phys. stat. sol. (a) 89, 617 (1985)

Subject classification: 20.1; 13.1; 22.1.2

*Laboratoire de Phase, Centre de Recherches Nucleaires, Strasbourg*[1])

# Determination of the Electron Effective Mass and Relaxation Time in Heavily Doped Silicon

By

A. SLAOUI and P. SIFFERT

Two models are considered to describe the near infrared (NIR) reflectance spectra of doped silicon. By comparing these calculated results to those found experimentally in the wavelength range from 0.8 to 2.6 μm, basic physical constants of silicon, like effective electron mass $m_e^*$ and relaxation time $\tau$ may be determined. This procedure is applied to heavily doped silicon, obtained by laser annealing of high dose dopant implantation. A new relationship is established between $m_e^*$ and $\tau$ for these hyperdoped silicon layers. Differences in behaviour as a function of doping level are observed above $10^{21}$ cm$^{-3}$, which will be discussed.

Dans ce travail, nous proposons deux modèles pour décrire les spectres de reflectivité dans la région proche infrarouge du silicium dopé. En comparant ces résultats calculés à ceux trouvés expérimentalement dans l'intervalle (0,8 à 2,6 μm), des constantes physiques de base telles que la masse effective des électrons $m_e^*$ et le temps de relaxation des porteurs peuvent être déterminées. Cette procédure a été appliquée au silicium hyperdopé obtenu par recuit laser de silicium implanté à forte dose. Pour les niveaux de dopage au dessus de $10^{21}$ cm$^{-3}$, la masse effective augmente sensiblement alors que le temps de relaxation reste pratiquement constant. Ces résultats sont largement discutés.

## 1. Introduction

Infrared techniques are widely used both in semiconductor research and industry to get information of impurity level and band structure. In particular, transmittance and plasma reflectivity experiments allow the determination of the effective mass of electrons $m_e^*$ and for probing the dopant profile parameters [1 to 6].

However, in silicon, by contrast to many other semiconductors [2], high carrier densities are needed to observe an effect on the reflectivity spectra, which may indicate a change in the effective mass.

Recently, new doping procedures, such as ion implantation followed by pulsed laser annealing, have allowed to reach active impurity concentrations in silicon well above the normal equilibrium solubility [7].

The goal of this paper is to show that it is possible to determine the electron effective mass and relaxation time accurately simply from the measurement of the reflectivity spectra in the NIR region for these heavily doped silicon samples. However, in this case, a theoretical model of the reflectance of an optically inhomogeneous material is needed. In the literature at least two models based on Drude's theory are, generally, considered:

(i) the first model assumes an almost uniform doped layer and determines $m_e^*$ from the relationship giving the plasma frequency as a function of carrier concentration [2, 3]. It should be noticed that this model neglects the imaginary dielectric constant, which can be important at the experimentally determined plasma frequency;

[1]) B.P. 20, F-67037 Strasbourg Cédex, France.

(ii) the second model assumes that the carrier profile versus depth is modelled by a sequence of uniformly doped layers [4, 6].

In this paper, we used the two former models, with the following modifications:

(i) in the first model, we took into account also the imaginary part of the dielectric constant;

(ii) in the second model, we considered that the active carrier concentration profile after implantation and annealing varies exponentially with depth.

These calculated values have been compared to the experimental spectra and we deduced $m_e^*$ and $\tau$ as a function of carrier concentration. These values are discussed and compared to other results given in the literature [1, 3].

## 2. Experimental Conditions

Polished 1.5 Ωcm p-type, (100)-oriented silicon wafers were implanted with $As^+$ ions at 80 keV and doses up to $5 \times 10^{16}$ cm$^{-2}$. The samples were annealed with a repetitive Q-switched YAG laser ($\lambda = 0.53$ μm), having a beam diameter of 100 μm, a pulse duration of 100 μs, and a repetition rate up to 5 kHz at 2.5 J/cm$^2$.

Sheet resistivity measurements indicated very low values, showing a good doping incorporation in the lattice. Rutherford backscattering measurements (RBS) confirmed the high concentration of dopants, well in excess of the thermodynamic solubility limit [7].

The optical reflectivity measurements were performed in the 0.8 to 2.5 μm range, using a Beckmann spectrometer, under nearly normal incidence. Typical results are shown on Fig. 1. It appears that the wavelength at which the reflectivity curve shows a minimum $\lambda_{min}$ shifts towards shorter wavelength when the implanted dose (or the active carrier concentration) is increased.

