Sunlight loss for femtosecond microstructured silicon with two impurity bands*

Fang Jian(方 健), Chen Chang-Shui(陈长水)†,
Wang Fang(王 芳), and Liu Song-Hao(刘颂豪)

Institute of Biophotonics, South China Normal University, Guangzhou 510631, *China*

(Received 12 January 2011; revised manuscript received 11 March 2011)

Black silicon, produced by irradiating the surface of a silicon wafer with femtosecond laser pulses in the presence of a sulfur-bearing gas, is widely believed to be a potential material for efficient multi-intermediate-band silicon solar cells. Taking chalcogen as an example, we analyse the loss of sunlight for silicon with two impurity bands and we find that loss of the sunlight can be minimized to 0.332 when Te^0(0.307 eV) and Te^+(0.411 eV) are doped into microstructured silicon. Finally, problems needed to be resolved in analysing the relationship between conversion efficiency of the ideal four-band silicon solar cell and the position of the introduced two intermediated bands in silicon according to detailed balance theory are pointed out with great emphasis.

Keywords: black silicon, solar cell with impurity bands, loss of sunlight

PACS: 42.25.Bs, 42.55.–f **DOI:** 10.1088/1674-1056/20/7/074202

1. Introduction

Silicon, the second richest element on earth, is widely used in the industry of semi-conductor. Compared with silicon, hardly any other elements can be predominant in the solar cell industry because of their limited abundance. Besides, silicon has many other advantages, for example, it is easy to purify and endures high temperatures, thus it is natural to believe that only silicon will be the most sustainable material for solar cells in the future. However, due to the wide band gap of silicon, sunlight with a wavelength of more than 1100 nm cannot be absorbed by crystalline silicon; therefore, the theoretical limiting efficiency for ordinary single crystalline silicon solar cell is only 29%. Based on this recognition, it is of great significance to bring up new cell structure and improve materials to increase the efficiency of solar cell. In 1997, by irradiating the surface of semiconductor with high-intensity femtosecond laser pulses, Professor Eric Mazur of Harvard University fabricated a new kind of material called "black silicon."[1] Researchers found that this new material had several unusual optical properties such as strong absorption of light with wavelength from 0.25 μm to 17 μm[2] and nice field emission characteristics; therefore, they predicted that black silicon had incomparable superiority to other materials in the solar cell field. Research results indicate that the enhanced visible light absorption of black silicon is mainly due to the multi-reflection caused by the periodic structure on its surface while the strong infrared absorption is mainly due to the deep energy levels,[3,4] which consist of impurities and defects introduced by laser-assisted chemical etching[5−8] within the band gap. Chalcogen is reported to be able to introduce impurity levels into the band gap of silicon.[9]

In the area of solar cells, the study on promoting the efficiency always gains the highest priority. At the end of the 20th century, Green[10] put forward the conception of the third generation of solar cells which included the intermediate band solar cell. In the intermediate band solar cell, transitions via intermediate energy band, in addition to transitions from the valence band to the conduction band, increase the generation rate of electron–hole pair. In 1997, Luque and Marti[11] built up the physical model of intermediate band solar cell based on detailed balance theory. Their research showed that the highest efficiencies of intermediate band solar cell can reach up to 63.1%, higher than the limiting efficiencies of the single solar cell and two tandem solar cells, 40.7% and 55.4%, respectively. In addition, they mentioned a series of methods to introduce intermediate band into the energy band

*Project supported by the Key Program of Natural Science Foundation of Guangdong Province of China (Grant Nos. 10251063101000001 and 8251063101000006) and the National Natural Science Foundation of China (Grant No. 60878063).

†Corresponding author. E-mail: cschen@aiofm.ac.cn

© 2011 Chinese Physical Society and IOP Publishing Ltd

structure of ordinary solar cells , while, among which, the simplest is impurity doping.[12] However, all these calculations and discussions are based on a three-level absorption model. In 2002, Brown and Green[13] discussed the situation when multi-impurity bands were doped, but there was no specific calculation. Our group has discussed the sunlight loss of black silicon with one purity band.[14] In this study, by improving the three-level absorption model, we advance and introduce a method to study the relationship between the sunlight loss of materials and the location of the introduced impurity level in silicon when two impurity bands are doped, with the example of chalcogen. This study would provide an easy way to purposefully choose the appropriate two doping impurities, which is significant to make ideal multi-band gap solar cells based on black silicon.

