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14. ABSTRACT
This report describe our work using p-type heterostructure devices as a platform to study band structure and band offset of heterojunction device structures. The goal is to understand
the field-induced and temperature dependent changes in the valence band (VB) structure and relative properties used for designing
and fabricating devices, such as absorption properties, carrier transports at the non-zero field condition, band parameters including the VB splitting energies, effective masses, and the band alignment at

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Band structure and band offset characterization of semiconductor heterojunctions

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and fabricating devices, such as absorption properties, carrier transports at the non-zero field condition, band parameters including the VB splitting energies, effective masses, and the band alignment at
interfaces of heterojunctions, etc., by looking into the inter-valence-subband (IVSB) transitions caused photo-response spectroscopy. These ideas were applied to HgCdTE , GaAs/AlGaAs and type II superlattice type detectors. Hence this work provides critical information for heterostructure device development, not only for p-type Heiwip devices but also for p-n junction devices, HgCdTE detectors, type II superlattice detectors and in general for future detector development efforts.

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

Received		Paper
01/03/2017	15	Yan-Feng Lao, A. G. Unil Perera, Y. H. Zhang,T. M. Wang. Band Offset non commutativity of GaAs/AlGaAs interfaces probed by internal photoemission spectroscopy, Applied Phylics letters, (07 2014): 171603. doi:
01/03/2017	25	Yan-Feng Lao, P. K. D. D. P. Pitigala, A. G. Unil Perera, E. Plis, S. S. Krishna, Priyalal S. Wijewarnasuriya. Band offsets and carrier dynamics of type-II InAs/GaSb superlattice photodetectors studied by internal photoemission spectroscopy, Applied Physics Letters, ( ): 181110. doi:
01/03/2017	27	R C Jayasinghe, Y F Lao, A G U Perera, M Hammar, C F Cao and H Z Wu. Plasma frequency and dielectric function dependence on doping and temperature for p-type indium phosphide epitaxial films, J. Phys.: Condens. Matter, ( ): 435803. doi:
01/03/2017	23	Yan-Feng Lao, P. K. D. D. P. Pitigala, A. G. Unil Perera, E. Plis, S. S. Krishna, Priyalal S. Wijewarnasuriya. Band offsets and carrier dynamics of type-II InAs/GaSb superlattice photodetectors studied by internal photoemission spectroscopy, Applied Physics Letters, ( ): 181110. doi:
01/03/2017	20	Seyoum Wolde, Y. F. Lao, P. K. D. D. P. Pitigala, A. G. U. Perera, L. H. Li, S. P. Khanna, E. H. Linfield. Low-frequency noise properties of p-type GaAs/AlGaAs heterojunction detectors, Infrared Physics & Technology, ( ): 99. doi:
01/03/2017	5	Y. F. Lao, A. G. Unil Perera, L. H. Li, S. P. Khanna, E. H. Linfield, and H. C. Liu. Tunable hot-carrier photodetector beyond the spectral limit, Nature Photonics, (03 2013): 412. doi:
07/21/2016	19	Sanjib Kabi and A. G. Unil Perera. Effect of quantum dot size and size distribution on the intersublevel transitions and absorption coefficients of III-V semiconductor quantum dot, Journal of Applied Physics 1, ( ): 124303. doi:
07/21/2016	18	A. G. U. Perera, Y. F. Lao, P.S. Wijewarnasuriya, S. S. Krishna. Band Offsets of III-V and II-Vi Materials studied by Temperature -Dependent Internal Photoemission Spectroscopy, Journal of Electronic Materials, ( ): 1. doi:

TOTAL: **8**

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(b) Papers published in non-peer-reviewed journals (N/A for none)

Received Paper

TOTAL:

Number of Papers published in non peer-reviewed journals:

