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Effect of Oxygen (O, S, Se, Te) in Microstructured Silicon on the Performance of Solar Cells

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Abstract*:* *Intermediate band (IB) solar cells hold promise for ultrahigh solar electrical energy conversion. Microstructured silicon, formed by irradiating the surface of a Si wafer with femtosecond laser pulses in the presence of sulfur-bearing gas, is widely believed to be a potential material for efficient multi-intermediate-bands (IBs) silicon solar cells. We have calculated the detailed balance limit of the efficiency for IB microstructured silicon solar cells, which is doped with oxygen (e.g.,O, S, Se, Te). The results indicate that the impurity levels introduced by oxygen dopant (O) and doped with chalcogen (S, Se, Te) have the opposite impact in silicon on the conversion efficiency of IB solar cells. The former is negative and the latter are positive. Then the issue of fabricating high efficiency IB solar cells based on femtosecond laser microstructured silicon is discussed in detail.*

Key words: *microstructured silicon; solar cell; chalcogen; Detailed Balance Theory*

1. INTRODUCTION

Nowadays, the most cost-effective high-efficiency solar cells are crystalline silicon solar cells. Surface texturization is commonly employed to enhance the light absorption in silicon solar cells (**Campbell P& Green MA ,1987**). Repeated pulsed laser irradiation of silicon in the presence of sulfur-bearing gases has been used to create microstructured silicon surfaces(**Wu C et al ,2001; Crouch C,2004; Sheehy M A et al,2005**; **Her T H et al,2000**); Researchers found that this new sort of material had extraordinary optical properties, including the strong absorption of light within the range of 0.25μm to 17μm(**Sheehy M A et al, 2005**; **Her T H et al, 2000; Liu Y et al. 2008**; **Tull, B et al 2009**; **Younkin R**, **2003**; **Crouch C H et al, 2004**), good field emission characteristics. Besides, these materials have potential applications like photo-detectors **(Carey J E**, **2005**) and light emitters (**Wu C**,**2002**) and so on. The incorporation of sulfur in the laser-irradiated surfaces was found effective to induce high sub-band-gap absorption (**Sheehy M A et al, 2005**; **Kim T G, 2006)**.

Research results have shown that the enhancement of visible light absorption of microstructured silicon is mainly attributed to laser induced periodic surface structures (LIPSS). And microstructured silicon absorbs up to 42% more light than flat silicon of the same thickness; the effect is even more dramatic for thinner films of Si. The strong infrared absorption is mainly due to the deep levels and dark spot defects in the band gap formed in the ultra-fast laser machining process (**Sheehy M A, 2007**,; **Bassam M A et al,(2008); Wang Y, 2009**). Chalcogenides are dramatic impurities in silicon (**Jansen R W & Sankey O F, 1986; Janzén E et al, 1984**), since they are capable of increasing the conversion efficiency of a solar cell by forming an Intermediate band (IB). It is widely believed that *O, S, Se*, and Te belong to substitutional impurities (**Tull, B et al, 2009**; **Younkin R**, **2003**; **Sheehy M A ,2007**), so oxygen is also attractive as IB. Recently, Oxygen is found abundant in silicon and its amount is determined by crystal growth processes while its existing form and content changes with annealing temperature and time **Tabbal Malek et al, 2007; Gimpel, Thomas et al, 2014)**. Generally, a donor level (E=160 meV) and an acceptor level (E=380 meV) into silicon can be introduced. Table.1 shows the reported impurity levels in silicon by doping with chalcogen (S, Se, Te)(**Janzén E et al ,1984**). Arakawa et al**(Tomohiro Nozawa & Yasuhiko Arakawa,2011)** have calculated the detailed balance limit of the efficiency for IB Silicon Cells with multiple intermediate bands by optimizing IB's energy levels. The reporters indicated that thermodynamic limit of IB Silicon Cells with 4 IBs is 74.6% which far exceeds 63% calculated in a previous study for the single IB case, and predicted the thermodynamic limit of IB Silicon Cells can ultimately approach nearly 80% by further increasing the total number IBs **(Nozawa Tomohiro & Arakawa Yasuhiko,2011)**.

