The Features of Impurity Thermal-Photovoltaic and thermal-Voltaic Effect of Polycrystalline Structures

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Abstract A model of a p-n junction in the area of the grain boundaries in polycrystalline p-n structures is proposed. Shown mechanism of formation of impurity thermal-voltaic and impurity thermal-photovoltaic effects in IGB. A concept of creating highly effective comparatively inexpensive solar energy converters will be justified by the results we obtained during the study of the ITPV and ITV effects. Proposed theoretical model and experimentally obtained results can be useful in study of poly-Si n+-p structures, for example during external treatment. They allow explaining why in certain temperature ranges, an additional local heating, or applied potential, or a local illumination of pre-heated surface of poly-Si n+-p structure containing deep level impurities, can dramatically change the flow of current. In other words, such external treatment become trigger mechanism for discharge of charges accumulated in IGB due to impurity related thermal voltaic or thermal and photo-voltaic effects.

Keywords p-n Junction, Inter-Grain Boundaries, Polycrystalline Silicon, Impurity Thermal-Voltaic and Impurity Thermal-Photovoltaic Effects, Solar Energy

1. Introduction

A new phenomenon we have recently discovered by experiments in the inter-grain boundaries (IGB) of polycrystalline silicon (PS) solar cell (SC). It is the so-called impurity photovoltaic effect, as well as the impurity thermal-voltaic effect (ITV) and the impurity thermal-photovoltaic Effect (ITPV) [1, 2]. The impurity photovoltaic effect leads to increasing the photocurrent owing to absorption of sub-zone photons, which allows significant increase in the single junction solar cell efficiency; the ITPV and ITV effects lead to formation and separation of additional electron-hole (*eh*) pairs with participation of impurities while increasing temperature of a semi-conductive structure [1, 2], Down-converter and Up-converter changing photon energy with impurity participation [3-8]. Therefore, this field of studies is a

perspective direction of photo-voltaics and thermal-photovoltaics.

A concept of creating highly effective comparatively inexpensive solar energy converters will be justified by the results we obtained during the study of the ITPV and ITV effects [1, 2].

2. Charged Inter-Grain Boundary Model

It is known that the inter-grain boundaries in the polycrystalline silicon solar cell are the centers where the defects are accumulated decreasing the solar cell efficiency, as well as the doping and residual impurities from an initial material which create localized charged states [1-3]. Filling of charged states in IGB results in changing the height of the potential barriers, which significantly influences the transfer of charge carriers (CC).

Several methods are commonly used to determine electronic properties of IGB, and a number of models are introduced in the literature to explain charge carrier transport within and between the grains. One of well studied, applicable to poly-Si elemental semiconductors is a model of thermoionic emission (see [3] and references therein). The model allows obtaining information on wide range of charge carrier energies and can be used for *p*- and *n*-type materials.

Figure 1 shows energy diagram of charged IGB in poly-Si suggested by the thermoionic emission model, where (a) and (b) represent *p*-type and *n*-type conductivity cases, respectively. The model predicts the existence of total electrical current J_{th} generated by main carriers flowing from left to right [3]:

$$J_{th} = A^* T^2 \exp(-\beta(\zeta + \varphi))(1 - \exp(-\beta U)), \quad (1)$$

where $\beta = e/kT$ is an inverse thermal difference of potentials, e is an electron, k is the Boltzmann's constant, T is temperature, A^* is the Richardson effective constant, U is an applied potential. Denoted as $e\varphi$ is the barrier displaced in forward direction (left), and $e\zeta$ is a Fermi level

which typically depends on dopant concentration in crystalline grains.

Figure 1. The zone diagram of the charged IGB in PS of p- and n-type.