(c) Presentations

Tunable hot-carrier photodetectors for terahertz frequency operation

Number of Presentations: 1.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

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01/03/2017	26	A. G. U. Perera,Y. F. Lao , P. K. D. D. P. Pitigala , S. P. Khanna , L. H. Li , E. H. Linfield ,H. C. Liu. Hot-carrier photodetector beyond spectral limit, 2013 IEEE Photonics Conference (IPC). 08-SEP-13, Bellevue, WA, USA. : ,
07/21/2016	17	A. G. U. Perera, Y. F. Lao. Temperature Dependent Internal Photoemission Spectroscopic Probe for band - Offset studies in III- V and II- Vi Materials, The 2015 US Workshop on the Physics and Chemistry of II-Vi materials. 05-OCT-15, Chicago, Illinois. : ,

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Number of Manuscripts:

Books

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TOTAL:

Patents Submitted

Patents Awarded

High operating temperature split-off band infrared detector with double and/or graded barrier

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Tunable hot carrier Photodetector

High Operation Temperature Split-Off Band Infrared Detectors”

Awards

Fellow IEEE

Fellow APS

Fellow SPIE

Graduate Students

NAME	PERCENT_SUPPORTED	Discipline
Dimuthu Bandara	0.50	
Dilip Chauhan	0.10	
Duleepa Pitigala	0.50	
FTE Equivalent:	**1.10**	
Total Number:	**3**	

Names of Post Doctorates

NAME	PERCENT_SUPPORTED
Yanfeng Lao	0.50
Sanjib Kabi	0.50
Diviya Somwansi	0.50
FTE Equivalent:	**1.50**
Total Number:	**3**

Names of Faculty Supported

NAME	PERCENT_SUPPORTED	National Academy Member
A. G. U. Perera	0.10	
Y. F. Lao	0.50	
FTE Equivalent:	**0.60**	
Total Number:	**2**	

Names of Under Graduate students supported

NAME	PERCENT_SUPPORTED	Discipline
Christopher Troy Thurman	0.05	Physics
FTE Equivalent:	**0.05**	
Total Number:	**1**	

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period:	1.00
The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:......	1.00
The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:......	1.00
Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):......	1.00
Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:......	0.00
The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense	0.00
The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields:	0.00

Names of Personnel receiving masters degrees

NAME	
Seyoum Wolde	
Dimuthu bandara	
Dilip Chauhan	
Total Number:	**3**

Names of personnel receiving PHDs

NAME	
Duleepa Pitigala	
Total Number:	**1**

Names of other research staff

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Sub Contractors (DD882)

Inventions (DD882)

5 High Operating temperature Split off Band infrared detector with double and/or graded Barrier

Patent Filed in US? (5d-1) Y
Patent Filed in Foreign Countries? (5d-2) Y
Was the assignment forwarded to the contracting officer? (5e) Y
Foreign Countries of application (5g-2): Canada

5a: A. G. U. Perera and S. G. Matsik

5f-1a: Georgia State University

5f-c: 29 peach tree center Avenue
Atlanta GA 30303

5 Tunable Hot carrier Photodetector

Patent Filed in US? (5d-1) Y
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Foreign Countries of application (5g-2): International

5a: A. G. U. Perera and Y. F. Lao

5f-1a: Georgia State University

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Atlanta GA 30303

Scientific Progress

Internal photoemission (IP) correlates with processes in which carriers are photoexcited and transferred from one material to another. This characteristic allows characterizing the properties of the heterostructure, for example, the band parameters of a material and the interface between two materials. IP also involves the generation and collection of photo carriers, which leads to applications in the photodetectors. We have studied the generic IP processes based on heterojunction structures, characterizing P type band structure and the band offset at the hetero-interface, and infrared photo detection including a novel concept of photo response extension based on an energy transfer mechanism between hot and cold carriers.