Table1. *Level energies for the chalcogen impurities S, Se, and Te in Si. And the energy is counted from the bottom of the conduction band in meV.*

Table 1 Level energies for the chalcogen impurities *S*, *Se*, and *Te* in Si

	E (meV)		E (meV)		E (meV)
S^0	318	Se^0	307	Te^0	199
$S_2{}^0$	188	$Se_2{}^0$	206	$Te_2{}^0$	158
S^+	614	Se^+	593	Te^+	411
$S_2{}^+$	371	$Se_2{}^+$	390	$Te_2{}^+$	
$S_c{}^0(X_1)$	110	$Se_c{}^0(X_1)$	116	$Te_c{}^0(X_1)$	127
$S_c{}^0(X_2)$	92	$Se_c{}^0(X_2)$	94	$Te_c{}^0(X_2)$	110
$S_c{}^0(X_3)$	82	$Se_c{}^0(X_3)$	53	$Te_c{}^0(X_3)$	93
$S_c{}^0(X_4)$	81	$Se_c{}^0(X_4)$		$Te_c{}^0(X_4)$	73
$S_c{}^0(X_5)$	57	$Se_c{}^0(X_5)$		$Te_c{}^0(X_5)$	65
$S_c{}^+(X_1)$	248	$Se_c{}^+(X_1)$	214	$Te_c{}^+(X_1)$	

Our group has discussed the sunlight loss rate of one impurity band **(Fang W et al, 2011).** and double-impurity-band chalcogenide-doped silicon **(Fang J et al, 2011)**. Previous research has investigated the relationship between solar cell efficiency and intermediate band position based on the four-band absorption model(**He H et al,2012**). Using the Detailed Balance Theory (**Fang W et al,2011; Fang J et al, 2011; He H et al, 2012; Luque A & Martí A,1997**) , the aim of this paper is to study the effect of the IBs solar cells on the conversion efficiency while the silicon is doped with oxygen(O, S, Se, Te), which is referred to as doubly-doped and singly-doped respectively if not specially indicated. That is to say, we use Detailed Balance Theory to discuss the ultimate conversion efficiency of microstructured silicon solar cells doped either with both oxygen (O) and chalcogen (S, Se, Te) or those only with chalcogen (S, Se, Te) in microstructured silicon. In the model, one important assumption is that no overlap exists between these IBs and the conduction band or the valence band. Then the theoretical conversion efficiency of the both solar cells with different band widths is pointed out with great emphasis.

2. Analysis of the Efficiency of the Multi-IBs Solar Cell Based on Femtosecond Laser Microstructured Silicon

Photoelectric conversion efficiency of conventional single junction solar cells can theoretically be improved by introducing IBs into the device. Ideally they allow electrons to be excited from the valence band to the conduction band via the intermediate band by absorbing the previously wasted sub-band-gap photons. The detailed balance limit represents the thermodynamic energy conversion efficiency limit of solar cells accounting for black-body radiation (**Luque A & Martí A, 1997**).

According to the calculation conditions in Ref. 24, we use the following calculation method for IB solar cells with n IBs to elucidate. In Fig.1.(a), the intermediate band position starts from the conduction band, where inter IB transitions are much less common because they have small line widths. In out calculation, a photon produces an electron hole pair at most, the portion of photon energy higher than Eg are all wasted.

However, a high-energy photon can generate a number of electron-hole pairs for its special structure of femtosecond laser microstructured silicon. And there is still no comparatively comprehensive understanding of this phenomenon up till now, so it must be noted that we do not consider the phenomenon of multiple carrier generation in femtosecond laser microstructured silicon.

