Modeling of Minibands for Si/SC Quantum Dot Superlattice Solar Cells

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ABSTRACT

The silicon (Si) / silicon carbide (SiC) quantum dot superlattice solar cells (SiC-QDSL) with aluminum oxide (Al₂O₃-QDSL) passivation approaches a high short-circuit current (J_{sc}) of 4.77 mA/cm² under AM1.5 and one sun illumination due to the quantum enhancement on effective bandgap and minimum transition energy. This value matches well with experimental measurement of 4.75 mA/cm². To further optimize the conversion efficiency through the geometry of Al₂O₃-QDSL, we introduce several parameters to define a complete QDSL configuration. A high conversion efficiency of 17.4% is optimized by using the QD geometry from experiment and applying hexagonal QDSL formation with an inter-dot spacing of 0.3 nm.

Keywords: Si/SiC Quantum dot, geometry parameters, solar cell, conversion efficiency

1 INTRODUCTION

By implementing the theory of the intermediate bands, the quantum dot (QD) solar cells are expected to reach a higher conversion efficiency [1-8] and surmount Shockley-Queisser limit [9-10]. Despite of the fact that some studies had provided guidelines to design an optimal core/shell quantum dots solar cell fabricated by III/V compounds [11-12], the design criteria for a low-cost quantum dot solar cell still remain vague. The preliminary result shows that both the efficiency of silicon (Si)/ silicon carbide (SiC) and germanium (Ge)/ Si OD solar cell decrease significantly in an ultra-dense OD configuration, where the planar dot-todot spacing is smaller than 1.3 nm, due to the reduction of effective bandgap [13]. The reduction of effective bandgap degrades the critical role of intermediate bands in the twophoton transition mechanism. Specifically, the intermediate bands serve as the "stepping stone" for the excited electrons that the adsorbed energy is not large enough to reach conduction band [14-15]. This mechanism makes large bandgap materials promising in the photovoltaic devices. In the ultra-dense OD configuration, the effective bandgap drops especially significant because the higher energy states can easily mix with continuous energy levels based on our early calculations [16-17]. To abate the drop of effective



Fig. 1. (a) Advanced top-down process with steps (i) Si/SiC stacked-layer deposition (ii) ferritin self-assembly (iii) neutral beam etching (iv) matrix regrowth. (b) The scanning electron microscopy image of the SiC-QDSL before passivation. (c) The illustration of the unit cell with two QDs for a L = 2 QDSL, and the physical parameters for the simulation. L increases as the number of QD layer increases.

bandgap, the most up-to-date Al_2O_3 passivation layer on Si/SiC QD superlattice (Al_2O_3 -QDSL) had been carried out in the experiment by using top-down process [18]. In order to further understand the character of Al_2O_3 passivation layer in QDSL, we applied the new finite element method and modified Luque theory [13] for the description of two-photon transition mechanism.

In this study, the geometry-dependent effective bandgap and minimum transition energy are studied for multilayer SiC-QDSL. Then, we find out the optimized structure of SiC-QDSL which can reach the highest efficiency. Following the same procedure of analyzing two-photon transition mechanism, the Al₂O₃ passivation layer treatment on SiC-QDSL was studied and compared with SiC-QDSL though the conversion efficiency.

2 TOP-DOWN FABRICATION AND COMPUTATIONAL MODEL

In the experiment, the QDSL is fabricated using a damage-free neutral beam etching (NBE) process [19-20]. A radio frequency sputtering system is used to deposit SiC film and Si film alternatively. In this step, we can accurately control the number of Si/SiC layers and corresponding thicknesses by managing the number of times and the duration of time for the deposition, respectively. Next step is to deposit ferritin molecules on the surface layers and removing the protein shell, the remaining uniform Fe cores



Fig. 2. Minimum transition energy for different zDot as a function of L in the square SiC-QDSL with h = 2 nm. Inset shows (i) effective bandgap (ii) minimum transition energy (iii) ground-state energy (iv) ground-state bandwidth.

act as the mask for the following etching treatment. The applied NBE creates a well-ordered vertical etching profile for its high selectivity between the Fe core and etched material. The final step is to remove the Fe mask and the SiC or Al_2O_3 matrix regrowth, shown in the Fig. 1(a), where Fig. 1(b) is the scanning electron microscopy (SEM) micrograph of QDSL. In this process, the coupling of wave function can be controlled by changing the inter-dot spacing and the number of layers. By adjusting the weight of polyethylene glycol (PEG) attached on the surface of ferritin, we can precisely control the inter-dot spacing between QDs on the same plane.

