

Influence of surface states on current–voltage characteristics of M-I-pSi solar cells

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Abstract. A detailed analysis of the M-I-pSi solar cell has been made considering all the components of the hole and electronic currents. The tunnelling current due to the surface states has been evaluated by taking a realistic distribution of surface states (using the reported experimental data) and their occupational probability, thus the calculations of the open circuit voltage V_{oc} and the short-circuit current density J_{sc} have been made for different positions of the impurity level (surface states) in the band gap. The location of the surface states has a significant effect on V_{oc} and J_{sc} . For surface states in the range of -0.15 eV to 0.15 eV no change of V_{oc} or J_{sc} is observed, but they decrease for surface states located at the two band edges. The theoretical results show a good agreement with the reported experimental results for V_{oc} and J_{sc} as a function of oxide thickness for realistic values of the various semiconductor parameters.

1. Introduction

MIS/SIS solar cells have attracted much interest in the last few years. Both n-type and p-type silicon has been used for the fabrication of these solar cells with controlled growth of the thin oxide layer. Instead of metal, transparent conductors (ITO and SnO_2) have been found to yield better results. Most of the experimental results that are available are for p-Si, but there has been limited detailed analysis of the tunnelling M-I-pSi structure. Kamal Rajkanan *et al* (1980) have used electrical equivalent models of MIS and the Schottky barrier diode to explain their data for an MIS solar cell and a low oxide thickness. However, it does not give any physical picture of the energy levels or the different current components. Green *et al* (1974), in their theory of M-I-pSi tunnel diodes, have shown that, when the insulating layer is thin, the semiconductor electron quasi-fermi level is pinned. This model has the basic limitation that, even in the presence of oxide, the theory treats MIS as a p–n junction. A realistic model should take into account the different mechanisms of charge transport through the oxide, as has been done by Card and Rhoderick (1971) for the n-Si substrate. With some modifications, the proposed model of Card and Rhoderick for M-I-nSi can reasonably explain the experimental results. In the present paper, this modified model (Bhatnagar *et al* 1988, Biswas *et al* 1989) has been extended to M-I-pSi. Explicit calculations have been made to determine the relative importance

of various physical processes. The effect of the surface-state position of V_{oc} and J_{sc} has been calculated as a function of oxide thickness and compared with the reported experimental data.

2. Theory

The band diagram of an MIS (p-Si) solar cell in equilibrium (zero-bias condition) is shown in figure 1. At equilibrium, the total potential difference V_B between the metal and the semiconductor is given as the poten-

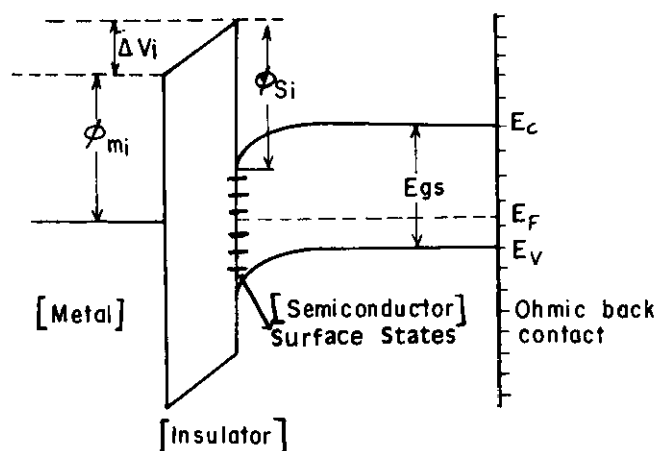


Figure 1. Band diagram of MIS solar cell.

tial drop across the semiconductor V_D and the oxide V_i , i.e.

$$V_B = V_D + V_i \quad (1)$$

when an external potential difference V is applied across the junction. When it is developed by the photovoltaic effect we have

$$V = \Delta V_i + \Delta V_D \quad (2)$$

where ΔV_i is the change in V_i and ΔV_D is the change in V_D .

The incident photons falling on the oxide semiconductor interface produce electron-hole pairs. The electron-hole pairs are neutralized by the electron current flowing from the metal to the semiconductor and the hole current flowing from the semiconductor to the metal if radiation recombination is neglected.

The electrons and holes can be transported in the following ways:

- (1) Electrons jumping over the barrier.
- (2) Tunnelling through the barrier.
- (3) Transport through the interface states (Sze, 1986).

These transport mechanisms are discussed below.

