Resonant Cavity–Enhanced Photodiodes for Spectroscopy of C–H Bonds

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Resonant cavity-enhanced photodiodes targeted within the spectral region of absorption by C–H bonds are demonstrated. The 3.0–3.3 μm region of the infrared spectrum contains many substances that are useful to measure spectroscopically. However, the measurement of individual substances requires a high spectral specificity, that is achieved by the resonant cavity photodiodes with spectral response widths of < 40 nm. Two material systems are investigated for μ3.3/C210μ3.7 absorption region by fiμ1,2/c25RCE up to 7.8 absorber on a GaSb substrate PD structure on an PD where reasonable. There are μ12μ3/V-based RCE μ3–PDs grown on GaSb substrates have PDs) for the mid-μPDs can overcome this challenge by PDs. The speci–PD was grown on a GaAs substrate PD to target a speci–PD. However, the MWIR has seen the μ51μ2021 cant developments — the original work is properly cited. The MWIR region contains absorption peaks of many substances, including CO2 at 4.3 μm and CO at 4.6 μm. The small part of this region between 3.0 μm and 3.3 μm contains absorption peaks of various substances due to stretching vibrations of the C–H bond. This bond is found within many notable organic compounds, including, hydrocarbons, alcohols, and certain nerve agents—making this wavelength range a salient target for RCE–PDs.

Methane (CH4) is one compound that is of particular focus as it is the primary component of natural gas and a significant contributor to global warming. There are currently many types of sensors available for methane sensing, including optical, calorimetric, pyroelectric, semiconducting metal oxide, and electrochemical sensors. Optical sensors can potentially offer excellent sensitivity; however, they can suffer from a lack of specificity—absorption peaks of other hydrocarbons can interfere with the detection. RCE–PDs can overcome this challenge by deselected all light outside a specific narrow band, which can be designed so that it only covers the absorption peak of methane. The specific wavelength of interest for methane detection is 3.3 μm.

For an RCE–PD to target a specific absorption peak, the detector has to be designed for a specific target wavelength, which determines the layer thicknesses and the absorber material. III–V-based RCE–PDs have previously been demonstrated at multiple wavelengths, from the shortwave infrared at 2.2 μm,[7] up to 7.8 μm.[8] However, the MWIR has seen the most effort.[9–12] RCE–PDs grown on GaSb substrates have become well established, whereas for the target of ≥3 μm, a lattice-mismatched RCE–PD was grown on a GaAs substrate by Green et al.[13] RCE–PDs on InAs substrates have also been touched upon by O’Loughlin et al.[11]

In this article, we demonstrate an RCE–PD structure on an InAs substrate that has been fabricated to target the methane absorption peak in the MWIR. Use of an InAs substrate allows for native use of the InAs binary absorber material, with minimal defects and dark currents, as well as sensitivity at 3.3 μm. Previous work has demonstrated an RCE–PD utilizing an InAs0.9Sb0.09 absorber on a GaSb substrate[10] that could also be adjusted to sense at 3.3 μm. This Letter analyses the performance of the InAs-based RCE–PD and offers comparisons with the InAsSb-based RCE–PD where reasonable.

1. Introduction

Resonant cavity-enhanced photodiodes (RCE–PDs) for the mid-wave infrared (MWIR) have seen significant developments recently, driven by the desire for improved gas sensing.[1,2] The narrow spectral response of this class of detectors allows for spectrally specific targeting of the individual gas absorption features. The MWIR region contains absorption peaks of many significant gases, including CO2 at 4.3 μm and CO at 4.6 μm. The small part of this region between 3.0 μm and 3.3 μm contains absorption peaks of various substances due to stretching vibrations of the C–H bond. This bond is found within many notable organic compounds, including, hydrocarbons, alcohols, and certain nerve agents—making this wavelength range a salient target for RCE–PDs.

