Theoretical modeling of polycrystalline thin-film photovoltaics

Muthuthanthrige Lilani Attygalle

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A Dissertation
entitled
Theoretical modeling of polycrystalline thin-film photovoltaics

by
Muthuthanthrige Lilani C. Attygalle

Submitted as partial fulfillment of the requirements for the
Doctor of Philosophy Degree in Physics

Advisor:  Dr. V. G. Karpov

College of Graduate Studies

The University of Toledo
May 2008
An Abstract of

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This work is aimed at developing realistic theoretical models of major thin-film photovoltaics (PV) which currently are CdTe based and CuIn(Ga)Se$_2$ based materials. We emphasize the physical and technological aspects that are unique to these types of PV and are not adequately reflected in the existing modeling software. They are: (1) the presence of CdS layer whose role remained poorly understood; (2) the electrostatic screening length larger than or comparable to the device thickness; (3) high density of states in the forbidden gap conducive of efficient hopping transport. We note however that the problem of lateral nonuniformities typical of thin-film PV is left beyond the present scope to avoid too much interference with already published results on that topic.

We collected and critically analyzed many facts indicative of the physics of operations of CdS-based thin-film photovoltaic junctions, including their major types with CdTe and CIGS absorber layers. Based on these observations we proposed a realistic physical model of CdS based junctions. Our model allows for field reversal in the depleted CdS layer. It is solved analytically and numerically, and predicts a variety
of phenomena, such as the lack of carrier collection from CdS, buffer layer effects, light to dark current-voltage curve crossing, and rollover.

Furthermore, we have numerically modeled the current-voltage characteristics and quantum efficiencies of devices with different electric field profiles including the standard p-n junction case and field reversal. Our quantitative modeling shows that the CdS polarization and its related field reversal turn out to be beneficial for photovoltaic technology making it more forgiving and reliable. Our understanding points at new venues in thin-film photovoltaic technology.

As another step in exploring more realistic models of thin-film photovoltaics we have developed a theory of long-range random potential caused by charge density fluctuations in thin nonmetal structures sandwiched between two conducting electrodes. This model applies to many practical systems including not only thin film photovoltaics but also classical p-n, and Schottky junctions. The lateral screening due to conducting electrodes leads to the screening length close to the structure thickness. We have analytically calculated the random potential amplitude for practically important cases of point defects, spherical grains, and columnar grains. Implications of our findings for polycrystalline devices are discussed.

As one other realistic feature we have investigated the defect-assisted tunneling (hopping) electron transport through non-crystalline Schottky barriers and junctions. We have shown that it can be a dominant mechanism winning over the barrier activated transport. A non-trivial interplay between the transverse tunneling and lateral device resistance is found explaining some phenomena that remained poorly understood, such as lay-down current-voltage characteristics and their light- to dark-
crossovers.

The above described findings are combined to elucidate the physical properties of ultrathin photovoltaics with thickness ($\lesssim 1 \, \mu m$) smaller than both the depletion width and diffusion length, applicable to the cases of amorphous, polycrystalline, and nano-structured devices. We show that three phenomena underlie the unique physics of such systems: (1) lateral screening by conducting electrodes, (2) leakiness due to defect assisted tunneling, and (3) gigantic capacitive energy conducive to shunting breakdown. These phenomena overlooked in the classical theory of photovoltaic operations need to be taken into account in the emerging technology of ultra-thin photovoltaics.
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Chapter 1

Introduction

This chapter introduces one of the renewable energies i.e., solar energy, brief introduction to four generation of photovoltaics (PV) and mainly discuss the second generation PV or non-crystalline PV.

1.1 Solar energy

The earth receives 174 petawatts of incoming solar radiation (insolation) at the upper atmosphere at any given time. After passing through the earth’s atmosphere, approximately half the insolation is in the visible electromagnetic spectrum with the other half mostly in the infrared spectrum (a small part is ultraviolet radiation). This energy drives climate and weather and supports virtually all life on Earth.

Solar power is used synonymously with solar energy or more specifically to refer to the conversion of sunlight into electricity. This can be done either through the photovoltaic effect or by heating a transfer fluid to produce steam to run a generator.
1.2 Photovoltaics

A solar cell or photovoltaic (PV) cell is a device that converts light into electricity using the photoelectric effect. The first working solar cells were constructed by Charles Fritts in 1883. These prototype cells were made of Se (selenium) and achieved efficiencies around 1%.

The first generation of solar cells are silicon wafer-based solar cells. Eventually it would be replaced by a second generation of lower cost thin-film technology, probably also involving a different semiconductor. Historically, CdS, a:Si (amorphous silicon), CuIn_xGe_1−xSe_2, CdTe and now thin-film p:Si (polycrystalline Silicon) have been regarded as key thin-film candidates.

Nowadays photovoltaics is likely to evolve, in its most mature form, to a third generation of high-efficiency thin-film technology. By high efficiency, what is meant is energy conversion values double or triple the 15-20% range presently targeted, closer to the thermodynamic limit of 93%. These new devices include photoelectrochemical cells, Tandem cells, polymer solar cells, nanocrystal solar cells, Dye-sensitized solar cells and are still in the research phase.

A hypothetical fourth-generation of solar cells may consist of composite photovoltaic technology, in which polymers with nano particles can be mixed together to make a single multispectrum layer. Then the thin multispectrum layers can be stacked to make multispectrum solar cells more efficient and cheaper based on polymer solar cell and multijunction technology.
1.3 Second generation of Photovoltaics

Non-crystalline semiconductor based second generation PV technologies are hydrogenated amorphous thin film and polycrystalline thin-films (II-VI semiconductor based solar cells and multi-layered solar cells). They are relatively inexpensive compared to the crystalline PV and yet demonstrate surprisingly high efficiencies in the range of $\sim 10\text{-}19\%$.

They are much lighter, and use less raw materials. Polycrystalline thin-films can also typically be more forgiving of small amounts of impurities in the material compared to single-crystal devices. In addition, thin-films are typically somewhat tolerant of, and to some extent even benefit from, “imperfect” boundaries between the crystallites, whereas single-crystal devices typically demand significant consistency from one unit cell to the next. Such tolerance results in thin-films being rather amenable to large-scale production. While all thin-films share these benefits, polycrystalline thin-film products currently have the benefit of a greater stability (i.e. longer service lifetime) than some of the amorphous-silicon thin-film products.

The technology of thin-film PV has reached a degree of maturity allowing its market development [1]. However understanding of these devices remains rather poor leaving the technology to rely mostly on trial-and-error approaches. This lack of scientific support, at least partially reflects inadequacy of the concepts developed earlier for the established PV technologies (crystalline Si and $A^{II}B^V$) and blindly applied to thin-film PV.

One obvious concern here is that after more than two decades of extensive research,
some features unique to thin-film PV have become apparent that are not readily understood in the crystalline PV physics framework. Such are, for example, variations between the characteristics of nominally identical devices, extremely high sensitivity to minute surface treatments, unusual degradation kinetics, and super-additive effects of independent factors.

Conceptually, the small film thickness and non-crystalline structure seem to be the key factors underlying the observed peculiarities; these factors are naturally ignored in the framework of crystalline PV physics. However, the prevailing model of thin-film CdS-based PV has been a p-n hetero-junction with the n-type CdS layer, based on the classical crystalline device physics concepts [2]. The model parameters include layer thickness, band offsets, doping and defect concentrations, and others specified by the existing software packages, such as SCAPS [3,4] and AMPS [5].

CdS-based solar cells include CdTe- and CuIn$_{1-x}$Ga$_x$Se$_2$ (CIGS)-based devices. CdS is said to act as the window layer for the above devices. In this work we will take into account that CdS has a unique property of being a very strong, pyro- and piezo- electric. Because the grains in a polycrystalline CdS film are put under lateral compression in the device, the piezo coupling generates surface charges and the electric field opposing that of the absorber layer. The corresponding potential barrier makes CdS insulating and falling beyond the standard p-n junction operations. This understanding explains how CdS becomes important in thin-film PV.

While various methods are used today to understand and improve thin-film photovoltaic devices, many questions remain unanswered. We believe that the classical p-n junction model developed and successfully applied to describe the 1$^{st}$ generation
crystalline devices, becomes unrealistic as applied to thin-film non-crystalline PV. In this dissertation we have investigated more realistic models of photovoltaic junctions using analytical and numerical methods.

We tried to account for the following features overlooked in the exciting classical models of photovoltaics.

1) Strong pyro- and piezo- electricity of CdS grains known in many applications [6–14].

2) Random electric potential in the presence of metal electrodes.

3) Hopping transport through thin-film structures.

4) The effects of hopping transport leakiness and gigantic capacitive energy on ultra-thin-film PV.
Chapter 2

Physical model of CdS-based thin-film photovoltaic junctions

This chapter introduces a list of our collected observations published in the literature that are not easily explained by the classical p-n junction model. We propose a novel device model naturally explaining that indicative facts. The p-n junction model is also discussed and comparatively simulated using the available software.

2.1 Introduction

While the current-voltage (J-V) fitting is often considered a major test for this type of modeling, it appears not conclusive enough, even when amplified with other tests, such as QE and C-V. For example, reasonable J-V fits can be obtained with strikingly different models (Fig. 2-1), which is not surprising: the diode-type J-Vs naturally occur with any barrier dominated electron transport. Similarly, different
structures with multiple fitting parameters and more than one barrier can provide comparable J-V, C-V and QE fits.

Underlying such a “crystalline” type modeling is the tacitly assumed understanding that thin-film PV is similar to their crystalline counterparts only with worse material parameters. This suggests that improving the latter to the level of crystalline PV will constitute the technology roadmap. Overall, this understanding has not brought much success. In particular, the suggestions of better material doping and recombination suppressing have been repeatedly made, lacking not only specific ways for their implementations, but any substantial experimental evidence in the realm of thin-film PV. It is natural then to assume that simply tweaking the parameters of p-n junction model may not be sufficient and new models are needed to understand the physics of thin-film PV. We believe that a new device model can be better shaped based on a list of what we call indicative facts that all together limit the model choice and, in particular, challenge the standard p-n junction model (see, Sec. 2.2). A list of such indicative facts is attempted in Sec. 2.3

2.2 P-n junction model

As it is usually described [15], the intimate contact between n- and p-type semiconductors allows for exchange of electrons and holes until an equilibrium situation is achieved. Electrons diffuse into the p-type material, leaving behind ionized shallow donor levels, and holes diffuse into the n-type material, leaving behind ionized shallow acceptor levels. Adjacent to the p-n interface, both semiconductors deplete of free
Figure 2-1: AMPS generated light and dark J-V characteristics for two different device models: the standard p-n junction (a), and this work model (b). For the case (a) we used the device parameters suggested in Ref. [2] including the back barrier, but without the buffer layer and deep defects in CdS. For the case (b) the reversed electric field was additionally introduced by creating two heavily doped ($10^{18} cm^{-3}$) interfacial layers and decreasing the carrier concentration in CdS to $2 \times 10^{16} cm^{-3}$.

carriers and a space-charge region (SCR) is established. The diffusion process stops once the drift current established by the electric field, exactly cancels the diffusion current, and a flat Fermi level is established throughout the device.

Fig. 2-2 further illustrates the principle of a p-n junction solar cell. Incident light (e.g., from the left) generates additional electron-hole pairs in the solar cell. If the generation occurs within the SCR, both carriers are readily swept out by the electric field. The hole quickly reaches the p-type region and the electron the n-type region; once both carriers are majority carriers, they can then safely traverse the quasi-neutral region (QNR) and be collected at external electrical contacts. In case of generation outside of the SCR, either in the n- or p-type bulk material, one of the two generated carriers is a minority carrier and must traverse to the SCR before
Figure 2-2: The p-n junction model of thin-film PV. Fat arrow shows the process of photo-generation. The rightmost barrier is due to the contact between the semiconductor and the metal electrode (often called back metal).

it recombines; the success of this diffusion transport depends on the quality of the material and is often expressed in terms of a carrier lifetime or a diffusion length.

2.3 Indicative facts

Our list of indicative facts, arbitrarily ordered below, may appear redundant or lacking some other observations; it remains open and calls upon further suggestions.

(1) The pressure dependent PV attributable to the piezo parameters of CdS [16] suggests a strong electric field in the depleted CdS layer. In addition, the energetically favorable CdS electric dipole orientation requires this field be opposing the average device field dominated by the photovoltaic effect. In other words, it suggests field reversal in the CdS layer.
(2) The “reach-through” band bending in CdTe caused by a buffer layer on the other side of CdS \cite{17,18} suggests the insulating CdS layer and the metal-insulator-semiconductor nature of the device overall.

(3) Pointing at the same is that using more conductive CdS does not improve the device. Moreover, the highest quality devices were fabricated with extremely resistive CdS \cite{1}. This is contrary to the p-n model that would have a stronger p-n junction when CdS is more of n-type.

(4) Buffer layers of certain morphology (for example, sputtered) strongly increase the device open-circuit voltage $V_{oc}$, while other chemically and electrically equivalent layers (such as chemical vapor deposited) do not cause this effect \cite{17,18}. This points at interfacial morphology and possibly its related internal stress acting through the piezo-effect \cite{16}.

(5) Absence of carrier collection from CdS \cite{1} may suggest the electric field reversal in CdS relative to that in CdTe or CIGS (consistent with the above item (1)). We note however that the p-n junction model \cite{2} attributes the lack of carrier collection to the extremely high recombination rate under the assumption that CdS is strongly doped and its depletion width is much shorter than its thickness. One other point of view is that there really is the carrier collection from CdS, hence, no need in explaining the lack of it \cite{19,20}. However, the lateral understanding does not agree the experimental data \cite{1}.

(6) Pointing towards field reversal in the CdS layer could be the negative quantum efficiency, $\text{QE}<0$ under the blue illumination \cite{19,21}. However, this effect has been reliably observed only under forward bias \cite{19}. In what follows we show that field
reversal does not imply the negative QE (see Fig. 3-3).

(7) Light and dark J-V crossover pointing at CdS related photoconductivity [22], and light J-V rollover in the fourth quadrant [1].

(8) “Interactive processing” implying that the component properties and recipe steps are not additive: everything has to be reoptimized when just one of the components changes or a buffer layer is incorporated [23].

(9) Considerable fluctuations between the photovoltaic parameters of nominally identical devices, say, “sister” cells on the same substrate or “sister” modules from the belt line.

2.4 Field reversal model

The diagram in Fig. 2-3 is consistent with all of the above observations. Its unique feature is the electric field reversal and “gull wing” singularity in the conduction band implying positive interfacial charges (due to the piezo-effect or defect states, or both). Following [2] we do not assume any significant band offset between the CdS and its tangent layers; however, adding a moderate offset does not change the model predictions. Also, we do not specify the band bending curvature; the depletion widths remain arbitrary within the requirement that they are greater than the corresponding layer thicknesses. Unlike the examples in Fig. 2-1, our model neglects the back field effects (rightmost part of the diagram).

In this framework, the lack of carrier collection from CdS is due to the field reversal, and the corresponding barrier in Fig. 2-3 is consistent with the CdS depletion
Figure 2-3: Phenomenological model of CdS based thin-film PV. \( \sigma \) represents the two-dimensional electron charge density. \( J_{L1} \), \( J_{L2} \) are the component 1 and 2 photocurrents, \( J_{s1} \) and \( J_{s2} \) are the corresponding saturation currents. \( J_R \) is the recombination current.

[24](see also results of QE modeling below). Under illumination or forward bias, the electrons accumulated in the “gull wing” region will generate the electric field flattening the singularity and suppressing the barrier. Hence, the electric current increase leading to the dark and light JV crossing, qualitatively similar to the CdS photoconductivity. On the other hand, the CdS barrier will limit forward current causing \( J(V) \) flattening (rollover) in the forward bias region.

The model of Fig. 2-3 is solved analytically, next. We introduce the layer dielectric permittivities \( \epsilon_{1(2)} \) and electron potential barriers \( V_{B1(2)} \) measured from the conduction band singularity to the maximum electron energy in the layer 1(2). The barrier \( W_{1(2)} \) is measured from the contact Fermi energy to the same maximum; hence, the saturation currents \( J_{s1} = J_{s1}^0 \exp(-W_1/kT) \) and \( J_{s2} = J_{s2}^0 \exp(-W_2/kT) \). Each
component is described by the diode characteristics
\[ J_1 = J_{s1} \left( \exp \left( \frac{qV_1}{kT} \right) - 1 \right) - J_{L1} \]
and \[ J_2 = J_{s2} \left( \exp \left( \frac{qV_2}{kT} \right) - 1 \right) - J_{L2} \] with the open circuit voltages respectively [25],

\[ V_{oc1} = \frac{kT}{q} \ln \left( 1 + \frac{J_{L1}}{J_{s1}} \right) \quad (2.1) \]
\[ V_{oc2} = \frac{kT}{q} \ln \left( 1 + \frac{J_{L2}}{J_{s2}} \right) \quad (2.2) \]

The CdS barrier is relatively low, \( W_1 < W_2 \) and \( J_{s1} \gg J_{s2} \). The photocurrent ratio can be estimated as \( J_{L1}/J_{L2} \sim 0.15 \) for a thick (up to 0.2 micron) CdS and is smaller for thin CdS.

The electric current continuity requires that \( J = J_1(V_1) = J_2(V_2) + J_R \) where \( J_R \) is the recombination current, \( V_1 \) and \( V_2 \) are the electric potential differences across the layers, \( V_1 + V_2 = V \). The electric potential distribution is found from the electrostatic problem, which simplifies because the electron density is exponentially high in the proximity of “gull wing” singularity and can be approximated by a self-consistent two-dimensional charge density \( \sigma \); hence, the electric potential linear in coordinate.

In this approximation, \( J_R = \gamma \sigma \) where \( \gamma \) accounts for the interfacial defect properties. The equilibrium value \( \sigma = \sigma_0 \) remains the model parameter.

The problem is further simplified by noting that the recombination is relatively inefficient in device quality structures (say, \( J_R \sim 0.1 J_{L2} \)) and can be treated as perturbation. Namely, \( \sigma \) will be found neglecting the recombination and then substituted into \( J_R = \gamma \sigma \).
The partial currents can be written in the form

\[
J_1 = J_{s1} \left[ 1 - \frac{\sigma}{\sigma_0} \exp \left( -\frac{\Delta V_{B1}}{kT} \right) \right] + J_{L1}, \quad (2.3)
\]

\[
J_2 = -J_{s2} \left[ 1 - \frac{\sigma}{\sigma_0} \exp \left( -\frac{\Delta V_{B2}}{kT} \right) \right] - J_{L2}, \quad (2.4)
\]

The barrier change is expressed through the standard electrostatics,

\[
\Delta V_{B1} = \frac{Vl}{l_2} - \frac{4\pi \sigma q l}{\epsilon}, \quad \Delta V_{B2} = -\frac{Vl}{l_1} - \frac{4\pi \sigma q l}{\epsilon}
\]

\[
\epsilon = \frac{\epsilon_1 \epsilon_2}{\epsilon_1 + \epsilon_2}, \quad l = \frac{l_1 l_2}{l_1 + l_2}. \quad (2.5)
\]

Substituting this into \( J_1 = J_2 \) determines the electron charge density \( \sigma \),

\[
J_1 = J_{s1} \left[ 1 - \frac{\sigma}{\sigma_0} \exp \left( \frac{-Vl}{l_2 kT} + \frac{4\pi \sigma q l}{ekT} \right) \right] + J_{L1}
\]

\[
= -J_{s2} \left[ 1 - \frac{\sigma}{\sigma_0} \exp \left( \frac{Vl}{l_1 kT} + \frac{4\pi \sigma q l}{ekT} \right) \right] - J_{L2} \quad (2.6)
\]

\[
\frac{\sigma}{\sigma_0} \exp \left( \frac{\sigma l}{kT \epsilon} \right) = \frac{J_{s1} + J_{s2} + J_{L1} + J_{L2}}{J_{s2} \exp(qVl/kTl_1) + J_{s1} \exp(-qVl/kTl_2)}. \quad (2.7)
\]

Substituting Eqs. (2.5) and (2.7) into Eq. (2.3) yields the integral J-V characteristics
\[ J = J_{s1} + J_{L1} - \frac{J_{s1} + J_{s2} + J_{L1} + J_{L2}}{1 + (J_{s2}/J_{s1}) \exp(qV/kT)} - J_R \quad (2.8) \]

with \( J_R = \gamma \sigma \) and \( \sigma \) from Eq. (2.7).

