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Low voltage epitaxially down bonded mid-IR diode optopairs for gas sensing in the 3.3-4.3 μm spectral range

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ABSTRACT

We describe "flip chip bonded" In(Ga)As and InAsSb heterostructure photodiodes and light emitting diodes ($\lambda=3.3\div 4.3 \mu\text{m}$) grown onto n-InAs substrate. The advantages of the construction include the possibility of coupling with immersion lenses through the contact free surface. The report presents U-I characteristic, spectral emission and response, and simulations of sensitivity of the optically coupled diode pair to methane and carbon dioxide gases.

Detector, Mid-infrared photodiodes, IR sensing, IR diode optopairs

1. INTRODUCTION

There has been an increased interest in ambient operating mid-infrared ($\lambda=3\div 5 \mu\text{m}$) low voltage/current light sources and detectors with respect to application in new spectroscopic analyzers. Optical components in this wavelength range are of particular interest for environmental monitoring, since most industrial gases have characteristic absorption bands in the above spectral range. Methane is the major target gas for intrinsically safe sensor instrumentation since it is explosive and can be found in many technological processes [1].

Several companies offer InAs diodes that are sensitive to radiation at the ν_3 methane band ($\lambda=3.3 \mu\text{m}$) and work at zero or negligible bias. Room temperature detectivity values as high as $1.2 \cdot 10^{10} \text{ cmHz}^{1/2}/\text{W}$ at $\lambda=3.3 \mu\text{m}$ for surface illuminated *In(Ga)As* [2] and InAs mesa photodiodes [3] as well as above room temperature operation of the p-InAsSbP/n-InAs diodes for methane sensing [4] and for negative luminescence emission [5] have been already reported. Photodiodes sensitive to 4.3 μm emission have been also described [6, 7], however, they have broad spectral response and were not optimized for optical instrumentation, e.g. they do not contain immersion elements that can increase outcoupling with other devices (LEDs).

Recently new epitaxially down bonded (or "flip chip bonded") diode design was proposed both for the 1 mW (CW) source [8] and $2 \cdot 10^{10} \text{ cm Hz}^{1/2}\text{W}^{-1}$ detector [9] grown onto heavily doped n⁺-InAs that enabled to fabricate immersion lens diodes $\lambda=3.3 \mu\text{m}$ with the narrow beam diagram. First experiments on coupling of the above diodes also been described [9], however no data was published so far on the sensitivity of optically coupled epitaxially down bonded LED-photodiode pair with immersion lenses with respect to gas sensing in the 3.3-4.3 μm wavelength range.

Here we characterize immersion lens "flip chip bonded" In(Ga)As and InAsSb based heterostructure photodiodes and LEDs that are active at 3.3-4.3 μm and present preliminary estimations of limit of detection for the optically coupled diode pairs with respect to methane and carbon dioxide gas sensing.

2. EXPERIMENTAL DETAILS AND DISCUSSION

2.1. Heterostructure characterization

Double (DH) heterostructures for “short wave” diodes ($\lambda < 3.6 \mu\text{m}$) were similar to those described in [8, 9] and were grown by the LPE method. Heterostructures consisted of heavily doped $n^+-\text{InAs}$ (Sn) (100)- substrates and two epilayers. They represented $1\div 1.5 \mu\text{m}$ thick wide-gap $n-\text{InAs}_{1-x-y}\text{Sb}_x\text{P}_y$ confining layer, $2 \mu\text{m}$ thick $n-\text{InAs}$ or $n-\text{In}(\text{Ga})\text{As}$ active region with small amount of Ga and $2\text{-}3 \mu\text{m}$ thick wide-gap $p-\text{InAs}_{1-x-y}\text{Sb}_x\text{P}_y$ (Zn) emitter or cap layer. In some cases the active region was grown from the melt with gadolinium. Gd doping produces a gettering effect, that is, reduces net donor concentration and improves carrier mobility and photoluminescence efficiency

