Comparative study of ZnMgO/GaAs and ZnMgO/Si solar cells

Wei Zhang and Naiyun Tang

Shanghai University of Electric Power, School of Electronics and Information Engineering, 200000, Shanghai, People’s Republic of China

* Author to whom any correspondence should be addressed.

E-mail: 1355133960@qq.com

Keywords: interface recombination, ZnO/GaAs solar cells, ZnO/Si solar cells, Mg content, ZnO carrier concentration, interface defects

Abstract

Because ZnO can be used as transparent conductive oxide or as an anti-reflective coating in the field of transparent electronics, ZnO/Si solar cells using ZnO as the emitter material have received widespread attention. Compared with Si, GaAs has a wider band gap, which makes its spectral response and solar spectrum match better than Si, so ZnO/GaAs solar cells have higher power conversion efficiency. However, during the manufacturing process of heterojunctions, it is inevitable that dangling bonds and defects will be generated at the interface, which increase the interface recombination and reduce the performance of solar cells. Based on this, in this study, three methods to reduce the interface recombination of ZnO/GaAs solar cells are proposed: doping Mg in ZnO, increasing the carrier concentration of ZnO, and reducing the interface defects between ZnO and GaAs. The results show that these three methods effectively improve the performance of ZnO/GaAs solar cells. After comparing the results with ZnMgO/Si solar cells, it is found that the performance of ZnMgO/GaAs solar cells is much higher than that of ZnMgO/Si solar cells.

1. Introduction

Crystalline silicon is currently the most widely used solar cell material in the photovoltaic market. It has the longest development time in photovoltaic power generation materials and the most mature industrial preparation process [1–3]. However, the manufacturing cost of crystalline silicon solar cells is high, as is that of manufacturing wafers, which consumes a significant amount of energy and pollutes the environment [4]. Therefore, other materials must be found that replace or reduce the use of crystalline silicon. Compared with Si, on one hand, ZnO thin film also has good electrical properties and optical properties, while on the other hand the manufacturing cost of ZnO is low, and it can be used as an anti-reflection layer for solar cells, thereby reducing the cost of surface texture [5–10]. Therefore, with the development of the solar cell industry, ZnO/Si solar cells using ZnO as the emitter material have received widespread attention in recent years [9–11]. However, in comparison with ZnO/Si solar cells, ZnO/GaAs solar cells are superior to ZnO/Si heterojunction solar cells in a number of respects. First, GaAs has a wider band gap, which makes its spectral response and solar spectrum match better than Si, so ZnO/GaAs solar cells have higher power conversion efficiency. Furthermore, the radiation resistance of ZnO/GaAs solar cells is better than that of ZnO/Si solar cells, so it is more suitable for space applications. Finally, the temperature resistance of GaAs is better than that of Si, which is conducive to ZnO/GaAs solar cells still maintaining high power at high temperatures. Based on these factors, research on ZnO/GaAs solar cells is necessary. However, extensive research has shown that the conduction band offset and interface defects in the heterojunction can affect the interface recombination, and ultimately affect the performance of the heterojunction solar cell. To improve the performance of heterojunction solar cells, three methods currently exist to reduce heterojunction interface recombination. First, ZnO/Si solar cells can make the conduction band of ZnO higher than that of Si by doping Mg in ZnO, which can greatly reduce the influence of the recombination center at the interface of the two materials [10–15]. Second, the carrier concentration of ZnO also has a certain effect on the interface recombination. Finally, the different crystal structures of ZnO and Si lead to a high concentration of defects [16–19]. Therefore, interface recombination can be reduced by
reducing the lattice mismatch between ZnO and Si. Some phenomena for reducing the electron affinity of ZnO by doping Mg in ZnO were reported by Knutsen et al. in 2013, who predicted that when the content of Mg in ZnO reaches 20%, the performance of ZnO/Si solar cells is the highest [13]. However, they did not consider that, in addition to the conduction band offset, the carrier concentration of ZnO and interface defects also have a certain effect on interface recombination. Further simulation was obtained by Askari et al. in 2018 [12]; although they considered the effect of carrier concentration of ZnO and interface defects, they did not study the specific relationship between the Mg content in ZnO and the conduction band offset. In addition, most studies in the field of heterojunction interface recombination have only focused on ZnO/Si solar cells, and there is little published data on ZnO/GaAs solar cells. To further improve the performance of solar cells, research on ZnO/GaAs is necessary. In this article, a simulation study of the effects of the above three methods on the performance of a ZnMgO/GaAs heterojunction solar cell is conducted in detail using Silvaco technology computer aided design (TCAD), and the results of the three methods are compared with ZnMgO/Si solar cells. The rest of this study is organized as follows. The simulation details and analysis are described in section 2, simulation results discussed in section 3, and conclusions presented in section 4.

