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Band Gap of Gallium Phosphide from 0 to 900°K and Light Emission from Diodes at High Temperatures

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The indirect energy gap E_g of GaP in the tenperature range from 0 to 900°K was determined from absorption measurements. Below 400°K, E_g was determined from absorption due to the creation of excitons at isolated nitrogen atoms substituted on P sites. This absorption was measured with wavelength-modulated exciting light. The intrinsic absorption edge was measured over the full temperature range by conventional transmission. Above 400°K, the gap was determined from a numerical fit of the intrinsic-edge absorption data to a theoretical expression using parameters obtained from low-temperature measurements, with E_g as the only adjustable parameter. The shapes of the experimental curves are in good agreement with the theoretical calculations. At 300°K, E_g is 2.261 eV. Light emission from diodes was studied from 300 to 900°K. The principal high-temperature emission line parallels the energy gap at about 45-meV lower energy, and is attributed to an exciton recombination.

INTRODUCTION

RECENT interest in the luminescent properties of GaP at high temperatures[1,2] emphasizes the need for accurate values of the energy gap E_g over the entire temperature range throughout which the crystals are stable. Knowledge of the variation of E_g with temperature is essential to the identification of some of the luminescent processes and to a better understanding of their origin.

Absorption measurements from 1.6 to 300°K were made by Dean and Thomas[3] and the results were used to obtain the exciton energy gap (E_{gx}). Their values for E_{gx} were deduced from the absorption thresholds for optical transitions with simultaneous absorption and emission of various phonons.

We present in this paper absorption measurements which enable us to determine the energy gap accurately from 0 to over 850°K. Below 360°K we employ the absorption peak associated with a bound exciton, the A line,[4] this line being due to a hole and electron trapped at an isolated nitrogen atom substituted on a phosphorus site.[5] This line remains sharp to much higher temperature than the rather poorly defined absorption thresholds due to the different phonons at temperatures above 120°K as observed by Dean and Thomas.[3] We obtain values for E_g which lie up to 6 meV above those of Dean and Thomas between 77 and 300°K, but which are in good agreement with the revised values reported by Dean *et al.*[6] more recently. At the higher temperatures, we determine the gap from a numerical fit of the intrinsic absorption data to a theoretical expression using parameters obtained from the low-temperature measurements of Dean and Thomas and this work, and where E_g is the only adjustable parameter.

We have also investigated light emission from diodes in the range of 300 to 900°K. The results are discussed in the last section of this paper.

EXPERIMENTAL

The absorption measurements were performed on samples prepared by two different methods. The bound-exciton A line absorption below 360°K was measured on melt-grown single crystals containing nitrogen. These crystals were grown by Blum of this laboratory in a BN crucible at about 1500°C under 10 atm of phosphorus pressure.[7] Crystallization was achieved by lowering the crucible through a sharp gradient. These crystals, although undoped, were p type with a hole concentration at 300°K of about 10^{17} cm^{-3}. The hole mobility was 110 cm^2/V sec at 300°K and 840 cm^2/V sec at 77°K.

The intrinsic absorption data for the total temperature range were obtained from vapor-grown single crystals. These were prepared by a PCl_3 chemical transport method similar to that employed by Oldham[8] and Kamath and Bowman.[9] PCl_3 vapor in a hydrogen carrier gas was passed over the Ga source material at 900°C at a rate of 10^{-3} mole/h. The PCl_3 reservoir was maintained at -30°C and the hydrogen flow was adjusted so that the partial pressure of the PCl_3 in the system was 3 mm. The GaP substrates were mounted vertically in the all-quartz system and held at 800°C. The temperature gradient in the deposition zone was 10°C/in. The deposition rate of the layer was 12 μ/h. After growth, the substrates were mechanically removed from the vapor-grown layers and the samples were polished to various thicknesses. Hall measurements

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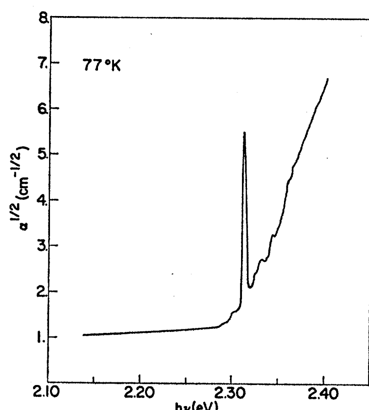

FIG. 1. An absorption spectrum of a GaP crystal doped with nitrogen. The absorption curve was calculated from a transmission spectrum taken at 77°K on wafer B 106, 0.18 cm thick.

