

# EFFECTIVE MASS AND INTRINSIC CONCENTRATION IN SILICON

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**Abstract**—Experimental observations bearing on density-of-states effective masses and on the intrinsic concentration in silicon are reviewed and correlated. These indicate effective masses to be temperature and energy dependent. The valence band structure as determined by Kane is used to calculate the temperature and donor density dependence of hole effective mass. A first order approximation to the explicit temperature variation of both hole and electron effective masses is made using the measured temperature dependence of the energy gap. When these temperature-dependent effective masses are substituted into the theoretical expression for intrinsic concentration the agreement with reported measurements of  $n_i$  is within the limits of error. Density-of-states effective masses at 300°K are found to be  $m_e^* = 1.18$  and  $m_h^* = 0.81$  in contrast to the generally used 4.2°K values of  $m_e^* = 1.06$  and  $m_h^* = 0.59$ .

**Résumé**—Des observations expérimentales ayant trait aux densités des masses effectives d'états et à la concentration intrinsèque dans le silicium sont revues et corrélées. Celles-ci indiquent que les masses effectives dépendent de la température et de l'énergie. La structure de bande de valence telle que déterminée par Kane est employée pour calculer la dépendance de la masse effective de trou sur la température et la densité de donneur. Une approximation de premier ordre relative à la variation de température explicite des masses effectives d'électrons et trous est faite en employant l'intervalle d'énergie en fonction de la température. Quand ces masses effectives qui dépendent de la température sont remplacées dans l'expression théorique de la concentration intrinsèque, l'accord avec les mesures reportées de  $n_i$  est dans les limites d'erreurs. La densité des masses effectives des états à 300°K ont été trouvées comme étant  $m_e^* = 1,18$  et  $m_h^* = 0,81$  contrairement aux valeurs généralement employées à 4,2°K de  $m_e^* = 1,06$  et  $m_h^* = 0,59$ .

**Zusammenfassung**—Experimentelle Beobachtungen der effektiven Zustandsdichtemassen und der Eigenleitungskonzentration in Silizium werden zusammengestellt und miteinander verglichen. Die effektiven Massen erweisen sich als energie- und temperaturabhängig. Die von Kane bestimmte Valenzbandstruktur wird dazu benutzt, um die Abhängigkeit der effektiven Löchermasse von der Temperatur und der Dotierung zu berechnen. Eine erste Näherung für die Temperaturabhängigkeit von Elektronen- als auch Löchermassen wird mit Hilfe der gemessenen Temperaturabhängigkeit des Bandabstandes berechnet. Wenn diese temperaturabhängigen effektiven Massen in die theoretischen Ausdrücke für die Eigenleitungskonzentration eingesetzt werden, so ergibt sich innerhalb der Fehlergrenzen Übereinstimmung mit den berichteten Messwerten. Die effektiven Zustandsdichtemassen bei 300°K ergeben sich zu  $m_e^* = 1,18$  und  $m_h^* = 0,81$ . Die allgemein verwendeten Massen für 4,2°K sind dagegen  $m_e^* = 1,06$  und  $m_h^* = 0,59$ .

## INTRODUCTION

THE INTERPRETATION of many bulk measurements and of the characteristics of minority or majority carrier junction devices depends on a knowledge of intrinsic concentration and effective masses.

In theory, the intrinsic concentration,

$$n_i = 2 \left[ \frac{2\pi m_0 k}{h^2} \right]^{3/2} (m_e^* m_h^*)^{3/4} T^{3/2} \exp\left(\frac{E_g}{2kT}\right) \quad (1)$$

where  $k$ ,  $m_0$  and  $h$  are physical constants and  $m_e^*$

and  $m_h^*$  are the density-of-states effective mass ratios for electrons and holes. The density-of-states effective mass is here defined as a scalar mass which accurately describes the density-of-states of a band which need not be ideal. That is, it may be degenerate and possess non-spherical energy surfaces distributed non-parabolically in  $k$ -space. Clearly, if the band were non-parabolic, such an effective mass would be a function of temperature and of doping density.

Ever since the earliest measurements of effective masses and energy gap in silicon there has been a large discrepancy between the values of  $n_i$  predicted by equation (1) and measured values. In general this has been ignored and values of  $n_i$  for temperatures lower than 400°K have been obtained by logarithmic extrapolation of the measured values of  $n_i$ . Such extrapolation automatically assumes temperature independent effective masses and a linear temperature variation for the energy gap. Furthermore, in the interpretation of some experiments effective masses are considered adjustable or unknown parameters. These approaches are not easily justified when available experimental observations could place these parameters within narrower limits and some simple calculations could give better values for conditions other than those where measurements have been performed.

It is the purpose of this paper to review and correlate the experimental observations on energy gap, intrinsic concentration and effective masses and to combine these with theoretical calculations using previous band structure calculations<sup>(1)</sup> to arrive at more realistic values for these parameters as a function of temperature.

#### ENERGY GAP

The temperature variation of the energy gap in silicon has been determined by MACFARLANE *et al.*<sup>(2)</sup> from optical absorption measurements and by HAYNES *et al.*<sup>(3)</sup> from measurements of recombination radiation. The former indicated that transitions occurred to an exciton state 0.0073 eV below the conduction band in good agreement with the calculated exciton energy of 0.01 eV. Recent electro-absorption experiments<sup>(4,5)</sup> have given support both for the existence of an exciton state in optical transitions and for the value and temperature dependence of the energy gap. FROVA

and HANDLER<sup>(4)</sup> obtained a value of  $Eg = 1.122$  eV at 296°K when an exciton energy of 0.01 eV was added. Similarly the results of WENDLAND and CHESTER<sup>(5)</sup> give 1.127 eV at 296°K. Using this value and the measured temperature variation of the transition involving emission of a TO phonon, the energy gap variation can be determined. The above measurements are compared in Fig. 1.

