172.3 meV with the $2P_{5/2}(\Gamma_8)$ state and the line at 181.0 meV with the $2P_{5/2}(\Gamma_7)$ state of a doubly ionized center. Taking 28 meV for the binding energy of the $2P_{5/2}(\Gamma_8)$ state we obtain a value of 200 meV for the ground state energy. We have chosen this value for the binding energy to be four times the single acceptor value used previously[2] to reflect the quadratic dependence of the effective Rydberg on the charge of the defect.

The absence of the 200-meV level in the FIR and luminescence spectra for uncompensated material can be explained by the double acceptor nature of the defect. In both cases the defect center is occupied by two holes for uncompensated material. Since the 200-meV energy reflects the energy with which one hole is bound to the fully ionized center, this level cannot be observed unless one of the two holes is first removed from the defect. This only occurs when the material is compensated as is the case for the Si-doped material.

One remaining question concerns the appearance of the 78- and 200-meV levels in the crystal compensated with silicon. In the uncompensated crystals, these levels are only observed in samples grown from melts containing less than 0.47 atom fraction of As and increases in concentration as the melt becomes more Ga rich. The crystal which was compensated with Si, however, was grown with 0.50 As atom fraction and was not expected to contain the 78-meV acceptor. The fact that we see this level indicates that the defect chemistry of the crystal has been significantly altered by the addition of Si to the melt. SIMS measurements have indicatd both Si (3×10^{16} cm^{-3}) and B(2×10^{18} cm^{-3}) impurities in substantial concentration. It is possible that these impurities may play a role in the incorporation of the defect.

In addition we cannot *a priori* reject a different identification of the defect as the defect B_{As} in view of the relatively high B content of this crystal. It should be pointed out that B_{As} and Ga_{As} defects should have very similar properties and that most of the arguments we have stated for a Ga_{As} identification of the defect work equally well for B_{As} defects. Nevertheless, to date we have found no correlation between the boron content and the 78-meV defect concentration in the crystals uncompensated with silicon.

In conclusion, we have observed an additional level associated with a residual acceptor in liquid encapsulated Czochralski GaAs by using infrared absorption, photoluminescence, and Hall measurements. The presence of this level indicates that the defect is a double acceptor consistent with an antisite Ga_{As} identification of the defect.

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Infrared to visible up-conversion using GaP light-emitting diodes

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Electroluminescence excited by infrared radiation has been observed in GaP light-emitting diodes (LED's) at low temperatures providing a new efficient method to convert infrared radiation within a broad spectral range into visible light. Using 10.6-μm radiation of a CO_2 laser an up-conversion quantum efficiency of 3.4×10^{-6} was found. If a low dark current photomultiplier is employed to detect the LED emission the dominant noise source is due to conversion of thermal background radiation yielding a noise equivalent power of NEP $= 1.6\times10^{-9}$ W/Hz$^{1/2}$.

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In recent years several techniques for conversion of infrared radiation into the visible spectral range have been realized. These permit infrared detection by sensitive photon counting detectors and infrared-to-visible image up-conversion. These techniques include optical mixing of infrared radiation with an intense visible laser beam in nonlinear crystals,[1-3] up-conversion utilizing the infrared quantum counter scheme proposed by Bloembergen,[4-6] and up-conversion fluorescence in semiconductors by an optical two-step excitation of electrons involving midgap impurity levels.[7,8]

In this letter we report on a novel method of efficient broadband up-conversion of infrared radiation relying on the photoionization of neutral shallow impurities in visible light-emitting diodes (LED's) by infrared radiation. It is most efficient at low temperatures ($T < 40$ K) when almost all carriers are bound to impurities. Then even at very high forward bias voltages the intrinsic electroluminescence of the LED is reduced to a very low level. Photoionization of impurities releases free carriers and induces a photocurrent through the diode and thus excites visible luminescence. This may be detected by sensitive optical detectors or may even be visually observed. The infrared long wavelength detectivity limit is determined by the binding energies of shallow impurities in the LED material.

The experiments were performed on commercially available GaP LED's emitting in the green spectral range of optimum photocathode performance between $\lambda_{vis} = 0.53$ μm and 0.57 μm. The infrared absorbing plastic cover of the LED was removed and the diode was mounted in an optical cryostat. The visible fluorescence was collected with $f/8$ optics and detected with a photomultiplier. Taking into account the radiation characteristics of the LED, the total emitted optical power P_{vis} could be determined. The diode was biased in series with a load resistor which allowed the measurement of the current.

