

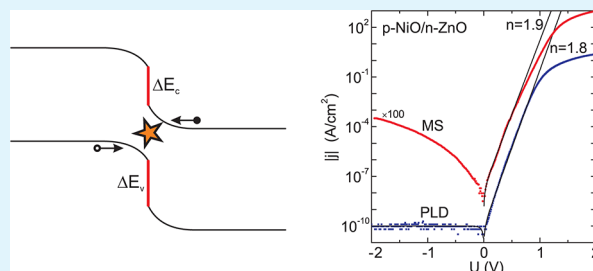
Interface Recombination Current in Type II Heterostructure Bipolar Diodes

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ABSTRACT: Wide-gap semiconductors are often unipolar and can form type II bipolar heterostructures with large band discontinuities. We present such diodes with very high rectification larger than 1×10^{10} . The current is assumed to be entirely due to interface recombination. We derive the ideality factor for both symmetric and asymmetric diodes and find it close to 2 in agreement with experimental data from NiO/ZnO and CuI/ZnO type II diodes. The comparison with experimental results shows that the actual interface recombination rate is orders of magnitude smaller than its possible maximum value.

KEYWORDS: interface recombination, type II band lineup, heterostructure, diode, trap, ideality factor



INTRODUCTION

Most wide-gap semiconductors, and in particular most oxide semiconductors, are unipolar, i.e. they are either n-type or p-type. From such materials, bipolar type II diodes can be constructed and represent interesting device perspectives for UV photodetectors, transparent solar energy converters, and junction field effect transistors. Wide-gap type II systems can exhibit large conduction and valence band offsets (NiO/ZnO,¹ CuI/ZnO²), but do not necessarily do so^{3–5} (Table 1).

Table 1. Conduction Band and Valence Band Offsets for Several Type II Heterostructures from Wide Gap Semiconductors

p/n	ΔE_c (eV)	ΔE_v (eV)	ref
NiO/ZnO	2.93	2.60	1
CuI/ZnO	1.37	1.74	2
Al _{0.12} Ga _{0.88} N/ZnO	0.45	0.11	3
SiC/ZnO	0.3	0.4	4
SiC/GaN	0.11	0.48	5

A NiO/ZnO pin-diode with small rectification of 6 (ratio of forward and backward current at ± 6 V) was reported in.⁶ A NiO/ZnO pn-diode with ideality factor of ~ 2 acting as UV photodetector was reported in.^{7,8} The fully transparent CuI/ZnO type II diode reported in⁹ exhibits high rectification of 6×10^6 and ideality factor around 2. Such a diode exhibits interface recombination as the dominant current transfer mechanism across the interface because the large conduction and valence band offsets block thermal currents.^{9,10}

The ideality factor of 2 due to trap recombination in the depletion layer of a pn diode was pointed out in ref 11. Heterostructure bipolar diodes are discussed in the book by Milnes and Feucht.¹² The type II band lineup in particular was theoretically analyzed in.¹³ The main conclusion of this paper

and current status of literature is that a symmetric type II diode exhibits an ideality factor of 2 and an asymmetric, i.e., p⁺n or n⁺p diode, exhibits an ideality factor of 1, similar to a Schottky diode. However, our analysis in the following predicts an ideality factor around 2 also for asymmetric diodes which is in agreement with experiments on asymmetric CuI/ZnO⁹ and NiO/ZnO diodes (this work). We note that for homo pn-diodes with trap recombination in the depletion layer, an ideality factor of about 2 is expected regardless whether the diode is symmetric or asymmetric.¹⁴

THEORY

We assume a heterostructure pn-diode made from two semi-infinite materials. The diode shall have depletion layers at zero bias, otherwise no good rectification will result and we do not consider such case. The interface is located at $x = 0$, the n-side (p-side) is at positive (negative) values for x . If the thickness of the n- and p-type materials is smaller than the depletion layers, our theory can be extended in the usual way by taking into account the contacts to the n- and p-type materials.