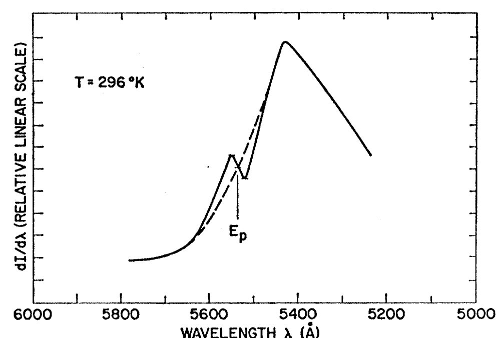

FIG. 2. Differential absorption as a function of wavelength for wafer B 106 at room temperature.

at room temperatures showed the deposited GaP to be n type with a carrier concentration of 3×10^{16} cm^{-3} and a mobility of 180 cm^2/V sec. The high quality of the vapor-grown crystals was confirmed by the 77°K mobility of 2100 cm^2/V sec.

Samples for absorption studies were lapped and polished using standard metallographic techniques. For absorption measurements at temperatures below 300°K the samples were mounted in an exchange-gas cooled Dewar which fitted into the sample compartment of a Cary model 14 spectrophotometer. A thermocouple was contacted to one corner of the sample to monitor the temperature. With this apparatus, the sample transmission could be easily measured at fixed temperatures of 77, 145, 195, and 245°K, and also at intermediate temperatures while the Dewar was slowly warming up. (The warm-up rate was about 1°K/min.) For transmission measurements above 300°K, the sample was mounted in a small heated cell which also fitted directly into the spectrophotometer beam.

From the measured transmission T the absorption coefficient α was calculated using the equation

$$T=(1-R)^2e^{-\alpha x}/(1-R^2e^{-2\alpha x})\,, \qquad (1)$$

where R is the reflectivity. We used a value of 0.29 for R.[10]

For the determination of the A-line absorption in crystals containing nitrogen we used transmission measurements in the temperature range from 6 to 270°K. At about 190°K the background absorption in the energy range of the A line is comparable to the A-line absorption. At 270°K the absorption due to the A line is but a small fraction of the total absorption and is located on a sharply increasing absorption curve with increasing photon energy. Since we were unable to determine accurately the peak of the A-line absorption above 270°K using the direct transmission method, we employed a technique developed by Gilgore *et al.*[11] of this laboratory, whereby the light prior to passing through the exit slit of a Bausch and Lomb 500-mm grating monochromator is deflected by a rotating transparent wobbling disk mounted in front of the slit. This results in wavelength modulation of the emerging light and permits direct recording of a differential transmission signal as a function of wavelength. We used a tungsten light source which had essentially a constant intensity I_0 in the wavelength range of the A line. Using this monochromator, we were able to measure $dI/d\lambda$ directly in the energy interval containing the A line. By comparing the differential transmission at 77°K to the transmission, we ascertained that the two techniques gave excellent agreement in the location of the absorption maximum. We were able to determine the peak position of the A line using transmission up to 359°K.

RESULTS

Figure 1 shows the absorption coefficient at 77°K as a function of photon energy for sample B 106 which has strong A line absorption. The A line absorption has a maximum at 2.3125±0.0005 eV. Along with this characteristic absorption, there is a considerable increase in the background absorption as well as some phonon-induced structure in the absorption edge. This additional absorption has recently been discussed[12] and will not be considered here. The A-line peak energy of this sample was measured up to 270°K. Up to 190°K the absorption line is sufficiently sharp so that the peak energy can be obtained directly. Above 190°K the background absorption must be taken into account and the peak energy can then be determined up to 270°K. Using the conventional absorption measurements, the uncertainty is too large above 270°K for any further analysis.