Among the most important aspects in a heterojunction consisting of two dissimilar materials is its heterointerface at which differences in band gaps give rise to a band offset across their interface. Accurate knowledge of band offsets and their temperature dependence will allow one to simulate and predict the device performances. Although a variety of methods have been developed, most of them cannot measure the band offsets at different temperatures. We demonstrated the temperature-dependent internal-photoemission spectroscopy (TDIPS) for heterojunction characterizations.1 This technique was applied to both III- V and II- VI materials.2,3,4 In addition we studied detectors based on various material systems to understand the band offsets. We also studied different material systems for infrared detection and showed various ways to improve the performance. Each of these ideas are summarized in the following sections

We use internal photoemission spectroscopy to determine the conduction band offset of a type-II InAs/GaSb superlattice (T2SL) pBp photodetector to be (+-)0:004 eV at 78 K, confirming its unipolar operation.2 It is also found that phonon-assisted hole transport through the barrier region disables its two-color detection mode around 140 K. In addition, photoemission yield shows a reduction at about an energy of longitudinal-optical phonon above the threshold, confirming carrier-phonon scattering degradation on the photo response. These results may indicate a pathway for optimizing T2SL detectors in addition to current efforts in material growth, processing, substrate preparation, and device passivation.

We have also studied the non-commutativity of band offset on the dependence on the order of the growth of the layers. This result is consistently confirmed by observations at various experimental conditions including different applied biases and temperatures. The GaAs/AlGaAs material system is believed to have a band offset without remarkable influence from the interface. However, We found a slightly higher (5–10 meV) valence-band offset at the GaAs-on-Al0.57Ga0.43As interface compared to that of the Al0.57Ga0.43As-on-GaAs interface, by using internal photoemission spectroscopy showing the importance of the existence of non-commutativity of the band offset.5

We employed internal photoemission spectroscopy to directly measure the valence-band Van Hove singularity, and identify phonons participating in indirect inter-valence band optical transitions.6 Photoemission of holes photoexcited through transitions between valence bands displays a clear and resolvable threshold. We also demonstrate the enhancement of optical phonon-assisted features primarily contributing to the photoemission yield. This result is evidence of the relaxation of photoexcited hot holes through intra-valence-band scatterings in heterojunctions, which contrast with intervalence-band scatterings in bulk GaAs material. Also, it was found that the valence band splitting energy of GaAs was found to remain unchanged, although degenerate doping introduces appreciable band tailings.

Photoluminescence measurements on GaAs and AlGaAs thin films revealed a dependency of incident light intensity, and temperature in Band Gap Narrowing in addition to the doping density. This will in turn change the barrier heights expected in the heterojunction devices. As a result, the valence band offset of p-doped GaAs/ AlGaAs heterojunctions were reduced under illumination and high temperatures. We presented evidence of incident-light-intensity causing barrier reduction7 at temperature >50 K causing zero valence band offsets in low-barrier heterostructures such as p-GaAs/Al0.01Ga0.99As, in addition to the dark-current increase by thermal excitations, causing the device failure at high temperatures.

Uncooled split-off band infrared detectors have been demonstrated with an operational device response in the 3–5 μm range. We have shown that it is possible to enhance this device response through reducing the recapture rate by replacing one of the commonly used flat barriers in the device with a graded barrier, which was grown using a “digital alloying” approach8. Responsivity of approximately 80 μA/W (D* of 1.4 x108 Jones) were observed at 78 K under a 1 V applied bias, with a peak response at 2.8 μm. This is an improvement by a factor of 25 times compared to an equivalent device with a flat barrier. This enhancement is due to improved carrier transport resulting from the superlattice structure, and a low recapture rate enabled by a reduced distance to the image force potential peak in the graded barrier. The device performance can be further improved by growing a structure with repeats of the single emitter layer as reported.

Photovoltaic infrared detectors have significant advantages over photoconductive detectors due to zero bias operation, requiring low power and having reduced low frequency noise. They also exhibit no thermally assisted tunneling currents, leading to higher operating temperatures. P-type emitter/graded barrier GaAs/AlxGa1xAs structures were tested as photovoltaic detectors in the infrared region, operating under uncooled conditions and without an applied bias voltage. A photovoltaic responsivity of 450 mV/W was obtained with a detectivity (D*) of 1.2 x106 Jones at a peak wavelength 1.8 micron at 300 K. Responsivity and D* increased to 1.2 V/W and 2.8 x106 Jones, respectively, at 280 K. A non-linear improvement in responsivity was observed with increased emitter thickness.9