2. Simulation details and analysis

A ZnO/Si solar cell is very similar to a ZnO/GaAs solar cell, except that GaAs is replaced by Si. Taking ZnO/GaAs solar cells as an example, the schematic structure used in the Silvaco TCAD simulation is shown in figure 1. A thin ZnO layer on a 180 μm thick p-type GaAs absorber layer is considered to be an emitter for the device. The thickness of ZnO layer is 0.08 μm. The values of several important material parameters used in the simulation are summarized in table 1. The electron affinity for ZnO material is chosen to be 4.35 for the initial analysis, although it varies from 4.1 to 4.7 [12, 14].

The energy band diagram of an ideal ZnO/GaAs heterojunction solar cell, which looks like a type-II heterojunction, is shown in figure 2. According to the Anderson energy band rule, the characteristics of the band

| Parameter                      | ZnO [12] | p-Si [12] | GaAs [20] |
|-------------------------------|----------|-----------|-----------|
| Thickness (μm)                | 0.080    | 180.00    | 180.00    |
| Acceptor concentration (N_A)  | —        | 1.36 × 10^{15} | 1.36 × 10^{15} |
| Donor concentration (N_D)     | 10^{18}  | —         | —         |
| Permittivity (ε_r)            | 9        | 11.2      | 13.5      |
| Electron affinity (χ_e) (eV)  | 3.73–4.35| 4.05      | 4.07      |
| Band gap (E_g) (eV)           | 3.3      | 1.12      | 1.42      |
| Mobility of electrons (μ_n) (cm² V⁻¹ s⁻¹) | 60     | 1300      | 8800      |
| Mobility of holes (μ_p) (cm² V⁻¹ s⁻¹) | 10     | 400       | 400       |
| Minority carrier lifetime of electrons (τ_n) (s) | 1 × 10^{-9} | 50 × 10^{-6} | 50 × 10^{-6} |
| Minority carrier lifetime of holes (τ_p) (s) | 1 × 10^{-9} | 50 × 10^{-6} | 50 × 10^{-6} |
| Effective density of states in conduction band (N_C) (cm⁻³) | 2.2 × 10^{19} | 2.8 × 10^{19} | 4.7 × 10^{17} |
| Effective density of states in valance band (N_V) (cm⁻³) | 1.8 × 10^{19} | 1.04 × 10^{19} | 7 × 10^{18} |

Figure 1. Schematic of ZnO/GaAs heterojunction solar cell.
alignment can be determined. The conduction band offset ($\Delta E_C$) and valence band offset ($\Delta E_V$) can be expressed as

$$\Delta E_C = \chi(\text{ZnO}) - \chi(\text{GaAs}), \quad (1)$$

$$\Delta E_V = (\chi(\text{ZnO}) + E_g(\text{ZnO}))(\chi(\text{GaAs}) + E_g(\text{GaAs})). \quad (2)$$