To simulate the experimental counterpart, we applied the new finite element method for the calculation of minibands formation in a boundary-free ODSL configuration. A unit cell defined by several structural parameters are shown in Fig. 1(c). r, h, and L are the radius, thickness of Si QD, and the number of layers, respectively. Two Si-QDs in the figure represent two layers of QDSL (L = 2). sDot and zDot are the smallest inter-dot spacing and layer-to-layer distance, which closely relate to the wave coupling from horizontal plane and vertical direction, respectively. Once we had defined a unit cell for a desire boundary-free ODSL configuration, the k-points space is defined in an irreducible Brillouin zone (IBZ) based on the symmetry of QDSL. In the IBZ, we sampled totally 45 kpoints for the Schrödinger equation extended in momentum space by Bloch theorem, as listed in Eq. (1).

$$\nabla \left(-\frac{\hbar^2}{2m^*} \nabla u_k(\vec{r}) \right) - \frac{i\hbar^2}{m^*} \vec{k} \cdot \nabla u_k(\vec{r}) + \left(V + \frac{\hbar k^2}{2m^*} \right) u_k(\vec{r}) = E_k u_k(\vec{r}),$$
(1)

where \overline{k} , E_k , \hbar , m^* , V, and $u_k(\vec{r})$ are the lattice wave vector, the quantum energy for specific wave vector, the reduced Planck's constant, the effective mass of carrier, the



Fig. 3. Effective bandgap as a function of L and zDots for the square SiC-QDSL with a fixing h = 2 nm.



Fig. 4. Conversion efficiency (solid lines) shows highly dependence on J_{sc} (dash lines). Despite of the fact that minimum transition energy and effective bandgap does not change with zDot, both J_{sc} and efficiency degrade as the increasing zDot due to lower $\boldsymbol{\nu}$.

potential energy, and the position-dependent Bloch function, respectively. For each k-point, the Schrödinger equation is discretized within a unit cell and solved in real space. After obtaining the minibands formation in both conduction and valence band, the effective bandgap (EB) and minimum transition energy are calculated to use the modified Luque theory which is based on detailed balance argument for the calculation of photoelectric characteristics.

3 RESULTS AND DISCUSSION

Figs. 2 and 3 study the impact of L and zDot on minimum transition energy and effective bandgap for SiC-QDSL, respectively. Among them, the effective bandgap is the minimum energy for the transition from the valence to conduction band, which delineates the coupling effect in the highest bounded-states, as the path (i) shown in inset of Fig. 2. The minimum transition energy, however, defines the minimum energy required to transit from intermediate to conduction bands that describes the confinement effect in lowest bounded-states, as the path (ii) of Fig. 2(b) inset.



Fig. 5. Measured (brown line) I-V curve of Al₂O₃-QDSL; The simulated $J_{sc} = 4.77 \text{ mA/cm}^2$ (symbol) is well matched with experimental $J_{sc} = 4.75 \text{ mA/cm}^2$.

Path (iii) and (iv) are the ground-state energy and groundstate bandwidth, respectively. Both minimum transition energy and effective bandgap saturate at L > 4 because the distance for coupling from one layer to another increase as the increasing L, h, and zDot. It is worth noticing that the drop rate of effective bandgap differs from that of minimum transition energy when introduces more layers or reduces the zDot. This is because, according to our early study, the wave function coupling is the major culprit of reducing effective bandgap and minimum transition energy since both the energy bandwidth for high and low energy states increase. However, there are more bounded-states generated in the high-energy interval than low-energy interval. Consequently, the high-energy states form a wider bandwidth and mixed with continuous energy levels, which results in the rapid decrease of effective bandgap [13], [17].

By using the effective bandgap, the minimum transition energy, and the ground-state bandwidth, we can calculate the conversion efficiency by assuming the full adsorption condition. As shown in the inset of Fig. (2), for the incident energy between 0.9–(iii)–(iv) and 0.9–(iii) eV, the electron can be excited from valence band to the intermediate band (ground-states of the minibands in valence quantum well), where 0.9 eV is the valence band shift between Si and SiC. On the other hand, the electron can be further excited from the intermediate band to the conduction band (ground-states of the minibands in conduction quantum well) by adsorbing the photon with the incident energy between (ii) and (i); whereas, the electron can bypass the intermediate band and transit from valence band to conduction band when the incident energy is higher than (i).