2. Analysis of sunlight loss for silicon doped with two impurity bands

Here, we take chalcogen as an example. The four-level structure of silicon after the introduction of two impurity bands is shown in Fig. 1. In this graph, $E_{\rm I1}$ stands for the distance between the impurity band 1 and the bottom of conduction band, $E_{\rm I2}$ stands for the distance between the impurity band 2 and the bottom of conduction band and the units of them are eV. $E_{\rm g}$ is the band gap of silicon at room temperature, we take $E_{\rm g} = 1.12$ eV in our calculation. As shown in Fig. 1, with appropriate sunlight, there can be six kinds of photon transitions after introducing two impurity bands into silicon. We assume that the energies needed for these six kinds of transitions are $E_{\rm g1}$, $E_{\rm g2}$, $E_{\rm g3}$, $E_{\rm g4}$, $E_{\rm g5}$ and $E_{\rm g}$ (listed in ascending order).

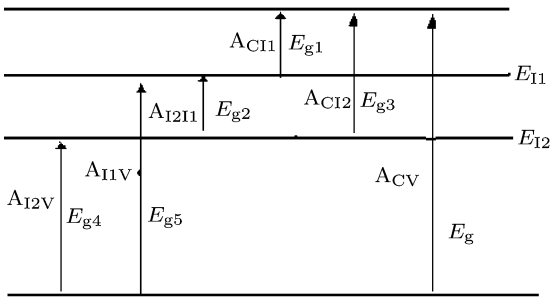


Fig. 1. Band diagram of silicon after the introduction of two impurity bands.

We made the following assumptions in our calculation:

1) $E_{\rm I1} < E_{\rm g/2}$, $E_{\rm I1} < E_{\rm I2}$;

2) photons with energy lower than $E_{\rm g1}$ cannot be absorbed at all;

3) a photon produces an electron–hole pair at most and the portion of photons with energy higher than $E_{\rm g}$ is all wasted;

4) photon selectivity is assumed such that photons with high energy preferentially excite the transition which needs higher energy. In Fig. 1, photons with energy between $E_{\rm g2}$ and $E_{\rm g3}$ will excite process $\rm A_{I2I1}$ while photons with energy between $E_{\rm g3}$ and $E_{\rm g4}$ will excite process $\rm A_{CI2}$.

According to assumption 2), photons with energy lower than $E_{\rm g1}$ cannot be absorbed at all, so this part of sunlight loss can be described as

$$E_1 = \int_0^{E_{\rm g1}} N(E) E \,{\rm d}E, \tag{1}$$

where E stands for the photon energy and $N(E)$ for the number of photons whose energy is E, in unit of $({\rm s\cdot cm^2\cdot eV})^{-1}$. According to assumption 4), the sunlight loss of photons with energy between $E_{\rm g1}$ and $E_{\rm g2}$ will be as follows:

$$E_2 = \int_{E_{\rm g1}}^{E_{\rm g2}} N(E)(E - E_{\rm g1}) \,{\rm d}E. \tag{2}$$

Similarly, there are

$$E_3 = \int_{E_{\rm g2}}^{E_{\rm g3}} N(E)(E - E_{\rm g2}) \,{\rm d}E, \tag{3}$$

$$E_4 = \int_{E_{\rm g3}}^{E_{\rm g4}} N(E)(E - E_{\rm g3}) \,{\rm d}E, \tag{4}$$

$$E_5 = \int_{E_{\rm g4}}^{E_{\rm g5}} N(E)(E - E_{\rm g4}) \,{\rm d}E, \tag{5}$$

$$E_6 = \int_{E_{\rm g5}}^{E_{\rm g6}} N(E)(E - E_{\rm g5}) \,{\rm d}E, \tag{6}$$

$$E_7 = \int_{E_{\rm g}}^{\infty} N(E)(E - E_{\rm g}) \,{\rm d}E. \tag{7}$$

The total loss of sunlight is

$$L = \frac{E_1 + E_2 + E_3 + E_4 + E_5 + E_6 + E_7}{\int_0^{\infty} N(E) E \,{\rm d}E}. \tag{8}$$

Figures 2–4 show the possible impurity bands in silicon band gap introduced by doping with sulfur, selenium and tellurium given in Ref. [15].

