THE DENSITY OF STATES IN HEAVILY DOPED REGIONS OF SILICON SOLAR CELLS

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ABSTRACT

The density of states (DOS) of crystalline silicon changes with the introduction of dopants due to the formation of an impurity band and band tails. Until now, the DOS of undoped silicon has been used to model silicon devices, regardless of the doping level. This approximation may not be satisfactory for the emitter and back surface field regions of silicon solar cells. Therefore, we measured the DOS by performing tunnel spectroscopy measurements on Schottky diodes fabricated on heavily doped silicon. We extracted the DOS from this data by calculating the quantum-mechanical tunnel probability through the Schottky barrier. The goal is to use silicon samples with varying phosphorus doping density in order to determine the DOS as a function of the phosphorus doping density. The use of this parameterisation (instead of the DOS of undoped silicon) is expected to improve the calculation of the minority carrier density in the emitter and back surface field region of crystalline silicon solar cells.

INTRODUCTION

The density of states (DOS) of crystalline silicon changes with increasing doping density N_{dop} in two ways:

(i) The impurity states interact with each other, forming an *impurity band* around the energy level of the dopant. This band broadens and it shifts towards the edge of the majority carrier band (due to the screening by charged carriers).

(ii) *Band tails* arise at the edge of the conduction and valance band due to disorder effects.

Near and above the Mott transition (at $N_{dop} = 3.2\times10^{18}$ cm^{-3}), the impurity band hosts mainly mobile electrons [1], which may cause a minor amount of additional band gap narrowing compared to theories that neglect the impurity band [2]. In a previous paper [3], we demonstrated that the real (non-ideal) DOS has considerable effects on the simulation of silicon solar cells due to its impact on the calculated Fermi energy. In this previous paper, we determined the DOS of heavily phosphorus-doped silicon using photoluminescence data from the literature. However, the used method did not allow us to extract the DOS at doping densities above 10^{19} cm^{-3} with sufficient precision. Abdurakhmanov *et al.* [4] derived the DOS of phosphorus-doped silicon from tunnel spectroscopy (i.e. from the differential conductance of Schottky diodes as a function of applied dc voltage at 4.2 K), using a mathematical method of Mahan *et al.* [5, 6]. In this paper, we present a similar but more detailed approach to extract the DOS of heavily doped silicon.

MEASURMENT METHOD

Fig. 1 shows the set-up for measuring the dc current I_{DC} and the differential conductance *dI/dV* of a Schottky diode as a function of dc voltage V_{DC}. For each fixed current I_{DC}, both *dI/dV* and V_{DC} need to be recorded. This is realised by driving a constant dc current through the Schottky diode and by superimposing a small-signal ac current (sine wave). V_{DC} and I_{DC} of the diode are measured using pre-amplifiers and voltmeters. Lock-in amplifiers are used to detect the *dV* and the *dI* response of the diode separately, from where *dI/dV* is calculated. The applied dc voltage is varied in order to measure the entire V_{DC} dependence of I_{DC} and *dI/dV*. The dc and ac currents are controlled via resistors R_{DC} and R_{AC}, which are chosen to keep the current amplitude of the sine wave smaller than the dc current step width. For all measurements, the diode was kept at 4.2 K in a liquid helium cryostat.

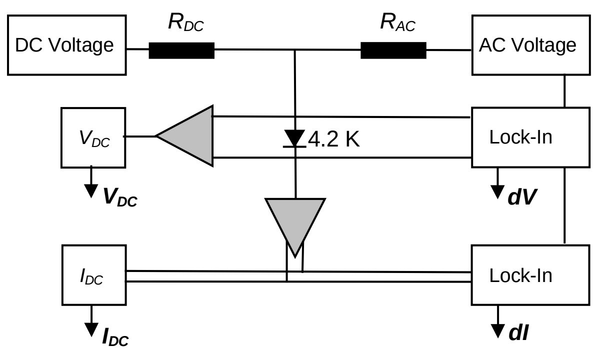

Fig. 1. Set-up for measuring the dc current and differential conductance (I_{DC} and *dI/dV*) of a Schottky diode as a function of the applied dc voltage V_{DC} (at 4.2 K).

SAMPLE FABRICATION

Schottky diodes were fabricated on phosphorus-doped Cz silicon wafers having a sheet resistance σ of 0.0053(1) $\Omega\cdot$cm, as determined by four-point probe measurements (the digit in the parenthesis represents the estimated error in the last digit of the previous value). Using the measurements of the σ-N_{dop} relation of Thurber *et al.* [7] and Mousty *et al.* [8], this sheet resistance corresponds to a doping density of $1.1(1)\times10^{19}$ cm^{-3}. Both the ohmic as well as the Schottky contacts were fabricated on the same side of the wafer. This wafer surface was polished, and we used photolithography to achieve small contact areas required for reliable resistance measurements (about 0.126 mm^2). The ohmic contact was realised by a local n^{++} diffusion, evaporation of titanium and palladium, and sintering at 400°C for 30 min, whereas the Schottky diodes were fabricated by gold evaporation onto the polished silicon. Fine gold wires were ultrasonically bonded to the contacts which form a four-point probe.