As shown in Fig. 1a), the holes are captured by the states on the boundary surface which locate above the Fermi level E_p . A corresponding positive charge is compensated by negatively charged acceptors in the region of the spatial charge. Thermoelectron emission creates current J_{th} running from left to right. Besides the current J_{th} on IGB there is current J_{ss} shown in Fig. 1. This current J_{ss} arises from dynamical equilibrium between capture of holes and their emission. To describe current J_{ss} we write

$$J_{ss} = Y_{ss} \delta\phi \quad (2)$$

In this formula Y_{ss} is the characteristic total conductivity of traps dependent on their energy distribution in space and on capture cross section. The current J_{ss} is identically equal to the derivative in time with respect to charge bound on the boundary surface; it is caused by changes in the barrier depth $\delta\phi$. On IGB the following striking phenomenon ought to arise. According to the process of hole capture and emission on the boundary surface, the width of the spatial charge region should vary in order for total electroneutrality to be kept. This, in turn, influences the whole zone diagram in Fig. 1a and the barrier height variation $\delta\phi$. The latter means that the current J_{ss} and the barrier height variation $\delta\phi$ are inversely proportional. The oscillation features of this inverse proportionality are completely defined by the trap features and the proportionality arises owing to applied voltage. Most important for IGB is the following fact. There is also current J_{th} resulting from thermoelectron emission through the barrier. This current is very sensitive to any changes in the barrier height. If a small change $\delta U \leq kT/e$ of voltage is applied then a periodic change of the barrier height in time arises; three different currents will run J_{th} , J_{ss} and shift current $J_{sc} = i\omega C_{HF} \delta U$, here C_{HF} is the high-frequency capacity of the spatial charge, $i = \sqrt{-1}$. The total current can be presented in the following form

$$J_{tot} = J_{th} + J_{ss} + J_{sc} \quad (3)$$

It is seen from formula (3) that the total current is

connected with the difference in capture and emission of CC on the IGB surface. In our opinion, when the quantity of the CC captures is more than emission then the barrier height increases a value of the current J_{ss} is negative; if vice versa then positive. Under such conditions J_{th} , J_{sc} decreases. This leads to decrease in conductivity [2].

3. Results and Discussion

Wafers having *p*-type electrical resistivity $\rho \sim 1 \, \Omega \cdot \text{cm}$ were made from molten secondary poly-Si [9]. Samples obtained from these wafers had thickness of $\sim 300 \, \text{mkm}$ and area of $1 \times 1 \, \text{cm}^2$ and are schematically depicted in Fig. 2(a). Similarly, n^+ -*p* structures were formed on same wafers by means of diffusion of phosphor at $1100 \, ^\circ\text{C}$ into the bulk down to the depth of $\sim 1.5 \, \text{mkm}$ (Fig. 2(b)).

The conductivity, surface and bulk resistivity measurements were carried out using modified and Van der Pauw four probe methods. Data were recorded in semi-automatic mode as samples were heated from 20 to $300 \, ^\circ\text{C}$. In Fig. 2 grains are denoted *P* and shown as the rectangles separated by the grain boundaries, i.e. regions marked 4. The dots within IGB in Fig. 2 illustrate recombination centers, concentration of which depends upon the diffusion of impurities into this region that takes place during crystallization of poly-Si in a graphite melting pot. A precursor mixture for poly-Si in this study was composed of silicon scrap and materials containing deep-level impurities. Similar composite material but without deep-level impurities has been used in fabrication of solar cells with efficiency of $\geq 12\%$ at electrical current of 1.5 A [2, 9].

Figure 2. A simplified diagram of a sample under study (a – for *p*-type poly-Si [9] and b – for n^+ -*p* structure based on it). 1 – poly-Si grains of *p*-type; 2 – n^+ phosphor diffusion layer; 3 – diffusion of phosphor along grain boundaries; 4 – area of boundaries, where dots illustrate the recombination centers in IGB between to neighboring grains; 5 – front mesh contact M_d and continuous back contact M_g .

To describe charge carriers transport between two neighbor grains (Fig. 2(a)) one needs to determine the height

of potential barrier in IGB region. The following equation was used in this study to calculate the barrier height based on experimental data that included temperature dependency of the conductivity and both surface and bulk resistivity ρ [3]:

$$\varphi \approx \frac{kT}{e} \ln \left(\rho e a A^* T / k \right) \quad (4)$$

Where a is a grain size.

