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DETERMINATION OF DOPING FACTOR, MOBILITY RATIO AND EXCESS CONCENTRATION USING PHOTOVOLTAGES AT EXTREME BAND BENDINGS

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Abstract—Photovoltages (surface photovoltage plus Dember voltage) were calculated and plotted, taking into consideration the influence of charge exchange between a continuum of surface states and the semiconductor. For moderate band bendings the photovoltage depends on several parameters which renders their reliable determination very difficult. For extreme band bendings, however, only doping factor, mobility ratio and relative excess concentration enter into given formulas. It is shown how by means of field-modulated photovoltage measurements using short pulses of light these three parameters could be determined reliably. Ge-samples with real surfaces were used. Good agreement between parameters determined in this way and otherwise indicates validity of the model and the approximations used in this work. The mobility ratio was found constant up to excess concentrations of about $10^{14}\,\mathrm{cm}^{-3}$. Possible extension of such measurements to semiconductors whose doping factors are very different from unity and applications are shortly discussed.

NOTATION

A	factor in expression for Q_{sc}, see eqn (6), (As/m^2)
b	mobility ratio μ_e/μ_h
k	Boltzmann's constant (J/K)
$n_0(x)$	concentration of quasi-free electron in equilibrium (m^{-3})
$n(x)$	nonequilibrium concentration of quasi-free electrons (m^{-3})
n_i	intrinsic concentration (m^{-3})
N_{ss}	concentration of surface states (m^{-2} J^{-1})
$p_0(x)$	concentration of quasi-free holes in equilibrium (m^{-3})
$p(x)$	nonequilibrium concentration of quasi-free holes (m^{-3})
p_0	bulk hole concentration in equilibrium (m^{-3})
Q_{sc}	charge in surface region (As/m^2)
Q_{ss}	charge in surface states (As/m^2)
T	absolute temperature (K)
v_D	Dember voltage (kT/q-units)
v_{ph}^+	photovoltage in the limit $y_0 \to -\infty$ (kT/q-units)
V_{ph}	photovoltage (V)
x	distance from surface (m)
y	surface potential in nonequilibrium (kT/q-units)
y_0	surface potential in equilibrium (kT/q-units)
$y(x)$	electrostatic potential in surface region (kT/q-units)
Y	surface potential in non-equilibrium (V)
Y_0	surface potential in equilibrium (V)
z	parameter defining exchange of electrons or holes
δn	bulk value of excess electron concentration (m^{-3})
δp	bulk value of excess hole concentration (m^{-3})
$\delta n(x)$	excess concentration of electrons (m^{-3})
$\delta p(x)$	excess concentration of holes (m^{-3})
Δy^+	surface photovoltage in the limit $y_0 \to -\infty$ (kT/q-units)
Δy^-	surface photovoltage in the limit $y_0 \to \infty$ (kT/q-units)
ΔY	surface photovoltage (V)
ϵ	absolute dielectric constant (F/m)
φ_0	Fermi-level in equilibrium (kT-units)
φ_n	quasi-Fermi-level for electrons (kT-units)
φ_p	quasi-Fermi-level for holes (kT-units)
λ	doping factor, ratio of p_0 and n_i
ρ	resistivity (VA^{-1} m)

1. INTRODUCTION

The electrically active doping of a semiconductor is usually described by the doping factor λ, defined as ratio of hole concentration in the bulk in thermodynamic equilibrium (p_0) and intrinsic concentration (n_i); $\lambda = p_0/n_i$. As λ is one of the most important parameters of a given semiconductor sample, many methods for its determination have been developed. Resistivities are measured with d.c.[2], a.c.[3], high frequencies[4, 5], microwaves[6] and eddy currents[8, 9]. Hall-measurements[10] are used often, optical methods[11, 12] have not found wide-spread application. When performing such measurements surface effects may lead to appreciable difficulties and errors[2, 13]. Contrarily, capacitance measurements make use of space charge effects in interface regions also for determinations of λ[14]. The method presented below also rests upon surface effects, but the Dember voltage introduces additionally the mobility ratio as a contribution from the bulk.

