Transformational Infrared Detectors for Medical and Environmental Sensing -"TIMES"

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ABSTRACT: Ultra-High Performance Mid- and Long-wavelength infrared resonant cavity-enhanced photodetectors (RCE-PDs) are demonstrated. Compared with the best existing conventional detectors, a ~50x reduction in absorber volume has been achieved, revealing a potential reduction in detector dark currents and noise by a similar factor. These are suitable for use as detectors for sensing a variety of important medical and environmental gases including CO2, CH4, N2O, acetone and glucose.

Keywords: Resonant Cavity-Enhanced Photodetectors; RCE-PDs; Molecular Beam Epitaxy; Medical Sensing; Environmental Monitoring; Medical Screening; Low Cost; Ultra-High Performance.

1. INTRODUCTION

New generation sensors working in the mid-wave infrared are expected to have transformational potential in the sensing of compound *spectral fingerprints* for a range of biomedical and environmental markers, e.g. [1-5]. Absorption lines or spectral fingerprints of glucose (for diabetes) and acetone (for many cancers), amongst others, could allow for early diagnosis, monitoring, treatment and improved clinical outcomes. CH4, CO2, CO and N2O could similarly be monitored in industrial environments for pollution control. Resonant cavity enhanced photodiodes (RCE-PDs) are a key candidate technology, with multiple orders of noise suppression predicted compared with existing sensors, whilst at the same time achieving accentuated sensitivity. In this ATTRACT programme a novel infrared detector architecture has been successfully design, fabricated, tested and developed. Sensitivity is focussed to a narrow (<100 nm) tuneable band[6] and noise suppression compared with conventional infrared detectors by several orders of magnitude is predicted by theory.[7,8] A thinned absorber is enclosed within a Fabry Perot cavity bounded by semiconductor Distributed Bragg Reflector (DBR) mirrors. Using Sb-based III-V materials, signature lines between 2-10 µm can be covered effectively; these include CO2, CH4, N2O, acetone and glucose, amongst others. If enhancements to detector sensitivity can be fully realised, these have the potential to allow monitoring of pollutant gasses, and also a range of ex-situ clinical traces for the diseases mentioned, for example in breath or on the skin.[9]

2. STATE OF THE ART

Infrared detectors generally use semiconductor materials (e.g. Si, HgCdTe, or III-V) with a bandgap smaller than the photon energy to convert incident photons into an electronic signal. For most purposes, the thickness of the absorber in state-of-the-art detectors is comparable to the wavelength of the radiation to be detected. Absorption occurs according to Beer's Law and carriers diffuse from the absorber to the electric field region (depleted of mobile electrons) to generate a current in the external circuit. Sensitivity is usually extended across a broad range of wavelengths corresponding to photon energies above the bandgap. Strong absorption (and thus good sensitivity) is usually ensured by using a thick absorber.

Detector	Absorber Thickness	Spectrum width	Quantum Efficiency	
Conventional	$\sim 1.0 \times \lambda$	2-4 µm	~50%	
RCE-PD	$0.025 \times \lambda$	0.05 µm	~70%	

 Table 1: RCE-PDs and conventional detectors.

3. BREAKTHROUGH CHARACTER OF THE PROJECT

The key performance metric for infrared detectors is the signal to noise ratio, sometimes expressed as Specific Detectivity D^* . The noise typically scales with the square root of the dark currents due to Auger (thermal) and Shockley Read Hall (defect related) processes. These are



predicted to scale linearly with the absorber volume when the thickness of the absorber is reduced, and this trend is exploited by the RCE-PDs developed in this project. Furthermore, in our new detectors, the signal - or quantum efficiency – is enhanced by using a Fabry Perot cavity, which recycles photons within a narrow resonant band. This allows the signal to noise ratio to be maximised, since the quantum efficiency is maintained whilst the noise is lowered. In addition to the reduction in the detector noise from the dark currents, our RCE-PD structures also reject radiation outside the narrow band of interest so that the photon noise from the scene is rejected and the D* enhanced still further. By developing a new type of RCE-PD, grown on GaSb using III-Sb materials, narrow gap absorbers including bulk InAsSb and type-II SLS, have been unlocked and demonstrated in this project. This extends the range of wavelengths covered to include the important mid- and long-wave infrared at wavelengths up to $10 \,\mu m$.

