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# Donor-Acceptor Pair Recombination Involving the First Excited State of a Donor in GaAs

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The photoluminescence spectrum of epitaxially grown *n*-type GaAs in the vicinity of the band-gap energy shows peaks whose temperature dependence and energy separations suggest the existence of pair recombination radiation involving the ground state and first excited state of a donor. Calculation based on this model and the use of hydrogenic wave functions for the ground state and the first excited state of the donor indicate that the recombination radiation arises from donor-acceptor pairs whose most probable separation is about 420 Å. This number is in reasonable agreement with the expectation based on the measured room-temperature conductivity of the sample.

## I. INTRODUCTION

DONOR-ACCEPTOR pair recombination has been investigated in many semiconductors.[1,2] However, pair recombination involving an excited state of a donor or an acceptor has not yet been observed. This is somewhat surprising in view of the fact that, because of the larger radius of an excited-state wave function, the transition from an excited state of a donor (say) to an acceptor at a distance of the order of the Bohr radius of electrons in the solid should have larger probability than that from the ground state of the donor to the acceptor.[3]

We report here experimental results on the photoluminescence spectrum of *n*-type GaAs in the range from 8250 to 8450 Å. The observed structure and temperature dependence of the spectrum can be interpreted quantitatively in terms of transitions from the ground state and the first excited state of a shallow donor to acceptors in GaAs. Although evidence for the existence of the donor excited states has been found for other semiconductors, we believe this to be the first observation of pair recombination involving an excited state and the first observation of an excited state of an impurity in GaAs. The relative intensities of the spectral lines are discussed, utilizing simple hydrogenic wave functions for the ground state and the first excited state of the shallow donors.

## II. EXPERIMENTAL NOTES

The photoluminescence spectrum of epitaxially grown GaAs was investigated between 10 and 22.5° K, using the technique described previously.[4] The sample was clipped on a copper block in an atmosphere of helium vapor and excited by the 6328-Å radiation from a He-Ne laser. The temperature was measured using a calibrated GaAs diode attached to the copper block. Since the sample was not immersed in a liquid, its temperature was higher than that indicated by the diode. A correction of +5° K was inferred by comparing the data obtained in the above manner with that obtained when the sample was immersed in liquid hydrogen. The correction was assumed to be the same at all temperatures because the thermal conductivity is very nearly constant in this temperature range. All the temperatures reported here are corrected temperatures. Unless otherwise specified, for the experimental results reported below the photon flux was $\sim 10^{21}$ cm$^{-2}$ sec$^{-1}$, which for a penetration depth of $\sim 1\ \mu$ gives a generation rate of $\sim 10^{25}$ cm$^{-3}$ sec$^{-1}$.

## III. EXPERIMENTAL OBSERVATIONS

The photoluminescence spectrum obtained with a high-resolution ($\sim$0.25 meV) spectrometer is shown in Fig. 1. Peak 1 is the usual "exciton" peak[5] and will not be considered further. The twin-peaks 2 are located at the approximate energy where donor-acceptor pair recombination has been observed previously.[6] The previous work did not resolve the two peaks, probably because of larger impurity content in those samples. The qualitative temperature dependence of twin-peaks 3 and twin-peaks 2 is identical; hence, we attribute twin-peaks 3 also to donor-acceptor pair recombination.

Figure 2 shows the behavior of peaks 2a and 2b as the temperature is varied. Note that the intensity of the higher energy peak ($I_{2a}$) increases with temperature while that of the lower energy peak ($I_{2b}$) decreases. Similar behavior has been observed in II–VI compounds,[7] as discussed below.

[1] J. S. Prener and F. E. Williams, Phys. Rev. **101**, 1427 (1956).
[2] D. G. Thomas *et al.*, Phys. Rev. **133**, A269 (1964).
[3] A simple calculation will show that the radiative lifetime for a transition from the ground state of a hydrogenic donor to an acceptor ground state will be shorter than that involving a donor excited state until a certain donor-acceptor separation distance $l$. Here $l$ is $3a_e$, where $a_e$ is the Bohr radius of electron in the solid. For pair separations larger than $l$ the lifetime for the transition involving the first donor excited state and the acceptor ground state becomes shorter than that involving the ground states of both impurities. Further increase of the pair separation makes the lifetime for the transition involving the second donor excited state and the acceptor ground state shorter than those involving the ground and the first excited state of the donor.
[4] R. C. C. Leite *et al.*, Appl. Phys. Letters **5**, 188 (1964).
[5] M. I. Nathan and G. Burns, Phys. Rev. **129**, 125 (1963).
[6] R. C. C. Leite and A. E. DiGiovanni, Phys. Rev. **153**, 841 (1967).
[7] L. S. Pedrotti and D. C. Reynolds, Phys. Rev. **120**, 1664 (1960); K. Colbow, *ibid.* **141**, 742 (1966).