Mobilities of electrons and holes can be determined with samples in thermodynamic equilibrium, e.g. by Hall-measurements. Whilst drift velocities and mobilities as function of temperature, doping and electrical field have been studied extensively[15], the mobility ratio $b = \mu_e/\mu_h$ in Ge and Si seems never to have been determined for the case that carrier concentrations far above those in thermodynamic equilibrium were present. This has led to rather crude assumptions in the evaluation of measurements performed with pin-structures[16]. As b also must be known reliably for the determination of certain surface parameters from photovoltage measurements[17, 18], investigations in this direction are desirable.

Reliable determination of optically induced excess concentrations are also necessary for such and other measurements. Evaluations of excess concentrations have been very inaccurate (a factor of ten uncertainty due to unaccurate values of surface recombination was stated in [19]) or somewhat tedious[18]. As a knowledge of the excess concentrations is equivalent to that of the quasi-Fermi-levels, whose position determines practically all processes in non-equilibrium decisively, reliable methods for such measurements are of considerable interest.

2. THEORY

The non-equilibrium quasistationary concentrations ($n(x)$ for electrons, $p(x)$ for holes) inside a space charge region near the surface of a semiconductor are usually described by the introduction of the quasi-Fermi-levels $\varphi_n kT$ *and* $\varphi_p kT$; see Fig. 1[20]. For the case of non-degeneration one writes as generalization of Maxwell's distribution

$$n(x) = n_i \exp[y(x) - \varphi_n] \tag{1}$$

$$p(x) = n_i \exp[\varphi_p - y(x)] \tag{2}$$

where $y(x)$ is the electrostatic potential in units of kT/q. Numerical calculations have shown recently that such a description in general will be a good approximation[21]. Introducing the excess concentrations δn and δp with the definitions $n(x) = n_0(x) + \delta n(x)$; $p(x) = p_0(x) + \delta p(x)$ ($n_0(x)$ and $p_0(x)$ are the concentrations in thermodynamic equilibrium) one obtains for the *bulk* values δn, δp (that is, for $y = 0$)

$$\varphi_n - \varphi_0 = \ln\left(1 + \frac{\delta n}{n_i}\lambda\right) \tag{3}$$

$$\varphi_p - \varphi_0 = -\ln\left(1 + \frac{\delta p}{n_i \lambda}\right). \tag{4}$$

Here it has been assumed that the condition $y = 0$ holds sufficiently well in a region of still horizontal φ_n and φ_p. Trapping in the bulk shall be neglected further on, which means that $\delta n = \delta p$.

The surface photovoltage is defined as $\Delta Y = Y - Y_0$ (difference of surface potentials in nonequilibrium and equilibrium). If the necessary parameters are given, ΔY can be obtained from the equation

$$\Delta Q_{sc} + \Delta Q_{ss} = 0 \tag{5}$$

where ΔQ_{sc} is the change of charge (per area) inside the space charge region ($x > x_0$ in Fig. 1) during nonequilibrium and ΔQ_{ss} the corresponding change of charge in surface states. Starting from the expressions of Q_{sc} given in [20] and using a simple model for charge exchange between a continuum of surface states[18], whose concentration (per area and energy) is designed by N_{ss} one obtains with the abbreviation $A = -(2n_i\epsilon kT)^{1/2}$

$$\begin{aligned} &A \cdot \operatorname{sign}(y)\Big[\lambda(e^{-y} - 1) + \lambda^{-1}(e^{y} - 1) + (\lambda - \lambda^{-1})y \\ &\quad + \frac{\delta p}{n_i}(e^{y} + e^{-y} - 2)\Big]^{1/2} - A \cdot \operatorname{sign}(y_0)[\lambda(e^{-y_0} - 1) \\ &\quad + \lambda^{-1}(e^{y_0} - 1) + (\lambda - \lambda^{-1})y_0]^{1/2} \\ &\quad + qkTN_{ss}\left[z \ln\left(1 + \frac{\delta p}{n_i}\lambda^{-z}\right) - \Delta y\right] = 0. \end{aligned} \tag{6}$$