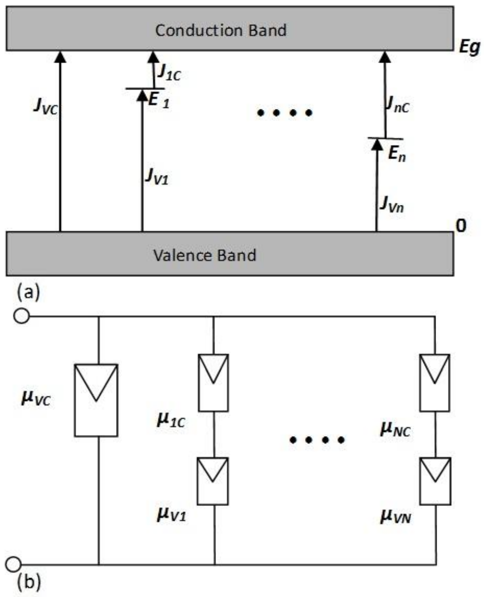

Fig1. *Energy band diagram and circuit diagram of IBs solar cell: (a) energy gaps and generated currents, where CB and VB are the conduction and valence band, respectively; (b) an equivalent circuit in terms of their associated chemical potential*

The Detailed Balance Theory (**Shockley W,1961; Bremner S P et al,1999**) assumes unity quantum efficiency in the limit so that the current coming out of a device is ascribed to the difference between the incoming and the outgoing photon flux. This current density emitted by a blackbody surface per unit surface area over the energy range $E_l \sim E_h$ is:

$$J = q[f_s \dot{N}_s(E_l, E_h, T_s, 0) - f_c \dot{N}_c(E_l, E_h, T_c, u)] \tag{1}$$

According to the Planck formula, the number of photons with energy between E_l and E_h which are emitted to the hemisphere at temperature T by the blackbody is:

$$\dot{N}(E_l, E_h, T, u) = \frac{2An^2\pi}{h^3c^2}\int_{E_l}^{E_h}\frac{E^2 dE}{e^{(E-u)/kT}-1} \tag{2}$$

Here q is the electronic charge; h is Planck's constant; c is the speed of light; k is Boltzmann's constant; E_l is the lower energy limit for the absorption process of interest; E_h is the upper energy limit; T_s is the temperature of the sun (modeled as a blackbody at a temperature of 6000K); T_c is the temperature of the cell (modeled at a temperature of 300K) and u is the chemical potential associated with the emitted radiation(**Wurfel P ,1982**).

For a given external voltage V applied to the solar cell, there is an equation:

$$qV = \mu_{Vn} + \mu_{nC} = \mu_{VC} \tag{3}$$

It is now possible to write down the equations describing the current due to carriers excited from the valence band to the k^{th} defect level [Eq. (4)], the current due to the carriers excited from the k^{th} defect level to the conduction band [Eq. (5)] and the current due to the carriers excited directly from the valence band to the conduction band [Eq. (6)], respectively

$$J_{Vk} = q[f_s \dot{N}_s(E_k, E_{k-1}, T_s, 0) - f_c \dot{N}_c(E_k, E_{k-1}, T_c, u_{Ck})] \tag{4}$$

$$J_{kC} = q[f_s \dot{N}_s(Eg - E_k, Eg - E_{k+1}, T_s, 0) - f_c \dot{N}_c(Eg - E_k, Eg - E_{k+1}, T_c, u_{kC})] \tag{5}$$

$$J_{VC} = q[f_s \dot{N}_s(Eg, +\infty, T_s, 0) - f_c \dot{N}_c(Eg, +\infty, T_c, u_{VC})] \tag{6}$$

The current flowing from the valence band to the intermediate band must be equal to the current flowing from the intermediate band to the conduction band, which is mathematically expressed as $J_{Vk}=J_{kC}$. Then with Eq. (3), we can extract the chemical potential u_{Ck} or u_{kV} (k = 1, 2 …. n).

Each absorbed photon only excites a single electron. The output power of the device is calculated as follows

$$P_{out} = u_{vc}(J_{VC} + J_{V1} + ... + J_{Vn}) \tag{7}$$

The efficiency η is defined as the ratio of the output electrical power over the input solar power. If the sun is modeled as a blackbody at temperature of T_s, then the incident power device received is given by $p_{in} = f_s \sigma T_s^4$, where, σ is the Stefan-Boltzmann constant.

