IOPscience iopscience.iop.org

Home Search Collections Journals About Contact us My IOPscience

Optical absorption measurements of band-gap shrinkage in moderately and heavily doped silicon

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1991 J. Phys.: Condens. Matter 3 8213

(http://iopscience.iop.org/0953-8984/3/42/016)

View the table of contents for this issue, or go to the journal homepage for more

Download details:
IP Address: 171.66.16.159
The article was downloaded on 12/05/2010 at 10:36

Please note that terms and conditions apply.

J. Phys.: Condens. Matter 3 (1991) 8213–8223. Printed in the UK

Optical absorption measurements of band-gap shrinkage in moderately and heavily doped silicon

S E Aw, H S Tan and C K Ong
Department of Physics, National University of Singapore, Kent Ridge, Singapore 0511

Received 4 March 1991, in final form 28 May 1991

Abstract. Optical absorption studies in the infra-red region around the fundamental energy gap have been carried out on both n- and p-Si samples in the range of concentrations from $3 \times 10^{14}\,cm^{-3}$ to $7.3 \times 10^{18}\,cm^{-3}$ for p-Si and from $6.5 \times 10^{16}\,cm^{-3}$ to $9.2 \times 10^{18}\,cm^{-3}$ for n-Si at room temperature (294 K). The transmission ratios were first measured for each sample in the range of wavelengths from about 0.9 μm to 2.5 μm. These ratios were then applied to calculate the reflectivity and the absorption coefficients for the samples. After correcting for free-carrier absorption, the band-gap shrinkage was then determined from the absorption coefficients for each sample. These results were then compared with those determined from other optical absorption studies, with those found by electrical device measurements and with those predicted from theories. It was found that even well below $3 \times 10^{18}\,cm^{-3}$, a reduction in band-gap energy ΔE_g could be determined for both n- and p-Si, in contrast to the earlier optical absorption studies which reported that none could be detected. Between $10^{18}\,cm^{-3}$ and $10^{19}\,cm^{-3}$ our experimental values are consistent with those determined by other optical absorption studies. Our results also show that even in the moderately doped regime, our values of $|\Delta E_g|$ are less than those found by electrical device measurements and those predicted by various recent theories. This is consistent with the findings of the other optical studies in the heavily doped regime. We also found that the gap shrinkage $|\Delta E_g|$ depends on the dopant concentration as $N^{1/3}$. This is in agreement with the experimental results of Wagner and Vol'fson and Subashiev as well as with the theoretical results of Mahan and Berggren and Sernelius.

1. Introduction

The phenomenon of band-gap narrowing of heavily doped silicon has been the subject of a number of intensive studies [1–17]. Theoretical considerations have suggested that at high dopant concentrations, the broadening of the impurity band and the formation of band-tails on the edges of the conduction and valence bands would lead to a reduction in the band gap of a semiconductor. This reduction in band-gap has an important significance in the determination of current–voltage characteristics of p–n junctions and the electroluminescent recombination radiation. Furthermore, a change in band-gap energy has a strong influence on the highest emitter efficiency that may be obtained for the highly-doped emitter region of a solar cell or a bipolar transistor.

Being one of the most important semiconductors in application, silicon has always enjoyed a great amount of attention in research. Not surprisingly, a large number of theoretical calculations on the reduction of the Si band gap as a result of heavy doping

have been performed [2–6]. In addition, the many experimental studies on the band-gap shrinkage performed in recent years are usually based on one of the following methods.

(*a*) Electrical measurements on bipolar transistors [7–9];
(*b*) low-temperature photoluminescence and excitation spectroscopy [10–14];
(*c*) optical absorption measurements [15–17].

Several papers and reviews [1, 4–6] have noted the discrepancies in the gap shrinkages obtained by the different experimental methods. The gap shrinkages ΔE_g determined from electrical measurements on bipolar transistors are much larger than those obtained by optical absorption measurements; while the results from photoluminescence experiments are generally higher than the values obtained by optical absorption measurements at low temperatures; yet are lower than those obtained by electrical device measurements. The determination of the gap shrinkage by optical absorption and by photoluminescence is more direct than that by electrical device measurements. Also, one may have some reservations concerning the accuracy of the results obtained by the electrical method because of the difficulties involved in the interpretation of such measurements. In device measurements, it has been assumed that the minority carrier mobility in the base is equal to the majority carrier mobility in the emitter region. (In fact, because of band-tailing at the minority band edge, the minority carrier mobility is probably smaller in the minority band.) This assumption has the effect of reducing the influence of the minority band tail on the gap, and narrowing results. It has also been assumed that the temperature dependence of carrier mobilities is the same in both n- and p-Si. This assumption is true only for low impurity concentrations such as $N < 10^{17}\ \mathrm{cm}^{-3}$. As the experiments are usually interpreted in terms of the Boltzmann statistics instead of the Fermi–Dirac statistics, the effects of degeneracy will be wrongly ascribed as a contribution to the narrowing of the band gap. These assumptions probably explain why the data of ΔE_g obtained from device measurements are generally much larger than those obtained from absorption measurements.

