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**ZnO as an anti-reflective layer for GaAs based heterojunction solar cell**

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**Abstract**

Currently, how to improve the efficiency of solar cells has attracted wide attention. ZnO film is one of the most effective films today, which can act as both emitter and anti-reflective coating of solar cells. In this paper, n-type ZnO/p-type GaAs solar cell is modeled by analyzing the band edge discontinuities, electric field distributions at the ZnO/GaAs interface and cell parameters with varying ZnO layer thickness, affinity values and carrier concentration. Moreover, in order to improve the band offset alignment at the heterojunction, Mg doped ZnO emitter is a possible alternative. Then, the thickness and carrier concentration of MgZnO emitter layer are studied and simulation results show stronger electric field, better fill factor and higher efficiency. After optimization of two solar cells by using Silvaco Atlas, it is observed that the conversion efficiencies of ZnO/GaAs and MgZnO/GaAs solar cells are 22.84% and 23.44% respectively.

**1. Introduction**

Thin film solar cells are widely researched and used for power generation due to their low production costs and high conversion efficiencies. ZnO is a high n-type conductive and excellent transparent thin film in the visible range. At room temperature, it has wide band energy around 3.37 eV under high concentration [1]. In addition, the costs of depositing ZnO thin films are low, where ZnO can act as n-type thin films with many p-type thin films such as Cu2O [2], CIGS [3], CdTe [4] and Silicon [5]. The ZnO/Si heterojunction solar cell has been researched which efficiency reaches 11.57% [6]. In such a device, ZnO acts as a transparent conducting oxide (TCO) and emitter to enhance light trapping [7]. The ZnO layer obtained by ALD method is a good choice for TCO application and serves as a n-type partner for the underlying p-GaAs substrate [8]. The surface area and defects of metal oxides are known to play an important role in photocatalysis activity, which can be recognized as the specific surface area, surface defects and band gap changes caused by doped ions. The surface of the ZnO was reported to be modified with the addition of doped ions, such as Co-doped ZnO, Ga-doped ZnO Mg-doped ZnO and so on, and its photocatalytic performance was well and significantly enhanced. The electrical conductivity behavior of the Co-doped ZnO thin films prepared by spin-coating method was studied in [9]. Ga-doped ZnO/Si photodiode displays high rectified ratio and relatively low leakage current [10]. In addition, GZO/Si heterojunction-based devices were successfully fabricated in NPs coated metal sol-gel process, which improved overall performance of equipment [11]. The performances of MgZnO/Si solar cell by varying the content of Mg were reported by Knutsen et al [12] and results shown that when the content of Mg was 20%, the solar cell got the best performances. In addition, Mg0.17ZnO0.83O could replace CdS as window layer and nearly reached the same efficiency in [13]. Extensive studies have shown that conduction band offset and interface defects in heterojunctions will affect the interface recombination and ultimately affect the performance of heterojunction solar cells. The doping Mg in the ZnO can make the conduction band of the ZnO higher than the Si, thus greatly reducing the influence of the composite center on the interface of the two materials. Therefore, the MgZnO/Si solar cell performs better than ZnO/Si solar cell [14]. GaAs is a direct bandgap semiconductor with band energy 1.4 eV and its absorption coefficient is 8000 cm⁻¹ which is 10⁴ times larger than silicon [15]. ZnO nanorod arrays were grown directly on GaAs via hydrothermal method to fabricate a
single-junction solar cell in [16] and reported maximum efficiency of 19.9%. The ZnO layer was grown by a sol–gel method as anti-reflection coating in the GaAs solar cell and it proves more efficient than without ZnO [17]. ZnO as anti-reflection coating prevents light to pass to the active region of the solar cell and increases light absorption [18].

