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Photo-n-p Junctions in ZnTe

Abstract: We have demonstrated ZnTe devices with efficient (about 1%) light emission at 77 °K in which the injection mechanism is a forward-biased photo-n–p junction. In one, Al and Cd are diffused into highly p-type ZnTe:P to produce an Al-doped region 70 μm deep with a 20 μm surface layer of average composition $Zn_{0.6}Cd_{0.4}Te$. Light emission (575 nm) is observed for 2.5 V. Similar results are obtained when Al alone is diffused in from an evaporated layer to a depth of about 50 μm. This latter device was earlier thought to operate by avalanche injection. Both structures with In contacts to the Al layer give open-circuit photovoltages of over 1.8 V at 77 °K. The all-ZnTe device, however, requires over 7 V to sustain light emission. While it is possible that efficient ZnTe devices made by vapor diffusing the Al are avalanche injection structures, efficient avalanche injection in a II-VI device has yet to be conclusively demonstrated.

Introduction

Efficient injection luminescence at room temperature in wide-gap II-VI compounds has been a frustratingly elusive goal. Electroluminescent p–n junctions have been prepared in CdTe,[1] (Zn,Cd)Te,[2] Zn(Se,Te),[3] and (Mg,Cd)Te,[4] all of which operate efficiently in the neighborhood of or below 77 °K. Self-compensation effects and other factors prevent the preparation of even moderately conducting p-type ZnSe, CdS and ZnO, or n-type ZnTe. These same factors limit the doping levels that one can obtain in junctions of p-type CdTe,[1] n-type (Zn,Cd)Te,[2] and both n- and p-type Zn(Se,Te).[3] In the latter system, in fact, only the photoconductivity of the two sides of the junction, sustained by the electroluminescence, permits the passage of any current at all.[3] At room temperature these limited doping levels, among other things, do not permit a high enough injection current and recombination density to overcome the effect of competing non-radiative recombination processes.

Avalanche injection, efficiently operative in producing luminescence in some GaAs p-type structures,[5] is free of the doping limitations which hamper the effectiveness of II-VI p–n junctions and could well permit the high recombination density required to overwhelm non-radiative processes at room temperature. We previously reported[6] a ZnTe structure in which the efficient emission of 540 and 575 nm radiation was attributed to avalanche injection. Impact ionization of electrons was considered to occur in a narrow, non-photoconducting region between a Li-doped bulk region (10^{17} holes-cm^{-3}) and a photoconducting, Al-diffused region that was insulating in the dark. Such devices, when "turned on" with light or voltage pulses, gave measured quantum efficiencies at 77 °K of over one percent at sustaining voltages of around 10 V.

In this paper we show that the light-emitting mechanism in both this and a new, improved device is that of a forward-biased p–n junction in which the conductivity of the n-side of the junction is sustained by photocarriers. The photocarriers are generated by the absorption of light emitted at the junction just as has been described for both sides of the junction in efficient Zn(Se,Te) diodes.[4]

Experiments

- *All-ZnTe devices*

Two techniques, which differed only in the source of the Al,[7] were used for diffusing Al into the Li-doped ZnTe substrate. In the first type a layer of Al was evaporated onto the substrate and fired for time intervals of from 5 min to 1 h at temperatures of 700 to 800 °C in a Zn atmosphere maintained by a Zn reservoir at the same temperature. The Al source in the second type was Al metal with a very small quantity of Te in the reservoir. Both procedures yield efficient light-emitting structures with similar switching behavior in their *I-V* characteristics, but there are marked differences in other properties which indicate that the injection mechanisms may be quite different.

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Both types of Al diffusion produce surface regions extending about 30 μm into the crystal which are insulating in the dark, but conducting when illuminated. The photoconductivity leads to the switching behavior shown in Fig. 1 for devices made by diffusion from the evaporated Al layer.[8] The onset of light emission when the device is in the high-voltage, low-current regime "switches" the device to the low-voltage, high-current regime with efficient light emission at 77 °K. The time required to switch is greater than 100 μsec, varies inversely with the value of the current in the high-voltage regime, and may be associated with a trap-filling process in the photoconducting Al-diffused region. In the case of diffusion from the evaporated Al, rather high photovoltages are observed at 77 °K, usually larger than half the band gap of ZnTe and up to 1.8 V. Increased light intensity often leads to decreased open-circuit voltages, but increased short-circuit currents. This behavior is consistent with more than one photovoltaic barrier, the origin of which is made clear by experiments described below. For diffusion from the vapor, only low photovoltages were observed, always less than half the ZnTe band gap and usually of the order of 0.3 V, a value appropriate to a metal-semiconductor contact. The high photovoltages observed for evaporated-Al diffusion were also originally attributed to the metal-ZnTe:Al contact.[7] Measurement of the capacitance C of a strongly illuminated diode (both types) as a function of reverse bias showed that C^{-2} varied linearly with V. This result was originally considered to be consistent with the metal-semiconductor contact barrier.