We treat the case of a type II diode as depicted in Figure 1 with conduction and valence band discontinuities, $\Delta E_c = \chi_n - \chi_p$ and $\Delta E_v = (\chi_n - E_g^n) - (\chi_p + E_g^p)$, that are so large that no thermionic minority carrier injection can occur at the temperatures given. Then the diode current is purely a recombination current via traps at the interface.

Here we do not consider any microscopic or dynamic details of the interface recombination that may be described with Shockley–Read–Hall kinetics.^{15,16} The equilibrium majority carrier concentrations in the neutral n- and p-regions are denoted as n_0 and p_0 , respectively. The minority carriers are

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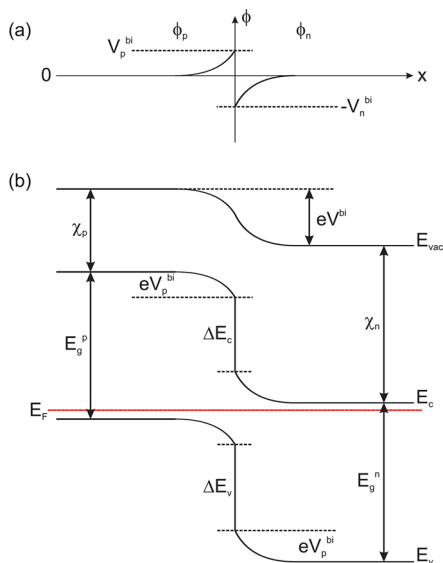


Figure 1. Type II heterostructure bipolar diode (symmetric case) for zero bias: (a) potentials ϕ_p and ϕ_n and (b) band diagram.

neglected, a good approximation for sufficiently large band gaps. We assume a very thin layer at the interface with traps leading to an interface recombination current density j_{if} . The current density in the n-layer (p-layer) is denoted j_n (j_p). Kirchhoff's law yields (for constant cross-section)

$$j_n = j_p = j_{if} \quad (1)$$

The voltage drop across the junction (Figure 1) at zero bias (and zero current) is denoted as built-in voltage and counted positive, $V^{bi} > 0$. The (positive) voltage drops on the n-side and p-side are denoted as V_n^{bi} and V_p^{bi} , respectively and $V^{bi} = V_n^{bi} + V_p^{bi}$. At zero bias, the potential in the depletion layers follows from the Poisson equations on the n- and the p-side. Far away from the interface the carrier densities take their equilibrium values. Throughout, we work in the Boltzmann approximation, i.e., with nondegenerate carriers. At the interface at zero bias

$$n_{if}^0 = n_0 \exp(-\beta V_n^{bi}), p_{if}^0 = p_0 \exp(-\beta V_p^{bi}) \quad (2)$$

with $\beta = e/kT$. We find

$$n_{if}^0 p_{if}^0 = n_0 p_0 \exp(-\beta V^{bi}) \quad (3)$$

If a bias voltage $U = U_n + U_p$ is applied ($U > 0$ for forward direction), the voltage drops are modified to

$$V_n = V_n^{bi} - U_n, V_p = V_p^{bi} - U_p \quad (4)$$

The effects of series and parallel resistance can be included later in the usual way.

A decisive question is whether the interface carrier densities depend on the applied voltage or not. If the carrier lifetimes at the interface are small, then excess carrier densities are small and $n_{if} p_{if}$ is close to its equilibrium value 3. This is the limit of fast interface recombination and yields the maximum possible current through such diode.