Many reports have reported some studies on the ZnO/Si solar cell [6, 19], and few experiments reported that ZnO/GaAs solar cell has higher efficiency, but the effects of various ZnO emitter parameters on the performances of GaAs based solar cell have not been studied and optimized. Hence, the present study is focused to analyze the device physics and carrier transport in ZnO/GaAs solar cell for varying emitter parameters in order to improve the performance of the cell. And the affinity values of ZnO layer are uncertain and vary depending on the annealing time [20].

In this paper, Silvaco-Atlas software is used to perform the numerical simulations to study ZnO/GaAs and MgZnO/GaAs solar cells. Firstly, the performances of the ZnO/GaAs solar cell is analyzed by varying the thickness of emitter layer, electron affinity values and donor concentration. Then, MgZnO/GaAs solar cell is modeled by varying emitter thickness and carrier density. Finally, the key parameters such as short circuit current density (Jsc), open circuit voltage (Voc), fill factor (FF) and efficiency (Eff) between ZnO/GaAs and MgZnO/GaAs solar cells are compared.

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**Table 1.** Material parameters used in the simulation of solar cell device [6, 28].

| Material Parameters                  | ZnO     | MgZnO   | GaAs                        |
|-------------------------------------|---------|---------|-----------------------------|
| Band Gap (eV)                       | 3.37    | 3.93    | 1.424                       |
| Permittivity                        | 9       | 8.49    | 13.2                        |
| Electron Affinity (eV)              | 4.35    | 3.8     | 4.07                        |
| Conduction band density of states (cm⁻³) | 2.2 × 10¹⁸ | 4.42 × 10¹⁸ | 4 × 10¹⁷                    |
| Valence band density of states (cm⁻³) | 1.8 × 10¹⁹ | 1.76 × 10¹⁹ | 9 × 10¹⁸                    |
| Acceptor concentration (cm⁻³)       | —       | —       | 5 × 10¹⁵                    |
| Donor concentration (cm⁻³)          | 10¹⁷–10¹⁹ | 10¹⁷–10¹⁹ | —                           |
| Electron Mobility (cm²Vs⁻¹)         | 100     | 16      | 3197                        |
| Hole Mobility (cm²Vs⁻¹)             | 25      | 4       | 252                         |
| Carrier Lifetime (s)                | 2.1 × 10⁻⁹ | 9 × 10⁻⁹ | 9 × 10⁻⁷                    |
| Radiative Recombination rate (/cm³s) | 1.1 × 10⁻⁸ | 1.1 × 10⁻⁸ | 1.3 × 10⁻¹⁰                |
| Thickness (µm)                      | 0.1–1   | 0.1–1   | 180                         |

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**Figure 1.** Structure diagram of the designed ZnO/GaAs solar cell.
2. Simulation methodology

The solar cell consisting of ZnO as emitter layer and GaAs as absorber material is modeled by Silvaco TCAD shown in figure 1. Each material parameters used in the simulation are listed in table 1. Several experimental studies reported ZnO affinity value of 4.35 eV in [21–23], so electron affinity of ZnO is chosen as 4.35 eV for initial studies as though it varies from 4.0 to 4.5 eV [24–26]. Mg,Ga1−x,ZnO/GaAs solar cell reaches high efficiency when value of Mg content is around 20%, so Mg0.2,Zn0.8O is chosen for further analysis. In the device model, the potential at mesh point is evaluated by solving the Poisson’s equation and carrier continuity equations [27]. The Poisson’s equation \( \nabla (\varepsilon \nabla \psi) = -\rho \) gives the relation between electrostatic potential and space charge density, where \( \varepsilon \) is the local permittivity, \( \psi \) is the electrostatic potential and \( \rho \) is the local space charge density. The continuity equations for electrons and holes are defined as follows.