Measurements of conductance and capacitance of externally illuminated structures as a function of the frequency (5 to 500 kHz) at 77 °K were generally consistent with two narrow (2 to 5 μm) regions of high resistance (10^6 to 10^9 Ω-cm).[7] For both types of Al diffusion the photoconductivity of the Al-diffused region was as much as a factor of 10 lower at room temperature than at 77 °K. This temperature dependence of the photoconductivity of the Al-diffused region contrasted markedly with that of ZnTe doped with Al from the melt. In the latter case the photoconductivity was higher at room temperature than at 77 °K and was definitely p-type from photo-Hall data. Unequivocal photo-Hall measurements on the diffused regions were prevented by contact problems and by the necessity for lapping off all but the region in question.

On the basis of the observations recounted above, two different operating mechanisms seemed equally consistent. (1) Avalanche injection, which is what we expected to see in these structures, might possibly result from impact ionization occurring in a thin, non-photoconducting region at the interface between the bulk crystal and the diffusion boundary. The electrons produced by this breakdown are swept into the ZnTe:Li region (where they recombine radiatively at a wavelength of about 540 nm). The diffused region is considered to be photoconducting, p-type, and the most desirable type of contact to it, an ohmic one. (2) The alternative model was that electrons are injected at the metal-ZnTe:Al contact. A space-charge-limited current of these electrons passes through the Al-diffused region without recombination into the ZnTe:Li at the diffusion boundary where radiative recombination occurs. Models of this behavior proposed for Si suggested that the p-type photoconductivity of the diffused region enabled a larger space-charge-limited current of electrons to be injected than would occur otherwise.[9] The photoholes were considered to migrate to the electron-injecting contact and to reduce the barrier for further injection of electrons. The lower the barrier voltage and the higher the fraction of the voltage falling across the Al-diffused region, the greater is the possible space-charge-limited current of electrons. For this mechanism the most desirable contact would be an injecting one.

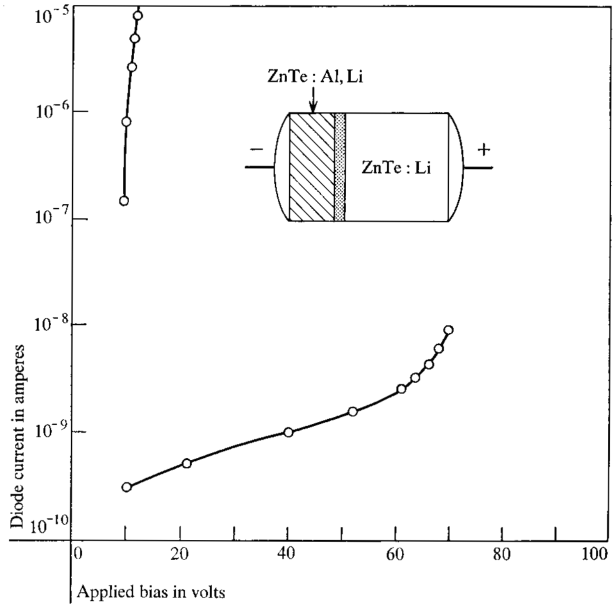


Figure 1 A typical dc current-voltage characteristic at 77° K of an evaporated, Al-diffused ZnTe device showing both the high-voltage, low-current regime and the low-voltage, high-current regime. In the latter state a substantial portion of the applied voltage falls across the darkly shaded region (see diagram of device in insert), while in the former the high applied voltage falls across the entire Al-diffused region.

- *Devices containing (Zn,Cd)Te*

To produce a definitely injecting contact to the supposedly p-type, photoconducting, Al-diffused layer, Cd (in a reservoir at 800 °C), as well as Al (from an evaporated layer), was diffused into p-doped ZnTe at 850 °C. While for a typical case the total width of the insulating region thus produced was about 70 μm, about 20 μm of the surface was converted to an average composition of $Zn_{0.6}Cd_{0.4}Te$. Earlier work indicated that a solid solution of this composition could be made reasonably n-type when doped with