Here the first term with square brackets represents the space charge in non-equilibrium ($\delta p \neq 0$), the second term the corresponding charge in equilibrium and the term with the factor N_{ss} is the change of charge in surface states. For $z = +1$ this equation considers the exchange of holes (only) between surface states and semiconductor, for $z = -1$ that of electrons. In contrast to calculations performed, e.g. in [22, 23] this equation gives charges exchange (that is: $\Delta Q_{sc} \neq 0$) for any value of the surface potential (if, of course, $N_{ss} \neq 0$) and not only holds (as e.g. the analysis in [24]) for the small signal case.

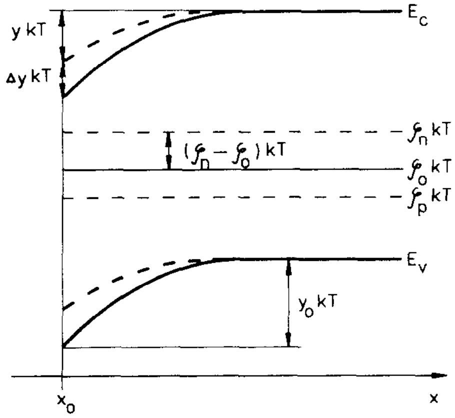

Fig. 1. Band bending in the surface region (surface at x_0) of a semiconductor; $y_0 kT/q$ and ykT/q are the surface potentials in equilibrium (Fermi-level $\varphi_0 kT$) and nonequilibrium (quasi-Fermi-levels $\varphi_n kT$ and $\varphi_p kT$). The surface photovoltage is $\Delta ykT/q$.

Using parameters pertaining to Ge at room temperature ($n_i = 2 \times 10^{13}\,\mathrm{cm}^{-3}$, $\epsilon_{rel} = 16$) solutions of (6) have been used for the curves in Fig. 2. Here the Dember voltage according to eqn (9) with $b = 2.09$ has been added so that these curves represent photovoltages between the (free) surface and a contact to a part of the sample which is in thermodynamic equilibrium. Curves like those in Fig. 2 show that for moderate band bendings ($|y_0| < 10$ in this case) all of the parameters λ, b, p/n_i, N_{ss}, z, y_0 have marked influence on the photovoltage and it is at least difficult to determine them from photovoltage measurements in this region. But for sufficiently large band bendings the behaviour is much simpler: Here the influence of N_{ss}, z and y_0 disappears! Further calculations and experiments will make use of this feature.

For sufficiently large positive values of y_0 ($y_0 \to \infty$) one obtains from (6) the simple expression for the surface photovoltage Δy^-(kT/q-units)

$$\Delta y^- = -\ln\left(1 + \frac{\delta p}{n_i}\lambda\right). \tag{7}$$

Accordingly we obtain in the limit of large negative band bendings ($y_0 \to -\infty$) for the surface photovoltage

$$\Delta y^+ = \ln\left(1 + \frac{\delta p}{n_i \lambda}\right). \tag{8}$$

In the deriviation of (7) and (8) it has been assumed that the band bending in nonequilibrium is not too small, e.g. $|y| \gtrsim 3$. This means that δp may not be too large; for the case of $\delta p \to \infty$ we always have $y \to 0$[18] and the surface photovoltage would be equal to $-Y_0$.