The use of wavelength-modulated exciting light allows us to determine the A-line peak energy to

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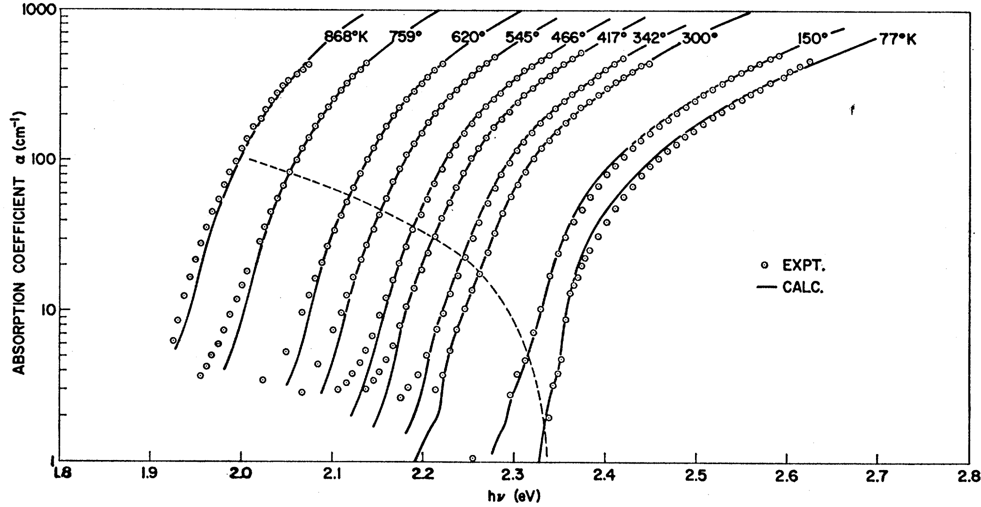

FIG. 3. The band-gap absorption for a high-purity GaP sample free of nitrogen for temperatures from 77 to 868°K. The experimental data is shown as circled points and the theoretical fit is given by the solid curves. The intersection of the dotted curve with the absorption curves at different temperatures yields the energy gap at each temperature and also shows the variation of α for Eg as a function of temperature.

considerably higher temperatures. A trace of $dI/d\lambda$ versus λ for sample B 106 at 296°K is shown in Fig. 2. The A-line absorption is again superimposed on the background absorption. The dotted line in Fig. 2 is the estimated $dI/d\lambda$ of the background. The intersection of the dispersion curve with the background then gives the peak energy of the A line. Analytically, the intersection occurs at the midpoint of the maximum and the minimum of the dispersion curve. It should be noted that the conventional optical transmission curve of this sample at 296°K shows essentially no sign of the A-line absorption. With the frequency modulation technique the A line was measured up to 359°K.

The results of Dean and Thomas[3] established a value of 2.338 eV for E_g at 0°K. The A line occurs at 2.318 eV or 20 meV from E_g. We assume here that the energy difference between the A line and E_g is temperature independent. Thus, the energy position of the A line up to 360°K gives us a precise value of E_g up to that temperature. The determination of E_g at $T>360$°K is given in the next section.

The absorption coefficients of high-purity vapor-deposited samples which are free of A-line absorption are shown in Fig. 3 for several temperatures between 77 and 868°K.

ANALYSIS OF THE INTRINSIC ABSORPTION SPECTRUM

The absorption of photons in the intrinsic absorption edge region leads to the creation of free and bound excitons as well as to the production of free carriers in the conduction and valence bands. Since the optical transitions in GaP are indirect, each of the above processes, except for the creation of bound excitons, requires the participation of a given phonon of energy $\hbar\omega_i$, which has the momentum to promote the electron from the valence-band maximum to the conduction-band minimum. The absorption coefficient describing the combined absorption processes is given by[13]

$$\alpha=\sum_{i=1}^{n}\frac{1}{h\nu}\frac{a_i}{\exp(\hbar\omega_i/kT)-1}\{(h\nu-E_{gx}+\hbar\omega_i)^{1/2}+[\rho_i\exp(\hbar\omega_i/kT)](h\nu-E_{gx}-\hbar\omega_i)^{1/2}\}+\sum_{i=1}^{n}\frac{1}{h\nu}\frac{b_i}{\exp(\hbar\omega_i/kT)-1}\{(h\nu-E_g+\hbar\omega_i)^2+[\rho_i\exp(\hbar\omega_i/kT)](h\nu-E_g-\hbar\omega_i)^2\}. \quad (2)$$