## 3. Analysis of the Results

### *3.1 Determination of the effective mass and relaxation time*

The presence of the arsenic atoms in subtitutional silicon lattice sites leaves electrons in the conduction band. According to the Drude theory [8], the dispersion and absorption of free carriers are given in terms of the real and imaginary parts of the dielectric constant as follows:

$$\varepsilon^*(\omega, x) = \varepsilon_r(\omega, x) + i\varepsilon_i(\omega, x) ,$$

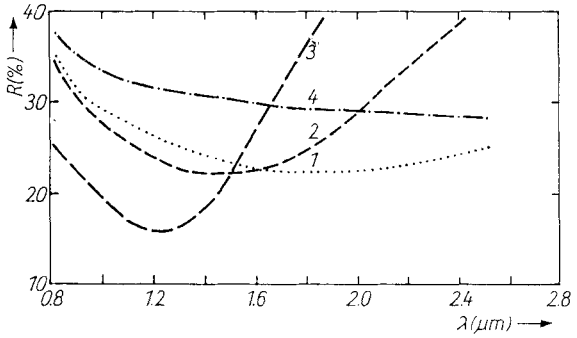


Fig. 1. Reflectivity spectra of ion-implanted ($As^+$, 80 keV) Si at several doses ((1) $5 \times 10^{15}$, (2) $10^{16}$, (3) $5 \times 10^{15}$ cm$^{-2}$) and YAG laser annealing. The reflectivity spectrum of undoped Si is also reported (4)

where

$$\varepsilon_r(\omega, x) = \varepsilon_\infty - \frac{4\pi N(x)\, e^2\tau^2}{m_e^*(\omega^2\tau^2 + 1)},$$
$$\varepsilon_i(\omega, x) = \frac{4\pi N(x)\, e^2\tau}{m_e^*(\omega^2\tau^2 + 1)}. \tag{1}$$

In these equation, $N(x)$ is the density of free carriers, $m_e^*$ the electron effective mass, and $\tau$ the relaxation time, $\varepsilon_\infty$ denotes the dielectric constant due to the highly bound core electrons and $\omega$ is the angular frequency.

For two situations of doping versus depth — uniform or exponential — the model yields the following results:

### *3.1.1 Inhomogeneous doping*

In this case the model is founded upon the solution of the following equation:

$$\frac{d^2E_y(x)}{dx^2} + \left(\frac{\omega}{c}\right)^2 \varepsilon^*(\omega, x)\, E_y(x) = 0 \tag{2}$$

which describes the propagation of the light in the medium, where $E_y$ is the intensity of the electric field.

As the arsenic concentration profile, after implantation and pulsed laser annealing, has been found experimentally to be asymmetric and non-homogeneous in depth, especially by SIMS [3, 9], we used for $N(x)$ the following expression:

$$N(x) = N_0 + N_{max} \exp\left[-\alpha(x - d)^2\right] \quad \text{for} \quad x \geqq d,$$
$$N(x) = N_0 + N_{max} \exp\left[-\beta(x - d)^2\right) \quad \text{for} \quad x < d, \tag{3}$$

where $N_0$ is the doping of the subtrate, $N_{max}$ the maximum concentration of dopants in the profile, and $d$ the depth location of this maximum from the surface. $\alpha$ and $\beta$ are adjustable parameters.

The value of the relaxation time $\tau$ appearing in (1) has often been assumed constant in the literature [1 to 4]. Here, we used the values of $\tau$ given empirically from Lambert's measurements [10]. The solution of (2) for this model yields the following value for the reflection coefficient [11]:

$$R(\omega) = \frac{[V(0) - 1]^2 + (cW(0)/\omega)^2}{[V(0) + 1]^2 + (cW(0)/\omega)^2}. \tag{4}$$

This coefficient depends on two unknown quantities $V$ and $W$ at the surface ($x = 0$), determined from the differential equations

$$\frac{dW}{dx} + W^2 - \left(\frac{\omega}{c}\right)^2 [V^2 - \varepsilon_r(\omega, x)] = 0, \qquad \frac{dV}{dx} + 2WV - \left(\frac{\omega}{c}\right)^2 \varepsilon_i(\omega, x) = 0. \tag{5}$$

The Milne numerical resolution method of these equations allows the calculation of $V$ and $W$ along the doping profile: one begins the calculation from the substrate, where the concentration $N$ is constant and step by step one progresses towards the surface [11].