4. PROJECT RESULTS (SCIENTIFIC)

Detectors were fabricated in a Class 100/1000 clean room. Mesa diodes were defined using a citric acid-based etchant and the common contact was made around the perimeter of the photomask unit cell. Since the detector Shot noise, I_n^2 , depends on the dark currents according to $I_n^2 = 2qI_0$ where q is the elementary charge and I_0 is the DC dark current, the signal to noise ratio of the detectors depends on the magnitude of the dark currents. The dark currents were measured using a low temperature probe station equipped with a radiation shield, which blocks background radiation from the 300 K scene. The dark current densities for both detectors are shown in Fig 4. Arrhenius plots can be used to show dark currents as a function of inverse temperature and find a characteristic activation energy which can reveal the nature of the dark current processes, allowing them to be mitigated. Dark currents can scale with temperature either with the full bandgap, Eg, of the absorber for *diffusion* limited regime or Eg/2 in the presence of defect limited performance. The former case is preferable since the dark currents fall faster with temperature as cooling is applied. In part (a) an Arrhenius plot shows the dark current density for the 3.4 µm detector at -0.3 V operating voltage: around 10⁻² A/cm² at 250 K operating temperature. The activation energy is taken from a fitted gradient, yielding 0.26 eV. This value is somewhat smaller than the full bandgap of the absorber (~0.3 eV) indicating that further improvements to the dark currents and noise should be possible. Part (b) shows the same dark currents as a function of voltage. The dark currents for infrared detectors further scale inverse-exponentially with the bandgap, hence rising exponentially for detectors operating at longer wavelengths. Part (c) shows the dark currents for the 7.7 µm detector and these are significantly greater, at around 10⁻¹ A/cm² at 1.0 V operating bias and 77 K operating temperature.

Once the noise is known for a given operating bias and temperature, the photoresponse of the detector is required in order to find the signal to noise ratio, which is finally expressed by convention in terms of a so-called specific detectivity. The photoresponse is usually measured in terms of the quantum efficiency which differs from the responsivity (A/W) by a factor of the photon energy. Spectroscopic sensing of infrared absorption signatures requires a stable resonance position. Figures 5 (a) and (b) show the detector photoresponse for the 3.4 μ m and 7.7 µm detectors, respectively. For the 3.4 µm detector, the width of the photoresponse varies between 43 nm at 175 K and 51 nm at 250 K. The position of the resonance maximum varies only weakly with temperature between 3.409 µm and 3.428 µm across the same temperature range. The weak dependence results from the change in



the refractive indices with temperature rather than the change in the bandgap of the absorber, which varies more strongly. For the 7.7 µm detector, the width of the resonance varies between 104 nm and 89 nm between -0.2 V and -0.8 V applied bias. Specific detectivity is illustrated for both detectors in Figure 6. The figures were calculated from the dark currents of Figure 4 and the photoresponse of Figure 5. The peak performance was taken to be at 3.415 µm and 7.706 µm, respectively. The performance level of the 3.4 µm detector can be compared to conventional commercial detectors operating at the same wavelength; for example, InAs and HgCdTe from Vigo System S.A. offer $3 \times \text{and } 4 \times 10^{10} \text{ cmHz}^{1/2}\text{W}^{-1}$ for 2-stage thermoelectric cooling (TEC).[10] While HgCdTe operating at 10.6 μ m boasting 10⁸ cmHz^{1/2}W⁻¹ is available for 2-stage TEC (our first proof of concept detectors operate at 77 K) we are confident that with development, the noise levels can be reduced. The fact that a high quantum efficiency is achieved for a thinned absorber indicates that the dark currents can be reduced, as reported in [6], allowing for highly significant reductions in noise, perhaps by several orders. This would allow the 7.7 µm device to operate with thermoelectric cooling.



4. PROJECT RESULTS (INSTRUMENTAL AND TESTING)





5. FUTURE PROJECT VISION

5.1. Technology Scaling

In this ATTRACT Phase 1, our consortium successfully demonstrated high quantum efficiency, narrowband and versatile RCE-PD technology within a laboratory environment, together with prototype electronic driver package. Our RCE-PDs have reached TRL 3 - 4 (with good indications that a cost-effective route to TRL 5-7 is possible within the framework of an ATTRACT Phase 2.

Proof of concept has been established and the next stage is to fully realize the noise suppression that is promised

by the design. We are confident that this can be achieved by modifying the device cavity by using a carefully tuned doping regime to flatten the bands and ensure the dark currents scale with the reduction in absorber volume.

In order to increase the TRL of this technology further, the current project partners will coordinate with already identified end-users of our technology. Throughout ATTRACT Phase 1, the team have been interacting with several systems integrators who are interested in various applications of the technology, including: Low-cost environmental gas monitoring, stand-off laser scanning imager and medical quantitative monitoring.

