Research Article

Si:HgTe Colloidal Quantum Dots Heterojunction-Based Infrared Photodiode

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1. Introduction

Infrared detectors have been explored for many optoelectronic applications, particularly for night vision detection, infrared guidance, thermal imaging, and optical fiber communication [1–4]. Currently, the most common materials used for infrared photodetectors are HgCdTe and InSb. Both are mature material technologies that can be used in integrating focal plane arrays with silicon-based readout circuits and provide good quantum efficiencies, but the complex integrated manufacturing process makes these photodetectors expensive [5–8]. New photodetectors must be created due to the drawbacks of existing detectors. The characteristics of the ideal photodetectors should include rapid response, high responsiveness, ease of production, and low cost [9–11].

In recent years, nanoparticles and quantum dots have attracted a great deal of interest in academia due to their unique properties and outstanding applications [12–15]. Colloidal quantum dots (CQDs) and nanoparticles are widely used in humidity sensors, antibacterial activity, anticancer activity, and optoelectronic devices [16–18]. CQDs, which provide solution processability, spectral tunability, and silicon-compatible fabrication, are providing solutions to such challenges. Near-infrared PbS-CQDs/silicon hybrid photoconductive have been illustrated. CQDs with narrower gaps are required to obtain longer wavelength infrared to further increase the spectral detection regions. Because of their strong absorbance in the mid-infrared and THz ranges, HgTe CQDs are promising infrared detector materials [19–22]. HgTe CQDs can be easily deposited on silicon-based readout circuits using the spin-coating method due to their solution processability [23]. As a result, it may be easily integrated with readout circuits without the need for a complicated electrical link between the detector and readout circuits. This can greatly simplify device manufacture and lower the cost [24–26]. Liu et al. [27] recently presented a HgTe CQDs photoconductive detector based on different ligand exchange processes on SiO2 substrates. However, the devices suffer from low responsivity (3.5 × 10⁻³ A/W) at infrared wavelengths. Utilizing a graphene common contact between short-wave infrared HgTe CQDs and a silicon substrate, Tang et al. [28] established a method for visible and infrared...
dual-channel detectors. Nevertheless, the photodiode for the CQDs has a detective of $5 \times 10^{10}$ Jones. In order to improve device performance, HgTe-CQDs/graphene and graphene/silicon contacts need to be optimized.

In this work, we describe the easy solution-derived synthesis and characterization of HgTe CQDs materials. In parallel, we report a HgTe-CQDs/silicon infrared photodiode and compared the effect of planar silicon with different resistivity on the performance of silicon-based HgTe CQDs photodiode. Under illumination with different wavelength lasers, obvious light response proves the feasibility of the silicon-based HgTe CQDs photodiode. Our devices have a 0.2 mA/W response at 1,550 nm. The device has a normalized detective of 4.4 $\times 10^{10}$ Jones, a high responsivity of 40 mA/W at 980 nm, and an external quantum efficiency (EQE) of up to 5.1%.

### 2. Experimental Section

#### 2.1. Materials. Mercury chloride (HgCl₂, powder, 99%), tellurium power (Te, ALaddin, 99.99%), trietylphosphine (TOP, ALaddin, 90%), oleylamine (OLA, ALaddin, 90%), dodecanethiol (DTT, ALaddin, 98%), methanol (ALaddin, 99.5%), toluene (99%), 1,2-ethanediithiol (EDT, ALaddin, 97%), and isopropanol (IPA, ALaddin, 99.7%). Except for oleylamine, which is dried overnight at 80°C under vacuum, all of these compounds are utilized as received. Highly hazardous mercury compounds are present. Take extra care when handling them.

#### 2.2. HgTe Colloidal Quantum Dots Synthesis. In a 100 mL three-neck flask under an argon environment, the HgTe CQDs were synthesized [29]. A typical synthesis involved heating a combination of 342 mg of HgCl₂ and 40 mL of oleylamine under vacuum to 110°C for 1 hr. In a three-neck flask, 1.27 g Te powder is combined with 20 mL of TOP. The flask is placed under vacuum and allowed to stand at ambient temperature for 5 min before being heated to 110°C. In addition, as the temperature is raised to 275°C, the solution is agitated until it turns a clear orange hue. When the reaction is complete (after 3 min), the HgTe CQDs are immediately washed with 20 mL of methanol, then dried overnight at 80°C under vacuum.

