# CONTACT RESISTIVITY ANALYSIS OF DIFFERENT PASSIVATION LAYERS VIA TRANSMISSION LINE METHOD MEASUREMENTS

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## Approval of the Thesis:

## CONTACT RESISTIVITY ANALYSIS OF DIFFERENT PASSIVATION LAYERS VIA TRANSMISSION LINE METHOD MEASUREMENTS

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## ABSTRACT

## CONTACT RESISTIVITY ANALYSIS OF DIFFERENT PASSIVATION LAYERS VIA TRANSMISSION LINE METHOD MEASUREMENTS

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Crystalline silicon (c-Si) homojunction solar cells constitute over 90% of the current photovoltaic market. Although the standard solar cells are cost effective and easy to process, their efficiency potential is unfortunately limited. Currently, more innovative cell concepts appeared with their high efficiency potential coupled with low costs. Since the recombination at surfaces and under metal contacts is one of the major obstacles against high conversion efficiencies, surface passivation has primary importance in solar cell design. However, the challenging part is reducing surface recombination and properly conducting electrical current simultaneously. To perform these requirements, depositing a thin interface oxide layer and a conductive thin film on top of it, under metal regions, namely passivation layer is a suitable solution. Simultaneously having low contact resistivity and recombination velocity is necessary for such structures. For this, different passivating contact structure have been applied by different research groups.

The goal of this thesis is to analyze 3 different passivating contact structures in terms of contact resistivity. Electron beam (e-beam) evaporated in-situ doped (n)

passivating contact, PECVD deposited in-situ doped (n) TOPCon passivating contact and LPCVD deposited and ex-situ doped (n) Poly-silicon passivating contact structures are the major type of investigated cell designs. The focus of this analysis is on the contact resistivity extraction of these layers. Oldest 1D-TLM contact resistivity extraction method coupled with the recently published 2D-TLM method is applied for all samples. Additional novel idea also presented in this work is applying a new contact resistivity evaluation method using 3D numerical simulations. This method could only be applied to a few samples within the scope of this thesis.

The trade-off between the contact properties ( $\rho_{contact}$ ) and the passivation quality (iV<sub>OC</sub>) is investigated for various oxide layers obtained via different methods and post annealing temperature following passivation layer deposition. The methods of extracting contact resistivity are also compared. 900 °C annealed HNO<sub>3</sub> sample shows as good contact resistivity as non-oxided sample with a contact resistivity of 0.9 m $\Omega$ •cm<sup>2</sup> using 1D-TLM evaluation and 0.56 m $\Omega$ •cm<sup>2</sup> using 2D-TLM evaluation. Differentiation of resistivity values between metal/TOPCon interface ( $\rho_{c1}$ ) and TOPCon/bulk interface ( $\rho_{c2}$ ) could be done via the 3D numerical simulation method with the help of plasma etching coupled with numerical simulations.  $\rho_{c1}$  and  $\rho_{c2}$  were found to be 0.1 and 0.25 m $\Omega$ •cm<sup>2</sup> respectively for this specific sample. The 3D numerical simulation technique developed for contact resistivity analysis can be applied to a wide variety of structures with as few as possible assumptions.

This work contributes to the research and development of high-efficiency silicon solar cells by providing new insights on the properties of passivating contacts. The methods of extracting contact resistivity are additionally compared and the most realistic evaluation method was also presented and performed on some of the samples.

**Keywords:** *passivating contact, silicon solar cells, specific contact resistivity, transmission line method.* 

## FARKLI PASİVASYON KATMANLARININ İLETİM HATTI MODELİ YOLUYLA KONTAK DİRENCİ ANALİZİ

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Kristal silisyum (c-Si) homo-eklem güneş hücreleri mevcut fotovoltaik pazarın % 90'ından fazlasını oluşturmaktadır. Standart güneş hücreleri maliyet açısından etkili ve kolay işlenmekle birlikte, malesef verimlilik potansiyelleri sınırlıdır. Son zamanlarda, düşük maliyetlerle üretilen yüksek verimlilik potansiyeline sahip daha yenilikçi kavramlar ortaya çıkmıştır. Yüzeylerdeki ve metallerin altındaki rekombinasyon, yüksek verimliliğin önündeki büyük engellerden olduğu için, yüzey pasivasyonu, güneş hücrelerinin tasarımında büyük öneme sahiptir. Bununla birlikte, hücre yapılarında, aynı anda yüzey rekombinasyonunu azaltmak ve elektrik akımını iletmek güçtür. Bu gerekleri yerine getirmek için, metal bölgeleri altındaki silisyum alttaş üzerinde çok ince bir oksit tabakası ve iletken ince bir filmin, yani pasivasyon tabakasının kaplanması uygun bir çözümdür. Bu tür yapılar için düşük kontak direnci ve düşük rekombinasyon hızının eş zamanlı sağlanması gereklidir.

Bu tezin amacı, bu yüksek verim potansiyelli hücrelerde kullanılan farklı pasivasyon yapılarını analiz etmektir. Yerinde (n) katkılı elektron demeti

buharlaştırma sistemi (EBPVD) ile hazırlanmış silisyum ince filmler, yerinde (n) katkılı plazma destekli kimyasal buhar biriktirme (PECVD) ile hazırlanmış silisyum ince filmler ve düşük basınçta kimyasal buhar biriktirme (LPCVD) ile hazırlanmış ve sonradan (n) katkılanmış pasivasyon katmanları incelenmiştir. Bu çalışmanın odağı, bu tabakaların kontak direnç analizi üzerinedir. 1 boyutlu iletim hattı modeli (1D-TLM) ve son zamanlarda yayınlanmış 2 boyutlu iletim hattı modeli (2D-TLM) uygulanmıştır. Bu çalışmada, 3 boyutlu sayısal simülasyonları kullanarak yeni bir kontak direnç değerlendirme yöntemi geliştirilerek, kontak direnci hesaplama yöntemlerine bir yenisi eklenmiştir. Bu yöntem, bu tez kapsamında sadece birkaç seçilmiş örneğe uygulanmıştır.

Kontak direnci ve pasivasyon arasındaki ödünleşime sıkça rastlanmıştır. Kontak direnci hesaplama yöntemleri de, bu çalışma kapsamında karşılaştırılmıştır. 900 °C sıcaklıkta tavlanmış nitrik asit oksitli numune, 1D-TLM değerlendirmesinden sonra yaklaşık 0.9 m $\Omega$ •cm<sup>2</sup>, 2D-TLM değerlendirmeden sonra 0.56 m $\Omega$ •cm<sup>2</sup> civarında kontak direnci gösterir. Metal/pasivasyon katmanı arayüzü ( $\rho_{c1}$ ) ile pasivasyon katmanı/alt taş arayüzü ( $\rho_{c2}$ ), bu yeni sayısal simülasyon yöntemi ile birlikte plazma aşındırmanın da yardımıyla ayrı ayrı hesaplanabilmiştir.  $\rho_{c1}$  ve  $\rho_{c2}$  bu spesifik örnek için sırasıyla, 0.1 ve 0.25 m $\Omega$ •cm<sup>2</sup> olarak bulunmuştur. Kontak direnci analizi için geliştirilen bu sayısal simülasyon tekniği, mümkün olan en az sayıda varsayım içerirken, çok çeşitli yapılara da uygulanabilir.

Bu çalışma, pasive edilmiş kontakların özelliklerine yeni bakış açıları sağlayarak yüksek verimli silikon tabanlı güneş hücrelerinin araştırılmasına ve geliştirilmesine katkıda bulunmaktadır. Kontak direnci hesaplama yöntemleri de karşılaştırılarak en gerçekçi değerlendirme metodu olan 3 boyutlu sayısal simülasyonlar yoluyla hesaplama yöntemi de bazı örneklerde sunulmuş ve uygulanmıştır.

Anahtar Kelimeler: pasifleştirici kontak, silikon güneş pilleri, spesifik kontak direnci, iletim hattı modeli.

Dedicated to all real explorers...

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# NOMENCLATURE

a-Si:H	Hydrogenated amorphous silicon
AM	Air Mass
Al	Aluminum
ARC	Anti-reflection coating
BSF	Back surface field
С	Capacitance
CB	Conduction band
c-Si	Crystalline silicon
$CO_2$	Carbon dioxide
Cz	Czochralski
CVD	Chemical Vapor Deposition
DI	Deionized
EBPVD	e-beam physical vapor deposition
ECV	Electrochemical capacitance voltage
E <sub>G</sub>	Energy band gap
$E_{M,F} \\$	Metal fermi level
eV	Electron volt
FE	Field emission
FF	Fill factor
FZ	Float-Zone
G	Photogeneration rate
GW	Gigawatt
HF	Hydrofluoric
HIT	Heterojunction with intrinsic thin layer
HJBC	Heterojunction Back Contact
HTJ	Heterojunction

IBC	Interdigitated-back-contact
ICP	Inductively coupled plasma
Io	Saturation current
IL	Light generated current
I <sub>SC</sub>	Short circuit current
I-V	Current-Voltage
J	Current density
$\mathbf{J}_{\mathrm{MPP}}$	Current density at maximum power point
$\mathbf{J}_0$	Dark saturation current density
J <sub>SC</sub>	Short circuit current density
kWh	Kilowatt-hour
LCOE	Levelized cost of electricity
L <sub>D</sub>	Diffusion length
LPCVD	Low pressure chemical vapor deposition
L <sub>T</sub>	Transfer length
MIS	Metal-Insulator-Semiconductor
MS	Metal-Semiconductor
MW	Megawatt
NAOS	Nitric acid oxidation of silicon
$N_0$	Photon flux
N <sub>D</sub>	Doping concentration
NREL	National renewable energy laboratory
PECVD	Plasma enhanced chemical vapor deposition
P(E)	Tunneling probability
P <sub>MPP</sub>	Power density at maximum power point
POLO	Poly-silicon on oxide
PV	Photovoltaic
R <sub>C</sub>	Contact resistance
RCA	Radio corporation of America
RPHP	Remote Plasma Hydrogen Passivation

R <sub>S</sub>	Series resistance
R <sub>SH</sub>	Shunt resistance
SE	Spectroscopic ellipsometry
SiN <sub>X</sub>	Silicon nitride
SiO <sub>2</sub>	Silicon dioxide
SPC	Solid phase crystallization
SRH	Shockley-Read-Hall
SQ	Shockley–Queisser
TCO	Transparent conductive oxide
TE	Thermionic Emission
$T_{\text{eff}}$	Effective Lifetime
TFE	Thermionic-Field Emission
Ti/Pd/Ag	Titanium/Palladium/Silver
Ti/Pd/Al	Titanium/Palladium/Aliminum
TLM	Transmission line method
TOPCon	Tunnel oxide passivated contact
U	Net recombination rate
V	Voltage
VB	Valence band
V <sub>bi</sub>	Built-in potential
$V_{MPP}$	Voltage at maximum power point
V <sub>OC</sub>	Open circuit voltage
WF <sub>M</sub>	Metal work function
WF <sub>SC</sub>	Semiconductor work function
QSSPC	Quasi-steady-state photoconductance
$\rho_c$	Specific contact resistivity
q	Elementary charge
η	Cell conversion efficiency
$\Phi_{\rm B}$	Schottky barrier height
Xd	Depletion width

## **CHAPTER 1**

## **INTRODUCTION**

## 1.1. Current Status of World Energy

The growth in the world economy, population and urbanization necessitates the developments in life-sustaining operations such as industry, electricity, transportation or food obtainment. With the expansion of these fields, global demand for energy rapidly rise which is primarily led by developing countries.

The Energy Information Administration (EIA)'s International Energy Outlook 2016 notes that global energy consumption will increase by 48 percent over the next three decades [1]. According to this outlook, while the dominant energy source will remain as natural gas, the fastest-growing energy sources are expected to be renewables and nuclear power between 2012 and 2040 with an increase rates of 2.6% and 2.3% per year respectively as illustrated in Figure 1. Coal, natural gas and renewable energy sources will contribute roughly same shares (28-29%) of electricity production in 2040, according to EIA's projection.



Figure 1: World energy consumption by source 1990-2040 [1].

When the current state of renewable energy sources is examined closely, it can be seen that the most additions of renewable energy are hydropower, wind and solar energy (Figure 2). Since 2013, while wind and solar photovoltaic (PV) technology have been dominating the market share, hydropower has remained at the same levels. According to the International Renewable Energy Agency (IRENA), the growth in the wind power (66 GW) and solar PV power (47 GW) in total, exceeded the hydropower in 2015, for the first time in the history. Moreover, solar PV technology is mentioned to be represented the most rapidly growing share in this field [2].



Figure 2: World net electricity generation from renewable power 2012-2040 [1].

Moreover, the need for cost effective clean energy systems has shown up while the demand is increasing worldwide. Renewable Energy Policy Network (REN21), reported that the cost of producing photovoltaic generators are dramatically declined by 58% in 2015 according to the 2010 costs owing to the enhancements in technology and manufacturing [3]. The cost of the electricity (called Levelized Cost of Electricity – LCOE) has reached values below 0.05 \$/kWh in some favorable places in the world. This value is very competitive with other energy producing sources. This trend is expected to sustain and to decrease another 57% by 2025 as against 2015 costs. By decreasing the cost, solar PV with many advantages, will be the main source of energy in the near future.

#### **1.2. History and Development of Photovoltaics**

Physical phenomenon describing the conversion of light into electricity is known as photovoltaic effect. Like many other discoveries in the history, photovoltaics began in the 1830's as a coincidence while French Physicist A.E. Becquerel was experimenting a solid electrode in an electrolyte solution. He observed the generation of electrical current in his experimental system. 40 years later, an English engineer Willoughby Smith observed a conductance rise with illumination via the difference in electricity travel through selenium in light and at dark, while testing the telegraph lines, by chance [4].

The first electricity generation from a PV device was carried out by W.G. Adams and R.E. Day using selenium material. In this way, they could prove that a solid material is able to transfer light into electricity without any additional source even if the output power was not sufficient to run every day electrical equipment in those days [4].

In 1914, photovoltaic features of metal-semiconductor surfaces and the existence of a barrier layer in PV devices were discovered by Goldman and Brodsky, followed by the theoretical explanation of energy barriers by Schottky in 1930's [5].

At that time, with an increasing attention on silicon for its use in PV field, the invention of single-crystal silicon ingot by a Polish scientist Jan Czochralski has led to production of monocrystalline solar cells [6]. A solar cell converts sunlight into electricity while producing current and voltage, acting like a diode when the light shines on it.

Even with a limited information about dopants and junction formation in PV devices, the first silicon solar cells were formed by cutting the ingot into the fractions including p type and n type zones with a natural junction and applying metal contacts to it, in 1941 [7]. Later on, in 1954, Chapin, Fuller and Pearson demonstrated the first modern silicon solar cell with an efficiency of 6% in Bell Laboratories [8]. They have proven their solar device by utilizing it to run a small Ferris wheel toy and a radio transmitter. This breakthrough has opened the first real prospects for solar PV with a huge improvement among its previous counterparts. The New York Times marked it as "the beginning of a new era, leading eventually to the realization of one of mankind's most cherished dreams", the next day on its front page [9].

Production of the first solar cells were expensive and mass production was a long way off. However, in less than a few decades, solar cells were started to be used in satellites and space-crafts for the space research and sun-powered automobiles. In 1970's, with the establishment of large photovoltaic companies, the worldwide photovoltaic module production gained steam. After that, large scale solar cell producers started to look for a way to produce cheaper PV devices with higher efficiency values. After 1980's, technology has been rapidly developed and more than 20% efficiency values were obtained in a few decades [4].

Figure 3 shows both the global solar panel prices/watt and installations per year. As can be seen from the figure, the price of solar PV was higher than \$100/watt in 1975 with the total amount of almost 2 Megawatts (MW) global installations. Until the 2015, the price has drastically decreased being around \$0.61/watt when installation amount has increased up to 65 Gigawatts (GW) [10].



Figure 3: Global solar panel prices/watt and solar panel installations per year [10].

It is obvious that lower solar panel prices are needed as well as the higher efficiency values in order to use solar energy much effectively. In terms of efficiency, there are fewer researches on solar panels, but solar cells are investigated since they are the core of the solar technology. The following well-known chart in Figure 4 is an up to date plot of compiled values of highest confirmed conversion efficiencies prepared by The National Renewable Energy Laboratory (NREL). In this impressive chart, all the different technologies are included, from crystalline and thin-film, to organic cells, dye-sensitized, perovskite cells, single- and multi-junction cells and more.

