

OPTIMIZATION OF NOVEL PASSIVATION AND CARRIER SELECTIVE
LAYERS ON CRYSTALLINE SILICON SOLAR CELL TECHNOLOGIES

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TECHNOLOGIES**

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I hereby declare that all information in this document has been obtained and presented in accordance with academic rules and ethical conduct. I also declare that, as required by these rules and conduct, I have fully cited and referenced all material and results that are not original to this work.

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ABSTRACT

OPTIMIZATION OF NOVEL PASSIVATION AND CARRIER SELECTIVE LAYERS ON CRYSTALLINE SILICON SOLAR CELL TECHNOLOGIES

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Photovoltaics offer a promising response to global energy needs in the pursuit of sustainability. As solar technology advances, researchers seek to enhance the efficiency of solar cells while simultaneously mitigating their costs. A notable innovation is the integration of novel passivation and carrier-selective layers, which has received a lot of attention and has the potential to change the field entirely.

In this thesis, the optimization of passivation layers commonly used in standard passivated emitter and rear contact (PERC) structures, such as silicon nitride (SiN_x), silicon oxynitride (SiO_xN_y), and aluminum oxide (Al_2O_3), has been investigated. Following the successful demonstration of the performance of these layers in p-type baseline PERC solar cells, the passivation layers were subsequently utilized in n-type PERC-like structures. The fabricated n-type carrier selective metal-compound full area rear contact and partial rear contact solar cell employs the optimized electron-selective magnesium oxide (MgO_x) thin film deposited using the ALD (Atomic Layer Deposition) method. Moreover, the ion implantation technique is

utilized to form the emitter, which allows for single-side doping by further simplifying the process flow and creating a controllable doping profile. Such an option will pave the way for silver-free (Ag-free) solar cell manufacturing, which is highly desirable for industrial applications.

It has been demonstrated as a proof of concept that MgO_x can serve as a highly effective electron-selective passivating contact for n-type crystalline silicon (c-Si) solar cells. The optimized and simple manufacturing methods resulted in a remarkable solar cell efficiency of 17.17% from the 43.50 cm^2 area of PERC-like carrier selective contact solar cells. To the best of our knowledge, the size of the solar cells with a MgO_x layer produced in this thesis study is larger than the size of similar solar cells that have been published in the literature, which shows the potential of the ALD deposited MgO_x to be applied to industrial-size Si solar cells. These findings suggest a promising potential for producing high-efficiency, cost-effective, dopant-free heterojunction solar cells.

Keywords: Crystalline Silicon Solar Cells, Passivation Layers, Carrier Selective Layers, PERC

ÖZ

KRİSTAL SİLİSYUM GÜNEŞ HÜCRESİ TEKNOLOJİLERİNDE YENİ NESİL PASİVASYON VE TAŞIYICI SEÇİCİ KATMANLARIN OPTİMİZASYONU

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Fotovoltaik sistemler, sürdürülebilirlik arayışında küresel enerji ihtiyaçlarına umut verici bir yanıt sunmaktadır. Güneş enerjisi teknolojisi ilerledikçe, araştırmacılar güneş hücrelerinin verimliliğini artırmayı ve aynı zamanda maliyetlerini azaltmayı hedeflemektedir. Yeni nesil pasivasyon ve taşıyıcı seçici katmanların güneş hücrelerine entegrasyonu kayda değer bir inovasyondur. Bu konsept büyük ilgi görmektedir ve alandaki dengeleri tamamen değiştirme potansiyeline sahiptir.

Bu tezde, PERC güneş hücresi yapısında yaygın olarak kullanılan silisyum nitrür (SiN_x), silisyum oksinitrür (SiO_xN_y) ve alüminyum oksit (Al_2O_3) gibi pasivasyon katmanlarının optimizasyonu üzerine çalışılmıştır. Bu tabakaların p-tipi temel PERC yapılarında başarılı performansının gösterilmesinin ardından, pasifleştirme tabakaları n-tipi PERC benzeri yapılarında kullanılmıştır. Üretilen n-tipi taşıyıcı seçici arka kontaklı güneş hücrelerinde, Atomik Katman Biriktirme (ALD) yöntemi kullanılarak optimize edilen magnezyum oksit (MgO_x) ince filmi, elektron-seçici tabaka olarak kullanılmıştır. Ayrıca, emitör yapısını oluşturmak için iyon implantasyon tekniği kullanılmıştır ve bu teknik sayesinde süreç akışı daha da

basitleştirilirken, kontrol edilebilir bir emitör profili sağlanmıştır. Böyle bir seçenek daha sonra endüstriyel uygulama için oldukça arzu edilen gümüş (Ag) içermeyen güneş pili üretiminin yolunu açacaktır.

MgO_x tabakasının, n tipi kristal silisyum (c-Si) güneş hücreleri için oldukça etkili bir elektron-seçici pasifleştirme katmanı olarak hizmet edebileceği kavram kanıtı olarak gösterilmiştir. Optimize edilmiş pasivasyon ve yük seçici katmanlar ve basitleştirilmiş üretim yöntemleri kullanılarak üretilen 43.50 cm² alanlı n-tipi PERC benzeri güneş hücrelerinden %17.17'lik kayda değer bir verimlilik elde edilmiştir. Bildiğimiz kadarıyla, bu tez çalışmasında üretilen MgO_x tabakalı güneş hücrelerinin boyutu, literatürde yayınlanmış benzer güneş hücrelerinin boyutundan daha büyüktür. Sonuç olarak, bu çalışma ALD ile üretilen MgO_x katmanının endüstriyel boyuttaki Si güneş hücreleri için uygulanma potansiyelini göstermektedir. Bu bulgular, yüksek verimli, maliyet etkin ve katkılama içermeyen heteroeklem güneş pilleri üretme konusunda umut vaat etmektedir.

Anahtar Kelimeler: Kristal Silisyum Güneş Hücreleri, Pasivasyon Katmanları, Yük Seçici Katmanlar, PERC



To my mother

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LIST OF ABBREVIATIONS

ABBREVIATIONS

ALD	Atomic Layer Deposition
ARC	Anti-Reflective Coating
BRL	Boron-Rich Layer
BSF	Back Surface Field
CB	Conduction Band
CSPC	Carrier Selective Passivating Contact
c-Si	Crystalline Silicon
CVD	Chemical Vapor Deposition
Cz	Czochralski
D	Diffusion Coefficient
D_{it}	Density of Interface Defects
EC	Conduction Band Energy
EF	Fermi Energy Level
E_{Fn}	Quasi-Fermi Level for Electron
E_{Fp}	Quasi-Fermi Level for Hole
E_G	Band Gap Energy
E_i	Intrinsic Energy Level
EV	Valence Band Energy
F(E)	Fermi-Dirac Probability Function
FF	Fill Factor
I_0	Saturation Current
I_L	Current Created by Light
I_{pv}	Photocurrent
I_{sc}	Short Circuit Current
iV_{oc}	Implied Open Circuit Voltage
J_{sc}	Short Circuit Current Density
LCO	Local Contact Opening
LPCVD	Low Pressure CVD
MOCVD	Metal-Organic CVD
N(E)	Density of States
PECVD	Plasma Enhanced CVD
PERC	Passivated Emitter and Rear Contact
PERL	Passivated Emitter and Rear Locally Diffused Cell
PERT	Passivated Emitter and Rear Totally Diffused Cell
PMP	Power Density at Maximum Power Point
PSG	Phosphosilicate Glass
PV	Photovoltaic
PVD	Physical Vapor Deposition
QSSPC	Quasi-Steady-State Photoconductance

Q_f	Fixed Charges
R_s	Series Resistance
R_{sh}	Shunt Resistance
SRV, S_{eff}	Surface Recombination Velocity
T	Temperature
TMA	Trimethylaluminum
VB	Valence Band
V_{oc}	Open Circuit Voltage
XPS	X-ray Photoelectron Spectroscopy
XRR	X-ray Reflectivity



LIST OF SYMBOLS

SYMBOLS

η	Solar Energy Conversion Efficiency
n_i	Intrinsic Charge Carrier Concentration
ρ_c	Specific Contact Resistivity
ρ	Resistivity
a	Lattice Constant
f_c	Contact Fraction
μ	Mobility
q	Elementary Charge
k	Boltzmann Constant
$\text{\AA}$	Angstrom
τ_{eff}	Effective Lifetime

CHAPTER 1

INTRODUCTION

The growing global energy demand creates a significant problem that continues to change the overall energy scenario worldwide. As economies expand, industries modernize, and populations grow, the need for energy across sectors increases. The phenomenon of rapid urbanization and the simultaneous expansion of emerging economies have resulted in a notable increase in energy consumption across several sectors, including transportation, manufacturing, residential, and commercial domains. In addition, contemporary living patterns, characterized by increased utilization of electronic devices, further contribute to the rise in energy demands. The increasing demand for energy is a considerable challenge for conventional energy sources, specifically fossil fuels, leading to concerns regarding the depletion of resources and impacts on the environment. Consequently, there is an increasing drive to investigate cleaner and more sustainable alternatives, such as renewable energy technology, in order to address expanding energy demands, mitigate carbon emissions, and promote a sustainable energy trajectory.

According to the International Energy Outlook 2021 (IEO2021) [1], it is projected that global energy consumption will experience nearly 50% growth within the next three decades, assuming the absence of major changes in policy or technology (Figure 1.1). In the year 2050, it is projected that renewable energy sources, such as wind and solar power, will experience remarkable growth and approach a level of dominance that is comparable to traditional energy sources.

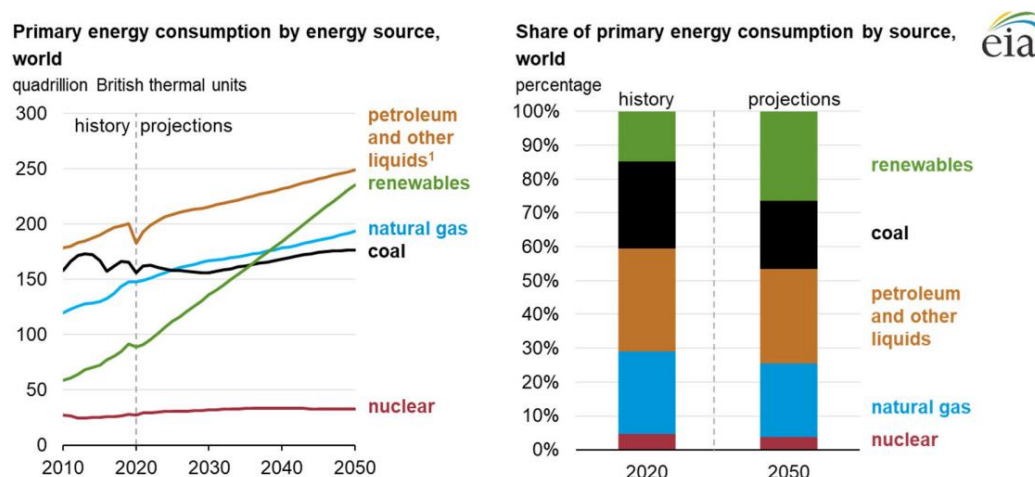


Figure 1.1 The global spread of energy consumption across different sources [1].

