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Efficient infrared upconversion in GaP

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Mechanisms for linear conversion of infrared to visible were investigated in extrinsic GaP. Efficient (1%) conversion of 10 micron to visible was observed in GaP:Zn,O. Several device applications are discussed and a quantum counter scheme involving III-V photocathodes is presented.

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INTRODUCTION

This paper describes a spectroscopic study of extrinsic semiconductor materials for infrared (ir) upconversion applications wherein impurity states provide a mechanism for upconversion of infrared to visible radiation.¹⁻⁴ An upconversion efficiency of $\sim 1\%$ for 10 μm to visible was observed in GaP:Zn,O, suggesting that efficient ir detection is possible using impurity doped semiconductors. Previous studies of linear ir upconversion have centered principally on rare-earth doped alkali halides.⁵⁻⁷ Several ir upconversion schemes employing in-gap semiconductor levels have been considered (Fig. 1) including upconversion to visible through shallow impurity and exciton states^{2,4,8} and deep traps.³

Certain impurity-doped semiconductors deserve consideration for ir upconverter applications because they have high radiative quantum efficiency—particularly at low temperature. Radiative quantum efficiencies approaching 100% have been reported^{9,10} in GaP:Zn,O. In addition, a number of other semiconductor features would be useful for device applications including broad ir and optical bias bandwidth, wide dynamic range, and utilization of material that is technologically well developed.

EXPERIMENTAL

A visible laser, usually a pulsed nitrogen laser pumped tunable dye laser, was used as the optical bias, and a pulsed infrared laser, either CO₂ (10 μm) or H₂O (23, 28, 33, 48, 55, and 78 μm) was used as the infrared signal. Samples were mounted in a cryostat, and sample temperatures could be varied from 4 K to room temperature. Fluorescence was observed using either a 1/4 or 1/2 M spectrometer and either an optical multichannel analyzer or a photomultiplier.

Upconversion of ir radiation was observed for wavelengths extending to 78 μm . Results are summarized in Table I. Materials studied (Table I) included GaP with impurities N, S, Zn, and O. Upconversion processes included (1) enhancement of visible fluorescence, (2) fluorescence from a level that does not fluoresce when ir is not incident, (3) fluorescence quenching, and (4) quenching of fluorescence from one impurity level along with enhancement of fluorescence from another impurity level.

Upconversion of 10 μm in GaP:Zn,O at 10°K was observed through enhancement of a broad emission between

710 and 780 nm. The optical bias was 645 nm. Care was taken to verify that enhancement was a photoeffect and not thermal. A calculation of efficiency based on the fluorescence data indicates an internal conversion efficiency of about 1%. Because this result required estimating the amount of light lost in the collection optics, spectrometer, etc., numbers were estimated conservatively, and we believe this is safely on the low side.

DISCUSSION

Spectroscopic observations in several systems (Table I) and the observed upconversion efficiency in GaP:Zn,O^{9,10} suggests several detector applications. For example, as a 10-

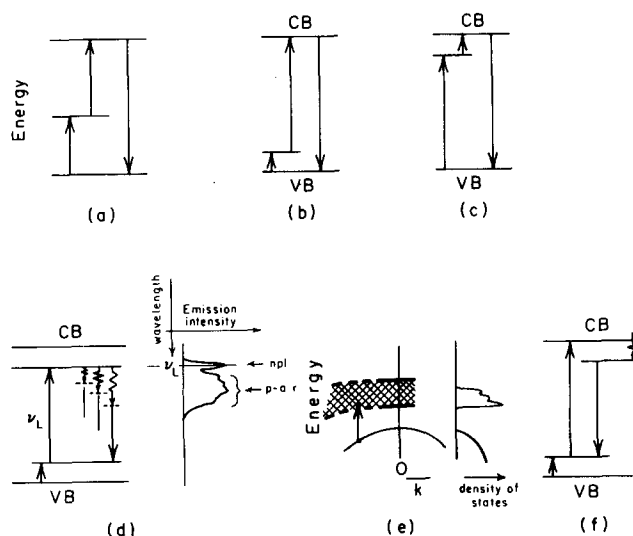


FIG. 1. Semiconductor ir upconverter diagrams. (a) Upconverter principle. Absorption of 2 photons (optical bias + signal) followed by emission at shorter wavelength. (b),(c) Schematic of processes employing acceptor and donor levels. VB = valence band, CB = conduction band. Similar processes may be considered for free and bound excitons. In (b) absorption of the optical bias occurs after absorption of ir; in (c) the bias is absorbed first. (d) Intraband process. npl = no-phonon line, p-a-r = phonon-assisted recombination, ν_L = bias photon frequency. Jagged arrow indicates phonon emission. This process would be more characteristic of an indirect gap material. Typically impurity intraband emission is broadened by phonon sideband emission, indicated on right, as well as other mechanisms including donor-acceptor pair distances and density effects. (e) ir absorption broadening mechanisms. k = wave vector. Acceptor level is broadened by density of impurities, and ir photon excites electron from valency band at $k \neq 0$. To the right is plotted hypothetical density of states. (f) Excitation by ir signal to acceptor, followed by excitation to conduction band, followed by nonradiative decay (e.g., trapping) to radiative donor or exciton level.

