Analytic description of the impact of grain boundaries on Voc

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Abstract—The impact of grain boundaries on the performance of polycrystalline photovoltaics remains an open question. We present a simplified description of dark grain boundary recombination current. The dark current takes the form of a diode equation, and the model provides closed form expressions for the reverse saturation current and ideality factor in terms of grain boundary and system parameters. This model applies under conditions relevant for thin film photovoltaics such as CdTe, namely for p-type absorbers with reasonably high bulk hole mobility, positively charged grain boundaries with high defect density, and grains which are not fully depleted. The dark recombination current can be used to predict the open circuit voltage for a given short circuit density, providing a simple closed form expression which shows how grain boundaries impact Voc.

Index Terms—polycrystalline solar cell, grain boundary recombination, open circuit voltage

I. INTRODUCTION

Thin films photovoltaics like CdTe and Cu(In,Ga)Se₂ exhibit high conversion efficiency despite their high defect density [1]. Grain boundaries are a primary source of defects, however so far polycrystalline samples outperform their single crystal counterparts [2]. This apparent dichotomy between the electrical and structural properties invites the unexpected question: “Can grain boundaries be beneficial for photovoltaic performance?” There is not a clear consensus on this issue. In our view there is not a universal answer to this question, it depends on the details of the grain boundary and bulk properties. Grain boundaries may improve the performance of samples with exceedingly poor bulk properties, but are always detrimental to samples with reasonably good bulk properties. In the best cases, grain boundaries assist carrier collection at zero bias, increasing the short circuit density Jsc. This is due to the built-in electric field accompanying charged grain boundaries which separates carriers and inhibits recombination (provided that carriers driven to the grain boundary core (majority carriers at the grain boundary core) [3], [4]. However in all cases grain boundaries are harmful for the open circuit voltage Voc [5], [6]. This is not surprising since Voc is reduced by recombination, and recombination is enhanced by grain boundaries when the device is under forward bias. However an intuitive, quantitative description of how grain boundaries reduce Voc is still lacking, despite previous numerical and analytical works [5], [6], [7]. This article describes our recently developed models which provide this simple relation between grain boundary properties and Voc.

II. GRAIN BOUNDARY RECOMBINATION

In a recent set of papers [8], [9], we have presented analytical expressions for the grain boundary dark recombination current. These expressions take the form of a general diode equation:

\[ J_{GB}(V) = J_0 \exp\left(\frac{qV}{n k_B T}\right), \]

where \( q > 0 \) is the electron charge, \( V \) is the applied voltage, \( k_B \) is the Boltzmann constant, and \( T \) is the temperature. The result of our work is closed form expressions for the reverse saturation current \( J_0 \) and ideality factor \( n \) in terms of grain boundary and system parameters. We also demonstrated that the dark recombination current can be used to accurately predict the open circuit voltage for a given short circuit current density. In particular, numerical simulations indicate that the following relation holds:

\[ V_{oc} = \frac{n k_B T}{q} \ln \left(\frac{J_{sc}}{J_0}\right). \]

The impact of grain boundary recombination on Voc can therefore be concisely quantified. This may enable rational approaches to mitigating the negative consequences of grain boundary recombination.

Our analysis showed that the system behavior depends on the grain boundary defect type (e.g. donor or acceptor), the location of the defect energy level(s) with respect to midgap, the applied voltage, and other factors. The system behavior can be classified into several regimes, where each regime has its own peculiarities and requires its own detailed analysis. The myriad of different cases can obscure the overall picture of grain boundary recombination. Despite the differences between different regimes, a single framework for understanding the system response can be presented, which offers useful perspective when viewing the multiplicity of cases. In this work we aim to provide a more global, qualitative description of our model of grain boundary recombination current.

Before discussing grain boundary recombination, it’s useful to rewrite Eq. 1 in a form which helps to frame our analysis. We write the dark recombination current as:

\[ J = N \left(\frac{\lambda}{\tau}\right) \exp\left(\frac{qV}{n k_B T}\right). \]
The form of Eq. (3) is fully general for thermally activated transport. Current density can always be written as the product of a density $N$ times a velocity: length $\lambda$ divided by time $\tau$. The exponential factor describes the classic diode voltage dependence with ideality factor $n$. Although Eq. (3) is generic, when applied to a 1-dimensional $p$-$n$ junction, the factors in Eq. (3) acquire quite specific physical interpretations. $N$ and $\tau$ correspond to the density and effective lifetime of the species controlling the recombination, and $\lambda$ is the length scale over which recombination occurs. The ideality factor $n$ is determined by the nature of recombination. An ideality factor $n = 1$ corresponds to minority carrier-controlled recombination, while $n = 2$ applies when both species contribute to recombination.