Solar energy, particularly photovoltaic (PV) technology, is considered a highly promising solution for effectively addressing the future energy issue while simultaneously protecting the environment. Solar energy utilizes the unlimited energy derived from the sun, providing an environmentally friendly, renewable, and everlasting means of generating electricity. In contrast to fossil fuels, solar energy generation is characterized by the absence of greenhouse gas emissions, thereby serving as a means to mitigate the negative impacts of climate change and diminish our carbon footprint. Moreover, solar PV systems have the potential to be installed on rooftops, on solar farms, and incorporated into buildings, thereby reducing the requirement for extensive land areas and alleviating the negative impact on habitats.

1.1 History and Development of Photovoltaics

The historical progression and evolution of photovoltaics extend over a period of more than one hundred years, representing a noteworthy trajectory of scientific breakthroughs, technological progress, and practical applications. The origins of photovoltaic energy can be attributed to the 19th century, specifically to the discovery made by French physicist Alexandre-Edmond Becquerel in 1839, wherein he identified the phenomenon called the photovoltaic effect [2]. Nevertheless,

significant advancements in understanding the process of transforming light into electricity were only achieved during the early 20th century. In the year 1905, Albert Einstein made a significant contribution to the scientific community by publishing an important work on the photoelectric effect [3]. The study offered valuable insights into the fundamental principles of quantum mechanics, shedding light on the complicated interactions of matter and light. His work established a theoretical basis for photovoltaics. Goldman and Brodsky identified photovoltaic properties of metal-semiconductor surfaces and a barrier layers in PV devices in 1914, followed by Schottky's theoretical explanation of energy barriers in 1930 [4]. The first working silicon solar cell was created in 1954 by a team of researchers at Bell Laboratories, namely Daryl Chapin, Calvin Fuller, and Gerald Pearson [5]. The silicon solar cell exhibited an efficiency of 6%, representing the starting point of the current era of photovoltaics. Since the 1980s, there has been an enormous growth in technology, resulting in the achievement of efficiency values above 20% within a span of a few decades.

During the 21st century, the photovoltaic business has witnessed significant expansion, with an exponential development. This growth may be attributed to several factors, including increasing awareness of the environment, the implementation of favorable regulations, and notable advancements in technology. Record-breaking efficiencies have been achieved thanks to developments in fabrication methods, the introduction of solar cells with multiple junctions specifically designed for space applications, and the introduction of revolutionary tandem solar cells. Today, photovoltaics have become a widely accepted and highly efficient source of renewable energy worldwide. Global solar installation capacities of 192 GW (IRENA) [6] to 268 GW (BNEF) [7] have been published for the year 2022. When considering the 167.8 GW of installed capacity in 2021 [8], it can be stated that the expansion of the photovoltaic (PV) industry aligns with the obvious increase in worldwide interest in solar energy.

The National Renewable Energy Laboratory (NREL) monitors the highest validated solar cell conversion efficiencies achieved in laboratories across photovoltaic

technologies from 1976 to the present (Figure 1.2) [9]. This outstanding chart involves crystalline, organic, thin-film, dye-sensitized, perovskite, single- and multi-junction, and additional photovoltaic technologies. The chart not only facilitates the tracking of progress but also serves as a source of inspiration for the development of more efficient and sustainable solar energy technologies. This is particularly crucial in light of the increasing global demand for clean and renewable energy sources. The necessity for reduced solar panel costs and increased efficiency values is evident in order to enhance the overall effectiveness of solar energy utilization.

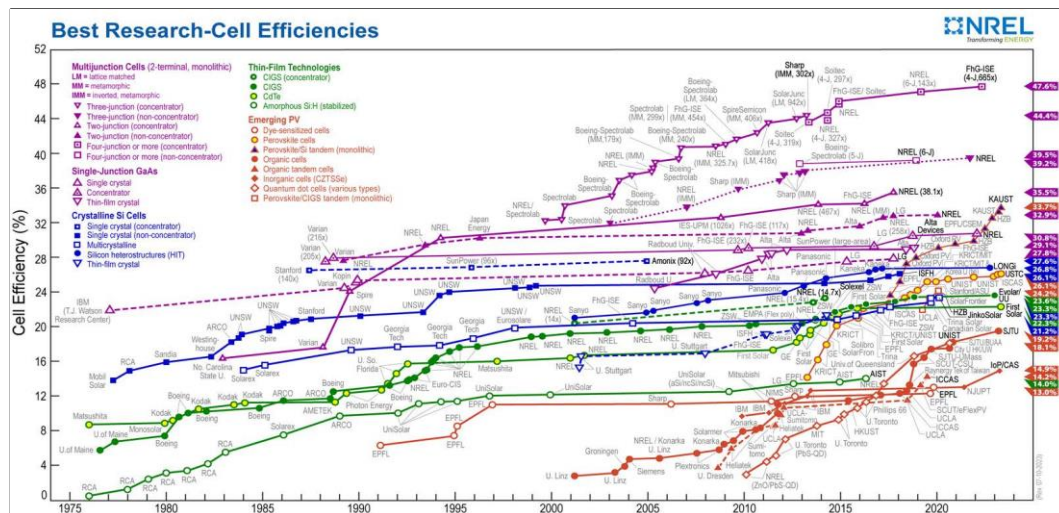


Figure 1.2. The best research-cell efficiencies [9].

Currently, the output of photovoltaic technology utilizing silicon wafers constitutes a majority share of over 95% [10]. Approximately 84% of the entire output of c-Si (crystalline silicon) is attributed to mono-crystalline technology [11]. Although silicon is not a suitable material for solar cell operation due to its unfavorable band gap and limited absorption properties, its numerous advantages, including convenient large-scale processing, reliability, longevity, abundance, and well-established material characteristics, present difficulties for alternative materials seeking to challenge its market dominance.

1.2 Principles of Solar Cell Operation

1.2.1 Photovoltaic Effect: From Light to Electricity

The solar cell can be defined as a two-terminal device that exhibits diode-like conduction in the absence of light and produces a photovoltage once exposed to solar radiation. A solar cell is composed of two distinct semiconductors, known as p-type and n-type silicon. Figure 1.3 illustrates a schematic representation of a solar cell, depicting the n-type and p-type layers as well as providing a comprehensive visualization of the depletion zone surrounding the junction between these layers [12].

P-type silicon is produced with the introduction of Group III elements, such as boron (B) or gallium (Ga), which possess one fewer electron in their outer energy level compared to silicon. The presence of boron in a silicon lattice results in the formation of an electron vacancy or "hole" due to the deficiency of one electron necessary for bonding with the adjacent silicon atoms. The production of n-type silicon involves the introduction of Group V elements, such as phosphorus (P) that possess an additional electron in their outermost energy level compared to silicon. The chemical bonding of the element occurs with neighboring silicon atoms, with the exception of one electron that remains uninvolved in the bonding procedure. Hence, there is an excess of electrons and holes in the n-type and p-type layers respectively. Once the n-type and p-type regions are brought into contact thereby creating a junction, the electrons in the n-type region diffuse towards the p-type region, whereas the holes in the p-type region diffuse towards the n-type region. Consequently, the formation of a "depletion region" occurs near the junction (Figure 1.3).

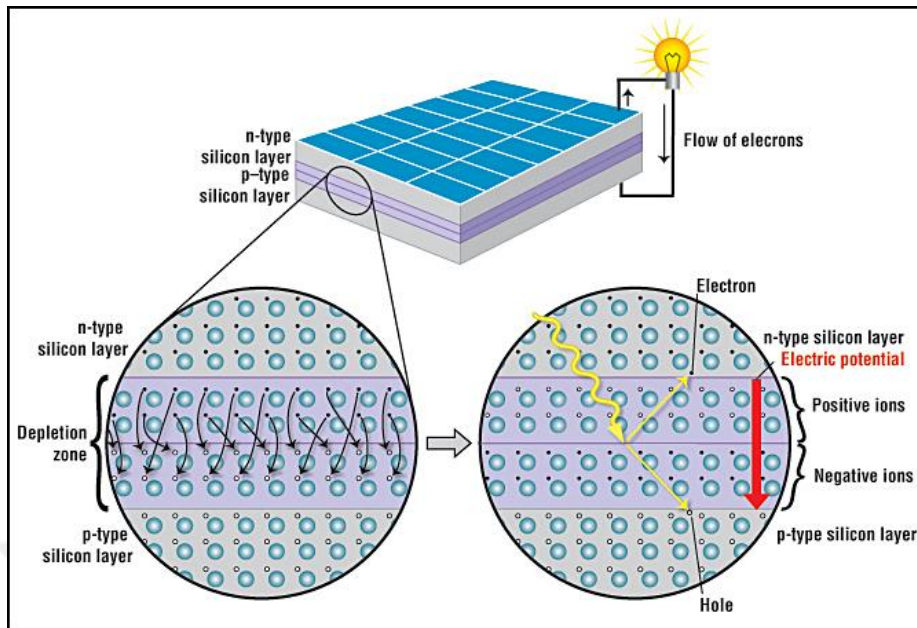


Figure 1.3. Schematic representation of the structure of a solar cell with a detailed illustration of the depletion zone around the junction [12].

Once all the holes in the depletion zone are filled with electrons, the p-type side comprises negatively charged ions, while the n-type side (where electrons were present) contain positively charged ions. The internal electric field created by these oppositely charged ions restricts electrons in the n-type layer from filling holes in the p-type layer.

When sunlight hits a silicon solar cell, silicon atoms absorb photons and transfer their energy to the electrons in the material, releasing electrons and creating holes (electron-hole pair) in the silicon. With the help of an electric field formed inside the solar cell, electrons move toward the n-type layer and holes move toward the p-type layer. The segregation of charge carriers generates a voltage difference between the two sides of the cell. Electrons migrate across the external circuit thanks to the contact between the n- and p-type layers, creating an electric current and a steady electrical charge.

1.2.2 Basic Solar Cell Characterization Parameters

Solar cell characterization parameters are crucial criteria to assess the performance and yield of solar cells. Solar energy conversion efficiency (η) is a decisive factor that significantly impacts the cost and sustainability of photovoltaic energy generation. The measurement of η is conducted in accordance with standardized conditions, wherein the incoming light is of the AM1.5 spectrum, resulting in an irradiation level of 1000 W/m^2 [13]. As the value of η increases, there is a corresponding decrease in the necessary amount of supply and area for a photovoltaic power plant. η principally represents the ratio of power that can be converted from incident sunlight through a solar cell to the power density of the incident light and described by the following equation:

$$\eta = \frac{FF \cdot V_{oc} \cdot I_{sc}}{P_{in}} = \frac{P_{mp}}{P_{in}} \quad (\text{Eq. 1.1})$$

where FF is the fill factor, V_{oc} is the open-circuit voltage, I_{sc} is the short-circuit current, P_{in} is the total power of the light incident of the cell and P_{mp} is the power of the maximum power point (also denoted as mpp). The fill factor (FF) can be visually represented as a quantification of the degree of "squareness" revealed by the current-voltage (I - V) curve of the solar cell, and it corresponds to the magnitude of the greatest rectangle that can be inscribed within the curve. Furthermore, J_{sc} is a parameter that denotes the current density, which refers to the amount of electric current passing through a certain surface area of the solar cell. The I - V characteristics of a PV cell may be represented using the ideal diode equation, both in the dark condition and when the cell is exposed to illumination, as expressed in Equation 1.2.

$$I = I_L - I_0 \left(e^{\frac{qV}{kT}} - 1 \right) \quad (\text{Eq. 1.2})$$

where I_0 is the saturation current of the diode, I_L is the current created by light, q is the elementary charge, V is the measured voltage of the cell, which can be either produced or applied, k represents the Boltzmann constant and T represents the temperature of the cell [14].