We have noted that, in the past, low-temperature photoluminescence and optical absorption measurements on the reduction of the Si band gap tended to focus on samples with impurity concentrations at and above $10^{18}\ \mathrm{cm}^{-3}$. This is partly because no gap shrinkage was detected below this concentration. For example, Vol'fson and Subashiev [15] could not detect any shift in the band-gap energy for concentrations below $10^{19}\ \mathrm{cm}^{-3}$ and Schmid [17] found only a shrinkage of 1.2 meV at a concentration of $2.8 \times 10^{18}\ \mathrm{cm}^{-3}$ for p-Si. Below this concentration, no gap shrinkage could be determined. However, on the other hand, from electrical device measurements, a gap shrinkage of 58 meV at a concentration of $2 \times 10^{18}\ \mathrm{cm}^{-3}$ was reported by Slotboom and de Graaff [7]. They also found a gap reduction of up to 20 meV for a concentration as low as $3 \times 10^{17}\ \mathrm{cm}^{-3}$. A similar result was also reported by Wieder [8]. Thus, it is the objective of the present work to investigate by optical absorption measurements whether there is any band-gap shrinkage in the range $1.5 \times 10^{16}\ \mathrm{cm}^{-3}$ to about $10^{18}\ \mathrm{cm}^{-3}$ for both n- and p-Si, and to determine their values if any. For concentrations from $10^{18}\ \mathrm{cm}^{-3}$ to about $10^{19}\ \mathrm{cm}^{-3}$, the reduction in band gap would be determined and compared with the data available in the literature.

2. Experimental details

Our samples were cut from commercially supplied n- or p-type single-crystal Si wafers. The carrier concentrations of the samples were determined from the resistivities

Table 1. The samples and their parameters.

Sample	Concentration (cm^{-3})	Dopant	Crystal orientation	Thickness (μm)
P1a	3.0×10^{14}	B	100	90 ± 5
P1b	3.0×10^{14}	B	100	150
P1c	3.0×10^{14}	B	100	265
P2	1.5×10^{16}	B	111	135
P3	3.3×10^{17}	B	111	120
P4	1.2×10^{18}	B	111	155
P5	7.3×10^{18}	B	111	115
N1	6.5×10^{16}	Sb	111	100
N2a	1.6×10^{18}	P	100	45
N2b	1.6×10^{18}	P	100	125
N2c	1.6×10^{18}	P	100	270
N3	6.4×10^{18}	P	111	80
N4	9.2×10^{18}	Sb	111	130

measured by the standard four-point probe technique. The samples were then lapped and polished mechanically to the required thicknesses. The polishing process was accomplished in several stages until the surfaces appeared mirror-like. The polishing compound (alumina) used in the final polish had a grain-size of 0.1 μm. The samples were then etched with a CP4 mixture of acetic, nitric and hydrofluoric acids in the following volume ratio: 5 (volume of 100% acetic acid); 3 (volume of 65% nitric acid); 3 (volume of 10% hydrofluoric acid). We chose to determine the sample surface reflectivity R at two particular dopant concentrations of 3.0×10^{14} cm^{-3} (p-type) and 1.6×10^{18} cm^{-3} (n-type) respectively. For each concentration, three samples of different thicknesses were prepared for this purpose. The samples and their parameters are listed in table 1.

The absorption measurements were performed with a Hilger and Watt infra-red monochromator. A lead sulphide photo-resistive cell was used as the detector. Its spectral response range covers 0.5 to 3 μm with maximum detectivity at 2.1 μm. The signal-to-noise ratio from the detector was enhanced with a lock-in-amplifier. The spectrometer was calibrated with the known near-infra red and visible-red emission lines of mercury, sodium and helium light sources; ranged from 0.69 to 2.06 μm.

The transmission measurements were performed at room temperature (294 K) by means of the usual sample-in sample-out technique. The transmission percentage for each wavelength was calculated and plotted against wavelength for all the samples. The percentage error in the measurements was less than 0.5%.