The reaction time can influence the nanoparticle sizes. By having removed the heating source and injecting a solution of 2 mL DDT and 18 mL toluene to stabilize the nanocrystals, the process was then quenched. The nanocrystals were redispersed in toluene after being precipitated and cleaned three times with a methanol solution. Before using, this solution needs to pass through a 0.1 μm polytetrafluoro ethylene filter. Sonication was occasionally necessary to achieve a tidy colloid. Aggregation must be avoided while creating high-quality films.

#### 2.3. Device Fabrication. Silicon substrates are cut into $1 \times 1$ cm sizes and thoroughly cleaned by sonicating with acetone for 15 min, cleaned with ethanol for 15 min, washed with deionized water for 5 min, submerged in HF acid for 60 s, rinsed with deionized water for 10 s, then dried completely with N₂ flow. During ligand exchange, mix 20 mL IPA and 0.2 mL EDT and a drop of HgTe-CQDs solution (40 μL) were spread over the surface and spun at 2,500 rpm for 40 s. Then a drop of dissolved EDT/IPA was put onto the HgTe CQDs film, allowed to wait for 60 s, and then spin-coating at 2,500 rpm for 1 min. The HgTe film was next washed with IPA before being annealed for 1 min at 60°C on the hot plate. The preceding procedures were repeated nine times and finally, top and bottom Ag electrodes were deposited onto the HgTe CQDs film and Si substrate with mask, respectively.

#### 2.4. Characterization. X-ray diffraction (XRD) was used to investigate the crystalline nature of the samples (Bruker AXS D8). By using Fourier transform infrared spectroscopy (FTIR) (Bruker, Vertex70v), we are able to measure the absorption spectra of HgTe CQDs at different temperatures while checking whether the ligand exchange is successful. A transmission electron microscope was used to measure the size of the HgTe CQDs (TEM, Talos, L120C). The electronic properties of the fabricated devices were characterized by measuring the current−voltage (I−V) curves using B2901A SYSTEM source meter with a pair of prods test systems. The bands used for the light source were 405, 520, 638, 980, and 1,550 nm. The semiconductor parameter analyzer platform design automation and the program LabExpress were used to measure the devices’ reaction times. The test procedure was conducted in a protected, dark box at ambient temperature.

### 3. Results and Discussion

TEM images of HgTe nanoparticles prepared at the temperature of 60, 70, 80, 90, 100, and 110°C are presented in Figure 1(a)−1(f) and the corresponding histograms of the size distribution are shown in Figure 2. The reaction time was maintained for 3 min while the reaction temperature increased from 60 to 110°C; the size of the synthesized HgTe CQDs frequently took the form of triangles or distorted circle shapes, as well as the size of HgTe CQDs increased. Typically, at temperatures of 60 and 70°C, and the reaction time is 3 min, the size of HgTe quantum dots does not change significantly. As the temperature continues to increase, the CQDs begin to aggregate into tetrapod-like shapes. The micrographs suggest that the HgTe nanoparticles are homogeneous and continuously grown with good orientation. The TEM images revealed that the CQDs ranged in size from 5 to 13 nm (Figure 3). The HgTe CQDs size distribution of temperature at 80°C and time at 3 min was homogeneous, which is very suitable to prepare thin films. They are bipolar and can form heterojunction junctions with N-type silicon. If the size is too large, the quantum dots are N-type and are not able to form heterojunction junctions with N-type silicon [29].

As shown in Figure 4, the spectrum of XRD of HgTe CQDs is produced at varied reaction temperatures. The large peaks are attributable to the nanostructure’s low crystallinity [30]. It is evident that as temperature rises, the diffraction peak’s full width at half maximum (FWHM) diminishes. According to Scherrer’s formula, the FWHM of the diffraction peak is
FIGURE 1: TEM images of the HgTe CQDs and the corresponding histograms of the size distribution: (a) 60°C; (b) 70°C; (c) 80°C; (d) 90°C; (e) 100°C; (f) 110°C.

FIGURE 2: Plot of HgTe CQDs size depending on the reaction temperature. The reaction time was maintained for 3 min.
inversely proportional to the crystal size. The XRD patterns showed some peaks at 23.9°, 39.59°, 46.8°, 57.1°, 62.8°, 71.7°, and 76.8° corresponding to the (111), (220), (311), (400), (331), (422), and (511) plane of zinc blende structure HgTe.

Figure 5(a) displays a series of absorption spectra for samples of various sizes that were deposited on indium tin oxide glass substrates and generated over a 3 min reaction period at temperatures of 70, 80, and 90°C. It can be seen that the smaller
particles give an absorption onset at higher frequencies. The first exciton absorption peak exhibits a red shift as the quantum dot’s size increases. It displays a monotonic trend in particle size-dependent absorption. The 10 and 6.7 nm CQDs’ absorption spectra clearly demonstrate intraband at 2,300 and 1,900 cm$^{-1}$, respectively. This indicates that the HgTe CQDs have a broad absorption range.