Methane (CH4) is one compound that is of particular focus as it is the primary component of natural gas and a significant contributor to global warming.[10] There are currently many types of sensors available for methane sensing, including optical, calorimetric, pyroelectric, semiconducting metal oxide, and electrochemical sensors.[12] Optical sensors can potentially offer excellent sensitivity; however, they can suffer from a lack of specificity—absorption peaks of other hydrocarbons can interfere with the detection.[5] RCE–PDs can overcome this challenge by deselected all light outside a specific narrow band, which can be designed so that it only covers the absorption peak of methane. The specific wavelength of interest for methane detection is 3.3 μm.[6]

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In this article, we demonstrate an RCE–PD structure on an InAs substrate that has been fabricated to target the methane absorption peak in the MWIR. Use of an InAs substrate allows for native use of the InAs binary absorber material, with minimal defects and dark currents, as well as sensitivity at 3.3 μm. Previous work has demonstrated an RCE–PD utilizing an InAs0.9Sb0.09 absorber on a GaSb substrate[10] that could also be adjusted to sense at 3.3 μm. This Letter analyses the performance of the InAs-based RCE–PD and offers comparisons with the InAsSb-based RCE–PD where reasonable.
2. Design

GaAs and GaSb substrates are usually favored over InAs for RCE-PDs in part because they allow for simpler distributed Bragg reflectors (DBR) to be used—AlGaAs/GaAs for GaAs substrates and AlAsSb/GaSb for GaSb substrates. These DBRs both include a binary layer, which is relatively simple to grow. In contrast, GaAsSb/AlAsSb ternary DBR layers are required for lattice-matched growth on InAs. This increases the complexity because both layer compositions need to be carefully controlled. The structure, as shown in Figure 1a, uses a DBR mirror above and below the cavity. A 12-pair DBR is used below the cavity and a 5.5-pair DBR above. The AlAs$_{0.16}$Sb$_{0.84}$ and GaAs$_{0.08}$Sb$_{0.92}$ layers used have an $\approx$20% lower refractive index contrast than AlAsSb and GaSb, although it would be simple to add more layers to counteract the loss in reflectivity.

The cavity consists of an nBn structure and a cavity spacer layer beneath. InAs is used for the n layers and AlAs$_{0.16}$Sb$_{0.84}$ is used for the barrier and filler layers. The use of a bulk binary absorber simplifies the cavity growth compared with other RCE-PDs and is more likely to produce a high-quality crystalline layer. InAs-based RCE-PDs have previously been demonstrated,[11] but it is not clear from previous research how the performance of InAs RCE-PDs compares with devices on GaSb. Devices were fabricated from the structure, grown by molecular beam epitaxy on an n-type InAs substrate (see Experimental Section).

3. Optical Characterization

The two detectors use similar designs but with the key differences in the absorber and substrate materials. The designs are otherwise similar, allowing for comparisons to be made based on optical measurements. A Fourier-transform infrared (FTIR) spectrometer was used to characterize the spectral response. The responsivity and quantum efficiency (QE) were calculated with reference to a commercial Vigo MCT detector of known responsivity. The normalized response of each detector is shown in Figure 2a. The exact wavelength of the resonance peaks is determined by a combination of the optical path lengths of the DBR layers and the cavity. These two structures could be fabricated with the same 3.3 μm resonance wavelength by simply altering the thicknesses of the DBR layers and the total cavity thickness.

It has previously been reported that the resonance peak wavelength shifts with temperature, with the majority of the shift attributed to changes in refractive indices of the cavity layers.[14,15] Figure 2b shows the temperature dependence of the resonant wavelength for the two devices. The gradient of the two fit lines shows clearly that the peak shift due to temperature is very similar for both devices—0.27 nm/K for the InAsSb-based device and 0.28 nm/K for the InAs-based device. The temperature dependence might be expected to reflect the resonant wavelength, $d\lambda/dT \propto |\alpha|$. However, this is not what is seen. This indicates that the layers in the cavity have lower temperature coefficients of the
refractive index for the InAsSb-based device. This is as expected from literature values of the temperature coefficients..

Figure 2c shows the temperature dependence of the full width half maximum (FWHM) of the resonance peak for the two devices. Both devices show a linear FWHM decrease of \( \approx 0.04 \text{ nm/K} \) with temperature. The dependence of the FWHM on the absorption coefficient has been modeled for the InAs-based structure and is overlaid on the same plot. The increase in FWHM above 250 K can be explained by an increase in absorption coefficient of \( \approx 18 \text{ cm}^{-1}/K \). The similarity in the FWHM variation for the two devices is expected, due to the similarity of the absorber materials. Below 250 K the InAs-based device shows a far stronger change of 0.16 nm/K, attributed to a higher rate of change of the absorption coefficient close to the band edge. This is not seen in the InAsSb-based device as the resonant wavelength is not close to the band edge.