The results of MACFARLANE *et al.*<sup>(2)</sup> are considered to be the most reliable because they were obtained using very high resolution ( $\sim 0.0015$  eV) equipment, they fall near the average of the other measurements and they give an extrapolated 0°K energy gap in good agreement with that obtained from measurements of intrinsic concentration. The experimental spread in these values is  $\pm 0.005$  eV. Uncertainty in the value of exciton energy is of the same order.

#### EFFECTIVE MASS OF ELECTRONS

Cyclotron resonance measurements indicate the constant energy surfaces of the silicon conduction band to be ellipsoidal. As a result longitudinal and transverse effective masses are observed. HENSEL *et al.*<sup>(6)</sup> have reported accurate measurements of these at 4.2°K:

$$m_l/m_0 = m_l^* = 0.9163 \pm 0.0004$$

$$m_t/m_0 = m_t^* = 0.1905 \pm 0.0001.$$

These values are in good agreement with those<sup>(7)</sup> reported earlier.

The density-of-states effective mass for one conduction band minimum is the geometric mean over the three axis. However, in silicon there are six minima and thus the density-of-states effective mass required in equation (1) must be the geometric mean averaged over the six minima, namely:

$$m_e^* = [6(m_l^* m_t^*)^2]^{1/3} \quad (2)$$

Using the results of HENSEL *et al.*<sup>(6)</sup>,  $m_e^* = 1.062$  at 4.2°K. This is the conduction band density-of-states effective mass generally quoted and used for silicon.

There is a substantial body of experimental data which indicates the electron effective mass to be dependent both on temperature and on donor density. In reviewing and comparing this work all values of effective mass will be converted to

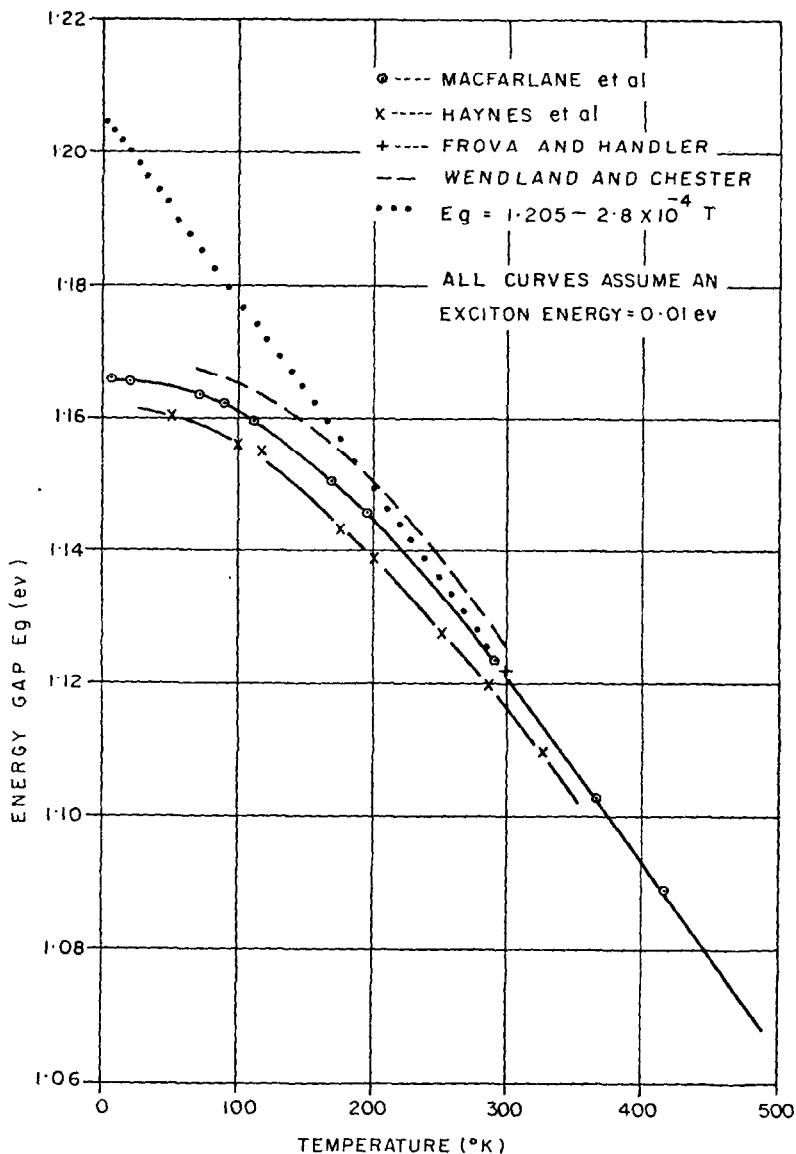


FIG. 1. Measured values of the silicon energy gap as a function of temperature assuming an exciton energy of 0.01 eV.

density-of-states effective mass averaged over six minima. In some papers conductivity effective mass,  $m_c^*$ , is reported. To convert this to density-of-states effective mass,  $m_l^*$  is assumed to be constant as indicated by the work of STRADLING and ZHUKOV<sup>(8)</sup> and the following expression is used

to obtain a value of  $m_l^*$  for use in equation (2):

$$\frac{1}{m_c^*} = \frac{1}{3} \left[ \frac{1}{m_l^*} + \frac{2}{m_t^*} \right]. \quad (3)$$

Magnetic susceptibility measurements by GEIST<sup>(9)</sup> on  $6 \times 10^{18} \text{ cm}^{-3}$  n-silicon and by SONDER