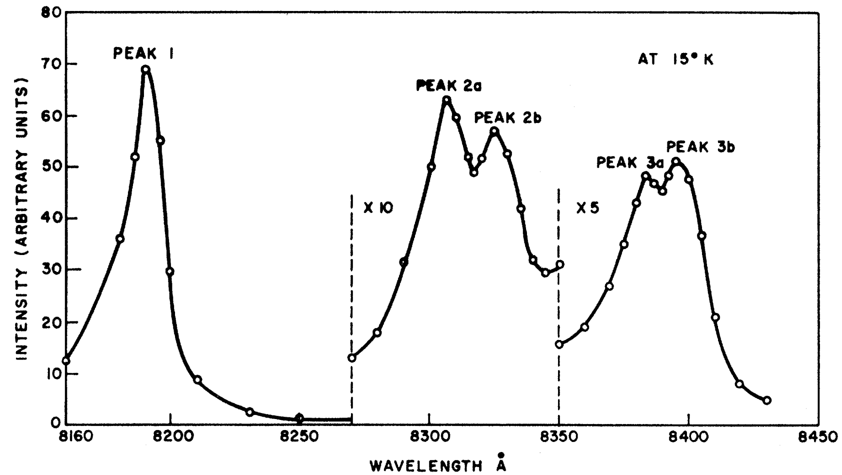


FIG. 1. Photoluminescence spectrum of $n$-type GaAs at 15° K. The points shown are representative points from a continuous recording.

Figure 3 shows a semilog plot of $(I_{2a}/I_{2b})$ versus $1/kT$. Note that it is a straight line with slope equal to 3.4 meV.

It should be mentioned that the spectrum was also measured with the sample under strain. Although the positions of all the peaks shifted by $\sim$50 Å, the separation between the peaks remained unchanged, indicating that strain was not responsible for the observed results.

The photoluminescence intensities of the emission bands were also measured as a function of the excitation light intensity. With the sample immersed in liquid $H_2$, the twin-peaks 2 and 3 began to saturate at photon flux above $\sim 10^{20}$ cm$^{-2}$ sec$^{-1}$. This indicates that the generation rate of excess carriers exceeds the recombination rate possible at the defects responsible for the observed luminescence bands. This observation is consistent with our model but it does not rule out other models. Hence, this will not be discussed further.

## IV. DISCUSSION

We have mentioned that observations similar to Fig. 2 have been reported for II–VI compounds.[7] In these, the lower energy peak (corresponding to our peak 2b) was attributed to donor-acceptor recombination and the higher energy peak (corresponding to our peak 2a), to a free-electron–to–acceptor transition. It is easy to see that such a model could explain the qualitative behavior of Fig. 2. However, it fails to account for the quantitative data of Fig. 3.

The fact that the ratio of intensities of the two lines varies as $\exp(-\Delta E/kT)$ immediately suggests that the ratio of the densities of electrons in the two initial levels is governed by Boltzmann statistics. The ratio of the density of free electrons to that of electrons on the donor $(n/n_d)$ must obey the Fermi statistics in general. It is true that this may be approximated by the Boltzmann statistics when the quasi-Fermi level for electrons *in the presence of the photoexcitation* is several $kT$ below the donor level. However, in our case the intensity of photoexcitation is such that the quasi-Fermi level would be above the donor level for $\tau$ (electron lifetime