The open circuit voltage and the fill factor values can be determined using the following mathematical expressions (Equation 1.3 and Equation 1.4) where n is the ideality factor changing between 1 and 2.

$$V_{oc} = \frac{nkT}{q} \ln\left(\frac{I_L}{I_0} + 1\right) \quad (\text{Eq. 1.3})$$

$$FF = \frac{V_{mp} \cdot I_{mp}}{V_{oc} \cdot I_{sc}} \quad (\text{Eq. 1.4})$$

The schematic representation of the current-voltage (I-V) characteristic of a solar cell under light is depicted in Figure 1.4 [15]. I_{sc} and V_{oc} refer to the values of the photocurrent and photovoltage under short-circuit and open-circuit situations, respectively. In both short-circuit and open-circuit conditions, the electric power output of a solar cell is zero. Maximum electrical power may be achieved at the maximum power point, which falls at the knee of the I-V curve. I_{mp} and V_{mp} are the current and voltage, respectively, that a solar cell generates at the maximum power point [15].

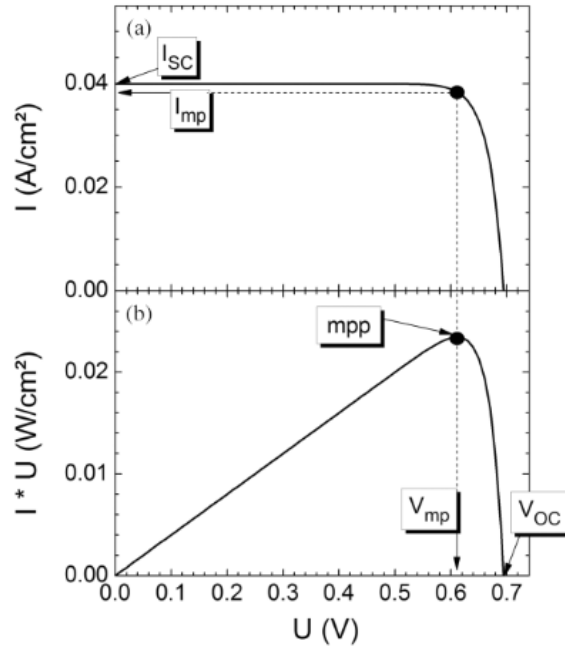


Figure 1.4. (a) An illustration of a current-voltage characteristic and (b) the corresponding power-voltage characteristic of a solar cell under light [15].

Figure 1.5 depicts the standard circuit representation of a solar cell or panel, which contains a current source, a single diode, and two resistors, one arranged in series and the other in parallel [16]. The term " I_{pv} " represents the photocurrent generated by the constant current source, whereas " R_s " represents the series resistance, which refers to the total resistance encountered by the current flowing through the device. The shunt resistance, denoted as " R_{sh} ", is utilized to consider the current leakage that occurs across the high conductivity shunts located across the p-n junction. Because shunt resistance provides an alternate channel for current, it should be infinitely high for a perfect solar cell, while series resistance should be as close to zero as possible since it causes a voltage drop when the current is flowing.

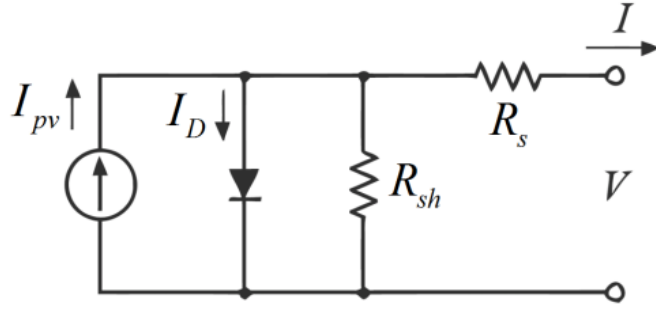


Figure 1.5. Equivalent circuit of a solar cell [16].

1.3 Objectives and Scope of this PhD Study

This thesis explores the enhancement of passivation layers commonly applied in the standard passivated emitter and rear contact (PERC) designs. These layers include silicon nitride (SiN_x), silicon oxynitride (SiO_xN_y), and aluminum oxide (Al_2O_3). Initially, the effectiveness of these layers was investigated and optimized in p-type PERC structures. Subsequently, these passivation layers were adapted for use in n-type PERC-like structures.

The n-type PERC-like solar cell that was created involves using an optimized electron-selective magnesium oxide (MgO_x) thin film. This film was deposited using the Atomic Layer Deposition (ALD) technique. Forming the emitter in this solar cell structure involves ion implantation, which allows single-side doping, streamlines the manufacturing process, and enables precise control over the doping profile.

It is anticipated that this will pave the way for the mass production of large size high-efficiency solar cells which is structurally similar to the PERC design, reducing silver (Ag) usage. This advancement is desirable and valuable for various industrial solar cell applications.

CHAPTER 2

FABRICATION AND CHARACTERIZATION METHODS

This chapter provides a comprehensive coverage of the fundamental principles behind semiconductor doping processes, as well as the concepts and techniques related to passivation and carrier selective layers. In Section 2.1, the significance of the doping process in semiconductor technology and common p and n-type dopants are covered. The various doping techniques, namely diffusion and ion implantation, employed in this thesis study are also described. The basic principles and development of carrier-selective contacts employing metal compounds instead of doped silicon to separate and collect charge carriers are additionally outlined. In Section 2.2, different types of the primary passivation and carrier selective layers employed in this thesis study, as well as their fabrication processes, such as Plasma Enhanced Chemical Vapor Deposition (PECVD) and Atomic Layer Deposition (ALD), are discussed. Section 2.3 presents a brief overview of the primary approaches of characterization that are commonly employed during this thesis study.

2.1 Methods for Charge Carrier Extraction

Charge carrier extraction may be attained by the implementation of several concepts, which can be classified into two categories: the manipulation of surface carrier concentrations and the establishment of asymmetries in carrier flows toward the contact. This section will provide a detailed explanation of all of the techniques employed in this thesis study for charge carrier separation in fabricated solar cells. Diffusion and ion implantation are the primary doping methods employed to intentionally introduce dopants into semiconductors in a controlled way, thereby

modifying their conductivity properties. The utilization of carrier-selective contacts is another popular approach in solar cell technology, aimed at the effective extraction and transportation of charge carriers (electrons or holes) with minimal recombination loss. Carrier-selective contacts are specially engineered designs that are utilized at the interfaces between different layers or materials included inside a solar cell. The primary objective of these devices is not the introduction of impurities but rather the enhancement of charge carrier flow optimization via the extraction of a certain charge carrier while effectively blocking the opposite charge carrier type.

2.1.1 Doping by Diffusion

Doping by diffusion is a technique employed to introduce dopant atoms into a semiconductor material by subjecting it to an environment containing the necessary dopant atoms in a gaseous state. The concentration of doping exhibits a systematically decreasing trend moving from the surface. The distribution of the dopant in the depth is mostly influenced by the temperature and the duration of diffusion.

Group III elements such as Boron (B) and Aluminum (Al) are widely employed as the dominant p-type impurity in silicon, whereas Group V elements such as Arsenic (As) and Phosphorus (P) are frequently utilized as n-type dopants, as previously mentioned. The dopant atom that belongs within the Group III elements is commonly referred to as an acceptor atom. Conversely, the dopant atom belonging to the Group V elements is recognized as a donor atom due to its capacity to transfer electrons [17]. The solubilities of these elements in silicon are very high, surpassing 5×10^{20} atoms/cm³ in the temperature range of diffusion, which spans from 800 °C to 1200 °C. The introduction of these dopants may be achieved by several methods, including solid sources such as BN for B, As₂O₃ for As, and P₂O₅ for P; liquid sources like BBr₃, AsCl₃, and POCl₃; as well as gaseous sources such as B₂H₆, AsH₃, and PH₃. Typically, the gaseous source is conveyed to the semiconductor surface by the

utilization of an inert gas, such as nitrogen (N₂), and subsequently undergoes reduction at the surface [18].

Figure 2.3 illustrates the schematic representation of the covalent bonds of pure silicon, phosphorus-doped silicon, and boron-doped silicon. The electrical composition of silicon is determined by the quantity and type of dopants inside it. The overall resistivity (ρ) of the material is determined by the combined contributions of electron and hole conductivity (Equation 2.1).

$$\rho = \frac{1}{q\mu_e n + q\mu_h p} \quad (\text{Eq. 2.1})$$

where n and p indicate the carrier concentration, whereas μ_e and μ_h denote the mobility for electron and hole, respectively. q represents the elementary charge. The values of μ_e and μ_h in semiconductors are dependent upon factors such as doping, temperature, and electric field.

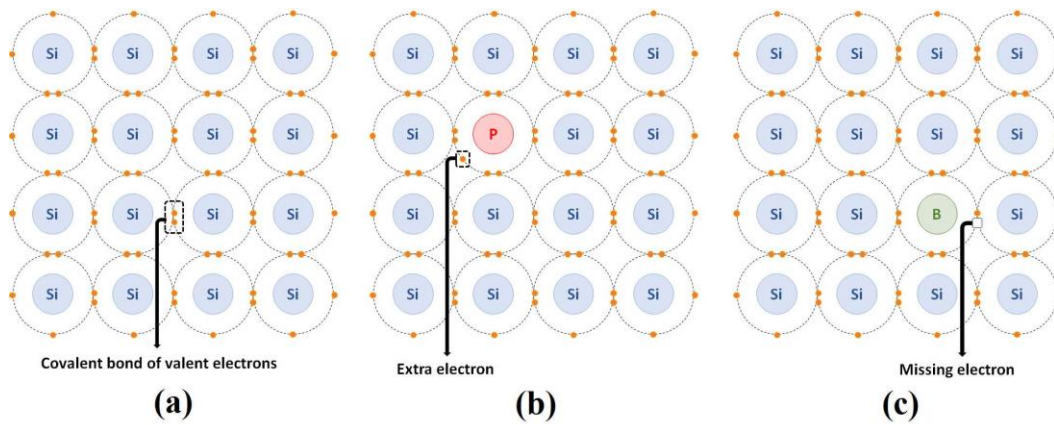


Figure 2.1. Schematic illustration of covalent bond of (a) pure silicon, (b) phosphorus doped silicon, (c) boron doped silicon [17].

The "Fermi Level" is the maximum energy level that the electron may occupy at absolute zero temperature. The valence and conduction bands, which are situated in close proximity to the Fermi level, play a crucial role in determining the electrical conductivity of solids. The electrons located in the outermost shell of an atom are typically referred to as valence electrons. The valence band (VB) refers to the band that is generated by a series of energy levels that contain the valence electrons and are located below the Fermi level. The conduction band (CB) refers to the energy level that contains the population of free electrons. Free electrons refer to the valence electrons that possess the ability to travel freely inside the atomic structure. These electrons play a crucial role in facilitating the conduction of electricity. The CB is located above the Fermi level. The band gap (E_G) refers to the difference in energy levels between the uppermost point of the VB and the lowermost point of the CB in insulators and semiconductors. In a system featuring discrete energy levels, the calculation of the probability for an electron to occupy a certain energy level, denoted as E , is accomplished by the utilization of the Fermi-Dirac probability function (Eq 2.2).

$$F(E) = \frac{1}{1 + \exp(\frac{E - E_F}{kT})} \quad (\text{Eq. 2.2})$$

The quantity of electrons present in the conduction band and the number of holes in the valence band are affected by the density of states. In the state of equilibrium, the quantity of electrons present in the conduction band and the holes in the valence band may be determined by;

$$n = \int_{E_c}^{\infty} N(E)F(E)dE \quad (\text{Eq. 2.3})$$

$$p = \int_{-\infty}^{E_v} N(E)(1 - F(E))dE \quad (\text{Eq. 2.4})$$

where $N(E)$ is the density of states, E_c is the energy of the conduction band edge, E_v is the energy of valence band edge.