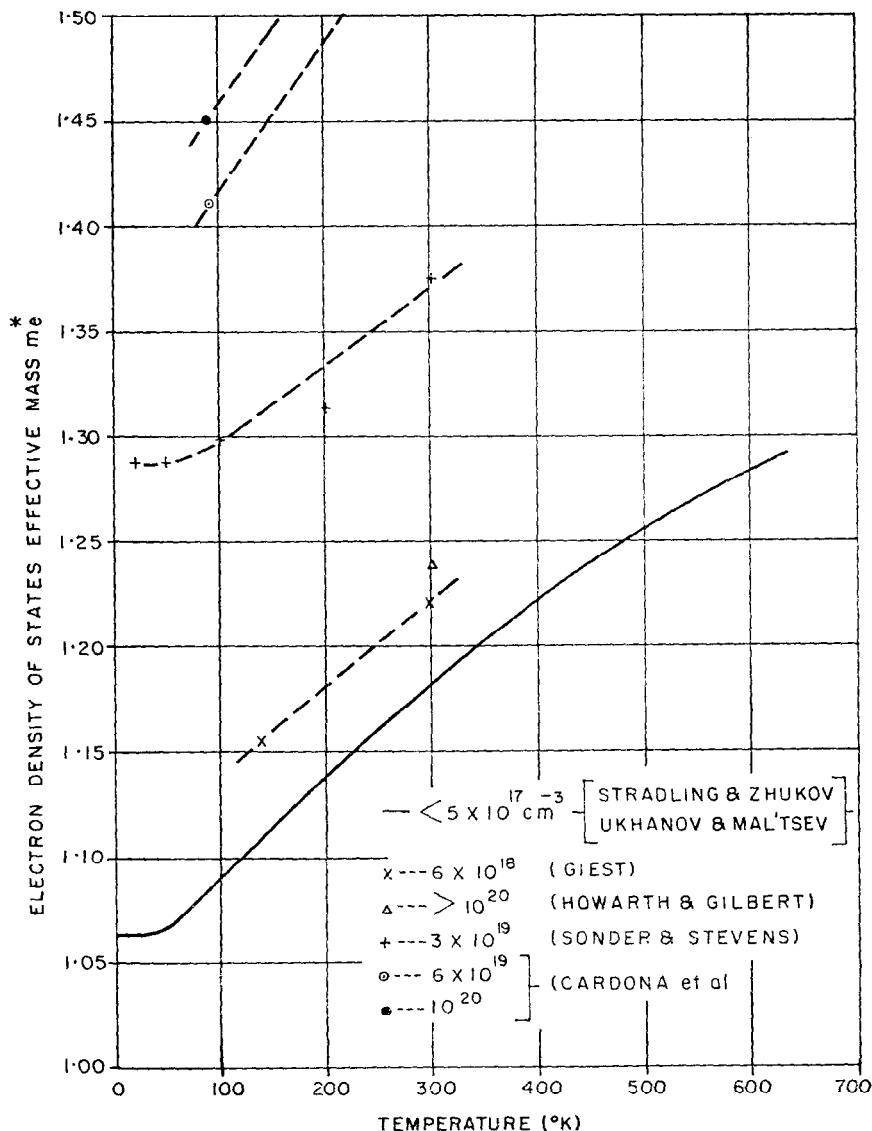


FIG. 2. Measured values of electron density-of-states effective mass in units of electron rest mass plotted as a function of temperature and illustrating the influence of donor density.

and STEVENS<sup>(10)</sup> on  $3 \times 10^{17}$  to  $3 \times 10^{19}$  n-silicon were the first experimental indications that electron effective mass was both temperature and donor-density dependent. The donor-density dependence received further confirmation in the specific heat measurements of KESOM and SEIDEL<sup>(11)</sup> performed on  $10^{19}$   $\text{cm}^{-3}$  n-silicon

below 4.2°K. Optical reflectivity measurements<sup>(12)</sup> on  $6 \times 10^{19}$  and  $1.1 \times 10^{20}$   $\text{cm}^{-3}$  n-silicon at 90 and 300°K indicated an increase in effective mass of 10 per cent with temperature and of 3 per cent with donor density. Similar measurements<sup>(13)</sup> (assumed at 300°K) on silicon having donor densities ranging from  $10^{19}$  to  $2 \times 10^{20}$   $\text{cm}^{-3}$

showed a trend involving an effective mass increase between 10 and 20 per cent. Piezoresistance studies<sup>(14)</sup> as a function of donor concentration were reported to indicate no donor-density dependence of effective mass. However, these experiments would not be sensitive to changes of the order of 10 per cent and if the ratio  $m_e^*/m_i^*$  varies with energy, as could be inferred from cyclotron resonance measurements,<sup>(8)</sup> then changes in  $m_e^*$  could be compensated in these observations and the experiment would be inconclusive.

Recent experiments by STRADLING and ZHUKOV<sup>(8)</sup> and by UKHANOV and MAL'STEV<sup>(15)</sup> have given convincing evidence for a temperature dependence of the electron effective mass. Stradling and Zhukov performed cyclotron resonance measurements on high purity silicon from 4 to 200°K. They found that  $m_i^*$  remained constant but that  $m_e^*$  increased with temperature for temperatures above 50°K. The constancy of effective mass below 50°K has also been indicated in high frequency magnetoconductivity experiments.<sup>(16)</sup> UKHANOV and MAL'STEV<sup>(15)</sup> performed Faraday rotation experiments on  $3.7 \times 10^{17} \text{ cm}^{-3}$  *n*-silicon over the temperature range 300–600°K and an increase of  $11 \pm 2$  per cent in effective mass was observed. Figure 2 shows the combined results of these two experiments as well as the results of the experiments on heavily doped silicon described earlier.

The above work indicates quite conclusively that the effective mass of electrons is temperature dependent. The evidence for donor-concentration dependence, also shown in Fig. 2, is variable and in some cases conflicting but most experiments have indicated an increase in effective mass for concentrations above  $10^{18} \text{ cm}^{-3}$ .

From simple considerations of the influences of temperature on band structure it can be shown that the temperature variation of effective mass shown in Fig. 2 is to be expected. Three mechanisms are primarily responsible for the temperature variation of effective mass.

- (a) The change of lattice spacing with temperature.
- (b) The temperature change of the Fermi-distribution function in a non-parabolic band.
- (c) The explicit temperature variation of the

band curvature due to the interaction between electrons and lattic vibrations.