MEASUREMENT RESULTS

Fig. 2 shows representative I_{DC}-V_{DC} and (dI/dV)-V_{DC} characteristics of an Au/n-Si Schottky diode, fabricated as described above. The dc current was ramped from -0.8 to 0.7 mA, the sine current had an amplitude between 10 and 500 nA and a frequency of 831 Hz.

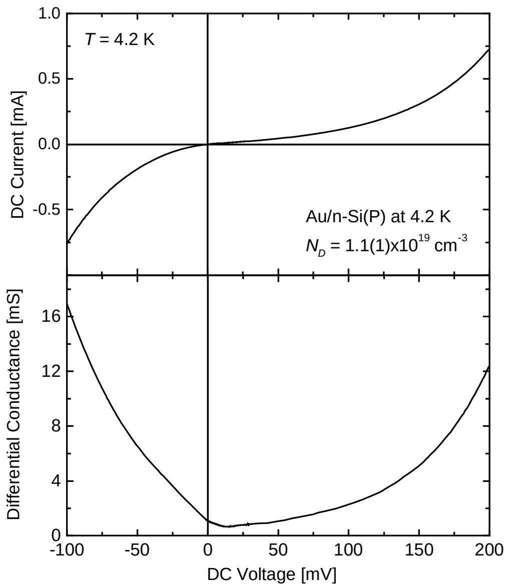

Fig. 2. Measured dc current and differential conductance (as a function of the dc voltage) of an Au/n-Si Schottky diode at 4.2 K, fabricated on $1.1(1)\times10^{19}$ cm^{-3} phosphorus-doped Cz silicon.

The (dI/dV)-V_{DC} characteristic of Fig. 2 reflects some important features of the DOS. Note that the current through the Schottky diode reflects both the tunnel probability and the DOS. Negative dc voltages in Fig. 2 correspond to a situation where the Schottky diode is reverse biased. In this case, electrons tunnel from the metal into the silicon (they are not thermally excited over the Au/n-Si barrier at 4.2 K). At large reverse bias, the electrons tunnel deep into the conduction band, where the DOS is large, leading to a high differential conductance. With decreasing reverse bias, electrons tunnel into regions of decreasing DOS, resulting in a lower differential conductance.

Going from reverse to forward bias, the tunnel direction changes, i.e. electrons tunnel from low energy states of the conduction band into states of the metal (note that silicon is degenerate at N_{dop} = 1.1×10^{19} cm^{-3} and T = 4.2 K). With increasing forward bias, the differential conductivity reflects the DOS near the conduction band edge. The minimum of the differential conductance corresponds to the minimum in the DOS. Beyond this minimum, the tunnel barrier becomes smaller, leading to an increase in the tunnel probability and hence in the differential conductance.

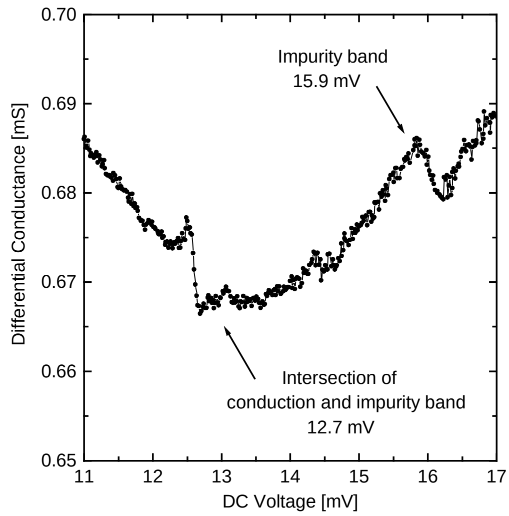

Fig. 3. Detailed measurement of the dI/dV versus V_{DC} characteristic between 11 and 17 mV at 4.2 K (low bias range of Fig. 2).

The real DOS deviates most from the intrinsic DOS near the conduction band edge. Therefore, a detailed measurement was performed between 11 and 17 meV, shown in Figure 3. As mentioned above, the minimum of dI/dV corresponds to the intersection between the conduction and impurity bands. Since we chose the energy of the conduction band edge to be zero, the minimum in Fig. 3 corresponds to the Fermi energy, which is 12.7 meV. A peak in dI/dV appears 3.2 meV above this minimum, indicating the maximum DOS of the impurity band. The feature just below 12.7 meV disappears if the sample is heated to slightly higher temperatures, whereas the feature of the impurity band stays the same. In accordance with Refs. 9-11, we interpret the first feature to arise from phonon-assisted inelastic tunnelling. The insensitivity of the second feature to small temperature changes strongly indicates that it is reflects the DOS.