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TABLE I. Upconversion observations. ^a

Sample	Observed Pump λ (μm) eV		Observed ir signal λ (μm) eV		Quantum gain (approx)	Est cutoff λ (μm)	Mechanism	Observed As ^b	Radiative efficiency ^c	Optimal pump (est) (μm)	Comments
(1) CdS ²	0.488	2.5	23–33	0.038–0.054	50	35	bound-free exciton	<i>F</i>	✓	0.488	Demonstration of direct up-conversion using resonant excitation of pump level.
(2) GaP:Zn,O	0.65	1.9	10.6	0.124	15	19	<i>e-h</i> pair recombination	<i>E</i>	✓	0.8	Measured conversion efficiency, ir-visible $\geq 1\%$.
(3) GaP:N ⁸	≥ 0.535	≤ 2.316	10–78	0.016–0.124	20–150	120	<i>bd</i> exciton free	<i>Q</i>	✓	0.535	Exciton bound to N with ≈ 10 meV.
(4) GaP:S ⁸	≥ 0.535	≤ 2.313	10–33	0.028–0.124	20–80	50	<i>bd</i> exciton free	<i>Q</i>	✓	0.536	Exciton bound to S with ≈ 19 meV.
(5) GaP:N,S ⁸	0.49	2.5	10–33	0.028–0.124	20–80	65	<i>bd</i> exciton-free- <i>bd</i> exciton	<i>Q,E</i>	✓	0.536	Employs both bound excitons in 4 and 5. Pumping with $\lambda \approx 5363$ Å should achieve high conversion efficiency. ^d
(6) GaP:Te	≥ 0.535	≤ 2.313	10–33	0.028–0.124	20–80	50	<i>bd</i> exciton free	<i>Q</i>		0.536	Exciton bound to neutral donor Te with 19 meV.
(7) GaP:Bi	≥ 0.535	≤ 2.3	10	0.124	20	12	<i>bd</i> exciton free	<i>Q</i>	^e	0.5904	Exciton bound to isoelectronic trap Bi.

^aData taken at $T \approx 10$ °K.^b*F* = Fluorescence; *E* = Fluorescence Enhancement; *Q* = Fluorescence Quenching.^cCheck indicates radiative quantum efficiency of fluorescing level 10% to 100% at 5 °K.^d0.5360 will directly excite exciton bound to neutral donor S. This center does not radiate efficiently. ir with $\lambda \leq 50 \mu\text{m}$ will photodissociate exciton, which may then bind to N. Quantum efficiency for N-bound exciton is very high, approaching 100% in samples easily available, and emission is broadened and easily detectable.^eEstimated for direct pump excitation to be $> 50\%$ based on studies of isoelectronic traps in GaP.

μm detector GaP:Zn,O should be fast (> 100 MHz) with good quantum efficiency, and high-quality material can be straightforwardly prepared. In addition, it is often required that the bias and/or signal have narrow frequency spread—either to precisely match absorption features in the material (for linear devices) or to achieve phase matching (in a nonlinear device). This tends to restrict applications somewhat. Typically both the signal and bias absorption features are broad in the extrinsic semiconductor materials. Thus in GaP:Zn,O and similar materials there should be a broad band ir response—extending from beyond $19 \mu\text{m}$ to the near ir.

It may be possible to take advantage of this method to use the negative electron affinity photocathode for the detection of middle and far infrared radiation. In commercial negative electron affinity devices, *p*-type GaP, GaAsP, and In-GaAsP are used.^{11–13} Heavy *p*-type doping is used—typically Zn(10^{18} – $10^{19}/\text{cm}^3$)—to achieve a very small band-bending region at the emitting surface. The work function of the semiconductor surface is lowered by the application of cesium and oxygen. The combination of work function lowering and band bending yields a high escape probability for photogenerated electrons from these III–IV materials.¹³ It may be possible to incorporate the acceptor level in a negative electron affinity device as the intermediate state in a quantum upconverter, thus using the ir to be detected to excite an electron to the acceptor site from the valence band, and then

exciting the electron to the conduction band with an optical bias—such as emission from a light emitting diode resonant with the energy difference between the acceptor state and the conduction band. Such a device could have a large surface and broad bandwidth (up to ~ 1 GHz).

Several problems deserve mention and further study for the development of a device. The intermediate state lifetime determines the requirement on optical bias intensity. Such lifetimes vary considerably; in GaP from ~ 10 ns to > 1 s, depending on the impurities. In order for the process to be efficient the ir absorption cross section must be large, and the pump intensity must be sufficient to provide the second excitation step before recombination occurs, e.g.,

$$n \gtrsim 1/\sigma T.$$

where n = number of bias photons per cm^2 s, σ = bias absorption cross section and T = intermediate state lifetime. In practice a source of noise may be the absorption of bias photons by valence band electrons; whether or not this occurs will in general depend on the semiconductor-impurity system. For a sensitive device, a low background of fluorescence is necessary. Thus if excitation by the optical bias occurs to the intermediate state from the valence band, the system would be unsuitable for a device with good detectivity—although the quantum efficiency may be high. In addition, the separation of the acceptor level from the valence band must be considered. If the doping level is as high as in

negative electron affinity devices, the valence band will be essentially degenerate with the acceptor level, and the effective acceptor density of states may be even higher than the valence band density of states. It would be necessary to reduce the acceptor doping to avoid degeneracy with the valence band, hence reducing the bending effect. Finally, for an efficient negative electron affinity type device it is also necessary that the ir absorption length be comparable to the carrier diffusion length.

The mechanism for upconversion in GaP:Zn,O is probably that indicated in Fig. 1(d), with the intraband states being those associated with the exciton bound to Zn-O.¹⁰ This mechanism suggests the possibility of an internal conversion efficiency greater than one—more than one visible photon produced for each absorbed ir photon. This is because the radiative recombination is intraband, and the lower state may be re-excited by another bias photon. Furthermore, there should be little absorption of the emitted radiation because most of the emission is through phonon-assisted sidebands [Fig. 1(d)]. Thus it may be possible to obtain gain in a classical sense in an optical system.

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