The influence of the first two mechanisms can be estimated from measured properties. By using a method similar to that employed by CARDONA *et al.*<sup>(12)</sup> the variation of effective mass resulting from the change in lattice spacing can be calculated from the measured elastic constants<sup>(17)</sup>, thermal expansion<sup>(18)</sup> and stress dependence of the effective mass.<sup>(6)</sup> This results in a very small increase ( $\sim 0.2$  per cent) in effective mass between 0 and 300°K. STRADLING and ZHUKOV<sup>(8)</sup> have estimated the effect of non-parabolicity to be an increase of about 1.5 per cent up to 100°K. Linear extrapolation of this result indicates an increase in effective mass at 400°K of the order of 6 per cent. If it is assumed that the density-of-states near the band edges must vary in a manner sympathetic with the temperature variation of the energy gap, the explicit temperature variation causes an increase in effective mass of about 5 per cent for each band at 400°K. The combination of these three effects gives a result in reasonable agreement with the lower experimental curve of Fig. 2. Furthermore, because of the dominance of the explicit temperature variation and the relative temperature invariance of the energy gap for temperatures below 75°K, it is not surprising that the effective mass is essentially constant for temperatures below 50°K.

#### EFFECTIVE MASS OF HOLES

The valence band in silicon consists of two degenerate bands and a third band split off by 0.044 eV.<sup>(19)</sup> The two degenerate bands interact to distort the ideal spherical symmetry and the parabolic distribution upon which the energy invariance of effective mass is based. DRESSELHAUS *et al.*<sup>(20)</sup> have shown that warped valence band maximum in silicon can be described by the following energy-momentum relation:

$$E(k) = \frac{-h^2}{8m_0} \{ A k^2 \pm [B^2 k^2 + C^2 (k_x^2 k_y^2 + k_x^2 k_z^2 + k_y^2 k_z^2)]^{1/2} \} \quad (4)$$

where  $k = (k_x^2 + k_y^2 + k_z^2)^{1/2}$ . Later, LAX and MAVROIDES<sup>(21)</sup> derived the following expression for density-of-states effective masses of the two

degenerate bands from equation (4):

$$m_i^* = \frac{m_0}{A \pm B'} [1 + 0.0333\gamma_i + 0.01057\gamma_i^2 - 0.00018\gamma_i^3 - \dots] \quad (5)$$

where  $B' = (B^2 + C^2/6)^{1/2}$ ,  $\gamma = \pm C^2/2B'(A \pm B')$  and "i" indicates light or heavy holes corresponding to the use of the plus or minus sign in the expression.

Cyclotron resonance measurements at 4°K are used to obtain values of the reciprocal mass constants  $A$ ,  $B$  and  $C$ . The following values obtained by HENSEL and FEHER<sup>(22)</sup> and corrected by BALSLEV and LAWAETZ<sup>(23)</sup> purport to be more accurate than previously reported values and are in reasonable agreement with those calculated by the  $k \cdot \vec{p}$  method.<sup>(24)</sup>

$$|A| = 4.27 \pm 0.02, \quad |B| = 0.63 \pm 0.08$$

and  $|C| = 4.93 \pm 0.15$ .

Using these values in equation (5)

$$m_1^* = 0.537 \quad \text{and} \quad m_2^* = 0.153$$

where  $m_2^*$  indicates the 4.2°K value of  $m_2^*$ .

The combined density-of-states effective mass is:

$$m_{12}^* = [(m_1^*)^{3/2} + (m_2^*)^{3/2}]^{2/3}$$

thus using the above values of  $m_1^*$  and  $m_2^*$

$$m_{12}^* = 0.591.$$

This is the valence band density-of-states effective mass generally quoted and used for silicon. However, since the same three factors which give rise to a temperature effect in the conduction band also affect the valence band, this value of effective mass can only be considered to apply in the region of 4.2°K. At higher temperatures the influence of these factors must be examined.

The effect of lattice expansion on hole effective mass can again be considered negligible but the non-parabolicity of the valence band has a large effect. To estimate this effect the measured effective masses of the doubly degenerate bands are considered to represent spherically symmetric bands where the constant energy surfaces are distributed in the manner indicated by  $k \cdot \vec{p}$  band structure calculations.<sup>(1,24)</sup> Furthermore, the effects of the third band must also be included since the occupation of this band will not be negligible if the spin-orbit splitting,  $\Delta$ , is comparable or less than

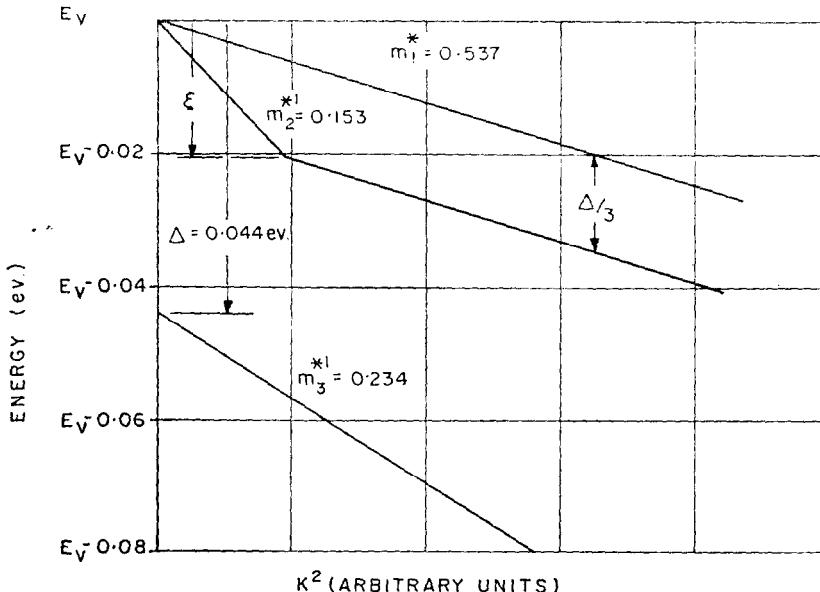


FIG. 3. The simplified valence band structure of silicon based on KANE'S<sup>(1)</sup> valence band calculations and measured properties of the valence band.