Basically, because the highest efficient devices requires high production costs and conversely the cheaper materials show low operating efficiency and durability, silicon material dominates the PV market currently. In other words, even though silicon is not the best material for solar cell operation because of its unsuitable band gap and low absorption properties, its advantages such as easy and large scale process conditions, availability, and well known material properties makes it difficult for other materials to compete.



Figure 4: The best research-cell efficiencies [11].

Crystalline silicon (c-Si) solar cells technology is the most common commercially used technology representing more than 90% of world PV cell market share owing to excessive amount of raw material available coupled with comparably high efficiencies than the competitors. c-Si PV cells are commonly produced from single-crystal (mono-crystalline) or multi-crystalline silicon wafers [12]. Recently, laboratory efficency values over 26% and over 21% have been demonstrated for monocrystalline and multi-crystalline solar cells, respectively.

With the new technology developments, solar energy is expected to continue improving steadily with higher cell efficiencies combining with lower production costs and hence to play a vital part in energy landscape in the near future.

#### **1.3.** Principles of Solar Cell Operation

#### **1.3.1.** Solar Irradiance

The surface of the sun, in other words photosphere, approximates a blackbody with a temperature about 6000 Kelvin. However, an object standing in a distance from the sun, like Earth, faces only a fraction of the overall power radiated by the sun. Solar irradiance means the power density received from the sun and it decreases as the distance from any object to sun increases. Whereas the solar irradiance reaches the Earth atmosphere is accepted to be almost constant, at the surface of the Earth it varies. This variation may be due to atmospheric effects such as absorption, scattering because of the water molecules and  $CO_2$  or some locational effects such as pollution, location, season or the time of the day. There is an air mass coefficient defined to characterize the solar spectrum after solar irradiance has reached to earth through atmosphere.

Air Mass (AM) is used to evaluate the distance of sun rays travelled through the atmosphere till the Earth's surface. It can be calculated as follows;

air mass = 
$$\frac{\text{path length travelled}}{\text{vertical depth of the atmosphere}} = \frac{1}{\cos(\theta)}$$
 (Eq. 1.1)

where  $\theta$  is 'zenith angle' that is the angle between position of the sun at the given time and its zenith. This means if the sun is 90 degrees above the horizon ( $\theta=0$ ), air mass can be calculated to be 1 and the spectrum is called 'AM1'. In this case, spectrum 'AM0' occurs outside the Earth's atmosphere (Figure 5). AM1.5 is usually taken to be the universal standard and it corresponds to the angle 48.2° between the position of Sun and zenith for a clear sunny day.



Figure 5: Air Mass changing with the zenith angle.

Figure 6 shows the change of spectral with respect to AM. In this figure, AM1.5 is separated into its components as 'AM1.5 Global' and 'AM1.5 Direct' where the former stands for both direct and diffuse radiation while the latter is only for direct radiation [13].



Figure 6: Solar energy spectrum of the atmosphere [14].

## 1.3.2. Basics of Semiconductors

Semiconductor is a material having electrical conductivity between metals and insulators. In other words, semiconductors conduct electricity less than a conductor such as gold or silver and conduct more than an insulator such as glass or ceramic. So, the flow of carriers can be controlled in the device owing to this semi-conducting behavior. Materials can be classified according to the band gap (Eg) which is defined as the minimum energy required to excite an electron from maximum attainable VB to the minimum attainable conduction band. While in insulators, valence band (VB) electrons are separated from the holes in the conduction band (CB) by a large gap, in conductors these two bands overlap. In semiconductor case, the gap is small enough so that some external alterations such as temperature, optical excitation and doping can increase conductivity. In the case of solar cell operation, sun ray photons having sufficient energy can excite the electrons to conduction band, and these electrons contribute to the power generation.

Semiconductor parts of the device are the most important regions of the solar cell and hence their properties mostly affect the solar cell performance. These materials can either be a single element from group IV of the periodic table for instance Ge or Si; a compound from combination of group III-V such as GaAs, InP or an alloy such as  $Al_xGa_{(1-x)}$ [15]. Silicon is the most widely used semiconductor material in solar cell technology.

The design and the operation performance of the solar cells primarily depend on the semiconductor material properties. Some main features affecting the performance of solar cell involves band gap energy (*Eg*), absorption coefficient ( $\alpha$ ), refractive index (*n*), mobility ( $\mu$ ), lifetime ( $\tau$ ) or diffusion length (*L*<sub>D</sub>), donor and acceptor atom concentrations, etc. [16]. Most of these properties will be discussed in detail in the following chapters.

With the atomic number of 14, silicon atom has 14 electrons around the nucleus in which outermost 4 of them are the valence electrons creating covalent bonds between Si atoms via sharing electrons. So, silicon can be bonded to 4 other Si atoms around it in crystalline form, which can be seen in Figure 7a. Coupled with the lattice constant of 5.4 Å, there can be found  $5 \times 10^{22}$  Si in each cm<sup>3</sup>. If there is no impurity atoms, the material can be called as 'intrinsic semiconductor' as in the figure below [15]. Intrinsic semiconductors contain electron and holes in which the carrier concentration  $n_i$  refers to the concentration of electron-hole pairs formed in consequence of breaking covalent bonds (Figure 7b). Eventually, concentration of electrons is equal to that of holes which is approximately  $1.5 \times 10^{10}$  per cm<sup>3</sup> in an intrinsic semiconductor at room temperature [16].



Figure 7: Schematic representation of covalent bonds in a silicon crystal lattice. No broken bonds (a), a bond broken and carriers (b).

The properties of the band gap of semiconductor is also one of the most vital properties affecting the performance of the solar cell. The band gap for silicon at 300 K is 1.12 eV [17]. In semiconductors, valence and conduction bands do not necessarily located at the same value of momentum. As shown in the Figure 8a, if the bottom of the CB has the same momentum with the top of the VB, it is called 'direct band gap semiconductor' while if they stay at different momentum values, it is called 'indirect band gap semiconductor' in which silicon is an example of (Figure 8b). In short,

electron should undergo both an energy and a momentum change in order to produce charge carriers in silicon case unlike the direct band gap semiconductors [18].



**Figure 8:** Schematic band diagrams for (a) a direct gap material, (b) and an indirect gap material [18].

### **1.3.3.** Light Absorption and Carrier Generation

Operation of a solar cell necessarily begins with light absorption by the active layer which leads to generation of electron-hole pairs if the incident photon has an energy equal or greater than that of the band gap of the bulk material. Generating an electron-hole pair basically means exciting a negatively charged electron into the conduction band while leaving a hole acting as positive charge, in the valence band. This generation occurs after photon absorption within the semiconductor at an arbitrary depth.

Absorption depth means how deep the sun light passes through the semiconductor before being absorbed and it is inversely proportional to the "absorption coefficient" of the bulk material. This is why the thickness of the device is important while designing a solar cell. Photons having higher energy, e.g. blue light, have shorter absorption depths and hence are absorbed near to the surface of solar cell and vice versa.

One can calculate the electron-hole pair generation rate at an arbitrary location in the solar cell using the equation below.

$$G = \alpha N_0 e^{-\alpha x}$$
 (Eq. 1.2)

where  $\alpha$  corresponds to absorption coefficient in (cm<sup>-1</sup>),  $N_0$  is the photon flux defined as the number of photons per unit area per unit time (cm<sup>-2</sup>s<sup>-1</sup>) at the surface and x is the distance (cm) of the photon penetrating into the material. Hence, it is obvious that the generation rate is highest at the surface and declines exponentially within the material. Furthermore, the incident light is the combination of different wavelengths. Thus, the generation rate also differs depending on the wavelength [19].

#### 1.3.4. Formation of p-n Junction and Carrier Transport

N type region corresponds to high electron concentration while p type region stands for high hole concentration. These regions are generally created by changing the number of electrons and holes in the semiconductor via 'doping' with materials from group III and V atoms for Si. Bringing n and p type regions together, p-n junction is formed. As can be seen in Figure 9 below, diffusion of electrons from n-region to p-
region and that of holes in the reverse direction occurs until the concentration of carriers becomes equal. Between the holes left behind in n-region and electrons passed to p-region an electrical field is induced. This induced electric field results in a drift current through the junction region. In this junction region, a built in potential  $V_{bi}$  is formed due to the Fermi level differences at equilibrium. In other words, concentration gradient of carriers leads to diffusion current, while the drift current depends on the electric field. Close to the junction, amount of bend bending and the strength of electric field as shown in the Figure 9 depends on the difference between Fermi levels of n and p type. Away from the junction, bulk conditions dominates and no electrical field or built in potential exists through the rest of the system.



Figure 9: Energy band diagram for the p-n junction in thermal equilibrium.

## **1.3.5.** Contact Formation and Carrier Collection

After the light absorption and carrier generation and separation within the p-n junction, the next step is the collection of these created carriers before they recombine and get lost. By placing ohmic metal semiconductor contacts at both n- and p-type sides of the junction, and connecting them to an external load, light-generated carriers

flow through this external circuit and collected. The difference in Fermi levels of both regions indicates the voltage measured on this load.

The collection probability refers to that the rate of carriers joining the lightgenerated current to the carriers generated by the absorption of light. This probability mainly depends on the diffusion length of carriers and the distance they have to penetrate until being collected. Collection probability decreases while getting far away from the junction, especially when the distance to the junction is larger than the diffusion length or when the surface passivation is so poor that the carriers recombine much more than being collected.

# 1.3.6. Basic Solar Cell Characterization Parameters

The performance and energy conversion capability of solar cells is assessed through current-voltage (I-V) characterization. The light shifts the dark I-V curve by an amount of light generated current along y-axis, as shown on the left side of Figure 10. In non-illuminated case, the PV cell behaves like a diode. When the intensity of light rises, current is generated by the solar PV cell, as illustrated in Figure 10.



Figure 10: I-V curve of solar cell and relevant electrical circuit.

I-V behavior of a PV cell can be modeled by the ideal diode equation under dark and illuminated conditions in the first quadrant as in Eq. 1.3 and Eq. 1.4 respectively.

$$I = I_0 (e^{qV/kT} - 1)$$
 (Eq. 1.3)

$$I = I_L - I_0 \left( e^{\frac{qV}{kT}} - 1 \right)$$
(Eq. 1.4)

where  $I_0$  is the saturation current of the diode,  $I_L$  is the light generated current, *q* is the elementary charge, *k* is Boltzmann constant, *T* is the cell temperature and *V* is the cell voltage measured which is either produced or applied.

Eq. 1.3 and 1.4 can be further expanded as the following equation, in this way electrical circuit model shown in the Figure 11 can be interpreted.

$$I = I_L - I_0 \left( e^{\frac{q(V+I.R_s)}{n.k.T}} - 1 \right) - \frac{V+I.R_s}{R_{SH}}$$
(Eq. 1.5)

Here, *n* refers to the diode ideality factor changing between 1 and 2 while  $R_s$  and  $R_{sh}$  refers to the series and shunt resistances respectively.  $R_s$  and  $R_{sh}$  are the internal parasitic resistances which affects the overall efficiency of the device. As shunt resistance provides an alternative path to the current, it should be infinitively high for an ideal solar cell, while the series resistance causes drop in voltage while current is flowing, it is desirable to have it as close to zero as possible.



Figure 11: Electric Circuit Model for a Solar Cell [20].

In a more detailed look, I-V curve ranges between 'short circuit current ( $I_{SC}$ )' and 'open circuit voltage ( $V_{OC}$ )', as in the Figure 12.  $I_{SC}$  is the maximum current at zero voltage and the  $V_{OC}$  is the maximum voltage at zero current. Maximum electrical power can be obtained at maximum power point which is located at the knee of the I-V curve. Furthermore, inverse slope of the I-V curve at zero voltage and zero current points can also give interpretations about  $R_s$  and  $R_{sh}$  respectively.



Figure 12: I-V and P-V curve for a solar cell.

The ratio of maximum power which is the product of  $V_{mp}$  and  $I_{mp}$  to the product of  $V_{OC}$  and  $I_{SC}$  gives another solar cell parameter 'fill factor (*FF*)'. *FF* is the measure

of the squareness of the I-V curve and can be calculated from the area of the largest rectangle fitting in the I-V curve or in other words via equation 1.6.

$$FF = \frac{V_{mp}. I_{mp}}{V_{oc}. I_{sc}}$$
(Eq. 1.6)

A photon incident on the cell having larger energy than the band gap of semiconductor makes one electron flowing in the external circuit. Maximum  $I_{SC}$  can be found using the photon flux for each wavelength of incoming photons by integrating the energy distribution over the whole range. Additionally,  $V_{OC}$  is ideally found by the following equation which is derived by setting zero voltage in Eq. 1.4 [21]. For maximum  $V_{OC}$ , saturation current  $I_0$  have to be minimized. With the decreasing band gap,  $I_0$  increases according to the saturation current equation (Eq. 1.8.),  $V_{OC}$  decreases and  $I_{SC}$  increases. As a consequence, there are optimal band gap semiconductors for each operation condition.

$$V_{\rm OC} = \frac{nkT}{q} \ln(\frac{I_{\rm L}}{I_0} + 1)$$
 (Eq. 1.7)

$$I_0 = 1.5 \ge 10^5 \exp(-\frac{E_g}{kT})$$
 (Eq. 1.8)

The most comprehensive and commonly used solar cell parameter is 'energy conversion efficiency ( $\eta$ ) ' which is the ratio of power that can be converted from incident sunlight via solar cell to the incident light power density and defined by the following equation as;

$$\eta = \frac{FF. V_{oc.} I_{sc}}{P_{in}} = \frac{P_{mp}}{P_{in}}$$
(Eq. 1.9)

where  $P_{in}$  is the total power of the light incident of the cell [22].

#### **1.3.7.** Loss Mechanisms Affecting Cell Performance

There are several factors leading to reduction in the expected performance of solar cells. Shockley–Queisser (SQ) limit refers to the maximum theoretical efficiency limit of a solar cell made from a single p-n junction. The effects which restricts the solar cell performance to even reach SQ limit is shown in Figure 13.



Figure 13: The major efficiency limits in the Shockley-Queisser limit at AM1.5 spectrum. Adapted from [23].

For a single p-n junction with 1.34 eV band gap, maximum conversion efficiency is calculated to be around 33% (at AM 1.5 solar spectrum). The main losses are due to photons with energy below band gap since they cannot be absorbed. Also

photons with energy above band gap results in performance losses because of the carrier relaxation at the edges of the conduction and valence bands. Moreover, we assume Sun as a blackbody having about 6000 K temperature while the solar cell is assumed to be a blackbody at 300 K, so that the radiation coming from the Sun cannot be totally captured by the solar cell at room temperature. "Other losses" term in the Figure 13 refers to the losses due to the tradeoff between low radiative recombination and high operating voltages [24].

However, it is important to note that this limit is not very appropriate for the crystalline silicon solar cells because of its indirect band gap. SQ limit is calculated based on radiative recombination mechanism, whereas in crystalline silicon cells dominant recombination mechanism is non-radiative (Auger recombination) [23]. Taking these propertis into the account, 29.43% efficiency limit is derived for silicon solar cells in 2013 [25].

Above all, there are additional intrinsic losses leading less efficient solar cells than expected by the theoretical limits.

## Short Circuit Current Losses

 $I_{SC}$  losses are mainly caused by 'optical' nature of the cells. Reflection losses because of highly reflective bare silicon and metal contacts on the front side of the cell reduces  $I_{SC}$  output of the cell. Additionally, bulk of the cell should be thick enough to absorb enough photon to produce charge carriers. Collection probability of these generated carriers is also important, so the recombination in the bulk and at the surface has also significant effect on  $I_{SC}$  losses.

### **Open Circuit Voltage Losses**

The main reason of  $V_{OC}$  losses is the 'recombination' in semiconductor. The process of that an electron and a hole combines before being collected at the corresponding contacts is called as "recombination". Low diffusion length resulting from low quality bulk material and weak passivation of the surfaces are main reasons

of high recombination and consequently reduce  $V_{OC}$ . Band gap energy has also impact on  $V_{OC}$  and with decreasing band gap energy,  $V_{OC}$  decreases as well.