The Poisson equation for the potentials ϕ_n (for $x \geq 0$, $\phi_n(x=0) = -V_n$, $\phi_n(x \rightarrow \infty) = 0$) in the depletion layers is (accordingly for ϕ_p ; for $x \leq 0$, $\phi_p(x=0) = V_p$, $\phi_p(x \rightarrow -\infty) = 0$)

$$\frac{d^2 \phi_n(x)}{dx^2} = -\frac{e}{\epsilon_n} (n_0 - n(x)) \quad (5)$$

with the dielectric constants $\epsilon_n = \epsilon_0 \epsilon_{r,n}$ ($\epsilon_p = \epsilon_0 \epsilon_{r,p}$). Here, we assume that the shallow impurities are fully ionized, i.e., $N_D^+ = n_0$ and $N_A^- = p_0$. From the potentials we derive the fields, e.g., in the n-region

$$E_n = -\frac{d\phi_n(x)}{dx} \quad (6)$$

Considering E_n as a function of ϕ_n and using $dE_n/d\phi_n = (dE_n/dx)(dx/d\phi_n) = -(dE_n/dx)/E_n = (d^2 \phi_n/dx^2)/E_n$ and $dE_n^2/d\phi_n = 2E_n(dE_n/d\phi_n)$, we write (analog for E_p)

$$\frac{dE_n^2}{d\phi_n} = -\frac{2e}{\epsilon_n} (n_0 - n(\phi_n)) \quad (7)$$

$$\frac{dE_p^2}{d\phi_p} = \frac{2e}{\epsilon_p} (p_0 - p(\phi_p)) \quad (8)$$

The continuity of the (normal component of the) displacement field at the interface calls for

$$\epsilon_n E_n(-V_n) = \epsilon_p E_p(V_p) \quad (9)$$

We neglect the majority carrier density in the depletion layer (so-called "abrupt approximation") and solve 7

$$E_n^2 = -\frac{2en_0}{\epsilon_n} \phi_n, E_p^2 = \frac{2ep_0}{\epsilon_p} \phi_p \quad (10)$$

Corrections to ϕ due to the majority carrier density in the depletion layer are only of the order of β^{-1} . At the interface we find for zero bias from 9

$$\epsilon_n n_0 V_n^{bi} = \epsilon_p p_0 V_p^{bi} \quad (11)$$

Introducing Q as a measure of diode asymmetry,

$$Q = \frac{\epsilon_n n_0}{\epsilon_p p_0} \quad (12)$$

we can now explicitly write for V_n^{bi} and V_p^{bi} in the zero bias case

$$V_n^{bi} = \frac{V^{bi}}{1+Q}, V_p^{bi} = \frac{V^{bi}}{1+Q^{-1}} \quad (13)$$

The symmetric diode case is $Q = 1$. We note that the image charge effect is typically small compared to n_0/p_0 , which can vary many orders of magnitude, thus we will neglect the ratio of dielectric constants in 12. In order to simplify, we choose $\epsilon_n = \epsilon_p = \epsilon_s$ in the following.

For finite bias,

$$V_n = \frac{V^{bi} - U}{1+Q}, V_p = \frac{V^{bi} - U}{1+Q^{-1}} \quad (14)$$

The currents due to drift and diffusion are (with the carrier mobilities $\mu_n < 0$, $\mu_p > 0$)

$$j_n = -e\mu_n n E_n - \mu_n kT \frac{dn}{dx} \quad (15)$$

$$j_p = e\mu_p p E_p - \mu_p kT \frac{dp}{dx} \quad (16)$$

Using $dn/dx = (dn/d\phi_n)(d\phi_n/dx) = -E_n(dn/d\phi_n)$, we can write

$$j_n = -e\mu_n E_n \left(n - \beta^{-1} \frac{dn}{d\phi_n} \right) \quad (17)$$

The boundary conditions are $E_n(\phi_n = 0) = 0$, $n(\phi_n = 0) = n_0$, and $E_p(\phi_p = 0) = 0$, $p(\phi_p = 0) = p_0$.