The intrinsic charge carrier concentration (n_i) for an undoped material is defined as

$$n = p = n_i \quad (\text{Eq. 2.5})$$

where n_i at room temperature for Si is $1.45 \times 10^{10} \text{ cm}^{-3}$.

For the doped material, the most appropriate method for determining the values of n and p is as follows:

$$n = n_i \exp(\frac{E_F - E_i}{kT}) \quad (\text{Eq. 2.6})$$

$$p = n_i \exp\left(\frac{E_i - E_F}{kT}\right) \quad (\text{Eq. 2.7})$$

where E_F is the Fermi energy level and E_i is the intrinsic energy level. Additionally the energy band gap (E_G) can be calculated using Equation 2.8.

$$E_G = E_C - E_V \quad (\text{Eq. 2.8})$$

Based on the Equations 2.6 and 2.7, it can be observed that with a rise in electron concentration, the position of E_F is shifted above that of E_i . In a similar vein, as the concentration of holes increases, then the position of E_F drops below E_i . Figure 2.4 depicts the energy band diagrams of n-type and p-type materials, displaying the parameters of E_C , E_V , E_F , and E_G .

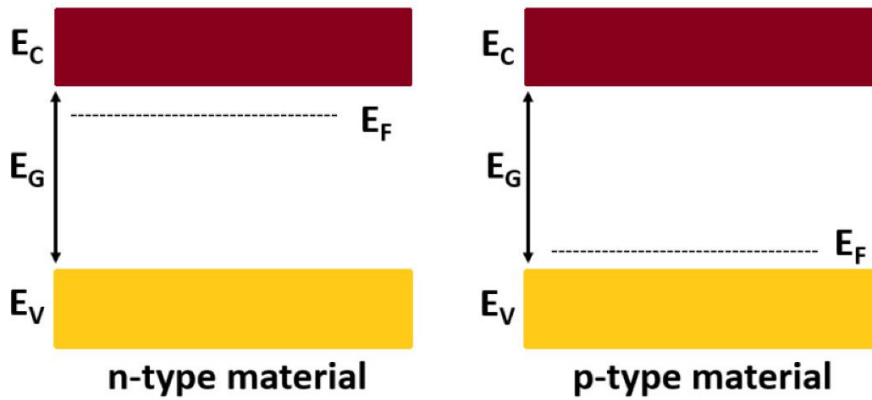


Figure 2.2. Schematic drawing of E_C , E_V , E_F and E_g of n-type and p-type semiconductor materials (Adapted from [13]).

The phenomenon of diffusion in a semiconductor may be described as a sequential process involving the atomic displacement of the dopant inside the crystal lattice.

Figure 2.3 depicts the two fundamental atomic diffusion mechanisms, namely the vacancy mechanism and the interstitial mechanism, where " a " represents the lattice constant. The open circles depicted in Figure 2.3 symbolize the host atoms that are situated at the equilibrium lattice locations. The solid dots in the diagram depict impurity atoms. At higher temperatures, the lattice atoms exhibit vibrational motion about their respective equilibrium positions inside the lattice. There exists a finite probability that a host atom may attain the energy necessary to escape from its lattice position and transform into an interstitial atom, consequently generating a vacancy. The phenomenon wherein an adjacent impurity relocates to occupy a vacant site, as seen in Figure 2.3(a), is referred to as vacancy diffusion. The phenomenon of interstitial diffusion occurs when an interstitial atom undergoes movement from one location to another without occupying a lattice site, as seen in Figure 2.3(b) [18].

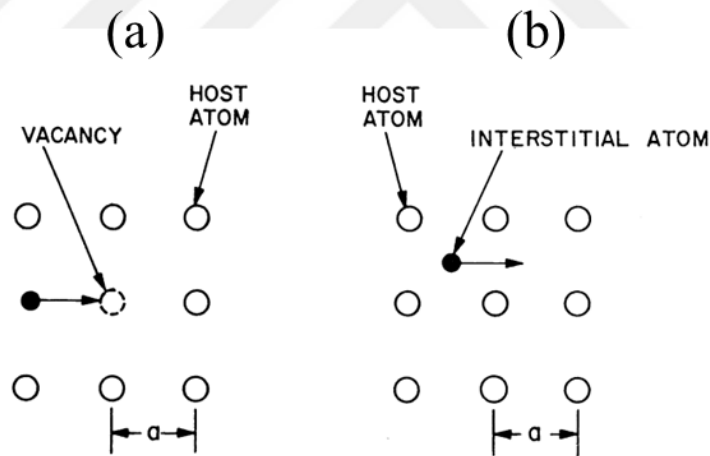


Figure 2.3. The mechanics of atomic diffusion in a two-dimensional lattice, (a) Vacancy mechanism, (b) Interstitial mechanism [18].

The diffusion coefficient (diffusivity) " D " is the parameter that characterizes the mobility of an atom, defect, or impurity inside a crystal lattice. The rate of diffusion for particles in an isotropic medium in one dimension may be mathematically described using Fick's first law;

$$J_x = -D \frac{\partial C}{\partial x} \quad (\text{Eq. 2.9})$$

where J_x : diffusion flux and C : concentration of particles in the material (Figure 2.4). The presence of a negative sign inside the Equation 2.9 indicates a counter-directional relationship between the diffusion flux and concentration gradient [19].

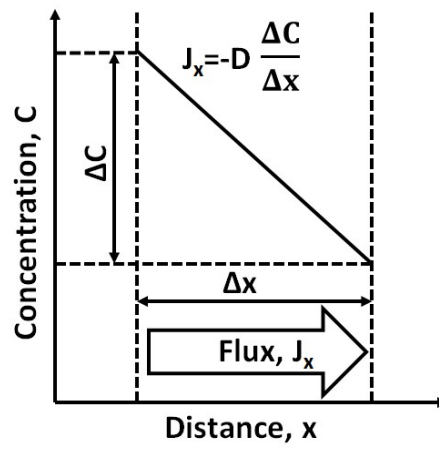


Figure 2.4. Illustration of Fick's first law [19].

Fick's second law extends the fundamental concepts of Fick's first law by incorporating the concept of diffusion in two or three dimensions [20]:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \quad (\text{Eq. 2.10})$$

According to Einstein's relation (or kinetic theory) (Equation 2.11), there is a direct correlation between temperature and the kinetic energy of dopants, resulting in an increase in their mobility and diffusivity:

$$D = \mu kT \quad (\text{Eq. 2.11})$$

where " μ " is the mobility, " T " is the absolute temperature, " k " is the Boltzmann constant, " D " is the diffusion coefficient [21].

2.1.2 Doping by Ion Implantation Method

The utilization of ion implantation has been scientifically demonstrated to enhance the efficiency of solar cells and streamline the manufacturing process for both conventional and cutting-edge cell designs. The ion implantation method is used to incorporate dopants into semiconductors at low temperatures, providing greater flexibility compared to diffusion. Ion implantation involves the process of vaporizing and ionizing dopant atoms, accelerating them, and subsequently separating them based on their mass-to-charge ratios [22]. The atoms are introduced into the crystal lattice, where they undergo collisions with the host atoms, resulting in energy loss. Ultimately, they settle at a certain depth within the solid. The determination of the average penetration depth is dependent upon the characteristics of the dopant, substrate materials and acceleration energy. The energy levels utilized in ion implantation span a range of a few hundred to several million electron volts, leading to the formation of ion distributions that exhibit penetration depths ranging from less than 10 nanometers to 10 micrometers. The crystal structure experiences damage as a result of the ion implantation procedure. The damage types include a non-equilibrium excess of vacancies and interstitials, the formation of vacancy clusters and interstitial clusters, and locally amorphized regions of the crystalline silicon [23]. Thus, it is standard procedure to perform an annealing step following ion implantation in order to facilitate the repair of the crystal lattice damage while promoting the drive-in of the implanted ions [24,25]. The impact of annealing on the crystal structure before and afterwards the post-annealing process can be seen in Figure 2.5.

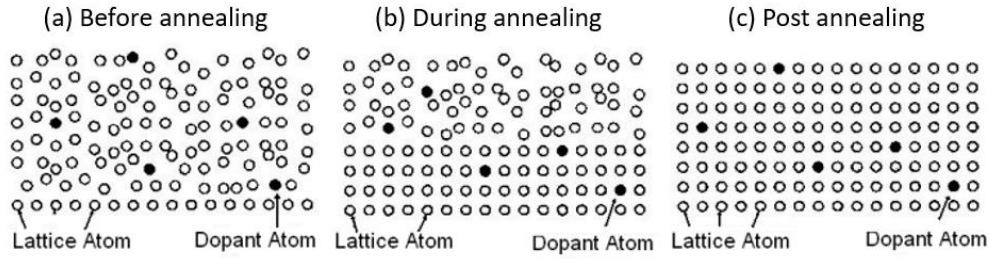


Figure 2.5. Visualization of the impact of post-annealing [26].

Ion implantation presents several benefits in comparison to diffusion doping for the incorporation of dopants into semiconductor materials. The thermal phosphorus diffusion technique is not well suited to the creation of one-sided and patterned emitters. Moreover, it is important to note that there are some challenges associated with the process of boron diffusion, such as the occurrence of a boron-rich layer (BRL). The ion implantation approach has several additional advantages, including precise doping control, selective doping, shallow junctions, high dopant concentration, reduced thermal budget, and minimal contamination risk. Notwithstanding these benefits, it is important to acknowledge that both ion implantation and thermal diffusion are vital methods for doping, and choosing one is dependent upon specific process needs and issues related to device design [27].