Under light, photons pass through the ZnO layer and are absorbed by the GaAs layer, which generates electrons in the GaAs conduction band, and such electrons belong to minority carriers. This minority carrier current plays a crucial role in the performance of solar cells. Knutsen et al. (2013) proved that the minority carrier current is significantly reduced due to conduction band offset. Similarly, the theory can also be used to explain ZnO/GaAs solar cells. The electron minority carrier current is given by [9].

$$I_n = kT \frac{\mu n_i N_a n_1^n_0}{N_c N_a} \exp \left( - \frac{|\Delta E_c|}{kT} \right) \left( \exp \left( \frac{qV}{kT} \right) - 1 \right), \quad (3)$$

$$I_{n2} = \int_0^{x_2} \exp \left( \frac{q\Psi(x)}{kT} \right) dx. \quad (4)$$

Subscripts 1 and 2 denote Si and GaAs material, respectively; $x_2 > 0$ is the extended depletion region of GaAs, where $n_i$, $N_a$, and $N_c$ denote minority carrier mobility and effective density of states in the conduction band respectively; $N_i$ and $N_a$ are intrinsic carrier concentration and acceptor concentration, respectively; $\Delta E_c$ is the value of conduction band discontinuity; and $V$ and $\Psi(x)$ are applied bias voltage and the potential function, respectively.

In addition to the conduction band offset, interface defects in the heterojunction also have an impact on the performance of the solar cell. Under the irradiation of incident light, a photon passes through the ZnO layer and is then absorbed by the GaAs layer, and an electron is excited in the conduction band of the Si layer, which belongs to the minority carrier. The minority carrier passes through the interface between ZnO and GaAs and moves to the front contact of the solar cell. During this propagation process, the electron recombines at the interface trap. Owing to the lattice mismatch between GaAs and ZnO, several defect states are generated. The energy levels of these defect states are located in the gap of the forbidden band. The trap centers belong to these states and have an effect on the carrier recombination, ultimately affecting the effective carrier life. This can be included in the model by determining the interface recombination velocity in the same manner as the Shockley-Read-Hall (SRH) recombination in bulk semiconductors [12]. The SRH recombination is expressed as follows:
\[
R = \frac{\tau_n}{\tau_n p + n_e \exp \left( \frac{E_{trap}}{kT} \right)} + \tau_p \left[ n + n_i e \exp \left( \frac{-E_{trap}}{kT} \right) \right],
\]

where \(\tau_n\) and \(\tau_p\) are the electron and hole lifetimes, respectively; \(n\) and \(p\) are the electron and hole densities, respectively; \(n_i\) is the intrinsic carrier concentration; \(E_{trap}\) is the difference between the trap energy level \((E_t)\) and intrinsic Fermi level \((E_i)\); and \(T\) is the lattice temperature \((\text{in K})\).

As described in equation (5), the carrier concentration also has an effect on determining the recombination rate.

3. Results

The first method evaluated was doping Mg in ZnO. The Mg content in ZnO can change the electron affinity of ZnO. The relationship between the Mg content and electron affinity of ZnO is shown in figure 3 [13]. As the Mg content in ZnO increases, the electron affinity of ZnO clearly decreases. However, owing to the limitation of the solubility of Mg in ZnO and the precipitation of the secondary phase, 20%–30% Mg content can be regarded as an upper limit [13].

