

New resistivity/dopant density model for compensated-Si

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Abstract: Models establishing relationships between electrical resistivity and dopant densities of silicon wafers/bricks are not applicable for compensated-Si, such as upgraded metallurgical grade silicon UMG-Si. To date, no satisfactory theoretical model has been able to explain precisely the variety of new experimental results and observations related to compensated-Si. In this study, a new approach considering equilibrium ionisation constants according to electrolyte theory was proposed, which reproduce, for single-doped Si, Thurber's curves of charge carrier's mobilities. When more than one doping species are involved, as in compensated-Si, a numerical algorithm has to be used for solving multiple equilibrium systems. The study of such systems demonstrates a particular behaviour known from buffered solutions. Equilibrium constants were calculated from thermodynamic properties of chemical compounds, and a new general theory was proposed using available knowledge of electrochemistry (Nernst equation, Butler-Volmer equation). Considering that the silicon/dopant systems constitute a weak electrolyte solid solution, it is concluded that the electrolyte solution theory provides a good physical model and mathematical framework to get a better understanding of solar cell's behaviour.

Key words: silicon; resistivity; compensated; UMG; boron; phosphorus

1 Introduction

Upgraded metallurgical grade silicon (UMG-Si) is typically 99.999% pure Si. UMG-Si is produced by purification of metallurgical grade silicon, which has a significantly less of only about 99%, by variety of metallurgical processes. The main challenge in the purification approaches is mostly related to the removal of two main electrically active impurities boron (B) and phosphorus (P), respectively.

When both donors and acceptors are present in silicon, it is called compensated-Si. The compensation phenomenon is typical for the UMG-Si. Since boron and phosphorus have antagonist effects on the electrical characteristics of Si, their overall quantity and their ratio need to be well controlled during crystallizations for instance, in order to achieve the required resistivity of the final products (wafers).

While the availability of UMG-Si is almost infinite for solar applications, its material characteristics are still poorly understood and pose a scientific challenge to researchers trying to expand its advanced utilizations.

The available information on compensated-Si in published literature is very limited. Reliable data only exists for monocrystalline single-doped silicon with boron or phosphorus. Furthermore, the models available for establishing relationships between electrical conductivity or resistivity and dopant densities are only based on empirical nature.

Based on new experimental data, it is found that those models which are available today are not applicable for compensated-Si. To date, no satisfactory theoretical model is able to explain precisely the variety of new experimental results and observations related to compensated-Si. Thus, a new approach is proposed in this work.

2 Theoretical review

2.1 Resistivity

The resistivity of Si is calculated using the following equation:

$$\rho = \frac{1}{q \cdot (\mu_p \cdot p + \mu_n \cdot n)} \quad (1)$$

where p and n are the hole and free electrons densities, respectively; q is the charge of electron. The mobilities of holes (μ_p) and electrons (μ_n) are generally derived from Thurber's curves.

2.2 Thurber's charge carrier mobility curves for Si

THURBER[1–2] from about 1975 to 1980, did research work to obtain an accurate relationship between the resistivity and dopant density of Si. The work was initiated because of disagreements between the measured values and those calculated using the existing relationships. Actual methods to convert dopant density to resistivity (and vice versa) are mainly based on his work[3].

Thurber assumed complete dopant ionization. According to Fig.1(a), for p-type Si,

$$\mu_p = f(p) = f(N_a) \quad (2)$$

$$\rho_p = \frac{1}{q \cdot \mu_p \cdot N_a} \quad (3)$$

According to Fig.1(b), for n-type Si,

$$\mu_n = f(n) = f(N_d) \quad (4)$$

$$\rho_n = \frac{1}{q \cdot \mu_n \cdot N_d} \quad (5)$$

2.3 Modification of Thurber's curves for compensated-Si

When both dopants are present, those mobility models are still applied in compensated-Si material. It is generally believed that both μ_n and μ_p have a functional dependence on the sum of acceptor and donor densities ($N_a + N_d$) to account for some "reduced mobility" in compensated-Si[4–5]. According to Fig.1(a), for p-type compensated-Si,