We first demonstrate this interpretation of Eq. (3) by evaluating the well-known 1-dimensional $p$-$n$ junction dark recombination current. For this system, dark recombination current is the sum of two contributions: the diffusion current and junction recombination current. Diffusion current is associated with minority carrier recombination in the neutral region. For concreteness, we suppose the system is a $p$-$n$ junction and consider recombination in the $p$-type region. Electrons are minority carriers, so $N$ is given by the equilibrium electron density in the $p$-type neutral region, which we denote $n_0^p$. The lifetime is set by the bulk electron lifetime, $\tau = \tau_{\text{bulk}}^e$. Minority carriers undergo simple diffusion in the neutral region, so the length scale of the minority carrier density profile is the diffusion length, $\lambda = \sqrt{D_{\text{bulk}}^e \tau_{\text{bulk}}^e}$, where $D_{\text{bulk}}^e$ is the bulk electron diffusivity. Recombination is determined by the minority carrier (electron) density, so the ideality factor $n = 1$. Substituting these factors for Eq. (3) reproduces the well-known result for diffusive dark current. We next apply the same analysis to junction recombination current. In this case the recombination occurs in the depletion region and involves both nonequilibrium electrons and holes. The equilibrium density of electrons and holes in the depletion region is given by $N = n_i$, where $n_i$ is the intrinsic density. The length scale over which recombination occurs is set by the depletion width $W$ of the $p$-$n$ junction, $\lambda \approx W$. The lifetime is determined by bulk recombination, $\tau = \tau_{\text{bulk}}$. Both nonequilibrium electrons and holes participate in recombination, so that $n = 2$. These factors correctly reproduce the junction recombination dark current.

For grain boundary recombination, the same interpretations of the parameters entering Eq. (3) apply. What remains is to identify the recombination species and its lifetime, and to determine the region over which recombination occurs. Doing so requires knowledge of how carriers behave in the 2-dimensional model, which we discuss next.

As in many analytical models, the key aspect of our treatment lies in the approximations we make. The initial problem in its fully general form is not analytically tractable, due to nonlinearities and its 2 (or 3)-dimensional nature. Reducing the problem to a more manageable form requires valid, simplifying assumptions, which in turn require sufficient knowledge of system behavior. The rough picture is that positively charged grain boundaries lead to downward band bending in most of the $p$-type absorber, providing a confinement potential for electrons. We assume one end of the grain boundary is in close proximity with the $n$-contact, so electrons are efficiently funneled into the grain boundary and the vast majority of electron current is carried along the grain boundary core. Hole current takes place in the grain bulk, and is directed towards regions of high recombination. We assume grains are not fully depleted. In practice this corresponds to grain sizes which exceed 1 $\mu m$ in CdTe. Hole current therefore requires very small gradients in the hole quasi-Fermi level. This fact leads to a key assumption: that the hole quasi-Fermi level $E_{FP}$ is approximately flat everywhere. This assumption is valid only for sufficiently high intragrain hole mobility; for typical material parameter values of CdTe, the intragrain hole mobility $\mu_p$ should exceed $30$ cm$^2$/V $\cdot$ s (see ref. [8] for details of this estimate).

We restrict our attention to the recombination at the grain boundary core, reducing the domain of interest to one dimension. However by itself this does not simplify the problem: The solution at the grain boundary depends on the solution in the grain interior, and the problem remains essentially 2-dimensional. The assumption of flat $E_{FP}$ is crucial here, as it implies $E_{FP_{GB}} = E_{FP_{bulk}}$. This relation provides a link between the grain boundary and grain bulk and enables the analysis of the two domains to be separated. The dimensionality of the problem is then reduced from 2 to 1.