By engaging with these potential end-users, the team has the opportunity to integrate RCE-PDs into laser systems (and it is to be noted we are also working with Resonant Cavity LED programmes that would reduce the cost below that of lasers), creating active infrared detector demonstrator systems capable of long-range standoff detection of hazardous chemicals or gases. The team have also defined other routes to developing a prototype demonstrator for medical applications by integrating RCE-PD technology into wearable sensors or handheld devices for monitoring medical compounds. By the end of Phase 2 we will work to ensure that the technology will reach a TRL of 6. Further, Amethyst (please see figure) is in the process of establishing itself as a Single Element RCE-PDs supplier, that is projected for our electronics packaging division to reach TRL levels in the 6-7 range.

5.2. Project Synergies and Outreach

The project team have been interacting with several system integrators throughout Phase 1, raising the profile of RCE-PD detectors. In Phase 2 of ATTRACT the partners intend to expand the project consortium by including potential end-users. This will enable the demonstration of RCE-PD technology within a relevant



industrial or medical environment for real-world applications. This will be as a highly accurate and discriminating gas or chemical sensor coupled with an active laser emitter for long range stand-off detection, or as a highly innovative wearable medical sensor. These opportunities, if a proof-of concept is successfully demonstrated, will enable a direct route to market for the technology through the end-users customer base. With several end-users already interested in the RCE-PD detectors the team is developing a varied customer base for this technology. However, we will also disseminate our technology 9after IP seis secure) by publishing our progress in scientific and academic journals, whilst showcasing our demonstrators created during Phase 1 of ATTRACT at scientific and industrial conferences.

5.3. Technology Application and Demonstration Cases

Industry and Societal Challenges:

With the development of infrared emitters advancing significantly in the past 50 years in comparison with the development of infrared detectors, RCE-PD's high performance, discriminatory narrow linewidth characteristics will revolutionise infrared detector technology. With the team's III-V material detector designs, being easily manufacturable and more environmentally friendly than other infrared detector materials, whilst demonstrating competitive performance, this creates a favourable market advantage. Detector designs for the RCE-PD can also be applied across all ranges of the

infrared spectrum, from SWIR to the LWIR, demonstrating the versatility of the technology, which can be applied to almost an infinite range of applications, including those in the environmental monitoring and

medical applications. The project team's goal for ATTRACT is to demonstrate the extraordinary potential of RCE-PD detectors to not only revolutionise the infrared detector market, but to contribute to providing a solution to many global challenges. The RCE-PD detector could provide unprecedented accuracy in detecting and identifying chemical or biological compounds by tuning the resonant wavelengths of the detector to that of the unique fingerprint spectral peaks of the chemical. This could provide a breakthrough in environmental monitoring data of greenhouse gases, assist in plastic sorting at recycling centres, or even the

non-invasive detection of biomarkers relating to diseases or medical conditions. In ATTRACT Phase 2, the project team will collaborate with potential end-users, integrating the RCE-PD technology with hardware developed by these users for specific applications, involving detection at range and wearable technology. Efforts to introduce the technology into plastic sorting applications will also explored during Phase 2 of the ATTRACT project.

The highest performance segment of the gas sensor market is dominated by products whose measurement principle is based on laser spectroscopy. Amethyst's RCE-PD detector technology allows a non-dispersive IR method to more closely approximate the performance of laser spectroscopy. The prices for such laser