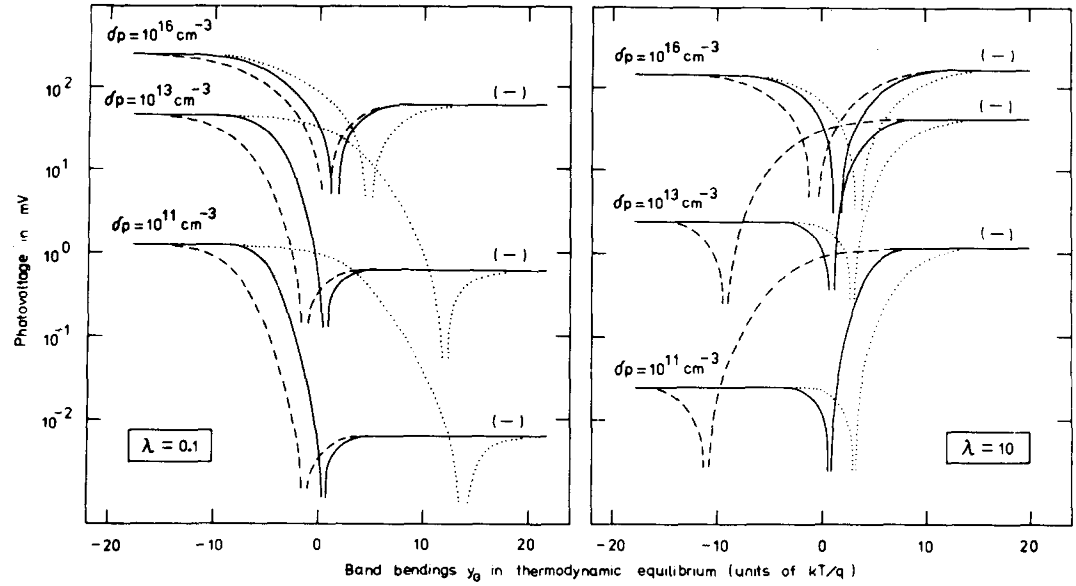

Fig. 2. Calculated photovoltages as function of band bending for two values of doping factor λ for three values of excess concentrations δp. ——, $N_{ss} = 0$; ----, $N_{ss} = 10^{12}\,\mathrm{cm}^{-2}\,\mathrm{eV}^{-1}$, exchange of electrons ($z = -1$ in (6)), ······, $N_{ss} = 10^{12}\,\mathrm{cm}^{-2}\,\mathrm{eV}^{-1}$, exchange of holes ($z = +1$ in (6)). Dember voltage calculated with $b = 2.09$, $n_i = 2.10^{13}\,\mathrm{cm}^{-3}$; $\epsilon_{\mathrm{rel}} = 16$, $T = 297$ K.

As (7) and (8) are (besides the sign, but this is simply a consequence of the usual sign convention in band diagrams) identical to those of (3) and (4) we have the possibility of an extremely simple and clear visualization: If the band bending y_0 is so extreme that only carriers of one sign give the dominating charge contribution near the surface, the space charge region behaves as if it would consist simply of a single (highly degenerated) level with the position $\pm ykT$ relative to the corresponding band edges. Upon illumination this level is shifted by the same amount as the corresponding quasi-Fermi-level; see Fig. 1.

To obtain the photovoltage we have to add in (7) and (8) the Dember-voltage, which with our nomenclature can be written as

$$v_D = \frac{b-1}{b+1} \ln\left(1 + \frac{\delta p}{n_i} \frac{b+1}{\lambda + b/\lambda}\right) \tag{9}$$

and we obtain finally the following expressions: For $y_0 \to +\infty$

$$v_{ph}^- = -\ln\left(1 + \frac{\delta p}{n_i}\lambda\right) + v_D \tag{10}$$

for $y_0 \to -\infty$

$$v_{ph}^+ = \ln\left(1 + \frac{\delta p}{n_i \lambda}\right) + v_D. \tag{11}$$

Equations (10) and (11) are used for the evaluation of the measurements.