Rewriting 17 as (both n and E_n depend on ϕ_n)

$$\frac{dn}{d\phi_n} = \beta \left(n + \frac{j_n}{e\mu_n E_n} \right) \quad (18)$$

and solving yields

$$n(\phi_n) = \exp(\beta\phi_n) \left(n_0 + \beta \frac{j_n}{e\mu_n} I_n \right) \quad (19)$$

$$I_n(\phi_n) = \int_0^{\phi_n} \frac{1}{E_n(\phi'_n)} \exp(-\beta\phi'_n) d\phi'_n \quad (20)$$

Accordingly

$$p(\phi_p) = \exp(-\beta\phi_p) \left(p_0 + \beta \frac{j_p}{e\mu_p} I_p \right) \quad (21)$$

$$I_p(\phi_p) = \int_0^{\phi_p} \frac{1}{E_p(\phi'_p)} \exp(\beta\phi'_p) d\phi'_p \quad (22)$$

At the interface on the n-side, $n_{if} = n(-V_n)$. Extracting j_n from 18 and using 2 and 4 yields

$$j_n = \frac{\mu_n kT}{I_n(-V_n)} n_0 \left(\frac{n_{if}}{n_0} \exp(-\beta U_n) - 1 \right) \quad (23)$$

Using the fast recombination approximation $n_{if}/n_0^0 \approx 1$, we finally obtain

$$j_n = \frac{\mu_n kT n_0}{I_n(-V_n)} (\exp(-\beta U_n) - 1) \quad (24)$$

$$j_p = \frac{\mu_p kT p_0}{I_p(V_p)} (\exp(-\beta U_p) - 1) \quad (25)$$

For discussion of the integrals I_n and I_p we first approximate the fields by their interface (extremum) values, $E_{if} = E_n(-V_n) = E_p(V_p)$,

$$E_{if} = -\sqrt{\frac{2\epsilon V^{bi} - U}{\epsilon_s n_0^{-1} + p_0^{-1}}} \quad (26)$$

Then the integral reads

$$\begin{aligned} I_n(-V_n) &\approx \frac{1}{E_{if}} \int_0^{-V_n} \exp(-\beta\phi'_n) d\phi'_n \\ &= -\frac{1}{\beta E_{if}} (\exp(\beta V_n) - 1) \end{aligned} \quad (27)$$

and

$$I_p(V_p) \approx \frac{1}{\beta E_{if}} (\exp(\beta V_p) - 1) \quad (28)$$

We note that a better analytical approximation of I_n is achieved by using the form 10 for the field. Introducing $y = -\phi'_n/V_n$, we can rewrite ($dy = -d\phi'_n/V_n$)

$$I_n(-V_n) = -\frac{2}{\beta E_{if}} \sqrt{\beta V_n} \exp(\beta V_n) \mathcal{D}(\sqrt{\beta V_n}) \quad (29)$$

where $\mathcal{D}(x)$ is the Dawson integral,

$$\mathcal{D}(x) = \exp(-x^2) \int_0^x \exp(y^2) dy \quad (30)$$

The function $\gamma(x) = 2\sqrt{x} \exp(x) \mathcal{D}(\sqrt{x}) / (\exp x - 1)$ varies between 2 and 1 and can be approximated by $\hat{\gamma}(x) = (2+x)/(1+x)$. Thus, a slightly better approximation for the integral is

$$I_n(-V_n) \approx -\frac{1}{\beta E_{if}} \left(\frac{\beta V_n + 2}{\beta V_n + 1} \right) (\exp(\beta V_n) - 1) \quad (31)$$

but the approximation 27 is sufficient for the following.

With 1, the diode current (still in the fast recombination approximation) can be written as $j = \pm(j_n j_p)^{1/2}$ (selecting the correct sign for forward and reverse direction) and is thus given by

$$\begin{aligned} j &= -eE_{if} \sqrt{-\mu_n \mu_p} \sqrt{n_0 p_0} \\ &\times \sqrt{\frac{(1 - \exp(-\beta U_n))(1 - \exp(-\beta U_p))}{(\exp(\beta V_n) - 1)(\exp(\beta V_p) - 1)}} \end{aligned} \quad (32)$$