Process Transfer		Single Photon Detectors			MCCEL-		
IP licence	MESA	Planar	Mid-IR	Single Photon Emitters	VUSELS		
Epi Design	Optimisation & design win	dow for manufacturability	Improve detectors quantum efficiency	Optimisation & design window for Optimisation manufacturability Manufacturability		ion & design window for urability	
	TOSHIBA 🖛 ICS	TOSHIBA		TOSHIBA		CAL RD M	
Epi Growth	Scale-up study – establish for key parameters affectin	growth process window g device operation IŒ	Process transfer & manufacturability	Scale-up study – establish growth process window for key parameters affecting device operation	Scale-up study – e process window fo affecting device op	stablish growth or key parameters peration	
Device/Process Design	TOSHIBA	TOSHIBA		TOSHIBA	Single-mode & yield	High polarisation stability	
Fabrication	Process-induced defect stu currents. Manufacturabilit	dy to minimise dark y and process transfer	Process optimisation, transfer & manufacturability	Process optimisation, transfer & manufacturability	optimisation	stability	
	CAMBRIDGE ICS	CAMBRIDGE	Lancaster 😳 🛑 🢡	CAMBRIDGE	ICS	COMPOUND SEMICONDUCTOR	
Packaging	Process, design and material optimisation for manufacturability for lead application			n In In I	Subcontracted (high-TRL, low innov)		
Assembly	Feasibility study on Phase II applications to understand impact on process/design/materials Miniaturisation, optimisa for manufacturability		misation <u>Microsem</u>				
Characterisation	TOSHIBA ICS	TOSHIBA	<u>AR\</u> ?	TOSHIBA	Linewidth, stability Reliability studies		
Validation (headline application)	Quantum cryptography	(BT) ?	Hyperspectral imaging.? Application lead?	?	Atomic clocks		
Specification Owner	TOSHIBA ICS			TOSHIBA			
Other applications & IAB / Foundry Proxy	Healthcare (bioluminescence detection, DNA sequencing)		Automotive LiDAR, healthcare, free-space comms, env monitoring,	Phase II: indistinguishable photons for quantum computing?		neters	
	TOSHIBA (BT)		imaging, vibr spectroscopy				

Figure 14: Current Strategy for Technology Commercialisation of RCE-PD: Amethyst is involved in a major collaboration with Universities, SMEs and manufacturing primes to exploit and commercialise the next generation of III-V electro-optical devices. ATTRACT Phase 2 will provide the ideal platform for full exploitation of this consortia.

spectroscopy instruments range from \$50K to \$200K. Key players include Picarro, Los Gatos Research (ABB), Tiger Optics and LI-COR. More information on these companies will be provided in the competition section. Our targeted niche market is researchers in the fields of soil, agriculture/forestry, hydrology, ecology and environmental studies. In 2018 there were over 200K such researchers in the United States alone (and we estimate twice that number globally). In recent years, a number of research consortia have formed to standardize data and increase accessibility.

We believe each of these sites is a potential location for an Amethyst Instrument, over 1600 units of sales. In addition to these, many researchers prefer to work independently of the consortia, or may wish to have additional instruments to use elsewhere. With these included, we estimate the total number of potential unit sales to be over 3000. At an average price of \$25K, that puts the Served Available Market (SAM) at \$75M in 2019. That is a cumulative "installed base" number, not an annual market size. To convert that to an annual market size, if we assume a saturated market and annual replacement rate of 15%, the SAM is in the range of \$12M to \$16M over the next decade. (This also includes a 3-4% growth rate of the installed base.)

Barriers to entry are relatively low. Brand recognition is strong for the key players, but customers are generally sophisticated and eager to test new technology and tools if there is perceived value. They are not difficult to locate and to communicate with because they publicize their research and contact information. The American Geophysical Union (AGU) operates regular conferences that are well attended by our target customers. There are no critical component technologies that are outside Amethyst control. There are no significant government regulations or licensing requirements. Since Amethyst's tool is bringing a new capability to customers, switching costs are not really a concern - - customers will most likely continue to use their existing tools even while incorporating Amethyst's tool into their research.

7

Amethyst plans to manufacture, assemble and sell its measurement systems via a direct-to-end-user channel. There is no need for an established player to provide access to customers. The SAM is fairly small, so scaling up production does not necessarily require a manufacturing partner. We will pursue initial sales through pilot demonstrations at one or more of the research networks identified above. This pilot approach will allow the company to focus its current resources on select direct relationship opportunities as it brings up a dedicated sales and marketing team. As an alternative option, there are large gas sensing players that do not participate in this high performance segment, and it may make sense to seek an alliance for purposes of fund raising and accelerating growth. This possibility will be explored further in Phase 2.

Patent Status	Description		
Granted	US #7,888,251 "Photo-assisted hydrogenation		
	process"		
	US #9,196,497 "Photolytic processing of		
	materials with hydrogen"		
Applied for and	US20120009769, "Annealing of amorphous In Si		
Published	Formed by Ion-Implantation: A Method To		
	Eliminate Residual Defects"		
	US20110070143, "Hydrogenation Of Polysilicon		
	Nanowires"		
	US20100327276, "Method and System for		
	Passivation of Defects in Mercury Cadmium		
	Telluride Based Optoelectric Devices"		
	US20090309623, "Method for Assessment of		
	Materials Defects"		
In Preparation	"Detection of Gases Using Resonant Cavity		
	Infrared Detectors"		
Exclusive	US #8,018,019 "Space-charge-free semiconductor		
Licenses	and method" (Univ. of Rochester)		
	US #8,274,096 "Unipolar Barriers for Reduction		
	of Surface Leakage Current and Semiconductor		
	Devices" (Univ. of Rochester)		
	US20180219110, "Low Dark Current, Resonant		
	Cavity-Enhanced Infrared Photodetectors" (Univ.		
	of Rochester)		
	WORLDWIDE APPLIED FOR		