In order to broaden the understanding of the detector characteristics, we measured and analyzed, at different temperatures and bias voltages, the dark noise spectra of GaAs/AlGaAs heterojunction infrared photodetectors.10 The noise and gain mechanisms associated with the carrier transport were investigated, and it was found that a lower noise spectral density is observed for a device with a flat barrier, and thicker emitter. Despite the lower noise power spectral density of flat barrier device, comparison of the dark and photocurrent noise gain between flat and graded barrier samples confirmed that the escape probability of carriers is enhanced by grading the barrier. This mechanism is important to achieve an improved response and hence the detectivity of the detector. The grading suppresses recombination owing to the higher momentum of carriers in the barrier. Optimizing the emitter thickness of the graded barrier to enhance the absorption efficiency, and increase the escape probability and lower the dark current, enhances the specific detectivity of devices.

Increasing the operating temperature of infrared detectors is a prime importance for practical applications. The use of split-off band transitions has been proposed for high operating temperature infrared detectors. Initial results showed increasing the potential barrier for free carrier emission has led to increases in operating temperature from 150 K for a detector with an 8 micron threshold to room temperature for detector with a 4 micron threshold. However, these detectors showed a low responsivity due to the capture of carriers in each emitter. A proposal was made to use graded barriers with an offset between the barriers on the two sides of an emitter as a method of reducing the capture in the emitters. Two GaAs/AlGaAs samples with a single graded barrier (Al fraction $x = 0.57$ to 1 and 0.45 to 0.75, respectively) were used to test the effects.8 The sample with the lower barrier show responsivity increased by a factor of 10 or more compared to the higher graded barrier sample and detectors without the graded barrier. The higher graded barrier sample, space charge build up causes almost all potential drop across the first barrier, and hence reduces the response. Based on the modeling it is believed that this effect will be greatly reduced in detectors with multiple periods of graded barriers and emitters, allowing the full gain effects of the graded barriers to be realized.

Based on this two barrier device, A photodetector operation based on a hot-cold carrier energy transfer mechanism has been demonstrated.11,12,13 Hot carriers injected into a semiconductor structure interact with cold carriers and excite them to higher energy states. The spectral response of common optoelectronic photodetectors is restricted by a cutoff wavelength limit λc that is related to the activation energy (or bandgap) of the semiconductor structure (or material) (Δ) through the relationship $\lambda c = hc/\Delta$. This spectral rule dominates device design and intrinsically limits the long-wavelength response of a semiconductor photodetector. We reported a new, long-wavelength photodetection principle based on a hot–cold hole energy transfer mechanism that overcomes this spectral limit. Hot carriers injected into a semiconductor structure interact with cold carriers and excite them to higher energy states. This enables a very long-wavelength infrared response. In our experiments, we observe a response up to 55 μm, which is tunable by varying the degree of hot-hole injection, for a GaAs/AlGaAs sample with $\Delta = 0.32$ eV (equivalent to 3.9 μm in wavelength). This idea could be used to develop long wavelength detectors with dark current associated with a shorter wavelength threshold device.

Minimizing the infrared reflection from the surface of a detector is an important criteria for applications. The reflection can also change with the incident angle of the light. Understanding this should lead to improved performance of the detectors. Oblique-angle deposited titanium dioxide (TiO2) nano-rods have attracted much attention as good antireflection (AR) coating material due to their low n profile. Therefore, it is necessary to better understand the optical properties of these nano-rods. TiO2 nano-rods grown on glass and Si substrates were characterized in the visible (0.4–0.8 μm) and infrared (2–12 μm) regions to extract their complex n profiles empirically.14 Application of these nano-rods in multilayer AR coatings on infrared detectors is also discussed. Optimization of graded index profile of these AR coatings in the broad infrared region (2–12 μm) even at oblique angles of incidence is discussed. The effective coupling between the incoming light and multiple nano-rod layers for reducing the reflection is obtained by optimizing the effect from Fabry–Perot oscillations. An optimized five-layer AR coating on GaN shows the reflectance less than 3.3% for normal incidence and 10.5% at 60° across the whole 2–8 μm spectral range.

