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RPPR Final Report

as of 04-Jan-2023

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Title: Hybrid silver selenide colloidal quantum dot - amorphous avalanche selenium infrared detectors (Electronics Sensing) (STIR)

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Major Goals: To aid and maintain highest level of mobility and situational awareness, future military systems in the Army are intended to conduct day/night and degraded visual environment [DVE] missions in conditions such as haze, dense fog, smoke, turbulence and even sand and dust to enable ground vehicle maneuvering [tanks, trucks etc.], automated human detection, vehicle detection and tracking, identify targets and perform threat assessment. In addition, threat warning systems such as infrared countermeasures and hostile fire indication are necessary on ground vehicles for missile and rocket mitigation and detection of small arms and rocket propelled grenade fire. All of these systems need to detect unresolved signals and operate at high speed and high frame rate, to catch short duration events with low false alarms. This motivates design of novel sensors and imaging architectures that are durable, affordable and can provide high performance and persistent surveillance. In this regard, infrared [IR] detectors and imagers have the powerful ability to resolve optical images in low visibility or obstructed environments. In the IR spectrum, there are four distinct windows: near-infrared [NIR, 0.7–1 μm], short-wavelength infrared [SWIR, 1–2.7 μm], mid-wavelength infrared [MWIR, 3–5 μm] and long-wavelength infrared [LWIR, 8–15 μm]. The technological advantage of extending the spectral response towards longer MWIR and LWIR lies in the fact that detectors do not require an illumination source for imaging [passive imaging] and have the ability to see through airborne obscurants such as smoke, mist, and fog. In particular, MWIR detectors are highly suited for first-responder and search-and-rescue, night driving, machine vision, and poor weather surveillance applications that require capabilities unmet by visible and NIR detectors.

The goal of this STIR project was to design hybrid SWIR and MWIR detectors by coupling recently discovered IR-active Ag₂Se colloidal quantum dots (CQDs) with amorphous-Selenium [a-Se] avalanche photodiodes, operating at room temperature [RT] with extremely low noise and SWaP-C compared to the well-established HgCdTe detectors that demand cryogenic cooling. Our proposed plan is to use intrinsic interband and degenerately doped intraband Ag₂Se CQDs as efficient IR photon absorbers and couple those to an a-Se transport layer utilizing an avalanche phenomenon to increase the signal-to-noise ratio [SNR] generating extremely sensitive IR detectors and imagers under photon-starved conditions. In practical avalanche detectors, the amount of enhancement in SNR is limited by excess noise caused by the stochastic nature of the avalanche impact ionization process and the optimal SNR typically occurs at very low gain values. The magnitude of noise enhancement depends on several factors such as intrinsic material properties, device structure, and biasing conditions. To address these issues, for the first time, we propose an IR QD sensitized solid-state a-Se photomultiplier that will achieve reliable and repeatable impact ionization gain without irreversible breakdown. This hybrid a-Se-QD sensor will successfully overcome the challenge of sensing, timing and quantifying low-light IR signals with high dynamic range, linear-mode operation, ultra-low dark current at RT, and noise-free avalanche gain. The outcomes of this project could potentially enable a low-cost, high performance IR imaging technology that will be ubiquitously utilized in a broad range of civilian and

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defense applications.

Accomplishments: The overarching goal of this research proposal was to fabricate a vertical-stack photodetector, using room-temperature, solution-processed IR Ag₂Se CQD photoconversion layer, with an a-Se layer acting as a wide-bandgap charge transport layer. Specific research tasks are listed below-

T1. Synthesis and materials characterization of IR Ag₂Se CQDs

T2. Design ligand exchange to reduce barriers for charge transport and improve mobility

T3. Design optimal colloidal deposition conditions on a-Se without crystallizing the same; and proof-of-concept-device fabrication

T4. Device characterization – fundamental properties such as absorption coefficient, carrier mobility and carrier lifetime, trap state location and density and device characteristics such as gain, 3dB bandwidth, responsivity, dark current, noise current and detectivity .