The performance versus Mg content in a ZnMgO/GaAs solar cell and a ZnMgO/Si solar cell is demonstrated clearly in figure 4. Both the ZnMgO/GaAs and ZnMgO/Si solar cells share a number of key features. First, the fill factor, open circuit voltage, and efficiency of both the ZnMgO/GaAs and ZnMgO/Si solar cells increase with increasing Mg content in ZnO. This shows that, in terms of improving the efficiency of these two solar cells, doping Mg in ZnO is indeed a feasible method. However, when the Mg content in ZnO reaches approximately 17%, the performance of these two solar cells hardly improves with increasing Mg content in ZnO. Second, the short circuit current density of both the ZnMgO/GaAs and ZnMgO/Si solar cells is almost constant, 28 and 31 mA cm\(^{-2}\), respectively. Moreover, there are a number of important differences between the ZnMgO/GaAs and ZnMgO/Si solar cells. First, the fill factor of the ZnMgO/GaAs solar cell is always greater than that of the ZnMgO/Si solar cell. When the Mg content is 0%, the fill factor of the ZnMgO/GaAs solar cell is 80.8 and that of the ZnMgO/Si solar cell is 72.7. When the Mg content is 17%, the fill factor of the ZnMgO/GaAs solar cell is 87.4 and that of the ZnMgO/Si solar cell is 81.5. The open circuit voltage of the ZnMgO/GaAs solar cell is thus always greater than that of the ZnMgO/Si solar cell. When the Mg content is 0%, the open circuit voltage of the ZnMgO/GaAs solar cell is 0.68 V and that of the ZnMgO/Si solar cell is 0.35 V. When the Mg content is 17%, the open circuit voltage of the ZnMgO/GaAs solar cell is 0.93 V and that of the ZnMgO/Si solar cell is 0.56 V. Finally, the efficiency of the ZnMgO/GaAs solar cell is always greater than that of the ZnMgO/Si solar cell. When the Mg content is 0%, the efficiency of the ZnMgO/GaAs solar cell is 15.5% and that of the ZnMgO/Si solar cell is 7.8%. When the Mg content is 17%, the efficiency of the ZnMgO/Si solar cell is 23.4% and that of the ZnMgO/Si solar cell is 14.4%. It seems possible that these results are due to the wider band gap of GaAs, which leads to higher open circuit voltage and efficiency of ZnMgO/GaAs solar cells.

However, the carrier concentration of ZnO has some effect on interface recombination in addition to the effect of conduction band offset between ZnO and GaAs.
The second method is to increase the carrier concentration of ZnO. Figures 5 and 6 reveal the relationship between the ZnO carrier concentration and the performance of ZnMgO/GaAs and ZnMgO/Si solar cells for different Mg contents, respectively. There are a number of similarities between the ZnMgO/GaAs solar cell and ZnMgO/Si solar cell. First, it can be seen from the data in figures 5 and 6 that the fill factor, open circuit voltage, and efficiency of the ZnMgO/GaAs and ZnMgO/Si solar cells all increase with increasing ZnO carrier concentration. This shows that, in terms of improving the efficiency of these two solar cells, increasing the ZnO carrier concentration is indeed an effective method. However, what is interesting in figures 5 and 6 is that when the Mg content in ZnO is high, with increasing ZnO carrier concentration, the performance of these two solar cells hardly improves. A probable explanation is that, under conditions of heavy doping, Auger recombination greatly reduces the lifetime of minority carriers. Second, the short circuit current density of the ZnMgO/GaAs and ZnMgO/Si solar cells is not affected by the carrier concentration of ZnO, and is almost a constant, i.e., 28 and 31 mA cm$^{-2}$, respectively. In addition, the ZnMgO/GaAs solar cell is different from the ZnMgO/Si solar cell in a number of respects. First, the fill factor of the ZnO/GaAs solar cell is always greater than that of the ZnMgO/Si solar cell under the same conditions. When the Mg content is 0% and ZnO carrier concentration is $1 \times 10^{18}$ cm$^{-3}$, the fill factor of the ZnMgO/GaAs solar cell is 80.8 and that of the ZnMgO/Si solar cell is 72.7. When the Mg content is 8% and ZnO carrier concentration is $3 \times 10^{19}$ cm$^{-3}$, the fill factor of the ZnMgO/GaAs solar cell is 87.5 and that of the ZnMgO/Si solar cell is 81.5. In addition, the open circuit voltage of the ZnMgO/GaAs solar cell is always greater than that of the ZnMgO/Si solar cell. When the Mg content is 0% and ZnO carrier concentration is $1 \times 10^{18}$ cm$^{-3}$, the open circuit voltage of the ZnMgO/GaAs solar cell is 0.68 V and that of the ZnMgO/Si solar cell is 0.35 V. When the Mg content is 8% and ZnO carrier concentration is $3 \times 10^{19}$ cm$^{-3}$, the open circuit voltage of the ZnMgO/GaAs solar cell is 0.93 V and that of the ZnMgO/Si solar cell is 0.56 V. What’s more, the efficiency of the ZnMgO/GaAs solar cell is always greater than that of the ZnMgO/Si solar cell. When the Mg content is 0% and ZnO carrier concentration is $1 \times 10^{18}$ cm$^{-3}$, the efficiency of the ZnMgO/GaAs solar cell is 15.5% and that of the ZnMgO/Si solar cell is 7.8%. When the Mg content is 8% and ZnO carrier concentration is $3 \times 10^{19}$ cm$^{-3}$, the efficiency of the ZnMgO/GaAs solar cell is 22.4% and that of the ZnMgO/Si solar cell is 14.1%.
Figure 5. Relationship between ZnO carrier concentration and ZnMgO/GaAs solar cell performances for different Mg contents.