There are 3 main recombination types named as; radiative (band to band) recombination, Shockley-Read-Hall (through defect level) recombination and Auger recombination. In a silicon solar cell, Auger and Shockley-Read-Hall recombination are more dominant because the radiative recombination is less probable for indirect band gap materials. Radiative recombination is reverse of absorption process in which an electron from the CB directly combines with a hole and emits the resultant energy as light Auger recombination is dominant in highly doped materials and in materials having high impurity levels. It involves three carriers. While two carriers recombine, the resulting energy is given to another electron in the CB which thermalizes back to the CB edges. Shockley-Read-Hall recombination, on the other hand, is a two-step process in which electrons are captured in an energy state in the forbidden region due to defects before combines with a hole [22].

# Fill Factor Losses

The parasitic  $R_{sh}$  and  $R_s$  resistances have a major impact on fill factor of solar cells. The main contribution of  $R_s$  comes from bulk resistance of semiconductor and the interface resistances between layers and also between the contacts and the bulk.  $R_{sh}$  on the other hand, caused by the defects and impurities near the junction that leads shorting of the junction, especially at the cell edges. High  $R_s$  values also act to reduce  $I_{SC}$  while low  $R_{sh}$  causes drop in  $V_{OC}$ .

#### 1.4. Monocrystalline Silicon Solar Cells

Semiconductor materials can be single- (mono-), multi-, poly-crystalline or amorphous depending on the size of the crystals constructing the material. For the silicon semiconductor bulk in a solar cell, either mono-crystalline or multi-crystalline materials are used. Although multi-crystalline silicon production is cheaper and more simple, grain boundaries within the material decreases its quality compared to the mono-crystalline ones (Figure 14).



Figure 14: Schematic representation bonds in silicon semiconductor (a) Monocrystalline (b) Multicrystalline [26].

Grain boundaries are known as regions of high recombination centers reducing carrier lifetime and electronic properties located at the boundaries between two crystal grains. Hence, with the well-defined band structure and regular arrangement of silicon atoms, single-crystalline solar cells have better material parameters although they are more expensive. Besides, with the drop in silicon price over the past years, single-crystal silicon has become much more attractive for solar cell production with a current market share of about 35% in 2015 [27]. Common mono-crystalline growth techniques include Czochralski (Cz) and Float Zone (FZ). Cz wafers are the most commonly used ones besides despite the high amount of impurity. FZ wafers are used to overcome this problem with its more complicated growth technique and higher cost.

# 1.4.1. Standard Silicon Solar Cell

A standard silicon solar cell consists of high concentration of dopants at the both sides of the wafer, phosphorus diffused front side and aluminum-doped back side as shown in Figure 15a schematically. Traditional solar cells generally based on p-type crystalline silicon (c-Si) wafer. This kind of  $n^+pp^+$  structure is generally named by "aluminum-back surface field (Al-BSF)" solar cells Figure 15a. In the textured p type silicon wafer, electrons and holes are extracted from the front and the back sides respectively. Silicon nitride on the front side acts both as surface passivation and anti-reflection coating (ARC) layer. Aluminum on the back side play a role as  $p^+$  dopant source besides back contact.



**Figure 15:** (a) Schematic of the standard Al-BSF solar cell [28], (b) Analysis of recombination losses (PC1D model) [29].

In a study published recently, this structure was modelled with representative industrial solar cell parameters using PC1D modelling program and predicted a maximum efficiency of 21.1% with the recombination loss analysis [29]. Standard fabricated silicon solar cells reached efficiencies up to 20.29% [30] for monocrystalline and 17.8% [31] for multicrystalline silicon substrates. It is obvious that the recombination at rear metal contact is dominant loss mechanism in addition to

the recombination in the absorber region, phosphorus diffused region and front surface (Figure 15b).

Fabrication of standard solar cell starts with the texturing of 180 µm thick ptype waferschemical cleanings, high temperature phosphorus diffusion. Since this diffusion is done on both sides, back side diffused region needs to be etched off or overcompensated by p doping. n<sup>+</sup> type layer on the front generally has sheet resistance of between 50-100  $\Omega$ /sq. An ARC layer is subsequently deposited to minimize the reflection from the cell and to passivate the surface. For metallization, front side fingers and busbars are made by Silver printing with appropriate masks. The rear side of the cells is fully covered by full Aluminum by the same printer. A subsequent firing step allows to form front contacts through silicon nitride layer. It also overcompensate P doped n-type region previously created during phosphorus diffusion on rear side by driving in Al into the bulk of Si, leading to creation of a p+ layer which provides an electric field called Back Surface Field (BSF) pushing the minority carriers away from the interface region.

### 1.4.2. High Efficiency Solar Cell Concepts

Although the standard solar cells are cost effective and easy to process, their efficiency potential is obviously limited. In the last two decades, new device concepts with high efficiency potential have been introduced and realized at R&D laboratories. Moreover, more recently, it has been shown that the cost of these highly efficient can be reduced to affordable levels. Among others, interdigitated-back-contact (IBC), silicon heterojunction (HTJ), passivating contact solar cells or even the combination of them have proven to be promising technology alternatives from both efficiency and cost point of view.

#### 1.4.2.1. Interdigitated Back Contact Solar Cells

In the IBC design, collection of both type of carriers is done at the rear side of the cell which allows fully optically active front side. This design is advantageous both in terms of optics and electronics because there is no trade-off between series resistance and grid shading. Since no metal is placed on the front side, high  $I_{SC}$  values are achievable as a result of high incident photon flux on the front side. Additionally, this cell structure is easier to interconnect and may be placed closer to each other in the module because it is not necessary to leave space between cells.

Although there are many possible fabrication sequences, the main goal is to create interdigitated  $p^+$  and  $n^+$  patterns, alternatively named as emitter and back surface field (BSF) respectively on the back side as shown in Figure 16. Boron diffusion is generally implemented to the back surface to transport holes selectively while phosphorus is diffused to gather electrons. The underlying reason of having larger emitter regions than BSF is that the electron mobility is higher than hole mobility. Hence, for better carrier collection, larger fraction of  $p^+$  region is preferred. The openings between these two regions must be large enough for less contact resistance losses and sufficiently small to have less recombination because of direct contact of the metal to the silicon. To avoid any possible shunt between back side electrodes, electrodes are generated slightly narrower.

Figure 16 shows the back contacted cell structure produced in a collaborative work of Australian National University, Trina Solar and PV Lighthouse in 2014, resulted in 24.4% cell efficiency from  $2 \times 2$  cm<sup>2</sup> cell area [32].



Figure 16: Cross-section representation of the IBC cells fabricated in [32].

It is also common to create an additional lightly diffused  $n^+$  layer on the front side to make electrons flow laterally through this layer before being collected from the back side. The design of IBC solar cells can vary according to the additional layers such as passivation and anti-reflection.

With the further developments mainly on reduction of edge losses and series resistance, SunPower broke the efficiency record with n type monocrystalline IBC technology (X-Series), achieving 25.2% on a full area (153.5 cm<sup>2</sup>), under one-sun operation, using industrial processes [33].

# 1.4.2.2. Silicon Heterojunction Solar Cells

Different from homojunction solar cells, two different semiconductor materials namely amorphous hydrogenated silicon and crystal silicon (a-Si:H and c-Si) rather than diffused emitter and c-Si create the p-n junction in heterojunction solar cells. Hydrogenated amorphous silicon is used for many years due to its excellent passivation quality on the c-Si surfaces.



Figure 17: Structure of Panasonic's heterojunction solar cell [34].

Although Sanyo was the pioneer of the c-Si heterojunction solar cells, they changed their brand name of solar modules Sanyo to Panasonic in 2012. Afterwards, Panasonic has broken the heterojunction conversion efficiency record with 24.7% in 2013 on 101.8 cm<sup>2</sup> solar cell area from the heterojunction with intrinsic thin layer (HIT) solar cell structure shown in Figure 17. HIT solar cell includes an intrinsic (i-type) and a p-type a-Si layers deposited on n type c-Si crystalline silicon wafer to form a p-n junction and also i-type and n-type a-Si layers on the opposite side to get a BSF structure. Additional Transparent Conductive Oxide (TCO) layers and electrodes are also produced on both sides of the cell [34].

Thanks to the intrinsic thin a-Si:H layer that gives us excellent surface passivation, HIT solar cells attains high  $V_{oc}$  values. Additional benefits of this structure includes low processing temperatures which is lower than 200 °C meaning less contamination and less damage on the bulk. It is believed that there are still some possibilities to further raise the conversion efficiency with higher quality of the a-Si film and more optimized front electrode size to reduce shadow loss and hence to gain much more from  $J_{sc}$ .

Further improvements and higher conversion efficiency on HIT cell structure came from Kaneka Corporation in 2015 by optimization of process conditions with 25.1% conversion efficiency on 151.9 cm<sup>2</sup> cell area. This is the latest world record in a both-side-contacted heterojunction silicon solar cells [35]. The main improvement

they have made was the reduction in interface carrier recombination which causes improvement in *FF* and hence in overall efficiency.

# 1.4.2.3. Passivating Contact Solar Cells

Since the recombination at surfaces and under metals is one of the major obstacle against very high conversion efficiencies, surface passivation has primary importance in solar cell design. However, the challenging part is decreasing surface recombination and conducting electrical current simultaneously. Recombination at contacts needs to be minimized in order to get low saturation current density ( $J_{0,contact}$ ). Furthermore, the requirement of carrier selectivity should be fulfilled allowing one type of charge carrier while blocking the other type which is necessary to get a high external open circuit voltage ( $V_{OC}$ ). To perform these requirements, the structure is created by generally depositing a thin interface oxide layer and a conductive thin film on the silicon wafer. In order to obtain high fill factor (*FF*) from such structures having several layers and interfaces, having low contact resistivity is also necessary for majority carrier transport.

Although in the literature "carrier selective" term is also used on behalf of "passivating", there are different conditions to be fulfilled for an ideal contact in a carrier selective structure. A great passivation layer may not be carrier-selective because it blocks both electrons and holes. Similarly, a perfect carrier-selective contact may not serve good passivation [36].

Doped silicon layer and very thin insulating layer is needed under the metal region in this structure (Figure 18). The silicon layer can be either deposited directly as polycrystalline silicon or as hydrogenated amorphous silicon. Phosphorus or boron dopants can be defined in situ [37] or they can be subsequently introduced by ion implantation [38], by thermal diffusion from a gaseous source [39] or from a doped oxide [40]. In order to crystallize the amorphous silicon layer and to activate dopants simultaneously, subsequent temperate process is performed. In most of the cases, this

temperature process is followed by a hydrogenation process from a plasma or annealing in a gaseous environment which includes nitrogen and hydrogen, to further improve passivation properties.

In 2015, The Fraunhofer Institute for Solar Energy Systems (ISE) achieved new world record from such a cell with a full area passivating back contact with 25.1% conversion efficiency. After one and half years later, they increased their former record by 0.6 % absolute, with the developments in the same cell structure (Figure 18), and their updated record conversion efficiency to 25.7% ( $2 \times 2 \text{ cm}^2$  area). This so-called TOPCon (Tunnel Oxide Passivated Contact) technology has shown the highest efficiency achieved to date for both sides-contacted monocrystalline silicon solar cells [41].



Figure 18: Structure of TOPCon solar cell [37].

This record cell structure includes very thin wet chemically grown tunnel oxide and Plasma Enhanced Chemical Vapor Deposition (PECVD) based in-situ phosphorus-doped a-Si:H layer which has been semi-crystallined after high temperature treatment. The cell properties will be discussed in detail later in experimental part of this thesis.

There are plenty of studies on passivating contact cell structures in the last years. Yet another both side contacted passivating contact structure has been studied by Energy Research Centre of the Netherlands (ECN) with their bifacial solar cell, namely PERPoly structure, shown in Figure 19. Bifaciality allows light to enter from both sides different from entire metal covered back surface TOPCon structure discussed.



Figure 19: Structure of PERPoly solar cell [42].

Another point of difference from the record efficient TOPCon cell structure is that they employed industial screen printed passivating contact cells in their 21.3% efficient PERPoly structure from large area (239 cm<sup>2</sup>) [42].

# 1.4.2.3. Novel Solar Cell Concepts

With the intention of pushing the efficiencies towards the theoretical limit of 29.43% (for a 110- $\mu$ m-thick Si wafer) [25], combinations of different high efficiency solar cell concepts have been recently on rise.

# Heterojunction Back Contact (HJBC);

Since heterojunction solar cells achieve high  $V_{OC}$  and FF values with their high minority lifetime advantage, and IBC solar cells promises good optical properties which enhances  $J_{sc}$  values. Higher efficiencies are achieved by combining these two concepts. In 2014, the highest efficiency in a silicon solar cell of 25.6% (144 cm<sup>2</sup>) was reached by a HJ back contact cell [43].

Recently, a Japan company, KANEKA Corporation has reported the world's highest conversion efficiency from mono c-Si solar cell with industrially compatible large-area cell (179.74 cm<sup>2</sup>). Associating interdigitated back contact design with an amorphous silicon/crystalline silicon heterojunction structure (Figure 20), they have achieved photoconversion efficiency of 26.6% which is an absolute improvement of 1% relative to the 25.6% [44]. This cell was the first to exceed 26% conversion efficiency among the equivalent c-Si technology counterparts.



Figure 20: The cell structure of Kaneka Corporation [45].

Additionally, they have shown practical attainable efficiency limit of HJBC cell as 27.1%, using their device design and fabrication processes with their best quality HJ passivation. KANEKA's real device result confirmed the potential of HJBC device with the approximately 10% reduction of the remaining loss to theoretical limit [45].

#### **IBC** with Passivating Contact;

Another structure combining two different cell concepts is introduction of passivating contacts to IBC structure. While IBC structure provides the optical gain, passivating contacts enable to get high open circuit voltages via low recombination rates at the surfaces. Recently, Institute for Solar Energy Research Hamelin (ISFH) has achieved a solar cell efficiency of 25% (3.97 cm<sup>2</sup>) from such a structure shown in Figure 21. This high efficiency was achieved with their "poly-Si on oxide" namely POLO structure which avoids recombination under metal contacts for both polarities on the back side.

The contact includes thin silicon oxide and doped polycrystalline silicon layer as in the case of TOPCon cell structure. However, here the difference is no contact is placed on the front side of the cell. For the electrical current conduction from thin silicon, they utilized localized current flow through pinholes in the oxide while in TOPCon structure, it has been done by tunneling effect which will be discussed in the next chapter, this thesis.



Figure 21: IBC with POLO junction cell structure of ISFH [46].

# **CHAPTER 2**

# THEORY

# 2.1. Background Information

#### 2.1.1. Contacts and Contact Resistivity

In this chapter, contact types including Schottky and ohmic contacts, their formation, contact resistance and resistivity parameters will be explained. Contacts between semiconductor and metal and the effect of the existence of an insulating layer between them will be discussed.

# 2.1.1.1 Metal-Semiconductor Contacts

The formation of metal-semiconductor (MS) contact is important for most of the electronic and photovoltaic devices. MS contacts do not necessarily have low resistances as contacted two metals because of the mismatch between the Fermi levels of metal and the semiconductor. This difference may also result in high resistance rectifying contact. In such a contact, the flow of carriers is easier in one direction than it is in the other direction. In Figure 22, the energy band diagrams of a metal and ntype semiconductor (a) before contact formation and (b) after contact formation in equilibrium case is drawn for the case of a Schottky contact formation.



**Figure 22:** Band diagrams of a metal and a semiconductor before Schottky contact formation (a), after Schottky contact formation in equilibrium (b).

When semiconductor and the metal are contacted, a barrier is formed at their interface which is responsible for current flow control.  $E_{M,F}$  corresponds to metal Fermi level. The delocalized electronic states lead conduction around this level. WF<sub>M</sub> is the metal work function that is the energy difference between vacuum and  $E_{M,F}$ . Similarly,  $WF_{SC}$  is semiconductor work function and  $\chi$  refers to the electron affinity [47].

If  $WF_M$  is greater than  $WF_{SC}$  (for n-type semiconductor), a Schottky contact is formed resulting in a barrier at the contact interface between metal and semiconductor. The energy difference between the metal work function and the electron affinity of semiconductor determines the Schottky barrier height denoted as  $\Phi_{B,n}$  and  $\Phi_{B,p}$  for n and p-type semiconductor respectively according to the Schottky-Mott rule [48]. This barrier height is important as it acts as a potential barrier against charge carriers and affects the electrical features of the device [49]. A Schottky diode is preferred in low voltage and high current applications because there is lower voltage drop across the diode terminals when current flows compared to a normal pn junction diode. Majority carriers are responsible for carrier transport in Schottky contacts while in p-n junctions minority carriers are the responsible ones.