Risks and Mitigation Strategies Employed

1] During our initial experiments, we noted that unless carefully handled, Ag₂Se CQDs are highly prone to aggregation during ligand exchanges. Aggregation leading to crystal growth is a huge issue for these CQDs since it would lead to change of phase from tetragonal to orthorhombic, loss of quantum confinement and move the SWIR and MWIR absorbance to the LWIR or beyond. In order to solve this issue, we employed the following strategies-
A] Designed a novel synthesis that leads to stable small SWIR and large MWIR Ag₂Se CQDs with similar chemical functionality. This results in easy and translatable processing conditions for a wide range of Ag₂Se CQDs of various sizes rather than optimizing ligand exchange conditions for every size of QDs obtained via various syntheses protocols.

B] Standard ligand exchanges employed for other classes of CQDs in soft Ag₂Se CQDs leads to large aggregation and loss of quantum confinement. We designed a new strategy that involves using controlled ligand exchanges to obtain extremely photoconductive [50 mA/W] lateral Ag₂Se CQD films [Figures 1 and 2]

2] Secondly, a-Se is also prone to crystallization with common solvents used during colloidal quantum dot deposition. We employed a robust design of experiments strategy to identify solvents and processing conditions that do not crystallize a-Se. This allows fabrication of devices in a p-i-n structure which allows deposition of CQDs directly on a-Se. In addition, we proceeded to fabricate devices in an inverted n-i-p structure that deposits a-Se on the CQD layer [Figure 1]. The challenge now was to deposit a metal contact on the a-Se which was mitigated by using cold or room temperature deposition of metal contacts. We successfully fabricated the entire device sequence without crystallizing the a-Se layer.

Major results

1] We used the ligand exchange and CQD deposition strategy used for lateral devices to fabricate vertical devices. Preliminary n-i-p vertical devices with ITO/CeO₂/Ag₂Se/a-Se/ITO full stack shows photo-response in the micro-ampere range [Figure 3]. The spectral photoresponse matches the absorbance spectrum of the quantum dots proving that the photoresponse originates from the CQDs. Note that a-Se does not absorb in the IR region of the electromagnetic spectrum.

2] By controlling the layer thickness and ligand exchange, and applying higher biases [till photoresponse is higher than dark current], we were able to improve the photoresponse by nearly 3 orders of magnitude from our first generation devices in the μ A/W regime to the mA/W levels [Figure 4]. On-off ratios that track the photocurrent to dark current ratios are high at lower biases but decrease as expected at higher biases.

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Training Opportunities: In the current period, the grant has trained three graduate students and four undergraduate students.

Undergraduate Students

Navkawal Mattu - developed synthesis and optical characterization skills with the dodecanethiol capped Ag₂Se colloidal quantum dots

Richard Li – designed the dipcoater for conformal coating of Ag₂Se quantum dots

Ana Vataj – working on solution phase ligand exchange for Ag₂Se CQDs

Jasmin Sabirin – working on mesoporous TiO₂ films for better charge extraction.

Graduate Students

Haavard Moelnaas – led experimental thrust on device fabrication and device characterization of Ag₂Se colloidal quantum dots

Shlok Joseph Paul – led experimental thrust on the synthesis and ligand exchange of Ag₂Se CQDs

Jiaqi Zuo – designing barrier layers for vertical photodiode devices

Results Dissemination: Heavy Metal-Free IR Photodetection using Ag₂Se Colloidal Quantum Dots, S. J. Paul, H. Mølnås, M. Scimeca, N. Mattu and A. Sahu, presented at the Gordon Research Conference, July 2022, Les Diablerets, Switzerland. [Poster]

Honors and Awards: None to report. I was awarded the DARPA Young Faculty Award for another project related to IR quantum dots. The technology we are developing in that project uses HgTe colloidal quantum dots. However, the working principle can easily be adapted for using Ag₂Se quantum dots instead.