Figure 6. Relationship between ZnO carrier concentration and ZnMgO/Si solar cell performance for different Mg contents.
carrier concentration is $3 \times 10^{19}$ cm$^{-3}$, the efficiency of the ZnMgO/GaAs solar cell is 23.4% and that of the ZnMgO/Si solar cell is 14.4%.

To further illustrate the relationship between carrier concentration of ZnO and Mg content in ZnO, figures 7 and 8 present the relationship between Mg content and ZnMgO/GaAs and ZnMgO/Si solar cell performance for different ZnO carrier concentrations. It can be clearly seen from the figures that when the Mg content is less than 17%, the fill factor, open circuit voltage, and efficiency of the ZnMgO/GaAs and ZnMgO/Si solar cells all increase with increasing Mg content in ZnO. What is noteworthy in figures 7 and 8 is that when the Mg content is
greater than 17%, regardless of the ZnO carrier concentration, the performance of the solar cells is the same; this shows that the effect of Mg content in ZnO on solar cell performance is dominant.

In fact, the lattice mismatch results in a high concentration of defects. In particular, the electron affinity of ZnO can reach 4.7 eV, the conduction band offset is large, and then the interface defect density has a greater impact on the SRH recombination.

The third method studied is reduction of the interface defect density of the heterojunction. The relationship between the interface defect density and performance of ZnMgO/GaAs and ZnMgO/Si solar cells is shown in figure 9. A number of similarities exist between the ZnMgO/GaAs and ZnMgO/Si solar cells. First, what the figure clearly shows is the steep decrease in the open circuit voltage and efficiency when the interface defect density is greater than a certain value. This means that interface defects do affect the performance of heterojunction solar cells. Second, the short circuit current density of the ZnMgO/GaAs and ZnMgO/Si solar cells is not affected by the interface defect density, and is almost a constant, i.e., 28 and 31 mA cm⁻², respectively. However, the ZnMgO/GaAs solar cell is different from the ZnMgO/Si solar cell in a number of respects. First, when the interface defect density is between 3 × 10¹² and 6 × 10¹² cm⁻², the open circuit voltage of the ZnMgO/GaAs solar cell drops sharply, from 0.92 to 0.69 V. When the interface defect density is between 2 × 10¹² and 4 × 10¹² cm⁻², the open circuit voltage of the ZnMgO/Si solar cell drops sharply, from 0.55 to 0.27 V. Second, when the interface defect density is between 1 × 10¹² and 5 × 10¹² cm⁻², the efficiency of the ZnMgO/GaAs solar cell decreases sharply, from 19.4% to 11.9%. Therefore, when the conduction band offset is large, the performance of the solar cell can be improved by reducing the defect density of the heterojunction interface. This can be achieved by introducing a buffer layer, such as a ZnS layer, the lattice constant of which is between ZnO and GaAs.