The peak responsivity for both devices is also significantly dependent on the temperature of the device, as shown in Figure 2d. The temperature of the highest peak responsivity impacts the real-world applications of the devices. The peak temperatures differ significantly—225 K for the InAsSb-based device and 350 K for the InAs-based device. The temperature dependence of the spectral response can also be largely attributed to the absorption coefficients of the absorbers. The InAs absorption coefficient at the resonant wavelength decreases rapidly below 275 K as the bandgap increases, reducing the overall absorption. Both devices show a slight decrease in responsivity above a certain temperature, which could be attributed to an increased absorption coefficient damping the resonant enhancement.

4. Electrical Characterization

The full optoelectronic characterization is presented for the InAs-based RCE–PD only. Select comparisons of the electrical properties of the two devices are made; however, it is important to note that these results do not necessarily represent the ultimate performance of each material system. Therefore, it is not possible to state that the performance of one is better than the other. The comparisons do offer insight into the temperature dependencies of each structure and allow educated expectations about the limitations of each material system to be formed.
The InAs-based RCE–PD was designed to target the absorption peak of methane at \( \approx 3.3 \mu \text{m} \). With reference to Figure 3a, it can be seen that the resonance peak coincides closely with the targeted absorption peak.\(^{[19]}\) This demonstrates the focused spectral targeting that RCE–PDs can achieve with appropriate calibration of the layer thicknesses. The targeted narrow linewidth allows for the measurement of methane concentrations with high spectral specificity. The quality factor of the InAs-based cavity was found to be in the range 80–137, increasing with temperature. Both devices demonstrate similar quality factors at 300 K, of 88 and 84, for the InAs and InAsSb-based devices, respectively, indicating that the higher-complexity DBRs in the InAs-based device did not compromise material quality. Figure 3b shows a coupled high-resolution X-ray diffraction (XRD) scan of the sample. Good lattice matching of the ternary mirror layers was confirmed, with all layers within 200 sec of the InAs substrate.

The external quantum efficiency was calculated from FTIR spectral response measurements. Temperature and voltage-dependent results are shown in Figure 4a. Results for the InAs-based device show that at 200 K and above there was a measurable response that monotonically increased with temperature up to 350 K, with a slight decrease at 375 K. Peak QE was measured to be 67% at 350 K, with a 300 K value of 52%—both measured with an applied bias voltage of \(-0.5 \text{V}\). Below 200 K there was no resonant response attributed to the cutoff wavelength of the InAs absorber falling below the resonant wavelength.\(^{[20]}\) For comparison, the InAsSb-based device achieves a peak QE of 66% at 225 K and \(-1.9 \text{V}\). The QE decreases slowly with temperature to a 300 K value of 57% at the same bias voltage. Both devices can achieve high room temperature quantum efficiencies, but only the InAsSb-based device can maintain these values at low temperatures. The significant decrease in QE at lower temperatures seen by the InAs-based device at this resonant wavelength is intrinsic to the absorber material. For shorter resonant wavelengths, the resonant response would be further from the cutoff wavelength and the QE would not decrease at low temperatures.

Leakage currents for the InAs-based device were measured between 100 K and 375 K at 25 K increments, as shown in Figure 4b. From these measurements, an Arrhenius plot was derived at an applied bias voltage of \(-0.3 \text{V}\), as shown in Figure 4c. Fitting to this plot reveals an activation energy of \(\approx 300 \text{meV}\), slightly lower than the bandgap of InAs of \(\approx 354 \text{meV}\). This activation energy indicates that the Shockley–Reed–Hall (SRH) mechanism does not dominate and Auger current is the most significant. A conventional InAs \(nBn\) detector with a 2 \(\mu\text{m}\)-thick absorber by Pedrazzani et al.\(^{[20]}\) is shown in the same figure, demonstrating a more than 50-fold decrease in leakage current that the resonant cavity structure achieves at room temperature. Also presented are measurements for the InAsSb-based device, which show an activation energy of 330 meV—approximately the bandgap of the absorber. It is likely that the InAs-based material system could also demonstrate an activation energy similar to the bandgap of the absorber with further refinement.