### 2.5 Model Predictions

The characteristic in Eq. (2.8) is mathematically quite different from that of the standard diode leading to a number of predictions, which we list in the approximation \( J_R = 0 \) next.

The system open circuit voltage and short-circuit current are

\[ V_{oc} = V_{oc2} - V_{oc1} \quad \text{and} \quad J_{sc} = \frac{J_{L2}J_{s1} - J_{L1}J_{s2}}{J_{s1} + J_{s2}}. \quad (2.9) \]

Because \( J_{s2}/J_{s1} \ll 1 \), the lack of carrier collection from CdS is predicted \( (J_{sc} \approx J_{L2}) \).

The dark to light J-V crossing takes place at

\[ V_X = V_{oc} + \frac{kT}{q} \left[ \exp \left( -\frac{qV_{oc1}}{kT} \right) + \exp \left( -\frac{qV_{oc2}}{kT} \right) \right], \quad (2.10) \]

slightly above \( V_{oc} \), consistent with the observations. In addition, Eq. (2.8) predicts a JV rollover more profound at low temperatures, which is indeed many times observed and attributed mostly to the back contact effects [26].

The slopes \( dV/dJ \) at \( V = 0 \) and \( V = V_{oc} \) give the short-circuit (‘shunt’) and
Figure 2-4: Left: AMPS simulated (a) vs. analytical (b) J-V characteristics for the same band diagram. Right: The proximity of conduction band singularity simulated by AMPS for the forward bias of 1 V in the dark and AM 1.5 light. [The “cusp” artifact is due to the artificial doped layer]. In this modeling the back barrier effects and recombination were eliminated; hence, JV crossing and rollover are due to the CdS barrier. Nevertheless, the device parameters $V_{oc} = 0.81$ eV, $J_{sc} = 20$ mA/cm$^2$, fill factor of 72%, and efficiency 12.8% appear realistic for CdTe PV. Note that thickness of the CdS layer is 200 nm, and artificial layers thicknesses are 10 nm each.

open-circuit (‘series’) resistances

$$R_{sc} = \frac{kT}{q} \left( \frac{\sqrt{J_{s2}/J_{s1} + \sqrt{J_{s1}/J_{s2}}}}{J_{s1} + J_{s2} + J_{L1} + J_{L2}} \right)^2,$$

$$R_{oc} = \frac{kT}{q} \frac{J_{s1} + J_{s2} + J_{L1} + J_{L2}}{(J_{s1} + J_{L1})(J_{s2} + J_{L2})}.$$ 

Assuming, for example, the typical [1] $J_{L1} \sim 0.1J_{L2} \sim 2$ mA/cm$^2$ and $J_{s2} \ll J_{s1} \sim J_{L1}$ yields $R_{oc} \approx (kT)/(qJ_{L1}) \sim 10\Omega$, in the ballpark of the observed series resistances for CIGS [27] and CdTe [28] based PV (this estimate changes when the alternative inequality $J_{L1} \ll J_{s1}$ takes place). In addition, the measured resistances can be affected by factors beyond the present model, such as the back field [26] and nonuni-
formity [29]. Defect assisted tunneling (hopping) transport through the CdS barrier would also have a noticeable effect on the above predictions.

Nevertheless, Eqs. (2.8) - (2.11) call upon experimental verifications including the temperature, light intensity and spectra dependencies.

Consider briefly the recombination effects. Eq. (2.7) predicts that $\sigma$ and thus $J_R$ is a maximum at

$$V_R = \frac{kT}{q} \ln \left( \frac{J_{s1}l_1}{J_{s2}l_2} \right) \approx V_{oc} - \frac{kT}{q} \ln \left( \frac{J_{L2}l_2}{J_{L1}l_1} \right).$$

(2.13)

Assuming the typical $J_{L1}l_1/J_{L2}l_2 \sim 0.01$, one can estimate $V_R \approx V_{oc} - 0.06$ eV. For realistic $l_1/l_2 \sim 0.1$, it follows from Eq. (2.7) that $J(R)$ drops sharply when $V > V_R$, while it decreases rather slowly for $V < V_R$. In other words, the recombination has almost no effect on J-V curve when $V > V_R$, while it decreases $|J|$ almost uniformly when $V < V_R$.

2.5.1 Numerical simulations of field reversal and similar models with polarized CdS

Originally, the AMPS software does not allow for charged surface states necessary to model the CdS dipole layer. This surface charges were created artificially by attaching two very thin CdS layers strongly p- and n- doped on both sides of the original CdS layer (we are grateful to A.L. Fahrenbruch who suggested to us this technique). We used the modeling parameters listed in tables 2.1 to 2.3. (Appendix A gives an introduction to AMPS numerical simulations.)
Table 2.1: Front and Back contact properties: e/h; refers to electron/hole properties, $\Phi_b$; barrier height; ($\Phi_{bn} = E_C - E_F$, $\Phi_{bp} = E_F - E_V$), $S$; surface recombination velocity.

<table>
<thead>
<tr>
<th>Input Parameters</th>
<th>Front</th>
<th>back</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Phi_b (eV)$</td>
<td>$\Phi_{bn} = 0.1$</td>
<td>$\Phi_{bp} = 1.0$</td>
</tr>
<tr>
<td>$S_e [cm/s]$</td>
<td>10'</td>
<td>10'</td>
</tr>
<tr>
<td>$S_h [cm/s]$</td>
<td>10'</td>
<td>10'</td>
</tr>
<tr>
<td>Reflectivity $R_f[1]$</td>
<td>0.1</td>
<td>0.8</td>
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Table 2.2: Layer properties: $W$; layer width, $\varepsilon$; dielectric constant, $\mu$; mobility, n/p; electron/hole density, $E_g$; band gap energy, $N_C$ and $N_V$; effective density of states, CHI; electron affinity.

<table>
<thead>
<tr>
<th>input parameters</th>
<th>CdS$_a$</th>
<th>CdS</th>
<th>CdS$_d$</th>
<th>CdTe</th>
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<tr>
<td>$W$ [nm]</td>
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<tr>
<td>$\varepsilon/\varepsilon_0[1]$</td>
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<td>10</td>
<td>10</td>
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<tr>
<td>$\mu_e$ [cm$^2$/Vs]</td>
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<td>100</td>
<td>320</td>
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<tr>
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<td>25</td>
<td>25</td>
<td>40</td>
</tr>
<tr>
<td>n,p [cm$^{-3}$]</td>
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<td>$n : 2 \times 10^{16}$</td>
<td>$n : 1 \times 10^{18}$</td>
<td>$p : 2 \times 10^{14}$</td>
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<td>1.5</td>
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<tr>
<td>$N_C$ [cm$^{-3}$]</td>
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<td>$2.2 \times 10^{18}$</td>
<td>$2.2 \times 10^{18}$</td>
<td>$8 \times 10^{17}$</td>
</tr>
<tr>
<td>$N_V$ [cm$^{-3}$]</td>
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<td>$1.8 \times 10^{19}$</td>
<td>$1.8 \times 10^{19}$</td>
<td>$1.8 \times 10^{19}$</td>
</tr>
<tr>
<td>CHI [eV]</td>
<td>3.9</td>
<td>3.9</td>
<td>3.9</td>
<td>3.9</td>
</tr>
</tbody>
</table>

2.5.2 Artificial layers and their parameters

The device modeling software AMPS as such does not allow for the interfacial charge modeling. Therefore it does not provide a tool to model the polarization CdS charges and their effects. To carry out the required modeling the two artificial narrow layers (10 % of the actual CdS thickness) containing high concentrations of shallow

<table>
<thead>
<tr>
<th>input parameters</th>
<th>CdS$_a$</th>
<th>CdS</th>
<th>CdS$_d$</th>
<th>CdTe</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N_{DG,AG}$ [cm$^{-3}$]</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>$D : 2 \times 10^{14}$</td>
</tr>
<tr>
<td>$E_A,E_D$ [eV]</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.75</td>
</tr>
<tr>
<td>$W_G$ [eV]</td>
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<td>-</td>
<td>-</td>
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<tr>
<td>$\sigma_e$ [cm$^2$]</td>
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<td>-</td>
<td>-</td>
<td>$10^{-12}$</td>
</tr>
<tr>
<td>$\sigma_h$ [cm$^2$]</td>
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<td>-</td>
<td>-</td>
<td>$10^{-15}$</td>
</tr>
</tbody>
</table>

Table 2.3: Gaussian(mid gap) Defect States: $N_{DG(AG)}$; acceptor-like (donor-like) defect density, $E_{A(D)}$; defect peak energy, $W_G$; distribution width, $\sigma$; capture cross section and e/h refers to electron/hole properties.
Figure 2-5: Left: AMPS simulated band diagram at thermal equilibrium; $3 \times 10^{18}$ cm$^{-3}$ shallow acceptors and $1 \times 10^{18}$ cm$^{-3}$ shallow donors at TCO/CdS and CdS/CdTe interfaces introduced respectively to emulate the polarization surface charge distributions. Right: J-V characteristics for the 1 Sun illumination.

donors and acceptors were added on the opposite sides of the original CdS to model the built-in reversal electric field in CdS. More specifically, in the case of Table 2.3, we have introduced $3 \times 10^{18}$ cm$^{-3}$ shallow acceptors and $1 \times 10^{18}$ cm$^{-3}$ shallow donors at TCO/CdS and CdS/CdTe interfaces respectively to emulate the polarization surface charge distributions. However we have tried many other parameter choices, including equal donor and acceptor concentrations in the above-mentioned artificial layers, as briefly described next.

The interfacial charge densities corresponding to the latter choice are then estimated as $\rho_{int} = n(p) \times W$ where $n$ or $p$ is found in the Table 2.3. The numerical values $\rho_{int,p} = 3 \times 10^{12}$ cm$^{-2}$, and $\rho_{int,n} = 1 \times 10^{12}$ cm$^{-2}$ are in the ballpark of typical interfacial charges in electronic devices [25] corresponding to roughly 0.01 $e$ per atom in the interface.
A comment is in order regarding the above-specified choice of interfacial charge density and the corresponding electroneutrality condition. The apparent disbalance between these negative and positive interfacial charges does not indicate the electroneutrality violation, since there are additional charges in the metal sides of the structure automatically adjusted by the AMPS program to maintain the electroneutrality condition (as is guaranteed the electrostatic equations underlying the AMPS routine described in the Appendix. A). A simple way to reveal the presence of such charges through the AMPS modeling is to simulate a metal semiconductor junction where the charge in the space charge (depletion) region seems to be unbalanced and yet is electrically balanced by the invisible (not shown in AMPS) opposite sign charge in the metal.

Instead of showing here the above example, we point at several more relevant AMPS related results in Figs. 2-5, 2-6 and 2-7. In particular Fig. 2-5 shows AMPS

Figure 2-6: Left: AMPS simulated band diagram at thermal equilibrium; where the acceptor and donor concentrations in the artificial layers are chosen equal. Right: J-V characteristics for the 1 Sun illumination.
generated band diagram and IV curves corresponding to the choice in table 2.3. This should be compared with the case of Fig. 2-6 where the acceptor and donor concentrations in the artificial layers are chosen equal. It is obvious that the difference between the two cases while noticeable, is not very significant, and that changing layer parameters serves more as a tool of fine tuning the band diagram, since the first order effects are significantly mitigated by the metal side charges. Our particular choice of Table 2.3 was dictated by a slightly closer similarity with the typical experimental IV curves.

Finally, in Fig. 2-7 we show the case of oppositely charged layers in the reverse order leading to what we call the “hunch-model”, whose relevance will be explained in Chapter 3 below. Here we just point at the fact that AMPS modeling with artificial strongly doped layers allows for simulating CdS dipole layer of both polarities and their corresponding device characteristics.

In the spirit of this model, we did not include the buffer layer, back field, and any recombination centers. Also the band offsets between layers are set to zero. Other parameters are chosen according to Refs. [2,15].

2.5.3 Results

The J-V and QE results for the field reversal model are shown in Fig. 3-3 and table 2.4. The higher band-gap in CdTe solar cells allows for higher open-circuit voltage, but also results in lower current compared to CIGS solar cells. Both quantum efficiency curves show some losses due to CdS absorption in the low wavelength region, $\lambda < 520$
Figure 2-7: Left: AMPS simulated band diagram at thermal equilibrium; where
the acceptor and donor concentrations in the artificial layers are chosen equal and
oppositely charged in the reverse order. Right: J-V characteristics for the 1 Sun
illumination.

nm. CdTe solar cells with their low doping and, hence, wide space-charge region
achieve generally better collection than CIGS devices [15].

<table>
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<th>Performance parameters</th>
<th>J&lt;sub&gt;sc&lt;/sub&gt; [mA/cm&lt;sup&gt;2&lt;/sup&gt;]</th>
<th>V&lt;sub&gt;oc&lt;/sub&gt; [V]</th>
<th>η (%)</th>
<th>FF (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>standard p-n junction model</td>
<td>21.37</td>
<td>0.87</td>
<td>14.78</td>
<td>75.6</td>
</tr>
<tr>
<td>field reversal model</td>
<td>20.48</td>
<td>0.86</td>
<td>12.48</td>
<td>71.0</td>
</tr>
<tr>
<td>“hunch” model</td>
<td>4.39</td>
<td>1.09</td>
<td>3.06</td>
<td>64.0</td>
</tr>
</tbody>
</table>

Table 2.4: Performance parameters of three models: J<sub>sc</sub>; short circuit current, V<sub>oc</sub>; open circuit voltage, η; efficiency and FF; fill factor.

2.6 Correspondence to the indicative facts

Following the list of facts in Sec. 2.3, we point here how they are consistent with
our model.

(1) Field reversal is a direct consequence of pyro-(piezo-) dipole orientation in a
PV device.
(2) Reach-through band bending is a direct result of the CdS layer depletion in the field reversal model.

(3) Again, the CdS depletion is consistent with our model.

(4) The role of buffers and surface morphology is explained as a precursor for the mechanical stress responsible for the CdS piezo-effect and the field reversal.

(5) The lack of carrier collection from CdS \( (J_{sc} \approx J_{L2}) \) is predicted by Eq. (2.8) with \( J_{s2}/J_{s1} \ll 1 \).

(6) See the QE modeling in Fig. 3-3 below.

(7) The nature of the light to dark curve crossing is illustrated by numerically simulated CdS barrier decrease under illumination in Fig. 2-4. The rollover appears a natural consequence of CdS barrier, although the back barrier in CdTe (beyond this model) can give a strong contribution to this effect [26].

(8) See items (2)-(4) in the above.

(9) Noncrystalline thin structures exhibit considerable random micro-nonuniformities strongly affecting the device performance across the distances greater than 1 cm and not self-averaging over the structure small thickness [30]. This and related issues go beyond the scope of the present junction model and need to be discussed separately.

In addition to the above, we have examined the approximation of two diodes in series underlying Eq. (2.8) (see Appendix B). The criterion of its applicability is that the thermalization time in the proximity of gull wing singularity is shorter than the electron lifetime; the latter dominated by activation above the CdS barrier. This criterion can be shown to result in the inequality \( V_B > E_F \) between the CdS barrier height and the distance between the Fermi level and the energy of “gull wing” singu-
larity. The latter can obey for realistic parameters, such as $V_B \sim 0.3 \text{ eV}$ and $E_F \sim (0.1-0.2) \text{ eV}$. Also, we have developed an alternative approach, based on the diffusion approximation (see Appendix B) showing that Eq. (2.8) remains approximately valid even beyond the range of $V_B > E_F$.

2.7 Conclusions

In conclusion, we have proposed a physical model that explains a variety of facts for CdS based photovoltaics. This model is solved analytically. The predicted properties differ considerably from that of the standard p-n junction and call upon further experimental verifications.

We verified our findings with numerical AMPS simulations. Two artificial narrow layers (10% of CdS thickness) containing high concentrations ($10^{18} \text{ cm}^{-3}$) of shallow donors and acceptors were added on the opposite sides of the original CdS to model the built-in reversal electric field in CdS. In the spirit of this model, we did not include the buffer layer, back field, and any recombination centers. As is seen from Fig. 2-4, the analytical and numerically simulated curves are reasonably close. The observed deviations appear legitimate, since our analytical result does not account for the carrier diffusion.

Overall, our model emphasizes interfacial properties, such as the interfacial morphology, related compression, and charges. In the terms of practical implications, they can be altered by tuning the deposition regimes, creating doping-induced stresses, and applying proper interfacial treatments (layers).
Chapter 3

Modeling of piezo-photovoltaic coupling effects on thin-film device performances

Piezo- and pyro-electricity in CdS based photovoltaics includes CdTe and CuIn(Ga)Se$_2$ based devices. The strong pyro- and piezo-effects in CdS significantly affect the electric field distribution and the physics of device operations [14]. Our quantitative modeling shows that the CdS polarization turns out to be beneficial for photovoltaic technology making it more forgiving and reliable.

3.1 Piezo-PV effect

Two major types of polycrystalline thin-film photovoltaics (PV) based on CdTe and CuIn(Ga)Se$_2$ (CIGS) absorbers include a thin CdS layer, [1] which empirically
appears important, even though understanding of its role remains rather poor. One hypothesis regarding the underlying physics of CdS layer is based on the recently observed pressure dependence of PV parameters in the above types of PV \[31–33\]. This observation was attributed to the strong piezo-effect in the hexagonal (wurtzite) phase of CdS well-known in many applications, yet overlooked in the PV community.

In addition, the hexagonal CdS crystalline structure exhibits a rather strong pyroelectric effect \[34\]. As it always takes place with the pyroelectrics, the spontaneous surface charges are related to the chemically different interfaces \[35\]. In the case of CdS, such are the Cd terminated (electrically more positive) and the S terminated (more negative) interfaces. The pyroelectricity can be significantly suppressed in CdS thin films due to the substrate clamping (constant strain or “clamped” boundary condition). Such a suppression makes the pyroelectric effects seemingly piezoelectric in origin \[36\].

Strong piezo- and pyro-effects present in both CdS crystals \[37\] and polycrystalline thin films \[36,38\] could be an important factor, since the CdS layer is naturally put in device under compression. Through the piezo-effect, the compression can translate into the dipole layer type of electrical polarization and considerable static voltage across the CdS film affecting the device operations.

One particular consequence of the above mentioned CdS polarization is that the “mainstream” understanding of CdS based PV as p-n junction ceases to apply. Instead, the electric potential distribution across the semiconductor junction can become non-monotonic with field reversal in the CdS region as discussed in the previous chapter. The physics of this field reversal is that dipoles of electrically polarized CdS
Figure 3-1: Conceivable band diagrams of CdS based PV. (a) p-n structure with n-type CdS and p-type absorber. (b) A “gull wing” potential shape structure; (+) and (-) mark the polarization charges. (c) The “hunch” model where electric field in CdS region allows for carrier collection. Dot-dashed lines show the Fermi level. For simplicity, the conduction band offset between the CdS and absorber is set to zero. The energy scale is for illustration only; a numerically simulated band diagram is shown in Fig. 2-4.

grains tend to align against the photovoltaic electric field to minimize the electrostatic energy $-\vec{P} \cdot \vec{E}$, where $\vec{P}$ is the polarization due to dipoles and $\vec{E}$ is the photovoltaic electric field (described in detail on Ref [39]).

### 3.2 Device operations and modeling

This section discusses the effects of CdS electric polarization on device operation. We consider the polarization of both signs (i.e. leading to the above described “sea-gull” shaped potential and the opposite one) in comparison with the “reference” (traditional) device structure that does not have a dipole layer. Correspondingly, we will consider the three device band diagrams in Fig. 3-1, two of which contain the dipole layers of opposing polarities representing the CdS region. More specifically we
will answer a question of how the major photovoltaic parameters, efficiency, open-circuit voltage ($V_{oc}$), short-circuit current ($J_{sc}$), and fill factor (FF) depend on the absolute value and sign of the electric field in the CdS region.