$$\mu_p = f(N_a + N_d) \quad (6)$$

$$\rho_p = \frac{1}{q \cdot \mu_p \cdot (N_a - N_d)} \quad (7)$$

According to Fig.1(b), for n-type compensated-Si:

$$\mu_n = f(N_a + N_d) \quad (8)$$

$$\rho_n = \frac{1}{q \cdot \mu_n \cdot (N_d - N_a)} \quad (9)$$

From experimental work with compensated-Si, it is observed that this model is not consistent with itself or with chemical analysis and cannot be used to predict an accurate resistivity from the dopant concentrations (and vice versa).

3 Applicability of weak electrolyte solution theory

Hole and electron densities (p and n) are generally assumed to be the same as their dopant densities (N_a and N_d) in single-dopant systems. This assumption is rarely verified. The general agreement in previous models was that incomplete dissociation of dopants has only negligible effects, however, for compensated-Si, it is not the case.

A new resistivity model is needed for multi-dopant Si systems (compensated-Si) which also has to be consistent with the proven Thurber's model for single-dopant Si systems. Looking for a theoretical model which can define a system including incomplete electronic dissociations of atomic species, complex kinetic equilibriums and transport of charged species, only one solution is fit for the couple of electrolyte solution theory and thermodynamics (semiconductors do not escape to the laws of thermodynamics).

3.1 Free electron and hole definitions

An electron hole (a hole) is a conceptual and mathematical opposite of a free electron. The concept describes the lack of an electron at a position where one could exist in an atom or atomic lattice. Atoms with an electron hole are defined as cations:

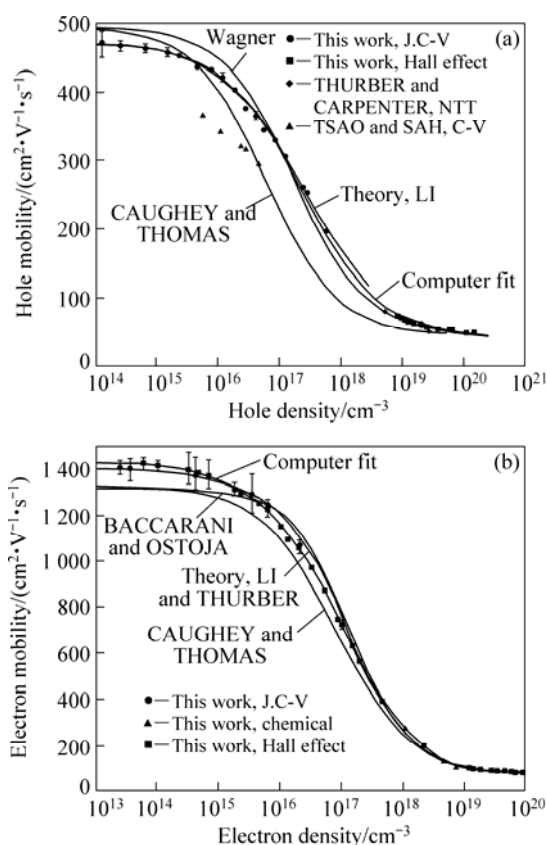


Fig.1 Thurber's curves describing relationships between carrier mobilities and dopant densities for boron (holes) (a) and phosphorus (free electrons) (b)

$$p=[\text{Si}^+] \quad (10)$$

Correspondingly, atoms with a free electron are defined as anions:

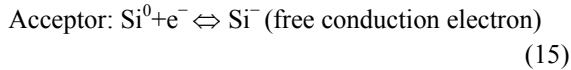
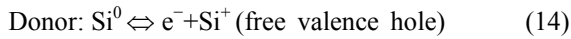
$$n=[\text{Si}^-] \quad (11)$$

3.2 Electrolyte definition

Electrolytes are substances that form ions when dissolved in solvents (usually water) and thus produce solutions that can conduct electricity. Strong electrolytes dissociate or ionize almost completely in a solvent, whereas weak electrolytes dissociate or ionize only partially. Doping reactions can be viewed in a way that is analogous to Brønsted-Lowry concept of the acid/base reactions. Both the reactions involve the transfer of one charged particle from a donor to an acceptor which is the particle being an electron in doping and proton in acid/base neutralization. When an acid donates a proton, that acid then becomes a conjugate base capable of accepting a proton. By analogy, when an n-type dopant donates an electron, afterward, that ionized dopant becomes a p-type specie that can accept an electron.