Our next assumption is that the grain boundary defect density is large. The charge of the grain boundary defect is equal to the defect density multiplied by a statistical factor related to the defect occupation and type (donor or acceptor, see Eq. (7)). If the defect density is very large, the statistical factor must be very small to ensure that the defect charge remains finite. A large defect density also implies that the statistical factor is independent of applied voltage [9]. This leads to a constraint which takes the place of the Poisson equation. The implications of this constraint depend on the details of the grain boundary, such as the position of the defect level with respect to midgap. This is the point at which different cases and their analysis bifurcate. We discuss these cases later. For now the salient point is that this assumption of high defect density provides another simplification to the problem.

Having made these assumptions, the problem can be reduced to a single 1-dimensional effective diffusion equation for the electron quasi-Fermi level $E_{FP_{GB}}(x)$, where $x$ is the coordinate along the grain boundary core. It’s not surprising that a description of grain boundary recombination would include a continuity equation for $E_{FP_{GB}}$: electrons are confined to the grain boundary and carry the recombination current there [5]. The 1-dimensional diffusive motion of electrons along the grain boundary is parameterized by the electron grain boundary diffusivity $D_{GB}$ and effective lifetime $\tau_{GB}$. These parameters can be expected to differ from their bulk counterparts due to the highly defective grain boundary core.
The grain boundary-confined electron diffusivity \( D_{\text{GB}}^e \) is likely reduced from the bulk value due to increased disorder scattering. \( D_{\text{GB}}^e \) enters as a free parameter in the model. The electron effective lifetime is reduced from its bulk value due to proximity to the grain boundary recombination centers. The recombination strength of the grain boundary is parameterized by an effective surface recombination velocity for electrons

\[
\bar{S}_{\text{GB}}^e = S_{\text{eff}}^e \lambda_n^{n-1} \tau_{\text{eff}}^{-n}.
\]

The effective lifetime \( \tau_{\text{eff}}^e \) is determined by the length scale of electron confinement \( L_E \) according to \( \tau_{\text{eff}}^e = L_E / S_{\text{eff}}^e \). The confinement length \( L_E \) is determined by the built-in potential around the grain boundary, which is associated with two length scales: the depletion width of the grain boundary and \( k_B T / (q E_{\text{GB}}) \), where \( E_{\text{GB}} \) is the magnitude of the electric field at the grain boundary. The appropriate choice for \( L_E \) depends on the regime of system behavior, but either choice gives qualitatively similar results. The diffusion length of electrons confined to the grain boundary \( L_{\text{GB}}^e \) is then given by

\[
L_{\text{GB}}^e = \sqrt{D_{\text{GB}}^e \tau_{\text{eff}}^e} = \sqrt{D_{\text{GB}}^e L_E / S_{\text{eff}}^e}.
\]

With this picture of the system in mind, we turn again to Eq. (3) and specify the factors entering the formula. The appropriate lifetime \( \tau \) for Eq. (3) is \( S_{\text{eff}}^e / d \), where \( d \) is the grain size (the appropriate \( S_{\text{eff}}^e \) depends on the grain boundary type). This amounts to taking all of the recombination centers concentrated on the grain boundary surface and smearing them out uniformly across the entire grain. This is the crudest approximation one can make to account for grain boundary recombination, and has been used rather successfully to describe polycrystalline Si solar cells [11]. For photovoltaics with high grain boundary defect density, simply re-scaling the \( \tau \) and applying 1-dimensional \( p-n \) junction theory is inadequate for determining \( N \), \( \lambda \), and \( n \). For these three parameters, the analysis proceeds differently according to the majority carrier type at the grain boundary core. As always, defect-mediated recombination is controlled by the minority carrier density. The minority carrier type depends on the Fermi level at the grain boundary core, which in turn depends on grain boundary defect properties (mostly the defect energy level).

Beginning with an \( n \)-type grain boundary core, holes are minority carriers, so \( N \) is the equilibrium grain boundary hole density, which we denote by \( n_{\text{GB}}^0 \). Since recombination is set by only one species, the ideality factor \( n = 1 \). The relevant \( S \) is that for holes: \( S = S_{\text{eff}}^p \). We consider a single donor+acceptor defect, in which case the effective surface recombination velocity is equal to the bare surface recombination velocity: \( S_{\text{eff}}^p = S_p \). (For other cases like the single donor defect and the continuum of donor+acceptor defects, the effective surface recombination velocity differs from the bare surface recombination velocity.) \( \lambda \) is determined by the region over which holes are available to flow into the grain boundary and recombine. The majority of the grain boundary length \( L_{\text{GB}}^p \) is embedded in \( p \)-type bulk, so holes are available for transport into the grain boundary from the grain bulk over approximately the entire grain boundary. Hence \( \lambda = L_{\text{GB}}^n \) (see Fig. 1(a)).