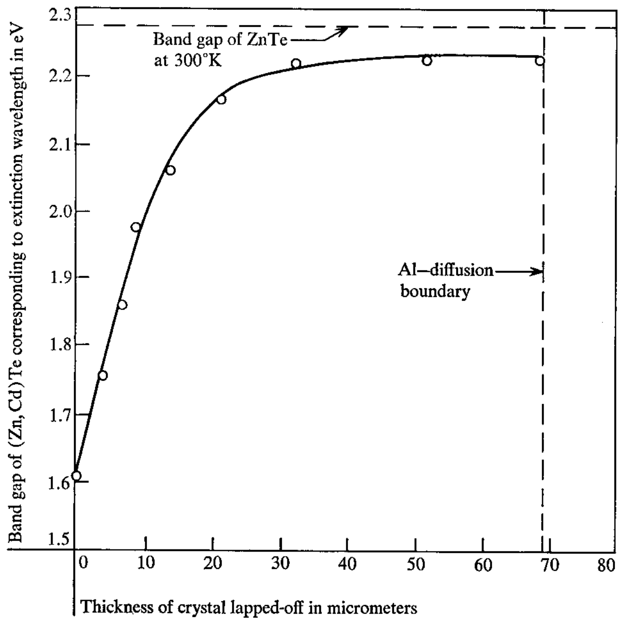


Figure 2 A plot of the estimated band gap of (Al,Cd)-diffused ZnTe device as a function of distance in from the diffused surface. A gap of 1.9 eV corresponds roughly to $Zn_{0.6}Cd_{0.4}Te$ at 300 °K.

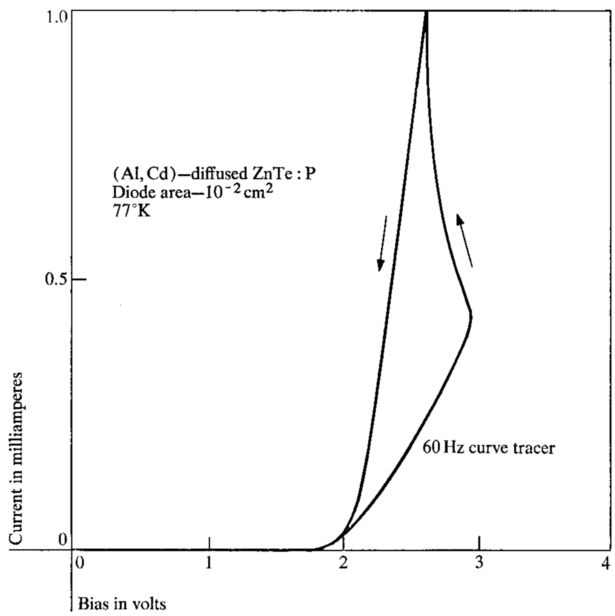
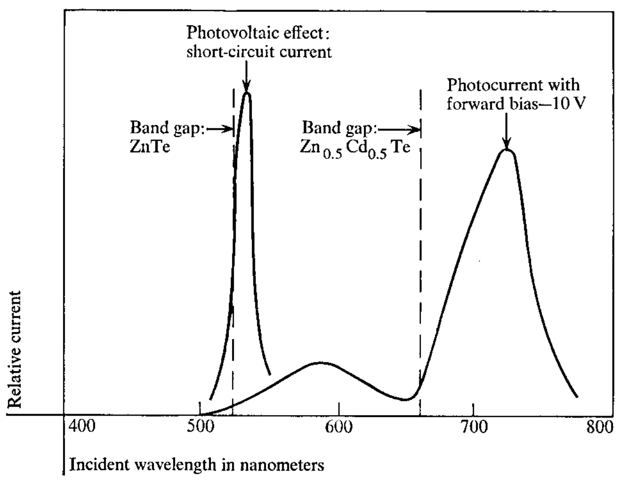


Figure 4 Current-voltage plot of the operation of an (Al,Cd)-diffused ZnTe device with an In contact to the diffused region. The 2 V intercept of the "return" trace is clearly that of a p–n junction in ZnTe. The hysteresis is caused by the necessity for light from the junction to sustain the conductivity of the n side.

Figure 3 A plot of the photovoltaic short-circuit current and the forward-biased photocurrent of an (Al,Cd)-diffused ZnTe structure as a function of wavelength. The photovoltaic response is that of a junction in ZnTe while the forward-biased photocurrent shows a large response at wavelengths characteristic of (Zn,Cd)Te.



Al.[10] The composition of the (Zn,Cd)Te alloy region at the surface was estimated by observing the wavelength for sharp extinction of transmitted light after measured thicknesses of the surface were lapped off. A monochromator was used to select the wavelength of the light transmitted through the crystal and the extinction was observed through a microscope (equipped with an inverter to extend the observations into the infrared). The results of these observations are shown in Fig. 2.