Also, as water, Si has an amphoteric nature:



3.3 Self-ionization of Si (electron-hole pair generation)

The reaction involves the transfer of a valence electron and its imaginary counterpart, a conduction hole*, to form two electrically conductive species:



$$K_{\text{Si}} = [\text{Si}^-] \cdot [\text{Si}^+] = n \cdot p = n_i^2 \quad (17)$$

Equilibrium constants are related to thermodynamic properties of the system:

$$K_{\text{Si}} = \exp\left(-\frac{\Delta G^0}{RT}\right) = \exp\left(-\frac{\Delta H^0 - T \cdot \Delta S^0}{RT}\right) \quad (18)$$

So, when $T=300$ K, it is obtained:

$$\Delta G^0 = -RT \ln(n_i^2) = -1.191 \text{ eV} (\text{spontaneous reaction}) \quad (20)$$

$$\Delta H^0 = E_g = 1.124 \text{ eV} (\text{endothermic reaction}) \quad (21)$$

$$\Delta S^0 = \frac{\Delta H^0 - \Delta G^0}{T} = 7.72 \times 10^{-3} \text{ eV} \cdot \text{K}^{-1} \quad (22)$$

* This concept has been implemented by opposition to the valence electron concept. In this way, a transfer reaction (permutation) can be considered as the mechanism for the hole formation to keep the stoichiometry of the reaction

3.4 Resistivity model for single-dopant systems

In single-doped Si (uncompensated), the mass balance and charge neutrality equations can be solved directly. The resulting function directly expresses the resistivity for p-type or n-type Si versus doping concentration (N_a or N_d).

3.5 Mathematical derivation

The acceptor doping reaction (Table 1) is



Table 1 Doping reaction of acceptor (before and after chemical equilibrium)

	Si^0	+	B^0	$\Leftrightarrow$	Si^+	+	B^-
Before equilibrium	Solvent		N_a		0		0
After equilibrium	Solvent		$N_a(1-\alpha)$		αN_a		αN_a

The ionization equilibrium constant is given as:

$$K_a = \frac{[\text{Si}^+] \cdot [\text{B}^-]}{[\text{B}^0]} = \frac{N_a \alpha^2}{1-\alpha} \quad (24)$$

where α is the ionization degree of boron. The solution to the quadratic equation is

$$\alpha = \frac{K_a}{2N_a} \left[\left(1 + \frac{4N_a}{K_a} \right)^{1/2} - 1 \right] \quad (25)$$

For uncompensated-Si the holes concentration is thus given as:

$$p = [\text{Si}^+] = \alpha N_a = \frac{K_a}{2} \left[\left(1 + \frac{4N_a}{K_a} \right)^{1/2} - 1 \right] \quad (26)$$

For p-type silicon, the resistivity Eq.(1) can be simplified as:

$$\rho_p \approx \frac{1}{\mu_p q p} = \frac{1}{\mu_p q (\alpha N_a)} \quad (27)$$

Eqs.(26)–(27) can be combined and the resistivity of p-type Si as a function of doping concentration can be expressed as:

$$\rho_p = \frac{2}{\mu_p q K_a} \left[\left(1 + \frac{4N_a}{K_a} \right)^{1/2} - 1 \right]^{-1} \quad (28)$$

3.6 Charge carrier mobility curves

The empirical mobility curves described by Thurber assumed complete dopant ionization. Thus, in the light of the proposed model, it is normal to observe that Thurber's curves are graphing an apparent mobility ($\alpha \mu_p$ and $\beta \mu_n$) in the ordinate axis rather than “pure” charge carrier mobility (μ_p and μ_n). The proposed model is

compared to Thurber's mobility curves by using the best data for compensated-Si (see Fig.2).