$kT$ . In silicon the effective mass of the third band  $m_3^{*'} = 1/A = 0.234$  and the spin orbit splitting  $\Delta = 0.044$  eV.<sup>(19)</sup> The band structure to be considered is illustrated in Fig. 3.

From Fig. 3 it is clear that the first band can be considered to be parabolically distributed in  $k$ -space and thus  $m_1^*$  is a constant. The second band, however, has an energy varying effective mass and in the general case can only be described

in terms of partial Fermi-Dirac integrals.

$$(m_2^*)^{3/2} = \frac{(m_2^{*'})^{3/2}}{F_{1/2}(\eta)} \int_0^{\xi/kT} \frac{\epsilon^{1/2} d\epsilon}{1 + \exp(\epsilon - \eta)} + \frac{(m_1^*)^{3/2}}{F_{1/2}(\eta)} \int_{\xi/kT}^{\infty} \frac{\epsilon_1^{1/2} d\epsilon_1}{1 + \exp(\epsilon_1 - \eta_1)} \quad (6)$$

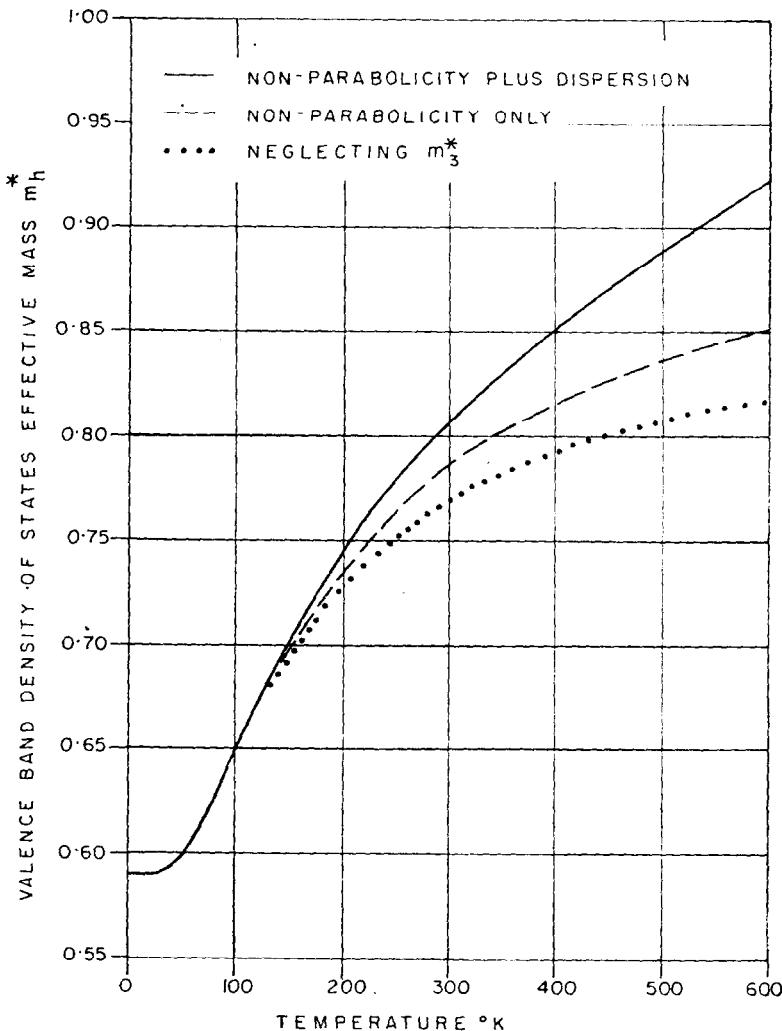


FIG. 4. Temperature dependence of the density-of-states effective mass of holes in units of electron rest mass calculated from the valence band structure of Fig. 3 (dashed line) and corrected for the explicit temperature dependence of the density-of-states (solid line). The contribution of  $m_3^*$  is subtracted in the dotted curve.

where  $\epsilon$  is energy in units of  $kT$  measured from the top of the valence band,  $\epsilon_1 = \epsilon - \Delta/3kT$ ,  $\zeta = \xi - \Delta/3$ ,  $\eta$  is the Fermi level,  $\eta_1 = \eta - \Delta/3kT$ ,  $F_{1/2}(\eta)$  is the Fermi-Dirac integral and the parameters  $\xi$  and  $\Delta$  are defined in Fig. 3.

Because the split-off band is displaced in energy, the apparent density-of-states effective mass at the top of the valence band is a function of temperature although the band itself is parabolically distributed.

$$(m_3^*)^{3/2} = \frac{(m_3^*)^{3/2}}{F_{1/2}(\eta)} \int_0^{\infty} \frac{\epsilon_2^{1/2} d\epsilon_2}{1 + \exp(\epsilon_2 - \eta_2)} \quad (7)$$

where  $\epsilon_2 = \epsilon - \Delta/kT$  and  $\eta_2 = \eta - \Delta/kT$ . In the case where  $\eta_2 \gg kT$  the ratio of the two Fermi-Dirac integrals in equation (7) reduces to a simple Boltzmann factor,  $\exp(\Delta/kT)$ .

The complete density-of-states effective mass,

$$m_h^* = [(m_1^*)^{3/2} + (m_2^*)^{3/2} + (m_3^*)^{3/2}]^{2/3}, \quad (8)$$

is obviously a complex function of temperature and of Fermi level or doping density. However, one further correction must still be applied. The explicit temperature variation can be estimated by assuming that the density-of-states is inversely

proportional to the energy gap. Thus  $(m_h^*)^{3/2} \propto Eg_0/Eg$ , where  $Eg_0$  is the energy gap at 0°K.

Equations (6), (7) and (8) have been evaluated numerically as a function of temperature and doping density and corrected for the explicit temperature dispersion. Figure 4 shows the variation of equation (8) with temperature and demonstrates the relative importance of the split-off band and temperature dispersion. It is clear that although the effects of the light hole band ( $m_2^*$ ) dominate the temperature dependence, the effect of the split-off band ( $m_3^*$ ) is not negligible even at 200°K. Figure 5 shows the variation of equation (8) with doping density and temperature. All values are corrected for temperature dispersion. Even at 0°K the effect of the split-off band is shown to be significant for concentrations in excess of  $3 \times 10^{19}$ . For higher temperatures its contribution becomes significant at lower concentrations and, as already stated, above 200°K it cannot be neglected for any concentration.