Electron injection from n-$Zn_{0.6}Cd_{0.4}Te$ into the insulating and supposedly photoconducting, p-type ZnTe would be greatly improved and possibly less dependent on the photoconductivity if the contact-injection, space-charge-limited-current model were correct. Further, if the photovoltages observed on the all-ZnTe devices have their origin at the metal to Al-diffused-region contact, and if the Cd-diffused structures simply place n-$Zn_{0.6}Cd_{0.4}Te$ in the role of the metal, then the wavelength dependence of the photovoltaic effect should be characteristic of a Schottky junction in (Zn,Cd)Te and not ZnTe. That this result was not the case is shown in Fig. 3. The wavelength dependence of the short-circuit current is very nearly that of ZnTe. Only when the (Zn,Cd)Te structure is forward biased is there photoconductive response prominent in the wavelength region characteristic of $Zn_{0.5}Cd_{0.5}Te$, as shown also in Fig. 3. In fact, with Au contacts to both ends of the device, adding red light to green light already shining on the junction lowers the open-circuit voltage by 0.2 V. These measurements strongly indicate that the Al-doped region is n-type in the light so that there is a p–n junction at the Al-diffusion boundary and a blocking, metal to n-type-semiconductor contact to the (Al,Cd)-diffused region. Changing this latter contact from Au to In, which should make a better ohmic contact to the photo-n-type Al region, produced the predicted improvements: much lower voltage thresholds for forward current and for light emission. Figure 4 shows the *I-V* characteristics of a typical (Al,Cd)-diffused device at 60 Hz. Extrapolation of the linear portion of the hysteresis loop to zero current yields a voltage intercept of slightly over 2 V. The quantum efficiency of the emission, shown spectrally in Fig. 5, is about 1% as measured with an integrating sphere type of apparatus at 77 °K.[11]

To determine unequivocally the position of the junction responsible for the photovoltaic effect and the dominant photoconducting regions, the device was scanned with a slit of light less than 5 μm wide. Light from a microscope illuminator was focused onto a 50 μm slit, the image of which was then projected through a microscopic objective (20×) onto the side of the junction device. The latter, mounted on a transistor header, could be positioned with micrometer adjustments in three directions and viewed in a stereomicroscope. Observations were made both at room temperature and at 77 °K in an uncoated glass dewar flask containing liquid nitrogen. Figure 6 shows the results of these measurements which definitely locate the junction responsible for the photovoltaic effect at the Al-diffusion boundary. Only when the system is forward biased is there a photoresponse detectable at the negative contact [the contact to the (Al,Cd)-diffused region]. Also shown in Fig. 6, correlated with photoscan measurements, are the location of the contact, the point of light emission, the average composition of the host lattice of the several regions of the device, and the average carrier concentrations and type in these regions. The average alloy composition[10] has been inferred from data such as that shown in Fig. 2 and the carrier concentrations were extracted from measurements of capacitance and conductance as a function of frequency at 77 °K for a strongly illuminated device. In comparison with the all-ZnTe device described above, diffusing in Cd and using In as a contact has lowered the resistance of both the contact region and that of the photoconducting Al-diffused region, allowing the efficient operation of the device at much lower voltages. A 75 μm diffusion of Cd and Al which was subsequently lapped to a 50 μm thickness allowed Hall-effect measurements down to 77 °K. About 4×10^{14} electrons-cm^{-3} were obtained for the illuminated specimen between 77 and 300 °K, with little significant variation with temperature. The photocarriers produced in the (Al,Cd)-diffused region are thus unequivocally identified as electrons.

Other measurements made on the (Al,Cd)-diffused ZnTe device further substantiate the photo-n–p junction character. Measurements of the diode capacitance as a function of reverse bias of the illuminated structure are shown in Fig. 7. In this case C^{-3} is linear with V, indicating a space-charge gradient of 1.5×10^{20} cm^{-4} and an estimate of $N_D - N_A$ on the photo-n side of 10^{16} cm^{-3}. This latter value is substantially higher than the average photocarrier density deduced from the capacitance- and conductance-vs.-frequency measurements (about 10^{14} cm^{-3}). The donors