In the equation $h\nu$ is the photon energy, a_i is a weakly temperature-dependent parameter[14] containing the density-of-states effective masses of electrons and holes, E_g is the energy difference between the conduction-band minimum and the valence-band maximum, and E_{gx} is equal to E_g minus the binding energy of the free exciton, which is taken as 0.010 eV.[3] The value of ρ_i is given by

$$\rho_i=(\Delta E+\hbar\omega_i)^2/(\Delta E-\hbar\omega_i)^2, \quad (3)$$

where

$$\Delta E=E_0(\Gamma_{15}\rightarrow\Gamma_1{}^c)-E_g. \quad (4)$$

E_0 is the direct energy gap. ΔE has a value of 0.56 eV at 300°K as determined by Zallen and Paul.[15] A more recent value for ΔE is 0.55 eV at 0°K.[6] ΔE also decreases slightly with increasing temperature but this variation has a negligible effect on ρ_i. We have used a constant

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TABLE I. Phonon energies and the coefficients for the evaluation of Eq. (2). The values listed in this table were obtained from Ref. 3.

Phonon mode	Phonon energy (meV)	Coefficient a_i (cm^{-1} $eV^{1/2}$)
TA	12.8	39.9
LA	31.3	151.0
TO	46.5	59.5
TA+LO	64.3	11.3

value of 0.55 eV over the full temperature range. The coefficient b_i is proportional to a_i, i.e., $b_i=Ca_i$.[13] With the exception of C the various constants particular to GaP and the origin of the constants are listed in Table I.

In the temperature range from 77 to 300°K, C is the only unknown value in Eq. (2). By curve fitting, using computer-generated values of α, we find that a value of $C=34$ $eV^{-3/2}$ leads to the best fit at the temperatures 77, 150, and 300°K. An equation can actually be derived for the constant C based on the theoretical considerations of Elliot[13] which has the form[16]

$$C=\frac{a_0^3(m_em_h)^{3/2}E^{3/2}}{\sqrt{2}\,8\hbar^3(m_e+m_h)^{3/2}},\qquad(5)$$

where a_0 is the exciton Bohr radius and E is the energy of 1 eV in ergs. If we assume a hydrogenic wave function for the free exciton with a binding energy of 0.010 eV[3] we calculate a Bohr radius of 6.5×10^{-7} cm. A conductivity mass for electrons of 0.32 has been reported by Zuhmakolov[17] and a value of 0.35 was reported by Hashimoto and Akasaki.[18] These values lead us to choose a value of 0.25 for m_e. For the hole mass we assume a value of 0.5. The evaluation of C based on the above estimates yields $C=43$ $eV^{-3/2}$. This is certainly in good agreement with the value of 34 $eV^{-3/2}$ arrived at from the fit to the experimental data.

Using the experimental value of $C=34$ $eV^{-3/2}$, we fit the high-temperature absorption data and thus determine the energy gap up to 900°K. The calculated absorption curves for each temperature are shown as the solid curves in Fig. 3. The agreement between theory and experiment for the absorption curves at 300°K and below are quite good. At 77°K there exists a small difference for the intermediate α values which does not occur if Eq. (2) is approximated by setting the ρ_i's equal to unity. The better agreement for all temperatures is however obtained by including the factor ρ_i.

All absorption curves show a tail at low energies which is more noticable at higher temperatures. This tail is due at least in part to lifetime broadening which is not taken into account in Eq. (2). In addition there may be some contribution from surface degradation

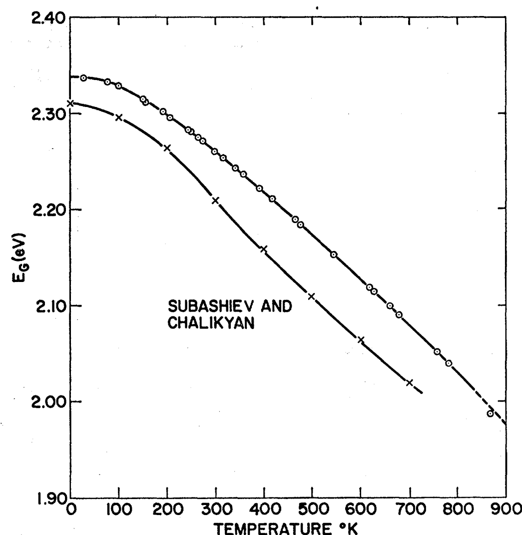

FIG. 4. The temperature dependence of the energy gap in GaP from 0 to 900°K. The circled points correspond to the present data while the crosses were obtained from Ref. 19.

caused by the higher temperatures. Microscopic inspection of the surface, however, after the high-temperature measurement showed little or no noticeable difference from the original surface finish.