Our analysis here is significantly based on the AMPS modeling [5] of the structure composed of the following layers: (1) TCO (transparent conductive oxide) playing the role of a metal contact; (2) slightly n-type CdS window layer (thickness 100 nm, donor concentration $2 \times 10^{16}$ cm$^{-3}$); (3) two artificial very thin CdS layers (10 nm) tangent to both sides of the layer (2) strongly doped with donors and acceptors and aimed at mimicking the electric polarization charges; [40] (4) p-CdTe absorber with acceptor concentration of $2 \times 10^{14}$ cm$^{-3}$. To simplify the picture we did not include the deep recombination defects in CdS layers; all other parameters of our AMPS modelling including the back barrier followed that of Ref. [2]. However, we have verified that adding the recombination centers suggested in Ref. [2] has a rather insignificant effect (of several relative percent) on the simulated parameters of models (b) and (c), unlike their known strong effect on the “standard” p-n junction structure (a).

Fig. 3-1 (a) represents the “main-stream” model of p-n type device with rather insignificant electric field in the CdS region that does not contain the strongly doped artificial very thin CdS layers tangent to both sides of the layer (2) [2]. This model (whose parameters here are not fine-tuned) is aimed at representing a reference point convenient for comparison with the dipole layer models.

The “gull-wing” model of Fig. 3-1, (b) describes a number of experimental facts, [21] such as the lack of carrier collection from CdS [1, 41] due to the field reversal according to this model (see chapter 2 in the above). The corresponding
barrier in Fig. 3-1, (b) is consistent with the CdS depletion and was independently suggested earlier based on a different argument [24]. Another feature of that model is that under illumination, the electrons accumulated in the “gull wing” region will generate an electric field suppressing the barrier. Hence, the electric current increases leading to the dark and light JV crossing, qualitatively consistent with the CdS photoconductivity [42–44]. On the other hand, the CdS barrier will limit forward current causing J(V) flattening (rollover) in the forward bias region. Characteristic of this model is the CdS polarization enhancing the electric field in the absorber layer thus improving the carrier collection and \( V_{oc} \) [14]. One consequence of such an electric field amplification is that the absorber layer inverts its conduction type close to the singularity (see Figs. 2-3, 2-4); for example, the p-type CdTe becomes n-type in the proximity of the CdS layer. The hypothesis of CdTe inverting its conduction type has been put forward earlier on different grounds [24,45].

The case of the opposite CdS polarity and negative fields in Fig. 3-1 (c) also has a strong effect on the electric field in the absorber. The underlying physics is that it creates the potential barrier for the electrons thus blocking the current from the absorber. On the other hand, this polarization allows for the collection of carriers generated in the CdS region (by high energy photons with wavelengths \( \lambda < 520 \) nm).

One important physical limitation to AMPS modeling for the band diagram (c) is that it does not account for the defect assisted tunneling (hopping) through the CdS. The latter becomes important when the electric field strength grows above certain value, such that the top of the valence band in the leftmost CdTe region approaches the Fermi level. This results in a very high concentration of holes giving rise to
Figure 3-2: Band diagram of CdS based device corresponding to the case of “hunch model” with strong enough polarization of CdS layer. Note the high concentration of holes giving rise to the hopping current between TCO and CdTe layer; due to the high electric field in CdS, the top of the valence band of CdTe approaches Fermi level.

Because the latter is directed against the photocurrent, it shunts the device open-circuit voltage. This phenomenon is included here through an artificial cutoff in the AMPS modeled $V_{oc}$ in the region of negative fields in Fig. 3-4.

The results of AMPS modelling of current-voltage characteristics and quantum efficiencies (Fig. 3-3) show a qualitative similarity between the standard p-n and gull wing models. An important difference is that the p-n model here allows for the carrier collection from CdS. To suppress the latter feature the existing more refined p-n junction models assume a very high concentration of recombination centers in CdS region in order to suppress the corresponding carrier collection never observed
Figure 3-3: AMPS generated light $J-V$ characteristics and quantum efficiencies (QE) for three different device models at 1 Sun: the standard p-n junction (a), gull wing potential (b), and the opposing field model (c).

experimentally [2,41]. We note that the curve (c) in Fig. 3-3 represents the current generated in the CdS region and does not show contribution from the CdTe layer. The quantum efficiency (QE) curves further confirm the above interpretation: lack of carrier collection from CdS in the gull-wing model, and lack of the carrier collection from the CdTe region in the “hunch” model of Fig. 3-1 (c).

The results of the above described modeling for the major PV parameters are summarized in Fig. 3-4 for a wide range of the CdS electric field strengths; here the positive and the negative field regions correspond respectively to the models (b) and (c) of Fig. 3-1. Shown in dashed line is the above mentioned cut-off of the AMPS predicted $V_{oc}$ aimed at accounting for hopping current through the CdS.

The negative field region has a significant part where the major PV parameters strongly decrease with the field strength. In particular, shown in solid lines $J_{sc}$ and efficiency strongly decrease due to the barrier blocking of the electron current in
Figure 3-4: Open circuit voltage ($V_{oc}$), short circuit current ($J_{sc}$), fill factor (FF), and efficiency (Eff) vs electric field strength $E$. The dashed branch of the $V_{oc}$ curve corresponds the shunting current cutoff beyond the AMPS modeling capabilities.

the “hunch” model of Fig. 3-1 (c); this decrease is predicted in the framework of AMPS modeling. Furthermore, taking into account the $V_{oc}$ cut-off effect (beyond AMPS modeling capabilities) will additionally worsen the efficiency. We note certain increase in PV efficiency in the narrow negative field region, to the left of field reversal line. However, the following quite an abrupt decrease makes the negative field domain less attractive because of PV parameter vulnerability to possible process fluctuations leading to the low performance region.

From the technological perspective, the range of positive fields (“gull-wing” region) in Fig. 3-4 is more forgiving, since the PV parameters there are relatively independent of the CdS field strength. Moreover, the device efficiency in that region is likely to be better than the AMPS predicted values due to the current leakage through the CdS barrier.
Figure 3-5: Towards the effect of CdS leakiness on the integral device $V_{oc} = V_{oc1} - V_{oc2}$. The three current voltage characteristics correspond to (1) CdS region when it is non-leaky, (2) absorber region, and (3) CdS region assuming significant leakiness and correspondingly low open-circuit voltage $V_{oc1}$.

We substantiate the latter prediction starting with the fact that AMPS generated $V_{oc}$ data in Fig. 3-4 remain relatively insensitive to the CdS electric field in the “gull-wing” region. This can be physically understood by approximating $V_{oc} = V_{oc2} - V_{oc1}$ where $V_{oc2}$ and $V_{oc1}$ are the contributions from the absorber and the CdS layers [21] represented by the two opposing diodes in series (Fig. 3-5). It follows then that increasing the electric field in CdS will increase both $V_{oc1}$ and $V_{oc2}$, leaving their difference $V_{oc}$ almost intact. However, allowing ceratin leakiness through the CdS will decrease $V_{oc1}$ without much effect on $V_{oc2}$ as illustrated in Fig. 3-5. Therefore the leaky (possibly nano-structured) CdS is conducive to the higher device $V_{oc}$.

In the limiting case of a very significant CdS leakiness ($V_{oc1} \ll V_{oc2}$ in Fig. 3-5), the slope of $V_{oc}$ vs. electric field strength $E$ in Fig. 3-4 should change its sign from the
negative (as presented) to positive. Its absolute value can be estimated (see Ref. [14]) as

$$\frac{dV_{oc}}{d\varepsilon} = l_1.$$

(3.1)

where $l_1$ is the CdS film thickness.

The latter translates into the experimentally verifiable stress dependence

$$\frac{dV_{oc}}{dT_j} = \frac{d_{3j}}{C_0},$$

(3.2)

where $d_{3j}$ is the piezoelectric tensor relating to the polarization $P$ to the stress $T_j$ and $C_0$ is the layer capacitance per unit area. We conclude that dipole layers have a strong effect on device operations and further broaden the scope of parameters in thin-film PV technologies. A region of not very large positive CdS fields appears most attractive technologically. This field region likely corresponds to the case of equilibrium polarization discussed in Ref. [14]. However, because the PV parameters are not very sensitive to the polarization strength in the “gull-wing” shaped potential region, the performance difference between the frozen-in and the equilibrium polarization cases (their preferential orientation can be achieved either in the course of film deposition (frozen polarization) or as a result of high-temperature treatments (equilibrium polarization) [14]) may be relatively insignificant.

### 3.3 Conclusions

In conclusion, the following points of our work seem to be most significant.
(1) The polarized CdS film can create either the gull-wing shaped electric potential distribution with field reversal in the CdS region or the opposite “hunch” type distribution.

(2) The gull-wing shaped electric potential distribution is generally beneficial for PV parameters making the technology rather forgiving with respect to variations in device and material parameters. In simple words this can be understood as the role of CdS barrier, which is so significant that defects and other more standard “spoilers” can be neglected compared to it.

(3) Our conclusions are generally consistent with the facts that (a) CdS is important, and (b) that various deposition and treatment technologies in CdTe and CuIn(Ga)Se$_2$ technologies lead to the devices of comparable efficiencies. We consider the latter as a consequence of only minor role of defects and imperfections for the case when the device operations are field reversal driven.
Chapter 4

Long-range random potential in thin-film structures

Here we develop a theory of long-range random potential caused by charge density fluctuations in thin nonmetal structures sandwiched between two conducting electrodes. This model applies to many practical systems including thin film photovoltaics and classical p-n, and Schottky junctions. The lateral screening due to the conducting electrodes leads to the screening length close to the structure thickness. We have analytically calculated the random potential amplitude for three practically important cases: point charged defects, spherical grains, and columnar grains. Implications of our findings for polycrystalline devices are discussed.

It is well known that statistical fluctuations in semiconductor charge density can create the long-range random electric potential on a space scale much greater than the characteristic distance between individual charges. The parameters of such fluctuations are determined by the screening length $l$. For example, the random potential
Figure 4-1: Top view and side view of real grain structures in thin-film PV: (a) SEM image of the CdTe surface of a polycrystalline CdS/CdTe cell (grains) [46]; (b) SEM microphoto of a CdTe layer Grown at 60°C substrate temperature, individual well defined columns are 50 Å diameter [47].

amplitude is estimated as [48]

\[ \delta \phi = \frac{e \delta N}{\epsilon l} \]  \hspace{1cm} (4.1)

where \( e \) is the elemental charge, \( \epsilon \) is the dielectric permittivity and \( \delta N \) is the fluctuation in the number of impurity (defect) charges in the region of linear dimension \( l \).

The typical theoretical analysis [49–51] describes random electric potential in infinite three-dimensional systems, hence, assuming large geometrical sizes \( L \gg l \). However many thin-film structures operate under the opposite condition \( L \ll l \), which we consider next.

More specifically, we consider a thin film semiconductor structure sandwiched between two metal electrodes. The semiconductor contains localized electric charges of impurities, grain boundary defects, etc. typical of thin film devices. The inequality
Figure 4-2: Side and top views of electric charge distributions in thin-film PV: (a) point charge distribution due to doping impurities or defects, mostly in amorphous materials; (b) surface charges at the interfaces of three-dimensional nano-particles (grains); (c) charges at the interfaces of columnar grains. Grey stripes in the top diagram represent metal electrodes.

$L \ll l$ means that the film behaves as a dielectric, i.e. it does not screen the electric field even though its forming material is semiconducting when bulk.

In such systems, the variations in charge density will create the random electric potential that is not limited by the film screening length $l$. Instead, the charge carriers in conducting electrodes will redistribute to maintain the electrode equipotentiality and thus provide the electrostatic screening. In what follows we discuss the questions of what is the corresponding screening length and the amplitude of random potential, and what are possible implications of such a random potential.

### 4.1 Systems and Parameters

Consider some systems of practical interest, in which the electrode screening can be significant. Thin film photovoltaic structures present one class of such sys-
tems including the major technologies based on a-Si:H, polycrystalline CdTe, and Cu(In,Ga)Se$_2$ [1]. Their related charge distributions are illustrated schematically in Fig. 4-2.

Many a-Si:H structures are of the p-i-n type (Fig. 4-3 (a)) with the intrinsic (i) component in between the strongly doped p- and n- layers. In the present framework, the charges in the i- layer generate the random potential, while p- and n- layers (in combination with their tangent metal electrodes) are responsible for screening. The typical i- layer has a thickness $L \sim 0.1 - 0.3 \mu m$, and mutually compensated charged point defect concentration $n \sim 10^{16} - 10^{18} \text{cm}^{-3}$ (see Ref. [52]).

The polycrystalline CdTe and Cu(In,Ga)Se$_2$ photovoltaic device thickness is in the range of 1-3 $\mu m$, which however has a trend to reduction in the future technologies [29, 53]. Their screening lengths (commonly referred to as the depletion widths) depend on the doping concentration and can be larger than device thickness [53,54].

It is believed that defect charges in polycrystalline films reside mostly on the grain boundaries, which grains have either roundish [55,56] or columnar [57,58] shape, as illustrated in Fig. 4-2. The existing technologies can make such systems with the average grain size $\langle R \rangle$ in any desirable range below or above the device thickness $L$; $\alpha \equiv \langle R \rangle/L$ of the order of several tenths with the relative dispersion $\delta R/\langle R \rangle \lesssim 1$ seems to be the most typical of the published data [1,55–58]. The grain boundary defect states are characterized by surface concentration ranging from $10^{10}$ cm$^{-2}$ to $10^{12}$ cm$^{-2}$ typical of interfacial charge density in semiconductor structures [59–61].

The classical p-n junction (Fig. 4-3 (b)) turns out to be another object falling into the class of systems with significant electrode screening. Indeed, the screening
Figure 4-3: Band diagrams of some structures with “electrode” screening: (a) p-i-n diagram of a-Si:H devices; (b) p-n junction with depletion width $L$, (c) Schottky barrier with depletion width $L$. Dashed lines show the ideal band diagrams without long-range random potential. Dash-dot lines represent the Fermi energies. The energy variations in transverse ($z$) direction are shown; the corresponding lateral variations of random potential are sketched in Fig. 4-4 below.

is absent in its depleted region, which in our present terminology is tantamount to $l > L$. That region is sandwiched between the p- and n- quasi-neutral regions where the screening lengths are relatively short, and which therefore play the role of metal electrodes.

Similarly, the Schottky barrier (Fig. 4-3 (c)) is yet another classical object with a depletion region sandwiched in between two conductive (“electrode”) layers, which determine its random potential screening and amplitude.

In what follows we consider three different cases covering the variety of systems. The first is statistical fluctuations in point charge concentration, $n = \langle n \rangle + \delta n$ where $\langle n \rangle$ is the average concentration, and fluctuations are spatially uncorrelated, obeying
the Gaussian statistics,

\[ \langle \delta n(r)\delta n(r') \rangle = \langle n \rangle \delta(r - r') \quad (4.2) \]

where \( r \) and \( r' \) are radius-vectors and \( \delta(r) \) is the delta-function. We will apply this description to the cases of Fig. 4-2 corresponding to the point charges (a) and roundish grains (b). In the latter case the delta function representation applies to the accuracy of \( \alpha^3 \ll 1 \).

The second is the case (c) in Fig. 4-2, which can be formally described by Eq. (4.2) where \( n \) stands for the \textit{two-dimensional} concentration of columnar grains, i.e. the number of columns per unit area of the film. Correspondingly, \( r \) should be replaced by the two-dimensional cylindrical coordinate radius-vector \( \rho \) parallel to the film plane, and \( \delta(\rho) \) becomes the two-dimensional delta-function. Similarly, this case could proceed from the elemental linear charges forming grain boundaries; the latter representation can be more relevant when the interfacial charge density rather than the total grain boundary charge is the physically defined quantity.

The third case of very large columnar grains whose radii are far greater than the film thickness, \( \langle R \rangle \gg L \), requires a separate consideration. We shall see that the latter inequality makes the grain boundary perturbation localized in it closest proximity \( \sim L \), which suppresses the random potential effects.

We note that our consideration below is limited to the assumption of identical electrodes, which remains a good approximation in all cases where the screening length in the electrode material is much shorter than thickness \( L \). Also, it is limited to the case of not too strong electric potential fluctuations that do not significantly
change the number of electrons in the film.

### 4.2 Qualitative considerations

The physics of electrode screening can be qualitatively understood based on the image charge concept. Strictly speaking, the applicability of the latter is limited to the case of one electrode. Indeed, for two parallel electrodes, the image charge created in one of them induces the second image in the other, which, in turn, will generate the third image in the former one, etc.

While not applicable quantitatively, the image charge concept still gives a clear qualitative picture for the case of two electrodes, based on a simple observation that a bare point charge between the plates will create substantial electrode polarization, i.e., image charges, in a region of characteristic lateral dimension $L$, same as device thickness, along the electrodes. Because the original and image charges effectively neutralize each other, they induce a potential decaying faster than that of a dipole. This is tantamount to the screening (correlation) length of the order of $L$.

The latter observation means, in particular, that statistical fluctuations in semiconductor charge density will generate a random potential (Fig. 4-4) of correlation length $\sim L$. Its amplitude $\delta \phi$ can be estimated in the “$\sqrt{N}$-approximation” corresponding to the correlation function in Eq. (4.2). If $N \gg 1$ is the average number of particles of electric charge $q$ each in the correlation volume $L^3$, then the typical
Figure 4-4: Sketch of the random potential fluctuations in arbitrary lateral direction for the cases of point charges (top), roundish or columnar grains of radius $R$ smaller than the film thickness $L$ (middle), individual columnar grains of large linear size $R \gg L$ (bottom); not to scale.

fluctuation in that number is $\delta N = \sqrt{N}$, and

$$
\delta \phi = \frac{q \delta N}{\epsilon L} = \frac{Q}{L \epsilon} \frac{1}{\sqrt{N}} = \frac{\phi}{\sqrt{N}}
$$

(4.3)

here $Q = qN$ is the integral charge in the correlation volume $L^3$.

Given the charge $Q$, Eq. (4.3) predicts $\delta \phi$ to decrease with $N$. In particular, $\delta \phi \ll \phi$ when $Q$ is uniformly dispersed over $N \sim nL^3 \gg 1$ point defects [Fig. 4-2 (a)]. However, the distributions (b) and (c) characterized by not very large $N \lesssim 10$ can generate rather substantial random potentials $\delta \phi \lesssim \phi$.

For the case of a columnar grain radius exceeding $L$, its grain boundary potential is about $q/\epsilon L$. Given the same grain boundary charge $q$, this potential is by the factor
of $\sqrt{N}$ weaker than the above estimated $\delta \phi \sim \sqrt{Nq/\varepsilon L}$ for the case of $N \gg 1$ grains of lateral dimension $\sim L/N$ each (Fig. 4-4).

We shall end this section by noting that the above random potential estimates are limited to the inner dielectric region, i.e. inner proximity of a semiconductor structure. Indeed, since the metal electrodes are equipotential, the random potential component must disappear in the electrode planes.

4.3 Quantitative Analysis

We start with a known solution [62] for the electric potential induced by a point charge $q$ at point $z = z_0$ on the $z$-axis between two infinite parallel grounded conducting planes at $z = 0$ and $z = L$ (see Fig. 4-5),

$$
\phi = \frac{4q}{\varepsilon L} \sum_{n=1}^{\infty} \sin \left( \frac{n\pi z_0}{L} \right) \sin \left( \frac{n\pi z}{L} \right) K_0 \left( \frac{n\pi \rho}{L} \right) \tag{4.4}
$$

where $\rho$ is the radial coordinate and $K_0$ is a modified Bessel function (see Ref. [62], p. 141; note however that here we use Gaussian units). This equation can be used to calculate the amplitude of random potential due to point charges. Because $K_0(x) \propto \exp(-x)$ for $x \gg 1$ we observe that the screening radius of a bare point charge between to metal planes is of the order on $L$, in agreement with our qualitative analysis in Sec. 4.2. Also, the sine function guarantees that there are no potential variations in the metal planes at $z = 0$ and $z = L$.