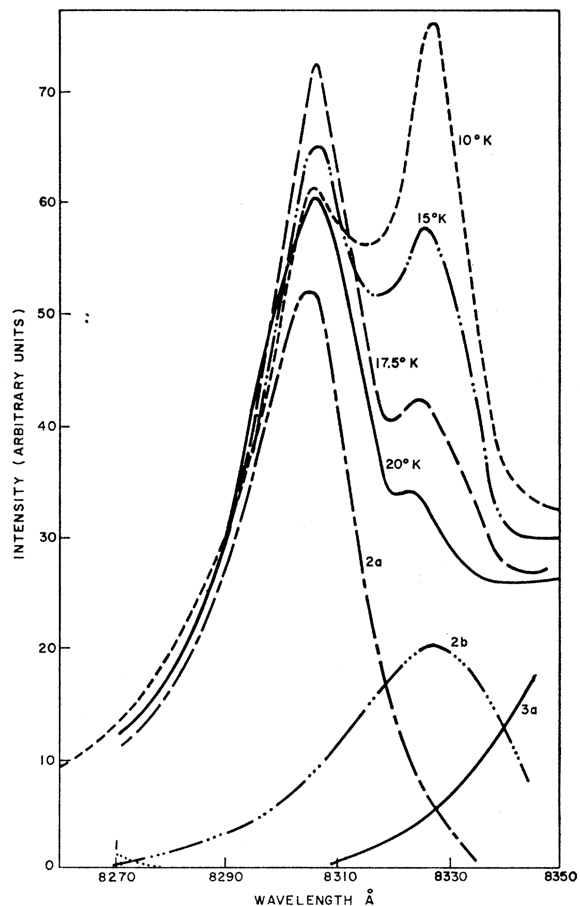


FIG. 2. Evolution of twin-peaks 2 with temperature. The resolution was $\simeq$0.25 meV. As an example of how the ratio $I_{2a}/I_{2b}$ (to be used in Fig. 3) was obtained from the experimental curves, the 20° K curve is shown resolved in its components 1, 2a, 2b, 3a in the figure. Here the numbers 1, 2a, etc., refer to the peaks marked in Fig. 1.

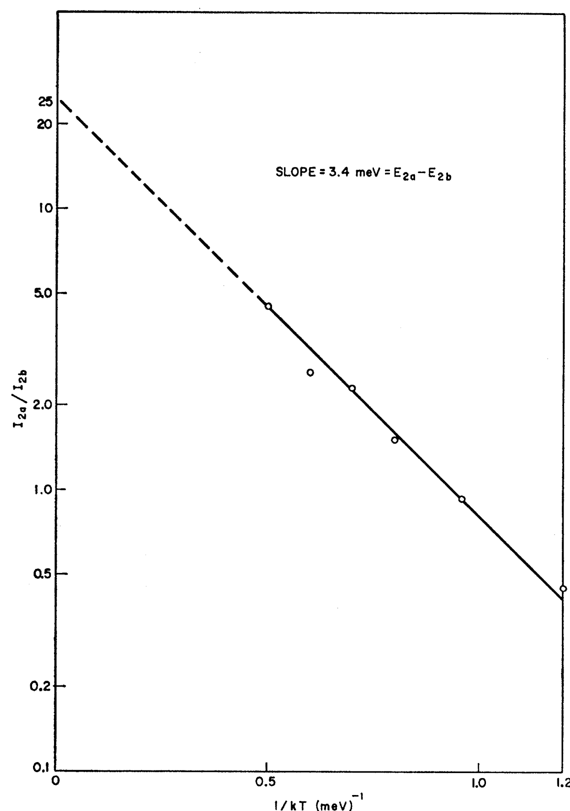


FIG. 3. Semilog plot of the ratio of intensities of twin-peaks 2 versus $1/kT$.

in the conduction band) greater than $10^{-11}$ sec. Since the measured $\tau$ for $n$-type GaAs is usually much longer it would appear that the observed Boltzmann factor cannot be explained if the higher energy peak 2a is attributed to a free-electron–to–acceptor transition. Indeed, for $\tau\sim10^{-10}$ sec and longer, the ratio $(n/n_d)$ would be approximately constant in the temperature range of Fig. 3.