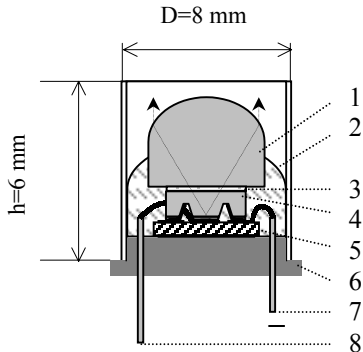
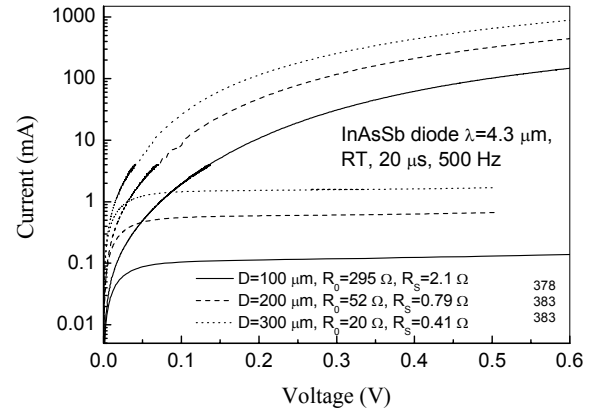


Fig.1 Construction of the immersion lens LED/photodiode.

1-CdSb or Si immersion lens
2-D=3.5 mm, 2- epoxy, 3-
chalcogenide “glue”, 4 –“flip
chip bonded” diode, 5-Si
submount, 6-TO-39 header, 7-
cathode, 8-anode

Fig.2 I-U dependence in InAsSb diodes with mesa diameter 300, 200 and 100 μm at room temperature



[¹⁰] and DH laser performance [¹¹]. Low residual concentration is a crucial factor for the device performance since the best photodiode parameters are achieved at “non symmetrical” doping profile e.g. p^+-n^- [¹², ¹³].

Lattice matched at heterojunction InAsSbP layers for “long wave” diodes ($\lambda > 4 \mu\text{m}$) were similar to those described in [5] and were grown at InAs plasticity temperatures ($650\text{-}720^\circ\text{C}$) by the LPE method on thin ($350 \mu\text{m}$) $n-\text{InAs}$ (111) substrates. Zn was used as a p-dopant for p-n junction

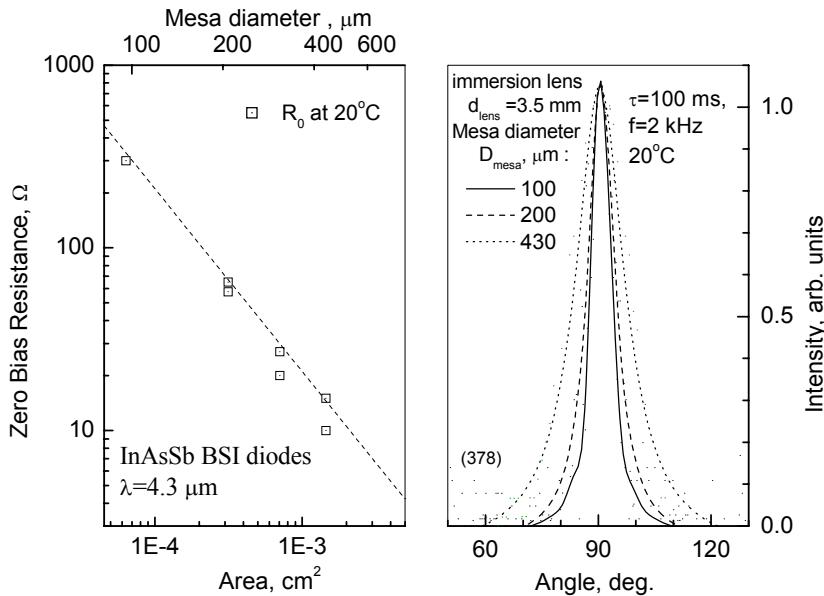


Fig.3 Shunt resistance vs mesa diameter/area (left) and far field diagram of immersion lens InAsSb LED (right) at room temperature. Dotted line on the left: $\sim 1/(D^2)$ function