Then the efficiency of solar cell is: $\eta = \frac{P_{out}}{P_{in}}$.

Using the formulas above we get the relationship between solar cell conversion efficiency and the voltage when one or two impurity levels are added to microstructured silicon. Results are shown in Fig.2-4. The incident spectrum which we choose is blackbody radiation where $f_s = f_c = 1$(i.e., maximally concentrated 46200 times) with the valence and conduction bands being unrestricted.

3. Results and Discussion

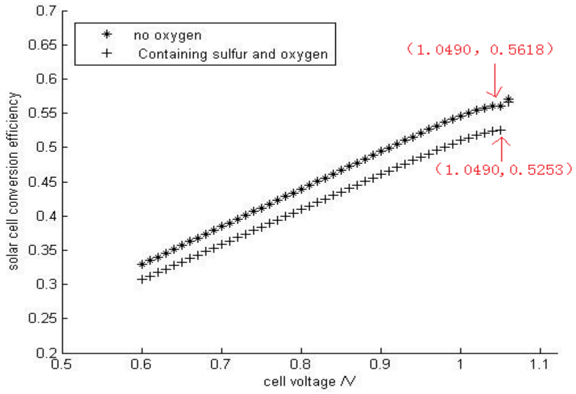

Fig2. *Relationship of solar cell conversion efficiency and the cell voltage when different sulfur with or without oxygen impurity levels are introduced into Si.*

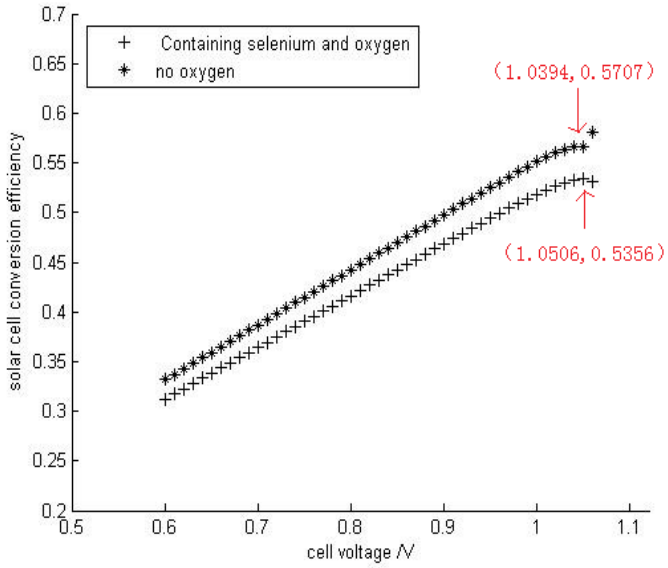

Fig3. *Relationship of solar cell conversion efficiency and the cell voltage when different selenium with or without oxygen impurity levels are introduced into Si.*

According to Fig.2-4, we can easily find that the limiting conversion efficiency of chalcogen（S, Se, Te）-doped silicon solar cells with oxygen dopant is lower than those without the existence of oxygen-doped, where the maximum limiting conversion efficiency of the silicon only doped with S, Se, Te is 0.5618, 0.5707 and 0.7118, respectively. The limiting conversion efficiency of chalcogen-doped silicon solar cells has the same order of magnitude when oxygen is present as a dopant. But the limiting conversion efficiencies of chalcogen-doped silicon solar cells with oxygen dopant are lower than those without the existence of oxygen-doped. According to the above analysis，we can work out that the impurity levels doped by oxygen in silicon have a negative impact on the conversion efficiency of IB solar cells. Thus, selecting the appropriate doping impurities and making clear effect of the impurity in the material on solar cell efficiency are absolutely necessary for high efficiency IB solar cells.