For a \( p \)-type grain boundary, similar reasoning immediately leads to \( N = n_{\text{GB}}^0 \), \( n = 1 \), and \( S = S_n \). The recombination length \( \lambda \) includes the region over which electrons are available to flow into the grain boundary. We delimit this region with \( x_0^p \): for \( x < x_0^p \), \( n_{\text{bulk}} > p_{\text{bulk}} \). Electrons flow into the grain boundary for \( x < x_0^p \) and propagate via diffusion along the grain boundary core for \( x > x_0^p \), where additional recombination occurs (see Fig. 1(b)). The total length over which recombination occurs is therefore \( x_0^p + L_{\text{GB}}^\text{diff} \), where \( L_{\text{GB}}^\text{diff} \) is the diffusion length of electrons confined near the grain boundary core. Based on the discussion of electron diffusion along the grain boundary given earlier, we have \( \lambda = x_0^p + L_{\text{GB}}^\text{diff} = x_0^p + \sqrt{D_{\text{GB}}^e L_E / S_{\text{eff}}^n} \).

In the case where electron and hole density are of comparable magnitude, we immediately anticipate that \( N = n_i \) and \( n = 2 \). To determine \( \lambda \), we note that both electrons and holes must be transported to the grain boundary for recombination (see Fig. 1(c)). Holes are available along almost the entire length of the grain boundary, as discussed earlier. However electrons are only available for \( x < x_0^p \). \( \lambda \) is therefore set by the electrons’ availability. Recombination is concentrated near the middle of the depletion region, and decays on a length scale of the electron diffusion length, so that \( \lambda = L_{\text{GB}}^\text{diff} \).

These cases are summarized in Table 1, and depicted in Fig. 1 (a)-(c).

### Table I: Recombination current parameters

<table>
<thead>
<tr>
<th>Type</th>
<th>Parameter</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>( n )-type</td>
<td>( N = n_{\text{GB}}^0 )</td>
<td>Grain boundary hole density</td>
</tr>
<tr>
<td>( p )-type</td>
<td>( N = n_i )</td>
<td>Grains boundary electron density</td>
</tr>
<tr>
<td>( n )-type</td>
<td>( \lambda = L_{\text{GB}}^n )</td>
<td>Grain boundary length for recombination</td>
</tr>
<tr>
<td>( p )-type</td>
<td>( \lambda = L_{\text{GB}}^p )</td>
<td>Grain boundary length for recombination</td>
</tr>
<tr>
<td>( n )-type</td>
<td>( S = S_{\text{eff}}^p )</td>
<td>Effective surface recombination velocity for electrons</td>
</tr>
<tr>
<td>( p )-type</td>
<td>( S = S_{\text{eff}}^n )</td>
<td>Effective surface recombination velocity for holes</td>
</tr>
</tbody>
</table>

### Fig. 1:
(a), (b), and (c) show the system geometry and the electron and hole current flow for \( n \)-type, \( p \)-type, and high recombination grain boundaries, respectively. Also shown is the length \( \lambda \) over which recombination occurs along the grain boundary core. The grain boundary is columnar and positioned at \( y = d/2 \). (d), (e), and (f) show the electron and hole density under forward bias through a slice of the neutral region perpendicular to the grain boundary for \( n \)-type, \( p \)-type, and high recombination grain boundaries, respectively. The grain boundary core is located at \( y = 2.5 \mu \text{m} \), and the blue (red) tick marks at the grain boundary core position indicate the values of \( \tau_{\text{GB}}^e (\tau_{\text{GB}}^p) \).
Having summarized our understanding of grain boundary recombination in qualitative terms, we next place it in more quantitative context by presenting the relevant governing equations. The key underlying equations provide the grain boundary occupation \( f_{GB} \), grain boundary charge \( Q_{GB} \), and grain boundary recombination \( R_{GB} \) in terms of carrier densities and the defect properties. These are all standard equations which can be found in textbooks [12], [13]. We start with the grain boundary occupancy:

\[
f_{GB} = \frac{S_p n_{GB} + S_p \pi_{GB}}{S_n (n_{GB} + \pi_{GB}) + S_p (p_{GB} + \pi_{GB})}.
\]