In a MS contact, main majority carrier transport is carried out by thermionic emission (TE) over the barrier to the metal. In a TE, the depletion region is wide to make electrons to jump over the potential barrier as in the Figure 23a. So the current flow in a Schottky contact governed by TE is given as below [50].

$$J_{S} = A^{*}T^{2}e^{(\frac{-2\Phi_{B}}{kT})}(e^{qV/kT} - 1)$$
 (Eq. 2.1)

where  $A^*$  is Richardson's constant, q is the elementary charge, k is the Boltzmann constant and T is the temperature. Hence, the resulting current has a non-linear relation with the voltage (Figure 23a) which depends on the barrier height and the temperature.



Figure 23: Conduction mechanisms for metal/n-semiconductor contacts. Thermionic emission (a), thermionic-field emission (b), field emission (c). Adapted from [51].

Ohmic contact is also one type of metal semiconductor contacts in which the Schottky barrier height is low, or negative (Figure 23c). In Figure 23, conduction mechanisms for metal/n-semiconductor contacts is shown with increasing doping concentration from a to c. For lowly doped substrates where  $N_D < 10^{17}$  cm<sup>-3</sup>, TE

dominates as in the Figure 23a case while b shows Thermionic-Field Emission (TFE) with intermediate doping  $10^{17} < N_D < 10^{19}$  cm<sup>-3</sup> and finally c shows high doping with  $N_D > 10^{17}$  cm<sup>-3</sup> in which the barrier is sufficiently thin making Field Emission (FE) to be the dominant mechanism [52].

Contrary to Schottky contacts, ohmic contacts allow carrier flow in both directions with very low contact resistances. Hence, ohmic contacts show linear current voltage dependence. Another way to achieve an ohmic contact is to decrease the depletion width so that carriers can tunnel by thermionic field emission (if the barrier height is also lower) or field emission (FE) through a thin barrier at interface (Figure 23b and Figure 23c) [51]. Current flow for semiconductor-metal tunneling contact case is given below.

$$J_{sm} = \frac{A^*T}{k} \int F_S P(E)(1 - F_m) dE$$
 (Eq. 2.2)

where  $F_s$  and  $F_m$  refers to the semiconductor and metal's Fermi-Dirac distributions while P(E) refers to the tunneling probability. If  $F_s$ ,  $F_m$  and P(E) is replaced, more explicit equation may be found as follows.

$$J_{sm} \alpha \exp(-2x_d \sqrt{\frac{2m^*(q\Phi_B - qV)}{h^2}})$$
(Eq. 2.3)

Here,  $x_d$  is the depletion region width, while  $m^*$  is the effective mass of the tunneling carrier and *h* is the Plank's constant.

#### 2.1.1.2 Metal-Insulator-Semiconductor Contacts

The interface of MS structure is modified by placing a thin insulator between metal and the semiconductor. The insulator acts as a tunnel barrier which allows one type of the charge carrier to tunnel with some probability. This insulator may either be a dielectric or sometimes a semiconductor like amorphous silicon as in the case of HTJ solar cells. Barrier width and barrier height have the major importance in this case because the tunneling probability mostly depends on these parameters.

Resultant Metal-Insulator-Semiconductor (MIS) contact has lower contact resistivity values than MS contacts [53]. However, still there is a trade-off between reduced resistance after lowering barrier height and increased resistance from the tunneling through the insulator. If the interlayer is amorphous silicon rather than a dielectric, it can be thicker than a dielectric film because the carrier transport mechanism will be different [54].

#### 2.1.1.3 Contact Resistance and Specific Contact Resistivity

In order to investigate the contact quality, suitable methods & evaluations and well-defined terms are needed to be measured and identified. In 1972, Berger has filled this deficiency by clearly describing the terms related to contacts of electronic devices [55]. *Contact resistance* ( $R_c$ ) is defined to be the additional resistance as an obstacle to reach ideal contact. It represents the resistance between semiconductor and metal contacts, which can be high depending on the electronic properties of the interface. A contact may behave like a nonideal contact due to the differences in work functions of metal and semiconductor, surface states or multiple foreign layers introduced inbetween.

In order to characterize metal-semiconductor interface independent of the contact geometry or semiconductor bulk characteristics, the term called as *specific* 

*contact resistivity* or *contact resistivity* ( $\rho_c$ ). When the current distribution at the contact is uniform, Eq. 2.4. can be used to determine contact resistivity.

$$\rho c = Rc \bullet Ac \tag{Eq. 2.4}$$

where  $A_c$  is the contact area. More widely used form to calculate  $\rho_c$  becomes as Eq. 2.5. which shows the ratio of total voltage drop  $V_c$  across the layers to  $J_c$  current density at the contact. More accurately, for a MS and MIS contact, the current transport is characterized by its specific contact resistivity which has the unit of  $[\Omega \cdot cm^2]$  and defined under dark conditions as;

$$\rho c \approx \left(\frac{\partial V}{\partial J}\right)_{V=0}$$
 (Eq. 2.5)

where *V* is the voltage applied and *J* is the current density.

The quality of the contact is characterized by contact resistance which is sometimes assumed to be negligible compared to the series resistance. Characterizing ohmic contacts includes many difficulties in terms of measurement and evaluation. Main difficulty is to separate the metal-semiconductor interface resistance from the semiconductor bulk resistance. There are some basic and also advanced methods to separate contribution of different interfaces which will be discussed later in this chapter.

# 2.1.2. Tunneling

Tunneling is a quantum mechanical concept in which carriers pass through a barrier that they are not able to do it in classical conditions. Because electron has wavelike property and the waves do not end suddenly at a barrier or a wall, contrary to the classical case, it can either tunnel through barrier, or decay out after certain penetration into the barrier. This can occur even if the energy of the electron is much smaller than the barrier height. In the classical case, only the carriers with enough energy can escape the barrier as in the case of TE. Using time dependent Schrödinger's equations, probability of electron tunneling can be determined [49].

Adding an insulator between metal and semiconductor interface results in change in work functions and reduces Schottky barrier height. As the tunneling probability depends on the barrier width, the thickness of insulator between metal and semiconductor should be well controlled. If the barrier is thin, insulator's additional resistance will be low enough to save the advantages of this Schottky barrier reduction. So the overall contact resistance will be lower as expected. As the tunneling barrier becomes thicker, additional resistance increases exponentially and dominates the total contact resistance. According to a simulation study done by Roy, A.M. in 2012, there is a lowest limit for the thickness of this insulator to get barrier reduction together with the highest limit to obtain low contact resistivity [56].

# 2.1.3. Recombination and Passivation

Electrons excited to the CB eventually decay back to the lower energy empty VB states removing a hole. This process is known as *recombination*. The average time passes between the generation of the carrier and their recombination is called *carrier lifetime*, which is a crucial parameter for devices. The ratio of excess concentration of carriers,  $\Delta p$  or  $\Delta n$ , to the net recombination rate, U (cm<sup>-3</sup>s<sup>-1</sup>), gives the carrier lifetime.

The recombination process is separated into two main types as *bulk recombination* and *surface recombination*. Since recently, the quality of wafers has been enhanced, the main recombination centers became the high carrier concentration regions and also the cell surfaces. To avoid these losses, surface states have to be "passivated." In order to have higher conversion efficiencies from a solar device, both of these recombination types must be minimized since they cause loss of carriers within the device.

Within the bulk, there are three types of recombination which are Shockley-Read-Hall (via defect states), Radiative (band to band) and Auger. The Radiative and Auger Recombination are intrinsic recombinations while Shockley-Read-Hall (SRH) Recombination is extrinsic with its high defect dependence. Furthermore, Auger and SRH recombination are the dominant ones for silicon solar cells because of its indirect band gap. These processes are shown in Figure 24.



Figure 24: Bulk recombination processes

Radiative recombination is reverse the of the absorption process and usually occurs in direct band gap semiconductors since an additional phonon emission is required to conserve momentum in indirect band gap materials. In Auger recombination case, electron recombining with a hole gives resulting excess energy to a second electron rather than emitting as a photon. Then, this second excited electron emits photon while relaxes back to its original position. Because, more than two carriers are included in this process, it is more likely to happen in highly doped materials. SRH recombination, on the other hand, is a two-step recombination mechanism including a defect level in the forbidden region in which electron gets trapped before relaxing to the valence band [22].

All types of recombination mechanisms must be taken into account to determine the lifetime of material. The bulk lifetime then can be found via the following equation.

$$\frac{1}{T_{bulk}} = \frac{1}{T_{radiative}} + \frac{1}{T_{SRH}} + \frac{1}{T_{Auger}}$$
(Eq. 2.6)

Surfaces also introduce additional recombination centers since the crystal lattice is incomplete at the surface resulting in dangling bonds. They promote the electron-hole recombination at the surfaces by acting as intermediary level for carrier transfer between CB and VB. The surface recombination rate is measured by the minority carrier transfer rate headed to surface which is called *surface recombination velocity*. Surface passivation is needed to reduce surface recombination and hence raise the efficiency of the device.

The lifetime of the material may be enriched by suppressing the surface recombination velocity via passivation. The passivation at the surfaces can be done either through reducing number of dangling bonds (chemical passivation) or reducing the concentration of one carrier type at the surfaces. Reducing number of dangling bonds is performed through growing or depositing a layer on top of the surface to chemically bind the dangling bonds to atoms. This layer can be a dielectric or amorphous silicon. This chemical passivation may also be performed by additional hydrogen atoms introduced to the surface via hydrogen annealing. Furthermore, reducing one type of carrier number at the surfaces is performed by introducing a field to the surface as a result of bend alignment at the physical junction, by an external bias or by a passivating dielectric layer (field effect passivation) [47]. Increasing surface dopant density decreases the surface recombination velocity especially for the surfaces passivated with a dielectric layers.

Bulk and surface recombination contributes together to the effective lifetime which is expressed by;

$$\frac{1}{T_{eff}} = \frac{1}{T_{radiative}} + \frac{1}{T_{SRH}} + \frac{1}{T_{Auger}} + \frac{1}{T_{Surface}}$$
(Eq. 2.7)

# 2.1.4. Passivating Contacts – Trade-off between passivation and contact resistivity

Traditional homojunction solar cells commonly have surfaces in direct contact with metal and remaining area is passivating with a dielectric. As the regions under the metal are critical obstacles against reaching high efficiencies with their high recombinative potential. However, reducing the metallized region is not a solution because of the limited carrier travel length, so it is necessary to provide passivation under these metallized areas. However, as the most of the passivating materials are insulators, decreasing the surface recombination and conducting the current at the same time is challenging. One way to achieve simultaneously both of these properties is to use hydrogenated amorphous silicon semiconductor with a very thin dielectric layer in between. This approach is also very similar to the MIS structures discussed in the previous sections where a microcrystalline silicon layer with a dielectric such as silicon dioxide is used. High efficiency values obtained for this structure were announced in 1980's [58]. Furthermore, most of the current back contacted cells with record efficiencies also utilize passivating contact to achieve very high  $V_{OC}$  values.

Recent passivating contact examples are the TOPCon technology [41] and POLO technology [46] that yields very high efficiency values using an ultra-thin silicon oxide layer and a heavily doped deposited silicon layer. The idea of using an ultra-thin silicon oxide layer between metal and semiconductor is based on the MIS structure and contemporarily applied to a p-n junction device. In the TOPCon device, this ultra-thin silicon oxide layer is required to allow one type of charge carrier while blocking the other type, based on the quantum mechanical tunneling approach as mentioned in the previous sections. Because of this selective tunneling issue, the oxide thickness must be well-controlled and usually less than 25 Å is required for current transport. The application of tunneling oxide and deposited n+ silicon layer at full back side of the n type solar cell structure (Figure 18) has led to 25.7% conversion efficiency for 4 cm<sup>2</sup> cell area [41]. However, for p type devices with p<sup>+</sup> silicon layer, these high efficiency values could not be achieved so far. It may be related to different pathways for carriers while tunneling, large valence band offsets and problems originating from boron defects. The band diagram of TOPCon structure is illustrated in the Figure 25a. On the other hand, in the POLO approach (Figure 25b), the current flow occurs through the pinholes generated intentionally within the oxide layer.



**Figure 25:** Band diagram of TOPCon structure (a), carrier flow in POLO approach (b).

As discussed also in the first chapter in this thesis, low saturation current density  $(J_0)$  is required as an indication of low recombination at the metallized  $(J_{0,contact})$  and non-metallized  $(J_{0,pass})$  surfaces separately.  $J_{0,pass}$  values are expected to be typically few orders of magnitude lower than  $J_{0,contact}$  ones. Hence, there exists a

trade-off between passivating the surfaces and obtaining good contact. The former is characterized by  $J_0$  (A·cm<sup>-2</sup>) while the latter is characterized by  $\rho_c$  ( $\Omega$ ·cm<sup>2</sup>). To show this trade-off between these parameters, Bullock et.al. performed a simulation on idealized solar cell structure (Figure 26). It is illustrated that to obtain high efficiencies, keeping both  $J_0$  and  $\rho_c$  low is a necessity [59].



**Figure 26:** Simulated resultant efficiency as a function of  $J_0$ ,  $\rho_c$  and the contact fraction (dotted lines). Adapted from [59].

It is apparent to achieve high power conversion efficiencies, obtaining  $J_0$  below 10 fA/cm<sup>2</sup> and  $\rho_c$  below 1 m $\Omega \cdot$ cm<sup>2</sup> is necessary. It also strongly depends on the contact fraction. For the full area contacts, in other saying, unity contact fraction, having higher contact resistivity is acceptable as long as the passivation is fairly high. Reduction in contact fraction constricts the carrier flow towards metal-silicon interface and results in reduced conduction. Hence, reducing the contact fraction requires gradually lower contact resistivity values in order to stay in high efficiency region according to simulation done by Bullock et al [59].

# 2.2 Characterization Techniques

In order to evaluate the properties of passivating layers used in this thesis work, different methods were used such as quasi-steady-state photoconductivity lifetime measurements, electrochemical capacitance-voltage, spectroscopic ellipsometry, secondary ion mass spectroscopy, raman spectroscopy and contact resistance measurement techniques. Yet, the focus of this thesis will be on contact resistivity analysis of these layers.

# 2.2.1 Quasi-steady-state Photoconductivity (QSSPC)

Minority carrier effective lifetime can be obtained either by transient or the Quasi-steady-state photoconductance method (QSSPC). For this purpose, Sinton Instruments WCT-120 lifetime tester is used and the measurement setup is illustrated and sketched in Figure 27.



**Figure 27:** Sinton Instruments WCT-120 lifetime tester. Illustration of the tool (a), Sketch of the setup (b).

Measurement starts with a short flash to generate excess charge carriers and enhance the conductance, after the flash is over, conductance decay again. Relatively longer flash is used in the QSSPC case than in transient measurements in order to keep generation rate constant over a short time. The setup records the conductance over time via the coil coupled to a radio frequency (RF) generator and calculates excess charge carrier density from the photoconductance change applying Eq. 2.8.

$$\Delta \sigma = qW(\mu_n + \mu_p)\Delta n \qquad (Eq. 2.8)$$

where  $\Delta\sigma$  refers to the variation in photoconductance, *W* is the thickness of the sample,  $\mu_n$  and  $\mu_p$  are the mobilities of electron and hole carriers respectively. After then, effective lifetime of the sample,  $T_{eff}$  is calculated by;

$$T_{eff} = \frac{\Delta n}{G - \frac{\partial \Delta n}{\partial t}}$$
(Eq. 2.9)

where *G* is photogeneration rate of the excess carriers. *G* can be neglected in the transient measurement while in the QSSPC technique, *G* becomes important. Implied open circuit voltage value can also be extracted from the measured data via the following equation. Implied circuit voltage indicates the maximum achievable  $V_{OC}$ in current state of the sample.

$$i\text{Voc} = \frac{kT}{q}\ln(\frac{np}{n_i^2})$$
(Eq. 2.10)

where *n* and *p* are the total electron and hole concentrations respectively,  $n_i$  is the intrinsic carrier density, *k* is the Boltzmann constant and *T* is the temperature of the sample.

