Infrared spectral distribution of photoconductivity and up-conversion in GaP light emitting diodes

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The spectral distribution of photoconductivity and infrared excited electroluminescence has been determined in GaP light emitting diodes at low temperatures by conventional infrared spectroscopic techniques. The observed photoresponse was found to be caused by ionization of shallow donors only, showing a peak sensitivity of 20 mA/W at 13-μm wavelength. Spectral structures for photon energies lower than the binding energies of shallow donors are attributed to electric field assisted photoionization. An external quantum efficiency of 3×10^{-3} was obtained being largely independent on the bias voltage and the wavelength of infrared stimulation.

I. INTRODUCTION

GaP light emitting diodes (LEDs) can be used as infrared photoconductors and as infrared to visible up-converters permitting infrared detection by sensitive photon counting detectors.[1,2] At low temperatures, when almost all charge carriers are bound to impurities the current and the electroluminescence of the LED are reduced to very low levels in the absence of infrared radiation even for rather high forward bias voltages. Infrared radiation ionizing shallow impurities induces a photocurrent through the diode and thus leads to visible luminescence.

This up-conversion method has several advantages compared, e.g., to the Bloembergen infrared quantum counter[3–5] or to nonlinear optical frequency mixing[6–8]: The energy difference between infrared (IR) and visible photons is supplied by the electrically injected carriers and not by a pump laser bias avoiding the necessity for spectral discrimination between the strong laser pump and the up-converted light. The IR spectral sensitivity is basically broad band and not limited by the requirement of resonant excitation of certain electronic states. The field of view of the up-converter is not restricted by phase matching conditions as in the case of nonlinear optical devices.[6] The major disadvantage of the LED up-converter is the necessity of liquid-helium cooling.

The present paper deals with spectroscopic investigations of GaP LEDs. The IR spectrum of photoconductivity was determined and the total IR-induced electroluminescence was measured as a function of the IR excitation frequency without spectrally resolving the visible emission. The results show that the IR sensitivity of GaP LEDs covers the near and middle infrared spectral range up to about 20-μm wavelength. At 13-μm wavelength the highest responsivity of about 20 mA/W was observed yielding a thermal background irradiation limited NEP $= 7\times10^{-11}$ W/$\sqrt{\text{Hz}}$ for photoconductivity, which is comparable to that of other infrared detectors operating at low temperatures.[9] The IR spectra show structures which may solely be attributed to donor excitations without any observable contribution from acceptors. In contrast to earlier measurements of extrinsic photoconductivity in n-GaP[10,11] a photoresponse was found far below the ionization energy of donors substantially extending the IR sensitivity to longer wavelengths. This observation is explained by assuming electric field ionization of infrared-excited donor states due to the high electric bias field in the diodes.

II. EXPERIMENTAL TECHNIQUE

A planar green emitting GaP:N diode prepared by liquid-phase epitaxy on Te-doped n-conducting substrate was applied. The doping materials were nominally Zn on the p-side and Te on the n-side. The substrate was fully covered by an alloyed Au:Ge metal electrode whereas on the p face a grid of thin Au:Zn strips was prepared as an electrode leaving about 85% of the surface free for IR irradiation into the wafer. The illuminated area of the sample was 5 mm^2.

The experimental arrangement for measuring the IR excitation-spectrum of photoconductivity and up-conversion is sketched in Fig. 1. The sample was mounted in a