A comment is in order regarding the above-mentioned condition of both electrodes being grounded. It originates from Ref. [62] and can be removed when the material
between the electrodes does not contribute to the electrostatic screening as assumed in this work. In particular, an external bias $U$ will not change the lateral distribution of electrons, hence linearly combining with the electric potential in Eq. (4.4), adding a trivial term $Uz/L$ to it’s right-hand-side. The latter term will have no effect on the electric potential fluctuations calculated next and can be omitted.

For the case of columnar grains, it is natural to start with the potential of a linear charge perpendicular to the electrodes, which can be readily obtained from Eq. (4.4),

$$\phi_L = \frac{8q}{\pi L \epsilon} \sum_{n=1}^{\infty} \frac{1}{n} \sin \left( \frac{n\pi z}{L} \right) K_0 \left( \frac{n\pi \rho}{L} \right)$$

where $q$ is now the integral linear charge and where summation includes odd numbers only (details are given in the Appendix C.2).

The electric potential by many charges can be represented as a sum of its average and fluctuation components,

$$\phi = \langle \phi \rangle + \delta \phi.$$
The random potential amplitude in a plane $z$ is defined as

$$\overline{\delta \phi}(z) = \sqrt{\langle (\delta \phi(z))^2 \rangle} \tag{4.7}$$

where the coordinate $z$ of the plane is arbitrary ($0 < z < L$), but fixed. The required averages are calculated along the standard lines [49]. For the case of point random charges one gets

$$\langle (\delta \phi)^2 \rangle = q^2 \int \int d\mathbf{r} d\mathbf{r}' \langle \delta n(\mathbf{r}) \delta n(\mathbf{r}') \rangle f(\mathbf{r}) f(\mathbf{r}')$$

$$= q^2 \langle n \rangle \int dr [f(r)]^2 \tag{4.8}$$

with the correlation function from Eq. (4.2) where the radius vector $\mathbf{r} = (z_0, \rho)$. The case of linear random charges is treated similarly with $f \rightarrow f_L$ and $\mathbf{r} \rightarrow \rho$.

The subsequent calculations are straightforward with all the integrals containing the Bessel functions tabulated [63]. For the case of point charges the final result takes the form

$$\overline{\delta \phi}(z) = \frac{4q}{\pi \epsilon} \sqrt{\langle n \rangle L} \left[ \sum_{n=1}^{\infty} \frac{\sin^2 (n \pi z/L)}{n^2} \right]^{1/2}. \tag{4.9}$$

Approximating the sum by the two leading terms (to the accuracy better than 10%) gives

$$\overline{\delta \phi}(z) = \frac{4q}{\pi \epsilon} \sqrt{\langle n \rangle L} \sin \left( \frac{\pi z}{L} \right) \left[ 1 + \cos^2 \left( \frac{\pi z}{L} \right) \right]^{1/2} \tag{4.10}$$

For the case of random linear charges corresponding to columnar structure, our cal-
Calculations yield

\[
\delta\phi(z) = \sqrt{\langle n \rangle} \frac{8q}{\sqrt{\pi^3\epsilon}} \left[ \sum_{n=1}^{\infty} \frac{\sin^2 \left( \frac{n\pi z}{L} \right)}{n^4} \right]^{1/2} \\
\approx \sqrt{\langle n \rangle} \frac{8q}{\sqrt{\pi^3\epsilon}} \sin \left( \frac{\pi z}{L} \right)
\]

(4.11)

where the latter approximation has the accuracy of better than 10%. Here \( q \) and \( \langle n \rangle \) are the average columnar grain charge and concentration respectively.

We now turn to the case (3) of very large columnar grains \( \langle R \rangle \gg L \). In accordance with the latter inequality the grain boundary regions farther than \( L \) apart do not interact. They are mutually independent and behave as infinite flat stripes of charge perpendicular to the electrodes. The electric potential generated by such a stripe will depend on the coordinate \( z \) perpendicular to the electrodes and on the distance \( x \) from the stripe (see Fig. 4-6).

We calculated the potential of a charged stripe as a superposition of contributions from its forming elemental linear charges described by Eq. (4.5), in which \( q \) is replaced with \( dq = L\sigma dy \) where \( \sigma \) is the surface charge density and \( dy \) is the elemental width in the \( y \) direction perpendicular to \( x \) and \( z \).

The potential due to one column grain,

\[
\phi_P = \frac{8q}{\pi\epsilon L} \sum_{n=1}^{\infty} \frac{1}{n} \sin \left( \frac{n\pi z}{L} \right) K_0 \left( \frac{n\pi \rho}{L} \right)
\]

(4.12)
Figure 4-6: Nonmonotonic electric potential of a charged standalone grain boundary with a fixed surface charge density numerically calculated from Eq. (4.19).

By substituting $q/L = \lambda = \sigma x \frac{d\alpha}{\cos^2 \alpha}$ and integrates over the $\alpha$ we get,

$$\phi_{strip} = \frac{8 \sigma x}{\pi \epsilon} \sum_{n=1}^{\infty} \frac{1}{n} \sin \left( \frac{n \pi \rho}{L} \right) \int_{\pi/2}^{\pi/2} \frac{d\alpha}{\cos^2 \alpha} K_0 \left( \frac{n \pi \rho}{L} \right)$$  \hspace{1cm} (4.13)

Let’s introduce a new variable $y = \frac{A}{\cos \alpha}$, here $A = n \pi x / L$.

$$\cos \alpha = \frac{A}{y}$$ \hspace{1cm} (4.14)

$$d\alpha = \frac{Ady}{y^2 \sqrt{1 - \frac{A^2}{y^2}}}$$ \hspace{1cm} (4.15)

By substituting back into Eq. (4.13),
\[ \phi_{\text{strip}} = \frac{8\sigma x}{\pi\epsilon} \sum_{n=1}^{\infty} \frac{1}{n} \sin \left( \frac{n\pi z}{L} \right) \frac{1}{A} \int_{A}^{\infty} \frac{ydy}{\sqrt{y^2 - A^2}} K_0(y) \tag{4.16} \]

To find out the integral we have again defined \( y^2 = A^2X \), then by using standard integral tables,

\[ \frac{1}{A} \int_{A}^{\infty} \frac{ydy}{\sqrt{y^2 - A^2}} K_0(y) = \frac{1}{2} \int_{1}^{\infty} dX (X - 1)^{-\frac{1}{2}} K_0 (A\sqrt{x}) \]

\[ = \frac{\pi}{2A} \exp(A) \tag{4.17} \]

\[ = \frac{\pi}{2A} \exp(A) \tag{4.18} \]

Finally by substituting above result on Eq. (4.16), the potential due to a thin sheet of charge, i.e. a stand-alone grain boundary is

\[ \phi_{\text{strip}} = \frac{4\sigma L}{\pi\epsilon} \sum_{n=1}^{\infty} \frac{1}{n^2} \sin \left( \frac{n\pi z}{L} \right) \exp \left( -\frac{n\pi x}{L} \right) \tag{4.19} \]

It is illustrated in Fig. 4-6.

We conclude that a stand-alone grain boundary creates the electric potential that at small distances is linear in coordinate, is screened at a distance of the order of film thickness \( L \), and has the amplitude \( \sim \sigma L/\epsilon \) comparable to that of a charged plane at distance \( \sim L \). These conclusions are fully consistent with the qualitative estimates in Sec. 4.2 above.
4.4 Numerical Estimates and Implications

For numerical estimates we assume certain realistic values, such as the film thickness of $1 \, \mu m$, the point defect concentration $n = 10^{16} \, cm^{-3}$ and the dielectric permittivity $\epsilon = 10$. For grain boundary charges we will use a moderate concentration [25] of surface states $n_s = 10^{11} \, cm^{-2}$ bearing the elemental charge $e$ each. The columnar or spheroidal grain radius $R = 0.3 \, \mu m$ will correspond to many typical structures mentioned in Sec. 4.1.

The estimates below deal with the random potential. This potential is rather insignificant when its amplitude is lower than the electron thermal energy, $\delta \phi \leq kT$. To the contrary, it can seriously impact the electron transport when $\delta \phi \geq kT$. For a particular photovoltaic application, the practically important range of $kT \sim 0.025$ eV corresponds to the criterion of random potential significance $\delta \phi \geq 0.1 - 0.2$ eV.

With the above in mind, the amplitude of point defect random potential (Fig. 4-2 (a)) is estimated from Eq. (4.10) with $q = e$, which yields $\overline{\delta \phi} = 0.02$ eV. The latter energy is rather insignificant on the scale of room temperature. However higher amplitude fluctuations $\delta \phi$ are found in the system with finite probability

$$\exp \left[ -(\delta \phi)^2 / 2(\overline{\delta \phi})^2 \right] \ll 1. \quad (4.20)$$

The regime of such Gaussian fluctuations is limited by the condition $\delta \phi \ll \delta \phi_{\text{max}}$ where $\delta \phi_{\text{max}}$ is the “maximum” characteristic fluctuation. It can be physically identified with the region of linear size $\sim L$ where the number of point charges differs
considerably from their average, \( \delta N \sim N \). Similar to the estimates in Sec. 4.2, one gets then \( \delta \phi_{\text{max}} \sim e^2 \delta N / L \epsilon \sim e^2 n L^2 / \epsilon \sim 1 \text{ eV} \). Gaussian fluctuations of rather high amplitudes can exist in the middle of the classical p-n junctions and Schottky barriers. For example, given the above numerical parameters, fluctuations with \( \delta \phi = 0.1 \) eV will be found there in concentration \( \sim L^{-2} \exp \left[ - (\delta \phi)^2 / 2(\overline{\delta \phi})^2 \right] \sim 10^3 \text{ cm}^{-2} \).

Consider next the case of spherical grains (Fig. 4-2 (b)). The charge per grain becomes rather large, \( q = 4 \pi n_s R^2 e \approx 10^3 e \). Using this in combination with the grain concentration \( \langle n \rangle = 3 / 4 \pi R^3 \approx 10^{13} \text{ cm}^{-3} \) leads to a significant fluctuation amplitude \( \overline{\delta \phi}_{\text{sph}} = 0.6 \text{ eV} \).

For the columnar grains (Fig. 4-2 (c)) we use \( \langle n \rangle = 1 / 4 \pi R^2 \approx 3 \cdot 10^8 \text{ cm}^{-2} \). This leads to \( q = 2 \pi RL n_s e \approx 2000 e \), which predicts a significant amplitude \( \overline{\delta \phi}_{\text{col}} = 0.5 \text{ eV} \) as substituted into Eq. (4.11).

Finally, consider a standalone grain boundary. Its electric potential is a maximum at \( z = L / 2 \) and can be estimated from Eq. (4.19) as \( \phi_{\text{max}} \approx 0.2 \text{ eV} \). We note that it is smaller than the typical fluctuations \( \overline{\delta \phi}_{\text{sph}} \) and \( \overline{\delta \phi}_{\text{col}} \) generated by many grains. The above estimates are illustrated in Fig. 4-4.

We now discuss possible implications of the above random potential, which appear somewhat different from those in bulk disordered systems [51]. Because of the lateral screening, the system, in general, can be thought of as a set of independent random micro-structures of linear size \( L \) each connected in parallel. Different electric potential distributions in their inner regions correspond to the exponentially different currents. Fluctuations in a half of micro-structures will set barriers to the current thus decreasing the effective area of current flow and the transverse conduction by
the factor of two.

Superimposed on the above average effect are strong effects of rare fluctuation, such as local tunneling currents under “triangle” barriers of Schottky or p-n junctions (Fig. 4-3). For example, the valence electrons in a region of high random potential will have to tunnel a shorter distance \( l_t = l_0^t (G - \phi)/G \) than the tunneling distance \( l_0^t \) without fluctuations. This effect is especially strong under reverse bias \( U \) where \( l_0^t \propto 1/\sqrt{|U|} \) shortens while the effective structure thickness \( L \propto \sqrt{|U|} \) increases making \( \bar{\delta\phi} \) bigger. Such local tunneling will result in “hot spots” of extremely high currents, which, from the above perspective, can be referred to as the Franz - Keldysh breakdown [64,65] in a disordered system. Experimentally, it is a common knowledge indeed that under high enough reverse bias, any junction ends up developing a hot spot instability, and this failure occurs under different biases in nominally identical devices.

As a next implication we point at phenomena involving photogenerated charge carriers, such as the photoconductivity or photovoltaic effect. Strong random potential in a polycrystalline structure will separate the electrons and holes spatially into parallel channels thereby suppressing their recombination. This can partially explain the unusually high effectiveness of polycrystalline thin-film photovoltaics [23].

A possible detrimental effect of fluctuation is the above-described enhancement in local tunneling causing spots of exponentially strong recombination. In addition, the parallel channels will enhance the recombination by effectively connecting the regions of opposite charge carriers [57]. Both these factors effectively increase the forward current \( J_f \), thus decreasing the open-circuit voltage \( V_{OC} \approx kT \ln(J_L/J_f) \),
where $J_L$ is the photocurrent [1,25]. These effects also representable in the terms of weak microdiodes can significantly decrease the system performance [29].

The above opposing tendencies can make the total effect of random potential on solar cell performance either positive or negative, depending on the system parameters (thickness, recombination kinetics, carrier generation rate, etc.). From the practical perspective, one can discriminate between two scenarios. The first is when the structure is thin enough to make the bulk recombination insignificant. In that case, the random potential will generally play a negative role resulting in local weak diodes and their related nonuniformity loss [29,66]. Practically, this suggests that the random potential should be suppressed, for example, by decreasing the grain size much below the structure thickness $L$ (which however can change the recombination rate through the grain boundary states thus adding more uncertainty).

The second scenario takes place when the bulk recombination is significant, i.e. $L$ is greater than the diffusion length. Such structures can benefit from increasing the random potential, which will suppress the bulk recombination thus increasing the photocurrent $J_L \propto \exp(V_R/kT)$, here $V_R$ is the recombination barrier. Taking into account that [51] $V_R$ is generally proportional to $\overline{\delta\phi}$ and that the voltage decrease is practically linear in $\overline{\delta\phi}$ (Ref. [29]), we conclude that the former exponential effect will dominate. Therefore such system performance can be optimized by tuning the random potential (through e.g. grain size) so that to suppress the bulk recombination and increase the current collection.

Overall we conclude that the random potential can significantly change the photocurrent and voltage in either direction. However the practical means of tuning
these effects are likely to impact other factors and more work is called upon to better understand these phenomena.

4.5 Conclusions

We have described the properties of long-range random potential in thin structures sandwiched between two conductive layers (“electrodes”). The underlying criterion of structure thickness $L$ being smaller than the screening length of its constituting bulk material, corresponds to many practically important systems including thin-film photovoltaics and classical p-n, and Schottky junctions.

We have shown that in such systems, the lateral screening length and the space scale of random potential are due to the electrons in the electrodes, and are close to the structure thickness $L$. The random potential amplitude here is described analytically in a closed form and is specified for three practically important cases of point defects, spherical grains, and columnar grains causing the potential fluctuations.

Finally, implications of our theory have been pointed out that strong random potential separate the electron and holes into parallel channels. It avoids the recombination and increase the photo current. However it creates conductive pathways that effect on transverse electron transport; examples, shunts, and this will decrease the system performances. It suggests some practical approaches to optimize the performance of thin-film photovoltaics through the device thickness, grain size, etc.
Chapter 5

Defect assisted tunneling

In this chapter we discuss defect-assisted electron transport through non-crystalline junctions. Our discussion starts with a simple toy model considering hopping paths through a rectangular barrier. We then extend our analysis to the case of a triangular barrier more adequate for semiconductor junctions.

Finally, we take into account that different hopping channels can be connected in parallel through a resistive electrode. Our theory predicts that under the typical working conditions, inter-defect tunneling can be a dominant current transport across a junction. Finally we point out possible implications of our findings.

5.1 Introduction

Applying a metal contact on a semiconductor generally results in Schottky barrier (SB), which affects the current flow. Here we discuss the electron transport through SB formed by non-crystalline semiconductors (amorphous and polycrystalline). De-
Figure 5-1: Mechanisms of electron transport through SB, (a) The direct thermal activation, (b) The direct tunneling, (c) The activation assisted tunneling, and (d) The thermally activated defect-assisted tunneling.

-effects are typical of non-crystalline materials and their SB regions. They can improve SB transparency by providing pathways for electron hopping. In what follows we concentrate on hopping transport through SB illustrated in Fig. 5-1 (d), which can dominate when the defect concentration is high enough.

The barrier transport across thin non-crystalline films is exponentially sensitive to the barrier parameters, such as thickness ($L$), height ($V_0$), the electron wave function radius under the barrier ($a$), and the density of localized defect states ($g$). Because of statistical fluctuations in defect concentration between different locations, the barrier transport turns out to be laterally non-uniform.

Tung’s model is the simplest model of laterally non-uniform SB transport [67]. It postulates the SB height fluctuations. However for SB to fluctuate, its height has
Figure 5-2: Energy-space diagrams for Schottky barrier; the equipotential metal surface and non-uniform tunneling distances due to variations of defect concentrations across the SB (a), and in-equipotential metal surface with non-uniform Schottky barrier heights and barrier thicknesses (b).

to be disconnected from the equipotential metal potential. In the Tung’s model, this is justified with a hypothesis of strong dipole layer separating the metal and semiconductor as shown in Fig. 5-2 (b). The conductivity of such an inhomogeneous SB is given by $\sim \exp(-V_0/kT)$, where $V_0$ is a random quantity.

Our approach illustrated in Fig. 5-2 (a) does not imply a dipole layer. Correspondingly the barrier height does not fluctuate. However, variations of defect concentration create strong fluctuations in hopping transport across the barrier.

Our approach here is conceptually close to a theory of transverse hopping conduction in thin amorphous films started in Ref. [68] and developed further in Refs. [69–72]. It applies to thin enough structures whose thickness $L$ is smaller than the correlation length $\ell$ of the percolation cluster responsible for the hopping conduction [50].

Under the condition $L < \ell$, the transverse hopping conduction is dominated by
Figure 5-3: Defect assisted electron tunneling pathways 1, 2 and 3 correspond to the regions of abnormally low, high and average transparency respectively, in real space.

rare configurations of defects forming quasi-linear paths with relatively small inter-defect distances [68–72]. While many aspects of such transport have been analyzed in the preceding work, its applications to device physics remains largely unexplored. Our work here is aimed to consider such applications to Schottky barriers and photovoltaic devices. This task is accomplished by extending the theory onto the case of systems with hopping between two resistive planar electrodes. The latter realistic addition significantly changes the features of transverse hopping conduction through thin structures.
5.2 “Toy model”

5.2.1 Optimum Channel

Consider electron hopping between equidistant $N \gg 1$ defect states along a rectilinear path, (Figs. 5-3, and 5-4). At each step the electron with comparable probabilities ($\sim 1/2$) can tunnel forth or back across the distance $L/(N + 1) \ll L$.

The hopping rate is proportional to the tunneling probability $\exp(-2L/aN)$, hence the corresponding conductance $R_{N}^{-1} \propto \exp(-2L/aN)$. Because $R_{N}^{-1}$ exponentially increases with $N$, an atypical path containing abnormally high number of defects becomes important, (see Fig. 5-3).