There is, as in the case of *n*-silicon, some experimental evidence which suggests that the effective mass of holes is temperature and acceptor-density dependent. CARDONA *et al.*<sup>(12)</sup> found an increase of about 12 per cent in optical effective mass

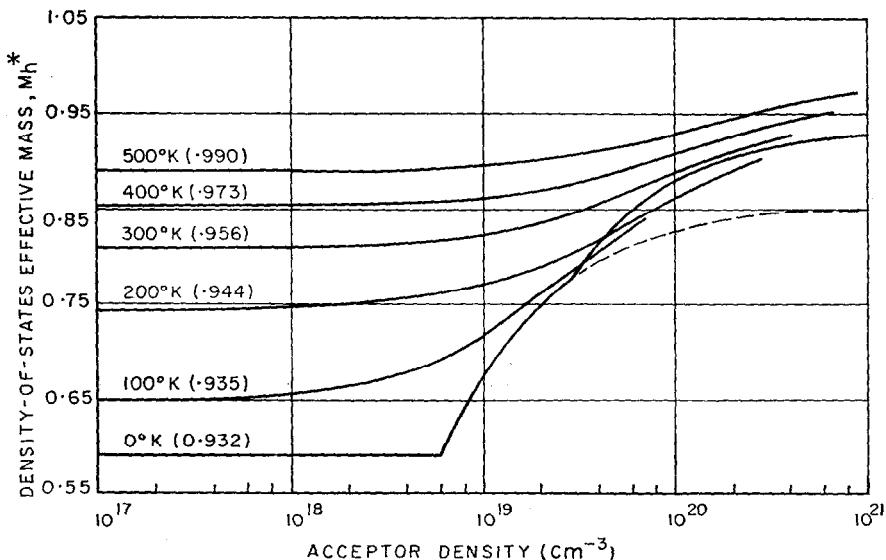


FIG. 5. The acceptor-density dependence of the density-of-states effective mass of holes as a function of temperature, calculated from the band structure of Fig. 3. Limiting values are bracketed.

between 90 and 300°K in heavily doped *p*-silicon. Since the influence of non-parabolicity on the temperature dependence of effective mass is reduced in degenerate material, this observation would appear to be in line with the expected temperature variation. GEIST<sup>(9)</sup> reported observations of a larger effective mass at 138°K than at 300°K in  $10^{19} \text{ cm}^{-3}$  *p*-silicon. However, since both values of effective mass were higher than the expected limit for degenerate material, some doubt is cast on these results. KEESEM and SEIDEL<sup>(11)</sup> measured the 0°K density-of-states effective mass to be 0.81 in  $4 \times 10^{19} \text{ cm}^{-3}$  *p*-silicon. A value of 0.815 is calculated for the same material using the band

structure of Fig. 3. Such close agreement with the measured value is probably fortuitous but it does support the use of calculations based on the simplified band structure illustrated in Fig. 3.

#### INTRINSIC CARRIER CONCENTRATION

Accurate measurements of the intrinsic carrier concentration in silicon were first reported by MORIN and MAITA<sup>(25)</sup> in 1954. They measured the Hall effect and the conductivity of *p* and *n* Czochralski-grown silicon from 10 to 1100°K. The purest material contained impurities in excess of  $2 \times 10^{14} \text{ cm}^{-3}$  and was suspected to contain *p-n* junctions, possibly as a result of oxygen conversion. From