3. Data analysis

The equation used to calculate the reflectivity R and the absorption coefficient α in this work is [18]

$$T = \frac{(1 - R)^2 \, e^{-\alpha d}}{1 - R^2 \, e^{-2\alpha d}} \tag{1}$$

where T is the transmission ratio and d the thickness of the plane parallel-sided sample.

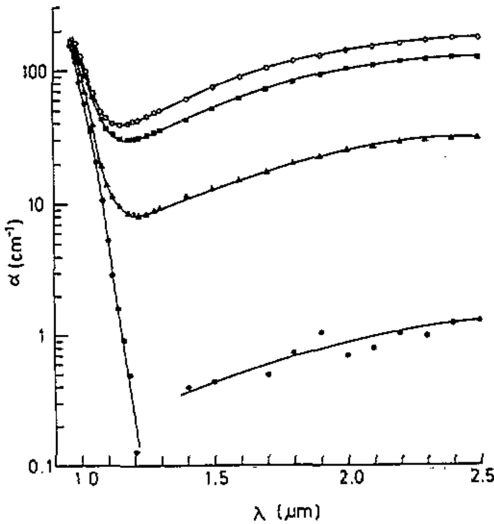

Figure 1. The absorption curves for n-Si samples at 294 K. (●) $6.5 \times 10^{16}\,cm^{-3}$; (▲) $1.6 \times 10^{17}\,cm^{-3}$; (■) $6.4 \times 10^{18}\,cm^{-3}$; (○) $9.2 \times 10^{18}\,cm^{-3}$.

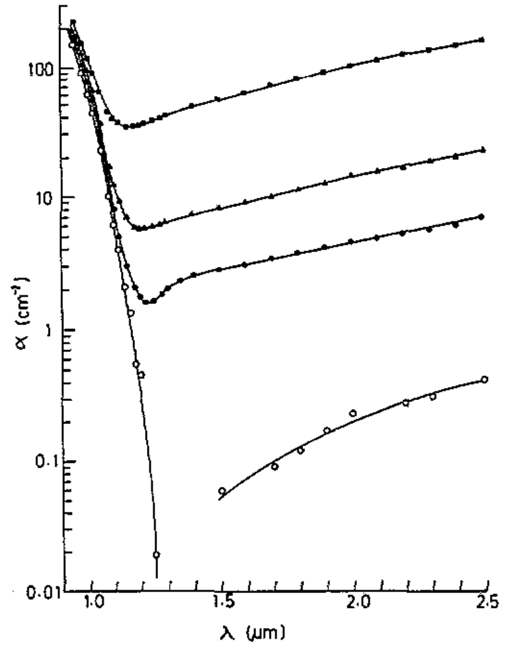

Figure 2. The absorption curves for p-Si samples at 294 K. (○) $1.5 \times 10^{16}\,cm^{-3}$; (●) $3.3 \times 10^{17}\,cm^{-3}$; (▲) $1.2 \times 10^{18}\,cm^{-3}$; (■) $7.3 \times 10^{18}\,cm^{-3}$.

The equation takes into account the infinite multiple internal reflections within the sample. By rearranging the equation into the form

$$\alpha = \frac{1}{d} \ln \left[\frac{(1-R)^2 + [(1-R)^4 + (2RT)^2)^{1/2}}{2T} \right] \tag{2}$$

and by considering the transmission ratios at the same wavelength for two specimens of different thicknesses, R and α are calculated simultaneously. The values of R for wavelengths ranging from 0.9 to 2.5 μm for a very lightly doped p-type sample ($N_A = 3.0 \times 10^{14}\,cm^{-3}$) and for a heavily doped n-type sample ($N_D = 1.6 \times 10^{18}\,cm^{-3}$) are separately determined. For the very lightly doped sample P1, R ranges from 0.32 at 0.9 μm to 0.25 at 2.5 μm. The R values of the heavily doped sample N2 are somewhat larger and ranges from 0.33 at 0.9 μm to 0.27 at 2.5 μm. Within the experimental uncertainty of ± 0.02, the R values we obtained are in satisfactory agreement with those reported earlier [19, 20] and those calculated from the refractive indices [21].

As the reflectivity values obtained from the transmission measurements on the N2 samples are closer to those found by other workers and since most of the samples studied in the present work are relatively heavily doped, the reflectivity values of the N2 sample were used to calculate the absorption coefficient α for all the other samples except the P2 sample because of its rather low dopant concentration ($1.5 \times 10^{16}\,cm^{-3}$). For this sample, the reflectivity values found for the P1 sample were used.