2.1. Transport by jumping over the barrier

The current through this mechanism can essentially be represented in the same way as for thermionic emission and can be expressed as

$$J_{ni} = J_{n0} \exp(-b_n \kappa_n^{1/2} \delta) [\exp(q\Delta V_D/KT) - 1] \quad (3)$$

where

$$J_{n0} = qV_n n_0 \exp(-qV_D/KT). \quad (4)$$

Apart from this, carrier transport can take place by tunnelling.

2.2. Transport by tunnelling through the barrier

The current due to tunnelling is given as

$$J_{n2} = qV_n \delta_n \exp(-b_n \kappa_n^{1/2} \delta) \quad (5)$$

and the hole tunnelling current as

$$J_p = qV_p \delta_p \exp(b_p \kappa_p^{1/2} \delta). \quad (6)$$

It may be noted that the tunnelling probabilities for electrons and holes are $\exp(-b_n \kappa_n^{1/2} \delta)$ and $\exp(b_p \kappa_p^{1/2} \delta)$ respectively, where δ is the insulator thickness. An explanation of all the symbols used in this analysis is given in table 1. These expressions for the tunnelling coefficients arise due to the fact that it is the tunnelling effective masses of the carriers that are being considered, and these are different from the free carrier masses considered previously (Card and Rhoderick 1971). The electron b_n and hole b_p tunnelling coefficients can be expressed as

$$b_n = (m_n^*/m_0)^{1/2} \quad (7)$$

$$b_p = (m_p^*/m_0)^{1/2} \quad (8)$$

where m_n^* and m_p^* are the tunnelling effective masses of electrons and holes respectively.

Following the pn-junction tunnel-diode theory, the effective masses can be written as

$$m_n^* = 2m_0 m_c^*/(m_c^* + m_0) \quad (9)$$

$$m_p^* = 2m_0 m_v^*/(m_v^* + m_0) \quad (10)$$

where m_c^* and m_v^* are the conductivity effective masses of electrons and holes in the conduction band and the

Table 1. Nomenclature and values of the variables and constants used in the analysis of the M-I-pSi solar cell.

Symbols	Description	Values	Reference
b_p, b_n, b_s	Tunnelling constant for holes, electrons and surface states	0.51, 0.74 and 0.6	[6]
$\kappa_p, \kappa_n, \kappa_s$	Barrier height for holes, electrons and surface states	3.2 eV, 4.6 eV	[1]
$\sigma_p, \sigma_n, \sigma_s$	Capture cross-section for holes, electrons and surface states	$\sim 10^{-21} \text{ m}^2$	—
V_p, V_n	Velocity of holes and electrons	$\sim 10^5 \text{ m s}^{-1}$	[15]
ϵ_i, ϵ_s	Permittivity of the insulating oxide and semiconductor	3.9, 11.9	[15]
g	Ground state degeneracy factor for donor and acceptor	2, 4	[15]
J_{sc0}	Short circuit current density when $\delta = 0$	350 A m^{-2}	—
L_p, L_n	Diffusion length for holes and electrons	$50 \mu\text{m}, 100 \mu\text{m}$	—
τ_p, τ_n	Life time for hole and electron	10^{-5} s	[15]
T	Absolute temperature	300 K	—
p	Density of holes in the valence band	—	[15]
n	Density of electrons in the conduction band	—	[15]
p_0	Density of holes in the valence band near the surface for thermal equilibrium	—	[6]
n_0	Density of electrons in the conduction band near the surface for thermal equilibrium	—	[6]
p_1, n_1	Density of holes and electrons when the Fermi-level energy coincides with the surface-state energy in equilibrium	—	[6]
K	Boltzmann constant	—	—
q	Charge on one electron	—	—
$g(E_s)$	Density of states in metal at energy $E = E_s$	—	—
E_s, E_f	Energy of surface state and Fermi-level position	—	—

valence band respectively. For the M-I-pSi structure, in which silicon is the substrate semiconductor, the values of b_n and b_p are calculated by taking

$$m_c^* = 0.28m_0 \quad (11)$$

$$m_v^* = 0.16m_0. \quad (12)$$

The transport of carriers takes place through the surface states and has an important effect on the total characterization.

