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# Development of Lead-free $Ag_2Te$ QDs-based Photodetector for SWIR Detection

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## Abstract

Recent advancements in autonomous driving and urban air mobility technologies have significantly increased the demand for infrared photodetectors. Short-wave infrared (SWIR) imaging provides improved image resolution compared with that of near-infrared imaging owing to its lower scattering and higher transmittance characteristics. Conventional commercialized SWIR-band photodetectors, such as InSb, Ge, HgCdTe, and InGaAs require complex manufacturing processes, resulting in high production costs and the need for additional cooling devices. Therefore, research on alternative materials, such as quantum dots (QDs), for SWIR photodetection is crucial. QDs are particularly promising candidates as photoactive materials owing to their relatively simple processing requirements and exceptional absorption characteristics at specific wavelength bands. $Ag_2Te$ QDs do not contain heavy metals (Pb, Hg, etc.), thereby complying with the European directive Restriction of Hazardous Substances. This study synthesized lead-free $Ag_2Te$ QDs with an absorption peak at 1670 nm, which corresponds to the eye-safe band, and fabricated a high-sensitivity SWIR photodetector. Additionally, to enhance the sensitivity of the device, P3HT (Poly(3-hexylthiophene-2,5-diyl)) and ZnO nanoparticles were incorporated as hole/electron extraction layers. As the results, the fabricated SWIR photodetector was confirmed to be capable of detecting an eye-safe wavelength laser of 1670 nm with a responsivity of up to 184.2%.

**Keywords:** SWIR, Photodetector, $Ag_2Te$ QDs, Lead-free QDs

## 1. INTRODUCTION

Recent advancements in industrial technology have led to active research in autonomous driving and urban air mobility technologies, resulting in a rapidly increasing demand for infrared photodetectors. Infrared photodetectors, which convert photons into electrical signals, are crucial in ensuring accurate object recognition and safety in low-light and adverse weather conditions. They are widely used in applications such as image detection, spectroscopy, and optical communication. Shortwave infrared (SWIR) in the range of 1000-2500 nm, facilitates improved image resolution compared with that of near-infrared (NIR) owing to its low scattering and high transmittance characteristics. The wavelength band above 1400 nm is considered eye-safe band because it is absorbed by the eye without penetrating the human retina. Therefore, there is an ongoing demand to develop photodetectors that can detect wavelengths within the eye-safe band of the SWIR spectrum, specifically those at or beyond 1400 nm. Initial research on photodetectors focused on bulk semiconductor materials, such as Ge and InAs. However, these materials were constrained by limited spectral ranges and could not be adapted for transparent or flexible devices, hindering their applicability in next-generation technologies. Conventional commercialized SWIR-band photodetectors are typically manufactured from bulk inorganic semiconductors, such as InSb, Ge, HgCdTe, and InGaAs. Although these materials exhibit high sensitivity and excellent stability, their fabrication processes are complex, involving high-pressure and high-temperature epitaxial growth of silicon and III-V semiconductor compounds. These conditions increase manufacturing costs, and additional cooling devices are essential to mitigate heat generation at room-temperature operation [1-3]. Therefore, the development of materials with nanostructures and narrow band gaps is required for photodetection in the SWIR band. Quantum dots (QDs) are the most representative candidates for such materials [4-7].

QDs are semiconductor compounds, typically on the order of several nanometers in size, and their electrical and optical

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properties can be precisely tuned via quantum confinement. These characteristics allows for precise control of the band gap based on the particle size, facilitating easier processing compared with that of conventional bulk semiconductors. Additionally, QDs exhibit excellent flexibility, photostability, and wavelength-specific absorption properties, making them suitable for photoactive materials. Recent investigations have focused on SWIR photodetectors based on PbS, PbSe, and $Hg_2Te$ quantum dots. However, these materials contain hazardous heavy metals, such as lead and mercury, which pose significant environmental and health risks and are subject to the Restricted Hazardous Substances (RoHS), a European directive that regulates the use of hazardous substances in commercial consumer electronics [8-10]. To address this issue, research has shifted towards non-toxic alternatives such as $Ag_2Te$ quantum dots, complying with the RoHS directive [11-13]. $Ag_2Te$ quantum dots can be synthesized via a simple solution process and used in the fabrication of photodetectors within an eye-safe wavelength band of 1400 nm or more by controlling the particle size. These QDs exhibit strong absorption characteristics in the SWIR band, comparable to that of typical heavy-metal-based quantum dots. Therefore, in this study, we synthesized lead-free $Ag_2Te$ quantum dots with an absorption peak at 1670 nm, which corresponds to the eye-safe band, and fabricated a high-sensitivity short-wavelength infrared photodetector using the synthesized quantum dots. The device was fabricated by depositing a thin film via spin coating. To facilitate smooth extraction of electron-hole pairs (EHP) generated by light irradiation on the electrode, P3HT (Poly(3-hexylthiophene-2,5-diyl)), a p-type conductive polymer material with high hole mobility, was employed as the hole extraction layer. Likewise, ZnO nanoparticles (NPs) exhibiting high electron mobility were employed as the electron extraction layer. P3HT, a p-type organic semiconductor material, exhibits high electrical conductivity and electroluminescence, making it suitable for applications in devices such as light-emitting diodes and organic field-effect transistors. Moreover, P3HT offers efficient hole extraction owing to the narrow gap between the energy levels of its Highest Occupied Molecular Orbital (HOMO) and the $Ag_2Te$ quantum dots. Following a similar principle, ZnO nanoparticles were incorporated as the electron extraction layer. An SWIR photodetector with enhanced photosensitivity due to optimal photocharge separation was fabricated utilizing these donor-acceptor materials. The characteristics of the synthesized $Ag_2Te$ quantum dots were evaluated using absorbance measurements and the responsivity characteristics of the fabricated SWIR photodetector were evaluated using a source meter unit (SMU).