The obtained heterostructures were processed by a wet photolithography into constructions with mesa diameter $D=430, 300, 200$ or $100 \mu\text{m}$ and were cut into chips of $\sim 1 \times 0.9 \text{ mm}^2$ dimensions. The latter contained gold “horse shoe” or “U” shaped (cathode) and circular anode contacts on the epise of the chip. Both chip contacts were connected to contact areas of a $1.5 \times 1.7 \times 0.4 \text{ mm}^3$

formation during the growth. The thickness of p-type layer was about $5 \mu\text{m}$. Due to high segregation coefficient phosphorus concentration diminishes within first $50\div 80 \mu\text{m}$ of InAsSbP layers providing the energy gap decrease along the growth direction with $\nabla E_g = 1\div 2 \text{ meV}/\mu\text{m}$ and a “window” effect for the light escaping from InAsSb narrow gap region.

The obtained heterostructures were processed by a wet photolithography into constructions with mesa

semiinsulating Si-submount by soldering. Si or CdSb lenses with $D=3.5$ mm were attached to the n^+ -InAs surface by a chalcogenide glass having refractive index of $n=2.6$ as shown in Fig.1.

2.2. InAsSb Diode pair ($\lambda=4.3$ μm)

Typical I-U characteristic of InAsSb diode with mesa diameter 300, 200 and 100 μm is presented in Fig.2. As seen from Fig.2 the forward bias (FB) current and the saturation current at the reverse bias (RB) are decreasing with mesa diameter. The latter can be described also in terms of zero bias resistance (R_0) dependence on mesa diameter shown in Fig.3 (left). The R_0A product constitutes to ~ 0.02 $\Omega\cdot\text{cm}^2$ in the whole 100-300 μm diameter range indicating negligible leakage current through the mesa surface. Measurements showed also the domination of thermal (Johnson) noise in the diodes. The presented data show also that by selecting device diameter it is easy to adjust diode

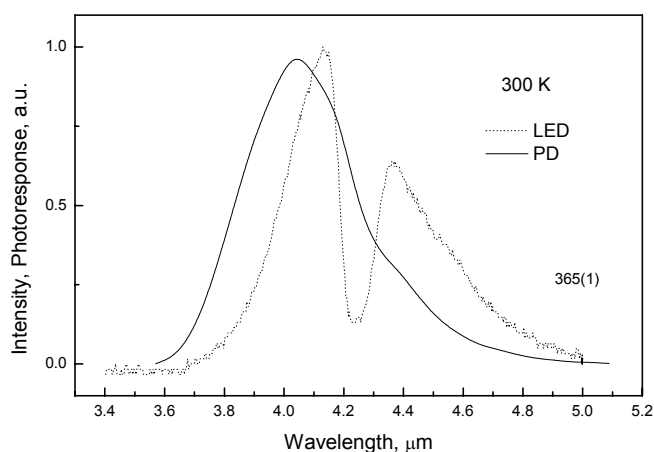


Fig.4 Response (solid) and emission (dotted) spectra of the same InAsSb diode at room temperature

resistance to that of the amplifier. The latter is especially important for longwave/narrow gap diodes whose standard shunt resistance amounts to several Ohms only [14]. The desired increase of shunt resistance goes along with the narrowing of the beam diagram in immersion lens diodes that is important for practical applications as shown in Fig.3 (right). InAsSb backside illuminated (BSI) diodes are characterized by narrow spectral sensitivity peaking at 4.0-4.2 μm with FWHM ranging from 0.5 to 0.6 μm as shown in Fig.4. Additional band narrowing can be achieved by spectral filtering using bandpass filters [see e.g. 15]. Peak sensitivity is shifted with respect to emission spectra of the same diode towards short wavelength by $\Delta\lambda=0.05$ -0.1 μm in conjunction with the broadband InAsSbP “window” transmission and carrier diffusion towards the p-n junction. Response spectra in Fig.4 was corrected for CO_2 gas absorption while InAsSb LED emission bears features of atmosphere CO_2 ($c=0.03$ % v/v) absorption at a path length of ~ 170 cm. It thus evident that optically coupled InAsSb pair is a gas sensor since photoresponse will depend on the amount of gas between the diodes.