Figure 3 shows results of calculation which suggest that the barrier grew exponentially from 0.3 eV to 0.8 eV as temperature risen from 20 up to 300 °C. It is evident that the data points recorded during sample heating and cooling overlap quite well. Data reported here for poly-Si formed from molten silicon precursor in graphite pot (—◇—) [9] agree with the data on samples fabricated using other techniques, such as the Chokralsky method of pulling crystal from the molten precursor containing up to 10% of technical silicon (—×—) [10] and the powder sintering metallurgy method (—△—) [11]. The observed potential barrier temperature change can be described within the frame of the modified Seto model [12], according to which the barrier height depends upon IGB boundary charge Q_i as shown in following Eq. (5):

$$\varphi = Q_i^2 / (8\epsilon\epsilon_0 e N_G) \quad (5)$$

Figure 3. Temperature dependence of potential barrier height in IGB determined using experimental results in poly-Si obtained by three methods - [9]; - [10]; - [12].

One may conclude from Eq. (5) that increasing charge Q_i on localized traps in IGB leads to the rise of potential barrier. With the rising temperature number of trapped charge carriers increases faster than their emission, and when temperature decreases this process reverses, i.e. the emission prevails the trapping process. Such process confirms the existence of a feedback link between current J_{ss} and change of barrier height $\delta\varphi$. More important fact is that in addition to the current J_{ss} such feedback link includes current J_{th} as well which forms due to thermoionic emission over the barrier. The current J_{th} is very sensitive to any variation in the barrier height, that is to the ratio of the

trapping and emission processes and thus to the temperature change. Consequently the total current, being a sum of two mentioned currents as Eq. (6) shows:

$$J_{tot} = J_{th} + J_{ss}, \quad (6)$$

significantly depends on the ratio of the trapping and emission of charge carriers on surface of IGB. When number of trapped charge carriers is higher than the emitted ones, charge will move on the trapping levels along the border between two neighboring grains as the conductivity of the traps and the barrier height increases. Let us define this direction of current J_{ss} as having negative sign. If the emission prevails the trapping, then charge moves in opposite direction, and one may define the direction of the current J_{ss} as having positive sign. It has been shown experimentally [13-15] that in former case J_{th} decreases which results in decreasing conductivity, and in later case the current J_{th} increases along with conductivity. As temperature increases, charge carriers within IGB region become excited and eventually liberated from the traps, and those obtained reasonably high kinetic energy start contributing into total electrical conductivity [13-15]. On the other hand, charge carriers with low kinetic energy are absorbed by surface region of IGB in the adjacent grain located on the path of moving charges thus they become removed from the flow. Similar mechanism is valid for IGB of n-type poly-Si (Fig.1(b)).

4. Model of p-n Transition In the IGB Region

It was defined in [12-15] that IGB have various complicated structures. Analysis of the chemical composition of some parts of the grain surface, i.e. the IGB region, showed the presence of the following complexes: Mg, S, Cl, Ca, and Fe. The atomic structure of IGB in crystals with covalent bonds has failures like decayed bonds that form additional energy levels in the forbidden zone [3, 16, 17]. Besides, the precipitates SiO_x or Si_yO_x are formed with oxygen atoms both in the near-surface region of the grains and in IGB [18]. While interaction of oxygen atoms with vacancies the different vacancy centers (A, E, H etc.) are formed. It is also known that the impurities of Pd, Na, Be, Cd, Au, Co, Pb, O, S, Mn form the deep acceptor levels within the range of 0.35-0.5 eV from the edge of the valent zone E_v ; Ag, Mn, Au, Cd, Zn, Ni, O form the acceptor levels located 0.35-0.5 eV lower than the edge of the conductivity zone E_c ; Cr, Se, Mn, Pb, Fe form the donor levels located 0.35-0.5 eV lower than E_c ; and C, Pd, Ag, Au, Mo, Ge, K, Fe, W form the levels located 0.35-0.5 eV higher than E_v [18]. Such vacancy centers are very sensitive to any outer influences. For example, in [20] the level changes were defined in the presence of impurities with the raise in temperature, within the temperature range 50-70 °C the trap level is $E \approx 0.15$ eV

and $E \approx 0,17$ eV; $100-170^\circ\text{CE} \approx 0,36$ eV; $325-350^\circ\text{CE} \approx 0,3$ eV. On the basis of these data with the help of the zone diagram of the charged IGB in PS of the p- and n-type in Fig 1a, b, a model of the zone diagram of the p-n transition in the IGB region can be presented as follows (Fig. 4)

