Narrow-Band Lead Salt Photodetectors and Solution-Processible Nanocrystal Photodetectors for the Midinfrared

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Introduction

Molecular absorption line strengths are much stronger in the midinfrared spectral range than in the near infrared and the visible. Thus, for sensitive gas analysis and atmospheric pollution monitoring highly efficient optoelectronic devices for the midinfrared are required. For portable gas detection systems, infrared spectrometers and other applications, one obvious requirement is to avoid the need for cryogenic cooling of the system components, including also the detectors. To achieve room temperature photodetectors we show two different approaches. One is the use of epitaxial PbTe detectors which we integrated monolithically on optical filter structure like λ/2 microcavities. The second is the development of photodetectors based on solution-processible nanocrystals.

Narrow-Band PbTe Photodetectors

The integrated PbTe detector consists of a 500-nm-thick PbTe photosensitive layer deposited on top of a microcavity filter, designed for a target wavelength of λ = 3.6 μm. The microcavity filter consists of two EuTe/$Pb_{0.94}Eu_{0.06}Te$ Bragg interference mirrors separated by a λ/2 $Pb_{0.94}Eu_{0.06}Te$ cavity layer [1]. For the bottom mirror, a single EuTe/PbEuTe layer pair is chosen, which is sufficient to obtain a reflectivity of 83%, whereas for the top mirror an odd number of layers (3) has to be used in order to obtain similar reflectivities in respect to PbTe. The samples were grown with excess Te flux resulting in a p-type doping of the PbTe layers with a hole concentration of 10^{17} cm^{-3} and a mobility of 1700 cm^2/Vs at room temperature. By adjusting the substrate temperature and the Te to Eu flux ratio during growth, n-type conductivity is obtained in the EuTe films. Mesas were fabricated by standard photolithography and chemical wet etching. Pt/Ti/Au pads are used as ohmic contacts for p-type PbTe whereas In contacts serve as n-type contacts for EuTe.

A cross sectional scanning electron microscope (SEM) image of the complete structure is shown in Fig. 1(a), where the chemical contrast between the layers was enhanced by selective plasma etching. In the SEM image, the PbEuTe and EuTe layers of the Bragg mirrors and of the cavity region as well as the photosensitive PbTe film on top of the structure can be clearly distinguished.

The high optical quality of the microcavity filter is demonstrated by the FTIR transmission spectrum depicted in Fig. 1(a). Within the wide stop band from 2.7 μm to 5 μm a narrow cavity resonance peak at 3.66 μm is observed, corresponding to the first order cavity resonance mode. The full width at half maximum (FWHM) of the peak is 100 nm, which corresponds to a cavity finesse of 27. The photovoltage spectrum of the device under backside illumination in Fig. 1(b) exhibits a single peak at 3.67 μm, which is just

above the PbTe band gap at room temperature. This resonance peak position coincides exactly with the strong O=C-H stretching bond absorption line characteristic for non-aromatic aldehydes. This is indicated in Fig. 1(b) by the characteristic absorption spectrum of acetaldehyde used e.g. in the production of perfumes, polyester resins, and basic dyes. Obviously the relative width of the photoresponse peak of $\Delta\lambda/\lambda = 2.7\%$ corresponds very well with the width of the acetaldehyde absorption peak. The single photovoltage peak of the detector coincides in position and line width with the peak found in transmission measurements. Therefore, the photovoltaic response of the detector is directly correlated to the filter transmittance. The broadband feature shown in Fig. 1(b) at shorter wavelengths (< 3 µm) is due to the transmission of the filter structure above the Bragg mirror stop band. This signal can be eliminated by adding a PbEuTe absorber layer underneath the microcavity filter structure, acting as long pass filter and blocking all radiation above the band gap energy. This would allow to obtain detectors with only a narrow-band photoresponse, which can be easily tuned to the molecular vibration-rotation lines of other gases just by adjusting the filter design. Such monolithically integrated detectors would perfectly meet the demands given by compact gas detection systems.