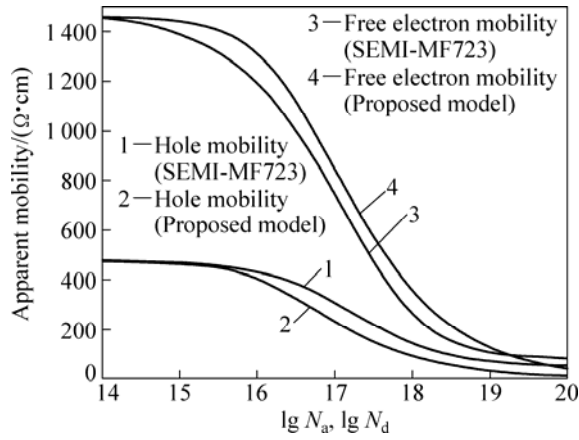


Fig.2 Apparent mobility of holes (boron) and free electrons (phosphorus) vs doping concentration from standard procedure SEMI-MF723 (derived from Thurber's curves) and proposed model ($K_a \approx 4.5 \times 10^{16}$, $K_d \approx 8.0 \times 10^{16}$, $\mu_p \approx 480 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$, $\mu_n \approx 1460 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$)

3.7 Resistivity model for multi-dopants systems

In compensated-Si, more than one doping types of species are present and the system's equilibrium cannot be solved analytically. In order to solve a multiple-equilibrium problem, as many independent algebraic equations as the number of participants are needed in the system being studied. For compensated-Si, three types of algebraic equations are used to solve the problem.

Equilibrium-constant expressions III:

$$K_{\text{Si}} = [\text{Si}^+] \cdot [\text{Si}^-] = 1.02 \times 10^{20} \quad (29)$$

$$K_a = \frac{[\text{Si}^+] \cdot [\text{B}^-]}{[\text{B}^0]} = 4.5 \times 10^{16} \quad (30)$$

$$K_d = \frac{[\text{Si}^-] \cdot [\text{P}^+]}{[\text{P}^0]} = 8.0 \times 10^{16} \quad (31)$$

Mass-balance equation II:

$$N_a = [\text{B}^0] + [\text{B}^-] \quad (32)$$

$$N_d = [\text{P}^0] + [\text{P}^+] \quad (33)$$

Charge neutrality equation I:

$$[\text{Si}^-] + [\text{B}^-] = [\text{Si}^+] + [\text{P}^+] \quad (34)$$

The best way to solve for $[\text{Si}^+]$ (or p) and $[\text{Si}^-]$ (or n) is numerically. This system of this equation is an analogue to the one used to solve the $[\text{H}_3\text{O}^+]$ concentration (or pH value) in a buffer solution made

from a mix of a weak acid and a weak base. The most important characteristic of a buffer solution is its resistance to change in pH value, so its resistivity can be viewed to be more stable than usual due to the addition of acid or base.

4 Other applications for new model

The weak electrolyte model may be successfully used to calculate the resistivity of compensated-Si and may improve the actual Thurber's empirical model. Furthermore, the electrolyte solution theory may also bring new answers to other phenomena observed in silicon solar cells.

4.1 Solar cell's IV curve

The usage of the Butler-Volmer equation (a fundamental equation for electrochemistry) can replace the Shockley ideal diode equation in the characteristic solar cell's equation. The Shockley equation is only a special case of Butler-Volmer equation where the cathodic polarization is $\alpha_c = 0$.