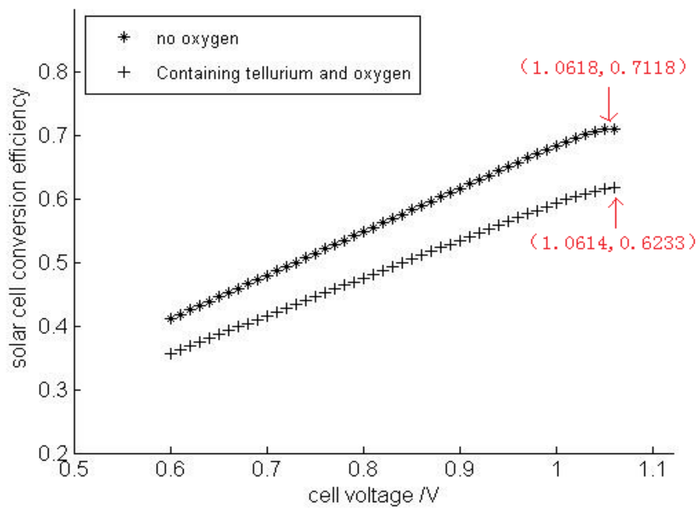

Fig4. *Relationship of solar cell conversion efficiency and the cell voltage when different tellurium with or without oxygen impurity levels are introduced into Si.*

However, the effect of overlap between IBs and the conduction and valence bands is ignored in this study. The three-band model (**Navruz T S&M Saritas, 2008**) has been used to investigate the decrease in efficiency of an IB solar cell due to band overlap. The problem may arise from a possible overlapping of forbidden gap. For example, the overlap would decrease voltage of solar cells, thereby reducing efficiency; they would also lead to distinct decrease of carrier mobility and thus short minority carrier lifetime。 About this, we will discuss it in detail in further research.

Moreover, an intermediate band very close to the other or a conduction band (or a valence band) could have a significant thermal emission of carriers, which would essentially short-circuit the bands. Thus, IB decreases the effective band gap and reduces the maximum potential of the device. In addition, the heavy doping effect brought about by high concentrations of impurity cannot be ignored because it would severely affect the solar cell efficiency. However, in the nanostructure heavily doped by chalcogenide, and in the condition that the deep-level sub-bands have been formed, it is possible for Auger effect(**Klimov V I et al, 2000; Wang L W et al, 2003; Klimov V I,2000**) to develop in the positive direction. That is, the electronic excitation probability is greater than the recombination probability, which makes one high-energy photon in microstructured silicon stimulate more than one electron. Thus quantum efficiency exceeding 100% could be obtained. Moreover, we will further discuss the situation where one phonon generates several electron hole pairs and the case with the existence of Auger effect.

4. Conclusions

Making efficient solar cells is an effective way to solve today's energy and environment problems. Solar cell with multi-IBs provides an innovative method for making highly efficient solar cells and impurity doping is a comparatively simple way to introduce IBs. The issue of how to select the appropriate doping impurities to maximize the efficiency of solar cells with multi IBs is highly concerned. Fortunately, the new material microstructured silicon with strong and broad band absorption spectrum is supposed to be the ideal material for intermediate-band solar cells. Based on this perspective, taking chalcogen as an example, we have calculated the detailed balance limit of the efficiency for IB microstructured silicon solar cells, either doubly-doped or singly-doped. The results indicate that the largest limiting conversion efficiency presents in tellurium-doped silicon solar cells, followed by selenium-doped silicon solar cells and then the limiting conversion efficiency of sulfur-doped silicon solar cells, while oxygen-doped ones do not exist. And among the above species the maximum limiting conversion efficiency is 76.15%. The limiting conversion efficiency of chalcogen-doped silicon solar cells also has the same order in the presence of oxygen dopant. But the limiting conversion efficiency of chalcogen-doped silicon solar cells with oxygen-doped is smaller than those without the existence of oxygen dopant. This shows that the impurity level by doped with oxygen in silicon has a negative impact on the conversion efficiency of IB solar cell.

Acknowledgements

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