However, the probability of finding such an abnormal path, $p_{N}$ exponentially decreases with $N$. Let $p$ be the probability of finding just one defect in a close proximity of the electron trajectory. The probability to find a trajectory with $N$ defects can then expressed as $p_{N} = p^{N} = \exp(-\lambda N)$, where $\lambda = \ln(1/p)$. The competition between $R_{N}^{-1}$ and $p_{N}$ resolves in the optimum paths that maximize the partial conductance:

$$p_{N}R_{N}^{-1} \propto \exp\left(-N\lambda - \frac{2L}{aN}\right), \quad \lambda \equiv \ln \frac{1}{p}. \quad (5.1)$$

A straightforward maximization gives the optimum number of defects:

$$N_{opt} = \sqrt{\frac{2L}{\lambda a}}. \quad (5.2)$$
Substituting this back into Eq. (5.1) gives the optimum conductance:

\[ R^{-1} = R_0^{-1} \exp \left( -2\sqrt{\frac{2L\lambda}{a}} \right) \]  

(5.3)

Eq. (5.3) shows the increase in current transport due to defects: reduction of the tunneling exponent from \( 2L/a \) to roughly, \( 2\sqrt{2L\lambda/a} \ll 2L/a \).

In a rough approximation the pre-exponential \( R_0^{-1} \), can be estimated as

\[ R_0^{-1} \approx \nu q^2 / kT \]  

(5.4)

here the hopping rate \( \nu \) is of the order of the characteristic phonon frequency, \( \nu \approx 10^{12} \) s\(^{-1}\).

To justify the latter approximation we consider two adjacent sites, where the potential difference of \( kT/q \), between these sites forces a direct current \( q\nu \), here \( q \) is the electron charge. The ratio of the potential difference and current gives the resistance between these two site which is equal to the inverse of the Eq. (5.4). Our approximate estimate is \( R_0^{-1} \approx 10^{-5} \Omega^{-1} \). A more exact derivation of the pre-exponential factor is done by Abrahams and Miller [73]. Their estimate depends on many parameters, such as the speed of sound, the deformation potential, etc. and generally predicts \( \nu \approx 10^{11} - 10^{14} \) s\(^{-1}\). The accuracy of the pre-exponential estimate is not very important here compared with the exponential effects.

Here and in what follows we assume that hopping is more efficient than direct thermal activation. The corresponding exponents must obey the inequality \( V_0/kT \gg \)}
Figure 5-4: A channel of \( N = 3 \) defects confined into cylindrical region of diameter \( \rho \) and \( L/N \) is the effective inter-center distance, where \( 2a \) is the electron localization distance.

\[ 2\sqrt{2L\lambda/a}, \text{ where } \lambda \gg 1, \text{ and } L = V_0/F, \text{ (} V_0 \text{ is the barrier height, } F \text{ is the strength of the electric field across the barrier)}. \]

It is convenient for our purposes to present the latter inequality in the form

\[ \alpha = \frac{V_0Fa}{8kT^2\lambda} \gg 1 \quad (5.5) \]

Even though \( \rho \) has not been exactly defined in the above, its related uncertainty appears insignificant under the logarithm in the final result of Eq. (5.3). It can be specified through a more comprehensive analysis [71], which yields

\[ \lambda = \ln \left( \frac{\lambda}{gkTaL^2} \right) \approx \ln \left( \frac{1}{gkTaL^2} \right), \quad (5.6) \]

and which will be more in detail outlined in the Appendix D.1.
5.3 Channels connected through a resistive electrode

So far we have considered electron transport through the barriers without any relation to other possible resistances, that the electron current may have to overcome. This is tantamount to the hopping channels connected through a superconductive electrodes. However if such resistances are present they may affect the barrier transport as shown below.

5.3.1 Physical models of barrier transport with resistive electrodes

Let us consider two examples of significant additional resistances. Our first example is a semiconductor structure that has two metal electrodes and two Schottky barriers as schematically shown in Fig. 5-5. In the real space the current path may not be straight since the optimum channels are not necessarily found in front of each other. Therefore the current flowing through the optimum channel of one barrier may have to flow in the lateral direction before it finds a conducting channel in the second barrier. In this system, sufficiently high lateral resistance will change the parameters of the optimum channel. In particular channels with resistance much lower than lateral resistance will not play a significant role. In the above described system, the current flow is organized in such a fashion as though there was a resistive electrode connecting individual conducting channels, which model we analyze in what follows.
Figure 5-5: A real-space diagram of current flow in a semiconductor structure sandwiched between two metal electrodes (a), the corresponding energy-space diagram of hole transport through two barriers in the sandwiched structure (b); dashed line shows the Fermi-level in the metal contacts.

Consider next another example of a typical band diagram (Fig. 5-6) corresponding to thin-film photovoltaics. In this diagram, again we have two barriers. One at the semiconductor interface is called the photovoltaic junction; another one is a Schottky barrier at the back contact. In this structure, the electron-hole pairs are generated randomly in real-space and are typically far from the conducting channels. These charge carriers need to be collected at the device terminals, which becomes possible through the optimum hopping channels. In finding such channels, the carriers have travel in the lateral directions and overcome the lateral resistance, for example, the lateral resistance of CdTe is $10^9 - 10^8 \, \Omega$, which is described by the above mentioned
circuitry with resistive electrodes.

5.3.2 The derivation of optimum channel parameters under the resistive electrode conditions

Each channel collects currents from the area of characteristic radius \( l \), of the order of inter-channel distances. The corresponding lateral resistance is not very sensitive to \( l \),

\[
R_l = \frac{r_s}{2\pi \rho} \ln \frac{l}{\rho},
\]

(5.7)

where \( r_s \) is the sheet resistance of the resistive electrode. In what follows we neglect the logarithmic dependance in Eq. (5.7), thus considering \( R_l \) as a constant parameter of the order of \( r_s \). The total integral conductance experienced by the current is given by

\[
\sum_i \frac{\exp(-\lambda N_i)}{R_l + R_{c,i}}
\]
where the channel resistance is \( R_{c,i} = R_0 \exp(2L/aN_i) \), \( N_i \) is the number of defects in the \( i^{th} \) channel, and the probability of forming such a channel is \( \exp(-\lambda N_i) \). Having introduced the optimum channel numbers, the latter equation takes the form

\[
\frac{1}{R} = \sum_i \frac{1}{R_0} \left\{ \frac{\exp[-\sqrt{2L\lambda/a}(N_i/N_{opt})]}{\exp[\sqrt{2L\lambda/a}(N_{opt}/N_i)] + (R_l/R_0)} \right\}.
\]

This sum is dominated by the maximum terms, with \( N_i \) satisfying the equation

\[
\exp[\sqrt{2L\lambda/a}(N_{opt}/N_i)] \left( (N_{opt}/N_i)^2 - 1 \right) = R_l/R_0.
\]

Its solutions define the optimum channel parameters.

\[
N_i = \sqrt{2L/\lambda a}, \quad R_l \ll R_0 \quad (5.10)
\]

\[
N_i = 2L/a \ln(R_l/R_0), \quad R_l \gg R_0. \quad (5.11)
\]

We observe that for \( R_l \ll R_0 \), the conductance is given by Eq. (5.3), which is independent of lateral resistance \( R_l \). In the opposite limiting case \( R_l \gg R_0 \) introduced in this case, the optimal conductance is given by

\[
R^{-1} \simeq R_l^{-1} \exp \left( -\frac{2L\lambda}{a \ln r} \right), \quad r = R_l/R_0. \quad (5.12)
\]
6.6

Figure 5-7: A thin-film of thickness $L$ sandwiched between 2-D parallel conductors is shown. A single channel of diameter $\rho$ presents within the given radius of $l$.

5.4 Critical area and mesoscopic fluctuations

Since the optimal channels are exponentially rare, Eq. (5.3) or Eq. (5.12) determine the conductivity of a film if the sample area is sufficiently large, so that there are many optimal channels within this area. If the latter condition is not obeyed, the conductivity of a film is governed by the most conducting non-optimum channels present in the sample. A related effect is that, since the pathways are statistically different, there will be lateral variations in the barrier transparency between nominally identical samples.

Consider a channel of $N$ defects confined into a cylindrical region of diameter $\rho$. For this region to present a recti-linear conductive path, its diameter $\rho$ must be smaller than the inter defect distance, $L_1 = L/N \gg \rho$, (see Fig. 5-4). $\rho$ can be defined from the condition that the radial dispersion of defects does not exceed the characteristics tunneling length, $\sqrt{(L/N)^2 + \rho^2} - L/N \leq a$. From here we get
\[ \rho = \sqrt{La/N}. \] Dividing the sample area \( A \) into a set of spots of area

\[ \rho_{\text{opt}}^2 = \frac{La}{N_{\text{opt}}}, \] (5.13)

will estimate the number of potential optimum channels. Each such spot becomes a base for an optimum channel with probability \( P_{N_{\text{opt}}} = \exp(-\lambda N_{\text{opt}}) \). Therefore the optimum channel concentration can be estimated as

\[ n_{\text{opt}} = \frac{1}{\pi \rho_{\text{opt}}^2} \exp(-\lambda N_{\text{opt}}). \] (5.14)

The condition that the sample area is large enough to accommodate at least one optimum channel defines the critical area for the case of non-resistive electrodes

\[ A_c = \pi \frac{La}{N_{\text{opt}}} \exp \left( \sqrt{\frac{2L\lambda}{a}} \right), \] (5.15)

\[ = \pi \sqrt{\frac{La^3\lambda}{2}} \exp \left( \sqrt{\frac{2L\lambda}{a}} \right). \]

For the alternative case of resistive electrodes, the area of an optimum channel can be found by substituting the optimum channel parameters given by Eq. (5.11) for \( R_l \gg R_0 \) in Eq. (5.13),

\[ \rho_{\text{opt}}^2 = \left( \frac{a^2}{2} \right) \ln r, \quad r = R_l/R_0, \quad r \gg 1. \] (5.16)

As a result the optimum channel concentration becomes,
Figure 5-8: The equivalent electric circuit of a set of parallel channels connected to a resistive electrode. Each channel is represented by a resistor of resistance $R_{c,i}$. The sheet resistance of the electrodes is $R_l$. The resistance of the optimum channel is $R_{opt}$.

$$n_{opt} = \frac{2}{\pi a^2 \ln r} \exp \left( -\frac{2L\lambda}{a \ln r} \right)$$

(5.17)

corresponding to the critical area,

$$A_c = \frac{\pi}{2} a^2 \ln r \exp \left( \frac{2L\lambda}{a \ln r} \right), \quad r \gg 1.$$  

(5.18)

The significance of results in Eqs. (5.15), (5.18) is that they define the characteristic area below which fluctuations in transverse conduction do not self average.

### 5.4.1 Transversal Barrier Resistance

Consider the triangular barrier (Fig. (5-9))

$$V(x) = V_0 - Fx,$$

(5.19)
where $x$, is the linear coordinate and $F$ is the strength of the electric field across the barrier. $V_0$ is measured from the Fermi-level and the thickness of the barrier is determined by the depletion width $L$. The defect assisted tunneling is characterized by some activation energy $\delta E$ and the number of defects $N$. The inter-defect tunneling distance can be expressed as,

$$L_1 = \frac{L}{N} = \frac{V_0 - \delta E}{FN}.$$  \hspace{1cm} (5.20)

We have carried-out a procedure of direct optimization of the conduction of many parallel channels characterized by their respective variational parameters $N$ and $\delta E$ as described in the Appendix D.3. As a result the optimum channel conductance is given by

$$R^{-1} \approx R_0^{-1} \exp \left( -2 \sqrt{\frac{2V_0 \lambda}{Fa}} \right).$$  \hspace{1cm} (5.21)

It depends on the barrier height $V_0$ and temperature $T$ with $\lambda$ given by the solution of the equation,

$$\lambda = \ln \left( \frac{\lambda}{2g(V_0/F)^2aT} \right).$$  \hspace{1cm} (5.22)

Note that introducing $(V_0/F) = L$ makes Eq. (5.21) fully identical to the earlier written Eq. (5.3) for a rectangular barrier. Note also that our result in Eq. (5.21) coincides with the corresponding result of Ref. [72] to the accuracy of multipliers under the logarithm in the expression for $\lambda$.

For the case of resistive electrode regime described in Sec. 5.3, our optimization
Figure 5-9: Schottky barrier approximated into a triangular barrier of height $V_0$, width $L$: electron hopping with activation $\delta\mathcal{E}$ through the barrier.

procedure layed-out in the Appendix D.3 gives

\[ R^{-1} \approx R_0^{-1} \exp \left( \frac{-2V_0\lambda}{F_a \ln r} - \frac{\ln r}{\lambda} \right) \] (5.23)

### 5.4.2 Current-voltage characteristics

To describe the current-voltage characteristics of a triangular barrier, we start with the diode equation,

\[ J = J_0 \left[ \exp \left( \frac{V_e}{kT} \right) - 1 \right] \] (5.24)

where the saturation current

\[ J_0 = J_{001} \exp \left( -\frac{w_0}{kT} \right), \] (5.25)
Figure 5-10: Energy band diagram of SB under forward bias (a) and reverse bias (b); $E_{FM}$ and $E_{FS}$ are the fermi level corresponding to metal and n-type semiconductor and $L_s$ is the depletion width.

i.e. in the standard model, $J_0$ is governed by the barrier height $w_0$. In our model, because of the barrier transport is dominated by hopping, the factor $\exp(-w_0/kT)$ will be replaced by the corresponding hopping exponential according to whether the barrier is under forward bias or reverse bias.

Under forward bias, the SB height is reduced to $(V_0 - V)$ and the corresponding electric field $F$ is $(V_0 - V)/L$ with $L = \sqrt{2\epsilon_s(V_0 - V)/qN_D}$, (see Fig. 5-10) [25]. Assuming n-type semiconductor with donor concentration $N_D$, the forward bias hopping exponential becomes,

$$J_{FB} = J_{001} \exp \left[-2 \sqrt{\frac{2\lambda}{a}} \sqrt{\frac{2\epsilon_s(V_0 - V)}{qN_D}} \right]. \quad (5.26)$$

For the case of reverse bias, (Fig. 5-10,b) SB height is $V_0$ and the electric field
$F = V_0/L$ where the barrier thickness $L = V_0 \sqrt{2\epsilon_s q N_D (V_0 - V)}$. The hopping exponential for this case is given by,

$$J_{RB} = J_{001} \exp \left[-2 \sqrt{\frac{2\lambda}{a}} \sqrt{\frac{2\epsilon_s}{q N_D}} \frac{V_0}{\sqrt{V_0 - V}} \right]$$  \hspace{1cm} (5.27)$$

(note that $V$ is negative here) Eq. (5.26) and (5.27) can be approximated by the expression,

$$J_0 = J_{001} \exp \left[-2 \sqrt{\frac{2\lambda}{a}} \sqrt{\frac{2\epsilon_s}{q N_D}} \frac{V_0 \sqrt{V_0 - V}}{2V_0 - V} \right]$$  \hspace{1cm} (5.28)$$

where $V < V_0$. Substituting Eq. (5.28) into Eq. (5.24) yields the current-voltage characteristics for transverse hopping conduction

$$J = J_{001} \exp \left[-2 \sqrt{\frac{2\lambda}{a}} \sqrt{\frac{2\epsilon_s}{q N_D}} \frac{V_0 \sqrt{V_0 - V}}{2V_0 - V} \right] \left[ \exp \left( \frac{Ve}{kT} \right) - 1 \right]$$  \hspace{1cm} (5.29)$$

For the case of resistive electrode the hopping exponential can be similarly obtained from Eq. (5.23) and is given by,

$$J = J_{002} \exp \left[ -\frac{2\lambda}{a \ln r} \left( \sqrt{\frac{2\epsilon_s}{q N_D}} \frac{V_0 \sqrt{V_0 - V}}{2V_0 - V} \right) - \frac{\ln r}{\lambda} \right] \left[ \exp \left( \frac{Ve}{kT} \right) - 1 \right]$$  \hspace{1cm} (5.30)$$

In the terms of a widely used jargon, Eqs. (5.29) and (5.30) describe the current-voltage characteristics of a *leaky* SB.

A graphic example of the latter is shown in Fig. 5-11 for realistic model parameters corresponding to the experimental results of Ref. [74]. The reverse-bias leakage current of the Schottky diode is significantly higher compared to that of the standard
Figure 5-11: Examples of a leaky diode current-voltage characteristics compared to standard diode corresponding to the parameters $V_0 = 1.0 \text{ eV}$, $\lambda \sim 5$, $N_D = 10^{12} \text{cm}^{-3}$ and $L/a \sim 1000$; these parameters are selected so as to obtain $J$-$V$ close to experimental observations. In both reverse bias (left) and forward bias (right) regimes the leaky diode currents are higher.

diode (“soft” reverse characteristics). The forward-bias characteristics also shows a difference in current level for the two types of diodes. In both regions, higher current level since the electron hopping transport across the barrier is easier compared to thermal activation.

5.5 Numerical estimates

We start with the estimate for the inter-defect tunneling distance $L_1$,

$$L_1 = \frac{L}{N} \quad (5.31)$$
for a realistic barrier thickness \( L \sim 0.5 - 1 \mu m \) and the characteristic electron localization radius of \( a \sim 10 - 30 \text{ Å} \). Assuming also the defect density of states \( g = 10^{15-17} \text{ cm}^{-3} \text{ eV}^{-1} \) and \( \lambda \sim 2 - 5 \) in Eq. (5.6), we can estimate \( N_{opt} \sim 8 - 14 \), which translates into \( L_1 \sim 35 - 125 \text{ nm} \), in the ballpark of tunneling distances in semiconductor structures (tunneling junctions, etc.)

The optimum channel cross-section area \( \rho_{opt}^2 \sim 10^{-12} \text{ cm}^2 \) can be found by substituting the latter estimates in Eq. (5.13). The corresponding critical area, in Eqs. (5.15), (5.18) varies in a very broad interval depending on the system parameters, \( A_c \sim 10^{-8} (r \gg 1) - 10^{28} (r \ll 1) \text{ cm}^2 \). The measured specific transverse resistance will be by the factor of \( \exp(-S) \) lower, i.e. in the range \( (10^9 - 10^{48}) \Omega \) for \( r \ll 1 \). For the case of \( r \gg 1 \), the measured specific transverse resistance is about \( 10^9 \Omega \).

For triangular barrier model using Eq. (5.19), we estimate \( F \sim 3 \times 10^4 \text{ e V/cm} \). Assuming \( V_0 \sim 1 \text{ e V}, kT \sim 0.025 \text{ e V}, a = 2 \times 10^{-7} \text{ cm} \) gives \( \lambda \sim 5 \). The corresponding triangular barrier thickness \( L = V_0/F \lesssim 3 \mu \text{ m} \).

### 5.6 Implications and Predictions

1. *The non-uniform SB barrier transport revisited*
Three major observations of real SB operations differ from the classical theory predictions [67]. They are,

(a) *J-V characteristic curve-forward bias*

The observed smaller steepness phenomenologically described by the non-ideality factor \( n \), i.e. \( V/kT \rightarrow V/nkT \) or by renormalizing the temperature \( T \rightarrow (T + T_0) \) [75]. Both descriptions make the J-V curve less steep (see Fig. 5-11).

(b) *J-V characteristic curve-reverse bias*

The reverse current increases in absolute value instead of saturating (soft-reverse characteristics).

(c) *SB parameters*

The measured SB parameters depend on the characterization techniques, such as capacitance and I-V.

These features have been previously highlighted and qualitatively explained by Tung [67] in the model of fluctuating SB height (see Sec. 5.1 above). Our interpretation of these features are as follows.

(a) The greater than unity ideality factor is explained by the thermally activated hopping with the energy \( \delta E \) lower than classical SB height [see Eq. (D.21) in Appendix D.3]. In addition \( \delta E \) is temperature dependent and decrease with \( T \) increase. This makes the J-V curve less steep that the classical theory prediction. Comparing the classical activation current
\[ \exp(-V_0/kT) \] with that of defect assisted tunneling shows that the latter dominates when

\[ T < \frac{\lambda V_0 Fa \ln r}{k (Fa(\ln r)^2 + 2V_0\lambda^2)} \]  

(5.32)

For the above discussed numerical values of parameters the inequality in the Eq. (5.32) holds for room temperature and below.

(b) Soft reverse characteristics (see Fig. 5-11) can be explained by the reverse bias current-voltage characteristics in Eq. 5.29. When SB is under reverse bias, the barrier gets relatively narrow (see Fig. 5-10) and electrons can more efficiently flow across the barrier using defect assisted tunneling. As a result the current increases in absolute value.