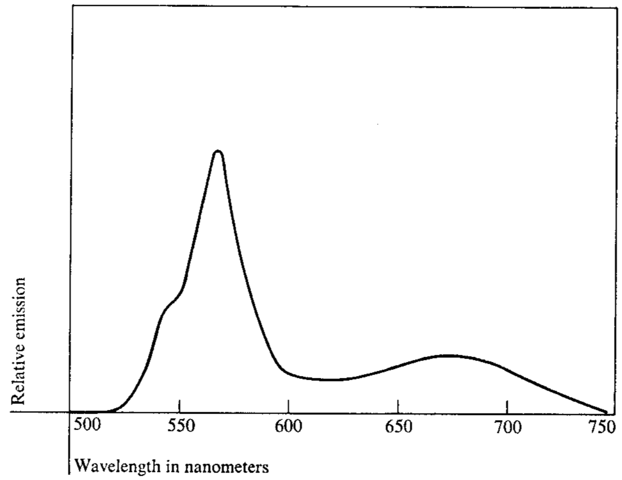
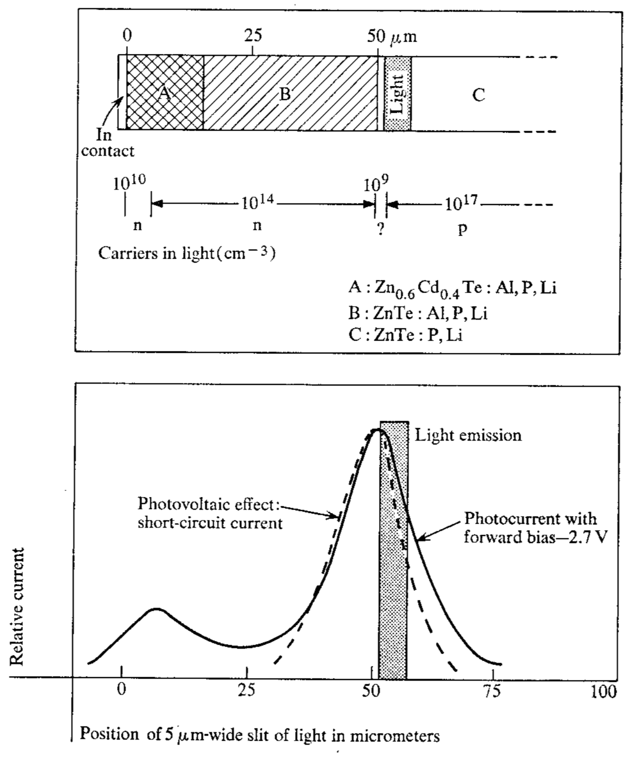


Figure 5 Wavelength spectrum of the electroluminescence from an (Al,Cd)-diffused ZnTe device (77 °K). The emission-band peaking at 680 nm is characteristic of ZnTe doped with P.

Figure 6 The experimental results of scanning an (Al,Cd)-diffused ZnTe device with a 5 μm-wide slit of light. The bottom diagram shows both the photovoltaic short-circuit current and the forward-biased photocurrent as a function of the position of the slit on the device. The top diagram shows on the same scale the position of the In contact, the (Zn,Cd)Te:Al region, the extent of the Al diffusion, and the point of light emission at 77 °K. The top diagram also shows the approximate concentration of carriers present in the different regions consistent with the measurements of capacitance and conductance as functions of frequency.



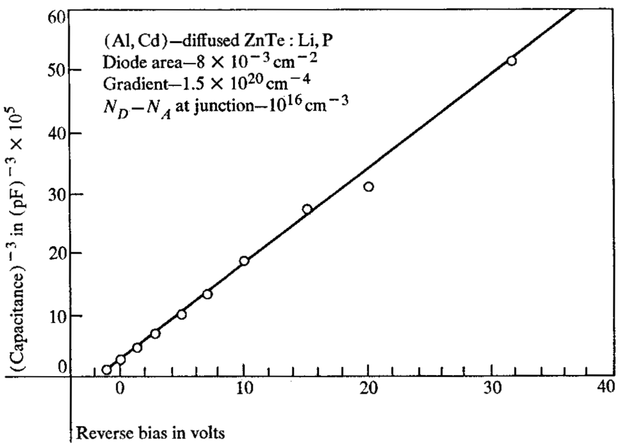
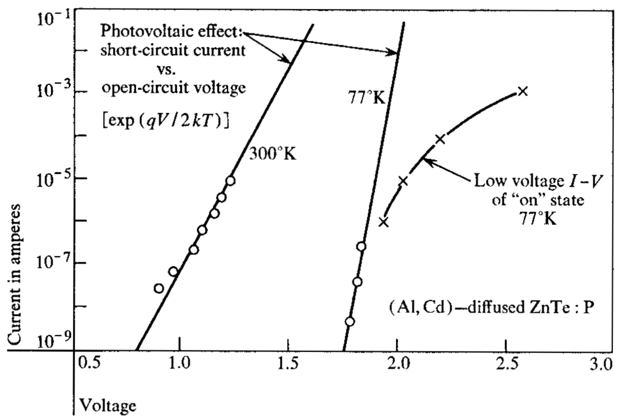


Figure 7 Reverse-biased capacitance measurements on an (Al,Cd)-diffused ZnTe device.