Some important features can be seen if we consider the ratio v_{ph}^+/v_{ph}^- which in a logarithmic scale is plotted in Fig. 3 as function of $\log \lambda$ for some values of $\delta p/n_i$. For sufficiently small $\delta p/n_i$ a straight line is obtained. It is easy to show that in this case we obtain from (9), (10) and (11)

$$\frac{v_{ph}^+}{v_{ph}^-} = -\frac{b}{\lambda^2}. \tag{12}$$

This shows that for small signals the evaluation of b or λ from suitable measurements is extremely simple.

Further we obtain for the special case $\lambda = 1$ immediately $v_{ph}^+/v_{ph}^- = -b$ for arbitrary values of $\delta p/n_i$ (only for the special case of small signals this was shown in [25]). Finally we obtain for $\delta p/n_i \to \infty$ that $v_{ph}^+/v_{ph}^- \to -b$ for all values of λ. Therefore it is possible to choose the sensitivity in respect to λ by selecting an appropriate value for $\delta p/n_i$.

There remains the question if the system (9), (10), (11) is well conditioned for the determination of λ and $\delta p/n_i$. For a large range of parameters this is answered by Fig. 4. Here curves of constant v_{ph}^+ (positive parameters at the curves) and v_{ph}^- (negative parameters) are plotted; the axes represent $\delta p/n_i$ and λ. Only well defined intersection points exist which means that from the two values v_{ph}^+ and v_{ph}^-, values for λ and $\delta p/n_i$ can be determined with an accuracy which is comparable with those of the measurements.

3. EXPERIMENTAL PROCEDURE AND RESULTS

Experiments were performed using an improved version of the apparatus described in [17, 18]. Short pulses of light (duration about 1 μs) produce non-equilibrium carriers which give rise to photovoltages. These are measured between a contact (positioned sufficiently far away from the illuminated region) and a semi-transparent SnO_2 film on glass, insulated by mica from the opposite (illuminated) surface of the semiconductor. The modulating field voltage is applied in the form of pulses

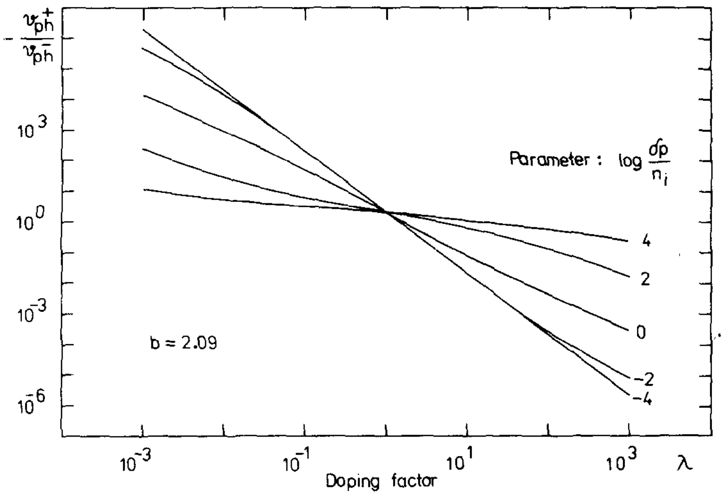

Fig. 3. Calculated ratio of photovoltages for extreme band bendings as function of doping factor (double logarithmic) with log $\delta p/n_i$ as parameter. Straight lines result for the limiting cases $\delta p \to 0$ ($v_{ph}^+/v_{ph}^- \sim \lambda^{-2}$) and $\delta p \to \infty$ ($v_{ph}^+/v_{ph}^- \sim \lambda^0$).