(c) Tung has discussed the dependance of (SBH) Schottky barrier height on the technique measurements. Examples are Capacitance-Voltage technique (C-V), Current-Voltage technique (I-V), and Photo-Response (PR) technique. According to his model, the C-V method gives the average SBH of the entire SB diode while SBH measured using I-V or PR is smaller than that of C-V technique. Since the displacement current takes place in C-V technique, the hopping mechanism cannot explain it. But I-V and PR measurement techniques can determine the more transparent regions for the defect assisted tunneling because those regions correspond to the higher tunneling probabilities.

We shall end this section with briefly mentioning the ballistic electron emis-
sion microscopy (BEEM) in terms of hopping transport. The BEEM spectra represent the collector current as a function of the tip bias voltage supposedly above or equal to the SBH. The measured current varies in the lateral directions when the tip scans the semiconductor structure. The existing interpretations have used Tung’s model to understand such fluctuations [76, 77]. According to the philosophy, discussed of this chapter, electrons can use the available efficient hopping channels of the non-crystalline semiconductors. As a result, the BEEM spectra can reflect fluctuations in hopping transverse conduction rather than SBH. This issue remains unresolved in the present framework.

2. Implications for Photovoltaics

Here we discuss some implications of transverse hopping transport related to thin-film photovoltaic devices. More specifically, we consider the cases of leaky CdS layer and the leaky back contact junction.

A recent work on thin-film photovoltaics [78] has pointed out that very thin non-crystalline films can be leaky due to shunting like pathways formed by chains of \( N \gg 1 \) defects [71]. CdS in contact with TCO forms a triangular shape barrier (from field reversal model described in Sec. 2.4 above) [21]. The defect assisted tunneling appears beneficial for that kind of barrier. As explained in Fig. 3-5 above, leaky diode formed by CdS help to increase the open circuit voltage \( (V_{oc}) \) of a CdS based thin-film solar cell. This effect is due to decrease in CdS barrier resistance. Therefore highly resistive CdS with high defect con-
Figure 5-12: Different samples of CdS/CdTe thin-film solar cells can show very different J-V curves [80]; “standard” J-V curve, where dark J-V curve flatness is not very strong (a), and normal light J-V curve accompanied by a very flat dark J-V curve (b).

centration, ideally almost amorphous, is expected to serve the best, which is consistent with the observations [79].

One another implication is that defect-assisted tunneling transport through the CdS barrier can have a noticeable effect on the device model develop for CdS based CdTe solar cells as described in Sec. 2.4 above [81]. In particular when effective enough, such hopping will eliminate the J-V rollover and move light- to dark J-V crossing to the high current region. In addition, it can contribute to the observed variations between nominally identical cells, since the most effective hopping pathways can vary between the cells of finite area smaller than the critical area $A_c$ [see Eqs. (5.15), (5.18) above] [71].

The back contact SB formation in the above mentioned thin-film PV devices,
constitutes the phenomenon known as the back barrier or back diode (see Fig. 5-6), or back surface field. It can effect all the major PV, such as CdTe, and CIGS [1]. The device containing a back barrier can operate in either standard (back diode) or reach through diode regime [26]. We can apply the philosophy of defect assisted tunneling through a triangular barrier to either the back diode or reach through regime. A leaky back diode will reduce the barrier resistance due to shunting like pathways and there by reducing the roll-over [25,26].

The last implication here is the dark JV lay-downs observed for CdS based thin-film solar cells. The lay-downs correspond to very high resistance in the dark current regime, while the light resistance remains typical. Hence unusually low current at the light to dark crossover. It is observed that the degree of flatness, its particular shape and the voltage where the curves take-off vary between different samples (see Fig. 5-12 above) [80]. The lateral resistance of the CdTe of the device is inversely proportional to the light intensity [25]. Under the dark conditions the extremely high lateral resistance will increase the barrier resistance, and this high resistance cannot be over come by the defects in that region (see Sec. 5.3). Therefore above the light to dark crossover, this will decrease the dark current to almost zero. However when the light hits on those samples the high lateral resistance drastically decrease and defect assisted tunneling can dominates the transparent regions of the barrier by increasing the current above the light to dark crossover.
5.7 Conclusions

We have shown that defect-assisted tunneling can dominate the Schottky barrier transport mechanism in non-crystalline semiconductors. Specifically we have derived the current-voltage characteristics, introduced the critical area and suggested an alternative to Tung’s fluctuation of SBH model. The effects of strong electric field across the triangular shaped SB and lateral resistance are discussed.

Finally, we have applied our results to explain two of the commonly observed effects that so far remained puzzling: (a) positive role of very resistive CdS layers with high defect concentration (typically, CBD (Chemical Bath Deposition) grown), and (b) lay-down current-voltage characteristics in CdTe/CdS photovoltaics.
Chapter 6

Ultra-thin-film photovoltaics

We consider physical properties of ultrathin photovoltaics with thickness ($\lesssim 1 \mu m$) smaller than both the depletion width and diffusion length, applicable to the cases of amorphous, polycrystalline, and nano-structured devices. Three phenomena underlie the unique physics of such systems are: (1) lateral screening by conducting electrodes, (2) leakiness due to defect assisted tunneling, and (3) gigantic capacitive energy conducive to shunting breakdown. We give numerical estimates and discuss practical implications of these phenomena. Much of the discussion below is based on the results obtained in Chapter 4 and Chapter 5.

The current trends in thin-film photovoltaics call for reduction in device thickness in order to increase the commercial attractiveness and address concerns of availability of some chemical elements, such as In in CuIn(Ga)Se$_2$ and Te in CdTe devices [1, 82]. This moves the technology to the range of submicron thickness. However even laboratory scale devices demonstrate unexpectedly drastic efficiency losses when they are well in the submicron range [53, 54, 83]. Here we show that significant changes
Figure 6-1: Electric charge distributions in thin-film PV: (a) point charges due to doping impurities or defects; (b) surface charges at the interfaces of three-dimensional nano-particles (grains) in organic or some polycrystalline photovoltaics; (c) charges at the interfaces of columnar grains.

are expected indeed for devices of submicron thickness $l$ shorter than the depletion width ($L_{\text{dep}}$) and the diffusion length ($L_{\text{dif}}$). The latter conditions define a regime of device operation and stability that we call ultrathin photovoltaics (UTPV).

6.1 Physical model

In our model, a thin semiconductor structure is sandwiched between two electrodes and contains localized states and electric charges of impurities, grain boundary defects, etc. (Fig. 6-1). In what follows we discuss three of its characteristic features:

1. Because of $L_{\text{dep}} > l$, the film behaves as a dielectric; screening by the electrodes determines its electric potential distribution.
2. Due to $L_{\text{dif}} > l$ the recombination is insignificant, and efficiency is limited by the leakage current.
3. Large geometrical capacitance $C \propto 1/l$ makes the stored energy $CV^2/2$ gigantic, conducive to the dielectric breakdown.
As discussed in chapter 4, statistical fluctuations in semiconductor charge density make the electric potential vary between the electrodes. The spacial and energy amplitude of these variations are determined by the electrode polarization, which can be quantitatively described based on the known potential of a point charge between two metal planes. A qualitative understanding is facilitated by the intuitive image charge concept. A bare point charge creates a substantial electrode polarization, i.e. image charge, in a region of characteristic length $l$, same as device thickness. Because the original and image charges effectively neutralize each other, they induce a potential decaying faster than that of a dipole. This is tantamount to the screening (correlation) length of the order of $l$.

We recall that the amplitude of a random potential (Fig. 6-2) of correlation length $\sim l$ can be estimated in the ‘$\sqrt{N}$-approximation’ for all three important cases of electric charge distribution illustrated in Fig. 6-1 [see Eq. (4.3)].

The main conclusions on this amplitude were that grain size comparable to the
device thickness is the most efficient source of fluctuations; either very small or very large in diameter grains create a weaker random potential.

Figure 6-3: CdTe/CdS solar cell (not to scale). The polycrystalline structure of a CdTe film is shown. \( L \) is the characteristic screening length of nonuniformity in the lateral directions [see Eq. (6.3)]

The implications of random potential can be understood based on the equivalent circuit of \( l \)-sized micro-diodes connected in parallel through the resistive electrode (e.g. transparent conductive oxide) (see Fig. 6-3). Strong random potential fluctuations \( \delta \phi > kT/e \) are detrimental causing loss in open circuit voltage, fill factor, and device efficiency [29]. Our consideration in chapter 4 predicts that suppressing such loss requires either very small or very large particle size compared to the device thickness.

6.3 Leakage currents

This section is based on the above results in chapter 5. We recall that thin non-crystalline films are leaky due to shunting-like pathways formed by untypical chains of \( N \gg 1 \) defects [71] [Fig. 6-4 (a)]. In such pathways, short inter-defect distances \( l/N \) exponentially increase the probability of electron tunneling \( \exp(-2l/Na) \) and
related hopping conduction, where \( a \) is the characteristic electron localization radius on a defect, typically, \( a \sim 10 - 30 \) Å. Geometrically each pathway is presented by a cylinder of length \( l \) and radius \( \rho = \sqrt{la/N} \) determined by the condition that the radial distribution of defects about the cylinder axis does not suppress tunneling, i.e. \[ \sqrt{(l/N)^2 + \rho^2} - l/N \leq a \] (see Eq. (5.13)).

For uncorrelated defect distributions, the probability of finding a \( N \)-defect pathway \[ R_{pN} = (p_1)^N \equiv \exp(-N \Lambda) \]. Its hopping resistance \( R = R_0 \exp(2l/Na) \) with the preexponential \( R_0 \sim kT/\nu e^2 \sim 10 \text{ K}\Omega \) where \( \nu \sim 10^{13} \text{ s}^{-1} \) is the characteristic phonon frequency [84]. Combining these equations yields the probabilistic distribution of pathway resistances,

\[
P(R) \propto \frac{1}{R} \exp \left[ -\frac{2l \Lambda}{a \ln(R/R_0)} \right]. \tag{6.1}
\]

It is a maximum at the optimum resistance \( R_{opt} = R_0 \exp(\sqrt{2\Lambda l/a}) \) (same as derived in chapter 5 by another arguments) compromising between the pathway efficiency.
and probability (with $N_{opt} = 2\sqrt{l/\Lambda a}$). Taking into account thermally activated hopping [71] yields a more exact definition of $\Lambda \approx -\ln(gl^2akT) \sim 2 - 5$, where $g$ is the defect density of states.

Eq. (6.1) predicts a broad distribution of local shunt resistances. Low $R$ pathways decrease local $V_{oc}$. A criterion for this shunting effect can be established by considering a diode in parallel with ohmic shunt, whose current-voltage characteristics are $J = J_0 \{\exp[e(V - V_{oc})/kT] - 1\}$ and $J = V/R$ [Fig. 6-4 (b)]. It is straightforward to show for such a circuit that a substantial ($\gtrsim kT/e$) decrease in $V_{oc}$ takes place when $R \ll V_{oc}/J_0$. Using $J_0 \approx J_L \rho^2$ yields

$$R \ll V_{oc}/(J_L a \sqrt{l_a}) \equiv R_l$$

where $J_L$ is the photo-current density. As a rough estimate, $R_l \sim 10^{14} \Omega$ for a 1 $\mu$m thick structure with $V_{oc} \sim 1$ V and $J_L \sim 0.01$ A/cm$^2$.

We now introduce the concept of critical thickness $l_c$, below which the device suffers a significant leakage loss. A local shunt effect spans the characteristic distance [29]

$$L = \sqrt{kT/eJ_L \rho_{sh}}$$

where $\rho_{sh}$ is the electrode sheet resistance; typically $L \sim 1 - 10$ mm. The number of potentially shunting pathways in the latter region of influence can be estimated as $L^2/\rho^2$. A significant leakage takes place when at least one of them has a resistance
below $R_l$, i.e. $(L/\rho)^2 \int_0^{R_l} P(R)dR = 1$, which yields a definition for $l_c$,

$$\frac{L^2}{a\sqrt{l_c a}} \exp \left( -\frac{2l_c \Lambda}{a \ln(R_l/R_0)} \right) = 1. \quad (6.4)$$

Using the above numerical parameters results in $l_c \sim 0.1 - 0.3 \, \mu m$. This should be understood rather as a lower bound estimate. In particular, the shunt non-ohmicity $[J \approx (V/R) \exp(\sqrt{eV/kT})$, see [72]] or correlated defect distributions will increase the above $l_c$. In general, we expect $l_c$ in the submicron range.

To conclude this section, we predict the existence of critical device thickness in the submicron region, below which the leakage currents will harm the device performance. This implies that decreasing the film thickness below $l_c$ may not be technologically viable.
6.4 Dielectric breakdown

Shunting is a known degradation mechanism in thin film photovoltaics [85]. We consider a chemistry independent mechanism of shunt generation in UTPV driven by the decrease in capacitive energy \( W = CV^2/2 \) via shunt induced voltage decrease. This is similar to the scenario discussed in Ref. [86].

A shunt of resistance \( R \gg \rho_{sh} \) decreases the device potential by \( \delta V \approx V \rho_{sh}/R \ll V \) in the neighborhood of area \( L^2 \) where \( L \) is given in Eq. (6.3). For a cylindrical capacitor of thickness \( l \) and area \( \pi L^2 \) about the shunt, the change in stored energy is (see Fig. 6-5)

\[
\delta W \approx W \frac{\rho_{sh}}{R} \quad \text{with} \quad W = \frac{\varepsilon L^2 V^2}{4l}.
\]

It is extremely large even for highly resistive shunts due to gigantic capacitive energy \( W \sim 10 \text{ GeV} \) (in the ball park of nuclear energies!) corresponding to the typical \( V \sim V_{oc} \sim 1 \text{ V}, \) \( l = 1 \mu \text{m}, \) and \( L = 3 \text{ mm} \).

The above \( W \) suffices to generate a huge number, \( W/w \sim 10^9 \) defects assuming the defect generation energy of \( w \sim 10 \text{ eV} \), enough to form a structure altered path of diameter \( \sim 0.1 \mu \text{m} \) through a \( 1 \mu \text{m} \)-thick film. In reality, shunting occurs upon much lighter structural transformations of just several defects forming a pathway with the above defined resistance \( R_l \) [Eq. (6.2)].

Given a shunt resistance, the number of its forming defects is proportional to the device thickness, thus requiring the energy \( W_D \propto l \). Because \( W \propto L^2/l \), the ratio \( W/W_D \) describing the possibility of shunting is dominated by the dimensionless
parameter

\[ \alpha = (L/l)^2 \gg 1. \]  \hspace{1cm} (6.6)

Remarkably, \( \alpha \) of UTPV \((L \sim 1 \text{ mm}, l \sim 1 \mu\text{m})\) is of the same order of magnitude as that of the ultrathin oxides in the modern integrated circuits \((L \sim 1 \mu\text{m}, l \sim 1 \text{ nm})\). In the latter technology, the dielectric breakdown remains a major bottleneck and a subject to numerous studies (see the review [87]). Based on this analogy, the dielectric breakdown is expected to become a major degradation mode in UTPV, thus calling upon immediate remedies. A more quantitative analysis of its nucleation kinetics in ultra-thin oxides [86] may be relevant for UTPV.

One counterintuitive consequence of the above is a higher breakdown vulnerability under low illumination, “from dusk till dawn”. This happens because the area \( L^2 \propto 1/J_L \) of shunt influence increases and so do its related capacitance, stored energy, and \( \alpha \). More exactly, since \([1] V_{oc} \approx (kT/q) \ln(J_L/J_S)\), the energy \( W \propto L^2V_{oc}^2 \) is a maximum at low light \( V_{oc} \approx 2kT/q \approx 50 \text{ mV} \).

To summarize this section, we predict shunting to be a characteristic degradation mode of UTPV, especially detrimental under low light.

A comment is in order regarding the case of polymer UTPV where flexible atomic structure is conducive to strong polaron effect accompanying the electron localization. This exponentially increases the hopping resistance \( R_0 \), [84] thus improving the device vulnerability to leakage [Eq. (6.4)] and dielectric breakdown.
6.5 Conclusions

In conclusion, the characteristic physics of UTPV is due to the phenomena of electrode screening, current leakage, and shunting instability. Their respective practical implications include (1) grain (particle) sizes either much larger or much smaller than the device thickness, (2) the existence of critical thickness, below which the device performance is strongly affected by the leakage currents, (3) the dielectric breakdown conducive to shunting, especially under low illumination. The above effects originate from purely statistical ("fundamental") fluctuations in the charge and defect density, which cannot be suppressed by technology improvements and are not accounted for by the standard device modeling. As a potential remedy we point at properly designed interfacial layers that increase the defect chain resistances thereby mitigating the leakage and breakdown vulnerability.
Chapter 7

Conclusions

In this dissertation, five different and important aspects regarding thin film photovoltaics, classical p-n, and Schottky junctions were addressed:

7.1 Summary

1. *A field reversal model of CdS based photovoltaic junctions*

We have proposed a physical model that explains a variety of facts for CdS based photovoltaics by introducing the concept of field reversal. This model is solved analytically. Its predicted properties differ considerably from that of the standard p-n junction and call upon further experimental verifications.

The field reversal model emphasizes the interfacial properties, such as the interfacial morphology, related compression, and charges. In the terms of practical implications, they can be altered by tuning the deposition regimes, creating doping-induced stresses, applying proper interfacial treatments (layers), and
external bias during the cell fabrication.

2. Operations of piezo-photovoltaics

We have considered effects of piezo- or pyro- polarization in CdS layer on device operations, which further broadens the scope of parameters in thin-film PV technologies.

We show that the polarized CdS film can create a gull-wing shaped electric potential distribution with field reversal in the CdS region and its related electric potential drop is on the order of $\lesssim 1$ V. We prove that the gull-wing shaped electric potential distribution is generally beneficial for PV parameters making the technology rather forgiving with respect to variations in device and material parameters.

3. Long range potential fluctuations

We have theoretically described the properties of long-range random potential in thin structures sandwiched between two conductive layers (“electrodes”) discussed. The underlying criterion of structure thickness $L$ being smaller than the screening length of its constituting bulk material, corresponds to many practically important systems.

We have shown that in such systems, the lateral screening length and the space scale of random potential are due to the electrons in the electrodes, and are close to the structure thickness $L$. The random potential amplitude here is described analytically in a closed form and is specified for three practically important
cases of point defects, spherical grains, and columnar grains.

Such random potential can significantly change the photocurrent and voltage in either direction.

4. **Defect assisted tunneling**

We have shown that defect-assisted tunneling (hopping) transport mechanism can dominate the Schottky barrier formed by non-crystalline semiconductors. We have considered such a transport in a strong electric field of a Schottky barrier in a variety of systems that can have significant lateral resistances. Our results explain the observed leakiness of many practical junctions. Our theory offers a natural alternative to the well-recognized Tung’s model of fluctuating barrier heights.

5. **Ultra thin-film Photovoltaics (UTPV)**

We have shown that the unique physics of UTPV is due to the phenomena of electrode screening, current leakage, and shunting instability. Their respective practical implications include (1) grain (particle) sizes either much larger or much smaller than the device thickness, (2) the existence of critical thickness, below which the device performance is strongly affected by the leakage currents, (3) the dielectric breakdown conducive to shunting, especially under low illumination. The above effects originate from purely statistical (“fundamental”) fluctuations in the charge and defect density, which cannot be suppressed
by technology improvements and are not accounted for by the standard device modeling.
Appendix A

Numerical Simulations

This chapter introduces the technique of numerical simulations of semiconductors, particularly in solar-cell applications, and discusses the relevant physical models for transport, recombination, and generation. Subsequently, baseline parameter sets are presented that describe CIGS and CdTe thin-film solar cells; their characteristics are chosen to be similar to CIGS and CdTe record cells [2]. These baselines are used as a starting point for more complex models. The work presented here used the AMPS software developed at the Pennsylvania State University by S. Fonash et al. Its development was supported by the Electric Power Research Institute. The term AMPS abbreviates “Analysis of Microelectronic and Photonic Structures” and represents a computer code which allows the analysis of a broad variety of device structures under illumination or voltage bias or both. A detailed description of the solution techniques can be found in the AMPS manual [5]. Using as much experimental data as is available, modeling represents a meet-in-the-middle process where theory and experiments come together and find agreement in the calculated and experimental output. In the
agreement lies the gain in knowledge, transferring the information that was used for
the modeling to the experimental device. Nonetheless, modeling can be misleading
because of its complexity, and near-identical results for a limited data set can of-
ten be found using different assumptions. Therefore, every result must be carefully
checked, preferably through a set of experimental data.