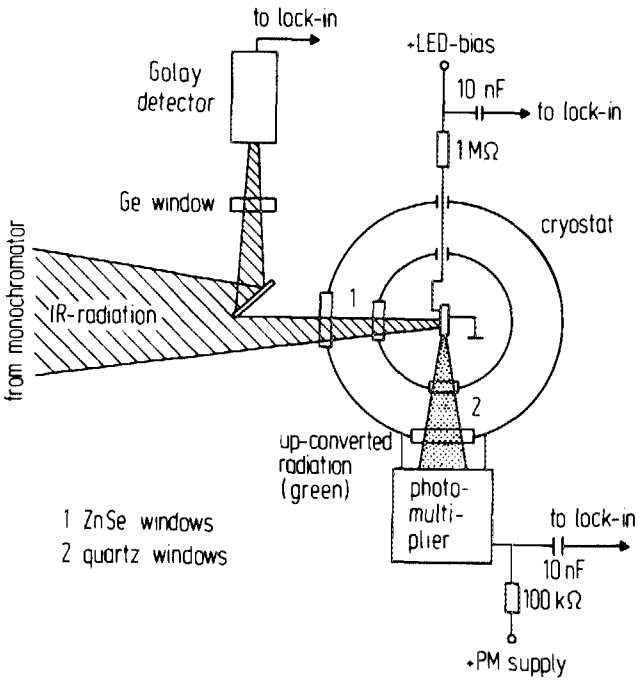

FIG. 1. Experimental arrangement for determining the IR spectrum of photoconductivity and up-conversion luminescence. For details see text.

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temperature variable cryostat with IR transparent ZnSe windows and quartz windows for observing the visible luminescence. The IR radiation of a 30-W output power Nernst glower was spectrally resolved by a Jobin-Yvon HRP single grating monochromator yielding a bandwidth of 50 nm. The output of the monochromator was geometrically split into two beams, one beam was focused on the sample, the other beam was directed on a Golay detector.

The photoconductive signal was normalized by the spectrally flat response of the Golay detector which had a diamond window. The visible fluorescence intensity radiated out of one edge of the LED wafer was determined by a Hamamatsu R928 photomultiplier and divided by the photoconductive signal in order to evaluate the IR spectral dependence of the external LED quantum efficiency η_{LED}. All signals were measured simultaneously by standard lock-in technique.

The electrical properties of GaP diodes at low temperatures are characterized by the prevention of double injection into the junction below a critical voltage. Above this threshold voltage double injection occurs yielding S-type current voltage characteristics and rapid increase of the current by several orders of magnitude.[1,12,13] For the diode of the present investigation the breakdown voltage varied with temperature from 80 V at 2.4 K to 6 V at 40 K. In all measurements the bias voltage was kept well below the onset of double injection in order to ensure stable operation and to avoid excess current noise.

III. INFRARED SPECTRA

A. Photoconductivity

A photoconductive signal was observed in forward and reversed bias conditions without significant difference in the spectral dependence. The photocurrent was strongly dependent on the sample temperature. Details of the temperature dependence will be discussed below. Best signal-to-noise ratio was obtained at about 10 K. At this temperature double injection instability occurred at 20 V forward bias voltage limiting the bias voltage applicable across the diode. Figure 2 shows the photoconductivity spectrum normalized by the Golay detector signal in the range from 480 to 1150 cm^{-1} for 5.6 and 17.6 V bias voltage and a temperature of 11 K. In Fig. 3 the photoconductive signal is plotted for the whole spectral range investigated up to the band edge of GaP.