The performance of the above pair coupled with spherical mirror $R=13$ cm is shown in Fig.5 by the dependence of Signal to Noise Ratio (SNR) measured in the $\Delta f=1$ MHz band vs LED pulse current at single pulse. Shown in Fig.5 is also the limit of detection (LOD) (right scale) with respect to the CO_2 gas that was draftily estimated using the response of the pair to the test gas (dU/U)_{test} and signal/noise ratio (SNR) in the following manner: $\text{LOD}=(c\cdot L)_{\text{test}} U/(dU\cdot\text{SNR})$ where c – is the gas

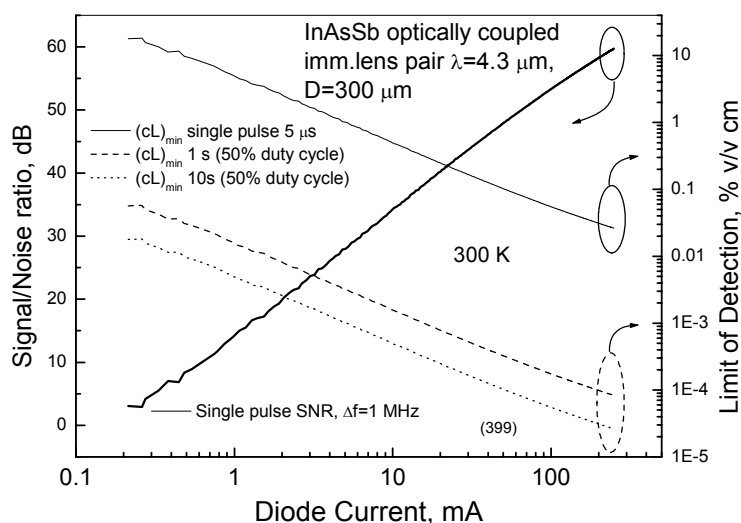


Fig.5 Signal to Noise ratio (left) of mirror coupled InAs diode pair with immersion lenses and LOD (right) vs LED current at single pulsing and averaging over 1 and 10 s (duty cycle 50%, room temperature)

concentration and L is the optical path. The dU/U value that is the change of the photodiode signal on an introducing the gas between diodes was taken as 0.2 for $(c \cdot L)_{\text{test}} = 0.051$ cm in accordance with gas transmission shown in Fig.4. As seen from Fig. 5 the «alarm» concentration of 0.2 % v/v can be detected at path of 1 cm and single LED current pulse of 24 mA only. Subsequent integration of 1 mA signal pulses during 1 and 10 s produces ability to detect of ~ 160 and ~ 50 ppm of CO_2 correspondingly.

2.2. InAs Diode pair ($\lambda = 3.3 \mu\text{m}$)

Room temperature FB current follows Shockley formula with ideal factor slightly differing from the unity ($\eta = 1.067$). The latter value is an indication of good quality of a p-n junction and is a distinguishing feature from nominally similar diodes with $\eta = 3.5$ measured in [16]. As soon as the bias approaches the barrier potential ($U = 0.35$ eV) an exponential current growth is followed by a linear I-U dependence with serial resistance as low as 0.13Ω . The RB (or “dark”) current in a $300\text{-}\mu\text{m}$ wide diodes exhibits saturation at ~ 0.01 mA and slight increase to ~ 0.02 mA at $U = -1$ V with negligible recombination-generation and $1/f$ noises. Dark current grows on a temperature increase.