Fig. 4 shows phonon peaks occurring at higher dc voltages. Some of them have been interpreted in Refs. 9-11, for example as inelastic tunnelling assisted by TO phonons at the centre of the Brillouin zone (Γ).

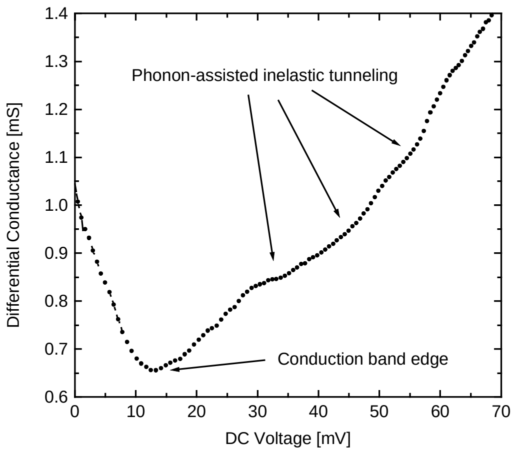

Fig. 4. Detailed measurement of the *dI/dV* versus V_{DC} characteristic between 20 and 70 mV at 4.2 K (medium bias range of Fig. 2).

CALCULATION OF THE DOS OF HEAVILY DOPED SI

Mathematically, the current as a function of voltage of a Schottky diode at 4.2 K can be described as [5]

$$I = \gamma \int_{\mu_F - V}^{\mu_F} dE\, P(E)\, e^{-W(V,E)} , \qquad (1)$$

where the Fermi distribution is approximated by a step function. *P(E)* represents the DOS of electrons of phosphorus-doped silicon as a function of energy *E* ($E = 0$ at the conduction band edge). The factor $e^{-W(V,E)}$ is the tunnel probability of electrons through the barrier (calculated using Franz's two-band model [12] and the WKB approximation [6]). μ_F is the Fermi energy in respect to the conduction band edge, and γ is a scaling factor.

Differentiation of Eq. (1) with respect to the voltage results in the following expression for the DOS [13]:

$$P(\mu_F - V) = \gamma^{-1}\left(\frac{dI}{dV} - \frac{I}{V_o(V)}\right) e^{W(V,\mu_F - V)} \qquad (2)$$

$$W(V,E) = \begin{cases} \dfrac{1}{E_o} \displaystyle\int_0^{\mu_F + V_B - V - E} d\eta \sqrt{\frac{\eta\left(1 + \eta/E_g\right)}{\eta + E}} , & V < \mu_F \\[2ex] \dfrac{1}{E_o} \displaystyle\int_0^{\mu_F + V_B - V} dt \sqrt{\frac{(t - E)\left(1 + (t - E)/E_g\right)}{t}} , & \mu_F < V \end{cases}$$

$$V_o^{-1}(V) = \begin{cases} \dfrac{1}{E_o}\sqrt{\dfrac{V_B\left(1 + V_B/E_g\right)}{\mu_F + V_B - V}} , & V < 0 \\[2ex] \dfrac{1}{E_o}\sqrt{\dfrac{(V_B - V)\left(1 + (V_B - V)/E_g\right)}{\mu_F + V_B - V}} , & 0 < V < \mu_F \\[2ex] \dfrac{1}{E_o}\sqrt{1 + (\mu_F + V_B - V)/E_g} , & \mu_F < V \end{cases}$$

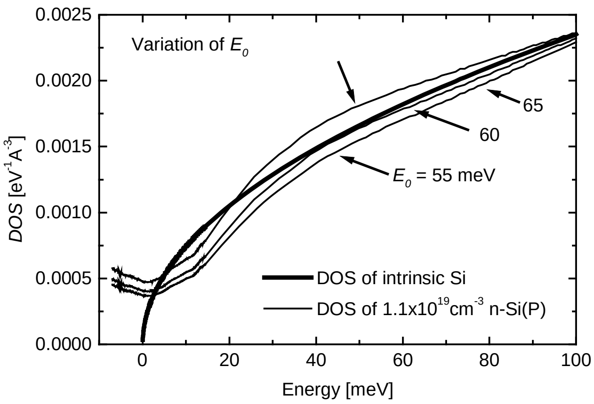

Fig. 5. The DOS calculated from experimental data (Fig. 2) for three different E_o values (solid lines) and the DOS of intrinsic silicon (bold line). For this calculation, V_B was 0.8 V and μ_F was 13 meV (see Fig. 3). The conduction band edge energy was set to be zero.