Protocol Activity Status:

Technology Transfer: Nothing to Report

PARTICIPANTS:

Participant Type: PD/PI

Participant: Ayaskanta Sahu

Person Months Worked: 2.00

Project Contribution:

National Academy Member: N

Funding Support:

Participant Type: Graduate Student (research assistant)

Participant: Shlok Joseph Paul

Person Months Worked: 6.00

Project Contribution:

National Academy Member: N

Funding Support:

Participant Type: Graduate Student (research assistant)

Participant: Havard Moelnaas

Person Months Worked: 6.00

Project Contribution:

National Academy Member: N

Funding Support:

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Participant Type: Graduate Student (research assistant)
Participant: Jiaqi Zuo
Person Months Worked: 2.00
Project Contribution:
National Academy Member: N
Funding Support:

Participant Type: Undergraduate Student
Participant: Navkawal Mattu
Person Months Worked: 3.00
Project Contribution:
National Academy Member: N
Funding Support:

Participant Type: Undergraduate Student
Participant: Jasmin Sabirin
Person Months Worked: 1.00
Project Contribution:
National Academy Member: N
Funding Support:

Participant Type: Undergraduate Student
Participant: Richard Li
Person Months Worked: 3.00
Project Contribution:
National Academy Member: N
Funding Support:

Participant Type: Undergraduate Student
Participant: Ana Vataj
Person Months Worked: 2.00
Project Contribution:
National Academy Member: N
Funding Support:

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Partners

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I certify that the information in the report is complete and accurate:

Signature: Ayaskanta Sahu

Signature Date: 12/30/22 10:39PM

Abstract:

Hybrid silver selenide colloidal quantum dot - amorphous avalanche selenium infrared detectors

To aid and maintain highest level of mobility and situational awareness, future military systems in the Army are intended to conduct day/night and degraded visual environment (DVE) missions in conditions such as haze, dense fog, smoke, turbulence and even sand and dust to enable ground vehicle maneuvering (tanks, trucks etc.), automated human detection, vehicle detection and tracking, identify targets and perform threat assessment. In addition, threat warning systems such as infrared countermeasures (IRCM) and hostile fire indication (HFI) are necessary on ground vehicles for missile and rocket mitigation and detection of small arms and rocket propelled grenade fire. All of these systems need to detect unresolved signals and operate at high speed and high frame rate, to catch short duration events with low false alarms. Current technology that involves radar, night-vision devices, and visual watches has been relatively unchanged since decades and is pretty much obsolete which provides a compelling motivation to design novel sensors and imaging architectures that are durable, affordable and can provide high performance and persistent surveillance. In this regard, infrared (IR) detectors have the powerful ability to resolve optical images in low visibility or obstructed environments. By extending the spectral response towards longer Mid-wave IR, detectors do not require an illumination source for imaging (passive imaging) and have the ability to see through airborne obscurants such as smoke, mist, and fog thus rendering them highly suited for applications that require capabilities unmet by visible and near-IR detectors.

Our aim is to design novel Mid-wave and Short-wave IR detectors and imagers by coupling recently discovered IR-active Ag_2Se colloidal quantum dots (CQDs) with amorphous-Selenium (a-Se) avalanche photodiodes, operating at room temperature with extremely low noise and SWaP-C (size, weight, power and cost) compared to the well-established mercury cadmium telluride (HgCdTe) detectors. In particular, this project aims to use Ag_2Se CQDs as a new environmentally benign and non-toxic IR photon absorber and couple those to an a-Se transport layer utilizing an avalanche phenomenon to increase the signal-to-noise ratio (SNR) generating extremely sensitive IR detectors and imagers under photon-starved conditions. Our approach focuses on ameliorating the issues with typical CQD-based detectors and a-Se avalanche detectors by coupling and exploiting the best features of both technologies to deliver a highly efficient IR detector.