In Fig. 3, to consider a more realistic case, hexagonal QD system is considered for the calculation of conversion efficiency under an ultra-dense Si/SiC QDSL configuration, where the definition of structural parameters remains the same as square QD system. It is clear to see that hexagonal QDSL outweighs square QDSL from the perspectives of J_{sc} and efficiency due to a higher QD volume ratio, in Fig. 4. However, despite of the fact that both minimum transition energy and effective bandgap are independent of zDot



Fig. 6. Benchmarking the simulated conversion efficiency of square SiC- and Al₂O₃-QDSLs as a function of L and zDot. Al₂O₃-QDSL outweighs SiC-QDSL for h = 4 and sDot = 0.3 nm. The efficiency and J_{sc} degrade as more L are introduced; however, the SiC-QDSL behaves otherwise that it only degrades when overcoupling occurs, when zDot < 1.5 nm.

when h > zDot, both J_{sc} and efficiency are reduced because of the decreasing QD volume ratio (v). Although it seems that the conversion efficiency of 18% is high for the SiC-QDSL, the conversion efficiency is extremely sensitive to process variation such as h and zDot. For instance, 1 nm difference in the zDot can result in the 4% reduction in the conversion efficiency for both hexagonal and square SiC-QDSL. The optimal points for hexagonal and square systems are zDot = 1 and 2 nm. It is the result of the balance between effective bandgap and QD volume ratio. To be more specific, the effective bandgap reduces as the decreasing zDot, which leads to the reduction of opencircuit voltage and conversion efficiency. On the contrary, the QD volume ratio increases as the decreasing zDot. A large QD volume ratio leads to the large J_{sc} and conversion efficiency.

Fig. 5 is the measured I-V characteristics (brown line) of Al₂O₃-QDSL [18] and the calibrated J_{sc} (symbol) in the simulation, where *r*, *h*, sDot, and zDot are 3.2, 4, 10, and 2 nm, respectively, and L = 4. The calibrated bandgaps of Si and SiC are 1.6 and 3.0 eV, respectively, which are in agreement with our recent study on SiC-QDSL [16]. Most importantly, the calibrated bandgap of Si is larger than 1.12 eV (monocrystalline Si), which reflects the bandgap widening effect of Si in nanoscale [21]. We further estimate the J_{sc} and conversion efficiency with respect to L and zDot for SiC- and Al₂O₃-QDSL by fixing h = 4 nm. As shown in Fig. 6, even the QD volume ratio is the same, Al₂O₃-QDSL shows a good compatibility between minimum transition energy and effective bandgap, which leads to a high J_{sc} and efficiency. Especially, the reduction of effective bandgap is insignificant for the ones with small zDot. On the contrary, for eight-layer (L = 8) Al_2O_3 -QDSL, the highest conversion efficiency is obtained at the smallest zDot we studied. The SiC-QDSLs, however, lose the compatibility between effective bandgap and minimum transition energy. Because the coupling of minibands becomes intense as L increases with small zDots, the conversion efficiency of few-layer SiC-QDSL is larger than the SiC-QDSL with multiple layers (black > red > green). Therefore, both J_{sc} and efficiency degraded when zDot < 2nm (e.g. green line), but not for the SiC-QDSLs with large zDots.

4 CONCLUSIONS

In summary, by considering geometry parameters, QDSL formation, and passivation layer, Al_2O_3 -QDSL solar cells outweigh SiC-QDSL solar cell in terms of high J_{sc} and efficiency due to a good compatibility between minimum transition energy and effective bandgap. Therefore, a high conversion efficiency of 17.4% is optimized by using the QD geometry from experiment but applying hexagonal QDSL formation with an inter-dot spacing of 0.3 nm.

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REFERENCES

- W. Walker, O. Thériault, J. F. Wheeldon, and K. Hinzer, "The effects of absorption and recombination on quantum dot multijunction solar cell efficiency," *IEEE J. Photovolt.*, vol. 3, no. 3, p. 1118, July. 2013.
- [2] A. W. Walker, O. Thériault, and K. Hinzer, "Carrier dynamics in quantum-dot multijunction solar cells under concentration," *IEEE J. Photovolt.*, vol. 4, no. 4, p. 1095, July. 2014.
- [3] A. W. Walker, O. Theriault, and K. Hinzer, "The dependence of multijunction solar cell performance on the number of quantum dot layers," *IEEE J. Quantum Electron.*, vol. 50, no. 3, p. 198, Mar. 2014.
- [4] T. Nozawa and Y. Arakawa, "Theoretical analysis of multilevel intermediate-band solar cells using a drift diffusion model," *J. Appl. Phys.*, vol. 113, no. 24, p. 243102, Jun. 2013.
- [5] W. Hu, M. M. Rahman, M.-Y. Lee, Y. Li, and S. Samukawa, "Simulation study of type-II Ge/Si quantum dot for solar cell applications," *J. Appl. Phys.*, vol. 114, p. 124509, 2013.
- [6] A. M. Kechiantz, L. M. Kocharyan, and H. M. Kechiyants, "Band alignment and conversion efficiency in Si/Ge type-II quantum dot intermediate band solar cells," *Nanotechnology*, vol. 18, no. 40, p. 405401, Sept. 2007.
- [7] Y. Okada, N. J. Ekins-Daukes, T. Kita, R. Tamaki, M. Yoshida, A. Pusch, O. Hess, C. C. Phillips, D. J. Farrell, K. Yoshida, N. Ahsan, Y. Shoji, T. Sogabe, and J.-F. Guillemoles, "Intermediate band solar cells: Recent progress and future directions," *Appl. Phys. Rev.*, vol. 2, no. 2, p. 021302, 2015.