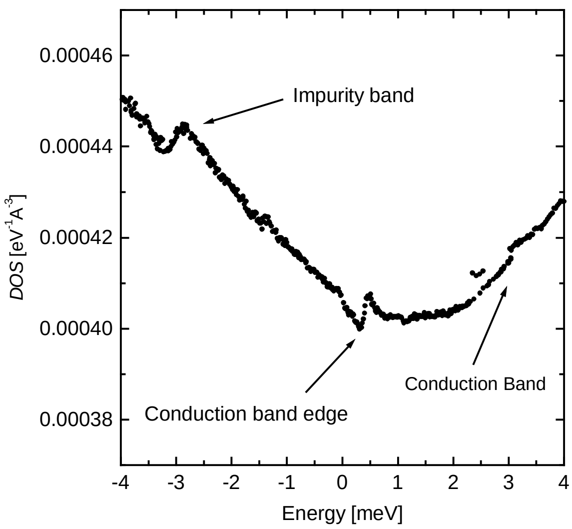

Fig. 6. The DOS calculated from the experimental data of Fig. 2 for E_o = 60 meV, μ_F = 13 meV, and V_B = 0.8 V in the energy range between –4 and 4 meV (small energy range around the conduction band edge of Fig. 5).

Eq. (2) contains four unknown parameters: The tunnel energy E_0, the Au/n-Si potential barrier V_B, the equilibrium Fermi energy μ_F and the scaling factor γ.

The scaling factor is obtained by fitting the measured DOS to the intrinsic DOS at high energies far away from the conduction band edge. As mentioned above, the Fermi energy is 12.7 mV and a value of V_B = 0.8 V is chosen for the Au/n-Si contact [14]. In Figure 5, we varied the remaining parameter E_o between 55 and 65 meV, using V_B = 0.8 V and μ_F = 12.7 meV. The calculated DOS is most consistent with the intrinsic DOS at medium energies, if we chose $E_o \approx 60$ meV. The mathematical approach used in this work is based on Ref. 5 and relies on consistency arguments. This limitation should be overcome by developing more refined mathematical models.

The feature that we interpreted in Fig. 3 as impurity band is too small to be seen in Figure 5. Therefore, we show this feature with higher resolution in Figure 6. There, it becomes apparent that it is superimposed by the phonon hump. A more detailed analysis is necessary to distinguish between the DOS and phonon peaks.

CONCLUSION

We measured the *I-V* and the *(dI/dV)-V* characteristics of Au/n-Si Schottky diodes at 4.2 K. These diodes were fabricated on $1.1(1)\times10^{19}$ cm^{-3} phosphorous-doped Cz silicon. We extracted the DOS of these doping densities from these measurements by calculating the quantum-mechanical tunnel probability through the Schottky barrier. For such calculations, we used a similar but more detailed approach than Mahan *et al*. However, our calculations are based on self-consistency arguments (as is the method of Mahan *et al*.), and a refined method needs to be developed to obtain a more accurate DOS.

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REFERENCES

[1] T.F. Rosenbaum *at al*. *Phys. Rev.* **B27**,1983, pp. 7509 - 7523.

[2] A. Schenk, *J. Appl. Phys.* **84,** 1998, pp. 3684 - 3695.

[3] D.H. Neuhaus, P.P. Altermatt, and A.G. Aberle, *Sol. Energy Mater. Sol. Cells* (in press).

[4] K.P. Abdurakhmanov, S. Mirkhmedov, and A.T. Teshabaev, *Sov. Phys. Semicond.* **12**, 1978, pp. 457-459.

[5] G.D. Mahan and J.W. Conley, *Appl. Phys. Lett.* **11**, 1967, pp. 29-31.

[6] J.W. Conley and G.D. Mahan, *Phys. Rev.* **161**,1967, pp. 681 - 692.

[7] W.R. Thurber *et al*., *J. El. Chem. Soc.* **127**, 1980, pp. 1807 - 1812.

[8] Mousty *et al*. *J. Appl. Phys.* **45**, 1974, pp. 4576 - 4580.

[9] G. Salace and J.M. Patat, *Thin Solid Films* **207** 1992, pp. 213 - 219.

[10] D.E. Cullen *et al*., *Phys. Rev*. **B2**, 1970, pp. 3157 - 3169.

[11] H.G. Busman et al. *Z. Phys.* **B59**, 1985, pp. 439 - 443.

[12] W. Franz, Handbuch der Physik, vol. 17 (Springer-Verlag, Berlin, 1956), p. 275.

[13] Details about the derivation will be given in a forthcoming paper.

[14] S.M. Sze, Physics of Semiconductor Devices, 2nd ed. (John Wiley, Singapore, 1981), p. 206.