The overarching goal of this research proposal is to fabricate a p-i-n vertical-stack photodetector, using room-temperature, solution-processed IR Ag_2Se CQD photoconversion layer, with an a-Se layer acting as a wide-bandgap charge transport layer. The ultimate aim is to demonstrate devices based on this hybrid a-Se:CQD system that would demonstrate high detectivity in the SWIR and the MWIR spectral regions, operating at high temperature ($> 200\text{K}$) accessible through a solid-state Peltier cooling device. The success of this project will have a huge impact on the IR imaging and sensing area which is currently dominated by the toxic HgCdTe detectors operating at cryogenic temperatures and enable a low-cost, high performance IR imaging technology that will be ubiquitously utilized in a broad range of defense applications. Also, our success will provide a road map for integrating CQDs in mainstream commercial IR applications and not just restrict to military and astronomy applications. Additionally, through this proposed work, we plan on advancing our fundamental and practical understanding of Mid-IR detector technology by focusing on the structure-property relationship of IR-active CQDs.

Objectives:

The overarching goal of this research proposal was to fabricate a vertical-stack photodetector, using room-temperature, solution-processed IR Ag₂Se CQD photoconversion layer, with an a-Se layer acting as a wide-bandgap charge transport layer. Specific research tasks are listed below-

- T1. Synthesis and materials characterization of IR Ag₂Se CQDs
- T2. Design ligand exchange to reduce barriers for charge transport and improve mobility
- T3. Design optimal colloidal deposition conditions on a-Se without crystallizing the same; and proof-of-concept- device fabrication
- T4. Device characterization – fundamental properties such as absorption coefficient, carrier mobility and carrier lifetime, trap state location and density and device characteristics such as gain, 3dB bandwidth, responsivity, dark current, noise current and detectivity .

Findings:

- T1. Synthesis and materials characterization of IR Ag₂Se CQDs –

Designed a novel synthesis that leads to stable small SWIR and large MWIR Ag₂Se CQDs with similar chemical functionality. This results in easy and translatable processing conditions for a wide range of Ag₂Se CQDs of various sizes rather than optimizing ligand exchange conditions for every size of QDs obtained via various syntheses protocols.

- T2. Design ligand exchange to reduce barriers for charge transport and improve mobility –

Standard ligand exchanges employed for other classes of CQDs in soft Ag₂Se CQDs leads to large aggregation and loss of quantum confinement. We designed a new strategy that involves using controlled ligand exchanges to obtain extremely photoconductive [50 mA/W] lateral Ag₂Se CQD films [Figures 1 and 2]

- T3. Design optimal colloidal deposition conditions on a-Se without crystallizing the same; and proof-of-concept- device fabrication –

a-Se is also prone to crystallization with common solvents used during colloidal quantum dot deposition. We employed a robust design of experiments strategy to identify solvents and processing conditions that do not crystallize a-Se. This allows fabrication of devices in a p-i-n structure which allows deposition of CQDs directly on a-Se. In addition, we proceeded to fabricate devices in an inverted n-i-p structure that deposits a-Se on the CQD layer [Figure 1]. The challenge now was to deposit a metal contact on the a-Se which was mitigated by using cold or room temperature deposition of metal contacts. We successfully fabricated the entire device sequence without crystallizing the a-Se layer.

- T4. Device characterization – fundamental properties such as absorption coefficient, carrier mobility and carrier lifetime, trap state location and density and device characteristics such as gain, 3dB bandwidth, responsivity, dark current, noise current and detectivity .

We used the ligand exchange and CQD deposition strategy used for lateral devices to fabricate vertical devices. Preliminary n-i-p vertical devices with ITO/CeO₂/Ag₂Se/a-Se/ITO full stack shows photo-response in the micro-ampere range [Figure 3]. The spectral photoresponse matches the absorbance spectrum of the quantum dots proving that the photoresponse originates from the CQDs. Note that a-Se does not absorb in the IR region of the electromagnetic spectrum.

By controlling the layer thickness and ligand exchange, and applying higher biases [till photoresponse is higher than dark current], we were able to improve the photoresponse by nearly 3 orders of magnitude from our first generation devices in the uA/W regime to the mA/W levels [Figure 4]. On-off ratios that track the photocurrent to dark current ratios are high at lower biases but decrease as expected at higher biases.