The ratio of occupation densities of any two levels (a and b) in a solid can be a Boltzmann factor, regardless of the position of the quasi-Fermi level, if and only if (i) each level has the same finite number of states and (ii) the two levels are mutually exclusive, i.e., the occupation of a state $a_i$ prevents the occupation of the corresponding state $b_i$ and vice versa. We note that the ground and the first excited states of an impurity in a semiconductor form precisely such a system. For a donor, let $n_x(n_g)$ be the density of electrons in the first excited (ground) state, $\beta_x(\beta_g)$ be the degeneracy of the first excited (ground) state and $|\Delta E_{xg}|$ be the energy difference between the two levels. Then, we must have

$$n_x/n_g=(\beta_x/\beta_g)\exp(-|\Delta E_{xg}|/kT)\cdots \quad (1)$$

*regardless of the position of the quasi-Fermi level.*

In view of this, the following model is proposed to explain our experimental results. The crystal has one shallow donor and two acceptors. At very low temperatures, when only the ground states of the impurities are occupied, the recombination between the donor and the acceptors gives rise to two peaks (peaks 2b and 3b). As the temperature is raised the first excited state of the donor begins to be occupied. (The occupation of the excited states of the acceptors can be neglected because the acceptors are deeper.) Hence peaks should appear at energy $\Delta E_{xg}$ above the peaks due to ground state, where $\Delta E_{xg}$ is the difference between the first-excited-state energy and the ground-state energy of a hydrogenic donor in GaAs. Since the population of an excited state increases with temperature, the higher energy peak should increase in intensity as the temperature is increased. This explains the qualitative behavior of Fig. 2. Moreover, for a hydrogenic donor, $\Delta E_{xg}=E_0(1-\frac{1}{4})$, where the donor ground-state energy $E_0$ is given by[8]

$$E_0=(m^*/m)(\epsilon_0^2/\epsilon^2)\times13.6\text{ eV}=5.1\text{ meV}.$$

Here the values $m^*/m\simeq0.06$ and $\epsilon/\epsilon_0=12.53$ were used.[9] Hence $\Delta E_{xg}=3.8$ meV, which agrees well with the experimental value $E_{2a}-E_{2b}\simeq3.7$ meV. The smaller apparent value of $E_{3a}-E_{3b}$ may be explained by the fact that the twin-peaks 3 are broader than twin-peaks 2. However, we do not have a good explanation for this at the moment.

Note also that the ratio of the intensities of peaks $2a$ and $2b$, $I_{2a}/I_{2b}=(n_x/t_x)/(n_g/t_g)$. Here $t_x(t_g)$ is the lifetime for the recombination of an electron in the first excited (ground) state of a donor with a hole at an acceptor when the donor-acceptor pair separation corresponds to the peaks in the emission band 2. Using this along with Eq. (1), the straight line of Fig. 3 is easily explained. Also the slope in Fig. 3 (3.4 meV) agrees well with the estimated $\Delta E_{xg}$ (3.8 meV) and the observed energy separations $E_{2a}-E_{2b}=3.7$ meV. At high temperatures where $(\Delta E_{xg}/kT)\rightarrow0$, the ratio $(I_{2a}/I_{2b})$ reduces to $(\beta_xt_g/\beta_gt_x)$. Extrapolation of the straight line in Fig. 3 gives the value 25 for this quantity. Hence we have $(t_g/t_x)\cong25(\beta_g/\beta_x)\simeq6.25$ since $(\beta_g/\beta_x)=\frac{1}{4}$.

We have also observed that peaks 2a and 3a are not broadened by increasing the temperature. This and their rather large widths agree with expectation from donor-acceptor pair transitions in which the width is determined by fluctuations of the Coulomb interaction energy because of the random distribution of donors and acceptors.

At this point one must consider the possibility that the first excited ($n=2$) states form a band and merge with the conduction band. We find that, although the radius of the excited-state wave function is relatively large, banding of the $n=2$ state is quite possibly a

[8] R. A. Smith, *Semiconductors* (Cambridge University Press, London, 1959), p. 62.

[9] O. Madelung, *Physics of III–V Compounds* (John Wiley & Sons, Inc., New York, 1964).

small effect. This is mainly because only the relatively few donors whose ground states are unoccupied contribute to banding of the $n=2$ states (principle of exclusion).[10] Kaplan[11] has recently observed a sharp transition at 5 $cm^{-1}$ in InSb having a donor density of $6\times10^{13}$ $cm^{-3}$. This was attributed to a transition from the second excited state ($n=3$) of the donor to the first Landau level. If $\alpha_0$ is the appropriate Bohr radius, and $N_D$ the density of donors contributing to banding, $\alpha_0 N_D^{1/3}$ is the parameter that determines the condition for merging.[12] The value of $\alpha_0 N_D^{1/3}$ for the first donor excited state in our GaAs sample is approximately the same as the value of $\alpha_0 N_D^{1/3}$ for the second donor excited state in Kaplan's experiment.