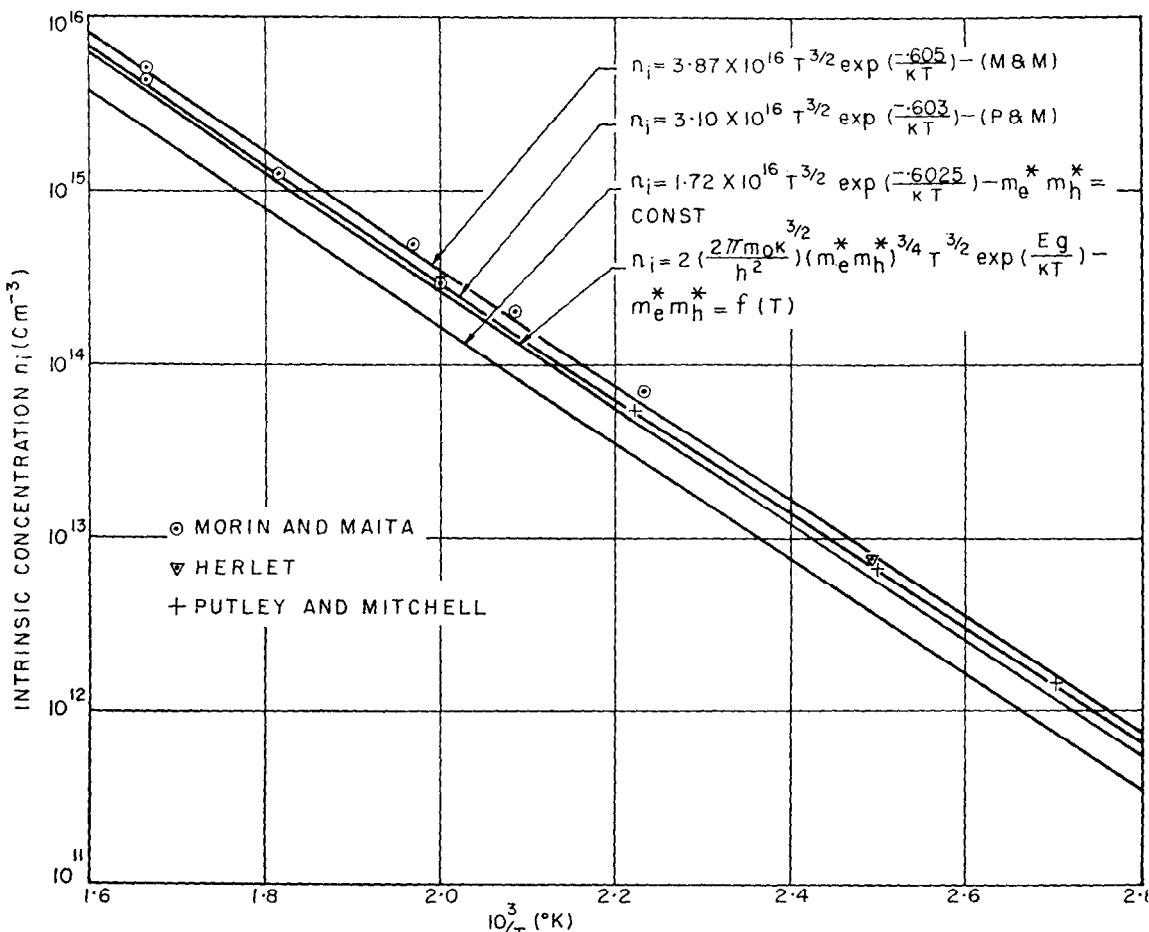


FIG. 6. Experimentally determined values of intrinsic concentration compared to those calculated from theory using the temperature dependent effective masses of Figs. 2 and 4, the energy gap measured by MACFARLANE *et al.*<sup>(2)</sup> and an exciton energy of 0.007 eV.

in these measurements the intrinsic concentration down to 450°K was calculated and below 700°K was accurately described by the expression

$$n_i = 3.88 \times 10^{16} T^{3/2} \exp(-0.605/kT). \quad (9)$$

HERLET<sup>(26)</sup> used the forward characteristics of *p-n* junctions to extend the measurements of  $n_i$  down to 250°K. These results were also fitted by equation (9) but since they relied upon the separate determination of other junction parameters they were accurate only to  $\pm 20$  per cent.

In 1958 PUTLEY and MITCHELL<sup>(27)</sup> reported measurements of Hall effect and conductivity from 20 to 500°K on very pure ( $\sim 10^{13} \text{ cm}^{-3}$ ), oxygen-free silicon. The values of  $n_i$  obtained are plotted, with those reported by Morin and Maita and by Herlet, in Fig. 6 and are accurately described by the expression:

$$n_i = 3.10 \times 10^{16} T^{3/2} \exp(-0.603/kT). \quad (10)$$

These measurements were estimated to contain an experimental error of less than 5 per cent and, therefore, agree within experimental error with those of Herlet. However, the difference of 25 per cent between these results and those reported by Morin and Maita is not easily explained in terms of experimental error. Since the measurements of Morin and Maita were performed on much more doubtful materials, the results reported by Putley and Mitchell must be considered the most reliable.

When an exciton energy of 0.01 eV is added to the energy gap values reported by MACFARLANE *et al.*,<sup>(2)</sup> the energy gap,  $Eg = 1.205 - (2.8 \times 10^{-4})T$  for temperatures above 300°K. If this expression is used in equation (1) together with the 4.2°K effective mass values

$$n_i = 1.72 \times 10^{16} T^{3/2} \exp(-0.6025/kT). \quad (11)$$

This is obviously in poor agreement with the experimental expressions, equations (9) and (10).

If the effective masses shown in Figs. 2 and 4 are used in conjunction with the values of energy gap reported by Macfarlane *et al.* and an exciton energy of 0.007 eV is assumed, equation (1) yields values of  $n_i$  having an average disagreement of  $\sim 14$  per cent with Putley and Mitchell's measured values. Figure 6 compares these calculated values of  $n_i$  with the measured values and with values computed from equations (9), (10) and (11).

Because the interpretation of Hall measurements depends on a knowledge of the dominant scattering processes and these are not completely understood in silicon, the experimental values of  $n_i$  suffer from an uncertainty not due solely to experimental error. The overall uncertainty in the results of Putley and Mitchell is estimated to be in the region of 15 per cent. When temperature dependent effective masses are employed in equation (1) the agreement is within these limits. Of course, the calculated values themselves suffer from an uncertainty due to the inaccuracies in  $m_e^*$ ,  $m_h^*$  and  $Eg$ . The calculations already described lead one to believe that  $m_e^*$  as shown in Fig. 2 is accurate to 5 per cent while  $m_h^*$  as shown in Fig. 4 is accurate to 10 per cent. These coupled with the uncertainty in  $Eg$  lead to an overall uncertainty of about 30 per cent in the calculated values of  $n_i$ . On this basis the calculated values must be considered to give the correct temperature dependence for  $n_i$  at temperatures below 300°K where  $Eg$  and  $(m_e^* m_h^*)$  are both non-linear functions of temperature. However, the measured values of Putley and Mitchell must be considered to give a more accurate magnitude for  $n_i$ . If  $n_i$  is calculated from equation (1) assuming an exciton energy of zero, the values are almost identical with those measured by Putley and Mitchell. With this adjustment values of  $n_i$  can be calculated for temperatures lower than 300°K with a degree of confidence not previously possible. Figure 7 shows the calculated values of  $n_i$  between 700 and 230°K and compares them to measured values in this region.