2.1.3 Carrier-Selective Contacts Using Dopant-Free Materials

Solar cells are dependent on the successful generation of electrons and holes, as well as the subsequent collection of the aforementioned photoexcited charge carriers at electrodes that are separated from each other. A significant number of contacts utilized in the industrial production of solar cells rely on heavily doped silicon, which might result in negative outcomes such as Auger recombination or parasitic absorption. The exploration of various contact techniques that might potentially enhance performance, reduce costs, simplify processing is of great significance, considering the widespread implementation of c-Si solar cells. One method that has

the potential to address the above-mentioned concerns is the utilization of metal compounds as a layer that selectively carries charge carriers. A “carrier-selective” contact utilizing dopant-free materials in solar cells indicates a unique design that enables the effective extraction and selective transportation of charge carriers (electrons or holes) without utilizing conventional doping methods. The number of successful selective-contact performances of these materials is rapidly escalating, with the most notable solar cell demonstrations already above 23% [28]. One of the main potential benefits of selective contacts made from metal compounds is the broader range of optical characteristics they can offer. For instance, numerous metal oxides and alkali metal halides are entirely transparent throughout both the visible and infrared regions of the spectrum, effectively suppressing parasitic absorption. Additionally, the diverse selection of refractive indices these compounds provide creates possibilities for customizing anti-reflection properties and the light-trapping abilities of solar cells. Another advantage is their ability to reduce recombination losses, which are one of the major factors limiting solar cell performance. These layers can be designed to create an electric field that aids in the separation of photo-generated charge carriers. Carrier-selective layers enable electrons and holes to travel with minimal resistance towards their respective electrodes, by creating a favorable energy gradient, thereby increasing V_{oc} and improving charge collection efficiency [28]. Furthermore, these films have the advantage of being deposited at low temperatures ($T < 200\text{ }^{\circ}\text{C}$) or via solution-processing methods [29,30] which suggests a higher potential for simplifying the manufacturing process and reducing overall costs. However, despite the potential for enhancing efficiency, various obstacles must be addressed before considering the industrial deployment of such connections. The primary concerns connected with these materials are mostly related to their inadequate stability, limited compatibility with abundant electrodes, and limited ability to be produced using conventional industrial processes.

Figure 2.6 illustrates the schematic representation of the working mechanism of a silicon solar cell, incorporating selective layers for hole and electron carriers. The process of light absorption results in a non-equilibrium distribution of carriers, hence

requiring the use of separate quasi-Fermi levels, namely E_{Fn} for electrons and E_{Fp} for holes. The quantity referred to as the implied voltage (iV_{oc}) is defined as the difference in free energy existing between the two quasi-Fermi levels. The driving forces behind the electron current (J_n) and hole current (J_p) can be attributed to the gradients of the quasi-Fermi levels and the conductivities of electrons and holes. The selective layers on both sides of the absorber layer are intentionally engineered to exhibit a significant difference in their conductivities for electrons and holes, resulting in a voltage build-up (V_{ext}) between the metal contacts [28].

For the solar cell to work efficiently, as illustrated in Figure 2.6, the contacts between the absorber and both electrodes need to display a substantial asymmetry in conductivity that promotes one of the carriers. For instance, achieving efficiencies above 25% mainly requires the hole contact to have a resistance below $1 \Omega \cdot \text{cm}^2$ to holes and above $500 \Omega \cdot \text{cm}^2$ to electrons, and vice versa [31]. Therefore, selective transport arises from an imbalance in the conductivities of electrons and holes, with the p-n junction serving as one specific example of this asymmetry.

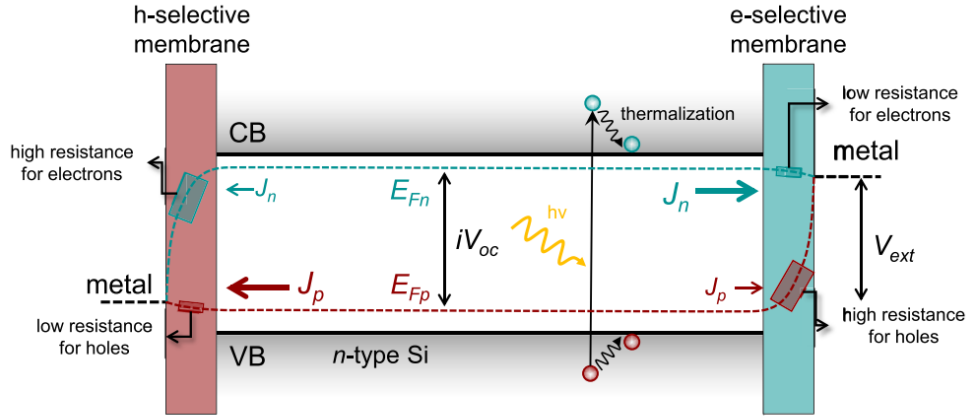


Figure 2.6. Schematic representation of the working mechanism of a silicon solar cell that incorporates symmetrical electron and hole selective layers [28].

Würfel et al. showed that selective transport is also possible without any doping, in cases where the mobility asymmetry is sufficiently pronounced [32,33]. Such contacts, frequently referred to as "carrier-selective" must have several crucial characteristics, as was discussed previously by Glunz et al. [34]. Apart from being tailored for optical performance, these attributes encompass passivation, conductivity, and selectivity. Regarding optical properties, front contacts should be transparent, while back contacts can be either transparent or reflective. A high separation of quasi-Fermi levels within the absorber is made possible by good passivation, which also results in high iV_{oc} values. To achieve a high fill factor, conductivity is crucial for reducing resistive losses at the maximum power point. Selectivity aids in reducing the amount of voltage lost within the contact, resulting in an actual V_{oc} that is close to or equal to the iV_{oc} . Selectivity metric (S) can be defined as in Equation 2.12 [35] where $j_{0,c}$ is the contact recombination current density and ρ_c is the specific contact resistivity. $k_B T/q$ means the thermal voltage (V_{th}) at a temperature of 298.15 K.

$$S = \frac{k_B T}{q j_{0,c} \rho_c} \quad (\text{Eq. 2.12})$$

Hence, for example, for a hole selective contact, the electron conductance ρ_n and hole conductance ρ_p can be defined as in the Equation 2.13 and 2.14 [35]. Decreasing the contact area fraction within the device leads to a reduction in the effective recombination parameter and a simultaneous enhancement in the effective contact resistance. The contact fraction, denoted as f_c , is a well-established parameter that provides tailoring the design of solar cells. Modifying this parameter changes the effective contact recombination parameter, denoted as J_c , and the effective contact resistance, referred to as ρ_c , within the device while ensuring that the selectivity remains unchanged.

$$\rho_n = \frac{V_{th}}{f_c j_c} \quad (\text{Eq. 2.13})$$

$$\rho_p = \frac{\rho_c}{j_c} \quad (\text{Eq. 2.14})$$

Figure 2.7 displays the periodic table, which emphasizes the elements employed in effective demonstrations of selective contacts based on metal compounds for crystalline silicon (c-Si) solar cells [28]. One simple method for electron transport is to use low work function metal oxides between the external metal electrode and the internal silicon absorber. Low work function metal oxides, which have a small conduction band offset with n-Si, e.g., titanium oxide (TiO_x) [36,37], zinc oxide (ZnO_x) [38], zirconium oxide (ZrO_2) [39], tantalum oxide (TaO_x) [40], magnesium oxide (MgO_x) [41–43] have recently been investigated as electron selective contacts for n-Si solar cells. For instance, the interface between TiO_x and Si exhibits a small amount of conduction band offset ($\Delta E_c \sim 0.05$ eV) and a significant valence band offset ($\Delta E_v \sim 2.0$ eV), which facilitates the passage of electrons from silicon to TiO_x while effectively limiting the migration of holes from silicon to TiO_x [44].

Conversely, high work function transition metal oxides (TMOs), e.g., molybdenum oxide (MoO_x) [45,46], vanadium oxide (VO_x) [47–51], tungsten oxide (WO_x) [52,53], and nickel oxide (NiO_x) [54] have recently been investigated as hole selective contacts for p-Si solar cells with their advantages of low optoelectrical losses [55]. Despite having relatively large work functions of about 6.0 eV, these materials have an n-type characteristic. As a result, compared to n-type crystalline silicon (c-Si), the Fermi levels are significantly lower. The Fermi levels of these TMOs align when they are combined with c-Si, creating an energy band bending of around 0.8 eV on the c-Si surface. This effect is very similar to that of the p-type amorphous silicon (a-Si:H) layer. This results in a large conduction band offset on the Si surface from the point of view of band alignment, producing an efficient inversion layer with hole accumulation. Hence, the heterojunction operates in a manner similar to a p-n junction, enabling the establishment of a theoretically significant built-in potential [56].

A	AE	TM														Ha		
I	II	III	IV	V	VI	VII	VIII		I	II	III	IV	V	VI	VII	VIII		
H		cation (electron contact) cation (hole contact) anion (or anion constituent)														He		
Li	Be										B	C	N	O	F	Ne		
Na	Mg										Al	Si	P	S	Cl	Ar		
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr	
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe	
Cs	Ba	*	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	**	Lr	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Nh	Fl	Mc	Lv	Ts	Og
*	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb				
**	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No				

Figure 2.7. Periodic table emphasizing elements utilised in metal compound based selective contacts for c-Si solar cells [28].

FF values in the literature above 80% have indeed been attained for a large number of the contacts based on metal compounds, indicating the possibility of efficient charge carrier extraction. Additionally, by using specialized a-Si:H passivation layers, contacts relying on metal compounds can achieve V_{oc} values that are comparable to the best doped-silicon contacts [28]. This proves that while some metal compound materials can create a considerable asymmetry in carrier conductivity, they fall weak when it comes to surface passivation. This emphasizes how crucial it is to increase their selectivity, preferably without using a special silicon-based passivation layer, to be able to challenge the current state of carrier selective contacts.

The characteristic properties of the magnesium oxide thin film and its band alignment when combined with n-type c-Si bulk together with the charge transport

mechanism are elaborated in more specific and detailed information in Section 3.3 and Chapter 5.

2.2 Thin Film Deposition Techniques

This section will provide the main thin film deposition methods employed in this thesis study for the fabrication of the fundamental passivation and carrier-selective layers. There are many major thin film deposition processes frequently used in the production of solar cells. The categorization of deposition techniques may be primarily determined by the source of the vapor species, whether they are created through physical mechanisms or chemical, electroless, or electrochemical processes. These techniques include physical vapor deposition (PVD), chemical vapor deposition (CVD), and solution growth. Photovoltaics commonly employ several PVD techniques, such as thermal evaporation, sputtering, and electron beam evaporation. Also, numerous CVD methods are regularly utilized including Plasma-Enhanced Chemical Vapor Deposition (PECVD), Metal-Organic Chemical Vapor Deposition (MOCVD), Atomic Layer Deposition (ALD), and Low-pressure CVD (LPCVD) [57].

The primary emphasis of the study conducted in this thesis is on research about passivation and carrier-selective thin films. Thus, this section will present comprehensive details about the synthesis of these structures, mainly using the PECVD and ALD techniques. Silicon nitride (SiN_x)-containing anti-reflective coating (ARC) structures and SiN_x /Silicon oxynitride (SiO_xN_y)-containing passivation layers have been produced using the PECVD technique. Additionally, two separate ALD machines are employed, one for coating the MgO_x carrier selective layer and the other for the deposition of an aluminum oxide (AlO_x) passivation layer.

2.2.1 Plasma-Enhanced Chemical Vapor Deposition (PECVD)

Figure 2.8 depicts the operational mechanism of the plasma-enhanced chemical vapor deposition (PECVD) technique. This technique involves the introduction of a combination of inert gases and reactant gases between the substrate that is grounded and the cathode. The cathode is subjected to the RF power, resulting in the ionization of the inert gas. This ionization process leads to the establishment of capacitive coupling between the substrate and cathode. The process of ionizing inert gas molecules promotes the dissociation of the reactant gas, enabling its interaction with other gas molecules or the substrate material. This interaction ultimately leads to the creation of a new chemical compound on the surface of the substrate. The technique of PECVD comprises a series of chemical reactions without the simultaneous generation of heat, making it a viable option for depositing materials on substrates that are sensitive to high temperatures. The method generally runs at comparatively low temperatures, often ranging from 250 °C to 350 °C, as opposed to standard CVD procedures. PECVD offers an important advantage in the generation of ions via the inert gas, enabling the bombardment of the developing thin film coating. This is of great significance in regard to its impact on several aspects such as growth kinetics, nucleation, stress, structure, and characteristics of the material being deposited [58,59].