The observed LED photoconductivity spectrum is quite different from those of both GaP:Te and GaP:Zn.[11] In the latter cases photoconductivity sets in sharply close to the ionization threshold of donors or acceptors, respectively. Above the threshold structures due to phonon-assisted recombination of charge carriers into impurity bound states were observed. The structures in the LED spectra, however, have a different origin. In Fig. 2 the ionization energy[14] of Zn acceptors from the ground state to the valence band $1s_{3/2}\rightarrow\Gamma_8$ and that of Te donors $1s(A)\rightarrow\Delta_1$ and $1s(A)\rightarrow X_1^c$ corresponding to transitions from the ground state into the Δ_1 minimum of the conduction band and into the band edge at the X-point zone boundary, respectively, are indicated by arrows. The photosignal of the LED assumes a maximum just at the quantum energy of the $1s(A)\rightarrow X_1^c$ transition of Te whereas for the Zn ionization transition $1s_{3/2}\rightarrow\Gamma_8$ no structure at all could be observed though the sample was irradiated through the p face. Thus acceptors in the p side of the diode do not contribute to the photoconductivity under the present cw excitation conditions. This must be due to the very fast free-to-bound donor decay of holes and the correspondingly low steady-state concentration of IR-generated holes.[2] Below the ionization energy of Te of about 740 cm^{-1} distinct structures occur which cannot be attributed to ionization of Zn acceptors. A comparison of the spectral position of these structures to the well-known energy levels of Te donors in GaP[14] shows that the low-frequency edges of the observed photoconductivity structures just correspond to the donor transitions $1s(A)\rightarrow 3p_0, 2p_{\pm}$ and $3p_{\pm}$ whose spectral positions are also indicated by arrows in Fig. 2 Thus, IR-excited transitions between bound Te states also contribute to the photoconductivity.

There are, however, some additional prominent struc-

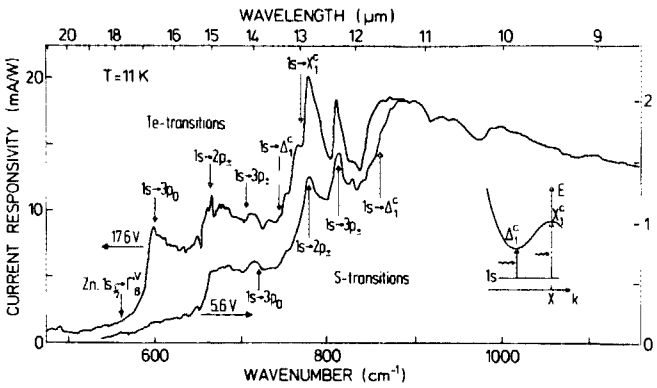

FIG. 2. Spectral dependence of current responsivity of a GaP:N (Zn, Te) LED at 11 K and for 5.6- and 17.6-V bias voltage. Impurity transitions are indicated by arrows. Insert: IR-induced transitions from the 1s donor ground state to the Δ_1^c and X_1^c points of the conduction band.

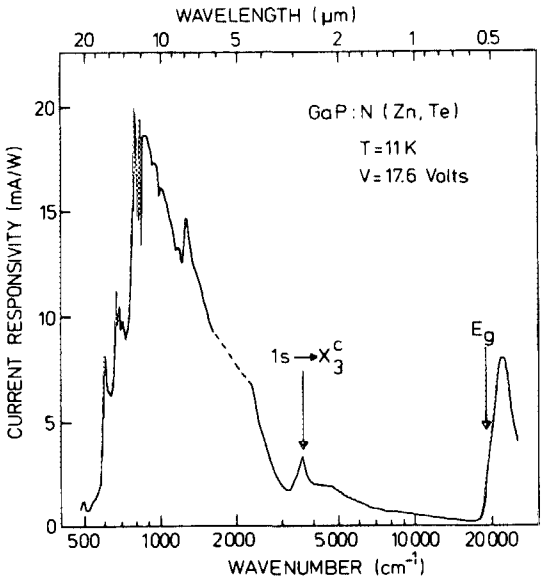

FIG. 3. Spectral dependence of current responsivity of a GaP:N (Zn, Te) LED for wave numbers larger than 480 cm^{-1}. The temperature was 11 K, the bias voltage 17.6 V. The $1s(A)\rightarrow X_3^c$ transition energy and the energy gap E_g are indicated.

tures in the photoconductivity spectrum, namely the peak at 810 cm^{-1} and the edge at 860 cm^{-1}. These structures agree quite accurately with the spectral positions of the $1s(A)$-$2p_{\pm}$ transition (810 cm^{-1}) and the $1s(A) \rightarrow \Delta_1$ ionization threshold (860 cm^{-1}) of sulfur. Thus, besides the intentional n-doping material Te, the diode must contain a substantial amount of S which is an almost unavoidable impurity in GaP. The strong photoconductivity peak at 780 cm^{-1} and the structure at 710–720 cm^{-1} which were identified as $1s(A) \rightarrow X_1^c$ and $1s(A) \rightarrow 3p_{\pm}$ transitions of Te may also have contributions due to S as indicated in Fig. 2.