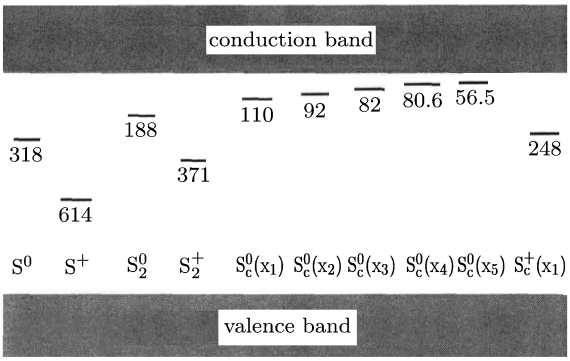


Fig. 2. Impurity bands in silicon band gap introduced by doping with sulfur.

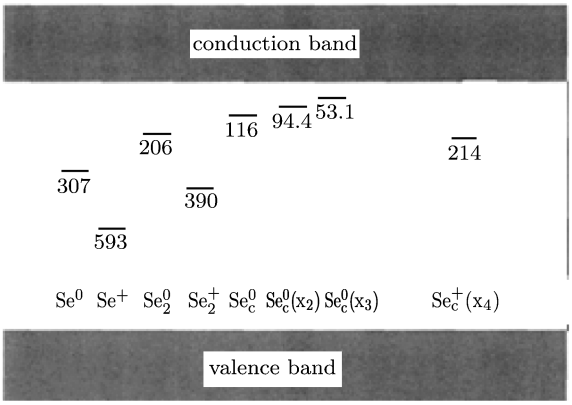


Fig. 3. Impurity bands in silicon band gap introduced by doping with selenium.

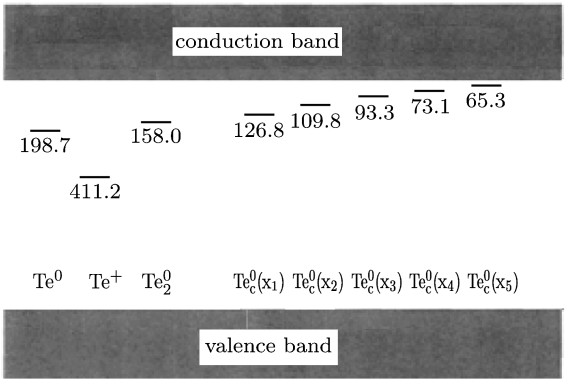


Fig. 4. Impurity bands in silicon band gap introduced by doping with tellurium.

Note that in assumption 1), even if $E_{I1} > E_{g2}$, $E_{I1} > E_{I2}$, according to the symmetry theory, we will still obtain a similar formula and the same results. In other words, we make such an assumption just for the convenience of our calculation. With MATLAB software, we calculate the sunlight loss after the introduction of two impurity bands of chalcogen to silicon, the results are shown in Tables 1, 2 and 3.

According to these tables, we can easily find out that the minimum loss of sunlight for silicon after the introduction of two impurity bands is 0.332. In other words, in order to obtain the highest absorption rate of sunlight, we should introduce Te^0(0.307 eV) and Te^+(0.411 eV) into the band gap of silicon to form two impurity bands.

Table 1. Sunlight loss when two impurity bands of sulfur doped.