The responsivity and leakage current measurements were used to calculate the voltage and temperature dependence of the specific detectivity at the resonant wavelength, as shown in Figure 4d. The calculated values take into account both Johnson and shot noise. For the InAs-based device, the highest values of \(8 \times 10^{10} \text{cm} \sqrt{\text{Hz/W}}\) were achieved at both 200 and 225 K and an applied bias voltage of \(-0.3 \text{V}\). At higher temperatures, the specific detectivity decreases monotonically, whereas a room temperature (300 K) value of \(2.5 \times 10^{10} \text{cm} \sqrt{\text{Hz/W}}\) was achieved with the same applied bias voltage. Select measurements for the InAsSb-based device are shown for comparison, exhibiting a slightly lower 300K value of \(\approx 1.5 \times 10^{10} \text{cm} \sqrt{\text{Hz/W}}\). However, at lower temperatures, the InAsSb-based device demonstrates significantly higher performance; at 200 K, a value of \(\approx 5 \times 10^{9} \text{cm} \sqrt{\text{Hz/W}}\) was measured. A similar comparison is also made to a commercial InAs photodiode available from Teledyne Judson.\(^{[21]}\) The InAs-based RCE–PD outperforms the commercial detector at room temperature but does not match the highest performance achieved at 188 K.

![Figure 3](image-url)
5. Conclusion

A high-quality RCE–PD was grown on an InAs substrate with the purpose of spectral sensing of methane and other compounds with C–H bonds. The resonance wavelength of $\approx 3.3\mu m$ lines up well with the targeted absorption peak and would allow for measurement of methane concentrations with high spectral specificity. A maximum quantum efficiency of 67% was measured at 350 K and a maximum specific detectivity of $2.5 \times 10^{10} \text{cm}\sqrt{\text{Hz}}/\text{W}$ demonstrate the high sensitivity. The combination of high specificity and high sensitivity shows the ideal properties for spectral sensing that the RCE–PD design possesses.

Comparisons with a previously grown RCE–PD with an InAsSb absorber showed that both material systems would be suited to spectral sensing in the absorption region of the C–H bond. Comparable quality factors indicate that the more complex DBRs in the InAs-based device do not compromise device performance. The InAs-based device had favorable high-temperature performance, with a spectral response that increased with temperature up to 350 K. Significantly, the high performance of this device could be utilized without cooling.

6. Experimental Section

Device Fabrication: Both device structures were grown by molecular beam epitaxy (VEECO GENxplor) on InAs and GaSb substrates, respectively. The substrates were first degassed at 350 °C before being placed in the growth chamber. Immediately before growth, surface oxides were removed by heating the substrates above the growth temperature—dependent on the substrate. An $\approx 1\mu m$-thick buffer layer of the same material as the substrate was grown prior to the structure growth. SUMO cells provided the group III fluxes, whereas valved cracker cells provided the fluxes for $\text{As}_2$ and $\text{Sb}_2$. All layers were grown at $1 \text{ML s}^{-1}$. The layers in the cavity were n-type doped with GaTe, whereas the DBRs were not intentionally doped. The exact compositions and thicknesses of the layers were calibrated by test samples prior to the growth of the final devices.

Postgrowth, XRD analysis was used to determine lattice matching for all ternary alloys—measurements were carried out on a Bruker D8 Discover X-ray diffractometer. The top DBR was etched to allow titanium/gold contacts to be placed on the top layer of the cavity. The top cavity layer was then etched to define the device mesas. Standard lithography and etchants were used throughout.

A similar FWHM for both devices indicates that both have high spectral specificity. The InAsSb-based device exhibited the highest sensitivity of $\approx 5 \times 10^{10} \text{cm}\sqrt{\text{Hz}}/\text{W}$, at 200 K, but would require thermoelectric cooling to achieve it.
FTIR Characterization: The optical properties of the devices were studied by a Bruker Vertex 70 FTIR spectrometer. The spectral response was measured with the device held in place inside a cryostat outside of the FTIR, with the beam from the FTIR directed onto the device. The responsivity and spectral response were calculated with reference to a commercial HgCdTe detector (Vigo PVM−2TE-12-1 × 1), with known responsivity. The photosensitive area of the device was considered to be the area of the top DBR.

Current−Voltage Measurements: The current−voltage characteristics of the devices were measured inside a cryogenic probe station (Lakeshore TTPX). The devices were surrounded by an integrated cold shield, to reduce thermal radiation onto the device. The current was measured as the voltage was swept from zero in the positive and then negative direction consecutively.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are openly available in research directory — Lancaster University at http://www.research.lancs.ac.uk/portal/en/datasets/inas-rce-pds(5ba0cc89-bcdb-4356-9c43-bb8ef0833f6b).html. doi:10.17635/lancaster/researchdata/415.

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