The relative strength of the photosignal below the ionization threshold of S was found to be strongly dependent on the electric bias voltage whereas above the threshold no change of the structure of the spectrum occurred except an overall increase of the signal with rising bias voltage. Figure 2 contains a recording determined at 5.6-V forward bias voltage in comparison to a measurement at 17.6 V for a 11 K sample temperature in both cases. The curves are scaled in such a way that they coincide in the ionization continuum of shallow donors. Transitions to bound excited states are obviously enhanced by the electric bias field. The effect increases with decreasing binding energy of the excited states. The measurement also shows that the peaks at 780 and 810 cm^{-1} have a noticeable voltage dependence relative to the S-ionization threshold at 860 cm^{-1} indicating that they too are at least partly due to excited donor levels, thus supporting the above identification of S transitions.

To demonstrate more drastically the influence of the electric field on the transition between bound donor states a measurement at 2.4 K has been performed where the diode sustained much higher forward bias voltages. Figure 4 shows the photoconductivity at 80-V forward bias corresponding to about 3×10^4 V/cm in the space charge region of the diode. The subthreshold structures are now of about the same height as those belonging to the ionization continuum.

The observed significant electric field enhancement of the photoresponse close to transitions between donor bound states suggests that tunneling of IR excited electrons out of the impurity potential occurs. The large electric bias field considerably lowers the coulomb barrier in the vicinity of an impurity ion yielding a tunnel probability which increases when the energy of incident photons approaches the impurity binding energy. Tunneling stimulated by IR irradiation may take place without involving excited donor states. In addition, if the photon energy is equal to a donor excitation energy resonant photoionization occurs.[15] Both effects qualitatively explain the almost steplike subthreshold structure of the photoconductivity spectrum in Fig. 2. Similar effects have recently been observed by Coon *et al.* in the extrinsic photoconductivity spectrum of Si:P prepared in form of *p-i-n* diodes.[16]

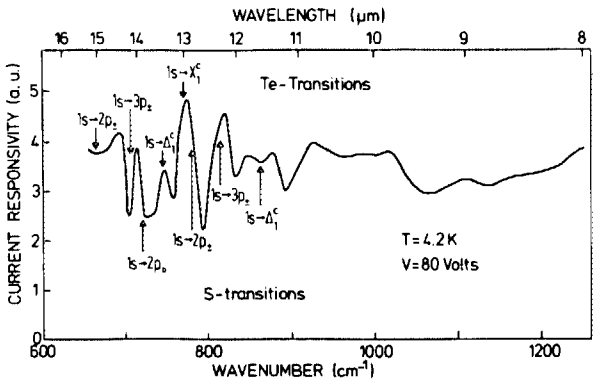

FIG. 4. Spectral dependence of photoconductivity of a GaP:N (Zn, Te) LED at 2.4 K for 80-V bias voltage. The transitions via excited donor states are strongly enhanced by the electric bias field.

At higher quantum energies a basically decreasing photoconductive signal is observed as it is expected for the photoionization of a hydrogenlike system as shown in Fig. 3. The small peak at 3640 cm^{-1} ($\lambda = 2.75\ \mu m$) corresponds to transitions from $1s(A)$ donor states to the upper zone boundary conduction band edge X_3^c. Above the energy gap $E_g \cong$ 19 000 cm^{-1} the signal shows again a strong peak. Besides these there are some minor structures in the spectral range above 900 cm^{-1} whose origin is not yet clear. They cannot be related to phonon-assisted recombination of charge carriers as it was observed in the extrinsic photoconductivity of homogeneously doped GaP crystals.[11]