## 2. EXPERIMENTAL

### 2.1 Synthesis of $Ag_2Te$ QDs

The $Ag_2Te$ quantum dots were synthesized from silver iodide-oleylamine (AgI-OLAm) and tellurium oxide-dodecanethiol (TeO2-DDT) precursors using a colloidal method. First, to prepare the Ag precursor solution, a mixture of 10 mmol AgI and 10 mL OLAm was stirred at 50°C for 1 h. Next, the Te precursor solution was prepared by stirring a mixture of 2.5 mmol $TeO_2$ and 10 mL DDT at 100°C for 1 h. A ligand solution containing 30 mL of OLA and 15 mL of 1-octadecene (ODE) was injected into a 3-neck flask and degassed at 100°C for 15 min in a vacuum to remove oxygen and moisture. Subsequently, it was heated to 160°C in an Ar atmosphere to synthesize quantum dots with the desired particle size. When the temperature reached the set point, 3 mL of AgI-OLAm solution was injected into the flask. After approximately 5 min of reaction time, 5 mL of the $TeO_2$-DDT solution was promptly injected, which resulted in a dark black color, indicating the nucleation of the $Ag_2Te$ quantum dots. After 30 min, the 3-neck flask was cooled to room temperature, and the synthesized solution was washed with methanol and toluene at a ratio of 4:1:1 to remove residual impurities. Finally, after centrifugation at 4000 rpm for 10 min to obtain $Ag_2Te$ quantum dot powder, and the resulting quantum dots were subsequently dispersed in hexane, a nonpolar solvent, at a concentration of 20 mg/mL to prepare an $Ag_2Te$ quantum dot solution.

### 2.2 Fabrication of the photodetector based on $Ag_2Te$ QDs

An SWIR photodetector based on $Ag_2Te$ quantum dots was fabricated by spin-coating a thin film onto an indium tin oxide (ITO)-patterned glass substrate. Prior to device fabrication, the ITO-patterned glass was sequentially washed with acetone, methanol, and IPA to remove impurities. After cleaning, a hole extraction layer was created on the cleaned substrate by spin-coating a p-type conductive polymer material, P3HT (20 mg/mL in chloroform) at 1,500 rpm for 15 s. Subsequently, a thin film was formed after annealing at 95°C for 30 min to remove the residual solvent. To create a photoactive layer for detecting infrared rays, the synthesized $Ag_2Te$ QDs (20 mg/mL in toluene) were spin-coated as a thin film at 1,500 rpm for 15 s, followed by annealing at 95°C for 30 min. Successively, an electron extraction layer was created by spin coating ZnO NPs (20 mg/mL in ethanol), which was subsequently annealed at 85°C for 30