The absorption coefficients for the n- and p-Si samples are shown in figure 1 and figure 2 respectively. It can be seen from the absorption curves that at the fundamental absorption edge (corresponding to λ of about 1.2 μm) the absorption rises steeply.

At longer wavelengths the absorption is entirely due to free carriers. To obtain the fundamental absorption for a given sample, it is necessary to subtract the free-carrier absorption from the total absorption. This is done by extrapolating the free-carrier absorption curve to wavelengths below 1.2 μm and then subtracting the free-carrier absorption from the total absorption.

For an indirect-gap semiconductor such as Si, the fundamental absorption is phonon assisted. For pure Si the absorption coefficient may be written as

$$\alpha = A^2 \left[\frac{(\hbar\omega - E_g + \hbar\omega_p)^2}{\exp(\hbar\omega_p/kT) - 1} + \frac{(\hbar\omega - E_g - \hbar\omega_p)^2}{1 - \exp(-\hbar\omega_p/kT)}\right] \tag{3}$$

where $\hbar\omega$ and $\hbar\omega_p$ are the photon and phonon energies respectively, E_g the indirect-gap energy and A^2 a constant which depends on the density-of-states, effective mass and temperature. The first term concerns a phonon absorption and the second term a phonon emission assuming single-phonon processes. In general, both longitudinal and transverse acoustic modes as well as optical modes should be accounted for [22], in which case the fundamental absorption coefficient is

$$\alpha = \alpha_{el} + \alpha_{al} + \alpha_{et} + \alpha_{at} \tag{4}$$

where e represents phonon emission, a represents phonon absorption and l and t represent longitudinal and transverse modes respectively. However, even at room temperature (294 K), we expect that, being lowest in energy, the 18 meV longitudinal acoustic (LA) phonon would be the dominating phonon involved in the absorption process. Furthermore, even if the phonons from other branches are also contributing partially towards the absorption process, the resultant effect will only be a slight modification to all our measured values of E_g by a more or less constant amount. Hence, on cancellation, it will have practically no effect on the values of band-gap shrinkage, ΔE_g, to be determined. We also assume that when $\hbar\omega > E_g + \hbar\omega_p$, the absorption is dominated by the phonon emission process. Hence from (3) it is observed that a plot of $\alpha^{1/2}$ versus $\hbar\omega$ should yield a linear relation with an intercept of $(E_g + \hbar\omega_p)$ at zero absorption.

For a doped semiconductor the absorption coefficient due to phonon emission process is given by [17]

$$\alpha = \frac{8A^2}{\pi}\frac{\xi^2}{1-\exp(-\hbar\omega_p/kT)}\int_0^1 \frac{x^{1/2}(1-x)^{1/2}}{1+\exp[(E_F - \xi x)/kT]}\,dx \tag{5}$$

where $\xi = \hbar\omega - E_g - \hbar\omega_p$ and E_F is the Fermi level measured from the band edges. In the case of a heavily doped semiconductor, the states near the extrema of the band (conduction band for n-type; valence band for p-type) would be occupied. This has the effect of increasing the minimum energy required to transfer an electron from the valence band to an unoccupied state in the conduction band. Such an effect is known as Moss–Burstein's Shift [23, 24] and its influence in our attempt to determine E_g from the absorption data has been included in (5) [25].

In order to make use of (5), it was necessary to calculate the Fermi level energy for each sample by either of the following equations:

$$E_F - E_C = kT\ln(N_D/N_C) \qquad \text{n-Si samples} \tag{6a}$$

$$E_F - E_V = kT\ln(N_A/N_V) \qquad \text{p-Si samples} \tag{6b}$$

where E_C, N_C are the energy and density of states of the conduction band edge and E_V,

Table 2. The band gap (E_g) and gap shrinkage ($-\Delta E_g$) of our samples.

Dopant	Concentration (cm^{-3})	$-E_F$ (meV)	[Curve fitted] E_g (eV)	[Curve fitted] $-\Delta E_g$ (meV)	[Intercepts] E_g (eV)	[Intercepts] $-\Delta E_g$ (meV)
p-type	3.0×10^{14}	265	1.103	—	1.105	—
	1.5×10^{16}	166	1.103	~0	1.105	~0
	3.3×10^{17}	86.7	1.096	7	1.098	7
	1.2×10^{18}	53.8	1.091	12	1.094	11
	7.3×10^{18}	7.9	1.083	19	1.086	19
n-type	6.5×10^{16}	154	1.100	3	1.101	4
	1.6×10^{18}	72.5	1.091	12	1.094	11
	6.4×10^{18}	37.2	1.086	17	1.087	18
	9.2×10^{18}	27.9	1.080	23	1.083	22