This modification has the advantage to improve the experimental fitting (as compared to the one diode model) and to fully conserve physical parameters meaning (as compared with the two diodes model). This simple modification may describe the complete IV curve (including reverse breakdown shown in Fig.3(b)).

$$i = i_o \left\{ \exp \left[(1 - \alpha_c) \frac{q(V - iR_s)}{kT} \right] - \exp \left[-\alpha_c \frac{q(V - iR_s)}{kT} \right] \right\} + \frac{V - iR_s}{R_{sh}} - i_L \quad (35)$$

4.2 Solar cell's degradation

When initially exposed to illumination or to an applied forward bias voltage, solar cells may exhibit a degradation of their performances. This phenomenon is referred as light induced degradation (LID). This effect is due to the activation of a specific metastable defect in Cz-Si or multi-Si, a conclusive explanation is still to be found. However, it is clearly correlated to the simultaneous presence of boron and oxygen in silicon[6]. The effect of LID on the performance IV curve is shown in Fig.4, both V_{oc} and i_{sc} decrease, lowering the efficiency of cells.

V_{oc} and i_{sc} are related together by the recombination current i_o (also called dark saturation current):

$$i_o \approx i_{sc} \exp \left(-\frac{qV_{oc}}{kT} \right) \quad (36)$$

LID takes place due to an increase of the recombination current from the regenerated state to the

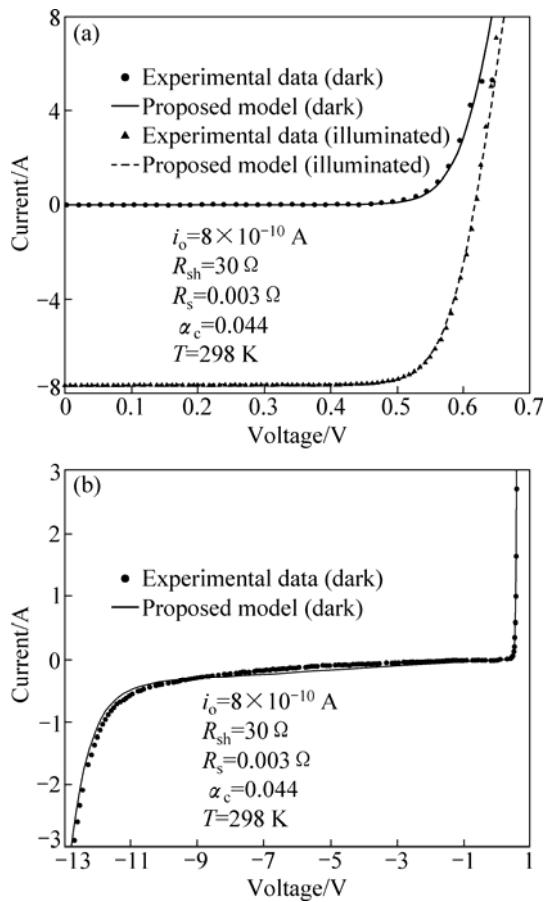


Fig.3 Solar cell IV curves (a) Dark and illuminated forward IV curves from experimental data and proposed model and (b) Dark IV curve showing reverse and forward bias characteristics

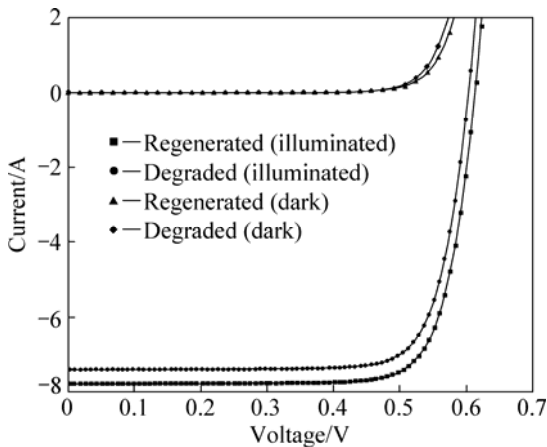


Fig.4 Solar cell's regenerated and degraded IV curves from experimental data and proposed mode

degraded state. The recombination current at junction is fixed by two phenomena: diffusion and drift currents. The later is produced under the influence of an applied electric field E_0 (or qV_{bi}). If this field is weakened ($E < E_0$), the recombination current i_0 would increase. Such a weakening of the internal electric field could happen if

polar molecular species are present in the junction acting as a dielectric.