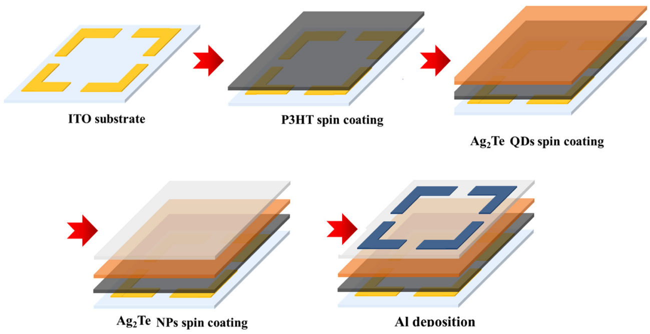


**Fig. 1.** Schematic of fabrication of the SWIR photodetector.

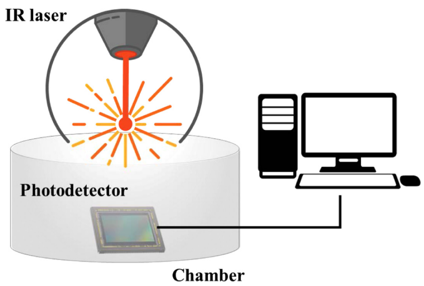


**Fig. 2.** Schematic of the SWIR photodetector measurement system.

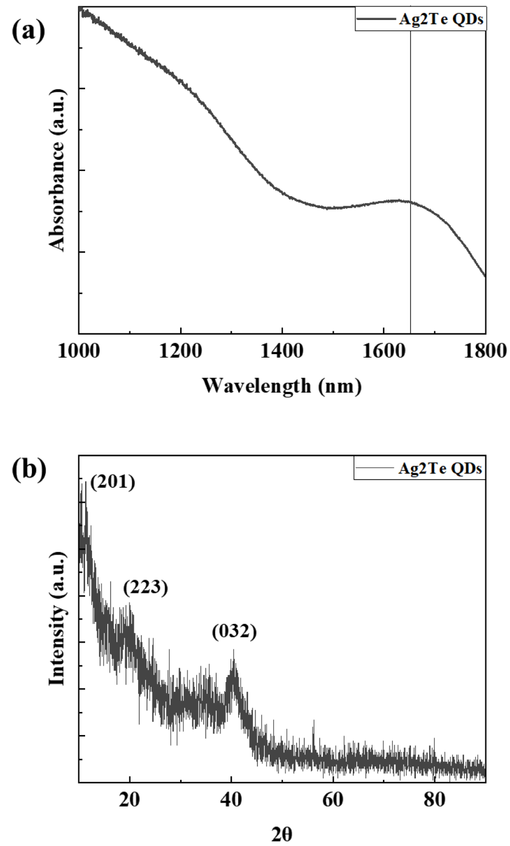


**Fig. 3.** (a) Absorbance and (b) XRD patterns of the synthesized $Ag_2Te$ QDs.

minutes. Finally, Al was deposited to a thickness of approximately 150 nm via thermal evaporation to form an electrode, thereby completing the fabrication of the SWIR photodetector with a sensing area of 9 $mm^2$.

## 3. RESULTS AND DISCUSSIONS

### 3.1 The characterization of $Ag_2Te$ QDs

To evaluate the SWIR absorption characteristics of the synthesized $Ag_2Te$ quantum dots, absorbance analysis was performed employing an Ultraviolet Visible Near Infrared (UV-Vis-NIR) spectrometer (Cary 5000, Agilent). As shown in Fig. 3, the $Ag_2Te$ quantum dots were observed to have an absorption wavelength peak of 1670 nm and a full width at half maximum (FWHM) of approximately 100 nm. Additionally, X-ray Diffraction (XRD) was performed to confirm the crystallinity of the synthesized $Ag_2Te$ quantum dots, and the results indicated that it had peaks of (201), (223), and (032), which are similar to those of $Ag_2Te$. Therefore, it was confirmed that the synthesized $Ag_2Te$ quantum dots were capable of detecting SWIR light in the 1670 nm wavelength band with high selectivity while ensuring retina safety and protection against heavy metal toxicity, as they operate within the eye-safe band and are lead-free.

### 3.2 The characterization of SWIR photodetectors based on $Ag_2Te$ quantum dots

To analyze the characteristics of the fabricated $Ag_2Te$ quantum-dot-based SWIR photodetector, it was fixed with a probe tip in a darkroom measurement chamber. A light source (Thorlabs, SLS202L/M), covering the SWIR band, was installed and the response characteristics of the device to light irradiation were measured. The dark current ($I_{dark}$), corresponding to the device current value when no infrared light source is irradiated, and the light current ($I_{light}$), corresponding to the device current value when the infrared light source is irradiated, were measured to evaluate the response characteristics and response/recovery speed. The SWIR photodetector fabricated in this study is based on the principle of the photoconductivity. As shown in Fig. 4, when voltage is applied to the fabricated device and a light source is irradiated, electron-hole pairs are formed in the $Ag_2Te$ quantum dots, which are the photoactive layers, resulting in an increase in the overall conductivity corresponding increase in current. To compare the response at varying applied voltages, measurements were conducted and compared at 1 V and 2 V through an SMU