The measurement output also gives the inverse lifetime graph on the main purpose of extracting total saturation current density  $J_0$  measured under high injection conditions. From the slope of the linear fit to this graph,  $J_0$  value is extracted. However if the sample does not include diffused conductive surfaces or the low injection levels are used instead of high injection levels, then it is less possible to get linear fit and extracted  $J_0$  value does not have a physical meaning [60].

## 2.2.2 Electrochemical capacitance-voltage (ECV)

Wafer profiler CVP21 tool is used to quantify the doping profiles via active carrier concentration measurement within the semiconductors by Electrochemical Capacitance Voltage (ECV) profiling method. The measurement setup is shown in the Figure 28. Even though it is a destructive method, it provides limitless measurement depth through the sample and easiness in sample preparation.



Figure 28: ECV Measurement Setup. Adapted from [61].

This method includes etching the surface of the cell and measuring the concentration of the carriers repeatedly in order to identify the electrically-active dopant concentration for each depth. Electrolyte within the sealing ring etches the surface and the ring opening identifies the contact area. A Schottky diode is utilized between sample and an electrolyte and charge of the ions in the solution decides carriers to be attracted or repelled. As a result, when the depletion region is created, ionized donors generate a capacitive effect. By applying an external voltage, the width of depletion layer can be changed and hence the capacitance changes accordingly.

Equations for depletion width and capacitance is given by

$$W_d = \left(\frac{2(\emptyset - V)\varepsilon_0\varepsilon_r}{qN}\right)^{1/2}$$
(Eq. 2.11)

$$C = A(\frac{qN\varepsilon_0\varepsilon_r}{2(\emptyset - V)})$$
(Eq. 2.12)

where  $W_d$  stands for the depletion region, *C* corresponds to capacitance,  $\emptyset$  is the built in potential, *V* is the applied bias voltage, *A* is the contact area and,  $\varepsilon_0$  and  $\varepsilon_r$ are the permittivities of free space and the semiconductor respectively.

From the capacitance, determining carrier concentration, N, is done through the Equation 2.13 [61].

$$\frac{1}{C^2} = \frac{2(\emptyset - V)}{QN\varepsilon_0\varepsilon_r A^2}$$
(Eq. 2.13)
## 2.2.3 Spectroscopic Ellipsometry (SE)

Spectroscopic Ellipsometry (SE) is a non-destructive and contactless thin film characterization technique. Generated light in an initial polarization state interacts with the sample surface and reflected from the surface with a different polarization state. This change in the polarization states allows the analysis of the layer in terms of some properties such as layer thickness, refractive index, absorption coefficient or even crystallinity (Figure 29).



Figure 29: Configuration of Spectroscopic Ellipsometry.

Main measured data in SE are called as amplitude ratio,  $\Psi$  and phase shift,  $\Delta$ . These parameters are related to the intensity of decoupled s and p components of the reflected light via Equation 2.14. Measured amplitude ratio and phase shift can be transferred to many other parameters as refractive index or thickness of the layer by doing some computer analysis. This computer analysis part includes modelling and adjusting fit parameters to estimate the fit parameters [62].

$$\rho = \frac{R_p}{R_s} = tan \Psi e^{i\Delta}$$
 (Eq. 2.14)

where  $\rho$  is the reflectance ratio. The film thickness and optical band gap of silicon layers after deposition were determined by SE, in this thesis study.

# 2.2.4 Raman Spectroscopy

Raman spectroscopy is a technique providing information about molecular vibrations and crystal structures of the concerned material. Monochromatic light is generated by laser in visible, near infrared (IR) or near ultraviolet (UV) range and used to irradiate the sample. The molecule interacted with the incoming photon change its rotational and vibrational states. Raman bands results from change in polarizability of molecule after interaction. Hence, scattered laser photons is shifted which can be detected in Raman system via CCD camera. This shift in energy gives information about vibrational modes of the molecule.

In this thesis, Raman spectroscopy was used in order to examine the crystallinity of the a-Si deposited layers after the annealing steps. Since the asdeposited a-Si Raman peak and the peaks of other crystallized layers differs in peak frequency, crystallinity of the deposited layers can be checked after annealing steps.

### 2.2.5 Contact Resistivity Measurements

In order to enhance the cell performances, accurate determination of contact resistivity is needed especially when the cell structure has passivating layers with multiple interfaces and is contacted with a fraction less than unity. There are number of ways to assess the performance of ohmic contacts to semiconductors and quantify the contact resistivity  $\rho_c$ .

The methods used so far in the literature are usually for conventional simple cell structures withouth many layers and the  $\rho_c$  values reported are not accurate but indeed relative values. Hence, it is very important to determine contact resistivity of these

high efficiency cell structures accurately. Furthermore, it is desired to differentiate the several interface contributions. Discussing and comparing different approaches on contact resistivity determination of different cell structures including passivating layers is the main purpose of this thesis. Additionally, a numerical model using solar cell simulation tool Quokka 3 to evaluate accurate contact resistivity and separate out the contributions from different interfaces is developed and applied on some of the structures. This numerical simulations also offers information about individual layers aside from the interfaces.

# 2.2.5.1 1D Transmission Line Method Evaluation

To define the specific contact resistivity within the metal semiconductor interface, Transmission Line Method (TLM) was first suggested for planar ohmic contacts by Shockley in 1964 [63]. In this technique, contacts were separated by variable distances from each other and the current is constrained to flow from one metal contact into semiconductor sheet and up into second metal contact pad. From the voltage drop associated with this current flow, the total resistance encountered is calculated. This voltage drop measurement can be done by a multimeter and from the ratio of voltage drop to current applied, total resistance is obtained. This resistance between any two contacts can be plotted as a function of distance between these contacts as illustrated in Figure 30 below.



Figure 30: Plot of the total resistance as a function of distance between metal structures together with a linear fit.

The resistance of a single contact is identified as the sum of the metal resistance and contact resistance. However, since the resistance of metal in the contact is so small that contact resistance dominates, metal resistance can be disregarded.  $R_C$  in Figure 30 refers to the contact resistance at the metal/semiconductor interface. Incrementing separation between the metal pads are named as d1, d2... (Figure 31) and having more altered gap distances yields more precise results with the need of least 3 different gap distances. The resistance value at the zero gap distance interception gives twice of the contact resistance which can be found from the plot by extrapolating to d=0. Slope of the linear fit gives the sheet resistance divided by the contact length Z. However, as the contact resistance is influenced by the size of the contact, as an alternative, contact resistivity is used as a point of evaluation and comparison.



Figure 31: Typical arrangement for a TLM pattern. Cross section (a), top view (b).

The lateral current flow through the semiconductor is usually uniform, yet the fraction of vertical flow between semiconductor and metal contacts is not the same throughout the metal. Hence, the physical length and width of the contact does not state the real active contact area. Major current transfer from the semiconductor to the metal contact pads or vice versa occur at the edges of the contacts and it declines moving away from the edge, as illustrated in Figure 32. This behavior is known as "current crowding effect" which was developed by Hower et al. [64] and decides the effective length of the contact. Then, transfer length,  $L_T$ , ought to be taken into consideration and can be measured from the interception at R=0 by extrapolating to the horizontal axis. This interception point refers to  $-2L_T$ .



Figure 32: Sketch of current flow path showing the transfer length.

Apart from the extraction of transfer length from the interception point of the linear fit, more accurate determination can be done via numerical solution of Eq. 2.16 for  $L_T$  after sheet resistance calculation from the slope. For small metal distances linearity of the R(d) curve fails. Therefore, larger pad distances are desired for sheet resistance extraction from the slope but smaller pad distances are also crucial for accurate interception points. Then, all parameters are known to find contact resistivity which is calculated via Eq. 2.17 assuming to have electrically long contact  $W>L_T$ [65].

$$R_{sheet} = m * Z \tag{Eq. 2.15}$$

$$R_C = \frac{R_{sheet}}{Z} * L_T * \operatorname{coth}(\frac{W}{L_T})$$
(Eq. 2.16)

$$\rho_c = R_{sheet} * L_T^2 \tag{Eq. 2.17}$$

Even though some parameters are extracted using the simple analytical theory of TLM, it should not be forgotten that there are so many assumptions which are not compatible with up-to-date designs. Assumptions cover;

- The effect of bulk is disregarded.
- Thin conductive layers (diffusion, poly Si, etc.) are not involved.
- Metal layer resistance is ignored.
- Current trails from the edges of the metal are ignored.
- Only one effective interface is taken into the account.

Hence, 1D-TLM measurement overestimates the contact resistivity value because of the ignored additional resistances (from bulk, metal and different interfaces) which can not be clearly separated from contact resistivity. There are numerous TLM evaluations including the correction for the current flowing around the contact edges or using circular structures in order to discard this effect [66]. However, there is no non-assumptive evaluation which gives definite contact resistivity values.

#### 2.2.5.2 2D Transmission Line Method Evaluation

Since the 2 dimensional (2D) current transport through the bulk of the silicon was ignored in standard 1D TLM evaluation, Eidelloth and Brendel suggested an analytical expression for extraction of the contact resistivity from TLM measurements taking the current flowing through the bulk into consideration for samples with any thickness [67]. Even if this method stands for correcting the bulk effect, it does not comprise a lateral edge effect correction. The metal layer is also expected to be infinitively conductive as in 1D TLM case. They additionally provide numerical simulations in order to verify the experimental results.

This method accounts for the thickness and the resistance of the bulk semiconductor since they both affect the length and the curvature of the current streamlines (See Figure 33). Likewise 1D TLM evaluation, R(d) plot should be formed as well as the interception point with the resistance axis, b, and the slope, m at large gap distances. Dimensionless geometry factors ( $G_{2D-TLM}$ ,  $G_{1D-TLM}$ ,  $G_{CM}$ ) were defined in order to extract contact resistivity value. After the ratio of interception point to slope, b/m is extracted from the plot, using the related equations, 2D bulk corrected contact resistivity value can be obtained independent of the contact length Z in line with the paper of Eidelloth and Brendel [67].

$$\gamma = \frac{W^2 \rho_b}{\rho_c h} \tag{Eq. 2.18}$$

$$\delta = \frac{h}{W}$$
(Eq. 2.19)

where  $\gamma$  is used in order to calculate  $G_{1D-TLM}$  from the usual solution of 1D-TLM theory.  $\delta$  becomes a part of these calculations when  $G_{CM}$  is calculated.  $G_{CM}$  is described as  $G_{2D-TLM}$  factor when contact resistivity goes to zero, in other words  $lim_{\rho c \to 0}$ ( $G_{2D-TLM}$ ) by conformal mapping approach.

$$G_{1D-TLM} = \sqrt{\gamma} \operatorname{coth} \sqrt{\gamma}$$
 (Eq. 2.20)

$$G_{CM} = 1 + \gamma + \gamma \frac{\delta}{\pi} (ln4 - \ln\left(e^{\frac{\delta}{\pi}} - 1\right))$$
(Eq. 2.21)

Combining these two formulas produces an analytical expression for  $\rho_c$  which is valid for arbitrary thickness and bulk resistance (Eq.2.22). It is obvious that  $G_{1D-TLM}$  refers to  $G_{2D-TLM}$  for infinitively small sample thicknesses.

$$\frac{b}{m}\frac{\rho_b W}{2\rho_c h} = 1 + \sqrt{((G_{1D-TLM} - 1)^2 + (G_{CM} - 1)^2)}$$
(Eq. 2.22)

 $(G_{1D-TLM}-1)$ ' term in the equation refers to the resistance by a supplementary transport length below the contact parallel to the surface.  $(G_{CM}-1)$ ' term represents the resistance due to vertical transport perpendicular to the surface below the contact. Contact resistance contribution is added as 1, unity. However, both in this and their subsequent work, it is stated that this model is not reliable for the values below 1 m $\Omega$ •cm<sup>2</sup> [46-67]. Furthermore, assumptions like single interface layer, current flow at the edges, infinitively high metal conductivity and not including thin conductive layers are still valid. Yet, this evaluation is more accurate than the 1D evaluation to some extent.

#### 2.2.5.3 3D Simulations via Quokka 3

In addition to the TLM measurements and 1D and 2D evaluations, another method is developed in order to evaluate contact resistivity using as less assumptions as possible. This section is based on the study done and to be published with the title of "On the determination of the contact resistivity for passivating contacts using 3D simulations" [68]. A 3D numerical model is used by the 3<sup>rd</sup> version of Quokka solar cell simulation tool in which a solver for ohmic carrier transport was additionally developed [69]. This simulation tool can be used constituting up to two conductive layers at each side of the bulk including sheet resistances and contact resistivities at the interfaces. Therefore, it may be used to represent TLM structures on more complicated devices having more than one interfaces and interlayers. Since devices including passivating layers are used in this thesis work, evaluation via Quokka 3 simulations were well suited for the main aim.

Physical properties like bulk resistance, thickness, size and position of the TLM patterns, gap distances between them should be well-defined to the simulation. Knowing the sheet resistance of each layer makes additional contribution. After defining the identical properties as experimental case, the contact resistivity can be extracted where the match between experimental R(d) data and simulation R(d) data occurs (See Figure 33). This contact resistivity represents the sum of contact resistivities at each interface between individual layers. The contact resistivities can be further distinguished using the same simulation tool if the silicon layer's conductivities are adequately high and an etching process is applied in between the metal pads to eliminate the conductive layers in-between.



Figure 33: TLM geometry as defined in Quokka3 (a), R(d) match between experimental data and the numerical simulations (b).

The only assumption in this case is the metal conductivity which is taken to be infinitively high because of some limitations about simulation tool. However, metal layer conductivity was also observed to have no sufficient effect on the result, with an additional simulation set [68]. Profitably, any specific geometry can be defined, 2 conductive layers at each side can be included with 2D bulk. Since an alike characterization device to the experimental structure is formed in the simulation tool, this technique seems to be the most precise evaluation way although it has a time-consuming structure which may be enhanced with future developments.

## 2.3 Concepts Investigated in This Thesis

There are many high efficiency and novel solar cell concepts apart from the conventional Al-BSF solar cell as presented in the first chapter of this thesis. On the purpose of examining contacts of some of these solar cells, characterization samples regarding to these cell concepts were fabricated and analyzed.

Electron beam (e-beam) evaporated in-situ doped (n) passivating contact, PECVD deposited in-situ doped (n) TOPCon passivating contact and LPCVD deposited and ex-situ doped (n) Poly-silicon passivating contact structures are the major investigated cell designs (Figure 34). e-beam evaporated structure is fabricated in e-beam evaporation system from Vaksis company in The Center for Solar Energy Research and Applications (GÜNAM) laboratories, Middle East Technical University, Turkey. Other two structures were fabricated in the tools from Roth and Rau company, located in Fraunhofer Institute for Solar Energy (ISE) laboratories, Germany.

All of the characterization samples are produced by both side polished wafers. It is not necessary for TLM, ECV, Raman and SE measurements to have symmetrical samples as shown in the Figure 34, but for the QSSPC lifetime measurements, symmetrical samples are required. In order to carry out all the characterizations from the same sample, they were fabricated symmetrically. The e-beam evaporated in-situ (n) doped amorphous layers were fabricated symmetrically on top of a very thin tunnel silicon dioxide layer (Figure 34a). One of the well-known methods to obtain poly-crystalline silicon layers is the solid phase crystallization (SPC) method by thermal annealing using in-situ doped amorphous layers as starting material. [70]. Thermal annealing of amorphous layers affects the grain size of deposited layer which can be analyzed via Raman measurements. After the characterization steps of QSSPC, Raman, metal TLM structures were defined on the front side for further characterization as contact analysis. The fundamental fabrication details will be described in Chapter 3. In the present study, the influence of thermal annealing temperature was investigated in terms of crystallinity, passivation and contact resistivity.

The other fabricated structure is PECVD based n-TOPCon passivating layer (Figure 34b). This structure includes a very thin tunnel oxide on both sides. n type amorphous crystalline layer is symmetrically deposited by PECVD. Subsequently, a high temperature annealing step is applied to partially crystallize amorphous layer in addition to simultaneously obtain diffusion layer underneath and activate the dopants. This time, characterization steps include QSSPC and contact resistivity measurements. The influence of the different procedures to get thin tunnel oxide, annealing temperature after deposition of n-TOPCon layer and the metal type on contact resistivity was investigated.