B. Up-conversion

Infrared stimulated electroluminescence occurred solely at forward bias because only then the charge carriers can recombine near the p-n junction. The up-converted light intensity shows the same spectral dependence as the photoconductive signal. That means that the external quantum efficiency η_{LED} describing the ratio of the number of up-converted photons to the number of photoexcited electrons remains constant in the range from 670 cm^{-1} to more than 11 000 cm^{-1} as shown in Fig. 5. For the present diode η_{LED} was determined to be 3×10^{-3}. At higher wave numbers optical two-step excitations of electrons involving midgap impurity levels, namely oxygen,[17] enhance η_{LED} (see insert in Fig. 5) whereas at lower wavenumbers than 670 cm^{-1} the signal-to-noise ratio decreases to an unpractical low magnitude. The measured value for η_{LED} was found to be independent of the bias voltage at 4.2 K for voltages ranging from 5 to 120 V and at 11 K for voltages from 5 to 18 V.

The fact that η_{LED} does not depend on the infrared excitation wavelength shows that each charge carrier contributes to the up-converted light in the same way and that variations of the lifetime of the charge carriers in the bands due to phonon-assisted recombination[11] play no important role in the LED photoconductivity. This is also confirmed by the observation that there is no dependence on temperature and bias voltage.

The major part of the IR-induced visible luminescence is due to Zn-Te donor acceptor (DA) pair recombination. Two structureless bands were observed corresponding to the no phonon peak at 565 nm and the LO-phonon replica at 578-nm wavelength.[18] The fact that no distinct lines could be resolved indicates that the large electric bias field strength broadens the lines belonging to certain DA pair distances because of the random orientation of DA pairs in the electric field.[19] Besides DA pair recombination a weak contribution to the luminescence caused by the decay of excitons bound to nitrogen pairs (NN lines[20]) could be identified.

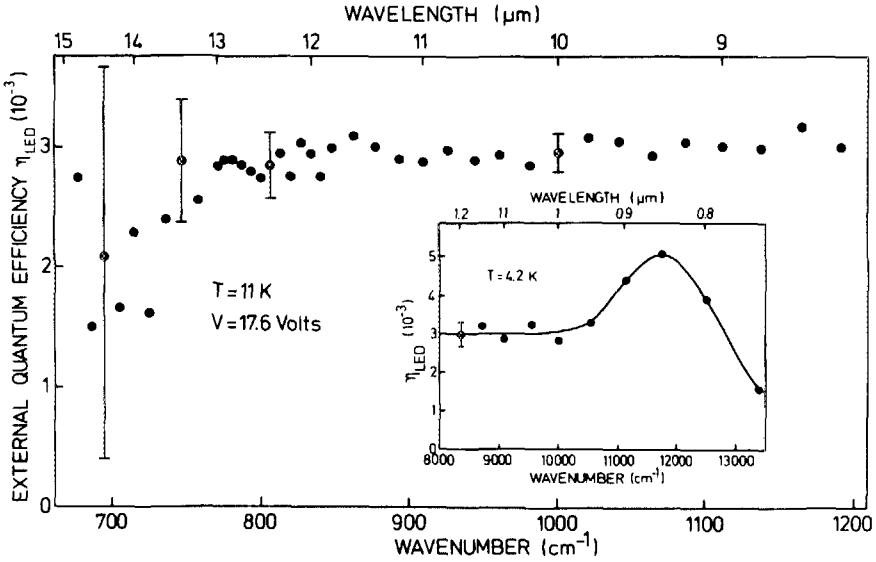

FIG. 5. External quantum efficiency η_{LED} of a GaP:N (Zn, Te) LED in the wave-number range from 670 to 1200 cm^{-1}. The same value of 3×10^{-3} is obtained up to about 11 000 cm^{-1}. The increase above this value (see insert) is caused by two-step excitations via deep impurity states.