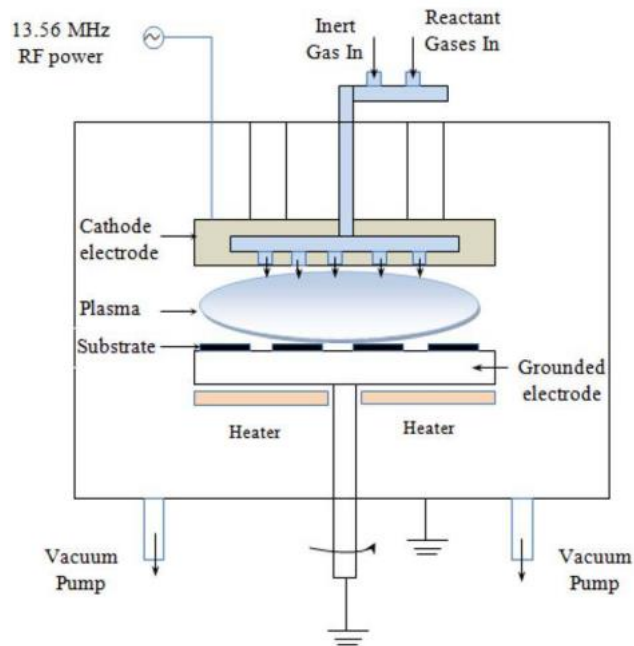


Figure 2.8. The operating principle of PECVD process [58].

PECVD has several other advantages apart from operating at low temperatures, such as providing uniform deposition, supporting effective coating on corners and steps, decreasing porosity, encouraging strong adherence to the substrate, and providing enhanced flexibility for working with different depositing materials. In addition, the ability to accurately manipulate process parameters in PECVD enables the tailoring of mechanical, chemical, electrical, and optical characteristics, as well as the stoichiometry and residual stresses of the deposited material. However, the technique exhibits some drawbacks, namely the production of hazardous by-products, challenges in achieving pure metal deposition, and the requirement for expensive process equipment [58,60].

2.2.2 Atomic Layer Deposition (ALD)

Atomic layer deposition (ALD) is a CVD method which has been receiving considerable interest owing to its remarkable characteristics, such as superior conformal pinhole-free coating and its capability to function throughout a broad

spectrum of pressures and temperatures. One of the primary benefits of atomic layer deposition (ALD) is its ability to provide uniform coverage on materials with high aspect ratios [61].

Unlike other CVD methods, ALD introduces gas precursors sequentially, not simultaneously. ALD introduces gas precursors sequentially rather than simultaneously, in contrast to the other CVD techniques. Each precursor is alternately turned on and off, with flows of inert purge gas in between. These sequential alternating pulses of gaseous chemical precursors that react with the substrate are called ‘half-reactions’. During the initial precursor pulse, reactant molecules adsorb onto the surface of the substrate. The degree of adsorption is determined by the process temperature, pressure, and time. The second precursor pulse is subsequently utilized after the chamber has been purged. The required thin layer gets formed as a result of the second precursor's reaction with the first precursor's adsorbed gases. Therefore, the ALD process relies on two key mechanisms: the chemisorption saturation process and the sequential surface chemical reaction. This series of sequential steps is referred to as the ‘ALD cycle’ and is represented in Figure 2.9. The process is intrinsically a surface reaction since the gases only interact at the surface, which contributes to its extremely conformal characteristics even on materials with high aspect ratios. Additionally, the ALD reaction is self-limiting, which means that the reaction stops as soon as all of the molecules from the initial precursor that have been adsorbed have been consumed. The cycle is repeatedly carried out to construct the film, with each cycle generally adding a monolayer or thinner thickness.

In Figure 2.9 (a) the substrate surface is shown. In (b) precursor A is introduced in a pulse and reacts with the surface and in (c) any excess precursor and reaction by-products are removed by purging with an inert carrier gas. Similarly, in (d) and (e) introduction of precursor B in a pulse and removal of excess precursor and reaction by-products are shown respectively. Excess precursor and reaction by-products are purged with an inert carrier gas. Steps (b) to (e) are repeated iteratively until the desired material thickness is attained (Figure 2.9 (f)).

ALD processes are commonly conducted at temperatures below 350 °C. The temperature range at which growth approaches saturation is unique to each ALD technique and is commonly referred to as the 'ALD temperature window'. Operating outside this ALD temperature window may occasionally result in unfavorable consequences, such as poor growth rates and non-ALD type deposition. These outcomes may be attributed to factors such as slower reaction kinetics or the condensation of precursor materials at low temperatures, as well as the thermal breakdown or rapid desorption of the precursor at high temperatures. In order to maximize the potential benefits of atomic layer deposition (ALD), it is necessary to perform the deposition procedure within the specified ALD temperature window [62].

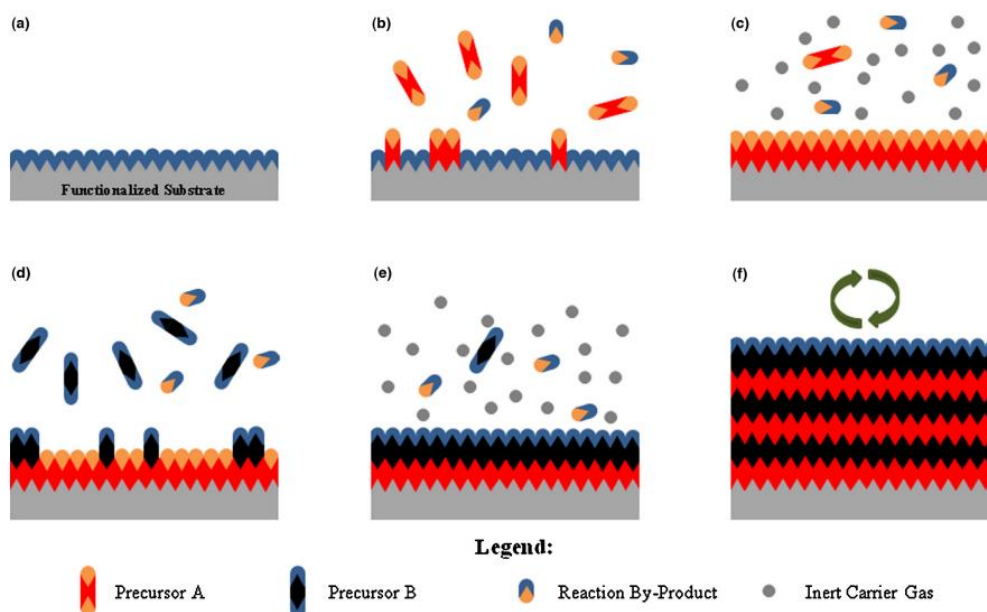


Figure 2.9. Representation of ALD process [62].

2.3 Characterization Methods

The main characterization techniques used within the scope of this thesis work is explained in this section.

2.3.1 I-V and SunsV_{oc} Measurements

Current-voltage (I-V) measurement is a fundamental technique used to evaluate the performance and characteristics of solar cells. The manufactured cells within this thesis study underwent I-V measurements using the “Spire Continuous Solar Simulator” under standard testing conditions. Important parameters such as short-circuit current (I_{sc}), open-circuit voltage (V_{oc}), fill factor (FF), and efficiency can be obtained as a result of these measurements. Moreover, an effective diode saturation current density, J_0 , can be determined for any solar cell based on its measured V_{oc} and J_{sc} , as outlined in Equation 2.15 [63].

$$J_0 = J_{sc} / [\exp\left(\frac{qV_{oc}}{kT}\right) - 1] \quad (\text{Eq. 2.15})$$

SunsV_{oc} measurement is a valuable method for analyzing the current-voltage curve of a diode while minimizing the impact of series resistance. In the context of lifetime samples, the quasi-steady state photoconductance (QSSPC) measurement holds the potential to indirectly predict the open-circuit voltage (V_{oc}) during initial manufacturing phases [64]. This predictive element is commonly referred to as implied V_{oc} (iV_{oc}). The QSSPC method, conducted using the Sinton WCT-120 lifetime tester, determines the iV_{oc} of the samples. The QSSPC approach is particularly well-suited for monitoring dopant diffusions and low-lifetime samples. The iV_{oc} value is commonly regarded as an upper threshold for the device, as it does not include the possible losses caused by metal-silicon recombination. The iV_{oc} for a p-type wafer can be mathematically expressed through the relationship between carrier concentration and voltage, as shown in Equation 2.16.

$$iV_{oc} = \left(\frac{kT}{q}\right) \ln\left(\frac{\Delta n(0) * [N_A + \Delta n(0)]}{n_i^2}\right) \quad (\text{Eq. 2.16})$$

where N_A is the doping of the substrate, n_i is the intrinsic carrier concentration in the silicon and $\Delta n(0)$ is the carrier concentration at the junction.

2.3.2 Transmission Line Method (TLM) and 4 Point Probe (4PP) Method

To define the specific contact resistivity (ρ_c) within the metal semiconductor interface, the Transmission Line Method (TLM) was first suggested for planar ohmic contacts by Shockley in 1964 [65]. In this technique, contacts are separated by variable distances from each other, and the current is constrained to flow from one metal contact into a semiconductor sheet and up into the second metal contact pad. From the voltage drop associated with this current flow, the total resistance encountered is calculated. This resistance between any two contacts can be plotted as a function of the distance between these contacts, as illustrated in Figure 2.10 below where L_T : transfer length, R_s : sheet resistance, R_c : contact resistance, Z : contact length.

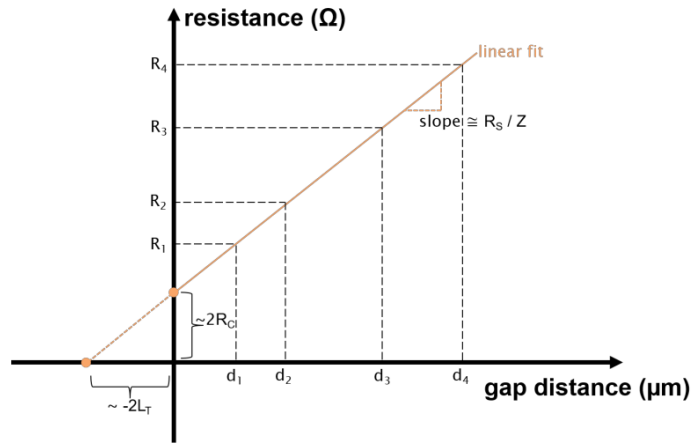


Figure 2.10. Plot of the total resistance as a function of distance between metal structures together with a linear fit [66].