Unfortunately, we did not have enough time to fully characterize the device characteristics such as the noise current and the 3dB bandwidth. We have been unable to measure the gain since the devices currently break down before we reach avalanche in a-Se. This issue can be resolved by utilizing high dielectric electron transport layers such as BaTiO₃ instead of CeO₂.

Figures:

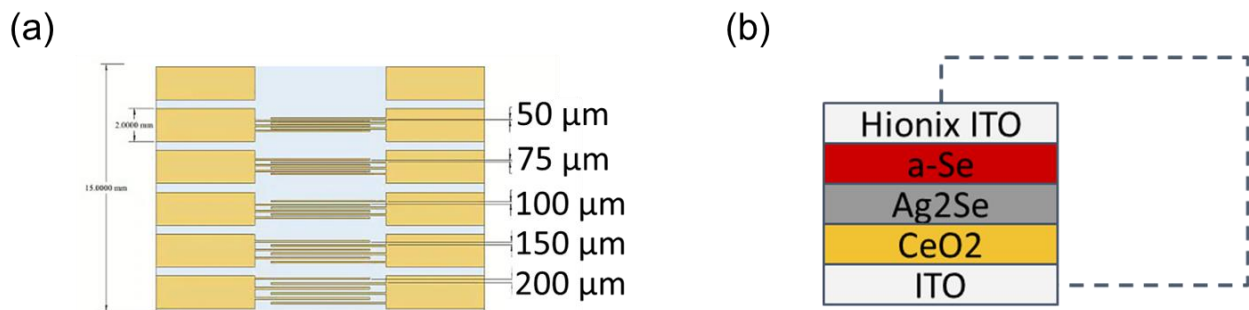


Figure 1: Photodetector device geometries. a) Lateral photoconductor geometry for sensing and detection. ITO interdigitated electrodes on glass substrate were purchased from Ossila Ltd b) Vertical photodiode geometry for imaging on an ITO/glass substrate with CeO₂ as the electron transport layer and a-Se as the hole transport layer.

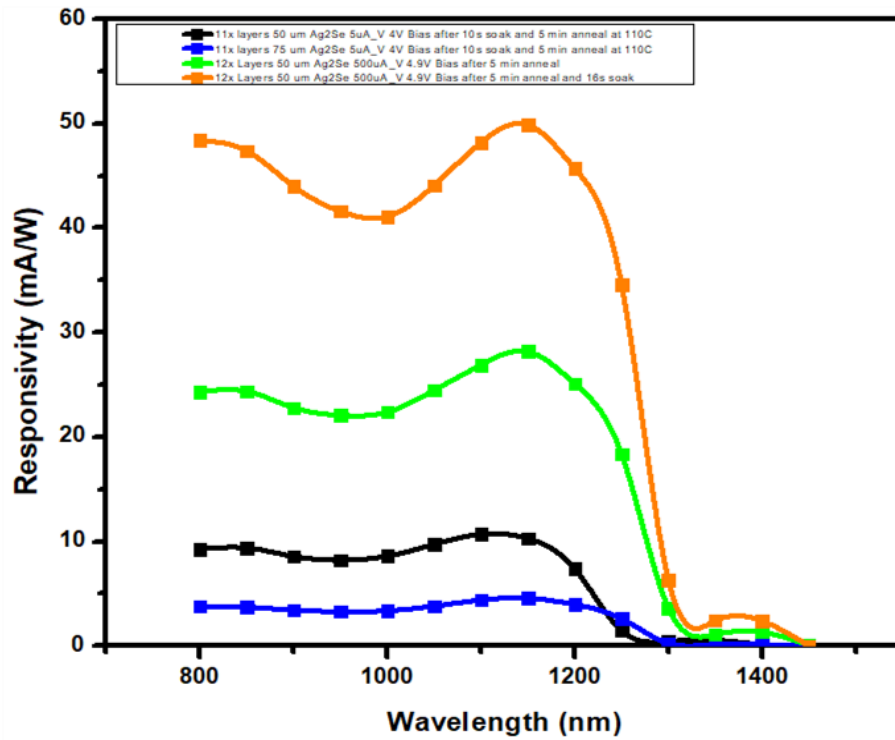


Figure 2: Maximizing responsivity of lateral Ag₂Se devices by controlled ligand exchanges, HCl additive treatment and annealing. Responsivity in lateral devices are currently at 50 mA/W which are the highest numbers reported to-date for Ag₂Se based SWIR devices.