\[
\frac{\partial n}{\partial t} = \frac{1}{q} \text{div} \overline{J}_n + G_n - R_n \tag{1}
\]

\[
\frac{\partial p}{\partial t} = -\frac{1}{q} \text{div} \overline{J}_p + G_p - R_p \tag{2}
\]

where \( \overline{J}_n \) and \( \overline{J}_p \) are the current densities of electrons and holes, which can be obtained by drift diffusion equations, \( n \) and \( p \) are the electron and hole concentrations, \( G_n \) and \( G_p \) are electron and hole generation rates and \( R_n \) and \( R_p \) are electron and hole recombination rates. The phonon transition occurs when there are traps in the semiconductor gap. Considering this phenomenon, recombination statistics is implemented by Shockley Read Hall (SRH) model as follows.

\[
R_{SRH} = \frac{pn - n_{ie}^2}{\tau_n \left[ n + n_{ie} \exp \left( \frac{E_{trap}}{kT} \right) \right] + \tau_p \left[ n + n_{ie} \exp \left( \frac{E_{trap}}{kT} \right) \right]} \tag{3}
\]

where \( E_{trap} \) is the difference between the intrinsic Fermi level and the trap energy level, \( n \) and \( p \) are the electron and hole densities respectively, \( n_{ie} \) is the intrinsic carrier concentration and \( \tau_n \) and \( \tau_p \) are the electron and hole lifetimes. Because ZnO and GaAs are heterojunctions, the interface recombination velocity is assumed to be \( 10^6 \text{ cm s}^{-1} \) in this work. The recombination at the interface is given by equation (4).

\[
R_{interface} = \frac{pn - n_{ie}^2}{\tau_n^{eff} \left[ n + n_{ie} \exp \left( \frac{E_{trap}}{kT} \right) \right] + \tau_p^{eff} \left[ n + n_{ie} \exp \left( \frac{E_{trap}}{kT} \right) \right]} \tag{4}
\]

Where \( \tau_n^{eff} = \frac{1}{\tau_n} + \frac{d_i}{A_i} n_{ie} \) and \( \tau_p^{eff} = \frac{1}{\tau_p} + \frac{d_i}{A_i} s \).

where \( \tau_n \) is the lifetime at node \( i \) along the interface and \( d_i, A_i \) are the length and area of the interface at each node. \( s \) and \( n \) are the recombination velocities of electrons and holes respectively. ZnO is a direct band gap semiconductor, so radiative recombination should be taken into account.

The solar cell is modeled under standard AM 1.5 G spectrum with intensity of 100 mW cm\(^{-2}\). Real part of the refractive index is used to calculate optical intensity and imaginary part of the refractive index is used to calculate the photogenerated carriers due to the absorption of light. The generation rate is calculated by:

\[
G = \eta_\text{h} \left( \frac{P_\lambda}{hc} \right) \alpha e^{-\alpha y} \tag{5}
\]

where \( \eta_\text{h} \) is the internal quantum efficiency, \( \alpha \) is the absorption coefficient.

The rest of the paper is composed as follows: some important parameters of ZnO/GaAs solar cell are optimized in section 3.1, such as ZnO thickness, affinity values and donor density; in order to improve the cell efficiency, the MgZnO/GaAs solar cell is designed and effects of MgZnO thickness and donor concentration on the cell are studied in section 3.2; finally, comparative performances of two cells are discussed in section 3.3.

3. Results and discussion

3.1. ZnO/GaAs solar cell

In order to prove the better performances of ZnO/GaAs solar cell, the key parameters between ZnO/GaAs, GaAs/GaAs are compared. The thickness of emitter is 0.6 \( \mu \text{m} \), and thickness of the donor concentration of the ZnO or GaAs is \( 10^{17} \text{ cm}^{-3} \), and the acceptor of GaAs is \( 5 \times 10^{15} \text{ cm}^{-3} \).
As we can see from the table 2, n-ZnO/p-GaAs solar cell performs better than n-GaAs/p-GaAs solar cell, so ZnO can act as emitter layer instead of GaAs. A thin ZnO deposition leads to the reduction of natural oxide bonds, such as Ga-O and As-O, which contribute to high defect density on GaAs surfaces. A wider band gap ZnO layer, compared with GaAs, enhances the absorption of the GaAs in short wavelength region and an increase in efficiency [29].