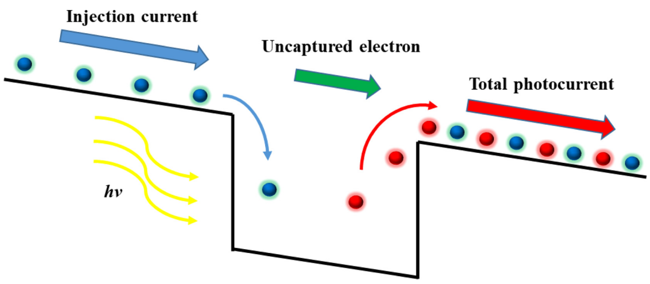


**Fig. 4.** Schematic diagram of the photoconductive effect.

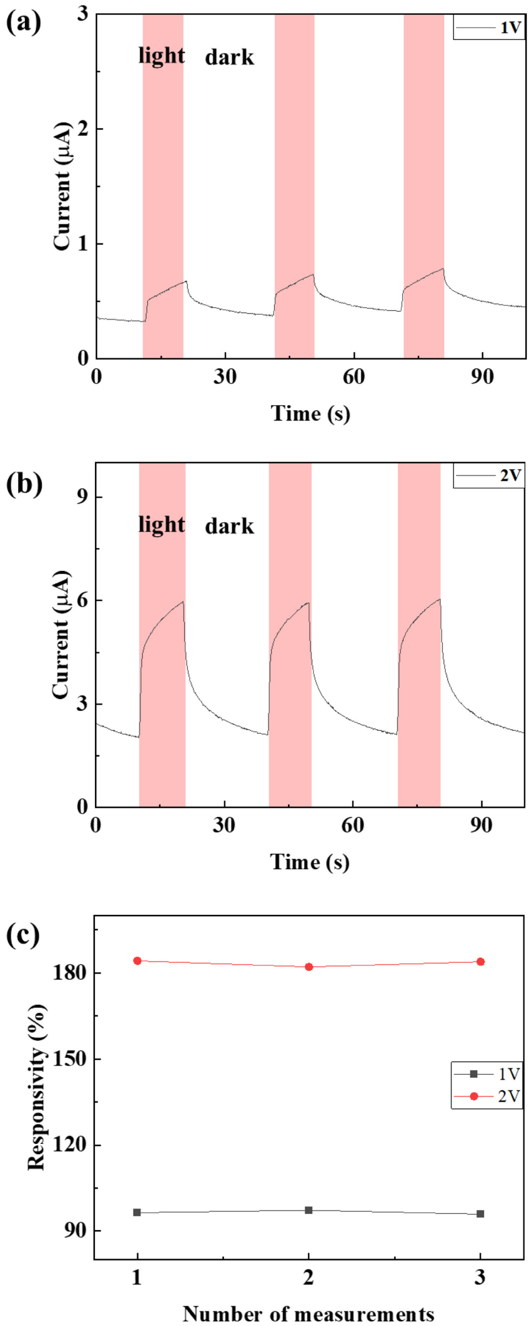


**Fig. 5.** Real-time current characteristics at (a) 1 V, (b) 2 V input voltage, and (c) responsivity comparison.

(B2902A, Keysight). As shown in Fig. 5, at 1 V, it was observed that on average, $I_{dark}$ = 0.37 μA and $I_{light}$ = 0.73 μA, yielding a current difference of approximately 0.36 μA and a response rate of 97.3%. At an applied voltage of 2 V, it was observed that on average, $I_{dark}$ = 2.09 μA and $I_{light}$ = 5.94 μA, yielding a current difference of approximately 3.85 μA and a response rate of 184.2%, which was relatively very high. This demonstrates that the response characteristics were approximately 1.89 times higher when 2 V was applied than when 1 V was applied; however, the response and recovery times were longer at 2 V. At an applied voltage of 3 V or higher, a decrease in the response was observed relative to 1 and 2 V, likely due to an increase in the dark current. Additionally, the response/recovery times of the photodetector were compared with those of T90, and were measured to be 6/11.4s and 5.4/12.5s at 1 V and 2 V, respectively.

## 4. CONCLUSIONS

In this study, we synthesized lead-free $Ag_2Te$ quantum dots, which exhibit an absorption wavelength of 1670 nm in the eye-safe SWIR band. An SWIR photodetector was fabricated using these QDs and its performance was analyzed by incorporating P3HT and ZnO NPs as hole/electron extraction layers. The synthesized $Ag_2Te$ quantum dots were characterized using UV-Vis-NIR spectrometry and XRD. The results indicate that the synthesized $Ag_2Te$ quantum dots exhibited an absorption wavelength peak at 1670 nm and a FWHM of 100 nm. This confirms that the synthesized $Ag_2Te$ quantum dots exhibit high selectivity for the SWIR wavelength of 1670 nm. An SWIR photodetector was fabricated based on the synthesized $Ag_2Te$ quantum dots, and the response characteristics of the device under IR irradiation and varying voltages were evaluated. The device exhibited a response of 97.3% at 1 V and 184.2% under 2 V. This was approximately 1.89 times greater in the response at 2 V compared to 1 V. Therefore, the SWIR photodetector based on $Ag_2Te$ quantum dots developed in this study is holds significant potential for in future applications in autonomous driving technology owing to its high response as well as eye-safety and lead-free properties.

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