(4)

In the above, \( n_{GB} \) and \( p_{GB} \) are the electron and hole carrier density at the grain boundary, respectively (note that \( n_{GB}, p_{GB}, \) and \( f_{GB} \) can vary as a function of position along the grain boundary core). \( \pi_{GB} \) and \( \pi_{GB} \) are the electron and hole density one would obtain if the Fermi level is positioned at the defect energy level \( E_{GB} \). If \( E_{GB} \) is measured from the valence band, then:

\[
\pi_{GB} = N_e \exp \left( \frac{(E_{GB} - E_0)}{k_B T} \right),
\]

(5)

\[
\pi_{GB} = N_e \exp \left( -\frac{E_{GB}}{k_B T} \right).
\]

(6)

The charge of the grain boundary is given by:

\[
Q_{GB} = q \rho_{GB} \times \begin{cases} 
(1 - f_{GB}), & \text{(donor)} \\
(1 - f_{GB}), & \text{(acceptor)} \\
(1 - 2f_{GB}), & \text{(donor + acceptor)}
\end{cases}
\]

(7)

Here \( \rho_{GB} \) is the two-dimensional defect density at the grain boundary core. Note that the charge of the defect state depends on its type (donor or acceptor). Experimental evidence indicates positively charged grain boundaries [10], so we restrict our attention to the donor and donor+acceptor cases (the acceptor case only yields negatively charged grain boundaries). Note that for the donor+acceptor case, both defects are assumed to be present at the same energy \( E_{GB} \). The donor and acceptor defects therefore compensate each other only when the Fermi energy is equal to the defects’ common energy level.

The grain boundary charge \( Q_{GB} \) is uncompensated by the surrounding depletion region charge. For a depletion width \( W \), the associated space charge is \( 2qN_A W \), where \( N_A \) is the doping and the factor of 2 arises from having depletion regions on both sides of the grain boundary. The relation \( Q_{GB} = 2qN_A W \) determines the equilibrium band bending between grain boundary and grain bulk.

The assumption we described earlier is that \( \rho_{GB} \) is “large”. The factors in parentheses in Eq. (7) must therefore be “small” for \( Q_{GB} \) to remain finite. For the donor case, this implies \( (1 - f_{GB}) \) is small, or \( f_{GB} \approx 1 \). For the donor+acceptor case, we have \( f_{GB} \approx 1/2 \); both donor and acceptor state are approximately half-occupied. As described in Ref. [9], large \( \rho_{GB} \) also implies the the factor in parentheses does not change with applied voltage; we can determine \( f_{GB} \) in equilibrium and use the same value under forward bias.

Having determined \( f_{GB} \), we can return to Eq. (4) and consider what values of carrier density \( n_{GB}, p_{GB} \) are needed to yield the correct value of \( f_{GB} \). We’ll consider the donor+acceptor case here as an example, in which \( f_{GB} = 1/2 \). In equilibrium, \( f_{GB} = 1/2 \) is satisfied by the carrier densities \( n_{GB} = \pi_{GB} \) and \( p_{GB} = \pi_{GB} \). This means that the Fermi energy is pinned to \( E_{GB} \) (see discussion preceding Eqs. (5), (6)). In equilibrium, the majority carrier type at the grain boundary core is therefore determined solely by \( E_{GB} \); if \( E_{GB} \) is closer to the conduction (valence) band, the grain boundary core is \( n \) (p)-type.