Final structure has very similar working principle as the TOPCon, where polycrystalline silicon passivating layers were used. Contrary to the TOPCon structure, the deposition of intrinsic amorphous layer is done via Low Pressure Chemical Vapor Deposition (LPCVD) for poly-crsytalline Si layers (Figure 34c). Subsequently, ion implantation method is used to implant this layer with Phosphorous to obtain n type doped layer, namely ex-situ doped. Next thermal treatment is done to crystallize the n type layer, to diffuse and activate the dopants as mentioned in the previous sections related to other structures investigated in this study.



**Figure 34:** Contact resistivity characterization structures investigated. e-beam evaporated in-situ (n) doped silicon layer (a), (n) TOPCon in-situ doped passivating layer (b), (n) Poly-silicon ex-situ doped passivating layer (c).

### **CHAPTER 3**

### SAMPLE PREPARATION

The concepts investigated in this thesis were separated into 3 sections as mentioned in the previous chapter. e-beam evaporated (n) layers were fabricated and characterized in GÜNAM laboratories. Other structures including (n) TOPCon and (n) poly-Silicon layers were entirely produced and characterized in Fraunhofer ISE laboratories.

### **3.1.** Fabrication Procedure for e-beam Evaporated Layers

n type shiny-etched float-zone (FZ) silicon wafers with 200  $\mu$ m thickness and 1  $\Omega$ ·cm base resistivity were used in fabrication and characterization in GÜNAM laboratories. n type amorphous silicon layers structures were fabricated symmetrically in order to be able to perform QSSPC measurements. The fabrication sequence can be seen in Figure 35 for both contact resistivity and passivation characterization samples.

Following the standard Radio Corporation of America (RCA) cleaning step, a short Hydrofluoric (HF) acid dip is performed. RCA cleaning is the very first step of silicon solar cell or characterization samples production [71]. This cleaning step is a must in order to remove metallic and organic residuals at the sample surface followed by dip samples into HF solution, rinse in the Deionized (DI) water and make it dry. RCA cleaning done in GÜNAM laboratory includes subsequent RCA-1 and RCA-2 cleaning procedures. Ingredients of these solutions were prepared and mixed with magnetic stirrer while it was heated up to  $70^{\circ}C \pm 5^{\circ}C$ . 10 minutes treatment for each cleaning solution was performed at this temperature.

Since these cleaning treatments oxidize the surfaces as mentioned in previous sections, HF dip and drying under nitrogen environment is performed to obtain clean surface. The surface after HF dip is expected to be hydrophobic which means non-wetting surface.



Figure 35: Simplified process sequence for the fabrication of the e-beam evaporated layers characterization.

Tunnel oxide formation was done symmetrically on cleaned surfaces of the wafer via wet chemical nitric acid oxidation method.

# Nitric Acid (HNO<sub>3</sub>) Oxide (NAOS)

NAOS refers to the Nitric Acid Oxidation of Silicon method. Wafers were dipped in boiling 68 wt% (i.e. azeotropic mixture with water) nitric acid solution at 100 °C to form thin (~1.4 nm) tunnel oxide layer on both sides. Azeotropic mixture

refers to a solution of two liquids (in this case nitric acid and water) in which the density does not change upon vaporization during boiling, in other words constant boiling solutions. Since the concentration of nitric acid remains constant, the process is accepted as reproducible. Atomic oxygen is the oxidizing agent reacting with the Si/SiO<sub>2</sub> interface after the breakdown of the reaction [72];

$$2HNO_3 \rightarrow 2NO + H_2O + 3O$$

Subsequent to tunnel oxide formation, n type amorphous layers were deposited by e-beam evaporation or in another saying e-beam physical vapor deposition (EBPVD) system at  $9.0 \times 10^{-8}$  Torr base pressure and approximately  $5 \times 10^{-8}$  Torr process pressure. The deposition was done when the substrate temperature was 400 °C temperature. Evaporation rate was kept at 1Å/s. Passive dopant concentration is expected around  $5.25 \times 10^{20}$  atoms/cm<sup>3</sup> according to the previous ToF-SIMS measurements.



Figure 36: Schematic representation of e-beam evaporation system. Adapted from [73].

The schematics of the EBPVD vacuum system is shown in the Figure 36. The material to be evaporated on substrate, which is silicon in this case, is melted by beam of electrons emitted from charged filament under high vacuum ( $10^{-6}$ - $10^{-7}$  Torr). The material to be evaporated is separated from the filament by a water-cooled crucible in order to protect the filament from possible contaminations. Electron beam bends towards the material with the help of magnetic field. Atoms of concerned material leaves target to coat the surface of substrate.

EBPVD is known with better control and higher deposition rates than the other vapor deposition systems. Impurity level is lower than thermal evaporation but higher than PECVD techniques. Although the uniformity of the layers is not as good as PECVD systems, EBPVD may be preferable in terms of lower cost and high directionality of the system.

e-beam evaporation customized system by Vaksis company used in the GÜNAM laboratories is sketched in Figure 37. This system includes additional effusion cells for p type and n type doping via boron element and gallium phosphide compound respectively. In this thesis, only n type was required and utilized. P atoms were separated from GaP compound by sublimation using a particular pyrolytic Boron Nitride crucible which causes efficient trap for Ga atoms.





Following the n type layer deposition, tube furnace annealing was done to obtain poly-silicon layers instead of amorphous ones. 2 different temperatures and time (800 and 900 °C, each for 2 and 4 hours) were employed to see the effect of temperature and time of annealing on layers in terms of different aspects. Crystallinity analysis via Raman and  $iV_{OC}$  measurements by QSSPC were done before and after this annealing step. SIMS was additionally performed in order to see the dopant profiles after annealing steps.

In order to define TLM pattern on top of these layers, TLM hard masks were prepared as shown in Figure 38 via laser cut. Hard masks were placed on top of the samples before putting them into the thermal evaporation system. Ag metal is thermally evaporated to form TLM contacts. The vacuum level in the thermal evaporation system was below  $1.0 \times 10^{-5}$  Torr.



Figure 38: Defined TLM pattern prepared by laser cut.

Metal pad widths of 600  $\mu$ m and lengths of 2000  $\mu$ m were used for TLM contacts. The range of gap distance between each metal is from 260  $\mu$ m to 480  $\mu$ m. Lower gap distances could not be obtained because of the limitations related to hard mask fabrication. A short anneal for contact formation was realized at 200 °C for 20

minutes. The setup for measuring I-V via four point probe measurements and Keithley Digital Multimeter were used to extract resistance associated to each different metal separations. Following to determination of resistance as a function of metal pad gap d for each sample, 1 and 2 dimensional TLM evaluations were implemented for contact resistivity analysis.

### **3.2.** Fabrication Procedure for (n) TOPCon Layers

Differently from the previous section, the fabrication of (n) TOPCon layers were carried out in Fraunhofer ISE Clean Room. For characterization of these layers, symmetrical samples were prepared whose cross-sections were shown in the Figure 34b. The fabrication sequence can be seen in Figure 39.



Figure 39: Simplified process sequence for the fabrication of the n-TOPCon passivating layers characterization.

n type shiny-etched float-zone (FZ) silicon wafers with 200  $\mu$ m thickness and 1  $\Omega$ ·cm base resistivity were used. Subsequent to RCA cleanings, a short Hydrofluoric (HF) acid dip is performed. Since RCA process leaves a thin oxide at the surface which should be removed afterwards, HF dip was performed to remove this thin oxide from the surface as mentioned before.

Next, a tunneling dielectric layer had to be defined on both sides of the clean sample. This layer may be one of various materials such as silicon dioxide, silicon nitride or aluminum oxide. However, silicon dioxide is mostly used tunneling dielectric thanks to its low fixed and interface trapped charge density potential in comparison with the other materials [75]. An extremely thin silicon dioxide layer is formed simultaneously on front and the rear side of the sample. Additionally, non-oxidized sample was also included in the experimental set of (n) TOPCon layers. Different ways were performed to grow thin oxide (1.3-1.5 nm) layers.

#### Nitric Acid (HNO<sub>3</sub>) Oxide (NAOS)

NAOS refers to the Nitric Acid Oxidation of Silicon method. Wafers were dipped in boiling 68 wt% (i.e. azeotropic mixture with water) nitric acid solution at 120 °C to form thin (~1.4 nm) tunnel oxide layer on both sides as mentioned in previous section.

### **Ozonated DI Water Oxide**

Ozone is a suitable wet chemical oxidizing material which can be used either for removal of contaminations on the wafer surface or surface passivation. Since ozone has a powerful oxidizing material, ozone based wet chemical oxidation is performed using ozonized DI water. Reactions that may occur during ozonated DI water oxidation is shown in Table 1.

Initial Step	Intermediate Step	Decompositon to O <sub>2</sub>
$Si-H + O_3$	$Si - HO_3$	$Si-OH + O_2$
$Si-H + O_3$	$Si-O + HO_2$	$Si-OH + O_2$
$Si-H + O_3$	$Si - OH + O_2$	$Si-OH + O_2$

Table 1: Possible reactions occur during formation of O<sub>2</sub> at silicon surface [76].

 $O_3$  reaching to the surface decomposes into  $O_2$  and atomic O. Atomic O has much shorter lifetime whereas  $O_2$  is less reactive and causes oxidation of Si-H bond. HO<sub>3</sub>, HO<sub>2</sub> or OH radicals are formed at intermediate steps resulting in formation of silicon oxidizing agent  $O_2$  at the end [76].

# Oxide from UV/O<sub>3</sub> Sources (Excimer and Hg vapor lamp)

There are also ozone based oxidation techniques. This time the oxidation is performed in dry atmosphere rather than wet-chemical oxidation.  $UV/O_3$  photo-oxidation is performed using two different sources as Hg vapor lamp and an excimer source in ozone ambient (Figure 40).



Figure 40: Reaction mechanisms and schematics of Hg vapor lamp (a), excimer system (b). Adapted from [77].

In the Hg lamp system, photons with different special wavelengths are generated in order to be absorbed by  $O_2$  to produce atomic O and generate  $O_3$  as a result of reaction between O and  $O_2$  at the same time (Figure 40). Simultaneously, in the chamber,  $O_3$  separates in  $O_2$  and some other radicals. Produced O and  $O_3$  reach and oxidize the wafer surface. Similarly, in excimer source systems, monochromatic UV light is generated resulting in similarly oxidizing the surface. The distance of the lamp to the surface to be oxidized can be varied as well as the time of exposure. The time and distance variations are expected to change the quality and the thickness of the oxide created.

After the thin tunnel oxide formation, 15 nm thin Phosphorus doped a-Si layer (n-TOPCon) was deposited by AK-400 PECVD tool (Figure 41) on both sides of the sample. Using the mixture of some reactive gases as SiH<sub>4</sub> (silane), CH<sub>4</sub> (methane) with dopant gas PH<sub>3</sub>, and forming the plasma, deposition of doped layer was carried out.

AK-400 PECVD tool includes a process chamber and a load lock parts separated as shown in Figure 40. Microwave and radio frequency power generators are used to excite the reactive gases and to fire the plasma. Subsequent to the electron excitation with the help of plasma environment, electrons start to make collisions with molecules and cause chemical reactions.



**Figure 41:** Schematic Representation of AK-400 PECVD tool at Fraunhofer ISE [78].

As a consequence of the difference between bulk plasma potential and surface potential, acceleration of ions towards the electrodes occurs, in other words ions are bombarded onto the substrate surface. As a result, some of the produced gas phase radicals hold on the substrate surface and initiate a chemical reaction there.

On the purpose of activating the dopants in deposited amorphous layer and moreover to partially crystallize this layer, subsequent furnace annealing was performed under N<sub>2</sub> environment. Samples were exposed to 800 - 900 °C temperatures. For lower temperatures, longer exposure times were utilized. For non-oxided samples, only 900 °C annealing was performed where an additional 800 °C annealing is added for other samples. The iV<sub>OC</sub> and lifetime results were obtained by QSSPC measurements after the furnace annealing step.

While annealing in the tube furnace, oxide may grow unintentionally, so this oxide was removed by short HF dip. In order to get further passivation, Remote Plasma Hydrogen Passivation (RPHP) technique was used. The RPHP tool used is shown in Figure 42. There is a microwave generator to obtain plasma from the gas mixture at about 400°C. A large number of atomic hydrogen H<sup>+</sup> is generated and since they are fast diffusers and active species for passivation of defects or impurities, they diffuse

and further reduce interface recombination. Pressure should not be high to prevent H collisions with each other. The wafers were exposed to hydrogen plasma for 30 minutes. Then, the passivation quality was checked again using the QSSPC technique.



Figure 42: Schematic Representation of RPHP tool at Fraunhofer ISE [79].

Then, the samples were prepared for contact resistivity analysis by utilizing a photolithographically defined TLM pattern. TLM contacts are formed by thermal evaporation of Ti/Pd/Ag or Ti/Pd/Al stacks and the following lift-off technique. The TLM geometry used is shown in Figure 43.

Metal pad widths of 600  $\mu$ m and lengths of 2000  $\mu$ m were used. The range of gap distance between each metal is from 20  $\mu$ m to 240  $\mu$ m. Resistance as a function of metal pad gap d was measured for each sample for further contact resistivity evaluations.

1 and 2 dimensional TLM evaluations were implemented after the R(d) plot formation. For one specific sample (HNO<sub>3</sub> oxided, 900 °C annealed sample), 3 dimensional evaluation was additionally included using Quokka 3 simulation. For a detailed analysis on the contact resistivity of this specific sample, plasma etching was applied to remove the conductive layers between metals and R(d) plot was also obtained after this removal. Microwave plasma source SLAN (SLit ANtenna) from JE Plasma Consult, was used for that purpose using  $SF_6$  as the reactant gas.



Figure 43: Transmission Line Method pattern defined by photolithography

# **3.3.** Fabrication Procedure for (n) poly-Si Layers

Similar to TOPCon passivating contact structure, symmetrical poly-silicon passivating layers were prepared on planar n-type FZ, 1  $\Omega$ ·cm, 200  $\mu$ m thick wafers. The fabrication was done in clean room of Fraunhofer ISE laboratories (Figure 44).



**Figure 44:** Simplified process sequence for the fabrication of the n-poly passivating layers characterization.

After similar RCA cleaning and the following oxide removal by HF, tunnel oxide formation was done by two wet chemical methods. Only nitric acid and ozonized DI water oxidation was carried out in poly-silicon contacts case. Then, undoped amorphous silicon was deposited via LPCVD reactor at 485 °C. The LPCVD deposition was separately done at the Institute for Microsystems Engineering (IMTEK), Freiburg. In LPCVD process, pressure is lower relative to the other Chemical Vapor Deposition (CVD) processes. Due to this low pressure, diffusion of reactant gases decline resulting more uniform and homogeneous layers [80]. Inside of a typical LPCVD reactor is shown in the Figure 45. Quartz tube is heated with the spiral heaters to preferred temperature at a low pressure. Reactive gases are sent to the tube to react with the substrate and form desired layer on the substrate surfaces. 40 nm

was the target thickness of a-Si for this study, nevertheless the real thicknesses were measured after the deposition using spectroscopic ellipsometry.



Figure 45: Schematic Representation of LPCVD Process [81].

Afterwards, ion implantation was used to dope this undoped a-Si layer with Phosphorus at 2 keV to form n type poly-silicon layer. 4 different doses were used between  $7.5e^{14}$  to  $15e^{14}$  cm<sup>-2</sup>. Ion implantation is one of the existing doping techniques which occurs via bombarding the sample surface with accelerated ions with the help of an electric field. Representation of a usual ion implanter is illustrated in Figure 46. Dopants are ionized within the ion source and accelerated by accelerator. Lenses are used to focus the ion beam. Desired ions are separated using mass separator with the help of their atomic mass differences. In order to remove the created additional damages during ion implantation process, annealing step is a must. Under the nitrogen ambience, samples were received 30 minutes annealing in tube furnace at temperatures of 850 °C and 900 °C.



Figure 46: Illustration of an Ion Implanter [81].

Next, wafers were exposed to RPHP at 400 °C for 30 min for further passivation. The passivation quality was analyzed by QSSPC technique before and after RPHP step. Additional ECV measurements were taken to clearly see the profiles of doping and the diffusion from poly layer to silicon for each ionization dose.