The procedure to analyze the experimental data is, then, as follows:

(i) assume a dopant profile characterized by the $\alpha$, $\beta$, $d$, $N_{max}$ parameters, which are estimated from the SIMS profile [9, 11];

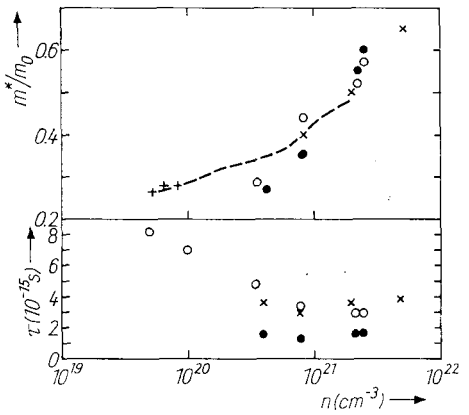


Fig. 2. Effective mass and relaxation time of free carriers as a function of carrier concentration for ion-implanted ($As^+$, 80 keV) Si after pulsed YAG laser annealing. The dashed line gives the effective mass of electrons calculated from the band structure data [12]; + [1], × [3], ● homogeneous profile, ○ inhomogeneous profile

(ii) suppose a relaxation time $\tau_0$ (for $N > 10^{21}$ cm$^{-3}$) and an effective mass $m_e^*$;
(iii) calculate the $V(0)$ and $W(0)$ quantities for each wavelength and deduce $R(\omega)$;
(iv) adjust $\tau_c$ and $m_e^*$ to minimize the deviation between the experimental and theoretical spectra for each dose value.

The parameters determined by following this procedure are shown on Fig. 2. It appears that $m_e^*$ increases from $0.288m_0$ for $N_e = 3.5 \times 10^{20}$ cm$^{-3}$ to $0.57m_0$ for $N_e = 2.5 \times 10^{21}$ cm$^{-3}$ ($m_0$ is the free-electron mass). The relaxation time decreases with higher doping levels, and saturates at $\tau_0 = 3 \times 10^{-15}$ s, for $N_e > 10^{21}$ cm$^{-3}$.

### *3.1.2 Uniform doping*

For $N(x) = N$, we have

$$1 + (\omega^2\tau^2)^{-1} \approx 1 \quad \text{and} \quad \alpha\omega_0^2 = 4\pi Ne^2(m_e^*)^{-1},$$

where $\omega_0$ is a constant frequency.

Consequently, (1) becomes

$$\varepsilon_r = \varepsilon_\infty - \frac{\alpha\omega_0^2}{\omega^2}, \qquad \varepsilon_i = \frac{\alpha\omega_0^2}{\omega^3\tau}. \tag{6}$$

We can write (6) as

$$\varepsilon_r = \varepsilon_\infty - \alpha\left(\frac{\omega_0\tau}{\alpha}\right)^{2/3}\varepsilon_i^{2/3} \tag{7}$$

which gives a relation between $\varepsilon_r$ and $\varepsilon_i$.

Another calculation [11] allows to write a second relation between $\varepsilon_r$ and $\varepsilon_i$

$$\varepsilon_r = -x + 0.5\left[\frac{1-R}{1+R}(1+x)\right]^2 \qquad x^2 = \varepsilon_r^2 + \varepsilon_i^2 . \tag{8}$$

This equation (8) allows to draw the curves $(\varepsilon_r, \varepsilon_i^{2/3})$ for a fixed $R$-value.

Under these conditions, $m_e^*$ and $\tau$ are obtainned as follows:

(i) for each dose $N$, the curve $(\varepsilon_r, \varepsilon_i^{2/3})$ at $R_{min}$ corresponding to $\lambda_{min}$, is drawn;
(ii) at the point $\varepsilon_r = \varepsilon_\infty$ and $\varepsilon_i = 0$ the tangent to this curve is traced;

(iii) we deduce the following parameters:

$$A = \alpha^{1/3}(\omega_0\tau)^{2/3}\,, \qquad B = \left(\frac{\omega_0}{\omega_{\min}}\right)\left(\frac{\alpha}{\omega_0\tau}\right)^{2/3} \tag{9}$$

which allow to determine $\alpha$ and $\tau$ and, consequently, $m_e^*$ and $\tau$;

(iv) finally, we check that for these values the experimental reflectance spectrum is formed.