2.3. Transport through the surface states

To introduce the effect of tunnelling through the surface states, let us consider surface states of density D_s having energy E_s evenly distributed in the energy range ΔE_s . The electrons tunnel from these surface states to vacant states in the metal. Similarly, a tunnelling current from the metal to the surface states exists. Let σ_{st} represent the capture cross-section of the surface states for tunnelling, and f_{so} and f_{mo} the occupational probability of surface states and metal respectively. The electron tunnelling from surface states to vacant states in the metal is given by J_{IM} :

$$J_{IM} = qD_s f_{so} \exp(-b_s \kappa_s^{1/2} \delta) \sigma_{st} V_m g(E_s) \Delta E_s \times [1 - f_{mo}(E_s)]. \quad (13)$$

The electron tunnel current from the vacant states of the metal to the surface states J_{MI} is

$$J_{MI} = qD_s f_s \exp(-b_s \kappa_s^{1/2} \delta) \sigma_{st} V_m g(E_s) \Delta E_s \times [1 - f_{so}(E_s)] \quad (14)$$

where V_m is the thermal velocity of electrons in the metal. The modified tunnelling coefficient has been expressed as $\exp(-b_s \kappa_s^{1/2} \delta)$. The value of b_s is taken as equal to the mean value of b_n and b_p as suggested by earlier workers in this field (Srivastava *et al* 1979), since no definite theory exists to calculate its value. The value of κ_s depends on the position of the surface state considered. In thermal equilibrium, the tunnelling current from surface states to vacant states in the metal is equal to the tunnelling current from the metal to the surface states. Therefore

$$J_{IM} = J_{MI}. \quad (15)$$

Substituting (13) and (14) into (15), we obtain

$$f_{so} = f_{mo}. \quad (16)$$

Due to the photogenerated voltage, the occupational probability will change from f_{so} to f_s and f_{mo} to f_m . The net tunnelling current through the surface states will be the difference between the current components, i.e. J_{IM} and J_{MI} . Hence, the net tunnelling current through the surface states can be given as

$$J_t = qD_s \sigma_{st} V_m g(E_s) \Delta E_s \times \exp(b_s \kappa_s^{1/2} \delta) [(1 - f_m)f_s - (1 - f_s)f_m]. \quad (17)$$

Using the Maxwell-Boltzmann approximation f_m can be related to f_{mo}

$$f_m = f_{mo} \exp(q\Delta V_D/KT). \quad (18)$$

Thus we obtain the net tunnelling current as

$$J_t = qD_s \sigma_{st} V_m g(E_s) \Delta E_s \times \exp(-b_s \kappa_s^{1/2} \delta) [f_s - f_{so} \exp(-q\Delta V_i/KT)]. \quad (19)$$

2.4. Evaluation of V_{oc} and J_{sc}

The current through the cell J is equal to the algebraic sum of the hole current J_p , the electron current $J_n = J_{N1} + J_{N2}$ and the current due to tunnelling at the surface state J_t

$$J = -J_p + J_n + J_t \quad (20)$$

The open-circuit voltage condition V_{oc} obtained when $J = 0$ and the short-circuit current condition J_{sc} when $V = 0$ and thus can be evaluated by substituting equations (3), (4) and (19) into equation (20).

2.5. Evaluation of the various parameters

The excess carrier density (δ_n is the electron density and δ_p is the hole density) has been calculated in the following manner. The electrons generated by light absorption reach the semiconductor/oxide interface. There, they either tunnel through the barrier presented by the oxide layer and recombine at the surface states or diffuse towards the semiconductor and recombine, depending upon the corresponding probabilities of each process. The value of δ_n can be evaluated by equating the above processes and hence is given by the following equation:

$$\delta_n = \frac{J_{sco} - J_{n0} \exp(-b_n \kappa_n^{1/2} \delta) [\exp(q\Delta V_D/KT) - 1] - (qL_n/\tau_n) n_0 \exp(-qV_D/KT) [\exp(q\Delta V_D/KT) - 1]}{qV_n \exp(-b_n \kappa_n^{1/2} \delta) + qV_n \sigma_n D_s f_s + qL_n/\tau_n \exp[-q(V_D - \Delta V_D)/KT]} \quad (21)$$

similarly

$$\delta_p = \frac{J_{sco} - qL_p/\tau_p \exp(-qV_D/KT)}{qV_p \exp(b_p \kappa_p^{1/2} \delta) + qV_p \sigma_p D_s f_s + qL_p/\tau_p \exp[-q(V_D - \Delta V_D/KT)]}. \quad (22)$$

The occupational probability has previously been considered to be independent of the position of the surface states. To arrive at a more accurate representation of the occupational probability we have adopted the following procedure. The initial occupational probability (thermal equilibrium condition) is given as follows:

(i) for donor states

$$f_{so} = \frac{1}{1 + g \exp[(E_F - E_S)/KT]} \quad (23)$$

(ii) for acceptor states

$$f_{so} = \frac{1}{1 + 1/g \exp[(E_F - E_S)/KT]} \quad (24)$$

In these equations it has been assumed that the surface states are situated at an energy E_S as in the Shockley-Read theory (Sze 1986) and also that the charge in each state can have only two possible values differing by the charge of one electron.