Figure 8 The photovoltaic effect measurements in the (Al,Cd)-diffused ZnTe device at 77 and 300 °K. The log of the short-circuit current is plotted against the open-circuit voltage for different levels of illumination. The results are consistent with space-charge-region recombination-current and the actual *I-V* characteristic at 77 °K (also shown) which is largely dominated by bulk and contact resistance at higher currents.



present in greatest concentration are evidently rather deep. (For diodes yielding lower estimated values of $N_D - N_A$, it has been observed that C^{-2} rather than C^{-3} is linear with V. The linear variation of $N_D - N_A$ evidently does not persist for more than a few micrometers into the photo-n region; a junction which is already this wide at no bias will appear abrupt rather than graded in the behavior of its capacitance with reverse bias. Even in lightly doped materials one cannot interpret an abrupt junction as a metal-semiconductor contact rather than a p–n junction.)

Photovoltaic measurements of the short-circuit current as a function of the open-circuit voltage for different levels of illumination are also consistent with the p–n junction character of the device. These quantities would have the same relation as that of current-to-voltage appearing across the junction.[1] Figure 8 shows this relation at both 77 and 300 °K. The short-circuit current varies with the open-circuit voltage as $\exp(qV/2kT)$, indicating a junction, as one would expect, governed by recombination in the space-charge region.[12] At 77 °K the low voltage *I-V* of the operating device at 60 Hz is seen to approach the photovoltaic data with decreasing current. At high current levels the device is largely dominated by various bulk and contact resistances, rather than by the junction.

• *Comparison of all-ZnTe devices with those containing (Zn,Cd)Te*

The electroluminescent devices prepared by diffusing the Al from an evaporated layer are very similar in characteristics to the photo-n–p junctions with (Zn,Cd)Te contacts. They probably also operate with the same mechanism. The light-scan experiment (see Fig. 6) gave the same result for these all-ZnTe devices, locating the source of the high photovoltage at the Al-diffusion boundary and near the point of light emission. The chief differences lie in the decreased contact resistance obtained with In on the (Zn,Cd)Te layer and in the increased photoconductivity of the Al-diffused region in the presence of Cd, as mentioned above. Another interesting difference is that while P-doped ZnTe substrates rarely produce efficient devices without Cd, only P- or (P,Li)-doped ZnTe crystals work when both Cd and Al are diffused in. The origin of this difference apparently lies in the different wavelength response of the two types of devices for the excitation and quenching of the photoconductivity of the Al-diffused regions. This wavelength dependence of the effect of external radiation on the forward current is shown for the two types of devices in Fig. 9.[8] The spectral dependence of the electroluminescent emission at 77 °K for the (Al,Cd)-diffused device [ZnTe:(P,Li) substrate] is shown in Fig. 10.[8] The P-doped structures contain an emission peak in their electroluminescence at 680 nm, while the structures containing only Li in the substrate do not. This wavelength, as seen in Fig. 9, strongly excites photocurrent in the (Al, Cd)-diffused devices, but quenches the forward current in those not containing Cd. The presence of P thus inhibits the stable operation of the all-ZnTe devices, but is required to promote stability when a (Zn-Cd)Te layer is present at the contact because of the 680 nm emission associated with P. The exact nature of the center actually responsible for this emission has not been determined. Studies of the effect of various thermal conditions on the green luminescence of melt-grown ZnTe:P have been made and will be reported.

As mentioned earlier, electroluminescent ZnTe devices made by diffusing Al from the vapor phase and from an evaporated layer have markedly different characteristics in several respects. Significantly higher sustaining voltages are required and these were never observed to be lower than 20 V for the vapor-diffused structures. Photovoltages, when observed, were always much less than half the ZnTe band

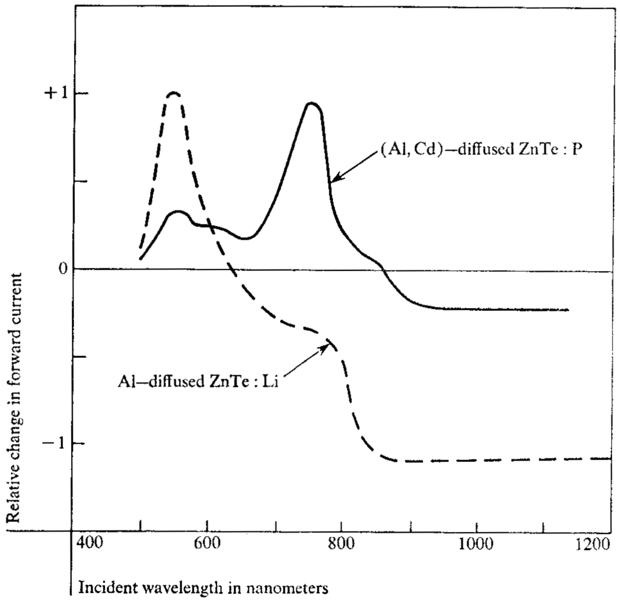


Figure 9 The wavelength dependence of the effect of external light on the forward current of both Al-diffused and (Al,Cd)-diffused ZnTe devices at 77 °K.