Infrared-induced luminescence has been observed by irradiating the LED with both a cw and Q-switched CO_2 laser, a Kr^+ laser at 0.799-μm wavelength, and an incandescent lamp whose visible spectrum was eliminated by a germanium filter. No visible emission, however, was induced by a D_2O laser at 66-μm wavelength emitting pulses of several kW peak power. These observations support the explanation of infrared excited electroluminescence given above. The binding energies of shallow impurities in GaP are of the order of 100 meV.[9] Thus the quantum energy of CO_2 laser radiation exceeds the binding energies of shallow impurities whereas the energy of 66-μm photons is too small to ionize either shallow donors or acceptors in GaP.

The experimental results presented in the following were obtained by using a CO_2 laser at $\lambda_{ir} = 10.6$ μm wavelength. Figure 1 shows the visible luminescence power P_{vis} as a function of the forward bias voltage for thermal background radiation and various intentional infrared irradiation power levels. In Fig. 2 the current forward bias voltage characteristics of the LED are displayed again for different infrared irradiation conditions including the low-temperature dark current and the current due to thermal background radiation only. The dark current was measured with the diode enclosed totally by a metal shield and immersed in liquid helium. Thermal background radiation is due to 300-K radiation accepted by the diode through the infrared transparent window of the cyrostat. The current resulting from thermal background radiation is about five orders of magnitude larger than the dark current demonstrating the pertinent high sensitivity of the LED. In all cases the current voltage characteristics have an Ohmic regime, i.e., $I \propto V$ at low voltages, followed by a square law region, $I \propto V^2$. Increasing the voltage further up to a critical threshold the current grows steeply by 10 orders of magnitude. This is indicated by the broken line in the dark current curve of Fig.

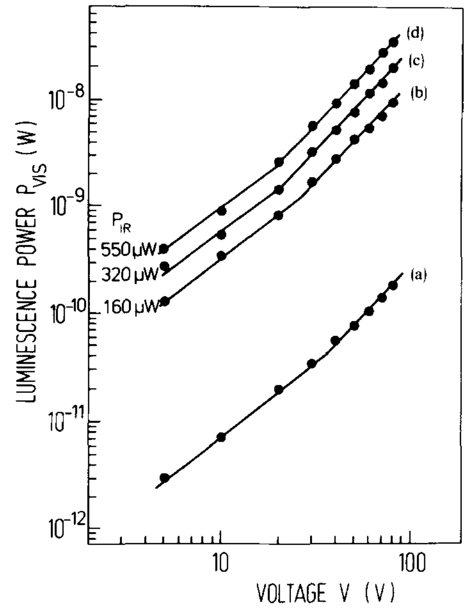

FIG. 1. Visible emission power P_{vis} as a function of forward bias voltage at 4.2 K for (a) thermal background radiation, (b)–(d) various infrared power levels at 10.6 μm as indicated.

2. These properties of the current voltage characteristics are well described by the theory of Ashley and Milnes concerning double injection into deep impurity levels.[10] At low temperatures GaP LED's behave like p-i-n structures containing partially occupied deep recombination centers which preferentially capture one type of carrier. Bhargava has identified oxygen contamination acting as deep recombination centers in GaP LED's.[11] The presence of oxygen in our samples was proved by observing the oxygen-zinc pair recombination fluorescence. At low voltages the current flow due to carrier injection through the contacts is blocked because electrons

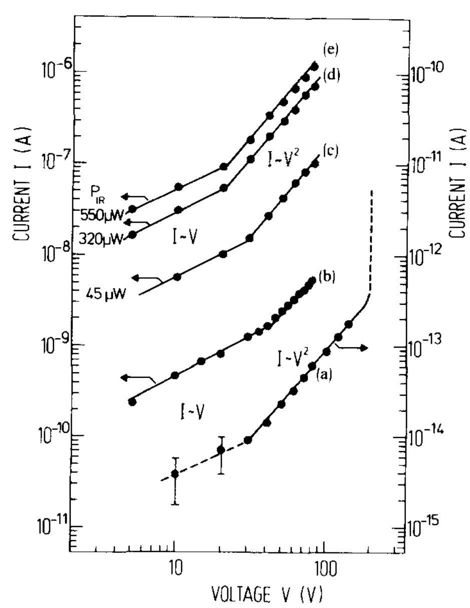

FIG. 2. Forward bias current-voltage characteristics at 4.2 K for various irradiation conditions: (a) dark current, (b) current due to thermal background radiation, (c)–(e) current due to intentional irradiation at 10.6-μm wavelength of different power levels as indicated.