The final occupational probability f_s is calculated by assuming that the electron capture rate U_n , the hole capture rate U_p and the tunnelling rate at surface states J_t/qD_s balance each other:

$$U_p - U_n + (J_t/qD_s) = 0. \quad (25)$$

U_n and U_p can be calculated using the Shockley-Read theory. The electron capture rate U_n can be expressed as

$$U_n = V_n n \sigma_n (1 - f_s) - V_n n_1 \sigma_n (1 - f_s) \quad (26)$$

similarly

$$U_p = V_p p \sigma_p f_s - V_p p_1 \sigma_p (1 - f_s). \quad (27)$$

Using the expressions for U_p , U_n and J_t from equations (26), (27) and (17) yields the following value for f_s

$$f_s = \frac{nv_n \sigma_n + p_1 V_p \sigma_p + f_{so} (J_{t0}/qD_s) \exp(-q\Delta V_i/KT) \exp(-b_s \kappa_s^{1/2} \delta)}{(n + n_1) V_n \sigma_n + (p + p_1) V_p \sigma_p + (J_{t0}/qD_s) \exp(-b_s \kappa_s^{1/2} \delta)}. \quad (28)$$

The change in the voltage developed across the oxide layer ΔV_i can be calculated in the following manner

$$\Delta V_i = (\delta/\epsilon_i) \Delta q_m \quad (29)$$

where Δq_m is the extra charge on the metallic side

$$\Delta q_m = -(\Delta q_s + \Delta q_{ss}) \quad (30)$$

Δq_s is the extra charge stored in the space charge layer and Δq_{ss} is the extra charge stored in the surface states. The values of Δq_s and Δq_{ss} are given as

$$\Delta q_s = (\epsilon_s/W) \Delta V_D \quad (31)$$

$$\Delta q_{ss} = qD_s(f_s - f_{so}). \quad (32)$$

Substituting Δq_s and Δq_{ss} in equation (30) and using (29), we find

$$\Delta V_i = \frac{(\delta/W)[(\epsilon_s/\epsilon_i)V] + (\delta/\epsilon_i)qD_s(f_s - f_{so})}{1 + (\delta/W)(\epsilon_s/\epsilon_i)} \quad (33)$$

2.6. Distribution of surface-state density

A number of distributions of the interface state density at the Si/SiO₂ interface in the bandgap of silicon have been reported (figure 2). An appropriate distribution

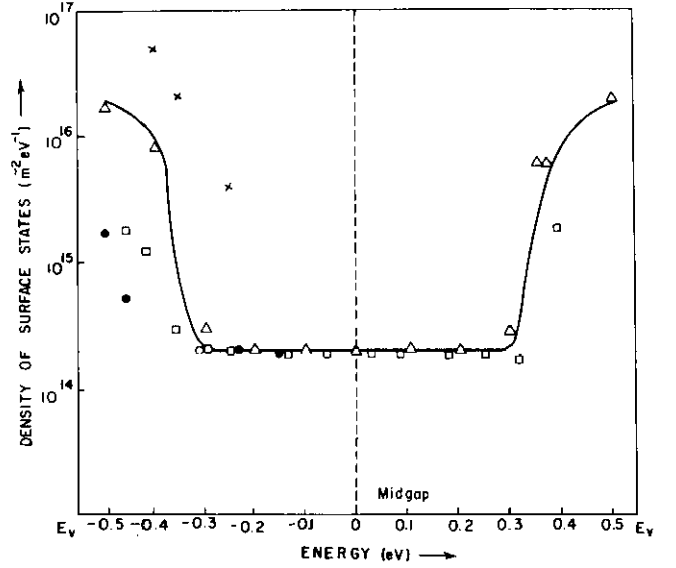


Figure 2. Density distribution of surface states against energy in the bandgap of Si at the Si/SiO₂ interface using the reported distributions: × [18], □ [17], Δ [19], ● [13].