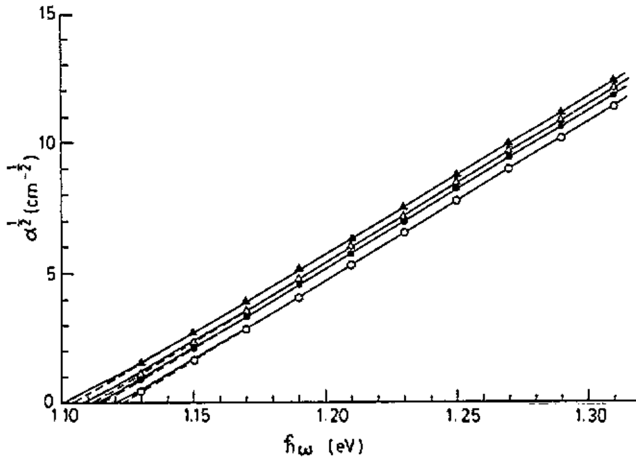

Figure 3. Graphs of $\alpha^{1/2}$ versus photon energy $\hbar\omega$ for p-Si samples. (○) 3.0×10^{14} cm^{-3}; (●) 3.3×10^{17} cm^{-3}; (△) 1.2×10^{18} cm^{-3}; (▲) 7.3×10^{18} cm^{-3}. The solid lines are the fitted curves using (5). The broken lines are extrapolated from the linear parts of the graphs.

N_V are the corresponding quantities of the valence band edge. N_D, N_A are donor and acceptor concentrations respectively. Since the Fermi level in (5) is measured with respect to the band edges, we have $E_C = 0$ and $E_V = 0$ for (6). The values of E_F thus calculated are listed in table 2.

We then determine the values of A^2 in (5) from the gradient of the linear portion of the graph of $\alpha^{1/2}$ versus $\hbar\omega$ for the purest sample (P1 with $N_A = 3.0 \times 10^{14}$ cm^{-3}) in this work. The experimental absorption data were then fitted with (5) in which the LA phonon energy $\hbar\omega_p$ was taken to be 18 meV. The value of E_g for each sample was thus obtained. The fitted curves for our p-Si samples are shown in figure 3. It was expected that the band-gap energy of our purest sample was essentially that of undoped Si. Therefore, its value was used as the reference in the determination of the magnitudes

of the band-gap shrinkage ΔE_g for the other samples. The values ΔE_g so calculated are also listed in table 2.

From figure 3 it was obvious that the experimental data as well as the fitted curves were essentially linear except the portions close to zero absorption. This prompted us to investigate whether we could determine the values of $E_g + \hbar\omega_p$ directly by extrapolating the linear parts of the graphs to zero absorption and read off the intercepts, as one would have done for a pure Si sample. In fact, from (5) we noted that when $\hbar\omega \gg E_g + \hbar\omega_p$ and with E_F negative in value, the term

$$\exp\left[\frac{E_F - (\hbar\omega - E_g - \hbar\omega_p)x}{kT}\right]$$

in the integral was essentially close to zero and the integral

$$\int_0^1 x^{1/2}(1-x)^{1/2}\,dx = [\Gamma(3/2)]^2/\Gamma(3) = \pi/8.$$

Hence (5) would become

$$\alpha \cong A^2 \frac{(\hbar\omega - E_g - \hbar\omega_p)^2}{1 - \exp(-\hbar\omega_p/kT)} \tag{7}$$

and therefore it was viable to use the zero-absorption intercepts of the $\alpha^{1/2}$ versus $\hbar\omega$ plots to determine the values of $E_g + \hbar\omega_p$. The values of E_g so obtained, together with the corresponding ΔE_g, are included in table 2. On comparison, it is interesting to note that the values of ΔE_g obtained from the two methods for each sample are in very good agreement.

4. Comparison of gap shrinkage with other experimental works

4.1. Optical absorption measurements

Experimental values of gap shrinkage, ΔE_g for both heavily doped n- and p-Si measured at room temperature (300 K) had been reported separately by Vol'fson and Subashiev [15], Balkanski *et al* [16] and Schmid [17]. For the purpose of making comparisons, these values are plotted with those of the present work in figure 4. The figure shows that our values of $|\Delta E_g|$ for both n- and p-Si are higher than those obtained by Schmid in the same regime; while our results for n-Si seem to be closer to Balkanski *et al*'s. However, at higher impurity concentrations ($\sim 10^{20}$ cm^{-3}) both Balkanski *et al*'s and Schmid's results tend to agree. The values reported by Vol'fson and Subashiev are generally lower than those obtained by the other groups especially for the less heavily doped samples. We also noted that Schmid reported a rapid decrease in $|\Delta E_g|$ for samples with impurity concentrations of less than about 5×10^{18} cm^{-3}. In fact a value as low as 1.2 meV was obtained for a p-Si sample of 2.8×10^{18} cm^{-3}. The present work on the other hand measured considerably larger $|\Delta E_g|$ in this moderately doped range. For example, a $|\Delta E_g|$ of about 11 meV has been obtained for a p-Si sample of 1.2×10^{18} cm^{-3}.