The four-point probe (4PP) is a commonly employed contact method utilized to measure and analyze doping density, resistivity, or emitter sheet resistance values. The elimination of contact resistance from the measurement result is achieved by the separated voltage and current electrodes. The flow of electric current is directed through the outer probes, resulting in the generation of an induced voltage in the inner voltage probes. Within the scope of this thesis, the Transmission Line Method (TLM) and the 4 Point Probe (4PP) measurements have been conducted automatically using the PV-Tools device. Equation 2.17 and 2.18 correlates the relation between R_c , R_s and ρ_c where W is the contact width of the TLM structure.

$$R_c = \frac{R_s}{Z} * L_T * \coth\left(\frac{W}{L_T}\right) \quad (\text{Eq. 2.17})$$

$$\rho_c = R_s * L_T^2 \quad (\text{Eq. 2.18})$$

2.3.3 X-ray Photoelectron Spectroscopy and X-ray Reflectivity

X-ray photoelectron spectroscopy (XPS) is a widely employed technique for elemental analysis. Based on the photoelectric phenomenon, XPS is a surface-sensitive quantitative spectroscopic approach. This method provides information about the chemical state of the components, the elemental composition and chemical state of a material, electronic structure, and electron state density. During the procedure, a sample is exposed to monochromatic X-ray radiation, leading to the emission of photoelectrons. The energies of these photoelectrons exhibit distinct characteristics corresponding to the elements present within the sampled volume.

A typical XPS spectrum provides a graphical representation of the number of electrons observed at a certain binding energy. Each element produces a unique set of XPS peaks. The observed peaks in the spectrum are indicative of the electron

distribution within the atoms, specifically the electron configurations associated with the 1s, 2s, 2p, 3s, and subsequent energy levels [67].

X-ray reflectivity (XRR) is another valuable technique employed for the structural characterization of thin films. This method is employed to gain helpful knowledge about thin films' density, roughness, and thickness properties. Within this thesis study, XRR is employed as a technique for evaluating film thickness. The technique involves the evaluation of diffraction peaks to establish a relationship with the thickness of the layer under investigation [68]. Utilizing XRR to compute the thickness of a monolayer film involves analyzing an X-ray reflectivity curve. Such a curve generally displays repetitive intensity oscillations linked to the thin film's thickness. The thin film's thickness can be determined by subjecting the derived oscillation pattern to a Fourier transformation. The oscillation curve obtained contains information about the layer's thickness and its refractive index [69].

2.3.4 External Quantum Efficiency and Reflection

The Bentham PVE300 instrument was utilized to measure the photo-responses of the fabricated solar cells at different wavelengths. External Quantum Efficiency (EQE) is a measure used to quantify the efficiency with which a solar cell converts incoming photons of light into electrical current. It is a critical parameter in characterizing the performance of solar cells, especially in understanding their response to different wavelengths of light. The Bentham PVE300 tool uses an adjustable monochromatic light source that combines xenon and halogen elements. An automated mirror mechanism selects the appropriate source: xenon for ultraviolet-visible (UV-VIS) and halogen for visible and near infrared (VIS-NIR) regions.

Crystalline silicon has a band gap energy of 1.12 eV, corresponding to a light absorption cut-off wavelength of about 1160 nm [70]. It is also referred to as an absorption edge wavelength. It is clear that a wavelength range of around 300 to

1200 nanometers is needed to be analyzed in EQE for the crystalline silicon photovoltaic cells.

The Bentham PVE300 tool is also equipped with a barium sulphate (BaSO_4) coated DTR6 integrating sphere for conducting measurements of reflectance and transmittance. When light strikes a photovoltaic device, it undergoes both specular and diffuse reflection. To capture both aspects, the sample is illuminated at an 8° angle of incidence, and this integrating sphere is utilized to gather the total of the reflected light.

2.3.5 Electrochemical Capacitance Voltage Profiling

The Wafer Profiler CVP21 tool is utilized to measure active carrier concentration and doping profiles in the doped layers within this thesis using the technique of Electrochemical Capacitance Voltage Profiling (ECV-Profiling). Alternating CV measurements with electrochemical etching steps can provide a comprehensive doping profile with a broad depth range of information.

The presence of ions in the etching solution adjacent to the interface can influence the movement of carriers, either attracting them (accumulation) or pushing them away (depletion) in the field-affected region. In order to measure carrier concentration using CV method, specific conditions must be established to create a region where carriers are depleted. In the case of a p-type layer, where the dominant carriers are holes, this state is achieved through the presence of positive ions in the etching solution. By applying a negative bias to the semiconductor beyond its equilibrium value, positive ions are drawn to the interface, and the holes are repelled and vice versa. The assessment of doping concentration is derived from the capacitance of the interface region between the semiconductor and the electrolyte [71].

2.3.6 Spectroscopic Ellipsometry

Spectroscopic ellipsometry (SE) is a surface-sensitive optical technique used for non-destructive characterization of materials. It involves analyzing changes in the polarization state of light as it reflects off a surface. This method provides detailed information about material properties, such as thickness, refractive index, and surface roughness, with high precision and sensitivity to the angstrom level. In this thesis study, the Semilab ellipsometer tool is utilized to analyze the thicknesses of thin film layers.



CHAPTER 3

OPTIMIZATION OF THIN FILM LAYERS

This chapter provides a comprehension of the optimization approach employed for various thin film structures utilized in solar cell technologies established within the context of the research conducted for this thesis. Additionally, the related consequences of these optimization efforts are discussed. The thin film structures mentioned in this regard include silicon nitride (SiN_x) and silicon oxynitride (SiO_xN_y), which have dual functionality as passivation layers and anti-reflective coatings (ARCs). Additionally, the optimization of the aluminum oxide (AlO_x) film, which is used specifically for passivation purposes, is discussed. Furthermore, the optimization of the magnesium oxide (MgO_x) thin film layer having electron selectivity is employed for its application in carrier selective functions.

3.1 Silicon Nitride and Silicon Oxynitride Film Optimizations

Silicon nitride (SiN_x) and silicon oxynitride (SiO_xN_y) films have a wide range of significant uses in the field of solar cells due to their distinctive characteristics and functions. Within the scope of this thesis, two principal applications of the layers SiN_x and SiO_xN_y or their stack layer $\text{SiN}_x/\text{SiO}_x\text{N}_y$ in solar cells are employed, namely as an anti-reflective coating (ARC) and as a passivation layer. SiN_x and $\text{SiN}_x/\text{SiO}_x\text{N}_y$ stack is commonly utilized as an ARC layer on the surface of solar cells which mitigates reflection losses by lowering the quantity of incident light that bounces back, thereby increasing the total light absorption and efficiency of energy conversion in the solar cell. The refractive index of the SiN_x film ranges from 1.8 to 3, whereas the SiO_xN_y film exhibits a broader range of 1.5 to 3.0 [72]. In addition, these hydrogenated layers function as a highly effective passivation layer, mitigating surface recombination and decreasing non-radiative recombination of electron-hole

pairs. Hence, the enhancement of carrier lifetime leads to an increase in the performance of the solar cell. In addition to these primary applications, silicon nitride and silicon oxynitride films can also serve as an etch mask, encapsulation layer, back surface field, diffusion mask, etc. The utilization of SiO_xN_y and SiN_x structures in a stack configuration can be bi-directional. In other words, depending on its position on the solar cell and the purpose of the application, it is possible to deposit the SiO_xN_y layer either on top of the SiN_x structure or vice versa. Their adaptability makes these layers important components in solar cell technology, improving the efficiency, reliability, and overall performance of photovoltaic systems.

The PECVD tool used in this thesis study is located in the Center for Solar Energy Research and Applications (GÜNAM) Photovoltaic Line (GPVL) is a pilot-size tube type with a 252 wafer capacity (18 rows, 7 columns, 2 wafers per interval) [72–74]. In this direct plasma tool operating at a low frequency of 50 Hz, wafers are positioned horizontally between graphite plates, with their surfaces facing each other. The procedure involves the generation of a capacitively coupled plasma that glows between the two wafers, as seen in Figure 3.1.

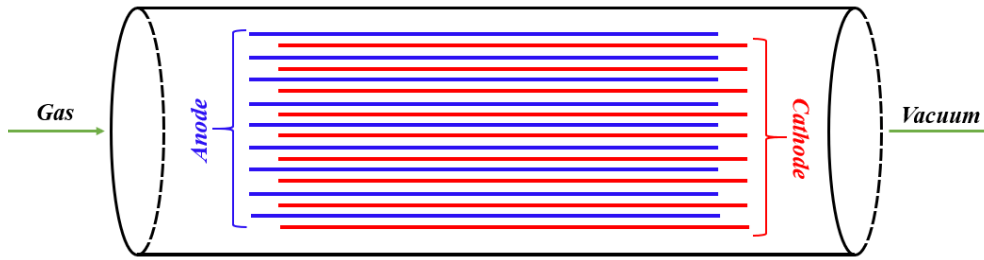
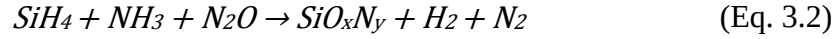
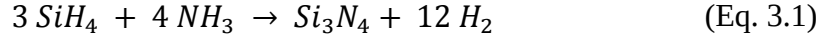


Figure 3.1. Top view of the horizontal tube of the industrial PECVD system [73].

By decomposition of silane (SiH_4), ammonia (NH_3), nitrogen (N_2) gases, SiN_x layer is coated on the surface of the wafers. Similarly SiO_xN_y is coated on the surface of the wafers by using nitrous oxide (N_2O) instead of nitrogen. Equation 3.1 and 3.2

represents the fundamental synthesis formulas of the reaction for the Si_3N_4 and SiO_xN_y layers [75,76].



For the optimization studies of ARC layer, large area 156 mm x 156 mm pseudosquare, 180 μm solar mono-c Si wafers are used. Reflectance is measured with an integrating sphere setup in 300 nm - 1200 nm range with 10 nm intervals. Film thickness and refractive index measurements are conducted via spectroscopic ellipsometer.

3.1.1 Uniformity Optimizations

In order to check the uniformity along the boat, textured samples along 5 rows and 7 columns (35 wafers in total) are treated through SiN_x deposition process. The rest of the graphite boat is filled with dummy wafers and after they reach a specific thickness during trials, dummy wafers are also replaced to prevent stress-induced bending and breakage.

To obtain uniformity along the boat, pressure, RF power, process gas flows, N_2 flow during deposition, RF duty cycle are employed as optimization parameters. The temperature of 5 different zones of the tube is kept constant at $\sim 450^\circ\text{C}$ during the plasma process for all runs. Additionally, the NH_3/SiH_4 flow rate is not varied during deposition trials and is kept at 3.5. The range of parameters employed is given below in Table 3.1. Pressure is varied between 100 Pa and 200 Pa, while the low-frequency RF power is changed from 1000 W up to 4500 W. As the boat is capable of processing 252 wafers, these correspond to power densities of 13 mW/cm^2 to 58 mW/cm^2 . Another parameter, the duty cycle of the plasma, which is defined by the

relative duration of the pulse-on time in plasma systems, is depicted in Figure 3.2 [77]. The duty cycle is the factor that determines the effective power density of the process. It is varied from 1/38 to 1/2 throughout the optimizations to find the best homogeneity across the boat. In addition, the presence of N₂ flow during the plasma process is investigated to see its effect on coating uniformity.