#### CARRIER TRANSPORT

Having obtained consistent evidence for agreement between theory and experiment both in the temperature dependence of effective masses and in their influence on the density-of-states, it is logical to examine the influence of effective mass variation on carrier transport. In the region between 100 and 300°K where lattice scattering is dominant, the Hall mobility in pure silicon is<sup>(27)</sup>

$$\mu_{Hn} = 1.2 \times 10^8 T^{-2.0} \text{ cm}^2/\text{V-sec}$$

$$\mu_{Hp} = 2.9 \times 10^9 T^{-2.7} \text{ cm}^2/\text{V-sec}.$$

Since acoustic lattice scattering is expected to give a  $T^{-1.5}$  temperature dependence of mobility, other factors obviously influence carrier scattering

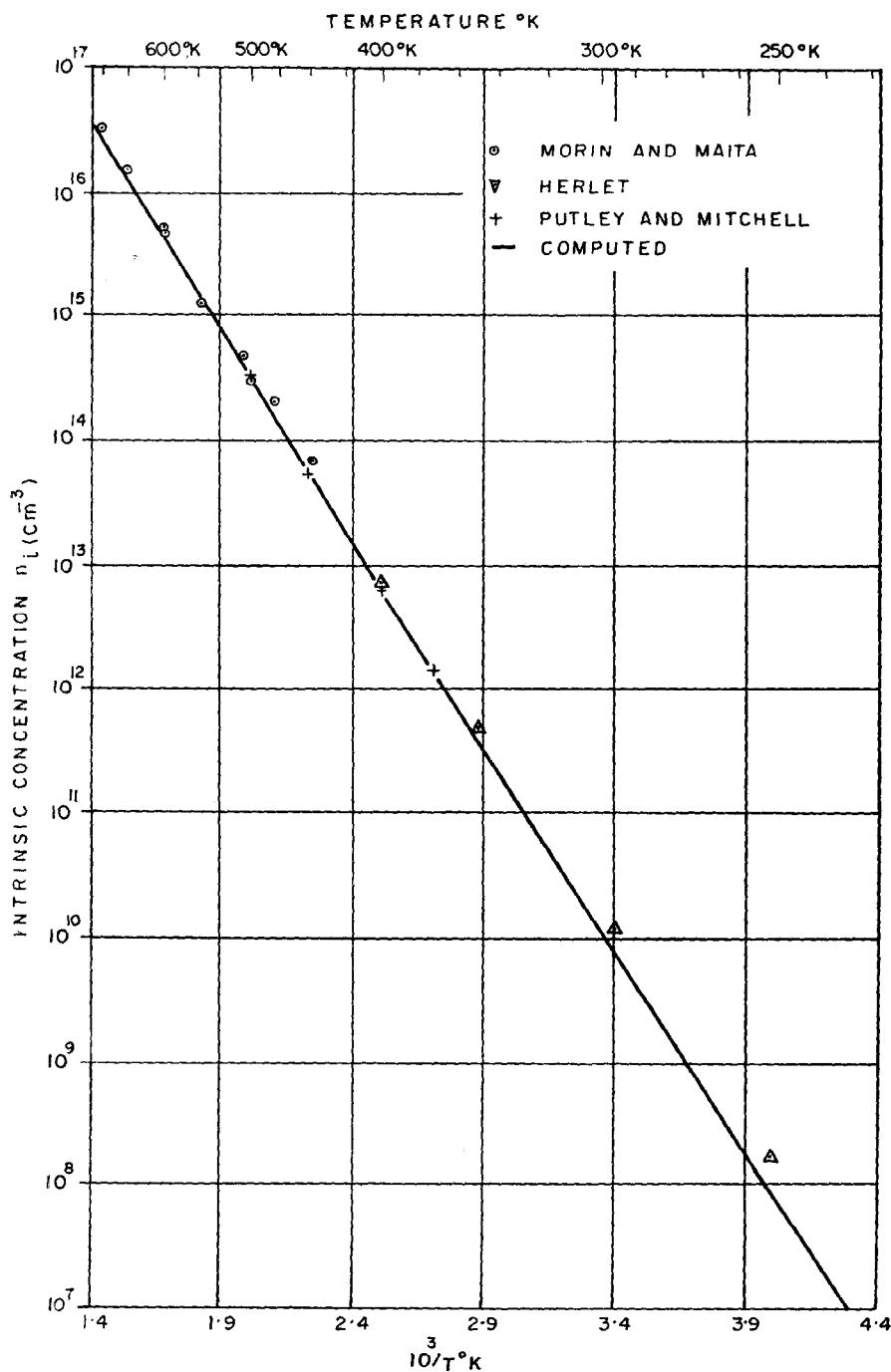


FIG. 7. Intrinsic concentration in silicon between 230 and 700°K calculated assuming  $E_{\text{ex}} = 0$  and compared to experimental measurements.

in silicon. Two factors have been suggested<sup>(28)</sup> to account for this difference.

- (a) The added influence of optical mode and intervalley scattering.
- (b) Effective mass variations due to a non-ideal band structure.

The effective mass variations presented earlier can be used to determine the effects of the latter and to deduce the approximate temperature dependence of the relaxation times.

$$\tau_n \propto T^{-1.8}$$

$$\tau_p \propto T^{-2.1}$$

These give a more realistic indication of the influences of intervalley scattering on electrons and of optical mode scattering on holes.

### CONCLUSION

The consideration of experimental and theoretical data on silicon band structure has shown that the effective masses in silicon are temperature and carrier-concentration dependent. For electron or hole concentrations less than  $10^{18} \text{ cm}^{-3}$  the latter is negligible and the effective masses at any temperature below 600°K are given in Figs. 2 and 4. For carrier concentrations above  $10^{18} \text{ cm}^{-3}$  valence band effective masses are given in Fig. 5 but less is known about the behaviour of the conduction band.

When temperature-dependent effective masses are employed, theoretical values of intrinsic concentration agree with the experimental values and, therefore, the low temperature values shown in Fig. 7 can be used with a degree of confidence not previously possible. It is interesting to note that, because of the compensating effects of the temperature varying effective masses and the non-linearity in the temperature variation of the energy gap, the expression for  $n_i$  derived by Putley and Mitchell [equation (10)] can be extrapolated down to 200°K with less than 6 per cent departure from the theoretical values.

### ADDED NOTE

Recent measurements<sup>(29)</sup> by infrared plasma reflection have indicated increasing effective masses for both holes and electrons with increasing concentration.

A calculation of effective mass change with lattice spacing using the pressure dependence of the energy gap<sup>(30)</sup> indicates a small decrease (~0.1 per cent) in effective mass between 0 and 400°K. This agrees in magnitude but not in sign with that calculated from the stress-dependence of effective mass. The important point here is that both approaches indicate the effect to be small.

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