- [8] W. Hu, M. Igarashi, M.-Y. Lee, Y. Li, and S. Samukawa, "Realistic quantum design of silicon quantum dot intermediate band solar cells," *Nanotechnology*, vol. 24, no. 26, p. 265401, Jun. 2013.
- [9] S. Rühle, "Tabulated values of the Shockley–Queisser limit for single junction solar cells," *Sol. Energy*, vol. 130, p. 139, Feb. 2016.
- [10] W. Shockley and H. J. Queisser, "Detailed balance limit of efficiency of p-n junction solar cells," J. Appl. Phys., vol. 32, p. 510, 1961.
- [11] S. Tomić, J. M. Miloszewski, E. J. Tyrrell, and D. J. Binks, "Design of core/shell colloidal quantum dots for MEG solar cells," *IEEE J. Photovolt.*, vol. 6, no. 1, p. 179, Jan. 2016.
- [12] D. Zhou, G. Sharma, S. F. Thomassen, T. W. Reenaas, and B. O. Fimland, "Optimization towards high density quantum dots for intermediate band solar cells grown by molecular beam epitaxy," *Appl. Phys. Lett.*, vol. 96, no. 6, p. 061913, 2010.
- [13] M.-Y. Lee, Y. Li, and S. Samukawa, "Miniband calculation of 3-D nanostructure array for solar cell applications," *IEEE Trans. Elec. Dev.*, vol. 62, no. 11, p. 3709, Nov. 2015.
- [14] A. Luque and A. Martí, "Increasing the efficiency of ideal solar cells by photon induced transitions at intermediate levels," *Phys. Rev. Lett.*, vol. 78, p. 5014, June 1997.
- [15] A. Luque, A. Martí, and C. Stanley, "Understanding intermediate-band solar cells," *Nature Photonics*, vol. 6, p. 146, Feb. 2012.
- [16] Y.-C. Tsai, M.-Y. Lee, Y. Li, M. M. Rahman, and S. Samukawa, "Simulation study of multilayer Si/SiC quantum dot superlattice for solar cell applications," *IEEE Elec. Dev. Lett.*, vol. 37, no. 6, p. 758, Jun. 2016.
- [17] Y.-C. Tsai, M.-Y. Lee, Y. Li, and S. Samukawa, "Miniband formulation in Ge/Si quantum dot array," *Jpn. J. Appl. Phys.*, vol. 55, p. 04EJ14, 2016.
- [18] M. M. Rahman, A. Higo, H. Sekhar, M. E. Syazwan, Y. Hoshi, N. Usami, and S. Samukawa, "Effect of passivation layer grown by atomic layer deposition and sputtering processes on Si quantum dot superlattice to generate high photocurrent for highefficiency solar cells," *Jpn. J. Appl. Phys.*, vol. 55, no. 3, p. 032303, Feb. 2016.
- [19] S. Samukawa, "A neutral beam process for controlling surface defect generation and chemical reactions at the atomic layer," *ECS J. Solid State Sci. Technol.*, vol. 4, no. 6, p. N5089, 2015.
- [20] S. Samukawa, "Ultimate top-down etching processes for future nanoscale devices: advanced neutral-beam etching," *Jpn. J. Appl. Phys.*, vol. 45, no. 4R, p. 2395, 2006.
- [21] Y. Cao, J. Xu, Z. Ge, Y. Zhai, W. Li, X. Jiang, and K. Chen, "Enhanced broadband spectral response and energy conversion efficiency for hetero-junction solar cells with graded-sized Si quantum dots/SiC multilayers," J. Mater. Chem. C, vol. 3, no. 46 p. 12061, 2015.