The values of $m_e^*$ and $\tau$ determined in this manner are reported also in Fig. 2. It appears that the behaviour of $m_e^*$ is similar to that found in Section 3.1.1. However, $\tau$ remains nearly constant when the doping level increases.

### *3.2 Discussion*

As indicated above, the values of $\tau$ and $m_e^*$ as determined by the two models are shown on Fig. 2 as function of the silicon doping level. On the same figure we report previously published results [1, 3] for arsenic-doped samples. In all cases, a significant and continuous increase of $m_e^*$ is observed, starting at a doping level of about $8 \times 10^{20}$ cm$^{-3}$.

Recently, optical effective masses of electrons in silicon have been calculated [12] for carrier densities up to $2 \times 10^{21}$ cm$^{-3}$. These results are also shown on Fig. 2. It appears that a satisfactory agreement with our experimental data is observed.

The increase of $m_e^*$ at high carrier concentration has often been attributed to electrons occupying a higher energy (and heavier mass) conduction-band valley, located about 0.15 eV above the conduction-band minimum. Indeed, the Fermi level reached a new valley of the conduction band, when the carrier concentration attained about $5 \times \times 10^{20}$ cm$^{-3}$, values beyond which $m_e^*$ starts to increase. However, recently van Driel [12] claimed that the second band does not have a sufficiently large density of states to influence the mass value. He suggested that the electron mass behaviour, which is observed experimentally, occurs primarly because of increasing warping of the (low-density) ellipsoidal constant energy surfaces with increasing Fermi energy. This author has shown that the constant energy contour of the lower conduction band at the $x$ point [13] has an ellipsoidal shape for the low Fermi energy and becomes more warped when this energy increases. To decide which model is correct, more precise calculations of the density of states are needed.

The optical relaxation time remains nearly constant with increasing doping (bottom of Fig. 2). Here, the main competing mechanisms are scattering by acoustic vibrations of the lattice and scattering by ionized impurity ions. As the first process is independent of carrier concentration $N$, while the second depends on it, it seems to us that the dominant process in the heavily doped n-type silicon is the scattering by acoustic vibrations. The absorption measurements seem to confirm this interpretation [14].

## 4. Conclusion

Physical fundamental constants, such as effective mass and relaxation time have been determined as a function of the free-carrier concentration, up to very high doping levels, which became possible by combining ion implantation and pulsed laser annealing. The experimental approach used was NIR reflectivity measurements on the heavily doped silicon.

The increase of $m_e^*$ above $N \geqq 10^{21}$ cm$^{-3}$ can result either from the filling of a new valley, or to the warping of the conduction band.

The dominant scattering process in the heavily doped n-type silicon is due to acoustic vibrations.

## References

[1] L. E. HOWARTH and J. F. GILBERT, J. appl. Phys. **34**, 236 (1963).
[2] W. G. SPITZER and H. Y. FAN, Phys. Rev. **106**, 882 (1957).
[3] M. MIYAO, T. MOTOOKA, N. NATSUAKI, and T. TOKUYAMA, Solid State Commun. **37**, 605 (1980).
[4] H. ENGSTROM, J. appl. Phys. **51**, 5245 (1980).
[5] M. PAWLIK, private communication.
[6] H. H. WAGNER and R. R. SCHAEFER, J. appl. Phys. **50**, 2697 (1979).
[7] A. SLAOUI, E. FORGARASSY, J. C. MULLER, and P. SIFFERT, J. Physique **44**, C5-65, 1983.
[8] T. S. MOSS, Optical Properties of Semiconductors, Academic Press, 1959.
[9] N. NATSUAKI, M. TAMURA, and T. TOKUYAMA, J. appl. Phys. **51**, 3373 (1980).
[10] L. M. LAMBERT, J. appl. Phys. **43**, 4612 (1972).
[11] A. SLAOUI, 3° cycle thesis, Louis Pasteur University, Strasbourg 1984.
[12] H. M. VAN DRIEL, Appl. Phys. Letters **44**, 618 (1984).
[13] J. R. CHELIKOWSKY and M. L. COHEN, Phys. Rev. B **14**, 556 (1976).
[14] L. N. STRELTSOV and V. V. TITOV, Soviet Physics — Semicond. **4**, 605 (1970).

*(Received January 17, 1985)*