Let’s consider an \( n \)-type grain boundary under forward bias. The terms \( n_{GB} \) and \( \pi_{GB} \) are much larger than \( p_{GB} \) and \( \pi_{GB} \) in the expression on the right-hand-side of Eq. (4). An applied bias voltage induces nonequilibrium electron and hole densities. Provided \( p_{GB} \) is much less than \( n_{GB} \), \( n_{GB} \) must remain fixed to the value \( \pi_{GB} \) to maintain \( f_{GB} = 1/2 \). This is demonstrated in Fig. 1(d), which shows the electron and hole density under forward bias through a slice of the system perpendicular to the grain boundary core. The small blue (red) tick mark at \( y = 2.5 \mu m \) indicates the value of \( \pi_{GB} (\pi_{GB}) \). In this plot, \( n_{GB} = \pi_{GB} \) while \( p_{GB} \). We can write the grain boundary hole density in terms of the bulk hole density using the assumption we described earlier:

\[
E_{GB} = E_{GB}^{bulk},
\]

This leads to \( p_{GB} = p_{GB}^{0} \exp (qV/k_B T) \). The minority carrier density increases exponentially with applied voltage. The same behavior holds for \( p \)-type grain boundaries, where majority and minority carrier types are interchanged with respect to the \( n \)-type grain boundary (see Fig. 1(e)).

Having determined the majority and minority carrier density, we can compute the grain boundary recombination \( R_{GB} \), given by:

\[
R_{GB} = \frac{S_n S_p (n_{GB}n_{GB} - n_i^2)}{S_n (n_{GB} + \pi_{GB}) + S_p (p_{GB} + \pi_{GB})}.
\]

(8)

For the \( n \)-type grain boundary, Eq. (8) simplifies to \( R_{GB} = \frac{S_n S_p (n_{GB} - n_i^2)}{S_n (n_{GB} + \pi_{GB}) + S_p (p_{GB} + \pi_{GB})} \). We argued previously that the length scale over which recombination occurs is equal to the entire grain boundary length \( L_{GB} \). Together these factors reproduce the diode equation terms for an \( n \)-type grain boundary as given in Table 1.

As the applied voltage increases, the minority carrier density \( p_{GB} \) dutifully increases exponentially and will eventually approach \( n_{GB} \). At this point further increases in the applied voltage push both \( n_{GB} \) and \( p_{GB} \) to exceed \( \pi_{GB} \). Now \( f_{GB} = 1/2 \) is satisfied by insisting that \( S_n n_{GB} = S_p p_{GB} \) (see Eq. (4)). This is the high-recombination regime. Returning to Eq. (8) and utilizing the relation \( n_{GB} p_{GB} = n_i^2 \exp (qV/k_B T) \), the maximum value of recombination along the grain boundary core can be found as:

\[
R_{GB}^{max} = \frac{S_n S_p n_i \exp \left( \frac{qV}{2k_B T} \right)}{2nk_i^2}
\]

(9)

In the high recombination regime, both nonequilibrium electrons and holes control the recombination. These carriers are transported to the grain boundary from the bulk. The
point of maximum grain boundary recombination occurs in the depletion region. In this regime an electrostatic potential gradient is also developed along the grain boundary which drives the high electron current. We showed that the electron and hole density profiles decay along the grain boundary over a length scale of $L_{\text{GB}}^\text{diff}$ in this case \[8\]. This leads to the recombination which decays away from its maximum value with the same length scale, as shown in Fig. 1(c) and the 3rd column of Table 1. This ends the analysis of the donor+acceptor case.

The analysis of the donor cases proceeds along similar lines. One important wrinkle is that $f_{\text{GB}} \approx 1$ in this case (see discussion following Eq. (7)). The defect is nearly fully occupied, which implies that for the same value of $E_{\text{GB}}$, the band bending is larger in the donor case than in the donor+acceptor case. This in turn implies the grain boundary hole density is suppressed in the donor case relative to the donor+acceptor case. For this reason, the effective hole recombination velocity is given by $S_{\text{p}}^\text{eff} = (1 - f_{\text{GB}}) S_{\text{p}}$. $(1 - f_{\text{GB}})$ is small by assumption, so the hole-controlled recombination is significantly reduced in the donor defect case \[9\].

III. CONCLUSION

We end the overview here, and refer the reader to references for a fuller and more rigorous derivation of the grain boundary dark current, as well as demonstrations that the grain boundary dark current can be used to predict $V_{\text{oc}}$. The type of analysis can be extended to consider a continuum of defect states, grain boundaries with arbitrary orientation, and networks of inhomogeneous grain boundaries. With this degree of model flexibility, we can begin to consider the behavior of realistic, inhomogeneous polycrystalline materials.

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