions for the Societal Challenges, including health and wellbeing, security and environment. Our team, especially Dr. Toni Pasanen, who will be responsible for this activity, will provide M.Sc. level students with explanation materials that will familiarise them with our technology and the main advantages of our innovation. He will also ensure smooth communication between the student team and our researchers at all phases of the project by organizing regular meetings between the parties.

We are also pleased to take part in the socio-economic study of ATTRACT e.g. by contributing with interviews and providing relevant material that will help to reach the goals of the study.

6. ACKNOWLEDGEMENT

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7. REFERENCES