The conclusions drawn from our model are not sensitive to an amount of banding of the $n=2$ states that is smaller than the energy difference between the $n=2$ state and the bottom of the conduction band. The observed Boltzmann factor, for example, does not require complete localization of the $n=2$ states, but it would seem to forbid significant degeneracy between the $n=2$ donor band and the conduction band.

We now present a simple calculation of the ratio of lifetimes ($t_g/t_x$) assuming hydrogenic wave functions for the donor ground and excited states.

For a donor at the origin and an acceptor at position **L**,

$$\frac{t_x}{t_g}(\mathbf{L})=\frac{\left|\int U^*_{gh}(\mathbf{r}-\mathbf{L})e\mathbf{r}U_{ge}(\mathbf{r})d\tau\right|^2}{\left|\int U^*_{gh}(\mathbf{r}-\mathbf{L})e\mathbf{r}U_{xe}(\mathbf{r})d\tau\right|^2}, \tag{2}$$

where $U_{gh}$ ($U_{ge}$) is the ground-state wave function for a hole (electron) on an acceptor (donor), while $U_{xe}$ is the wave function for an electron in the first excited state of the donor. $d\tau$ is the volume element. If the ground- (excited) state wave functions are written down in analogy with the wave function of $n=1$ ($n=2$) electron in a hydrogen atom, then for the case in which the effective Bohr radii for electron and hole ($a_e$ and $a_h$) are such that $a_h/a_e\ll1$, this simplifies to

$$\frac{t_g}{t_x}(L)=\frac{1}{32}\left[1-\frac{L}{a_e}+\frac{1}{2}\left(\frac{L}{a_e}\right)^2\right]\exp\left(\frac{L}{a_e}\right). \tag{3}$$

Let us define $L_{\text{eff}}$ as the value of $L$ at which the ratio $t_g/t_x$, calculated from Eq. (3), agrees with the experimentally determined value of 6.25 for $t_g/t_x$ (i.e., $L_{\text{eff}}$ is the pair separation corresponding to the peak in the emission band). Then we have $L_{\text{eff}}\simeq3.78\ a_e\simeq420$ Å.

[10] The exchange interaction between an $n=2$ electron in one donor with an $n=1$ electron in another may lead to some banding. However this process involves simultaneous tunneling of two electrons. Hence this is a second-order process and we believe that its contribution to banding is negligible.

[11] R. Kaplan, J. Phys. Soc. Japan Suppl. **21**, 249 (1966).

[12] N. F. Mott, Phil. Mag. **6**, 287 (1961).

The epitaxially grown samples of GaAs used in this experiment had a room-temperature carrier concentration of $5\times10^{15}$ $cm^{-3}$. Because of compensation, we would expect an impurity content $>5\times10^{15}$ $cm^{-3}$. However, in many other samples grown in this manner, the room-temperature carrier concentration was never greater than $5\times10^{15}$ $cm^{-3}$. Also, the position and width of the "exciton" line (peak 1) indicates a relatively pure sample. Thus the error will not be too large if we assume $N_D\simeq5\times10^{15}$ $cm^{-3}$. If we now define $L_0$ as the most probable distance between nearest-neighbor pairs, then $L_0=(1/2\pi N_D)^{1/3}$. Hence for $N_D\simeq5\times10^{15}$ $cm^{-3}$, $L_0=320$ Å.

If the pair recombination occurred only through the nearest-neighbor pairs, the peak in the emission band should correspond to a pair separation approximately equal to $L_0$. (It will not be exactly $L_0$ because of the dependence of the recombination lifetime on the pair separation.) However, the recombination through the pairs with separations larger than the nearest-neighbor pairs cannot be entirely neglected. The effect of recombination through such pairs will be to make the peak in the emission band correspond to a distance larger than $L_0$. The $L_{\text{eff}}$, as defined immediately after Eq. (3), is the pair separation corresponding to the peaks in the emission band 2. Thus the value of 420 Å calculated above for $L_{\text{eff}}$ from Eq. (3) and the experimentally determined value for $t_g/t_x$ is very reasonable and consistent with the impurity content of the sample deduced from electrical measurements.