Fig.6 presents shunt resistance (R_0) of the diodes vs mesa diameter. As seen from Fig.2 the

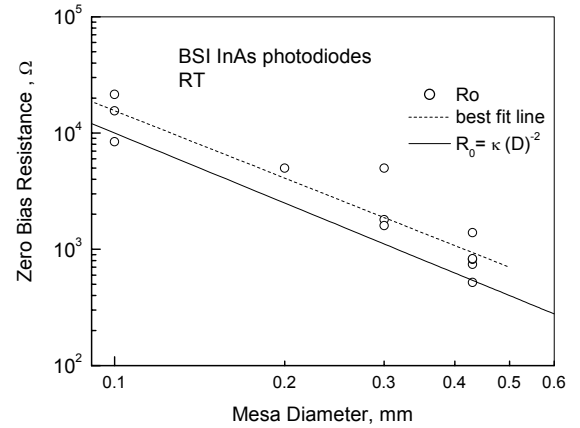


Fig 6 Shunt resistance vs mesa diameter in InAs diodes

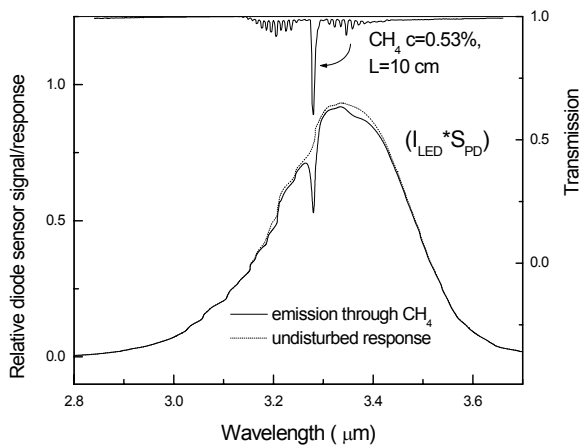


Fig.7 Methane transmission and product of spectral responsivity and emission for InAs diode at 20°C . Dip at $3.3 \mu\text{m}$ corresponds to methane absorption.

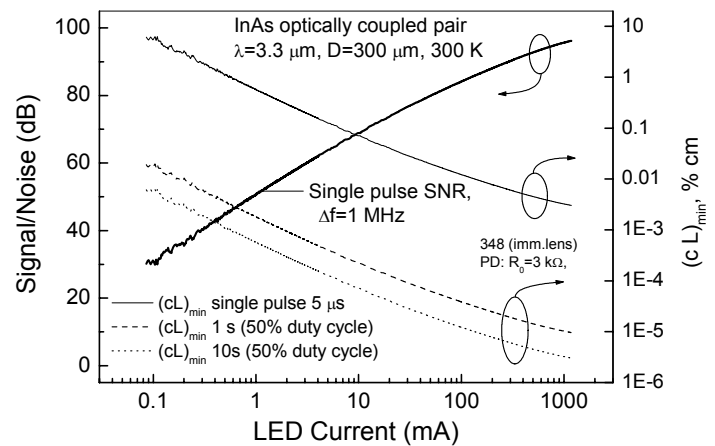


Fig.8 Signal to Noise ratio (left) of mirror coupled InAs diode pair and LOD (right) vs LED current at single pulsing and averaging over 1 and 10 s (duty cycle 50%, room temperature)

experimental values of zero bias resistance is proportional to diode area (or D^2) indicating as in case of InAsSb diodes negligible leakage current through the mesa surface. Johnson noise was main contributor to device noises.

InAs BSI diodes are characterized by narrow spectral sensitivity peaking at $3.3\text{-}3.4 \mu\text{m}$ with FWHM ranging from 0.5 to $0.7 \mu\text{m}$ in conjunction with the substrate thickness. Peak sensitivity is shifted with respect to emission spectra of the same diode towards short wavelength by $\Delta\lambda = 0.05\text{-}0.1 \mu\text{m}$. Low response of the BSI diodes at short wavelengths originates from light absorption in thick n^+ -InAs substrate. Fig.7 demonstrates room temperature spectral optopair response, that is, the product of LED emission and photodiode response spectra together with methane gas transmission and product of all above. As seen from Fig.7 there is good overlapping of methane absorption and pair response with $dU/U_{\text{CH}_4}^{\text{InAs}} = 0.027$ ($t = 20^\circ\text{C}$) for $L = 10$ cm pathlength and $c = 0.53\%$ v/v.