Since most of the work was focused on P type GaAs/AlGaAs material it was important to find out how other P type materials would perform as Infrared Detectors. In order to understand this issue, optical properties of p-type InP epitaxial films with different doping concentrations were investigated by infrared absorption measurements accompanied by reflection and transmission spectra taken from 25 to 300 K.15 A complete dielectric function (DF) model, including inter-valence band (IVB) transitions, free-carrier and lattice absorption, is used to determine the optical constants with improved accuracy in the spectral range from 2 to 35 μm. The IVB transitions by free holes among the split-off, light-hole, and heavy-hole bands are studied using the DF model under the parabolic-band approximation. A good understanding of IVB transitions and the absorption coefficient is useful for designing high operating temperature and high detectivity infrared detectors and other optoelectronic devices. In addition, refractive index values reported here are useful for optoelectronic device designing, such as implementing p-InP waveguides in semiconductor quantum cascade lasers. The temperature dependence of hole effective mass and plasma frequency is also reported. Along this line InGaN/GaN heterostructures were also studied.16 We reported on the studies of optical phonon modes in nearly defect-free GaN nanowires embedded with intrinsic InGaN quantum dots by using oblique angle transmission infrared spectroscopy. These phonon modes are dependent on the nanowire fill-factor, doping densities of the nanowires, and the presence of InGaN dots. These factors can be applied for potential phonon based photodetectors whose spectral responses can be tailored by varying a combination of these three parameters. The optical anisotropy along the growth (c-) axis of the GaN nanowire contributes to the polarization agility of such potential photodetectors.

We also studied the optical response of pristine and FeCl3-intercalated epitaxial graphene has been studied over the temperature range from 11 K to 296 K.17 The far-infrared (FIR) Drude conductivity of pristine graphene rises with increasing temperature, opposite to the behavior of intercalated graphene. This is a result of intercalation-induced p-type doping compensating the intrinsic n-doping in epitaxial graphene. Temperature-dependent Drude parameters are obtained by fitting the FIR response. This study demonstrates the influence of temperature variation on the optical properties of graphene, which should be a vital factor to be considered for graphene-based device applications.

We also studied solar cells by using molecularly organized dye on n- and p- type semiconductors. For example, a solar cell of configuration N-(DDD——D)-P with a molecularly organized dye J-aggregate (DDD—D) electronically coupled to n- and p-type semiconductors was illustrated by fabricating a model device, where TiO_2 and CuSCN are the n- and p-type substrates and D is the thiocyanate of a cationic pentamethine cyanine dye.18 Functional moieties in D anchors to TiO_2 establishing electronic coupling and serving as a template for assembly of a J-aggregated film. Bonding of sulfur in thiocyanate anions at the other end of the aggregate create the electronic coupling needed to facilitates transfer of holes to CuSCN. The cell exhibits photo-response originating from excitons generated in the bulk of the thick dye film as well as direct sensitized injection at the first interface. The dye molecular assembly is found to admit exciton transport over relatively long distances and significant hole mobility.

In summary we have studied P- type heterojunction infrared detectors using various techniques to improve the performance of the detectors. Different material systems were also atudied in order to implement the splitoff detector ideas in to toher material systems. The P type detection technique which use the internal photoemission spectroscopy was used to study the Band offsets, and the variation of that with temperature, non commutativity of the band offsets due to the order of the layers to name a few. A modification to the Fowler theory was developed to come up with a more accurate technique, i.e. Temperature dependent internal photemission spectrocscopy to determine the energy thresholds which determine the long wavelength threshold of the infrared detectors.

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Technology Transfer

We have interacted with US army scientists Dr. P.S. P. C. Wijewarnasuriya and Dr. K. K. Choi. A new method developed to study temperature dependence of the band structure using internal photoemission (TDIPS) was applied to HgCdTe detector samples grown by the Army research Lab scientists. In addition this method was also applied to Type II superlattice detectors. The specific ideas developed through the program were presented at several meetings where other researchers were present who might benefit from the band offset characterization, especially applied to HgCdTe and Type II detector structures.