A dielectric is material that may be polarized by an applied electric field (Fig.5). When a dielectric is placed in an electric field, electric charges do not flow through the material, as in a conductor, but only slight shift from their average equilibrium positions causes dielectric polarization. Because of dielectric polarization, positive charges are displaced toward the field and negative charges shift in the opposite direction. This creates an induced electric field (E_i) that partly compensates the field inside the dielectric (E_0). If a dielectric is composed of weakly bonded molecules, those molecules not only become polarized but also reoriented, so that their symmetry axis aligns to the field.

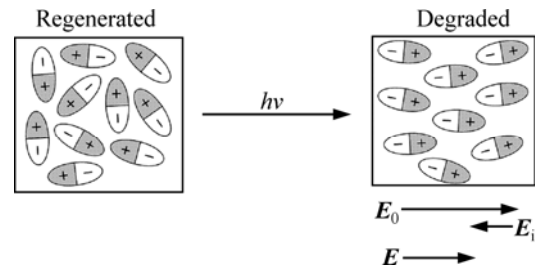
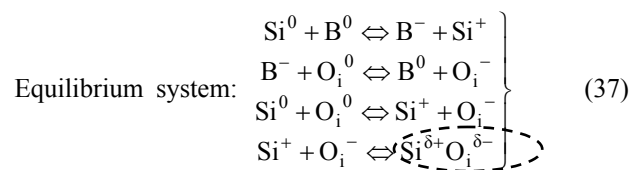


Fig.5 Proposed mechanism for LID: (a) Regenerated state with random orientation of polar oxygen complex; (b) Degraded state with reorientation of polar oxygen complex

The most probable mechanism for the formation of the weakly bonded molecule specie is an oxygen complex:



If the interstitial oxygen (O_i^0) density is high enough ($> 5 \times 10^{17} \text{ cm}^{-3}$), the Si- O_i complex becomes metastable in the presence of boron (Eq.(37)) and may be polarized by the internal electrical field E_0 (Fig.5).

LID occurs when doping with boron but not with gallium due to the stability of the Si- O_i complex.

5 Conclusions

1) Incomplete dopant ionization in silicon is assumed. It is derived that the theoretical equation giving the dopant density is in correspondence to resistivity for single-dopant Si systems. Comparing this equation to Thurber's model, it is able to demonstrate the validity of the starting assumption of the new model. This may lead to an improvement of the actual empirical model which

converts dopant density to resistivity (and vice versa).

2) When more doping species are involved, as in compensated-Si, a numerical algorithm is used for solving multiple equilibrium systems. The study of such systems demonstrates a particular behaviour known from buffered solutions, where adding dopant does not necessarily translate in a proportional response in conductivity (or inversely proportional in the case of resistivity).

3) Considering that the silicon/dopant system constitutes a weak electrolyte solid solution, it is concluded that the electrolyte solution theory provides a good physical model and mathematical framework to get a better understanding of solar cell's behaviour.

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一种新的补偿硅电阻率/掺杂浓度模型

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摘要: 硅片或硅块的电阻率与掺杂浓度的关系模型不适用于补偿硅, 如精纯冶金级硅(UMG-Si)。目前尚无合适的理论模型可以准确解释补偿硅实验和观测结果间存在的差异。基于电解液理论提出一种包含电离平衡常数的新方法, 可以得到单掺杂硅的电荷载子迁移率Thurber曲线。当掺杂硅中包含一种以上掺杂物质时, 需要采用数值算法来解决多重平衡系统。研究表明这类系统表现出一种缓冲溶液的特定行为。通过计算化合物的热力学参数获得平衡常数, 并利用现有的电化学知识(Nerust方程和Butler-Volmer方程)提出一个普遍理论。因为硅/掺杂物系统构成一个弱电解质固溶体, 电解质溶液理论为太阳能电池行为的认知提供了一个很好的物理模型和数学框架。

关键词: 硅; 电阻率; 补偿; UMG; 硼; 磷

(Edited by FANG Jing-hua)