Then, the samples were prepared for contact resistivity analysis, similar to TOPCon layers case. Photolithography was used for defining the same TLM pattern as in Figure 43. Ti/Pd/Al stack is deposited by thermal evaporation and following lift-off. TLM geometry and the dimensions are identical to the one in TOPCon passivating layer case. R(d) plot was drawn for each case subsequent to the I-V measurements via a probe station and Keithley 195/196 System Digital Multimeter (DMM). Various TLM evaluations including 1D and 2D were done following to measurements. Additional 3D evaluation using Quokka 3 simulation was also done for one particular sample (HNO<sub>3</sub> oxided, 850 °C annealed sample). For a detailed analysis on the contact resistivity of this specific sample, plasma etching was also applied to remove the conductive layers between metals and R(d) plot was also obtained after this removal.

# **CHAPTER 4**

# **RESULTS AND DISCUSSIONS**

The theory underlying passivation layers and characterization of these layers considering open circuit voltage and contact resistivity have already been described in detail in Chapter 2. The focus of this thesis is on the contact resistivity analysis of these layers. Implied  $V_{OC}$  is also discussed in order to analyze contact resistivity and contact passivation behavior at the same time. In this chapter, the effect of different parameters on passivation and contact resistivity are presented. Contact resistivity measurements were done via Transmission Line Method measurements as explained in previous sections. The evaluations were done via 3 different evaluation techniques one of them which is common old method in the literature [63]. The other method was proposed recently by Eidelloth and Brendel [67]. Third evaluation method was developed in this thesis work and could only be applied to one specific sample from two out of three passivation layer types [68].

# 4.1. (n) e-beam Evaporated Passivation Layer

Following the main cleaning steps, thin nitric acid oxides were formed wet chemically and symmetrically on the sample. The characterization of this thin tunnel oxide was not additionally done within the scope of this thesis since the wet chemical nitric acid oxide formation has already been optimized at GÜNAM laboratories. Following the oxide formations, deposition of n type doped a-Si layers were carried out via e-beam physical vapor deposition (EBPVD) system. Target thickness of this layer was about 40 nm and since the process has been already optimized, no further check for thickness was done. Before and after the n type doped a-Si layer deposition, Raman and QSSPC measurements were carried out. Then, solid phase crystallizations (SPC) were done in the tube furnace and additional Raman and QSSPC measurements were done in order to extract implied  $V_{OC}$  values before and after SPC step. For SPC, four combinations were performed including two different temperatures and 2 different annealing times. Figure 47 illustrates implied Voc values just after the (n) a-Si layer deposition, after 2 hours and 4 hours annealing at 800 °C and 900 °C temperatures.



Figure 47: Implied Voc values before and after Solid Phase Crystallization (SPC).

As can be clearly seen from the Figure 47, passivation is inversely proportional to the annealing temperature and annealing time as expected since high annealing temperatures increases the recombination velocity at the silicon-dioxide/c-Si interface. Annealing time has a positive impact on passivation quality since the crystallization

increases when the time of annealing increases. Whereas the iVoc was around 525 mV after the a-Si layer deposition, it reached almost 665 mV after 4 hours annealing at 800 °C. It can be further developed and optimized in order to reach best passivation with this layer.

Sheet resistance of the upmost layer was checked with 4-point-probe sheet resistance measurement. As the larger grain sizes were expected when increasing the annealing temperature and time, sheet resistance of these layers were expected to decrease when exposed to higher temperature treatments and longer times. Figure 48 shows the sheet resistance measurements from 4 different points on the sample including front side deposited and back side deposited layers. The layer shows high homogeneity within a layer and between front and back side of the same sample. The sheet resistance of the layer before any SPC annealing step measured around 300  $\Omega/\Box$ . For 900 °C annealing, longer annealing causes approximately 5  $\Omega/\Box$  drop in sheet resistance. For 800 °C annealing, increasing annealing time raises sheet resistance unexpectedly.



Figure 48: Sheet resistance of crystallized layers after different treatments

Raman spectroscopy measurements were also carried out just after the a-Si layer deposition and after SPC treatments. Figure 49a illustrates the Raman spectra measured from the sample revealing the presence of highly-crystalline (blue and green) and non-crystalline (black) as deposited layer and the partially crystallized states in between [82]. Highly crystalline silicon has very sharp peaks for instance the one centered at ~ 520 cm<sup>-1</sup> as can be seen in Figure 49a. Figure 49b exemplarily shows focused projection of the same Raman spectroscopy after background subtraction. a-Si peak which is at ~ 480 cm<sup>-1</sup> disappears after 900 °C, 2 hours annealing.



**Figure 49:** Raman spectroscopy of layer as deposited and after crystallization via variable conditions (a), exemplarily illustration of disappearance of a-Si peak after SPC (b).

Subsequently, TLM pattern was formed by hard mask and metal was defined by thermal evaporation using approximately 300 nm Ag. Following the metal formation, short anneal for contact formation was performed. For the TLM measurements, total resistances were measured for several different contact spacing and corresponding R(d) vs. resistance plots were created (Figure 50). As mentioned in Chapter 2, some of the parameters were extracted using simple analytical old TLM evaluation based on many incorrect assumptions.



**Figure 50:** Comparison of R(d) graphs of samples with varying annealing conditions for SPC.

Although there is no good linearity in the resistance vs. distance plots as shown in Figure 50, it is possible compare the contact quality of different conditions and even to extract contact resistivity values. From the R(d) plot, it is obvious that the lowest contact resistivity is obtained from the sample with 900 °C, 4 hours annealing from the interception point at d=0. Even though the other samples have quite close contact resistivity values to each other, 900 °C, 2 hours annealing shows the second lowest contact resistivity which is followed by the sample annealed at 800 °C, 4 hours annealing. The contact resistivity values were evaluated using oldest 1D-TLM method mentioned in Chapter 2. 2D bulk corrected method published by Eidelloth and Brendel were also performed and contact resistivities were extracted using the same R(d) data. The results are shown in Figure 51.



**Figure 51:** Contact resistivity values evaluated by 1D-TLM method (a), evaluated by 2D-TLM method (b).

Both 1D-TLM and 2D-TLM evaluation results shows that contact resistivity decreases with increasing annealing temperature and annealing time (Figure 51). However, extracted contact resistivity values are ultra-high for a good contact. The non-linearity in the R(d) graph were also a sign of poor contacting. The reason behind that maybe the quality of the metal layers deposited or the non-uniformity in the oxide layer in-between silicon layers. Increasing the annealing time or temperature may be a solution, however the passivation would reduce since there is a trade-off between contact resistivity and passivation.

# 4.2. (n) TOPCon Passivation Layer

Subsequent to main cleaning steps, thin tunnel oxides were symmetrically formed on the sample. The characterization of these tunnel oxides were not additionally done within the scope of this thesis since these oxide formations have already been studied in detail and optimized at Fraunhofer ISE. Following the oxide formations, deposition of n type doped a-Si layers were carried out via PECVD. Target thickness of this layer was about 15 nm and since the process has been already optimized, no further check for thickness was done.

Then, tube furnace anneal was performed and QSSPC measurements were done in order to extract implied  $V_{OC}$  values before and after hydrogenation step. In this part of the thesis, only after RPHP i $V_{OC}$  values will be given and compared to each other. Subsequently, TLM pattern was formed via photolithography and metal was defined by thermal evaporation. Ti/Pd/Ag and Ti/Pd/Al metals were used.



Figure 52: iVoc after RPHP of various oxide layers including Hg lamp oxide time and distance variations.

The data in Figure 52 originates from cooperation with the colleague F.Feldmann from Fraunhofer ISE. It shows the detailed passivation optimization of Hg lamp oxidation various time and exposure distances. For instance, Hg 0.5/1 represents the exposure from the distance of 0.5 cm between lamp and the sample for 1 minute. UV/O<sub>3</sub> stands for the excimer source. Surface passivation improves with longer exposure time and smaller distances for Hg lamp. Before continuing with the

contact resistivity measurements, one of these Hg lamp oxide samples was chosen. Since the best implied  $V_{OC}$  was obtained from the Hg 0.5 cm/3 min sample annealed at 800 °C, contact resistivity analysis work continued with only this sample for comparison with the other oxides. Best passivation was obtained from DI-O3 and excimer UV/O3 oxides amongst all oxide layers. However, only DI-O3 oxide was observed to be stable after annealing at 900 °C (Figure 53). For other oxides, increasing annealing temperature decreases the passivation quality. For no oxide sample, passivation is extremely poor with very low iV<sub>OC</sub> values even after RPHP.



Figure 53: iVoc after RPHP of various oxide layers including best Hg lamp oxide. Lines are for visual guide.

Figure 54 is an example for the R(d) graphs of samples with nitric acid oxide. The same analysis was carried out for each sample. For the sample with nitric acid oxide annealed at 900 °C, applied metal type does not change the contact resistivity with the value of around 2.1 m $\Omega \cdot cm^2$  after 1D-TLM evaluation. However, for the
sample annealed at 800 °C, Ti/Pd/Al metal leads to lower contact resistivity (4 m $\Omega$ ·cm<sup>2</sup>) than the Ti/Pd/Ag metal (6.75 m $\Omega$ ·cm<sup>2</sup>).



Figure 54: Comparison of R(d) graphs of samples with HNO<sub>3</sub> oxide

It is obvious that annealing temperature has a significant effect on passivation and contact resistivity. From Figure 55, it is observed that the contact resistivity is inversely proportional to the annealing temperature for 800-900 °C temperature range. The lower annealing temperature leads the better the passivation properties after hydrogenation step (Figure 53). This behavior can be attributed to the strong band bending at the poly-Si/c-Si interface which hinders carriers to diffuse into the bulk. Moreover, high annealing temperatures end up with the increasing of recombination velocity at the silicon-dioxide/c-Si interface and within diffused region through c-Si bulk. So, it is clearly seen that there is a trade-off between contact properties ( $\rho_{contact}$ ) and passivation quality (iV<sub>OC</sub>) in terms of annealing temperature.



**Figure 55:** Contact resistivities of the samples with Ti/Pd/Al metal evaluated using 1D-TLM (a), Ti/Pd/Al metal evaluated using 2D-TLM (b). Lines are for visual guide.

Figure 55a shows the contact resistivity value which is evaluated using old 1D-TLM method as discussed in the previous chapters for Ti/Pd/Al metal case. Figure 55b stays for the same samples as Figure 55a, but this time 2D-TLM evaluation was applied where 2D bulk correction was carried out. 2D-TLM evaluation gives much lower contact resistivity values than old 1D-TLM evaluation method since the old one already overestimates the contact resistivity. Still, 2D-TLM evaluation is not reliable enough as it was already stated in the publication of M. Rienäcker et al. (2016). This model is not applicable for small contact resistivity values such as  $\rho c \ll 1 \text{ m}\Omega \cdot \text{cm}2$ [46]. For some samples, 2D evaluation gives no result and could not be included especially when  $\rho_{\text{contact}}$  was very large (>30 m $\Omega \cdot \text{cm}2$ ) or very small (<1 m $\Omega \cdot \text{cm}2$ ).



**Figure 56:** Contact resistivities of the samples with Ti/Pd/Ag metal evaluated using 1D-TLM (a), Ti/Pd/Ag metal evaluated using 2D-TLM (b). Lines are for visual guide.

UV/O3 excimer lamp oxide shows worse contact properties than the other samples. Non-oxided sample shows low contact resistivity than the other samples as expected since no insulator layer is presented between the conductive layers. However, it is observable that 900 °C annealed HNO<sub>3</sub> sample shows as good contact resistivity as non-oxided sample with a contact resistivity around 0.50 m $\Omega$ •cm<sup>2</sup> after 2D-TLM evaluation. For samples annealed at 800 °C, DI-O<sub>3</sub> oxide shows higher contact resistivity than HNO<sub>3</sub> oxide whereas optimized Hg lamp with 0.5 cm/3 min exposure parameters shows the best contact resistivity. For samples annealed at 900 °C, results are much more close to each other. The contact resistivity of all samples are lower than that of samples annealed at 800 °C except UV/O<sub>3</sub> Hg lamp sample where  $\rho_{contact}$  is observed to be stable with increasing annealing temperature.

Additional 3D numerical simulation was carried out for one specific sample with good passivation properties using Quokka version 3. Since the simulation includes as few assumptions as possible and it represents very similar TLM structure to experimental case, results seem to be more reliable than the other two evaluation methods. However, simulation could not be implemented for all the samples since the simulation method is brand new and more time-consuming. After extracting the contact resistivity of one specific sample, others can be relatively estimated since trends are already known from 1D-TLM and 2D-TLM evaluations.

For the 3D Quokka Simulation, plasma etching was additionally applied to remove conductive layers between metals on the front side as illustrated in Figure 57. The chosen sample was the one with nitric acid tunnel oxide, annealed at 900 °C for 10 minutes with Ti/Pd/Al used for metallization . This specific sample has already shown larger than 1 ms lifetime after hydrogenation and QSSPC extracted overall sheet resistance was 39.8  $\Omega/\Box$  before etching step. R(d) plot before and after this etching step was obtained and realistic simulations were done trying to get a match between experimental R(d) graphs before plasma etching and R(d) graph that simulation gives. The same was applied for after plasma etching using the same sheet resistance and contact resistivity values also used before plasma etching. In this way, contact resistivity of each interface could be separated and the sheet resistance of TOPCon layer and diffused layers could be obtained.



Figure 57: The illustration of plasma etching applied to the front side of one specific (n) TOPCon sample.

Differentiation of resistivities between metal/TOPCon interface ( $\rho_{c1}$ ) and TOPCon/bulk interface ( $\rho_{c2}$ ) could be done via this new method with the help of plasma etching coupled with numerical simulations.  $\rho_{c1}$  and  $\rho_{c2}$  were found to be 0.1 and 0.25 m $\Omega$ •cm<sup>2</sup> respectively for the specific sample. TOPCon layer's sheet resistance was found to be 100 k $\Omega$ / $\Box$  where the underlying diffusion layer is much more conductive with the sheet resistance of 200  $\Omega$ / $\Box$ . Calculating the total resistance of the whole structure considering all the layers and the bulk as parallel resistances, sheet resistances are found to be around 33.31  $\Omega$ / $\Box$  and 39.98  $\Omega$ / $\Box$  before etching and after etching the front side respectively (Figure 58). After the etching of front side layers, total sheet resistance is expected to approach bulk resistance value which is 50  $\Omega$ / $\Box$ . The exact value of 50  $\Omega$ / $\Box$  sheet resistance would be expected if both sides of the sample were etched and no additional conductive layers left at the surfaces.



Figure 58: The match between experimental data and numerical simulations

For the sample mentioned above, contact resistivity values via different methods were obtained as tabulated in Table 2.

 Table 2: Contact resistivity values after different evaluation methods

1D-TLM	2D-TLM	Quokka 3
0.917 mohm.cm <sup>2</sup>	0.560 mohm.cm <sup>2</sup>	0.25+0.1 mohm.cm <sup>2</sup>

### 4.3. (n) Poly-Si Passivation Layer

The fabrication of poly silicon passivation layers has started with main cleaning steps as described in previous chapter. Subsequently, thin tunnel oxides were formed on both sides of the sample. These oxide formations have already been studied in detail and optimized at Fraunhofer ISE. It is known that wet chemical nitric acid oxidation and ozonized DI water oxidation yields approximately 1.3-1.4 nm oxide thickness as mentioned in previous section.

Subsequent to oxide formations, deposition of a-Si layers was done via LPCVD. Afterwards, Spectroscopic Ellipsometry (SE) measurements provided band gap and thickness of poly-Si layer from 3 random samples just before the ion implantation step. Target thickness of LPCVD deposited a-Si was 40 nm. SE yields the thicknesses as 35.1 nm, 36.1 nm and 36.3 nm from 3 different samples. Band gap of the LPCVD deposited layers were measured as 1.43 eV from each of these 3 samples.

During the following P implantation step, implantation dose was varied keeping the ion energy constant at 2 keV. Next, tube furnace anneal was performed and QSSPC measurements were done in order to extract implied  $V_{OC}$  values before and after hydrogenation step (Figure 59).



**Figure 59:** iV<sub>OC</sub> values as a function of P implantation dose before RPHP (a) after RPHP (b). Solid filled symbols represents 850 °C annealed, empty filled symbols represents 900 °C annealed samples.