obtained by curve fitting is shown in figure 2. The density of interface states near the conduction and valence bands, was found to be reproduced by the empirical equation

$$D_s = 6.190 \times 10^{16} E_s^2 - 2.92 \times 10^{15} E_s + 1.67 \times 10^{14} \quad (34)$$

and near the mid-point of the band gap the density of surface states is given by a constant value

$$D_s = 2 \times 10^{14}. \quad (35)$$

The distribution generated is used to find the value of D_s corresponding to a particular value of E_s . Various assumption are made:

(1) The surface states are independent states, i.e. no charge is exchanged between the surface states themselves.

(2) Since not much data is available on the distribution of the surface states as a function of oxide thickness, the distribution of surface states is considered to be independent of the oxide thickness.

(3) Surface states above the Fermi level are taken as donor type and below as acceptor type.

The J - V characteristic has been calculated by taking the initial value of the estimates of δ_n and δ_p by sub-

stituting f_{s0} for f_s in equations (21) and (22). From the estimates of δ_n and δ_p , f_s is calculated from equation (25). An iterative procedure is used until a consistent value of f_s satisfying equations (21), (22) and (25) is obtained. The J - V characteristic for a particular thickness of insulator and surface state position is calculated and V_{oc} and J_{sc} are obtained. The procedure is repeated for different thicknesses of oxide and various positions or the surface state varying from -0.45 eV to 0.45 eV (with the mid-point of the band gap as zero reference). For the present calculations we have used the silicon parameters for '1 ohm cm' resistivity given in table 1.

3. Results and discussion

Calculated values of V_{oc} and J_{sc} for different surface states located at an interval of 0.02 eV in the band gap of Si for an insulator thickness in the range of 6 – 18 Å are given in figures 3(a) and 3(b) respectively. From

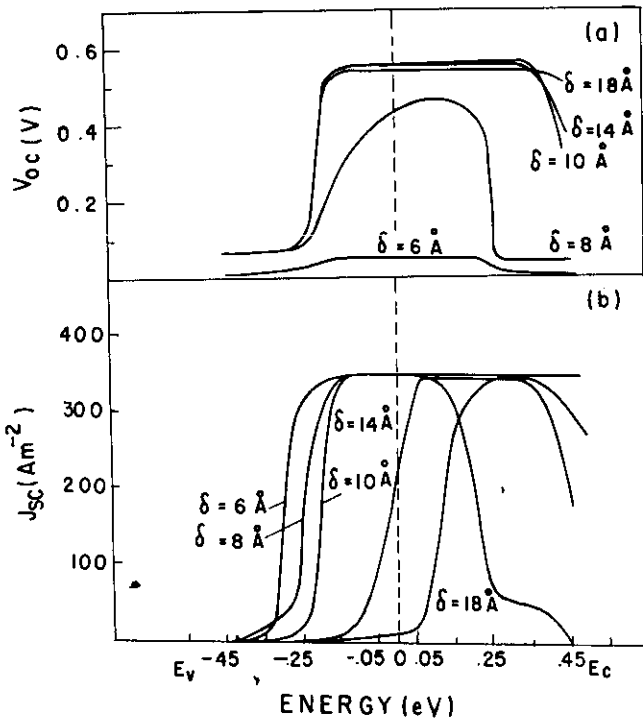


Figure 3. Variation of (a) open-circuit voltage V_{oc} and (b) short-circuit current density J_{sc} with the location of surface states in the band gap of Si for various values of the band gap width in the range 6 Å to 18 Å.

figure 3(a), it can be seen that for surface states located near the midpoint of the band gap (0.05 eV), V_{oc} increases with the increase in the insulator thickness and then saturates for higher thicknesses of oxide. It may be noted that the choice of the location of the surface states has a significant effect on V_{oc} . It is observed from figure 3(a) that when the surface states are located in the range -0.15 eV to 0.15 eV no significant change in V_{oc} with position takes place, but

it decreases when the surface states are located at the edges. The variation of J_{sc} for different oxide thickness (6 – 18 Å) has been studied at various surface-state positions (figure 3(b)). Studying the effect of oxide thickness on J_{sc} (for the surface states located near the midpoint of the band gap, say at 0 eV, as shown in figure 3(b)), it can be seen that J_{sc} remains constant when the oxide thickness increases from 6 Å to 10 Å but falls to lower values when the thickness further increases to say 18 Å. Studying the variation of J_{sc} for a particular thickness (say $\delta = 10$ Å) for different locations of the surface states across the band gap, J_{sc} shows a constant value for the surface states near the mid-point of the band gap (-0.15 to $+0.15$ eV) but decreases for the surface states near the edges of the band gap. This decrease is more drastic for surface states at the valence band edge. The curves are not symmetrical, due to the different occupational probabilities of the surface states near the conduction and valence band edges.