For the symmetric case and if the forward voltage U is sufficiently far away from flat-band condition, $\beta(V^{bi} - U) \gg 1$, the forward current density is

$$j \approx -eE_{if} \sqrt{-\mu_n \mu_p} \sqrt{n_{if}^0 p_0^0} (\exp(\beta U/2) - 1) \quad (33)$$

and the ideality factor is 2. In the case $Q \rightarrow 0$, i.e., a p^+n diode, $U_p \ll U$ and $V_p \ll V^{bi}$ the forward current for $\beta U \gg 1$, not too close to the flat-band condition, is

$$j \approx \xi_0 \sqrt{\beta U} (\exp(\beta U/2) - 1) \quad (34)$$

$$\xi_0 = e \sqrt{\frac{2kT(-\mu_n)\mu_p}{\epsilon_s(n_0 + p_0)}} n_0 p_0 \exp(-\beta V^{bi}/2) \quad (35)$$

Thus, the current for the one-sided diode also displays an ideality factor of approximately 2. We have numerically calculated the ideality factor of 32 as a function of Q (solid line in Figure 2) and find for all Q ideality factors close to 2. This is in contrast to the result in ref 13, where for asymmetric diodes ($Q \rightarrow 0$ or $Q \rightarrow \infty$) an ideality factor of 1 was predicted.

Now we relax the fast recombination condition and leave the currents in the form like in 23 using 27

$$j_n = -\frac{eE_{if}\mu_n}{\exp(\beta V_n) - 1} n_0 \left(\frac{n_{if}}{n_0} \exp(-\beta U_n) - 1 \right) \quad (36)$$

$$j_p = \frac{eE_{if}\mu_p}{\exp(\beta V_p) - 1} p_0 \left(\frac{p_{if}}{p_0} \exp(-\beta U_p) - 1 \right) \quad (37)$$

For general interface recombination, we may write

$$n_{if} = n_{if}^0 \exp(\beta(1 - \zeta)U_n) \quad (38)$$

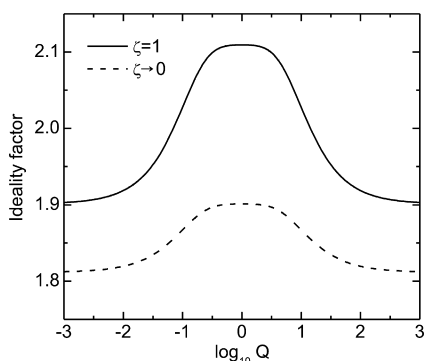


Figure 2. Ideality factor as a function of Q for fast ($\zeta = 1$, solid line) and slow ($\zeta \rightarrow 0$, dashed line) interface recombination. The slope of the characteristic has been calculated for $\beta V^{bi} = 40$ (about 1 eV at room temperature) and $U = V^{bi}/2$. The abscissa is the decadic logarithm of $Q = n_0/p_0$.

$$p_{if} = p_{if}^0 \exp(\beta(1 - \zeta)U_p) \quad (39)$$

with a coefficient $0 \leq \zeta \leq 1$; for the fast (slow) recombination limit $\zeta = 1$ ($\zeta \rightarrow 0$).

For $\zeta \ll 1$ and a symmetric diode ($Q = 1$) we find again an ideality factor of 2

$$j \propto \frac{1}{2} \zeta \beta U \exp(-\beta V^{bi}/2) \exp(\beta U/2) \quad (40)$$

For asymmetric diodes ($Q \rightarrow 0$), we find for the forward current density

$$j \approx \xi_0 \zeta \beta U \exp(\beta U/2) \quad (41)$$

Thus, also in the case of slow interface recombination the ideality factor is close to 2 as depicted as dashed line in Figure 2. In the case of an asymmetric diode, only the lowly doped side's carrier concentration is important; for a p^+n diode 41 reads (with conductivity $\sigma_n = -e \mu_n n_0$)

$$\xi_0 \approx \sqrt{2 \frac{kT}{e_s} \sigma_n \sigma_p n_0} \exp(-\beta V^{bi}/2) \quad (42)$$

■ COMPARISON WITH EXPERIMENTS

We compare our theory with experiments on type II diodes with large band discontinuities (see Table 1).