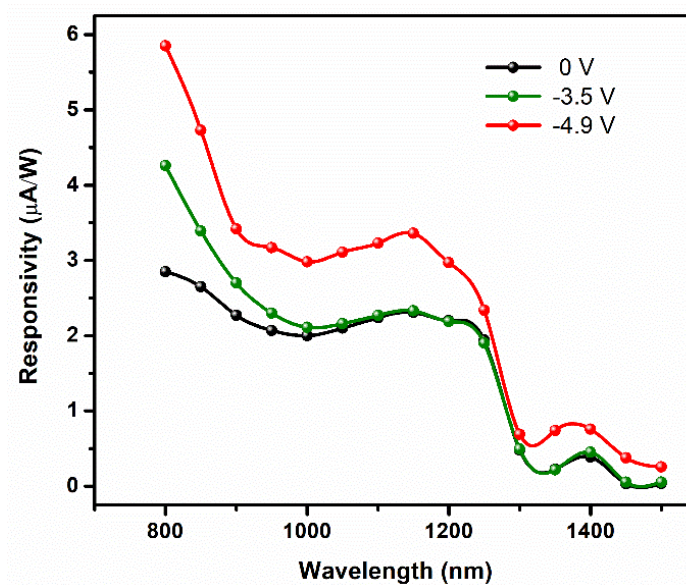
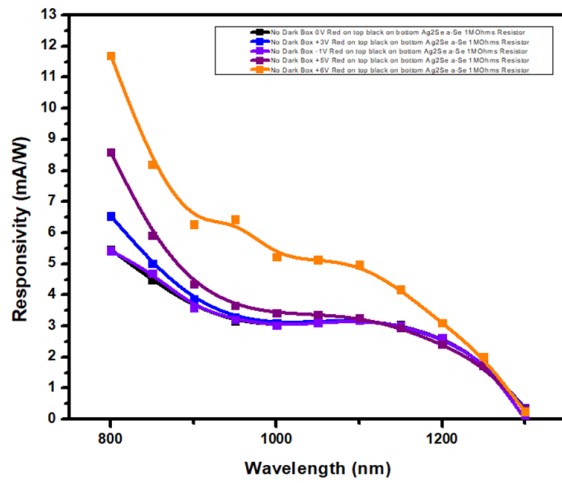


Figure 3: Responsivity in first generation vertical n-i-p devices (device structure shown in Figure 1b).

(a)



(b)

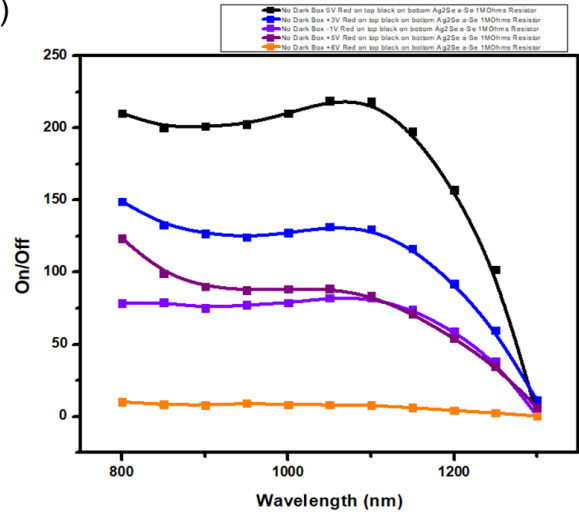


Figure 4: (a) Responsivity and (b) On-off ratios in second generation vertical n-i-p devices with optimized ligand exchange, layer thicknesses and applied bias. These devices show IR photoresponse ~ 6-10 mA/W which is the highest reported photoresponse for a vertical Ag₂Se device in the IR.