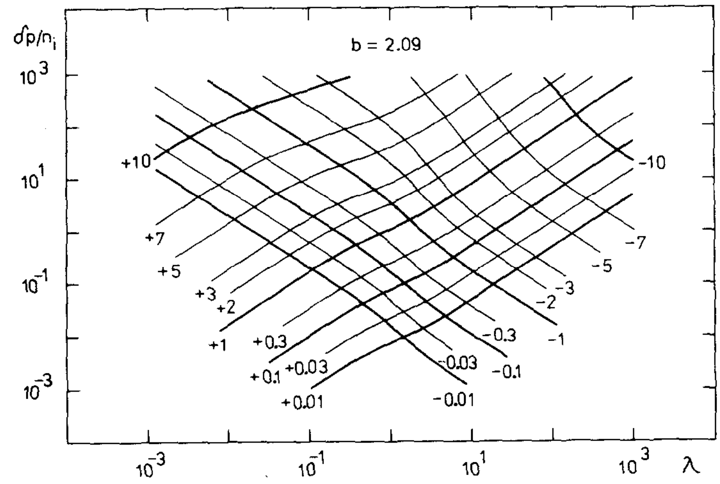

Fig. 4. Calculated curves of constant photovoltages at extreme band bendings; v_{ph}^+ for $y_0 \to -\infty$ and v_{ph}^- (negative parameters) for $y_0 \to +\infty$. Axes: Doping factor and relative excess concentration $\delta p/n_i$. For $b = 1$ straight lines would result.

which are automatically varied from pulse to pulse. Similar field modulation at real Ge surfaces has been used extensively for the study of electrical[26, 27] and optical[28] properties. Photovoltage pulses are recorded from the screen of an oscilloscope on continuously moving film and their peak values later measured using suitable magnification.

Results presented in Fig. 5 are peak values of photovoltage pulses as functions of a varying electrical field perpendicular to the surface. From curve to curve the intensity of light was varied by filters. As in the stationary state δp may strongly be afflicted by surface recombination, which may depend on the band bending, it is expedient to work in such a way that the duration of exciting pulses of light is much smaller than that of the recombination[25]. Then recombination cannot influence the results. Without such precaution a curve like those in Fig. 5 could not be considered to represent behaviour for a constant value of δp.

All of the curves in Fig. 5 (measured for three intensities of light) clearly show asymptotically horizontal branches for large values of the modulating field. Therefore we may safely assume that in these experiments the assumptions which led to eqns (10) and (11) could be realized. Photovoltages from the horizontal parts were used for the calculation† of λ, b and $\delta p/n_i$, using eqns (9), (10) and (11).

Values of λ and b for different Ge-samples obtained in this way are presented in the second and fourth column of Table 1. For all samples λ was also determined from the sign of the thermopower and the resistivity, using the measuring set described in [2]. These values appear in the third column. The mobility ratio also was obtained from the mobility values given in [10] (last column). We now can compare the values obtained from photovoltage measurements with those obtained quite otherwise. This allows to test the reliability of the method presented here.

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†Calculations were done using an HP 9820 A. A limited number of programs is available upon request.

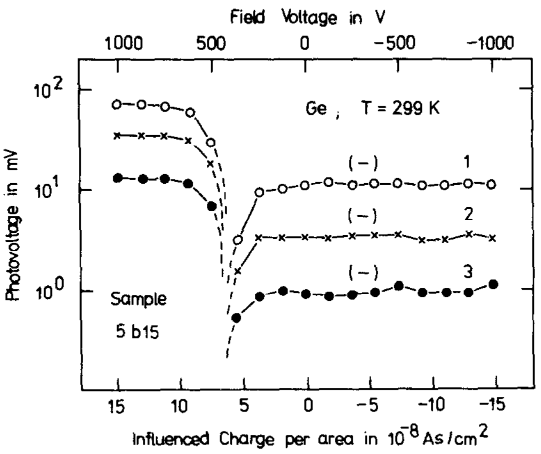

Fig. 5. Measured photovoltages: Ge-sample with real surface; three different intensities of exciting light pulses were used in the three runs, conditions otherwise identical. Values for λ and b from this measurement: see Table 1.

Table 1 demonstrates that the values for λ and b, obtained from photovoltages and otherwise, in all cases coincide within the inaccuracies stated. For nearly intrinsic material it is impossible to determine accurate values for λ from measurements of the resistivity ρ because the curves $\rho(\lambda)$ show a maximum in this region and the mobilities given in [10] are known only within an inaccuracy of ± 3%. Therefore in [29] λ also was determined using surface effects.