When synthesizing HgTe CQDs, we have used ligands with lengthy alkyl chains. The long-chain ligands can make the quantum dots have better dispersibility in the solution, which makes the synthesized quantum dots not easy to be oxidized, but hinders the transport ability between the quantum dots. To improve the conductivity of the CQDs film, we use EDT short-chain ligands (0.5 nm sizes) instead of DDT long-chain ligands. The ligand exchange process is finished using the spin-coating technique. As shown in Figure 5(b), after the ligand exchange, the ligand peaks are weakened, indicating that C–H bonds are reduced, and long-chain ligands are substituted.

To evaluate photoresponse characteristics, several parameters need to be determined. An important factor that describes the light–current transformation efficiency of the photodetector

<table>
<thead>
<tr>
<th>Number</th>
<th>Sample ($\Omega \cdot \text{cm}$)</th>
<th>Carrier lifetime (s)</th>
<th>Diffusion coefficient (cm$^2$ s$^{-1}$)</th>
<th>Mobility (cm$^2$ V$^{-1}$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.001–0.005</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>2</td>
<td>0.01–0.02</td>
<td>2.56</td>
<td>1.11</td>
<td>42.86</td>
</tr>
<tr>
<td>3</td>
<td>0.1–0.5</td>
<td>19.24</td>
<td>4.79</td>
<td>184.94</td>
</tr>
<tr>
<td>4</td>
<td>1–10</td>
<td>30.38</td>
<td>6.28</td>
<td>242.47</td>
</tr>
<tr>
<td>5</td>
<td>20–50</td>
<td>56.01</td>
<td>8.99</td>
<td>347.10</td>
</tr>
</tbody>
</table>

TABLE 1: Summary of silicon performance of different resistivity.

![Image](a) | ![Image](b) | ![Image](c) | ![Image](d)

FIGURE 6: (a) The structure of the HgTe-CQDs/silicon photodiode is depicted schematically and band diagram of HgTe:Si device; (b) the responsivity of the HgTe-CQDs/silicon photodiode with the silicon of different resistivities; (c) rectification ratio of the HgTe-CQDs/silicon photodiode with the silicon of different resistivities; (d) dark current of the HgTe-CQDs/silicon photodiode with the silicon of different resistivities.
FIGURE 7: (a) Photoresponse of HgTe-CQDs/silicon photodetectors under incident light of 405, 520, 638, 980, and 1,550 nm (30 mW/cm²) at a bias of 1 V; (b) photoresponsivity curves of the HgTe-CQDs/silicon photodiodes at 1,550 nm; (c) I–V curves of HgTe-CQDs/silicon heterojunction devices in the dark and under light illumination at 980 nm; (d) at 980 nm, rising and falling edges are used to estimate the rise time (T_r) and fall time (T_f); (e) photoresponse of HgTe-CQDs/silicon heterojunction under different bias voltages at 980 nm; (f) photoresponse of the HgTe-CQDs/silicon heterojunction under different light intensities at 980 nm.
is called responsivity [31, 32]. The $R$ is determined using the following formula as the photocurrent-to-light power ratio:

$$R = \frac{I_{\text{light}} - I_{\text{dark}}}{P} = \frac{I_{\text{ill}}}{P},$$

(1)

where the photocurrent of the device is $I_{\text{ill}}$ and the detector’s currents under light and darkness, respectively, are $I_{\text{light}}$ and $I_{\text{dark}}$. $P$ is the light power.

In order to compare photodetectors with various structures and regions, the normalized detectivity ($D^*$), is another crucial factor for assessing the performance of photodetectors [33]. This parameter emphasizes the detector’s capacity for detection. That is, the greater $D^*$, the more sensitive the device is to detecting optical signals. The following is the $D^*$ calculation formula:

$$D^* = R \sqrt{\frac{S}{2qI_{\text{dark}}}},$$

(2)

where $R$ stands for responsivity, $q$ for element charge, and $S$ for the effect of light absorption area when illuminated. Another crucial performance metric for the detector is its EQE, which measures photoelectric conversion efficiency and represents the capacity to transform photons into carriers [34]. The following formula is commonly used to define it:

$$\text{EQE} = R \times \frac{hc}{q\lambda} = R \times \frac{hv}{q},$$

(3)

where $v$ stands for the light frequency, $h$ stands for Planck’s constant, $\lambda$ for the incident light’s wavelength, and $c$ for the speed of light. The relationship between the external quantum efficiency and responsivity is inverse.