An asymmetric $p\text{-CuI}/n\text{-ZnO}$ diode was reported in.⁹ For the typical parameters $n_0 = 2 \times 10^{16} \text{ cm}^{-3}$, $p_0 = 5 \times 10^{18} \text{ cm}^{-3}$ ($Q = 4 \times 10^{-3}$), $\mu_n = 10 \text{ cm}^2/(\text{V s})$, $\mu_p = 5 \text{ cm}^2/(\text{V s})$, $\epsilon_{r,s} = 6.5$, $V^{bi} = 1.0 \text{ eV}$, we find $\xi_0 = 2.0 \times 10^{-5} \text{ A/cm}^2$. For $U = +0.5 \text{ V}$, the predicted current density for fast recombination 34 is $j = 1.5 \text{ A/cm}^2$. The experimental value is $j = 4.9 \times 10^{-4} \text{ A/cm}^2$ and thus in strong disagreement. We conclude that the fast recombination limit is not valid for the CuI/ZnO diode. Matching 41 and the experimental current density at $U = +0.5 \text{ V}$, we find $\zeta = 7.2 \times 10^{-5}$, justifying the assumption of slow interface recombination.

The NiO/ZnO diode reported in refs 7 and 8 is asymmetric, with $Q = n_0/p_0 = 0.17$ ($n_0 = 1 \times 10^{18} \text{ cm}^{-3}$, $p_0 = 6 \times 10^{18} \text{ cm}^{-3}$). Its ideality factor of 2 is in agreement with the theory laid out here. We have fabricated diodes from $n\text{-ZnO}$ (grown by pulsed laser deposition (PLD) on Al_2O_3) with (i) p -type amorphous NiO_x deposited by reactive DC magnetron sputtering and (ii) PLD. These diodes are also asymmetric: for (i) $Q \approx 10^{-3}$, $n_0 = 5 \times 10^{16} \text{ cm}^{-3}$, $p_0 \approx 5 \times 10^{19} \text{ cm}^{-3}$, for (ii): $Q \approx 0.1$. The

diodes exhibit high rectification of (i) 3×10^6 and (ii) 2×10^{10} for $\pm 2 \text{ V}$ and ideality factors of about 1.9 and 1.8, respectively (Figure 3). Again, the low current densities indicate slow

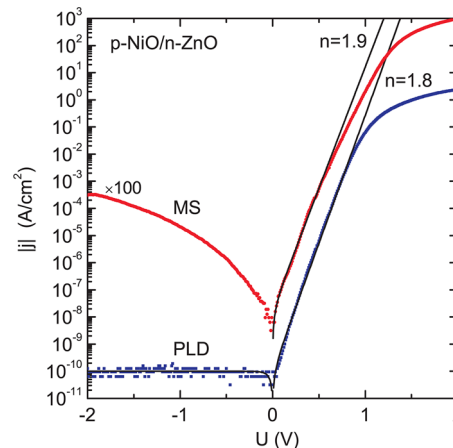


Figure 3. j - V characteristics of NiO/ZnO bipolar heterostructure diodes (at room temperature); the NiO_x has been fabricated with magnetron sputtering (MS) and pulsed laser deposition (PLD) as labeled. Solid lines are fits with ideality factors $n = 1.9$ and $n = 1.8$ as indicated.

interface recombination. The built-in voltage (from C - V measurements) is (i) 1.2 V and (ii) 1.1 V. Evaluating 41 and 42 for $U = V^{bi}/2$, we find for (i) ($\sigma_p = 100 \text{ S/m}$, $j = 3 \times 10^{-5} \text{ A/cm}^2$) $\zeta = 2 \times 10^{-5}$ and for (ii) ($\sigma_p = 1 \text{ S/m}$, $j = 2 \times 10^{-5} \text{ A/cm}^2$) $\zeta = 6 \times 10^{-5}$.

We summarize that the experimental ideality factors around 2 for all discussed asymmetric type II heterostructure diodes are in agreement with the present theory but not with.¹³ The experimental interface recombination rate in the present diodes is found to be 4–5 orders of magnitude smaller than its possible maximum value.

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Notes

The authors declare no competing financial interest.

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