4.2. Electrical measurements of bipolar transistors

Although the results of the present work show that our values, $|\Delta E_g|$, in the moderately doped samples are considerably larger than those reported in the other optical absorption

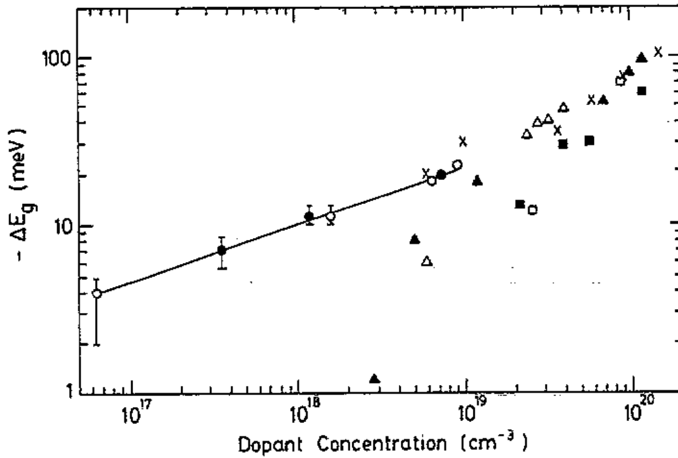

Figure 4. The band-gap shrinkages of n- and p-Si obtained by various groups with optical absorption at room temperature. Balkanski *et al*, n-Si (×); Vol'fson and Subashiev, n-Si (□), p-Si (■); Schmid, n-Si (△), p-Si (▲); present work, n-Si (○), p-Si (●).

studies, they are, on the other hand, much smaller than those values reported in the electrical measurements of Si bipolar transistors [7, 8]. For examples, for p-Si Slotboom and de Graaf [7] found a gap shrinkage of about 20 meV at $N_A = 3 \times 10^{17}$ cm^{-3} whereas our work showed a gap shrinkage of only 7 meV at $N_A = 3.3 \times 10^{17}$ cm^{-3}. For n-Si, a shrinkage of 63 meV at $N_D = 5 \times 10^{18}$ cm^{-3} was reported by Wieder [8]. In comparison we obtained only 17 meV at $N_D = 6.4 \times 10^{18}$ cm^{-3}. In conclusion, our results confirm that even in the moderately doped regime, the values of $|\Delta E_g|$ obtained by optical absorption method are consistently lower than those obtained by electrical device measurements. The disagreement, as discussed earlier in the introduction, is attributable to the dubious assumptions usually made in the less direct interpretation of electrical measurement results.

Direct comparison of our values of gap shrinkage with those obtained from photoluminescence experiments are not feasible because the photoluminescence results were acquired at liquid helium temperatures.

5. Dependence of gap shrinkage on impurity concentration

In the comparison of our results with those of the other experimental works, it is particularly instructive to highlight the dependence of gap shrinkage on impurity concentration. We noted that the dependence of $|\Delta E_g|$ on impurity concentration N found by Balkanski *et al* [16] was $N^{1/2}$ at 35 K and 300 K. Schmid [17], on the other hand, found $|\Delta E_g|$ to follow a critical behaviour, going to zero at the metal–insulator transition and varying slightly less than linearly with N at high doping. His results showed that

$$|\Delta E_g| \cong E_0 \left(\frac{N - N_c}{N_c}\right)^{\gamma} \qquad N \geqslant N_c \tag{8}$$

where $E_0 \cong 14$ meV, $N_c \cong 6 \times 10^{18}$ cm^{-3} and $\gamma \cong 0.8$ for the arsenic doped samples and $E_0 \cong 9$ meV, $N_c \cong 5 \times 10^{18}$ cm^{-3} and $\gamma \cong 0.8$ for the boron doped samples at low

temperature. At room temperature the high-doping values of $|\Delta E_g|$ were slightly smaller and the cut-off at N_c not as sharp.