Values for $\delta p/n_i$ used in these experiments were typically 0.2; 0.8 and 3.6; they could be determined within about ± 3%. This is a considerable improvement compared with results presented in [19], where in spite of carefully prepared samples and computer evaluations of photoconductivity measurements an uncertainty of about an order of magnitude for the excess concentration remained.

4. DISCUSSION

The photovoltages mentioned above were measured with an error of about ±3%. We believe that the position of all three Fermi levels $\varphi_0 kT$, $\varphi_n kT$ and $\varphi_p kT$ can be obtained in this way with an inaccuracy of not more than ± 1 meV relative to the intrinsic level. This should be useful for many investigations.

The good agreement between the values of λ and b in Table 1 is a strong indication for the validity of the model used. Then we expect that also other conclusions drawn from this model will be correct. This concerns, e.g. the existence and interpretation of photovoltage pulses with characteristic minima [17, 18]. Such pulses have now been observed and used in our laboratory when working with n- and p-type Si having much lower resistivities (~ 10 Ohm cm) than samples in earlier work and also at Ge. Such minima must appear if the model is correct and the Dember-voltage is present with values for b which are essentially those for the limit of small δp. As the measurements described here did not show any systematic deviation of b up to $\delta p \approx 10^{14}\,\text{cm}^{-3}$, which is about the value at which minima in the photovoltage pulses in high-resistivity Si appeared [17, 18] we believe that the interpretation given by us is correct and that presented in [23] cannot be applied in this case.

We will discuss now possible extensions of the method presented to substances where λ deviates far more from 1 than in the measurements presented here. The manufacture of many devices starts from Si for which $|\log \lambda|$ is of the order of 5 at room temperature. The direct application of the inherently accurate small signal case to material of this kind according to (12) would lead to photovoltage ratios of about 10^{10}. Such a ratio cannot be measured; with other words: the small signal surface photovoltage of strongly doped semiconductors disappears practically for strong accumulation. There are several possibilities to avoid this difficulty:

As already mentioned, the use of suitably large δp leads to a much reduced dependency of v_{ph}^+/v_{ph}^- from λ (see Fig. 3) and should make possible the application to materials which are strongly extrinsic. Furthermore, as already a moderate rise of the temperature leads to a strong increase of n_i, λ at higher temperatures will in general be much more near to 1 than otherwise, which makes its measurement by the method described above easier.

If only one of the parameters, e.g. λ, is wanted, a single photovoltage pulse, preferably in inversion, will suffice. This seems to be an attractive feature for phoduction control. The use of simple chemical substances like HF, which usually easily produces inversion at real surfaces of p-Si or corona charging of insulator covered Si [30] may be helpful in obtaining sufficiently extreme band bendings. The production of additional free carriers, e.g. by an additional optical pulse which precedes the excitation for the above-mentioned methods is also a possible means for diminishing the differences between inversion and accumulation in strongly doped semiconductors.

Finally some advantages should be mentioned, all of which are not inherent simultaneously to any of the other

Table 1. Doping factors λ and mobility ratios b for different G-samples from photovoltage measurements compared with values of λ from resistivity measurements and values of b from [10].

Sample	λ (from v_{ph})	λ (from ϱ)	b (from v_{ph})	b (from [10])
4 c 1	1.28 ± 0.01	1.50 ± 0.5	2.05 ± 0.07	2.09 ± 0.08
5 a 7	1.58 ± 0.05	1.50 ± 0.4	2.07 ± 0.2	2.09 ± 0.08
5 b 15	0.34 ± 0.01	0.35 ± 0.01	2.03 ± 0.06	2.09 ± 0.08

methods quoted: (i) The method presented here can be applied to samples either with real or insulator-covered surfaces. (ii) No preparation of contacts is necessary and even local damage due to hard point contacts may be avoided. (iii) No geometrical factors enter directly. (iv) The measuring principle allows optical scanning[31].

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