IV. TEMPERATURE DEPENDENCE OF THE PHOTOCURRENT

The photocurrent has been measured as a function of temperature between 2 and 40 K. Results for two different photon energies below and above the ionization energy of shallow donors are plotted in Fig. 6 showing basically the same behavior for both cases. Above 25 K a lower bias voltage has been applied to keep the diode in the low-current regime below the onset of double injection. With increasing temperature the responsivity first rises almost exponentially by two orders of magnitude then it remains constant up to 30 K and finally decreases at still higher temperatures which must be due to thermal depopulation of the donor ground state.

The rapid change of the photocurrent below 10 K may be qualitatively understood from the specific electronic properties of GaP LEDs. As mentioned earlier, below a critical bias voltage double injection into the junction is inhibited. Bhargava[12] attributed the prevention of double injection to the formation of an intrinsic region caused by deep-level recombination centers and adopted the theory of Ashley and Milnes[21] to explain the S-type current-voltage characteristics. On the other hand, Maeda[13] observed the formation of a high resistive section in the n region limiting the current through the diode again due to deep centers and applied a different theory presuming charge neutrality and taking into account boundary conditions. For both situations the distance between the carrier supplying diode sections and thus the electron transit time T through the sample decreases with increasing temperature. The number of neutral donors involved in the excitation process is not expected to change appreciably with temperature because only donors close to the cathode, where the deep recombination centers are occupied by injected electrons, contribute to photoconductivity. Thus the responsivity is governed by the photoconductive gain τ/T where τ is the lifetime of free electrons which itself rises with increasing temperatures. Therefore it seems conceivable that τ/T varies with temperature like the observed photocurrent below 10 K.

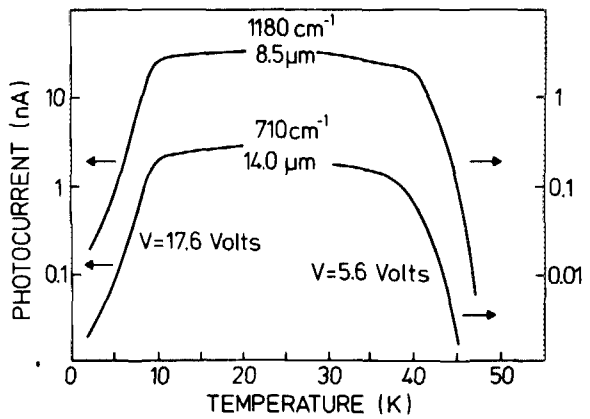

FIG. 6. Temperature dependence of the infrared-induced photocurrent in a GaP:N (Zn, Te) LED at 1180 and 710 cm^{-1}. 17.6 V (left curves) and 5.6 V (right curves) forward bias voltage. Above 25 K the bias voltage was reduced to avoid double injection.

The current noise being due to thermal background radiation[1] attains a minimum at the low-temperature edge in the flat top range of the response in Fig. 6. The photoconductivity noise equivalent power has been determined at 11 K, applying 17.6-V bias voltage for 13-μm wavelength, where the highest sensitivity was observed (see Fig. 2). For an aperture of 60° accepting room-temperature thermal radiation a value of NEP $= 7\times10^{-11}$ W/$\sqrt{\text{Hz}}$ was found.

V. CONCLUSION

In summary, we have shown that GaP LEDs are sensitive broadband IR detectors and up-converters which compare favorably with more commonly used photoconductors in the wavelength range around 10 μm. Below the double injection regime of the current-voltage characteristics much higher bias voltages may be applied across the diodes than to homogeneous samples of the same size. In many applications the drawback of liquid-helium cooling might be com-

pensated by the low price of the detector element itself. Further improvements in the device structure are conceivable, e.g., by irradiating the diode through the *n* face, higher donor doping and better suited luminescence centers. Higher recombination rates could be achieved by shifting the visible emission from donor-acceptor transitions to excitonic recombination.

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