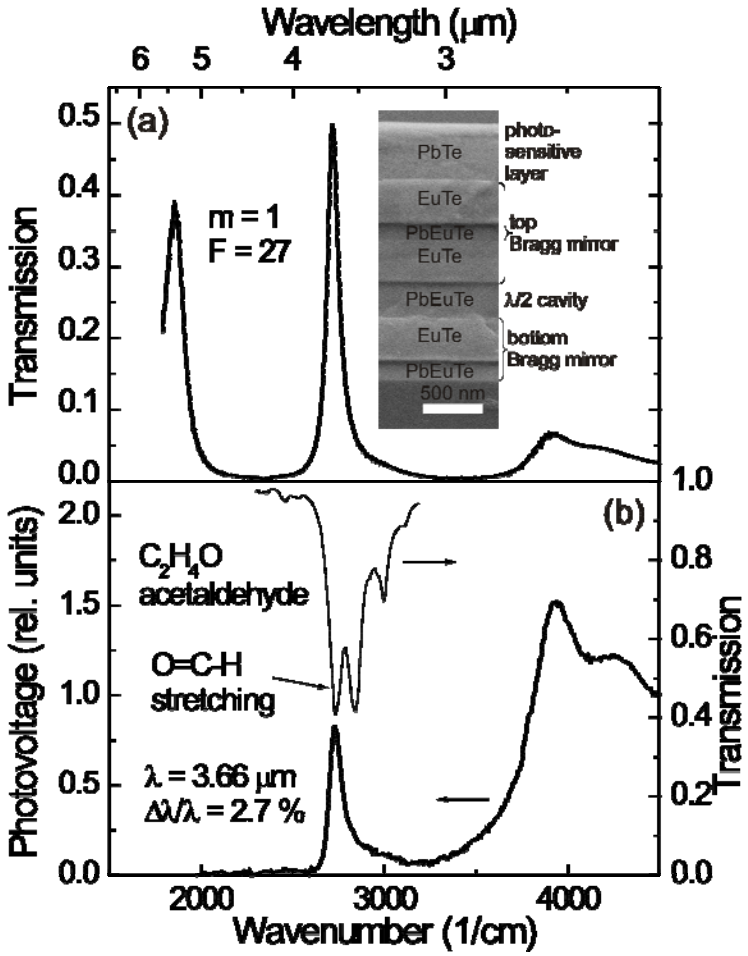

Fig. 1: (a) Transmission spectrum of the integrated PbTe photovoltaic detector on a λ/2 microcavity filter. The inset shows a SEM image of the device cross section. (b) Room temperature photovoltage spectrum of the integrated PbTe photovoltaic detector, compared to the absorption spectrum of acetaldehyde.

Nanocrystal Photodetectors for the Midinfrared

For the solution-processible photodetectors we used HgTe nanocrystals (NC), whose photoluminescence peak can be tuned between 1.2 and 3.5 µm by increasing the NC average size from 3 to 12 nm [2]. The HgTe NCs were prepared in aqueous solutions with hydrophilic thiols as stabilizers. A post-synthetic heat treatment increased the sizes of the NCs and pushed their bandgap to longer wavelength. Subsequently, a ligand exchange with dodecanethiol was carried out making the NCs soluble in commonly used organic solvents. The photoluminescence peak of the NCs can be tuned between 1.2 and 3.5 µm by increasing the NC average size from 3 to 12 nm [2].

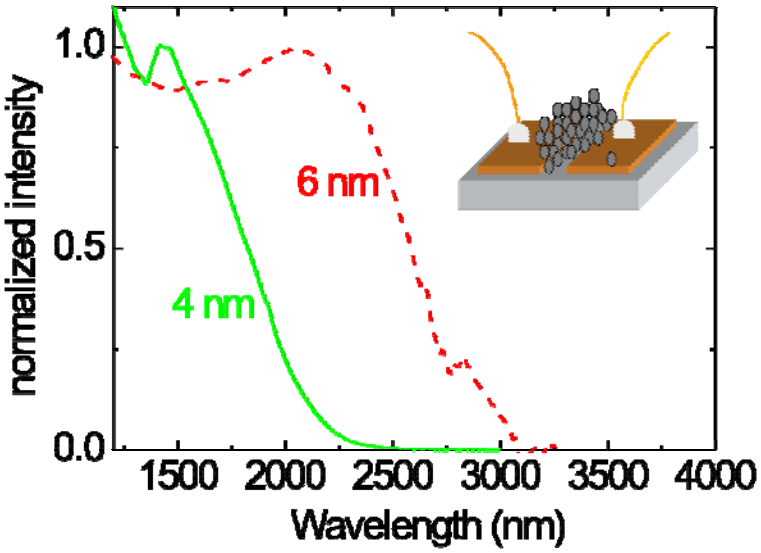

Fig. 2: Sensitivity spectra of HgTe NC photodetectors different in the NC size. The inset shows schematically the device structure.

For photoconductive devices NCs in solution were drop-casted on glass substrates and dried to form solid films. Cr/Au pads with a spacing of 50 µm serve as lateral contacts to the films. The sketch of the device structure is depicted in the inset of Fig. 2. The NC detectors were measured at room temperature and under ambient conditions. The normalized sensitivity spectra of the samples with different HgTe NC sizes are shown in Fig. 2. The onset of the photoresponse for 4 nm-big NCs is around 2.3 µm, whereas the onset for 6 nm-big NCs is shifted to longer wavelength due to the reduced confinement effect and is at 3 µm. The dark current of the NC detectors is about 10 nA. Illumination with a power of only 20 µW increases the current to 300 nA, thus the increase is more than a factor of 10. Measurements of the time behavior show that the time constant of the HgTe NC detectors is less than 20 µs, which is fast compared to organic semiconductor devices. The device structure is not yet optimized; nevertheless the sensitivity obtained from the HgTe NC detectors is 30 mA/W. A big advantage of the HgTe NCs in contrast to conjugated polymers is that they are photostable even under ambient conditions.

The ability to use solution-processible HgTe NCs gives future prospects for infrared devices on flexible or porous substrates and for highly integrated detector arrays.

Conclusion

In conclusion, we demonstrate monolithically integrated PbTe detectors, where the photosensitive PbTe layer is grown on top of a microcavity filter. The detectors show a single resonance in the photoresponse spectrum with a relative width of 2.7%. By adjusting the filter design, the peak wavelength and line width of the photoresponse can be matched to the characteristic absorption lines for various gases, as demonstrated for acetaldehyde. This makes these detectors ideal for molecule identification and quantification purposes in low-cost integrated systems.

Furthermore, we present solution-processible photodetectors based on HgTe NCs. With the size of the NCs the onset of the photoresponse can be tuned. We obtained an onset wavelength of 3 µm which is the longest wavelength demonstrated so far for NC photodetectors. These detectors offer a low-cost possibility to conventional photodetectors for the midinfrared due to the easy process handling.

Acknowledgements

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References

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