Several theoretical papers have appeared in the literature which give a quantitative variation of V_{oc} and J_{sc} similar to that observed experimentally. However, they (Sen 1982) have used unrealistic values of $\sigma_p \sim 10^{-25} \text{ m}^2$, while experimental values vary from 5×10^{-21} to $2 \times 10^{-20} \text{ m}^2$ (Kriegler *et al* 1979). We have tried to match our theoretical results with the experimental data in order to check the validity of the model and the numerical values of the different parameters. The values of V_{oc} and J_{sc} depend on the choice of values of the various parameters reported in table 1.

A comparison of previously obtained experimental values [9, 10, 11] with the theoretical ones can be conveniently examined from plots of V_{oc}/V_{ocmax} and J_{sc}/J_{scmax} as functions of oxide thickness. Such plots are shown in figures 4(a) and (b) respectively. One would

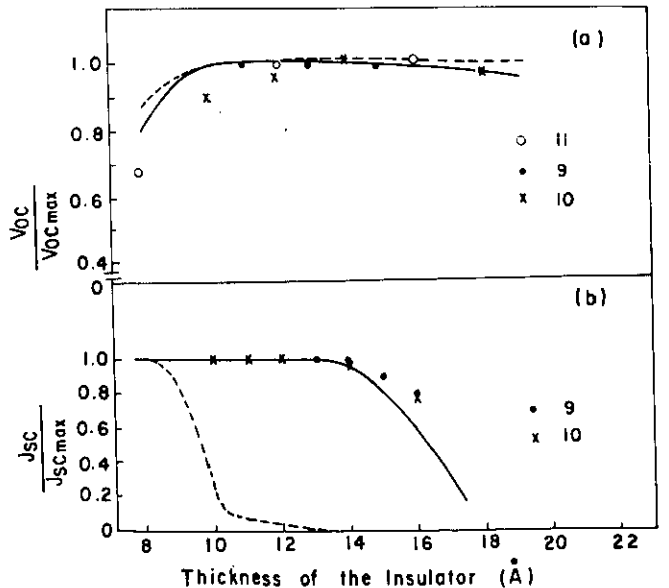


Figure 4. Variation of (a) V_{oc}/V_{ocmax} and (b) J_{sc}/J_{scmax} with insulator thickness for surface states located at -0.35 eV (broken curve) and 0.05 eV (solid curve), where \times indicates experimental results.

expect surface states to arise from the diffusion of electrode material or oxygen ions to the Si/SiO₂ interface. For the solar cells whose data has been reported in figure 4, the aluminium electrode material is expected to give surface states close to the valence band edge. Hence, theoretical curves have been drawn in the same figure for two situations (a) when the surface states are located at the band edges (-0.35 eV) and (b) when they are located near the mid-point of the band gap (0.05 eV). The experimental data closely match the curves for the surface states near the mid-point of the band gap. This suggests that surface states due to oxygen ions probably dominate the performance of the solar cell. Several authors have suggested that the degradation of M-I-nSi solar cells is due to the diffusion of oxygen at the interface and the increase of oxide thickness. Hence, it seems reasonable to assume that the surface states due to oxygen ions play a dominant role. It may be pointed out that the creation of any surface states at the edges (which may be due to Al) should lead to a drastic fall in J_{sc} and V_{oc} . The diffusion of aluminium in Al-pSi (with a thin oxide layer) is probably responsible for the drastic initial fall in V_{oc} and J_{sc} reported by Ponpon and Stiffert (1978).

4. Conclusions

Theoretical values of V_{oc} and J_{sc} have been calculated using a model of the M-I-pSi solar cell and realistic values of the semiconductor parameters (table 1). The values show very good agreement with the reported experimental data if the density of surface states is

assumed to be of the order of $10^{14} \text{ m}^{-2} \text{ eV}^{-1}$ and the impurity level (probably due to oxygen ions) is considered near the mid-point of the band gap.

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