Finally, for $L_{\text{eff}}\simeq420$ Å, the Coulomb energy involved in the pair recombination spectrum may be estimated as

$$e^2/4\pi\epsilon L_{\text{eff}}\cong2.5\text{ meV}.$$

Using this and the estimated band-gap energy[13] ($E_g\simeq1.520$ eV) the acceptors involved in the observed pair recombination spectra may be estimated from our results to be at energies 25.6 and 37.8 meV above the top of the valence band.

## V. SUMMARY AND CONCLUSIONS

Photoluminescence of $n$-type epitaxial GaAs disclosed two twin peaks such that the higher energy peak in each twin peak increases in intensity as the temperature is increased. Similar observations in II–VI compounds were explained by assuming thermal depopulation of shallow donors, the low- and high-energy peaks being due to donor-acceptor and free-electron–to–acceptor transitions, respectively. However, this model is unable to explain the observed Boltzmann intensity ratio obtained in our experiments. We have proposed a model in which the lower (higher) energy peak of each twin peak is because of the transition from the ground (first excited) states of donors and acceptors. This model explains all our results satis-

[13] M. D. Sturge, Phys. Rev. **127**, 768 (1962).

factorily. Moreover, using this model and the hydrogenic wave functions for the ground and the excited states of a donor, we have calculated the effective donor-acceptor pair separation corresponding to the observed peak in the emission band; the calculated number is consistent with the impurity content of the sample deduced from electrical measurements.

In conclusion, we may mention that the shallow donor states in GaAs may be masked by band-tail effects in more impure materials. This may explain why the excited donor states have not been observed previously in GaAs.

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# Band Inversion and the Electrical Properties of $Pb_xSn_{1-x}Te$†

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The electrical resistivity and Hall coefficient of $Pb_xSn_{1-x}Te$ alloys were determined as a function of temperature from 4 to 300°K. The measurements were intended as a test of Dimmock, Melngailis, and Strauss's band-inversion model in the immediate region of band crossing. The resistivity is characterized by a predominantly linear dependence upon $T$, and by the distinct breaks which occur in this dependence. The linearity is attributed to degenerate lattice scattering. The temperatures at which the breaks occur depend upon alloy composition, and are relatively independent of carrier concentration and carrier mobility. These break temperatures are in excellent agreement with band-crossing temperatures predicted on the basis of the band-inversion model. This fact, along with several other features of the results, strongly supports the band-inversion model.

## I. INTRODUCTION

PROPERTIES of the $Pb_xSn_{1-x}Te$ alloy system have been studied in several laboratories over the past few years.[1] It has been shown that these solids are semiconductors having the rocksalt crystal structure throughout the range $0 \leq x \leq 1$. Considerable interest has centered around the unusual dependence of the valence-conduction band gap $E_g$ upon alloy composition and temperature. This dependence is illustrated in Fig. 1, using a type of plot first presented by Dimmock, Melngailis, and Strauss[2] (DMS). The data represent experimental determinations of the magnitudes of $E_g$ by various optical[2-11] and electrical[9,11-13] methods. The assignment of negative values to the band gaps of SnTe is based upon the proposal by DMS that $E_g$ becomes zero at some intermediate alloy composition and that this is followed by an inversion of the states forming the valence- and conduction-band extrema. Their proposal was based upon a band model in which $E_g$ varies with alloying because of differences in the relativistic band effects associated with Pb and Sn. Such a model explains the observed variation of $E_g$ with $x$ and the change in sign of the temperature coefficient of $E_g$ in going from PbTe to SnTe.[2] Unfortunately, no experimental determinations of $E_g$ have been carried out near the proposed band-crossing points, and only two values are reported on the Sn-rich side of the alloy system. Efforts

† This work constitutes part of a thesis to be submitted to the University of Maryland by R. F. Bis in partial fulfillment of the requirements for the Ph.D. degree in physics.
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[2] J. O. Dimmock, I. Melngailis, and A. J. Strauss, Phys. Rev. Letters **26**, 1193 (1966).
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[8] I. Melngailis and A. R. Calawa, Appl. Phys. Letters **9**, 304 (1966).
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