As shown in Figure 59, implied  $V_{OC}$  increases with the P dose and reaches the highest value of about 715 mV and 727 mV following the annealing and after RPHP steps respectively. These values were obtained from the structure of (n<sup>+</sup>) poly-Si/HNO<sub>3</sub> oxide/n-Si/HNO<sub>3</sub> oxide/(n<sup>+</sup>) poly-Si for the highest implantation dose and annealing at 850 °C.

Another study from Fraunhofer ISE [81] has already revealed that the passivation of poly-silicon passivating layers is related to the doping profile at the interface of poly-Si and c-Si. They found that the passivation of LPCVD deposited and ion implanted poly-Si is dependent on implantation dose and energy, layer thickness, annealing temperature and time. In this thesis study, only the ion implantation dose and the annealing temperature and time were varied to see the passivation and contact quality.

Tunneling silicon dioxide and the doped poly-silicon layer collaboratively provides passivation properties due to the contributions of chemical passivation and field effect passivation respectively [83]. In this part of this thesis, we present the effect of both of them as a function of the oxide type or the doping density of poly-silicon layer.

Nitric acid oxidation shows slightly higher passivation than ozonized DI water oxidation both before and after RPHP process. Figure 60a represents the sheet resistance values extracted from QSSPC measurements while Figure 60b shows P-doping profiles from ECV measurements which were carried out by the F.Feldmann from Fraunhofer ISE. Sheet resistance shows the overall sheet resistance of symmetrical sample. The bulk resistivity (1  $\Omega$ ·cm), corresponds to the wafer sheet resistance of 50  $\Omega/\Box$  for a 200 µm thick wafer. If the sheet resistances of additional doped and diffused regions were considered as parallel resistances with the bulk, overall sheet resistances below 50  $\Omega/\Box$  can be expected as shown in Figure 60a.

It is clear that the doping density increases with the increasing implantation dose. P atoms were activated and diffused after annealing processes. Correlating the implied  $V_{OC}$  and ECV measurements, it can be understood that the higher annealing temperatures, in other words deeper diffusions leads to poorer passivation properties. This behavior has been also observed in the study of Yang et.al. [82] showing that shallow diffusion of dopants into the bulk leads to higher  $iV_{OC}$  values than the deep diffusion profiles. Thus, lower annealing temperature generates better passivation properties after hydrogenation step. This behavior can be attributed to the strong band bending at the poly-Si/c-Si interface as in the case of TOPCon. This prevents carriers to diffuse into the bulk. So the field effect passivation becomes dominant than the deeper diffusion of dopants case where the band bending is lesser. Moreover, high annealing temperatures end up with the increasing of recombination velocity at the silicon-dioxide/c-Si interface and within diffused region through c-Si bulk.



**Figure 60:** Sheet resistance values extracted from QSSPC measurements (a), Pdoping profiles from ECV measurements (b). Solid filled symbols represents 850 °C annealed, empty filled symbols represents 900 °C annealed samples.

As another result of deeper diffusion dopants, sheet resistance decreases with increasing annealing temperature since the larger grain size is expected from higher annealing temperatures. Sheet resistance is inversely proportional to the grain size of the deposited film.

Slight decrease in sheet resistance with increasing implantation dose is also observable since there are simply more activated dopants in higher dose implantations (Figure 60a). The behavior of decreasing sheet resistance with increasing implantation dose was also reported in many earlier studies [84].

Since the main focus of this thesis is on the contact properties of passivating layers, subsequent to photolithographical TLM Ti/Pd/Al metal pattern definition, metal evaporation and lift-off steps were done. Following TLM measurements and data collection, evaluations were carried out for each sample. For the TLM measurements, total resistances were measured for several different contact spacing and corresponding R(d) vs. resistance plots were created (Figure 61). Simple analytical old TLM evaluation which is based on many incorrect assumptions were performed.

For small distances, linearity of R(d) fails as observed in many TLM studies done in the literature. The main reason of this non-linearity for very small metal distances would be that the current is not necessarily face all the interlayers and resistances before reaching the nearby metal. For large distances, this becomes different and current starts to face all resistances before reaching the metal. Hence, for the very small metal gaps, resistance measured are lower than its actual value. The slope of the R(d) plot at linear region is mainly related to the sheet resistance and the interception at d=0 is related to the contact resistance. Figure 61 gives the comparison of R(d) plots of each sample. It is clear that the behavior of R(d) plots, slope and the interception points are similar for different oxides. However, annealing temperature has a clear effect especially on the interception point at d=0, so the contact resistivity. This can be seen from the difference of R(d) interception points between Figure 61a&b and Figure 61c&d. It is understood that the contact resistivity is inversely proportional to the annealing temperature for 850-900 °C temperature range.



Figure 61: Plot of the measured total resistance as a function of distance between metal structures

Similar slopes indicate similar sheet resistance values obtained from the samples. Similar sheet resistances have been also concluded from Figure 60, a slight expected change here may not be observable.

According to the very old TLM evaluation method and 2D bulk corrected method published by Eidelloth and Brendel, contact resistivities were extracted using R(d) data. For some samples, 2D evaluation gives no result as in the previous sections and could not be included in Figure 62 (especially if  $\rho_{contact}$  is very low).



**Figure 62:** 1D- and 2D- TLM evaluations of each (n) Poly-Si sample with DI-O<sub>3</sub> oxide-850°C annealed (a), DI-O<sub>3</sub> oxide-900°C annealed (b), HNO<sub>3</sub> oxide-850°C annealed (c), HNO<sub>3</sub> oxide-900°C annealed (d).

Contact resistivity decreases with increasing annealing temperature and increasing Phosphorous dose. Hence, we clearly observe the already mentioned tradeoff between contact properties ( $\rho_{contact}$ ) and passivation quality ( $iV_{OC}$ ) in terms of annealing temperature. The effect of doping on the contact resistivity is also seen in agreement with the literature. For all the annealing temperatures and different tunnel oxides, contact resistivity decreases with increasing implantation dose. This behavior is attributed to the fixed charge mechanism at the interface. At low implantation doses, drastic increase at contact resistivity is expected due to the strong increase in Schottky barrier [56].

Additional 3D numerical simulation was also carried out using Quokka version 3 for one specific poly-Si sample which also has good passivation properties. For the 3D Quokka Simulation, plasma etching was additionally applied to remove conductive layers between metals on the front side as illustrated in Figure 63. The chosen sample was the one with nitric acid tunnel oxide, annealed at 850 °C for 30 minutes and implanted with the highest P dose. This specific sample has already shown lifetime values larger than 2 ms lifetime after hydrogenation and QSSPC extracted overall sheet resistance was 43.5  $\Omega/\Box$  before etching. R(d) plot before and after this etching step was obtained and realistic simulations were done trying to get a match between experimental R(d) graphs before plasma etching results using the same sheet resistance and contact resistivity values for both of the cases. In this way, contact resistivity of each interface could be separated and the sheet resistance of poly-silicon and diffused layers could be obtained.



Figure 63: The illustration of plasma etching applied to the front side of one specific (n) poly-Si sample.

Figure 64 shows the match between experimental data and simulation output both before and after etching the conductive layers between metals on the front side. Since the etching was not applied to the back side, back side conductive layers were kept also in the after etching simulation input. This match gives the result of 0.21 m $\Omega$ •cm<sup>2</sup> total contact resistivity which was calculated as 3.45 m $\Omega$ •cm<sup>2</sup> using the old 1D-TLM and as 1.39 m $\Omega$ •cm<sup>2</sup> using the 2D-TLM evaluation method. This value represents the sum of the resistivities between metal/poly-Si interface ( $\rho_{c1}$ ) and poly-Si/bulk interface ( $\rho_{c2}$ ).



Figure 64: The match between experimental data and numerical simulations

Since LPCVD deposited poly-crystalline layer is more conductive than the TOPCon layer, R(d) plots before and after etching differs much more, hence the differentiation of resistivities between metal/poly-Si interface ( $\rho_{c1}$ ) and poly-Si/bulk interface ( $\rho_{c2}$ ) becomes easier.  $\rho_{c1}$  and  $\rho_{c2}$  were found to be 0.1 and 0.11 m $\Omega$ •cm<sup>2</sup> respectively. Poly-silicon layer sheet resistance was found as 15 k $\Omega/\Box$  where the underlying diffusion layer is much more conductive with resistance of 600  $\Omega/\Box$ . The sheet resistance of poly-silicon layer is much more than TOPCon sheet resistance in the previous section which is expected since the TOPCon layer is not totally crystallized layer. Additionally, less conductive diffused layer was also expected since the annealing temperature for this specific sample is lower than the annealing temperature for the chosen TOPCon sample. Calculating the resistance of the overall structure considering all the layers and the bulk, sheet resistance extracted from QSSPC (43  $\Omega/\Box$ ) before any etching step. After etching back of the front side, total sheet resistance is expected to approach bulk resistance value which is 50  $\Omega/\Box$ .

Calculated overall sheet resistance becomes approximately 46  $\Omega/\Box$  after etching the front side. 50  $\Omega/\Box$  sheet resistance would be expected if both sides of the sample were etched and no additional conductive layers left at the surfaces.

### **CHAPTER 5**

### CONCLUSIONS

With the increasing global demand of clean and cheap energy, renewables have become the major and growing part of current energy transformation of the world. Solar PV technology is expected to be the most affordable power available amongst all renewables in the near future. Developments on cost reduction and efficiency improvement are supposed to make PV more attractive investment. Within the solar PV technology, crystalline silicon (c-Si) homojunction solar cells dominates the market with the global share of over 90%.

In order to achieve high conversion efficiencies together with low fabrication cost, a novel cell structure has been presented in the literature, namely 'passivating contact' structure. This structure is generated via depositing thin and doped silicon layer underneath metal contacts and additionally inserting an ultra-thin insulator between this film and the bulk c-Si. The deposited film can either be an in-situ doped Si layer or an intrinsic Si layer subsequently doped via ion implantation. The aim of this cell structure is to passivate the c-Si surface while providing a good carrier transport through the metal contacts simultaneously. Lately, 25.7% ( $2\times 2 \text{ cm}^2$  area) record conversion efficiency has been reached by a bifacial monocrystalline silicon solar cell [41].

In 'passivating contact' structures, the most challenging part is the trade-off between the surface passivation and the contact quality. This thesis study focuses on the contact quality analysis of different passivating contact structures and the extraction of corresponding contact resistivity via different methods. The general observation is an enhancement in the passivation quality with the decreasing annealing temperature. However, the contact resistivity also tends to increase with decreasing annealing temperature. The aim is to find an optimum annealing temperature both keeping passivation and contact quality at a reasonable level. In addition to annealing temperature, doping concentration decreases the contact resistivity value. Increasing the doping concentration decreases the contact resistivity and sheet resistance of the layer at the same time while it contributes the passivation. Oxide layers formed via different methods were also examined in terms of their effect on passivation quality and contact resistivity. SiO<sub>2</sub> layers stacked with e-beam deposited (n) doped a-Si:H, PECVD deposited (n) doped TOPCon and LPCVD deposited (n) doped poly-Si layers have been analyzed within the scope of this thesis.

For the in-situ (n) doped TOPCon structure deposited via PECVD, it is obvious that contact resistivity of all samples annealed at 900 °C with various oxide layers are similar. For the samples annealed at 800 °C, nitric acid oxidation and Hg lamp oxidation with 0.5 cm/3 min exposure parameters show the lowest contact resistivity values. It is also apparent that the Ti/Pd/Ag metal causes higher contact resistivity values than Ti/Pd/Al metal. For the ex-situ ion implanted LPCVD deposited poly-Si layer, ozonized DI water oxidation and nitric acid oxidation indicated very similar contact resistivity values with below 10 m $\Omega$ •cm<sup>2</sup> for each sample even after 1D-TLM evaluation.

From a specific sample from TOPCon set, three different contact resistivity extraction methods were applied. The sample with thin nitric acid oxide and annealed at 900 °C has about 0.92 m $\Omega$ •cm<sup>2</sup> contact resistivity according to the old 1D-TLM evaluation and 0.56 m $\Omega$ •cm<sup>2</sup> according to the 2D-TLM evaluation method. 3D Quokka simulations has also been performed and illustrated that this sample has an overall contact resistivity of about 0.35 m $\Omega$ •cm<sup>2</sup>. This specific sample has shown 715

mV implied  $V_{OC}$  after hydrogenation step. Hence, not only the contact quality but also the passivation of this sample seems proper for a high efficiency cell design. It is worth to mention that the sample with no thin oxide layer shows similar contact resistivity values while it shows much worse passivation with an iV<sub>OC</sub> of 615 mV.

The same contact resistivity extraction methods were also applied for a specific sample from poly-Si set. The sample with nitric acid oxide and annealed at 850 °C has about 3.45 m $\Omega$ •cm<sup>2</sup> contact resistivity according to the old 1D-TLM evaluation and 1.39 m $\Omega$ •cm<sup>2</sup> according to the 2D-TLM evaluation method while the 3D Quokka simulations give about 0.21 m $\Omega$ •cm<sup>2</sup> overall contact resistivity. The contact resistivity values extracted from the numerical simulations could also be separated into components corresponding to different interfaces such as the interface between metal and passivation layer and the one between passivation layer and the bulk. The investigated sample has shown both excellent passivation quality with implied opencircuit voltage iV<sub>OC</sub> of 728 mV together with a low specific contact resistivity as extracted from the 3D numerical simulations. The 3D numerical simulation technique can be applied to wide variety of structures to be analyzed in terms of contact formation with as few as possible assumptions.

The TOPCon and poly-Si passivation layers that fabricated in Fraunhofer ISE laboratories have demonstrated excellent contact resistivity and passivation performances. These layers have already been optimized in terms of doping level and passivation in ISE laboratories when contact resistivity study have started. The samples fabricated in the GÜNAM laboratories were the first trials in order to start passivation layer study and optimize both in terms of passivation and contact quality. The samples fabricated via e-beam evaporation technique has shown almost 670 mV implied  $V_{OC}$  values after 4 hours annealing at 800 °C while 525 mV iV<sub>OC</sub> was extracted from the same sample prior to high temperature treatment. Only Ag metal could be deposited for these samples in contrast to the TOPCon and poly-Si ones which have Ti/Pd/Ag or Ti/Pd/Al metals. Additionally, hard mask definition of metal pattern was performed for the samples fabricated in GÜNAM laboratories while the TLM patterns of TOPCon and poly-Si layers were defined via photolithography. Samples fabricated

via e-beam evaporation system together with thin nitric acid oxidation and annealed at 800 °C and 900 °C for crystallization has shown around 370 m $\Omega$ •cm<sup>2</sup> and 320 m $\Omega$ •cm<sup>2</sup> respectively after 2D-TLM contact resistivity evaluation.

The higher contact resistivity values extracted from e-beam deposited passivation than the values extracted from other passivation layers could be caused by the non-optimized doping level coupled with the sheet resistances of layers deposited. Even though the contact resistivity values from e-beam deposited layers are not as low as the values from TOPCon and poly-Si layers, having higher contact resistivity (<100 m $\Omega$ ·cm<sup>2</sup>) is still acceptable as long as the passivation is fairly high for the full area contacts. SPC temperature and duration has not been optimized for such a passivating contact structure. Therefore, various temperature and time of annealing can be performed coupled with different doping levels of the deposited layer in order to optimize crystallization and conductivity of the deposited layer. Additionally, utilization of a better contacting metal is another possible pathway for further development of such layer. Hence, the optimization on the passivation quality coupled with the contact resistivity is needed for enhancement on these passivating layers.

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# **APPENDIX A**

# LIST OF PUBLICATIONS

G. Kökbudak, E.H. Çiftpınar, O. Demircioğlu, R. Turan, "Passivation of silicon solar cells via low temperature wet chemical oxidation" EUPVSEC Proceeding, 2016.

G. Kökbudak, R. Müller, F. Feldmann, A. Fell, R. Turan, S.W. Glunz, "On the determination of the contact resistivity for passivating contacts using 3D simulations" EUPVSEC Proceeding, 2017 (to be published).

H. Nasser, G. Kökbudak, H. Mehmood, R. Turan, "Designing and fabrication of n-cSi/MoO<sub>x</sub> heterojunction solar cells" SiliconPV Energy Procedia, 2017 (in press).