and holes are trapped in the partially filled centers building up a negative and a positive space-charge barrier in the vicinity of the cathode and anode, respectively. At the threshold voltage injected carriers gain sufficient energy to cross the potential barriers and double injection breakdown occurs transforming the semi-insulating sample into a conducting state. The current below the threshold is solely controlled by the free-electron concentration because O is a deep donor whose capture cross section is larger for electrons than for holes. For the Ohmic part of the characteristics the current is carried by infrared excited electrons because thermal excitation may be ignored at helium temperature. The free electrons must be produced close to the cathode where the deep donors are fully occupied by injected electrons and thus the distribution function is shifted up in energy providing a finite occupation of shallow donors. In the square law section of the characteristic the current is mainly due to injected holes whereas injected electrons are further trapped in the deep donors. Hole injection is enabled because the positive space charge at the anode is reduced by recombination with infrared excited electrons. Thus the current is recombination limited and its magnitude is again determined by the infrared induced free-electron concentration.[10]

In the square law part of the characteristic P_{vis} is found to be proportional to V^2 exactly like the current I (see Fig. 1). Thus $P_{vis} \propto I$ showing that the internal LED quantum efficiency is constant in this voltage range. In the Ohmic regime, however, P_{vis} depends on the voltage as V^α with $\alpha = 1.3$. Therefore, the LED quantum efficiency must vary with voltage like $V^{\alpha - 1} = V^{0.3}$. This behavior might be attributed to the fact that in this voltage range the transit time of holes is smaller than their lifetime. With rising voltage an increasing number of injected holes may recombine radiatively with infrared excited electrons.

The detectivity of the LED up-converter will be discussed for 80 V, the largest bias voltage below breakdown permitting stable operating of the device. The up-conversion quantum efficiency is defined by $\eta = (P_{vis}\lambda_{vis})/(P_{ir}\lambda_{ir})$. Setting $\lambda_{ir} = 10.6\,\mu$m and $\lambda_{vis} = 0.55\,\mu$m, $\eta = 3.4\times 10^{-6}$ was determined. The visible luminescence could readily be observed by the unaided eye at an infrared incident power on the diode of about $10\,\mu$W. Without intentional infrared irradiation the visible emission power due to thermal background radiation is $P^b_{vis} = 1.5\times 10^{-10}$ W (see Fig. 2). This radiation is the dominant noise source for photomultiplier detection. Thus the detectivity of the LED up-converter is background limited. The minimum detectable power P^{min}_{ir} may be estimated by setting $P^{min}_{ir} = (hc/\lambda_{ir})(\Delta i/e\beta\eta)$, where hc/λ_{ir} is infrared photon energy, Δi is the photomultiplier current noise due to P^b_{vis}, and β is a factor taking into account the fraction of visible photons converted into photoelectrons. Assuming an optical arrangement gathering 10% of the LED emission and taking into account the photomultiplier quantum efficiency of typically 10%, i.e., $\beta = 10^{-2}$, the noise equivalent power $\mathrm{NEP} = P^{min}_{ir}/(\Delta f)^{1/2}$ is found to be $\mathrm{NEP} = 1.6\times 10^{-9}\ \mathrm{W/Hz}^{1/2}$, where Δf is electronic bandwidth of detection.

The speed of the GaP LED up-converter emitting green light is determined by the lifetime of excitons bound to nitrogen and nitrogen complexes.[12] At liquid helium temperature the decay time of the green luminescence is of the order of 10 ns. The time constant of the detection device is not limited by the high resistance of the sample as it is usually the case for low-temperature extrinsic photoconductors. This was experimentally verified by observing temporally well resolved pulses of a Q-switched CO_2 laser. The visible luminescence followed the laser pulses instantaneously giving an upper limit of 25 ns for the detection time constant.

In conclusion, we have demonstrated that commercially available GaP LED's are well suited for detection and up-conversion of infrared radiation in a broad spectral range without limitations of resonant transitions. The observed quantum efficiency compares quite favorably with nonlinear optics up-converters in cw mode of operation.[1] The quantum efficiency could be improved by using diodes prepared on higher doped n-conducting substrates in order to reduce the infrared absorption length. By this the photon conversion efficiency could approach the internal LED quantum efficiency being of the order of 10^{-2}. Furthermore, a very simple infrared image converter may easily be built by employing a planar diode of appropriate size. Electrodes could be attached at the top and bottom of the wafer by alloying a grid of thin metal strips.

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