According to reference, it is found that the thickness of ZnO film is about 110 nm and the average refractive index is about 1.65 in the spectral region between 400 and 900 nm. For GaAs based solar cell, the refractive index of the anti-reflective coating is best satisfied with $n_{ARC} = \sqrt{n_{GaAs}n_{air}}$, where $n_{ARC}$, $n_{GaAs}$, and $n_{air}$ are refractive indices of the anti-reflective coating, air, and GaAs respectively. The refractive index of ZnO is about 1.65 near the optimum value of the best anti-reflective coating, which can be used for GaAs [17]. The peak intensity of the solar spectrum is approximately at wavelength of 600 nm. The required thickness of the ZnO layer as a perfect AR coating can be calculated as $d = \lambda / (4n_{ARC})$. The optimum thickness of the ZnO layer is about 90.9 nm for wavelength 600 nm, so the optimized modeled thickness was obtained as 0.1 $\mu$m for minimum reflection thickness.

| Solar cell      | $J_{SC}$ (mA cm$^{-2}$) | $V_{OC}$ (V) | FF (%) | Eff (%) |
|-----------------|-------------------------|--------------|--------|---------|
| ZnO/GaAs        | 27.76                   | 0.82         | 84.03  | 19.16   |
| GaAs/GaAs       | 13.54                   | 0.87         | 82.49  | 9.74    |

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3.1.1. Effect of ZnO thickness on the device performance

The section below describes that the thickness of ZnO layer is varied from 0.1 to 1 μm, while other input parameters are kept unchanged. Figure 2 illustrates the energy band of the solar cell extracted at the ZnO/GaAs interface. The peak electric field at the ZnO/GaAs interface is up to $4.1 \times 10^4$ V cm$^{-1}$.

The key parameters of the cell is studied by varying the thickness of the ZnO layer from 0.1 to 1 μm as illustrated in Figure 3. Figure 4 illustrates that on increasing the thickness of ZnO layer, band gap absorption of light (UV region) in the ZnO decreases. Therefore, what can be clearly seen in Figure 3(a) are the decreases in $J_{sc}$ and efficiency. $V_{oc}$ is dependent on both the photo-generated and saturation current given by $V_{oc} = \left(\frac{K T}{q}\right) \left(\ln \frac{J_{sc}}{J_0} + 1\right)$ [30]. Increase in the thickness leads to the drop in photo-generated current, thereby decreasing $V_{oc}$. When not considering series and shunt resistance, fill factor depends on open circuit voltage given by $FF = \frac{V_{oc} - \ln(V_{oc} + 0.724)}{V_{oc} + 1}$, where $V_{oc} = \frac{q}{neK T} V_{oc}$ [31]. In summary, it has been shown from this review that thinner layer can get better absorption from short wavelengths (300–450 nm) as shown in EQE curves. However, considering all the key parameters and EQE spectrum, 0.1 μm can be considered as the optimum thickness of ZnO emitter layer [19].

3.1.2. Effect of ZnO affinity on the device performance

The chapter that follows considers the effects of different ZnO affinity values. The electron affinity of ZnO was reported to be in the range of 4.0–4.5 eV in [24–26]. And the affinity values of ZnO layer are uncertain and vary depending on the annealing time [20]. The Conduction Band Offset (CBO) which represents the electron
The affinity difference between the ZnO buffer layer and the GaAs absorber layer was investigated in this numerical simulation. Figure 5(a) reveals that the band edge discontinuity between the two materials is significantly improved when changing CBO from $-0.45$ to $0.05$ eV. When CBO is reduced from $0.05$ to $-0.45$ eV, the barrier of electrons from n-side to p-side and the electric field at ZnO/GaAs interface are increased as the heterojunction becomes lower under equilibrium condition. The width of the depletion at the n-side changes little, but the depletion width at the p-side decreases as shown in the figure 5(b).