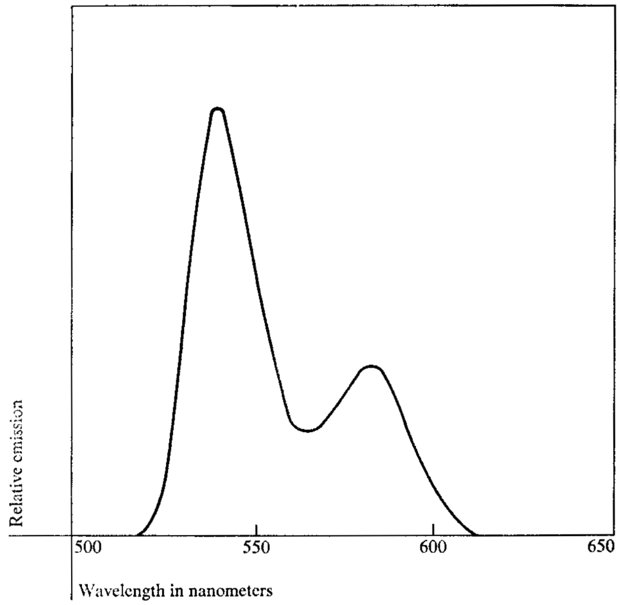
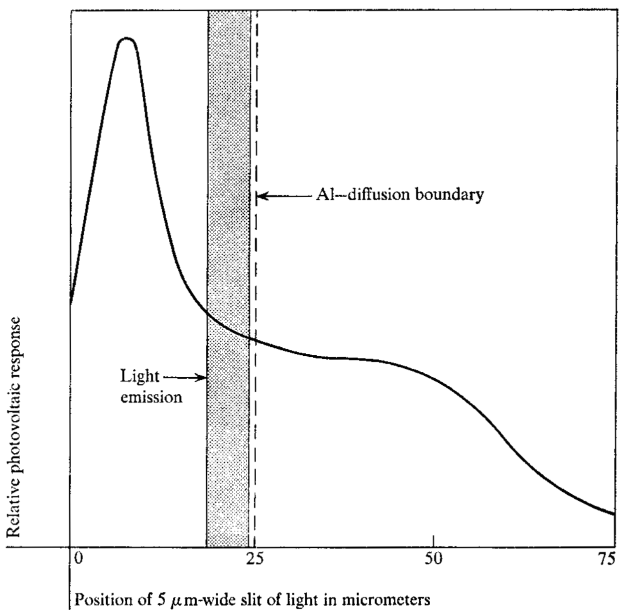


Figure 10 The wavelength spectrum of the electroluminescence of an Al-diffused ZnTe device (77 °K). Compare with Fig. 5. There is no red emission from ZnTe doped with Li.

gap at 77 °K (2.36 eV) and were usually of the order of 0.3 V. The light-scan experiment with these structures indicated a maximum photovoltaic response at 77 °K much nearer to the contact to the Al-diffused region than to the diffusion boundary, as shown in Fig. 11 (compare with Fig. 6). This result indicates that the Al-diffused region is p-type (from the sign of the contact photovoltage) and that the light-producing mechanism in these devices may be either avalanche injection at a non-photoconducting interface between the Al-diffusion and the bulk crystal or, more likely, injection of electrons at the metal contact and a space-charge-limited electron-current in the Al-diffused region, followed by recombination of these electrons near the diffusion boundary.

Table 1 presents a summary of the current status of the visible-light-emitting effectiveness of the various II-VI p–n homojunction systems that have been studied and reported to date (at 77 °K where thermal quenching does not dominate the recombination processes). The last column gives the relative effect on the human eye for a given input power. The characteristics tabulated for ZnTe are those of the (Zn,Cd)Te-contact device described in this report.

Figure 11 Experimental results of scanning a vapor-Al-diffueds ZnTe device with a 5 μm slit of light. Unlike devices made from diffusions from evaporated layers of Al, with and without Cd, the greatest photovoltaic response occurs nearer the contact than the diffusion boundary.