4. Conclusion

The present study was designed to determine the effect of interface recombination on ZnMgO/GaAs and ZnMgO/Si solar cells, and to conduct a comparative study of these two solar cells. Three methods for reducing the interface recombination of heterojunctions are proposed, namely, doping Mg in ZnO, increasing the ZnO carrier concentration, and reducing the heterojunction interface defects. The research has identified that the above three methods can reduce interface recombination and that the effect of Mg content in ZnO on solar cell
performance was dominant. The first major finding was that when the Mg content reached 17%, the efficiency of the ZnMgO/GaAs and ZnMgO/Si solar cells reached the maximum, i.e., 23.4% and 14.4%, respectively. The results of this study indicate that, in terms of improving the efficiency of solar cells, ZnMgO/GaAs solar cells are superior to ZnMgO/Si solar cells. The second major finding was that when the Mg content was less than 17%, the performance of these two solar cells can also be improved by increasing the ZnO carrier concentration, but the performance of solar cells cannot be improved without a limit. A probable explanation is that, under heavy doping conditions, Auger recombination greatly reduces the lifetime of minority carriers. The last major finding was that when the interface defect density reached a certain value, the performance of these two solar cells dropped sharply. This finding shows that the performance of these two solar cells can be improved by reducing the interface defects of ZnMgO/GaAs and ZnMgO/Si solar cells. This can be also achieved by introducing a buffer layer. To summarize, this study contributes to the understanding of interface recombination in heterojunction solar cells.

Conflict of interest

The authors declare that they have no conflict of interest.

ORCID iDs

Wei Zhang https://orcid.org/0000-0001-6717-0766

References

[1] Zhang W Y, Meng Q L and Lin B X 2008 Solar Energy Materials and Solar Cells 92 949–52
[2] Karaagac H, Parla M and Yengel E 2013 Materials Chemistry and Physics 140 382–90
[3] Pietruszka R, Witkowski B S and Luka G 2014 Beilstein Journal of Nanotechnology 5 173–9
[4] Green M A and Emery K 1993 Progress in Photovoltaic: Research and Applications 1 25–9
[5] Wang S F, Chen M J and Zhao X H 2010 Physica. B 405 4966–9
[6] Angelov O, Nichev H and Vassileva M S 2010 Physica Status Solidi A 07 1713–6
[7] Quemener V, Alnes M and Vines L. 2011 Solid State Phenomena 178–179 130–3
[8] Zahedi F, Dariani R S and Rozati S M 2013 Sensors and Actuators A: Physical 199 123–8
[9] Hussain B, Aslam A and Khan T 2019 Electronics 8 238
[10] Hussain B, Ebong A and Ferguson I 2015 Solar Energy Materials and Solar Cells 139 95–100
[11] Zhu L, Luo J K and Shao G 2012 Solar Energy Materials and Solar Cells 111 141–5
[12] Askari S S A, Kumar M and Das M K 2018 Semiconductor Science and Technology 33 115003
[13] Knutsen K E, Schilano R and Marstein E S 2012 Physica Status Solidi A 210 585–8
[14] Vallisree S, Thangavel R and Lenka T R 2018 Material Research Express 6 025910
[15] Coli G and Bajaj K K 2001 Applied Physics Letters 78 2861–3
[16] Zhu L, Shao G S and Luo J K 2013 Semiconductor Science and Technology 28 055004
[17] Zhu L, Shao G and Luo J K 2011 Semiconductor Science and Technology 26 085026
[18] Shang X Z, Wang Z Q and Li M K 2014 Thin Solid Films 550 649–53
[19] Nawaz M, Marstein E S and Holt A 2010 35th IEEE Photovoltaic Specialists Conf. 35 002213
[20] Jafari S N, Ghadimi A and Rouhi S 2019 European Physical Journal-Applied Physics 88 20401