Room temperature performance of optically coupled immersion lens diodes at different pumping currents is presented in Fig.8: left scale presents single pulse SNR of the pair at $\Delta f=1$ MHz coupled with spherical mirror. Fig. 9 presents signal variation of pair in which two immersion lens diodes are aligned in a manner that they both are looking “face-to face”. The latter means that no additional collimating elements have been used for the case. As seen from Fig.8 SNR as high as 4000 is already achieved at current as small as 20 mA. This indicates sufficient progress with respect to our previous results with the same SNR value at current pulse of 3 A [4]. It is clear that high aperture mirror Fig.8 is beneficial in terms of the SNR values with respect to “face-to-face” scheme in Fig.9 that exhibits sufficient reduction of the signal on a distance increase. However the construction of an instrument is always a compromise between the limit of detection (LOD), optical path, SNR and instrument dimensions (e.g. mirror diameter).

The LOD of the mirror coupled InAs diode pair was estimated in the same manner as for the InAsSb one and is presented in Fig.8 (left scale). As seen from Fig. 8 single pulse of 2 mA enable to detect 0.3 % v/v of methane at 1 cm path. The LOD at integration of 1 mA signals over 1s is around 18 ppm. The described pair can thus be used for intrinsically safe methane sensor that can operate even at explosive concentrations due to extremely low power consumption. Further decrease of the LOD can be achieved by the use of multipass [17, 14] or open path systems [1].

In conclusion we would like to note that from a standpoint of signal integration the low current pumping of the LED produces maximum value of the SNR ratio. The reason for this is sublinear dependence of LED emission at high currents originating from Joule heating, current crowding and Auger nonradiative recombination [5, 8, 14, 16]. That’s why low current 50% duty cycle regime of pair operation may be considered as “standard” for a diode couple. We can thus derive universal measure describing pair performance: unit current amplitude, unit current duration, unit path length limit of detection. The above values for InAsSb (CO_2) and InAs (CH_4) diode pairs activated at 50% duty cycle at room temperature constitutes to $\text{LOD}=160$ and $18 \text{ ppm}\cdot\text{cm}\cdot\text{mA}\cdot\text{s}^{1/2}$ correspondingly.

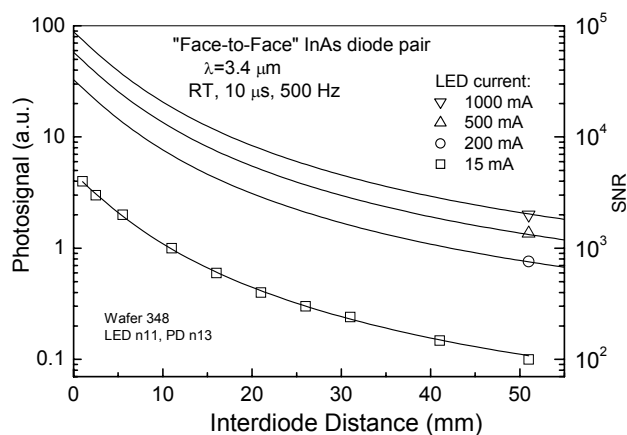


Fig.9 Room temperature signal to noise ratio (SNR) in InAs immersion lens diode pair at $\Delta f=1$ MHz vs interdiode distance at “face-to-face” viewing

3. SUMMARY

Narrow band ($\text{FWHM}=0.5\div 0.7 \mu\text{m}$) In(Ga)As and InAsSb optically coupled diodes ($\lambda=3.3\div 4.3 \mu\text{m}$) grown onto n-InAs substrates have shown ability to detect methane and carbon dioxide with the limit of detection as small as 0.3 % v/v at optical path of 1 cm and pumping single current pulse in the mA range. Low power consumption and bias voltage enable the application of these diodes for intrinsically safe sensors for explosive environment.

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