**A.0.1 Governing Equations**

The device physics problem is presented in the form of the Poisson equation and
the electron- and hole-continuity equations [25]

\[ \nabla \cdot \epsilon \nabla \phi = -q(p - n + N_{D^+} - N_{A^-}), \quad (A.1) \]
\[ \nabla \cdot J_n = q(R - G) + q \frac{\partial n}{\partial t} - \nabla, \quad (A.2) \]

and

\[ J_p = q(R - G) + q \frac{\partial p}{\partial t} \quad (A.3) \]

where \( \epsilon \) is the dielectric constant, \( \phi \) is the electrostatic potential, \( n \) and \( p \) are the free
carrier concentrations, \( N_{D^+} \) and \( N_{A^-} \) are the density of ionized donor and acceptor
levels, \( J_n \) and \( J_p \) are the electron and hole current density, \( R \) is the recombination
rate, and \( G \) is the generation rate. In this work, only steady state solutions are
investigated and, hence,

\[ \frac{\partial n}{\partial t} = 0, \quad (A.4) \]
and
\[
\frac{\partial p}{\partial t} = 0.
\]  \hspace{1cm} (A.5)

The recombination terms in Eqs. (A.2) and (A.3) have non-linear dependencies on the carrier concentrations \( n \) and \( p \). Hence, Eq. (A.1) Eq. (A.3) represent a set of coupled non-linear differential equations, which will be solved by numerical methods with the typical approach: (1) discretization (meshing) of the device, (2) discretization of Eq. (A.1) Eq. (A.3), (3) application of boundary conditions (contacts), and (4) solution of the resulting matrix equation by iteration. The solution consists of the three state variables \( \phi, E_{fn}, \) and \( E_{fp} \), which are sufficient to deduce all other characteristics in steady state conditions. All simulations utilize Fermi-Dirac statistics.

### A.0.2 Device model parameters

Three types of parameters are necessary before any AMPS simulation can be started:

- Material properties for each layer, including front and back contact
- Environmental conditions
- Modeling settings, i.e. model type, grid spacing for the numerical calculations, bias voltages for which J-V and QE output should be generated

Material Properties: The material parameters that define the field reversal model are listed in Tables 2.1 to 2.3.
Environmental conditions: The illumination is discretely defined and it can be calculated from the standard AM1.5 spectrum [2]. The number of incident photons/(cm$^2$s) was entered for wavelengths between 0.38 $\mu$m and 0.90 $\mu$m, with a step size of 0.02 $\mu$m. The temperature for this case was set to 300 K.

Modeling settings: The AMPS software can operate in two distinct modes: the density of state (DOS) mode or the lifetime mode. A description of both modes can be found in the AMPS manual [5]. In essence, the lifetime mode accepts inputs in the form of carrier lifetimes, which are assumed constant, independent of light and voltage bias, and does not address the underling recombination processes. The DOS mode allows the definition of multiple defect states, using densities, energy distributions, and capture cross-sections. Based on this information recombination current and defect occupancy is calculated using the Shockley-Read-Hall formalism. All modeling done for this work used the DOS mode.

The grid spacing was selected to be denser in the thinner top layers of the device, where more rapid changes are to be expected in the band structure. Selected biases were entered as necessary; by default AMPS calculates QE and band structure for thermodynamic equilibrium, maximum power point, and under open-circuit conditions.
Appendix B

Some methodical aspects of device modeling

This appendix deals with two aspects of (mostly analytical) device modeling that are often overlooked and misinterpreted. The first is representation of a device in the form of two sub-devices connected in series. The well-known example is the case when a semiconductor structure contains the built-in electric potential corresponding the main PV junction and the back contact Schottky junction. It is customary to present such structures as two diodes connected in series. But is such a representation always correct? Another example is provided by our field reversal model analyzed in chapter 1 as a series connection of two opposing diodes.

The second problem concerns the diffusion approximation for semiconductor structures with non-monotonic electric potential.
B.1 Model of series connection

Consider a PV junction of two semiconductor layers (1 and 2). It can be represented as a combination of two components. In CdTe device of chapter 2 (Fig. 2-3), CdS and its tangent metal contact form one component and, similarly, CdTe and its tangent metal contact is the other component. Given band edge energies, each of the components makes a diode of its own. While these two components appear connected in series the electrical characteristics of the entire system are not necessarily described by the equivalent circuit of two diodes in series; we consider next the criterion of such a description.

To clarify the latter statement we first discuss the simplest diode model of a built-in uniform field between two electrodes. By drawing an imaginary cross-section we divide it into two parts seemingly connected in series (Fig. B-1). However blindly applying here the equivalent circuit of two diodes in series leads to an absurd conclusion that the integral device current is determined by the smallest of the component currents. For example, thinning the component (1) will strongly decrease it and the entire device current down to infinitesimally small values.

The latter apparent paradox originates from a hidden assumption that the imaginary division of device in Fig. B-1 (a) makes the two diodes of Fig. B-1 (b). However, Fig. B-1 (b) assumes a new element, which is a metal layer between the components. If such a metal layer was real, then, indeed the integral current would by the minimum of two components. In particular, a system shown in Fig. B-1 (b) could be
Figure B-1: The simplest diode model (a) of a built-in uniform field and imaginary cross-section (dashed line) dividing it into two imaginary diodes connected in series (b).

implemented by using the interconnect metal whose work function

\[ w = w_1 + \frac{l_1}{l_1 + l_2} (w_2 - w_1), \]

where \( w_1 \) and \( w_2 \) are the work functions of the parts 1 and 2, and \( l_1 \) and \( l_2 \) are the thickness of semiconductor layers. The difference between the imaginary and real division is therefore due to the inter-device metal connector.

The final step in our analysis is to note that the concept of the interconnect metal is tantamount to that of thermal equilibrium in the gap between the two semiconductor layers (metal acts as the electron bath). This equilibrium obviously does not exist in the case of imaginary cross section of Fig. B-1 (a), which solves the paradox.

The required condition of equilibrium is that the electrons have time to thermalize before they leave the interconnect region, i.e. the escape time \( \tau_{esc} \) is greater than the thermalization time \( \tau_{Th} \). We apply this condition to the case of field reversal in
Fig. 2-3. For these two times we have obvious estimates

\[ \tau_{esc} \sim \tau_{0,esc} \exp\left(\frac{V_B}{kT}\right) \quad \text{and} \quad \tau_{Th} \sim \tau_{0,Th} \exp\left(\frac{E_{F1}}{kT}\right) \]

where \( V_B \) is the barrier to overcome in order to the electron can leave the system and \( E_F \) is the Fermi energy measured from the minimum of conduction band.

The pre-exponentials can be roughly estimated as

\[ \tau_{0,esc} = \frac{a_T}{v_T}, \quad \tau_{0,Th} = \frac{1}{\nu_D}, \] (B.2)

here \( a_T \) is the spacial amplitude of thermal oscillations in the proximity of gull-wing singularity, \( a_T \sim kT/|E|e \) where \( |E| \) is the characteristic electric field strength, \( v_T \) is the thermal velocity and \( \nu_D \) is the Debye frequency. It is straightforward to see under the typical conditions, \( \tau_{0,esc} \sim \tau_{0,Th} \sim 10^{-12} - 10^{-14}s \). As a result the condition of thermalization takes a simple form

\[ V_B > E_F + kT. \]

We now observe that the latter condition does not apply to the case of imaginary division of Fig. B-1 (a) \((V_B = 0)\). However this condition can be easily satisfied for the field reversal model of Fig. 2-3. Similarly, it is satisfied for the back barrier configuration that is similar to Fig. 2-3.
B.2 The diffusion approximation

The diffusion approximation is commonly applied to describe the Schotky barrier current-voltage characteristics. Here we extend it to the cases of non-monotonic built-in potentials of Figs. 3-1(b) and 3-1(c).

The approximation is based on the current representation and the Einstein relation for the diffusion coefficient.

\[
J_n = \sigma \mathcal{E} + e D_n \frac{\partial n}{\partial x} = \mu_n n e \frac{d\phi}{dx} + kT \mu_n \frac{\partial n}{\partial x}, \quad D_n = \frac{kT}{e} \mu, \quad (B.3)
\]

here \( \phi \) is the electric potential, \( \sigma \) is the conductivity, \( \mathcal{E} \) is the electric field in the depletion region, \( D_n \) is the diffusion coefficient, \( \mu_n \) is the mobility, \( n(x) \) is the electron concentration, \( k \) is the Boltzmann’s constant and \( T \) is the temperature. The hole current can be written similarly.

Eq. (B.3) can be integrated (using \( \exp\left[\frac{e\phi(x)}{kT}\right] \) as an integrating factor) to yield

\[
\frac{1}{\mu_n kT} \int J_n \exp\left[\frac{e\phi(x)}{kT}\right] dx = -n(0) \exp\left[\frac{e\phi(0)}{kT}\right] + n(l) \exp\left[\frac{e\phi(l)}{kT}\right]. \quad (B.4)
\]

The standard assumption is that the current density is independent of \( x \) and is separated out from the integral. Because the integrand in Eq. (B.4) varies exponentially, the integral is dominated by a narrow proximity of a point where the potential energy \( e\phi \) is a maximum. In that proximity, the potential can be linearized to give
\[ e\phi(x) = e\phi_{\max} - \mathcal{E}_{\max}e x, \]

and

\[ \frac{J_n}{\mu_n kT} \exp \left[ - \frac{e\phi(l)}{kT} \right] \exp \left[ \frac{e\phi_{\max}}{kT} \right] \frac{kT}{\mathcal{E}_{\max}e} = n(0) \exp \left[ \frac{e(\phi(0) - \phi(l))}{kT} \right] - n(l). \]  

(B.6)

The latter standard assumption that \( J_n \) is independent of coordinates is violated when photogeneration and recombination take place. For example, the photogeneration at a rate \( g \text{cm}^{-3}s^{-1} \) leads to the linear dependence \( \partial J_n / \partial x = -g \). In spite of this complication, Eq. (B.6) retains its form when the dependance \( J_n(x) \) is weak compared to \( \exp[e\phi(x)/kT] \). Indeed, the integral is still dominated by the narrow proximity of electric potential maximum, across which the current remains almost constant. As a result

\[ \frac{J(\phi(x) = \phi_{\max})}{\mu_n kT} \exp \left[ - \frac{e\phi(l)}{kT} \right] \exp \left[ \frac{e\phi_{\max}}{kT} \right] \frac{kT}{\mathcal{E}_{\max}e} = n(0) \exp \left[ \frac{e(\phi(0) - \phi(l))}{kT} \right] - n(l) \]

where \( J(\phi(x) = \phi_{\max}) \) is the current density at the point where \( \phi(x) = \phi_{\max} \).

Eq. (B.6) is a general result that will be now specified for the dark and light
conditions. In the dark conditions (no photocurrent) the boundary conditions are

\[ e \phi(0) = -w(0), \]  
\[ e \phi(l) = -w(l) - eu, \]  
\[ n_d(l) = n_d(0) \exp \left[ \frac{w(l) - w(0)}{kT} \right], \]  
\[ n_d(0) = N_c \exp \left[ \frac{-w(0)}{kT} \right], \]

where \( w(0) \) and \( w(l) \) are work functions of the two metal contacts at \( x = 0 \) and \( x = l \) respectively and \( u \) is the applied voltage and \( N_c \) is the effective density of states.

According to Fig. 2-3, the maximum potential can be either at \( x = 0 \) or \( x = l \). At \( x = l \), it becomes \( \phi_{max} = \phi(l) \) and applying the boundary conditions from Eq. (B.8), yields

\[ J_p = J_{s0} \left[ \exp \left( \frac{eu}{kT} \right) - 1 \right]. \]  
\[ J_n = J_{s0} \left[ 1 - \exp \left( -\frac{eu}{kT} \right) \right]. \]

where \( J_{s0} = \mu_p \mathcal{E}_{max} e n_d(l) \). Similarly for the case of \( \phi_{max} = \phi(0) \)

Consider next the system under illumination where the electron-hole pairs are generated and the electron concentrations \( n(0) \) and \( n(l) \) are changed. Adding the
photogenerated electron concentration gives

\[ n_d(l) + \delta n(l) = n(l), \quad (B.14) \]
\[ n_d(0) + \delta n(0) = n(0), \quad (B.15) \]

here \( n_d(l) \) and \( n_d(0) \) are the dark electron concentrations and \( n(l) \) and \( n(0) \) are the electron concentrations under the illumination. The corresponding hole concentrations can be written as similarly. Substituting these new concentrations into Eq. (B.6) gives

\[
\frac{J_n}{\mu_n kT} \exp \left[ \frac{-e\phi(l)}{kT} \right] \exp \left( \frac{e\phi_{\max}}{kT} \right) \frac{kT}{(-E_{\max})} = n_d(l) \left[ \exp \left( \frac{e\phi(l)}{kT} \right) - 1 \right] + \delta n(0) \exp \left[ \frac{e(\phi(0) - \phi(l))}{kT} \right] - \delta n(l).
\]

We conclude that in all cases the J-V characteristics is determined by the maximum potential in the device. The position of \( \phi_{\max} \) varies between different models. For a particular field reversal model, \( \phi_{\max} \) can be found at either \( x = 0 \) or \( x = l \). On the other hand, the maximum point is in between the two electrodes for the “hunch” model of Fig. 3-1(c).
Appendix C

Long range potential

Here we consider the details of calculation underlying the results in chapter 4.

C.1 Point charges

The known electric potential induced by a point charge $q$ at point $z = z_0$ on the $z$-axis between two infinite parallel grounded conducting planes at $z = 0$ and $z = L$ (see J. D. Jackson ‘Classical Electrodynamics’- 3$^{rd}$ edition, equation (3.20)) [62]

$$\phi = \frac{4q}{\epsilon L} \sum_{n=1}^{\infty} \sin \left( \frac{n \pi z_0}{L} \right) \sin \left( \frac{n \pi}{L} \right) K_0 \left( \frac{n \pi \rho}{L} \right)$$  \hspace{1cm} (C.1)

where $\rho$ - the radial coordinate, $K_0$ is the modified Bessel function; (here we use Gaussian units).

Statistical fluctuations in point charge concentration are introduced by, $n = \langle n \rangle + \delta n$ where $\langle n \rangle$ is the average concentration, and fluctuations are spatially uncorrelated,
obeying the Gaussian statistics,

\[ \langle \delta n(r) \delta n(r') \rangle = \langle n \rangle \delta(r - r') \quad (C.2) \]

where \( r \) and \( r' \) are radius-vectors and \( \delta(r) \) is the delta-function. The electric potential by many charges can be represented as a sum of its average and fluctuation components,

\[ \phi = \langle \phi \rangle + \delta \phi. \quad (C.3) \]

The random potential amplitude in a plane \( z \) is defined as

\[ \overline{\delta \phi}(z) = \sqrt{\langle (\delta \phi(z))^2 \rangle} \quad (C.4) \]

where the coordinate \( z \) of the plane is arbitrary \((0 < z < L)\), but fixed. For the case of point random charges one gets

\[ \langle (\delta \phi)^2 \rangle = q^2 \int \int dr dr' \langle \delta n(r) \delta n(r') \rangle f(r)f(r') \]

\[ = q^2 \langle n \rangle \int dr [f(r)]^2 \quad (C.5) \]

with the correlation function from Eq. (C.2) where the radius vector \( r = (z_0, \rho) \) and \( f \) is the electric potential induced by a point charge \( q \) at \( z = z_0 \). The case of linear random charges is treated similarly with \( f \rightarrow f_L \) and \( r \rightarrow \rho \), here \( f_L \) is the potential induced by a linear charge.

The dispersion of the random potential for the point charge distribution is given
by,

\[
\langle (\delta \phi)^2 \rangle = \left\langle \left( \frac{4q}{\pi \epsilon L} \right)^2 \int \int \delta N(\vec{r}) \delta N(\vec{r}') d^3\vec{r} d^3\vec{r}' \sum_{n,n'=1}^{\infty} \sin \left( \frac{n\pi z_0}{L} \right) \sin \left( \frac{n'\pi z_0}{L} \right) \sin \left( \frac{n\pi z}{L} \right) \times \sin \left( \frac{n'\pi z}{L} \right) K_0 \left( \frac{n\pi \rho}{L} \right) K_0 \left( \frac{n'\pi \rho'}{L} \right) \right\rangle
\]  

with

\[
\langle \delta n(\vec{r}) \delta n(\vec{r}') \rangle = \langle n \rangle \delta(\vec{r} - \vec{r}')
\]  

By substituting this into Eq. (C.6) and using \(d^3\vec{r} = dz_0 d\rho \pi \rho\) we get,

\[
\langle (\delta \phi)^2 \rangle = \left\langle \left( \frac{4q}{\pi \epsilon L} \right)^2 \sum_{n,n'=1}^{\infty} \delta_{n,n'} \sin \left( \frac{n\pi z_0}{L} \right) \sin \left( \frac{n'\pi z_0}{L} \right) \int \sin \left( \frac{n\pi z}{L} \right) \sin \left( \frac{n'\pi z}{L} \right) dz_0 \int \rho K_0 \left( \frac{n\pi \rho}{L} \right) K_0 \left( \frac{n'\pi \rho'}{L} \right) d\rho \right\rangle
\]  

By using the following standard integrals,

\[
\int_{0}^{L} \sin \left( \frac{n\pi z_0}{L} \right) \sin \left( \frac{n'\pi z_0}{L} \right) dz_0 = \delta_{n,n'} \frac{L}{2}
\]  

\[
\int_{0}^{\infty} \rho d\rho K_0 \left( \frac{n\pi \rho}{L} \right) K_0 \left( \frac{n'\pi \rho}{L} \right) \approx \frac{L^2}{\pi^2} \frac{\ln \left( \frac{n}{n'} \right)}{(n^2 - n'^2)} \approx \delta_{n,n'} \frac{L^2}{\pi^2} \frac{1}{2n^2}.
\]
The final result takes the form

\[ \overline{\phi}(z) = \frac{4q}{\pi \epsilon} \sqrt{\langle n \rangle L} \left[ \sum_{n=1}^{\infty} \frac{\sin^2 \left( \frac{n \pi z}{L} \right)}{n^2} \right]^{1/2} \]  \quad (C.11)

C.2 Columnar charges

The random distributions of point charges can distribute over a columnar grain boundary to make a line charge. The corresponding potential,

\[ \phi_L = \int \phi \lambda dz_0, \]  \quad (C.12)

\[ = \int_0^L \frac{4q}{L} \frac{1}{\pi L \epsilon} \sum_{n=1}^{\infty} \sin \left( \frac{n \pi z}{L} \right) \sin \left( \frac{n \pi z_0}{L} \right) K_0 \left( \frac{n \pi \rho}{L} \right) dz_0 \]  \quad (C.13)

\[ \phi_L = \frac{8q}{\pi L \epsilon} \sum_{n=1}^{\infty} \frac{1}{n} \sin \left( \frac{n \pi z}{L} \right) K_0 \left( \frac{n \pi \rho}{L} \right), \]  \quad (C.14)

here \( \lambda \) is the linear charge density. The potential due to many such line grain boundaries,

\[ \phi = \overline{\phi} + \delta \phi, \]  \quad (C.15)

here \( \delta \phi \) is the random potential fluctuations. The columnar grains are randomly distributed in a thin semiconductor layer. The concentration of such grains \( n \) can be defined as,

\[ n = \bar{n} + \delta n \left( \bar{\rho} \right), \]  \quad (C.16)
here $\bar{n}$ represents the average concentration. The correlation function,

$$\langle \delta n(\vec{\rho})\delta n(\vec{\rho}') \rangle = \bar{n}\delta(\vec{\rho} - \vec{\rho}'). \quad \text{(C.17)}$$