In order to understand comprehensive influences of thickness and affinity value of ZnO affinity on solar cell, contour graphs are plotted in figure 6. The thickness of the ZnO emitter layer is varied from 0.1 to 1 μm and

![Figure 6](image)

**Figure 6.** Influence of solar cell parameters on emitter layer thickness and affinity (a) $J_{sc}$ (b) $V_{oc}$ (c) fill factor (d) efficiency.

![Figure 7](image)

**Figure 7.** External quantum efficiency for different values of ZnO affinity.
value of ZnO affinity is varied from 4.0 to 4.5 eV. Jsc depends on the photon absorption and carrier generation rate. Because of this, Jsc is almost independent of ZnO affinity. Figure 6(b) shows that Voc performs better in the CBO range of 0.05 to $-0.2$ eV and $-0.4$ to $-0.45$ eV. In case of fill factor, it shows excellent performance in the affinity range of 4.0 to 4.25 eV as seen in figure 6(c). On the optimization of efficiency parameter, affinity values ranging from 4.0 to 4.2 eV and 4.5 shows improved performance as seen from the figure 6(d). As we can see from the figure 6, ZnO affinity values contributed more to Voc, fill factor and efficiency than ZnO thickness. Jsc and Voc decrease with the increase of thickness, however, the affinity value has little effect on the Jsc, and the Voc decreases first and then increases with the increase of affinity values, so the cell efficiency decreases with the increase of thickness, and decreases first and then increases with the increase of affinity values.

Figure 7 shows that external quantum efficiency keeps almost unchanged at different values of ZnO affinity, which is independent of ZnO affinity. In summary, it has been shown from this chapter that 4.1 eV is considered as optimum affinity value for the emitter layer. In addition, what can be evidently seen in the figure 6 is that thickness has less effect on the performances of device when compared to ZnO affinity. Therefore, considering the finger spacing [27], thicker emitter layer is recommended and 0.4 $\mu$m can be considered as the optimum thickness of the emitter layer.

### 3.1.3. Effect of ZnO carrier concentration on the device performance

This part is focused on the effect of emitter donor density. The donor concentration of the ZnO layer is varied from $10^{17}$ to $10^{19}$ cm$^{-3}$, while thickness and electron affinity are selected as 0.4 $\mu$m and 4.1 eV respectively. Figure 8(a) illustrates the energy band alignment for varying ZnO carrier concentration. Figure 8(b) shows that with the increase of ZnO donor density, a strong electric field is established at the heterojunction, which improves the collection of photogenerated carriers and the conversion efficiency. In addition, due to the recombination of electron concentration with more holes, the width of depletion region at the n-side decreases and that at the p-side increases.
Figure 9 illustrates that the cell parameters depend on the concentration of ZnO carrier. This is obvious in figure 9(a) that there has been a decline in $J_{sc}$ and a rise in $V_{oc}$. Increase in availability of majority carriers which raises the probability of recombination \cite{22} in the emitter layer may be the reason for decrease in $J_{sc}$. Strong electric field reduces the recombination of free carriers, which may play an important role in increasing $V_{oc}$. In addition, the development of stronger built-in electric field may lead to the increase of fill factor and efficiency.

3.2. MgZnO/GaAs solar cell

MgZnO/GaAs solar cell is modeled with value of Mg content of 20%. The effects on the thickness and donor concentration of MgZnO emitter layer are studied and the key parameters are compared with ZnO/GaAs cell in the following parts.