Impurity bands	S^0	$S^0_c(x_1)$	$S^0_c(x_5)$	$S^0_c(x_4)$	$S^0_c(x_2)$	$S^0_c(x_1)$	S^+_2	S^0_2
S^+(0.614)	0.336	0.336	0.367	0.352	0.350	0.346	0.338	0.333
S^0_2(0.188)	0.359	0.383	0.395	0.394	0.394	0.393	0.341	NA
S^+_2(0.371)	0.349	0.345	0.351	0.348	0.347	0.349	NA	0.341
$S^0_c(x_1)$(0.11)	0.361	0.383	0.443	0.443	0.347	NA	0.349	0.393
$S^0_c(x_2)$(0.092)	0.363	0.384	0.456	0.456	NA	0.347	0.347	0.394
$S^0_c(x_4)$(0.0806)	0.364	0.384	0.461	NA	0.456	0.443	0.348	0.394
$S^0_c(x_5)$(0.0565)	0.366	0.386	NA	0.461	0.456	0.443	0.351	0.395
$S^+_c(x_1)$(0.248)	0.364	NA	0.386	0.384	0.384	0.383	0.345	0.383

Table 2. Sunlight loss when two impurity bands of selenium doped.

Impurity bands	Se^0	$Se^0_c(x_4)$	$Se^0_c(x_3)$	$Se^0_c(x_2)$	$Se^0_c(x_1)$	Se^+_2	S^0_2
Se^+(0.593)	0.338	0.335	0.364	0.351	0.346	0.340	0.334
Se^0_2(0.206)	0.365	0.391	0.391	0.389	0.389	0.337	NA
Se^+_2(0.390)	0.342	0.338	0.349	0.342	0.340	NA	0.337
$Se^0_c(x_1)$(0.116)	0.366	0.388	0.439	0.439	NA	0.340	0.389
$Se^0_c(x_2)$(0.094)	0.367	0.388	0.455	NA	0.439	0.342	0.389
$Se^0_c(x_3)$(0.053)	0.371	0.390	NA	0.455	0.439	0.349	0.391
$Se^0_c(x_4)$(0.214)	0.366	NA	0.390	0.388	0.388	0.338	0.391

Table 3. Sunlight loss when two impurity bands of tellurium doped.

Impurity bands	Te^0	$T^0_c(x_5)$	$Te^0_c(x_4)$	$Te^0_c(x_3)$	$Te^0_c(x_2)$	$Te^+_c(x_1)$	Te^0_2
$Te^+(0.411)$	0.332	0.345	0.344	0.339	0.337	0.335	0.333
$Te^0_2(0.158)$	0.391	0.410	0.410	0.410	0.410	0.410	NA
$Te^0_c(x_1)(0.127)$	0.390	0.431	0.430	0.431	0.431	NA	0.410
$Te^0_c(x_2)(0.11)$	0.389	0.443	0.443	0.443	NA	0.431	0.410
$Te^0_c(x_3)(0.093)$	0.390	0.456	0.456	NA	0.443	0.431	0.410
$Te^0_c(x_4)(0.073)$	0.391	0.470	NA	0.456	0.443	0.430	0.410
$Te^0_c(x_5)(0.065)$	0.391	NA	0.470	0.456	0.443	0.431	0.410

Indeed, during our calculation, we have to confess the fact that we did not take into account the fact that one high-energy photon can generate numerous electron–hole pairs in silicon, because energy released in the transition of electrons excited by high energy photons, from excited states back to the conduction band, is no longer released in the form of heat as by crystal collision. We stimulate electrons from the valence band to the deep level or from a deep level to the conduction band due to the introduced deep level sub-bands in the non-equilibrium supersaturated process. In order to modify this flaw, we can introduce a coefficient g to describe the reused probability of the remaining energy of high-energy photons after the first transition. Therefore, Eqs. (2)–(7) can be modified more precisely to the following forms:

$$E_2 = \int_{E_{g1}}^{E_{g2}} N(E)(E - E_{g1})(1-g)\mathrm{d}E, \quad (9)$$

$$E_3 = \int_{E_{g2}}^{E_{g3}} N(E)(E - E_{g2})(1-g)\mathrm{d}E, \quad (10)$$

$$E_4 = \int_{E_{g3}}^{E_{g4}} N(E)(E - E_{g3})(1-g)\mathrm{d}E, \quad (11)$$

$$E_5 = \int_{E_{g4}}^{E_{g5}} N(E)(E - E_{g4})(1-g)\mathrm{d}E, \quad (12)$$

$$E_6 = \int_{E_{g5}}^{E_{g6}} N(E)(E - E_{g5})(1-g)\mathrm{d}E, \quad (13)$$

$$E_7 = \int_{E_g}^{\infty} N(E)(E - E_g)(1-g)\mathrm{d}E. \quad (14)$$

However, we have not found any comprehensive understanding of this phenomenon and we cannot give a clear definition for coefficient g, so we just give the modified formula here and leave it to further discussion in the future. Moreover, our study is only an analysis of sunlight loss for solar cell of microstructured silicon doped with two chalcogen impurity bands. In order to calculate the maximum efficiency of this kind of solar cell. We should make further analysis of the relationship between conversion efficiency of the ideal four-band silicon solar cell and the position of the introduced two intermediated bands in silicon according to detailed balance theory. In addition, we will further discuss the case that one phonon generates several electron–hole pairs and the case that several middle levels (more than two) are introduced in the future. Nevertheless, taking chalcogen as an example, we do find an easy method to choose two appropriate impurity bands to minimize the sunlight loss for solar cells of microstructured silicon.

3. Conclusion

Facing the serious crisis of energy and environment, many countries have paid more attention to studying new energy including efficient solar cells. As has been reported, solar cells with multi intermediate bands provides a completely new idea, because making high efficient solar cells and impurity doping is a comparatively simple way to introduce intermediate bands. Therefore, the topic of how to select appropriate doping impurities to maximize the efficiency of solar cells with multi intermediate bands is highly concerned. Luckily, the new material, black silicon, with strong wide spectrum absorption, is supposed to be the ideal material for intermediate band solar cells. Based on this recognition, taking chalcogen as an example, we analyse the enhanced absorption of sunlight in microstructured silicon with two impurity bands. Our calculations show that the loss of sunlight can be minimized to 0.332 when Te^0(0.307 eV) and Te^+(0.411 eV) are introduced into microstructured silicon. This calculation can be extended to the situation where more than two impurity bands are introduced. Based on this calculation, we will make further analysis of the relationship between conversion efficiency of the ideal four-band silicon solar cell and the locations of the two intermediated bands introduced in silicon according to detailed balance theory in future.

References

[1] Her T, Finlay R J and Wu C 1998 *Appl. Phys. Lett.* **73** 1673

[2] Liu Y, Liu S and Wang Y 2007 *Laser Phys.* **18** 1148

[3] Sheng G F, Li Y W and Hou S Q 2003 *Chin. Phys.* **12** 385

[4] Meng W Z and Song L Q 2006 *Chin. Phys.* **15** 2713

[5] Crouch C H, Carey J E, Shen M and Mazur E 2004 *Appl. Phys.* A: *Materials Science & Processing.* **79** 1635

[6] Tull B R, Winkler M T and Mazur E 2009 *Appl. Phys.* A: *Materials Science & Processing.* **96** 4

[7] Bassam M A, Parvin P and Coste H 2008 *Appl. Surf. Sci.* **254** 2621

[8] Wang Y L, Liu S Y and Wang Y 2009 *Mater Lett.* **63** 2718

[9] Feng Z X, Hou Y B, Shi Q M, Qin L F, Li Y, Zhang L, Liu X J, Teng F, Wang Y S and Xia R D 2010 *Chin. Phys.* B **19** 038601

[10] Green M A 2001 *J. Appl. Phys.* **9** 576

[11] Luque A and Marti A 1997 *Phys. Rev. Lett.* **78** 5014

[12] Jiao B C and Zhang X D 2011 *Chin. Phys.* B **20** 037306

[13] Brown A S and Green M A 2004 *J. Appl. Phys.* **5** 97

[14] Wang F, Chen C S and Liu S H 2010 *Appl. Phys.* A: *Mater. Sci. & Proce.* DOI: 10.1007/s00339-010-6095-0

[15] Reference solar spectral irradiance: ASTM G-173 *http://rredc.nrel.gov/solar/spectra/am1.5/ASTMG173/ASTMG173.html*