Dependence of the energy gap on temperature is shown in Fig. 4 along with that reported by Subashiev and Chalikyan.[19] It should be noted that our results in the temperature range of 77 to 300°K are now in good agreement with those of Dean and Thomas[3] after the revision reported by Dean *et al.*[6] The energy-gap values obtained from absorption measurements by Subashiev and Chalikyan[19] are at least 35 meV lower than our results. The disagreement between the earlier and the present results is probably due not to a major difference in the data but rather to the difference in the way the energy gap was determined from the data. In the earlier work[19] the straight-line portion of the curves of $\alpha^{1/2}$ versus $h\nu$ were extrapolated to $\alpha=0$. This method when applied to our data will also give lower values than we report. Since we have determined E_g directly up to 369°K from the sharp-absorption A line we believe that the data is also quite reliable in the higher-temperature range. The values of E_g and dE_g/dT from 0 to 900°K in 100°K intervals are shown in Table II. In the higher-temperature region, the variation of E_g with T becomes nearly linear and dE_g/dT is about 4.5×10^{-4} eV/°K between 400 and 700°K.

It has long been recognized that in the absence of phonon structure in the absorption edge it is difficult to determine experimentally the energy gap of materials which have indirect optical transitions. In the case of GaP where the phonon structure was clearly observed at low temperature[3] and a sharp exciton line was seen

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TABLE II. Temperature dependence of the energy gap.

Temp. (°K)	Eg (eV)	dEg/dT (10^{-4} eV/°K)
0	2.338	0
100	2.329	2.26
200	2.298	3.40
300	2.261	4.10
400	2.218	4.26
500	2.173	4.50
600	2.127	4.62
700	2.080	4.82
800	2.031	5.18
900	1.975	...

to nearly 400°K, the energy gap is well established. We have plotted a curve in Fig. 3 which intersects each of the absorption coefficient curves at the value of E_g for that temperature. At 77°K, E_g occurs at $\alpha=1.7$ cm^{-1}, whereas at 863°K E_g corresponds to an $\alpha=108$ cm^{-1}. The behavior is entirely consistent and expected. In fact, at 1.6°K, E_g should not fall onto the absorption curve at all unless the smallest phonon energy is less than the binding energy of the free exciton. In GaP the lowest energy phonon is 12.8 meV for the transverse acoustic mode and the exciton binding energy is 10 meV, so that the absorption threshold is 2.341 eV and E_g is 2.338 eV. With increasing temperatures the photon absorption can be assisted by phonon absorption from the lattice and hence E_g should occur at increasing values of α. This is clearly demonstrated in Fig. 3.

ELECTROLUMINESCENCE AT HIGH TEMPERATURE

We have previously studied the green-diode emission in the temperature range of 27 to 300°K,[20] and red-diode emission up to 700°K.[2] Electroluminescence studies of both green- and red-emitting diodes have now been extended up to 900°K. Methods of junction preparation and diode fabrication were previously described[21] and details of the measurements are also given elsewhere.[22] We present here only the peak energy dependence on temperature for diodes doped with Zn and S, Zn and Te, and Zn-O and Te. The results are shown in Fig. 5. Efficient Zn-O doped diodes emit essentially all of the light in the red band at 300°K. With increasing temperature the intensity of the red emission decreases and the recombination radiation appears in a line close to the band edge, denoted by the letter "H" in Fig. 5. Above 550°K the H line dominates the emission. The fact that the red band does not follow the temperature dependence of the energy gap is not surprising since the oxygen donor level is nearly 1 eV below the conduction band.[22]

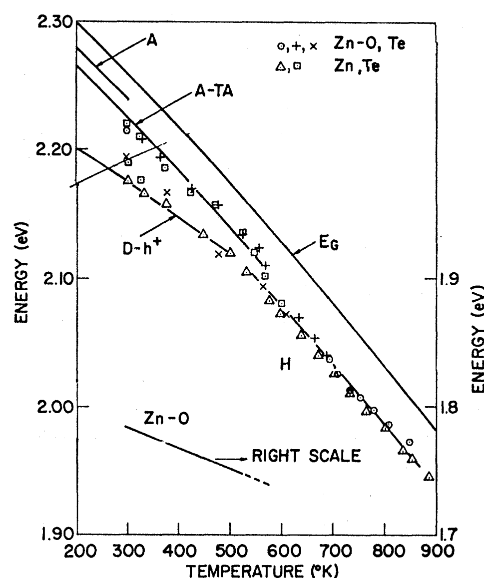

FIG. 5. Peak energies versus temperature for several diodes and the relation of the emission to the variation in energy gap with temperature.