Conclusions

All of the experimental results described above are unequivocally consistent with a photo-n–p junction in the (Al,Cd)-diffused ZnTe:P structures. Doping (Zn,Cd)Te with Al diffused in from an evaporated layer apparently introduces enough donors to convert the crystal to insulating n-type, and allows predominantly n-type photoconductivity. This is apparently also true for devices made of ZnTe without Cd since, in this case too, a photovoltage approaching the band gap of ZnTe is produced at the Al-diffusion boundary by external illumination at 77 °K. Only in the case of electroluminescent ZnTe devices produced by diffusion of Al from the vapor into ZnTe:Li is a different mechanism likely. The latter system probably involves

Table 1 Visual effectiveness of II-VI p–n homojunctions at 77 °K.

Material	*Peak wavelength of emission* (nm)	*Voltage at 0.1 A-cm^{-2}* (V)	*Quantum efficiency* (%)	*Power efficiency* (%)	*Visible output* (lm/W)
CdTe[a]	850	1.5	12	12	10^{-5}
(Zn,Cd)Te[b]	700	1.8	6	6	0.15
(Mg,Cd)Te[c]	680	2.0	1 (?)	1 (?)	0.09
Zn(Se,Te)[d]	620	50.0	18 (70 °K)	1	2.0
ZnTe	540, 575	3.0	1	0.8	5.0

[a] G. Mandel and F. Morehead, *Appl. Phys. Letters* **4**, 142 (1964).
[b] F. Morehead and G. Mandel, *Appl. Phys. Letters* **5**, 53 (1964).
[c] R. Yamamoto, M. Inoue, K. Itoh, and T. Shitaya, *Japan. J. Appl. Phys.* **6**, 537 (1967).
[d] M. Aven and W. Garwacki, *J. Appl. Phys.* **38**, 2302 (1967).

electron injection from the metal-semiconductor contact rather than the avalanche injection that was the original object of these investigations. Like all of the other p–n junctions produced with such arduous effort in only a few II-VI systems, efficient electroluminescence is observed only at low temperatures; at this point it appears unlikely that preparative procedures exist that will yield a sufficiently heavily doped p–n junction in any wide-gap II-VI compound to permit efficient injection luminescence at room temperature (with the possible exception of yet to be developed procedures involving ion implantation[13]). For example, 10^{16} cm^{-3} is apparently too light a carrier concentration on the p-side for CdTe to give efficient electroluminescence at 300 °K[1]; in the cases of ZnTe and Zn(Se,Te)[3] it is unlikely that the carrier concentration on the photoconducting sides of the p–n junctions is even 10^{15} cm^{-3}. A high density of recombining electrons and holes is required to overwhelm thermal quenching at higher temperatures and simply cannot be achieved in lightly doped p–n junctions. Avalanche injection in wide-gap II-VI's may be capable of producing the required high recombination density, but a good avalanche injection structure has yet to be made in II-VI's.

Acknowledgments

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References

1. G. Mandel and F. Morehead, *Appl. Phys. Letters* **4**, 142 (1964); F. Morehead, *J. Appl. Phys.* **37**, 3487 (1966).
2. F. Morehead and G. Mandel, *Appl. Phys. Letters* **5**, 53 (1964).
3. M. Aven and W. Garwacki, *J. Appl. Phys.* **38**, 2302 (1967).
4. R. Yamamoto, M. Inoue, K. Itoh, and T. Shitaya, *Japan. J. Appl. Phys.* **6**, 537 (1967).
5. K. Weiser and J. F. Woods, *Appl. Phys. Letters* **7**, 225 (1965).
6. B. L. Crowder, F. Morehead, and P. R. Wagner, *Appl. Phys. Letters* **8**, 148 (1966).
7. M. I. Nathan et al., "Research on Injection Luminescence in Wide Gap Semiconductors," *Final Technical Report, June 27, 1966 to June 26, 1967, Contract DA-44-009-AMC-1674(X)*, U. S. Army Engineers Research and Development Laboratories, Fort Belvoir, Virginia.
8. F. Morehead and B. L. Crowder, *Proceedings of the International Conference on Luminescence*, Budapest, 1966.
9. K. L. Ashley and A. G. Milnes, *J. Appl. Phys.* **35**, 369 (1964); A. Many and G. Rakavy, *Phys. Rev.* **126**, 1980 (1962).
10. F. Morehead and G. Mandel, *Phys. Rev.* **137**, A294 (1965).
11. G. Cheroff, C. Lanza, and S. Triebwasser, *Rev. Sci. Instr.* **34**, 1138 (1963).
12. C. Sah, R. N. Noyce, and W. Shockley, *Proc. IRE* **45**, 1228 (1957).
13. J. P. Donnelly, A. G. Foyt, E. D. Hinkley, W. T. Lindley, and J. O. Dimmock, *Appl. Phys. Letters* **12**, 303 (1968).

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