Vol'fson and Subashiev's [15] experiments at room temperature for both n- and p-Si showed that the gap shrinkage depends on N as

$$|\Delta E_g| = \begin{cases} A(N^{1/3} - N_0^{1/3}) & N > N_0 \\ 0 & \text{otherwise} \end{cases} \tag{9}$$

where $A \sim 2.5 \times 10^{-6}$ meV cm and $N_0 \cong 1.4 \times 10^{19}$ cm^{-3} for p-Si and $A \sim 3.4 \times 10^{-6}$ meV cm and $N_0 \cong 1.8 \times 10^{19}$ cm^{-3} for n-Si.

On the other hand, from their respective electrical measurements using bipolar transistors, Slotboom and de Graaff [7] and Wieder [8] reported an empirical relation which showed a much more complicated dependence of $|\Delta E_g|$ on N. The relation is

$$|\Delta E_g| = 9(F + [F^2 + 0.5]^{1/2}) \text{ [mV]} \tag{10}$$

where $F = \ln(N/N_0)$ and $N_0 \cong 10^{17}$ [cm^{-3}].

Another study which we should also mention is the low-temperature photoluminescence and excitation spectroscopy measurements on heavily doped Si performed by Wagner [10]. He found the dependence of $|\Delta E_g|$ on N was $N^{1/3}$ for concentrations above the critical Mott's density for the insulator–metal transition.

With the data of the present work on both n- and p-Si, the graph of $\log|\Delta E_g|$ plotted against $\log(N)$ (figure 4) is a straight line of gradient 0.33. This indicates that our values of $|\Delta E_g|$ also vary as $N^{1/3}$ and are thus in fair agreement with the findings of Vol'fson and Subashiev and Wagner. More specifically our data show that

$$|\Delta E_g| = AN^{1/3} \tag{11}$$

where $A = 1.0 \times 10^{-5}$ meV cm. Furthermore Schmid found that $|\Delta E_g|$ would disappear when $N = N_c \cong 5\text{–}6 \times 10^{18}$ cm^{-3} and Vol'fson and Subashiev found that $|\Delta E_g|$ would disappear when N is less than $1.4\text{–}1.8 \times 10^{19}$ cm^{-3}. However our data show that $|\Delta E_g|$ is still measurable below these concentrations and, in fact, if a cut-off concentration does exist at all, our data suggest that it should be below 10^{16} cm^{-3}. This estimate is supported by our finding that the ΔE_g for our 1.5×10^{16} cm^{-3} p-Si sample was too small to be measurable.

6. Comparison of gap shrinkage with theoretical works

Some theoretical works on the shrinkage of the band gap of heavily doped Si have been reported recently [1, 4, 5]. The calculations were based on the many-body theory to find quantitatively various energy contributions arising from a degenerate electron gas, electron–donor interaction, hole–donor interaction and hole self and correlation energies. The final numerical results were obtained after some appropriate approximations were made. In the work by Berggren and Sernelius [5], an attempt had been made to improve upon the results reported by Abram *et al* [1]. They then compared their results with Mahan's [4] results and finally concluded that their results agreed well although the details of the calculations were very different. It appears that their works are the most ambitious of the recent theories on the topic. Thus, it is appropriate that we compare our experimental results with their theoretical results. It must be borne in mind, however, that our results were obtained at 294 K while the theoretical calculations apply for 0 K.

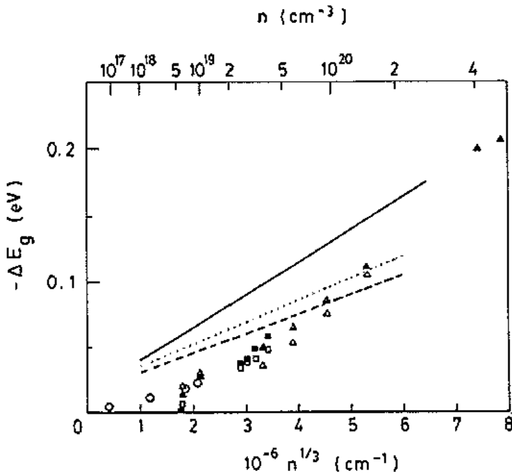

Figure 5. Comparison of experimental and theoretical values for $|\Delta E_g|$ in n-Si at different impurity concentrations. The full line refers to the calculation by Berggren and Sernelius for the case of a random arrangement of donor ions. The dotted line shows the same results for the case of the donors arranged in an FCC lattice. The broken line gives the results of Mahan's variational calculation, also for the FCC lattice. The experimental values reported by various groups are shown as follows. Balkanski *et al*, 35 K (▲), 300 K (△); Schmid, 4 K (■), 300 K (□); present work, 294 K (O).