In Fig. 4 besides the Fermi level E_p there are levels E_i in the p and n region. These levels for the p and n region are the recombination centers forming the barrier height in IGB and connected with impurity segregation [13-20], as shown in Fig. 1a and b. Under the action of voltage or lightning the electron-hole pairs are formed which have sufficiently high kinetic energy and participate in electroconductivity. Some part of CC with insufficient kinetic energy can be absorbed by the recombination center, as stated above. Then the formed currents can be presented as follows

$$J_{tot} = J_{tot(pn)} + J_{ss(pn)} + J_{sc(pn)} \quad (7)$$

The energies of the recombination centers E_{gt} in the region of the p-n transition are shown in Fig. 4. While capture and emission of CC from the surface the currents J_{sp} and J_{sn} are formed, which results in changing the barrier height of the p-n transition. A striking phenomenon should be noted that capture and emission of CC occur not only from the surface of the p-n transition but also from the acceptor and donor levels E_i in the p and n regions, respectively. This process leads to changes in dark current. It is known that the current of the p-n transition is defined by the sum of the photo-current J_f and the dark one J_t ; $J_{pn} = J_f + J_t$. In our case the total current can be presented as follows

$$J = J_{tot} + J_{pn} = J_{tot(pn)} + J_{ss(pn)} + J_{sc(pn)} + J_f + J_t \quad (8)$$

Figure 4. A zone model of the p-n⁺ transition P and n⁺ are the region of p and n⁺-type, respectively

As seen from formula (5), the changes in capture and emission of CC in IGB under outer actions lead to changing the characteristic of the p-n transition in the IGB region.

5. Mechanism of Formation of Impurity Thermal-Voltaic and Impurity Thermal-Photovoltaic Effects in IGB

As seen in Figs. 1 and 4 and formula (8), the characteristics of the p-n transition are defined by capture and emission of CC in the inter-grain layer. Under usual conditions, operation of the p-n transition in the IGB region is connected with formation and separation of the electron-hole pairs (eh) with participation of impurities while lightning or voltage. We impose the following conditions for the p-n transition to operate.

1. If the CC capture prevails over the CC emission in the inter-grain layer then the currents $J_{ss(pn)}$, $J_{sc(pn)}$ are negative (-) and the current $J_{tot(pn)}$ is also negative. In this case, the total current of the p-n transition tends to zero. This is connected with the high concentration of impurities in the inter-grain layer.

2. If the number of the CC capture and emission is equal then the currents $J_{ss(pn)}$, $J_{sc(pn)}$ and $J_{tot(pn)}$ tend to zero. In this case, the total current of the p-n transition is defined by the sum of photocurrent and dark current. This is observed when there are no impurities in the inter-grain layer.

3. When the CC emission prevails over the CC capture then these currents are positive (+). In this case, the total current is defined by formula (8). This takes place for the mean concentration of impurity in the inter-grain layer.

It is known that while voltage the acceptor and donor states in the level E_{gt} are formed in the region of the p-n transition. The CC capture in the region of the p-n transition leads to increase in the acceptor and donor states in the p-n transition. With the raise in temperature the tunneling of CC occurs. It should be noted that besides the CC tunneling in the region of the p-n transition the CC emission from the recombination centers (the levels E_i in the p and n regions) occurs and thermal generation of electron-hole pairs takes place in these regions. As shown in Fig. 4, all the thermally generated carriers move to the boundaries of the p-n transition, i.e. to E_{gt} , and increase tunneling.

It is evident that this mechanism can be for the first and second cases. But in the first case because of great quantity of impurities in the inter-grain layer there is metallic conductivity, i.e. there are no p-n transitions. In the second case no thermal generation is observed because of the absence of impurities in the IGB region.

Thus, the ITV and ITPV effects manifest themselves in the third case only, i.e. for the mean concentration of impurities in the inter-grain layer and with the raise in temperature.

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