The corresponding potential fluctuation is given by

$$\delta\phi(\vec{\rho}) = \frac{8q}{\pi L\epsilon} \delta n(\vec{\rho}) \sum_{n=1}^{\infty} \frac{1}{n} \sin\left(\frac{n\pi z}{L}\right) K_0\left(\frac{n\pi \rho}{L}\right) d\vec{\rho}$$

leading to the correlation function

$$\langle \delta\phi(\vec{\rho})\delta\phi(\vec{\rho}') \rangle = \left\langle \int d\vec{\rho} d\vec{\rho}' \left( \frac{8q}{\pi L\epsilon} \right)^2 \sum_{n,n'=1}^{\infty} \frac{1}{nn'} \sin\left(\frac{n\pi z}{L}\right) \sin\left(\frac{n'\pi z}{L}\right) \right.$$ \[
\times K_0\left(\frac{n\pi \rho}{L}\right) K_0\left(\frac{n'\pi \rho'}{L}\right) \delta n(\vec{\rho})\delta n(\vec{\rho}') \right\rangle \]

$$= \left\langle \left( \frac{8q}{\pi L\epsilon} \right)^2 \sum_{n,n'=1}^{\infty} \frac{1}{nn'} \sin\left(\frac{n\pi z}{L}\right) \sin\left(\frac{n'\pi z}{L}\right) \int d\vec{\rho} d\vec{\rho}' K_0\left(\frac{n\pi \rho}{L}\right) \right.$$ \[
\times K_0\left(\frac{n'\pi \rho'}{L}\right) \delta n(\vec{\rho})\delta n(\vec{\rho}') \right\rangle \]

Using here Eq. (C.17) and the fact that $d\vec{\rho} = 2\pi \rho d\rho$, we get

$$(\delta\phi(\rho))^2 = \bar{n} \sum_{n,n'=1}^{\infty} \frac{2\pi}{nn'} \left( \frac{8q}{\pi L\epsilon} \right)^2 \sin\left(\frac{n\pi z}{L}\right) \sin\left(\frac{n'\pi z}{L}\right) \int_0^{\infty} \rho d\rho K_0\left(\frac{n\pi \rho}{L}\right) K_0\left(\frac{n'\pi \rho}{L}\right). \quad \text{(C.20)}$$

From standard integral evaluations,

$$\int_0^{\infty} \rho d\rho K_0\left(\frac{n\pi \rho}{L}\right) K_0\left(\frac{n'\pi \rho}{L}\right) \approx \frac{L^2}{\pi^2} \frac{\ln\left(\frac{n}{n'}\right)}{n^2 - n'^2}. \quad \text{(C.21)}$$
Figure C-1: On calculating the potential due to a thin sheet of charge: $2h$ is the distance between two line charges, $x$ is the perpendicular distance from the sheet to the point of observation $P$.

By substituting this into the Eq. (C.21) we get,

\[
(\delta\phi(\rho))^2 = \frac{L^2}{n^2} \left(\frac{8q}{\pi L \epsilon}\right)^2 \sum_{n,n' = 1}^{\infty} \frac{2\pi}{nn'} \sin\left(\frac{n\pi z}{L}\right) \sin\left(\frac{n'\pi z}{L}\right) \ln\left(1 - \frac{n}{n'}\right) \ln\left(\frac{n}{n'}\right) \ln\left(\frac{n'}{n}\right) \ln\left(\frac{n'}{n}\right). \tag{C.22}
\]

When $n \Rightarrow n'$, $\delta\phi$ for the columnar electric charge distribution in a polycrystalline material can be approximately calculated as,

\[
\delta\phi \simeq \sqrt{n} \frac{8q}{\sqrt{\pi^4 \epsilon}} \left[\sum_{n=1}^{\infty} \sin\left(\frac{n\pi z}{L}\right) \right]^{1/2}. \tag{C.23}
\]

### C.3 A thin charge strip between metal electrodes

The potential due to a thin sheet of charge can be calculated as follows. Consider that sheet as a set of linear charges. The potential at point $P$ is evaluated by
introducing the following notations (see Fig. (C-1)).

\[
\rho \cos \alpha = x \quad \text{(C.24)}
\]

\[
dh = d(x \tan \alpha)
\]

\[
dh = x \frac{d\alpha}{\cos^2 \alpha}
\]

\[
\lambda = \sigma dh
\]

\[
\lambda = \sigma x \frac{d\alpha}{\cos^2 \alpha}
\]

where \(\sigma\) is the surface charge density and \(\lambda\) is the linear charge density.

The potential due to one linear charge \(q\) is,

\[
\phi_P = 8q \frac{\pi \epsilon}{L} \sum_{n=1}^{\infty} \frac{1}{n} \sin \left( \frac{n\pi z}{L} \right) K_0 \left( \frac{n\pi \rho}{L} \right) \quad \text{(C.25)}
\]

By substituting \(q/L = \lambda = \sigma x d\alpha/\cos^2 \alpha\) and integrating, we get

\[
\phi_{strip} = 8\sigma x \frac{\pi \epsilon}{L} \sum_{n=1}^{\infty} \frac{1}{n} \sin \left( \frac{n\pi z}{L} \right) \int_0^{\pi/2} \frac{d\alpha}{\cos^2 \alpha} K_0 \left( \frac{n\pi \rho}{L} \right) \quad \text{(C.26)}
\]

Introducing a new variable \(y = \frac{A}{\cos \alpha}, A = n\pi x/L\), one gets

\[
\cos \alpha = \frac{A}{y} \quad \text{(C.27)}
\]

\[
d\alpha = \frac{Ady}{y^2 \sqrt{1 - \frac{A^2}{y^2}}} \quad \text{(C.28)}
\]

Eq. (C.26) becomes
\[ \phi_{\text{strip}} = \frac{8\sigma x}{\pi \epsilon} \sum_{n=1}^{\infty} \frac{1}{n} \sin \left( \frac{n\pi z}{L} \right) \frac{1}{A} \int_{A}^{\infty} \frac{y dy}{\sqrt{y^2 - A^2}} K_0(y) \quad (C.29) \]

To evaluate the integral we again define \( y^2 = A^2 X \), then by using the standard tables of integrals,

\[
\frac{1}{A} \int_{A}^{\infty} \frac{y dy}{\sqrt{y^2 - A^2}} K_0(y) = \frac{1}{2} \int_{1}^{\infty} dX (X - 1)^{-\frac{1}{2}} K_0 \left( A \sqrt{x} \right) \quad (C.30)
\]

\[
= \frac{\pi}{2A} \exp(A) \quad (C.31)
\]

Finally by substituting the above result into Eq. (C.29), the potential due to a thin strip of charge is

\[
\phi_{\text{strip}} = \frac{4\sigma L}{\pi \epsilon} \sum_{n=1}^{\infty} \frac{1}{n^2} \sin \left( \frac{n\pi z}{L} \right) \exp \left( \frac{-n\pi x}{L} \right) . \quad (C.32)
\]

This shows that far from the strip the potential exponentially decays.
Appendix D

Defect assisted tunneling

This appendix provides more in detail derivations of results in chapter 5.

D.1 Optimum channels between resistive electrodes

Consider the right hand side of Eq. (5.8). The terms under the summation sign have the form

\[
\frac{\exp(-\eta x)}{\exp(\eta/x) + r}, \quad \eta = \sqrt{2L\lambda/a}, \quad (D.1)
\]

\[
x = N_i/N_{opt}, \quad r = R_i/R_0.
\]

They are maximum under the condition

\[
\exp(\eta/x) \left( \frac{1}{x^2} - 1 \right) = r. \quad (D.2)
\]

Consider the following constraints,
(1) \( \exp(\eta/x) \gg 1 \) when \( \eta \gg 1 \),

(2) \( r \exp(-\eta/x) \ll 1 \) if \( x \sim 1 \)

(1) and (2) gives, \( |1/x^2 - 1| \ll 1 \).

If \( x = 1 \), then \( 1/x^2 - 1 = 0 \) and it shows that Eq. (D.2)) cannot be satisfied. Otherwise if \( x \ll 1 \), then \( |1/x^2 - 1| \) is not very small.

Consider \( x = 1 - \delta \) where \( \delta \) is small, then \( 1/x^2 \simeq 1 + 2\delta \). Substituting this on the Eq. (D.2)), we get \( \delta = r/2 \exp(-\eta) \). This gives \( x = (1 - r/2 \exp(-\eta)) \) which is equivalent to \( N_{i-opt} \sim N_{opt} \). Finally, we get the optimum channel parameter given by Eq. (5.10).

Similarly, when \( r \gg 1 \)

\[
\exp(\eta/x) = r. \tag{D.3}
\]

We get \( x = \eta/\ln r \) and it gives the optimum channel parameter given by Eq. (5.11).

**Raikh and Ruzin Model**

Here we explain the derivation of the optimum conductance corresponding to Raikh and Ruzin model [71].

The partial conductance across a rectangular barrier can be written as the product of the probabilities of forming a channel and hopping in a given channel. It takes the form

\[
R^{-1} = R_0^{-1} \exp \left[ \frac{-2L}{Na} - \frac{\delta z}{a} - \frac{(\delta \rho)^2 N}{La} - \frac{\delta E}{kT} - N\lambda \right] \tag{D.4}
\]

where \( L \) is the film thickness, \( N \) is the number of defects, \( \delta z \) is the uncertainty in the \( z \) direction, \( \delta \rho \) is the uncertainty in the radial direction and hopping between
localized states may involve activation by $\delta \mathcal{E}$ (see Fig. D-1).

The optimization of the above equation with respect to the variables $\delta \rho$, $\delta z$, $N_{\text{opt}}$ and $\delta \mathcal{E}$ gives

$$\delta \rho_{\text{opt}} = \sqrt{La},$$

$$\delta z_{\text{opt}} = N_{\text{opt}}a,$$

$$N_{\text{opt}} = \sqrt{\frac{2L}{a\lambda}},$$

$$\delta \mathcal{E}_{\text{opt}} = N_{\text{opt}}kT.$$  \hspace{1cm} (D.5)

Substituting these optimized values into Eq. (D.4) yields Eq. (5.3). Also by substituting the above optimized values in the Eq. D.6, we can get Eq. (5.6).

$$\lambda = -\ln \left[g\delta \mathcal{E}\delta z(\delta \rho)^2\right].$$  \hspace{1cm} (D.6)

**D.2 Channels connected through resistive electrode**

For the case of resistive electrodes, we consider the following constraint: set the resistance of the optimum channel equal to the resistance of the lateral electrode. (Note: we consider that the contribution from the terms $\delta z$ and $\delta \rho$ is negligible)

$$R_t = R_0 \exp \left(\frac{2L}{Na} + \frac{\delta \mathcal{E}}{T}\right).$$  \hspace{1cm} (D.7)
The partial conductance,

\[ R^{-1} = R_0^{-1} \exp \left[ \frac{-2L}{Na} - \frac{\delta E}{T} - N\lambda \right]. \]  

(D.8)

By Lagrangian multiplier method we can optimize the Eq. (D.7) and Eq. (D.8).

\[ \frac{-2L}{Na} - \frac{\delta E}{T} - N\lambda - \Lambda \left( \frac{\delta E}{T} + \frac{2L}{Na} \right) = \Phi(N, \delta E) \]  

(D.9)

where \( \Lambda \) is the Lagrangian multiplier.

\[ \frac{\partial \Phi}{\partial N} \equiv \frac{2L}{N^2a} - \lambda - \Lambda \left( \frac{-2L}{N^2a} \right) = 0, \]

\[ \frac{2L}{N^2a} (1 + \Lambda) - \lambda = 0. \]  

(D.10)

\[ \frac{\partial \Phi}{\partial \delta E} \equiv -\frac{1}{T} + \frac{N}{\delta E} \frac{\Lambda}{T} = 0, \]

\[ -\frac{1}{T} (1 + \Lambda) + \frac{N}{\delta E} = 0. \]  

(D.11)

By using Eq. (D.10) and Eq. (D.11) the optimized parameters \( N \) and \( \delta E \),

\[ \delta E_{opt} = \frac{T \ln \frac{R_l}{R_0}}{(1 + \lambda)}, \]  

(D.12)

\[ N_{opt} = \frac{2L}{\lambda a \ln \frac{R_l}{R_0}} (1 + \lambda) \simeq \frac{2L}{a \ln \frac{R_l}{R_0}}. \]  

(D.13)

By substituting above optimal values on Eq. (D.8), we get the optimum conductance
given by Eq. (5.12).

**D.3 Triangular barrier model**

The purpose of this section is to explain the derivation of Eq. (5.21). The probability to find a defect channel,

\[ w_N = \left[ g\delta \delta z(\delta \rho)^2 \right]^N, \]

\[ w_N = \exp [-N\lambda], \]

(D.14)

here \( \lambda = -\ln [g\delta \delta z(\delta \rho)^2] \), \( g \) is the defect density of states (number of states per volume per energy—that is taken to be a constant),

The hopping rate is proportional to the tunneling probability, hence

\[ R^{-1} = R_0^{-1} \exp \left[ -\frac{2L_1}{a} - \frac{\delta z}{a} - \frac{(\delta \rho)^2 N}{La} - \frac{\delta \mathcal{E}}{T} \right]. \]

(D.15)
By substituting $L_1$ from Eq. (5.20) into Eq. (D.15) we get,

$$R^{-1} = R_0^{-1} \exp \left[ \frac{-2(V_0 - \delta \mathcal{E})}{FaN} - \frac{\delta z}{a} - \frac{(\delta \rho)^2 FN}{a(V_0 - \delta \mathcal{E})} - \frac{\delta \mathcal{E}}{T} \right].$$  (D.16)

The partial conductance supplied by $N$-defect chains is proportional to the product of the above two probabilities (Eq. (D.14) and Eq. (D.16)) and has the form

$$R^{-1} = R_0^{-1} \exp \left[ \frac{-2(V_0 - \delta \mathcal{E})}{FaN} - \frac{\delta z}{a} - \frac{(\delta \rho)^2 FN}{a(V_0 - \delta \mathcal{E})} - \frac{\delta \mathcal{E}}{T} - N\lambda \right]$$  (D.17)

where $R_0$ is a constant of the order of $\nu q^2/kT$, $\nu \sim 10^{13}s^{-1}$ is the characteristics phonon frequency and $q$ is the electron charge. The integral current through the barrier is determined by the optimum chains, which deliver a maximum to the latter exponent. Optimizing that exponent with respect to the variables $\delta \rho$, $\delta z$, $N$ and $\delta \mathcal{E}$ gives the optimum current and the corresponding chain parameters;

$$\delta \rho_{opt} = \sqrt{\frac{a(V_0 - \delta \mathcal{E})}{F}},$$  (D.18)

$$\delta z_{opt} = N_{opt} a = \sqrt{\frac{2a(V_0 - \delta \mathcal{E})}{F(1 + \lambda)}} \approx \sqrt{\frac{2a(V_0 - \delta \mathcal{E})}{F\lambda}},$$  (D.19)

$$N_{opt} = \sqrt{\frac{2(V_0 - \delta \mathcal{E})}{Fa(1 + \lambda)}} \approx \sqrt{\frac{2(V_0 - \delta \mathcal{E})}{Fa\lambda}},$$  (D.20)

$$\delta \mathcal{E}_{opt} = \frac{V_0}{\lambda(2\sqrt{\alpha} - 1)}.$$  (D.21)
here \( \alpha = (V_0 Fa/8T^2\lambda) \gg 1 \). By substituting those optimum parameters into Eq. (D.17) we can derive the optimum conductance,

\[
R^{-1} = R_0^{-1} \exp \left( -2N_{opt}(1 + \lambda) - \frac{\delta\mathcal{E}_{opt}}{kT} \right) \quad \text{(D.22)}
\]

\[
\simeq R_0^{-1} \exp \left( -2N_{opt} \lambda - \frac{\delta\mathcal{E}_{opt}}{kT} \right), \quad \lambda \gg 1
\]

\[
= R_0^{-1} \exp \left( -2 \sqrt{2\lambda(V_0 - \delta\mathcal{E}_{opt})} - \frac{\delta\mathcal{E}_{opt}}{kT} \right).
\]

By substituting \( \delta\mathcal{E}_{opt} \) from Eq. (D.21) into the above equation, we get

\[
R^{-1} \simeq R_0^{-1} \exp \left[ -2 \left( \frac{2\lambda}{Fa} \left( V_0 - \frac{V_0}{\lambda(2\sqrt{\alpha} - 1)} \right) \right)^{1/2} \right] \quad \text{(D.23)}
\]

\[
\times \exp \left[ -\frac{V_0}{\lambda(2\sqrt{\alpha} - 1)kT} \right].
\]

We consider \( \alpha \gg 1 \) and \( \lambda \gg 1 \), then we get the optimum conductance,

\[
R^{-1} \simeq R_0^{-1} \exp \left( -2 \sqrt{\frac{2V_0\lambda}{Fa}} \right). \quad \text{(D.24)}
\]

Next we give the details of derivation of Eq. (5.23). The following constraint is imposed: sets the optimum channel resistance equal to that of a resistive electrode:

\[
R_t = R_0 \exp \left( \frac{2(V_0 - \delta\mathcal{E})}{Na} + \frac{\delta\mathcal{E}}{T} \right) \quad \text{(D.25)}
\]
The partial conductance

\[ R^{-1} = R_0^{-1} \exp \left[ \frac{-2(V_0 - \delta \mathcal{E})}{Na} - \frac{N\lambda}{T} - N\lambda \right]. \quad (D.26) \]

By Lagrangian multiplier method we can optimize the Eq. (D.25) and Eq. (D.26) to derive the optimum conductance,

\[ \frac{-2(V_0 - \delta \mathcal{E})}{Na} - \frac{\delta \mathcal{E}}{T} - N\lambda - \Lambda \left( \frac{\delta \mathcal{E}}{T} + \frac{2(V_0 - \delta \mathcal{E})}{Na} \right) = \Phi (N, \delta \mathcal{E}) \quad (D.27) \]

where \( \Lambda \) is the Lagrangian multiplier.

\[
\frac{\partial \Phi}{\partial N} \equiv \frac{2(V_0 - \delta \mathcal{E})}{N^2 Fa} - \lambda - \Lambda \left( \frac{-2(V_0 - \delta \mathcal{E})}{N^2 Fa} \right) = 0, \\
\frac{2(V_0 - \delta \mathcal{E})}{N^2 Fa} (1 + \Lambda) - \lambda = 0. \quad (D.28)
\]

\[
\frac{\partial \Phi}{\partial \delta \mathcal{E}} \equiv \frac{-1}{T} + \frac{N}{\delta \mathcal{E}} - \frac{\Lambda}{T} + \frac{2}{FaN} (1 + \Lambda) = 0, \\
\frac{2}{FaN} (1 + \Lambda) - \frac{1}{T} (1 + \Lambda) + \frac{N}{\delta \mathcal{E}} = 0. \quad (D.29)
\]

By using Eq. (D.28) and Eq. (D.29) we find the optimum parameters

\[ N_{\text{opt}} = \frac{2V_0}{Fa \lambda \ln r} (1 + \lambda) \approx \frac{2V_0}{Fa \ln r}, \quad (D.30) \]
\[ \delta \mathcal{E}_{opt} = \frac{T \ln r}{(1 + \lambda)} \approx \frac{T \ln r}{\lambda}. \]  (D.31)

By substituting above optimal parameters into Eq. (D.26) we get Eq. (5.23).
Bibliography


[5] AMPS is a software package developed by Penn State University and aimed at simulating semiconductor multilayer devices.


[40] We are grateful to A. L. Fahrenbruch who suggested this method of AMPS modeling.


[80] D. Shvydka and V. G. Karpov. unpublished data.