In figure 5, we replotted the theoretical results obtained by Mahan (by variational calculations) and by Berggren and Sernelius respectively. Since the theoretical calculations are for n-Si, only the experimental results of n-Si samples are used for comparison. The results of Balkanski *et al* at 35 K and 300 K, Schmid's results at 4 K and 300 K and our results are plotted together in figure 5 for comparison. The experimental values show an order-of-magnitude agreement but, except for N in excess of $10^{20}\ cm^{-3}$, the experimental values are significantly less than the predicted theoretical values. However, on examining the dependence of band-gap shrinkage on impurity concentration, we found that the $N^{1/3}$ dependence was demonstrated theoretically by Berggren and Sernelius and was also evident in Mahan's work. Therefore, our experimental results (see (11)) together with those of Wagner and Vol'fson and Subashiev do seem to provide partial support to the theories mentioned.

7. Conclusion

In the present optical absorption study of moderately doped Si, band-gap shrinkages have been detected for both n- and p-Si for impurity concentrations well below $3 \times 10^{18}\ cm^{-3}$. This is in contrast to the earlier reports by Vol'fson and Subashiev and Schmid. However, below the impurity concentration of $10^{18}\ cm^{-3}$, the gap shrinkages we found were much lower than those measured by using Si bipolar transistors. This observation is consistent with that corresponding to more heavily doped samples [6]. Between $10^{18}\ cm^{-3}$ and $10^{19}\ cm^{-3}$, our values of gap shrinkage generally agree with those measured by Balkanski *et al*.

A comparison with the theoies by Berggren and Sernelius and by Mahan showed that our values of gap shrinkage are lower than predicted. This observation also applies to the gap shrinkages obtained in the other known optical absorption studies.

The dependence of the gap shrinkage, $|\Delta E_g|$, on impurity concentration N has also been investigated. We found $|\Delta E_g|$ to vary empirically as $N^{1/3}$ which gave support to the theoretical findings of Mahan and Berggren and Sernelius. The $N^{1/3}$ dependence was

also in agreement with the experimental results reported by Wagner, and Vol'fson and Subashiev.

References

[1] Abram R A, Rees G J and Wilson B L H 1978 *Adv. Phys.* **27** 799
[2] Inkson J C 1976 *J. Phys. C: Solid State Phys.* **9** 1177
[3] Lanyon H P D and Tuft R A 1979 *IEEE Trans. Electron Devices* ED-**26** 1014
[4] Mahan G D 1980 *J. Appl. Phys.* **51** 2634
[5] Berggren K F and Sernelius B E 1981 *Phys. Rev.* B **24** 1971
[6] Bennett H S 1985 *Solid State Electron.* **28** 193
[7] Slotboom J W and de Graaff H C 1976 *Solid State Electron.* **19** 857
[8] Wieder A W 1980 *IEEE Trans. Electron Devices* ED-**27** 1402
[9] Tang D D 1980 *IEEE Trans. Electron Devices* ED-**27** 563
[10] Wagner J 1984 *Phys. Rev.* B **29** 2002
[11] Schmid P E, Thewalt M L W and Dumke W P 1981 *Solid State Commun.* **38** 1091
[12] Selloni A and Pantelides S T 1982 *Phys. Rev. Lett.* **49** 586
[13] Dumke W P 1983 *Appl. Phys. Lett.* **42** 196
[14] Dumke W P 1983 *J. Appl. Phys.* **54** 3200
[15] Vol'fson A A and Subashiev V K 1967 *Sov. Phys. Semicond.* **1** 327
[16] Balkanski M, Aziza A and Amzallag E 1969 *Phys. Status Solidi* **31** 323
[17] Schmid P E 1981 *Phys. Rev.* B **23** 5531
[18] Pankove J I 1971 *Optical Processes in Semiconductors* (Englewood Cliffs, NJ: Prentice-Hall) p 93
[19] Fan H Y and Becker M 1951 *Symposium Volume of Reading Conference* (London: Butterworths Scientific) p 132
[20] Jellison Jr G E and Lowndes D H 1982 *Appl. Phys. Lett.* **41** 7
[21] Li H H 1980 *J. Phys. Chem. Ref. Data* **9** 561
[22] Macfarlane G G, McLean T P, Quarrington J E and Roberts V 1958 *Phys. Rev.* **111** 1245
[23] Moss T S 1954 *Proc. Phys. Soc.* B **67** 775
[24] Burstein E 1954 *Phys. Rev.* **93** 632
[25] Haas C 1962 *Phys. Rev.* **125** 1965