Table 1 shows the electrical parameters for the five different kinds of silicon substrates used in this work. We tested carrier lifetime, diffusion coefficient, and mobility. It can be seen that the #5 sample presents a higher carrier lifetime, diffusion coefficient, and mobility. The higher the resistivity of silicon, the lower the impurity concentration and the higher the mobility, which is consistent with the theory. Due to the high doping concentration of the #1 sample, parameters such as carrier lifetime were not measured. Then we fabricated HgTe–CQDs/silicon photodetectors and measured their key parameters. The structure of the photodiode based on HgTe–CQDs/silicon heterojunction is shown in Figure 6(a). The photovoltaic voltages produced by HgTe–CQDs/silicon channel surfaces are employed for photoelectric detection. A light-absorbing layer is provided by the HgTe CQDs film. Figure 6(a) depicts the corresponding energy band diagram. We used a silicon substrate that was n-doped. On top of this n-contact, a p-type HgTe CQD layer is deposited. The actual photosensitive region is 0.2 cm$^2$ and the device size is 1 × 1 cm$^2$. The responsivity, reflection ratio, and dark current for HgTe–CQDs/Si photodetectors with different Si substrates are shown in Figure 6(b)–(6d), respectively. Clearly, the device uses the Si substrate with a resistivity of 20–50 Ω cm and exhibits the highest responsivity and reflection ratio, as well as the lowest dark current, demonstrating its suitability for visible and near-infrared light detection.

Thus, we carried out a detailed characterization of the device. Figure 7(a) depicts the detected light response of HgTe–CQDs/silicon photodiode, demonstrates a broad spectral response between 405 and 1,550 nm. Figure 7(b) shows photoresponsivity curves of HgTe–CQDs/silicon photodiodes at 1,550 nm. The device responds at 1,550 nm with a lowest dark current, demonstrating its suitability for visible and near-infrared light detection.

Table 2: Si:CQDs PD performance is compared to CQDs-based PD in terms of device performance.

<table>
<thead>
<tr>
<th>Devices</th>
<th>Operating temperature (K)</th>
<th>Responsivity (A/W)</th>
<th>Detectivity (Jones)</th>
<th>Time response (ms)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si/HgTe-based photodiode</td>
<td>300</td>
<td>$4 \times 10^{-2}$</td>
<td>$4.4 \times 10^{10}$</td>
<td>0.36</td>
<td>This work</td>
</tr>
<tr>
<td>HgTe CQDs-based photoconductor</td>
<td>300</td>
<td>$3.5 \times 10^{-3}$</td>
<td>$6.6 \times 10^{7}$</td>
<td>–</td>
<td>[27]</td>
</tr>
<tr>
<td>Si/Graphene/HgTe-based photodiode</td>
<td>300</td>
<td>0.9</td>
<td>$5 \times 10^{9}$</td>
<td>–</td>
<td>[28]</td>
</tr>
<tr>
<td>HgTe CQDs-based phototransistor</td>
<td>260–300</td>
<td>0.56</td>
<td>$2 \times 10^{10}$</td>
<td>0.012</td>
<td>[37]</td>
</tr>
<tr>
<td>Si/PbSe-based phototransistor</td>
<td>300</td>
<td>648.7</td>
<td>$7.48 \times 10^{10}$</td>
<td>0.0732</td>
<td>[38]</td>
</tr>
</tbody>
</table>
photodetector’s photocurrent. As shown in Figure 7(f), the light intensity-dependent response of the HgTe-CQDs/silicon device was investigated further. The optical response was significantly improved when the incident light power intensity was increased from 5.1 to 234.3 mW/cm². Then, we contrast a variety of performance metrics for a HgTe-CQDs/silicon photodetector with a variety of conventional photodetector types in Table 2. It can be seen that our silicon-compatible HgTe quantum dot device is in the leading position.

4. Conclusion

To summarize, we described a silicon-based infrared photodiode made at room temperature using a solution technique. We explore the influence of silicon resistivity on the performance of these photodiodes. The silicon substrate with a resistivity of 20–50 Ω-cm has optimal performance parameters. Further, these HgTe-CQDs/Si photodiodes had a broad response spectrum, ranging from 405 to 1,550 nm. The device reaches a high external responsivity of 0.2 mA/W for 1,550 nm incident light at room temperature. In addition, the photodetector offers quick response times ($T_r/T_f = 380/360 \mu$s) and a decent response of 40 mA/W at 980 nm. The remarkable performance of the HgTe-CQDs/silicon photodetector implies that this material has a bright potential in the optoelectronic industry.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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References