3.2.1. Effect of MgZnO thickness on the device performance

The band gap of Mg$_{x}$Zn$_{1-x}$O is 3.8 when $x$ is 0.2, which is lower than ZnO. Therefore, MgZnO layer forms a v-shape barrier with GaAs as shown in figure 10(a). In addition, a stronger electric field built in at the heterojunction due to the clear spike-like configuration as portrayed in figure 10(b) and peak electric field is up to $8 \times 10^4$ V cm$^{-1}$. The trends of cell parameters are similar to that displayed in ZnO case. Figure 11(a) shows that $J_{sc}$ decreases from 28.72 to 27.14 mA cm$^{-2}$ as the thickness increases from 0.1 to 1 $\mu$m and $V_{oc}$ has a slightly decrease but higher than ZnO/GaAs solar cell. Moreover, it is evident in figure 11(b) that fill factor increases slightly and efficiency decreases significantly, which may be attributed to that photon generation rate decreases at the heterojunction. It seems that thinner layer shows better performances, but considering the finger spacing for the solar cell, 0.4 $\mu$m thickness is considered as the optimum thickness.
3.2.2. Effect of MgZnO carrier concentration on the device performance
In this study, the donor concentration of the MgZnO layer is varied from $10^{17}$ to $10^{19}$ cm$^{-3}$ and thickness is maintained at 0.4 μm. As $\Delta E_c$ is reduced to 0.27 eV, a v-shaped barrier is formed at the interface for lower concentration of $10^{17}$ cm$^{-3}$. However, as the carrier concentration increases, the v-shaped barrier at the heterojunction decreases as shown in the figure 12(a). It is evidently seen in figure 12(b) that with the increase of donor concentration, the depletion width of n-side and p-side decreased. As explained in the ZnO/GaAs solar cell, more electrons from the n-side can easily recombine with the hole, which forms stronger electrons in the electric field at the heterojunction.

Figure 13 shows that the dependence of cell parameters on MgZnO carrier concentration is the same as that of ZnO/GaAs solar cells. With the increase of carrier concentration, $J_{sc}$ is found to decrease slightly due to the increase of recombination of high energy photons in the emitter. $V_{oc}$, fill factor and efficiency increase with the MgZnO doping concentration because photo-generated carriers are swept across the junction by the drift motion created by the stronger electric field, but they increase slowly in the range of $10^{18}$ to $10^{19}$ cm$^{-3}$.

3.3. Optimized comparative performance of ZnO/GaAs and MgZnO/GaAs solar cell model
In this paper, the ZnO/GaAs solar cell is analysed with optimized parameters above ($t_{ZnO} = 0.4$ μm, $\chi_{ZnO} = 4.1$ eV, carrier density of $10^{19}$ cm$^{-3}$), which obtains efficiency of 22.84%. Similarly, the MgZnO/GaAs...
solar cell is modeled with 0.4 μm emitter thickness and donor concentration of 10^{19} \text{ cm}^{-3}, which obtains efficiency of 23.44%. The compared parameters can been seen in table 3. What can be clearly seen in this table that cell parameters are improved for MgZnO/GaAs cell when compared to ZnO/GaAs cell, which may stream from the reduced band discontinuities between two materials at the interface. The study implies that ZnO is an excellent transmitting layer but MgZnO performs better with GaAs.

4. Conclusions

In summary, ZnO/GaAs heterojunction solar cell is optimized by the thickness, electron affinity and carrier concentration of ZnO emitter under AM1.5, which obtains efficiency of 22.84%. Compared with ZnO/Si solar cell in [6], the efficiency is improved significantly. As the ZnO thickness increases, the cell parameters descend, but considering finger spacing for the cell, 0.4 μm thickness is considered as the optimum thickness. Affinity values have a great impact on the cell parameters, but considering experiment value, 4.1 eV is considered as the optimum affinity. In addition, the effects of carrier concentration on the solar cell demonstrates that a higher doping concentration increases $V_{oc}$, fill factor and efficiency but decreases $J_{sc}$. In order to improve the cell parameters, MgZnO/GaAs is modeled with MgZnO thickness and donor concentration. The results imply that MgZnO significantly improves the band discontinuities with GaAs and gets stronger electric field at the heterojunction. After simulations of MgZnO thickness and donor density, the efficiency reaches 23.44%. Hence, MgZnO shows excellent performances than ZnO which can act as excellent transmitting and anti-reflective coating layer.

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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