Diodes doped with Zn and S, or Zn and Te, behave quite similarly. In diodes made from purer material in which the red line due to oxygen is essentially absent, the 300°K emission is dominated by two lines. One line labeled A-TA is believed to be due to recombination of excitons bound to isolated N atoms substituted on P sites with the simultaneous emission of a transverse-acoustical-mode phonon.[20,23] The energy and temperature dependence of the other line, labeled D-h$^+$, is consistent with the capture of free holes by the shallow donors S and Te.[20] A given diode may show only the A-TA or the D-h$^+$ line at 300°K while other diodes may show both components. With increasing temperature the D-h$^+$ line decreases in intensity and merges into line H. The A-TA line terminates at about 550°K and also merges into line H. The latter emission line then has a temperature dependence parallel to that of the band gap and can be easily seen up to 900°K. In fact, the efficiency above 600°K appears almost temperature-independent. It is interesting to consider what the origin of line H is. Since all emission lines terminate in the H line, it might suggest an intrinsic recombination process. It may in fact be the recombination of a free exciton with the emission of a 31.3 meV longitudinal-acoustic-mode phonon. The peak energy is not inconsistent with this assignment. However, since for instance at 760°K the band width at half maximum is about 0.13 eV and the absorption coefficient at the peak of the H line is about 20 cm^{-1} and α rises to 83 cm^{-1} at $E_g=E_H+0.45$ eV, the peak energy and the linewidth may well be influenced by self-absorption. The fact that the H line parallels the band gap and

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occurs at a greater energy separation from E_g than the A-TA line is sufficient reason for assigning the H line to an exciton recombination. Whether it is a free exciton or an exciton bound to a N atom with the emission of a higher-energy phonon can not be readily decided on the basis of the present results.

SUMMARY

We have determined E_g as a function of temperature from 0 to 900°K. In the low-temperature range of 6 to 369°K, E_g was determined directly from the A-line absorption. Over the complete temperature range, absorption curves as functions of photon energy were fitted to a theoretical expression with E_g being determined by the best fit. High-temperature diode emission shows an exciton line that parallels the band gap up to 900°K.

ACKNOWLEDGMENTS

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Noise Properties of n-Type Gold-Doped Silicon*

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Measurements are reported of noise in n-type gold-doped silicon at reduced temperatures, both in thermal equilibrium and under optical illumination. The noise level is at least as low as predicted by generation-recombination theory; the shape is complex. Usually, two relaxation times and sometimes three are discernible. The spectrum often has a local maximum, even in thermal equilibrium. Several detailed three- and four-level models are described; their behavior is calculated and compared with experiment. The gross features of the spectra, viz., the temperature and light-intensity dependence of the relaxation times, the occurrence of negative plateau coefficients, and the interrelation between optical and thermal results can be explained if, besides the known gold levels, another level is postulated, situated slightly below the gold-acceptor level. Several features suggest that this level may stem from paired ionized gold-acceptor and shallow-donor impurities.

1. INTRODUCTION

THE properties of gold-doped silicon have been widely investigated, and although the gross features of this material are quite well understood, the details of some experimental results have not been fully explained, as may be seen, e.g., in the review article by Bullis[1] and from the work of Glinchuk *et al.*[2] In the present paper, we give the results of a study of the electrical properties of n-type gold-doped silicon by means of noise measurements. The noise of interest here is generation-recombination (g-r) noise, which stems from fluctuations in the electronic transition rates among the various participating energy levels of the material; in some cases, the nature of the noise spectra may be modified by transport of the charge carriers, i.e., by diffusion or drift.

Detailed studies have been made on the noise properties of germanium with impurities such as nickel, gold, and manganese which give rise to well-defined deep-lying energy levels in the forbidden band gap.[3–6] Similar measurements have been made on gallium arsenide.[7] To our knowledge, no measurements have been reported for silicon with deep-lying energy levels. The measurement of noise in materials with deep energy levels such as gold-doped silicon not only provides information about the specific material under investigation, but, more generally, can be a convenient means of studying g-r processes involving known donor or acceptor states. For crystals which contain as impurities only the common dopants which produce shallow electron-energy states in the band gap, the probability of transitions between these levels and the conduction or valence bands is very small until extremely low temperatures

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