Table 2: Status of Granted and Filed Patents

5.4 Technology Commercialization.

To commercialise RCE-PD technology, Amethyst will engage with end users as of prime importance and have taken the initiative to contact several potential customers throughout the duration of ATTRACT Phase 1. ATTRACT Phase 2 will endeavour to integrate advanced RCE-PD detectors into existing laser systems developed by a potential end-user who has already shown an interest in the detector technology. This will develop a stand-off gas sensor with significant improvements in performance and detection range in comparison to the existing system. The project team are also currently interacting with medical experts and specialised electronics companies to explore the potential of RCE-PD technology to be integrated into wearable sensors for non-invasive biomarker detection. Plastic sorting is another application the team would like to introduce this technology to, Amethyst have industrial contacts that could provide a route to make this possible.

Reliable, volume supply of photonic components (single-mode low-power lasers, single photon emitters and detectors) are key to enabling vast number of applications for the emerging E/O technologies across Europe, computing, communication, sensing and metrology. There is a pressing need for proven platform technologies for these components due to several factors:

• As critical components E/O systems, the stability, efficiency and reliability of these photonic components must be proven in order

to qualify E/O modules for real applications and this is a major barrier to technology adoption. Whilst some Innovate UK projects have demonstrated a small number of successful devices, there is significant further R&D required towards robust devices for reliable applications.

- Low-yielding processes present a high bill of materials for E/O modules, resulting in low adoption of E/O technologies and low-volume production. Public intervention is required for industrial research to address manufacturability challenges of these components.
- Majority of European collaborative R&D projects include design, fabrication and testing of photonic components as a parallel strand, either on or off the critical path activities across our European partners.

Intellectual Property Landscape:

RCE-PD infrared detector and the novel system architecture. The company aggressively pursues IP protection of its technologies. Amethyst currently has eleven US and European patents either granted or filed and has a portfolio of technologies held as trade secret. Table 2 presents a summary of some of the patent protections Amethyst has or is seeking for this program.

A preliminary examination of the intellectual property landscape identified no patents that would block introduction of our products into the market. Since our competition uses technically different measurement methods (i.e. laser spectroscopy), it is unlikely that they would hold IP that blocks Amethyst from entering the market.

5.5. Envisioned Risks

The main risks to a potential Phase 2 of the TIMES project would be the development of a commercial supply chain for developing RCE-PDs at scale, since currently these are developed on an academic MBE reactor which lacks both the capacity and quality for large-scale industrial manufacturing of the devices. In order to mitigate this, Amethyst will develop this required supply chain through known partners and contacts who have access to industrial-level equipment, whilst Lancaster University can use their reactor to fine-tune and optimise the design for specific applications. Another core risk for the industrialisation of RCE-PDs is that the detector electronics will need to be modified for each intended application._For small volume system sales, Amethyst can provide custom detector electronics for these applications. To scaling up production for higher volume sales Amethyst may seek assistance to an industrial partner and provide know-how to modify and manufacture detector electronics in bulk.

5.6. Liaison with Student Teams and Socio-Economic Study

As a innovate IR&D SME Amethyst enjoys remarkable close and in-depth interactions with major Universities and national laboratories, including our work at European sites, such as Fraunhofer. For example, Lancaster University has collaborated with Amethyst Research Ltd since 2012 and they are a key strategic partner for the University including a Knowledge Transfer Partnership (KTP).

Furthermore, we have an Industrial Hot Desk for Amethyst and host Amethyst staff on site on a frequent basis so they can access our specialist clean room facilities and interact with our expert faculty and their KTP associate with us.

Amethyst's support was instrumental in Lancaster being awarded funding for the Collaborative Technology Access Programme (cTAP) facility that offers businesses managed access to a suite of cutting-edge instrumentation. The £11.3M investment (including over £9M from European Regional Development Fund) includes a £1M start of the art Molecular Beam Epitaxy (MBE) machine used to manufacture semiconductor devices. Without Amethyst evidencing clear industry demand for this type of capability, it would have been difficult to obtain this level of funding, and bring this capability to the European consortia.

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