Table 3.1 Parameter Set Used for Optimization of SiN_x ARC Layer

	<i>Pressure (Pa)</i>	<i>Power (W)</i>	<i>N₂ Flow</i>	<i>RF on/off Duty Cycle</i>
Min	100	1000	Off	1/38
Max	200	4500	On	1/2

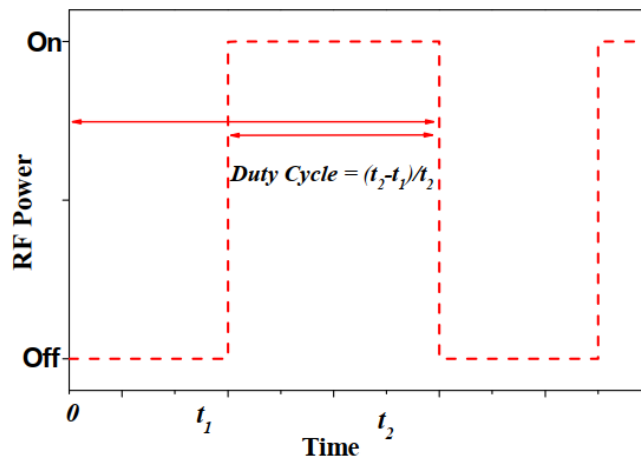


Figure 3.2. Duty cycle representation [74].

Through numerous experimental runs involving different pressure settings, a notable observation is made regarding the influence of pressure on the uniformity along the boat. Specifically, when the pressure is increased from 100 Pa to 200 Pa, the coating tendency shifted from being in favor of the gas side to the pump side. Moreover, no coating is detected at the lower and upper limits of this pressure interval for the pump

and gas sides, respectively. However, it was found that moderate pressure levels proved to be more effective in achieving a well-distributed coating across the entire boat, resulting in the absence of any uncoated samples, as shown in Figure 3.3.

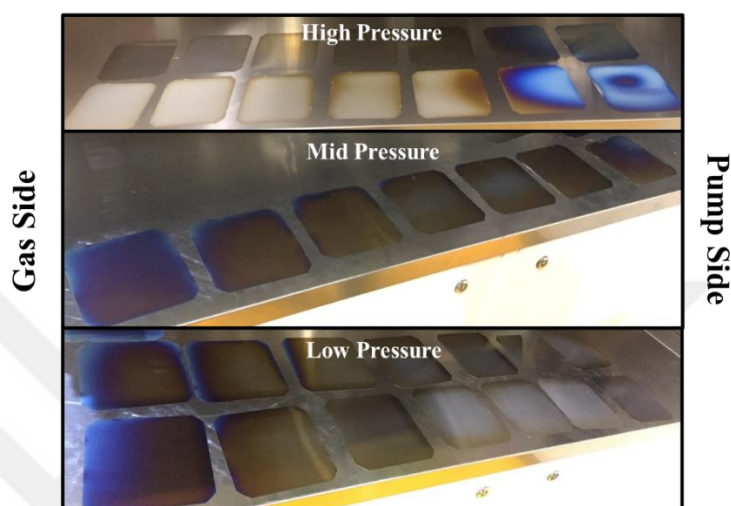


Figure 3.3. Effect of pressure on uniformity along the boat.

Similarly, it is discovered that adjusting the amount of N_2 flow has an influence on the PECVD boat's level of uniformity, as seen in Figure 3.4. An increase in N_2 flow provides a significant improvement in coating distribution, which reaches a breakthrough point at 1000 sccm and starts to be ineffective after this point.

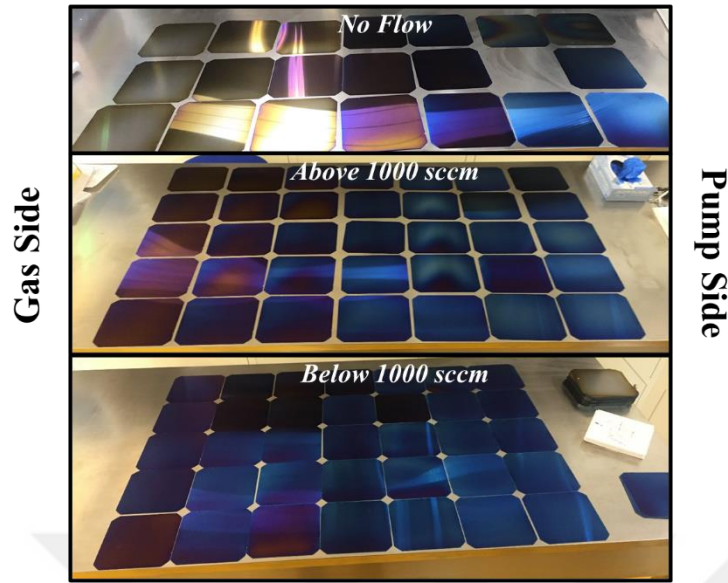


Figure 3.4. Effect of N_2 flow on uniformity along the boat.

3.1.2 Thickness Optimizations

Spectroscopic ellipsometry is carried out on 35 wafers coated with the optimized SiN_x recipe shown in Section 3.1.1. The samples are selected from different coordinates in x and y directions which represent specific regions at the boat. The average center thickness of the samples is found as 80.3 ± 20.6 nm. However, outliers with 117.2 nm maximum and 51.5 nm minimum values, resulted in 66 nm thickness difference at most in the sample set. The average of refractive index extracted from ellipsometry measurements from the center of the cells at 632.8 nm is found as 2.19 with 0.12 standard deviation where the optimum value for least optical loss should be around 2.0 [78]. Thickness and refractive index distribution schematics of the 35 wafers are shown in the Figure 3.5.

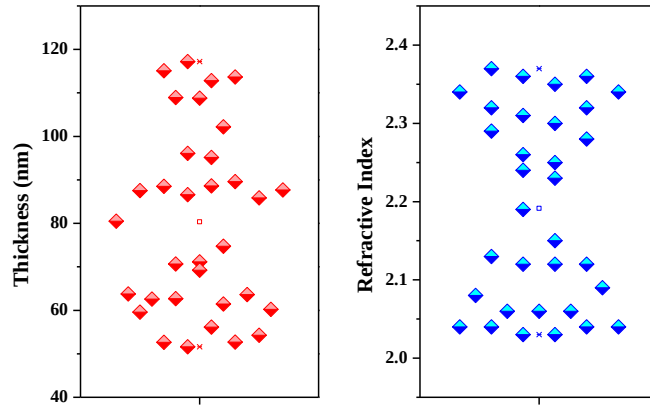


Figure 3.5. Thickness and refractive index uniformity on samples.

Figure 3.6 shows that the samples with higher refractive index have lower thickness. Due to the decrease in the density of SiN and Si-H bonds, the thickness of the layer increases. The less dense the material the lower the refractive index is obtained. Alternatively, as layer becomes denser, its refractive index increases as well as it becomes thinner [79].

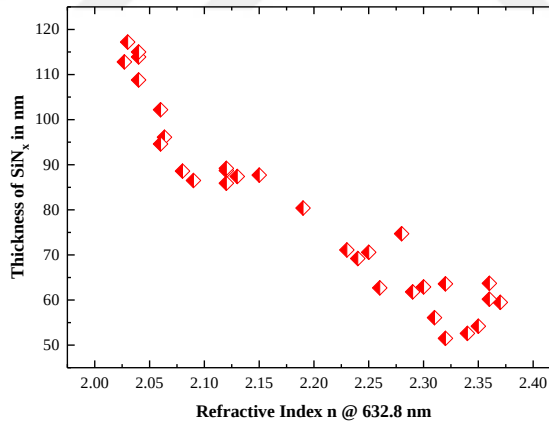


Figure 3.6. Refractive index vs thickness.

3.1.3 Reflection Optimizations

Reflection measurements are carried out at 5 different points of the same 35 samples where four of them are from the corners and one is from the middle. Average

weighted reflectance of the textured samples with optimized ARC recipe is calculated to be around 6.46 % as in Figure 3.7.

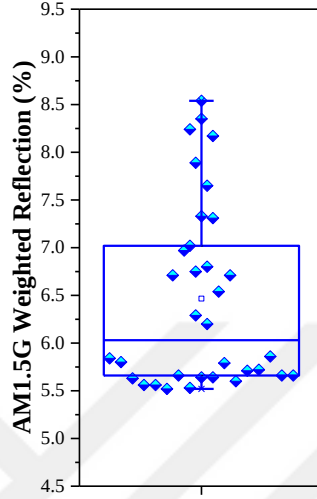


Figure 3.7. The reflection uniformity on the boat.

3.1.4 Passivation Optimizations

The primary aim of the above-mentioned adjustments is to optimize the conditions of the pilot-size tube PECVD tool. As a result, primarily the single SiN_x layer is employed to find the optimized production conditions of the PECVD tool. Additionally, for a more comprehensive exploration of SiO_xN_y optimizations, a detailed study can be found in the thesis written by Canar, H. H. (2023) [72].

The main purpose of integrating SiN_x and SiO_xN_y layers is to achieve effective passivation. This section of the thesis examines the optimization of passivation performances of both SiN_x and the stacks of SiN_x and SiO_xN_y layers. The surface passivation phenomena involve two main concepts: one is the reduction of the density of interface defects (D_{it}) through chemical passivation, and the other is the decrease in electron or hole concentration at the surface, known as field effect passivation. In the chemical passivation, during the annealing or firing step, the

hydrogen which is present in such hydrogenated films is released and passivates the dangling bonds at the surfaces, lowering the D_{it} of the interface state density. In field effect passivation, the presence of an insulating film leads to passivation thanks to the fixed charges (Q_f) contained within the film. SiN_x films and SiN_x/SiO_xN_y stacks possess positive fixed charges, whereas Al_2O_3 films carry negative fixed charges [72]. These films act as effective shields for minority carriers, i.e. either holes or electrons on the surfaces, thereby reducing surface recombination through the field effect passivation mechanism [80].

To evaluate the passivation capabilities of the produced films, symmetrical samples are prepared with double-sided SiN_x layers and SiO_xN_y/SiN_x stack coating using the middle rows of each column on the boat. These samples are fabricated using solar-grade, double-sided pyramid-textured n and p-type Czochralski (Cz) mono-crystalline silicon wafers with resistivity ranging from 1 to 3 $\Omega.cm$. The implied V_{oc} (iV_{oc}) of the samples is determined using the quasi-steady-state photoconductance method (QSSPC), using a Sinton WCT-120 lifetime tester, after firing at a peak temperature of 800 °C, as shown in Figure 3.9. For both types of crystalline silicon wafers, by depositing a few nanometers of SiO_xN_y film with a refractive index of 1.73 beneath the 95 nm SiN_x film (Figure 3.8) with a refractive index of 1.96, iV_{oc} improves due to reduced D_{it} , resulting in lower surface recombination. For both wafer types, iV_{oc} values of 700 mV have been achieved with the application of a thin SiO_xN_y film at the Si interface [72]. The reason for similar passivation performances observed in both wafer types may be the dominance of chemical passivation in this case.

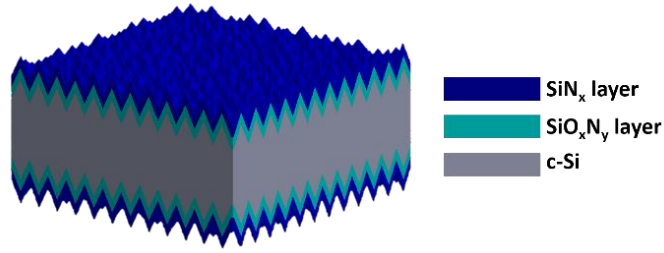


Figure 3.8. 3D representation of the symmetrical $\text{SiO}_x\text{N}_y/\text{SiN}_x$ passivation sample.

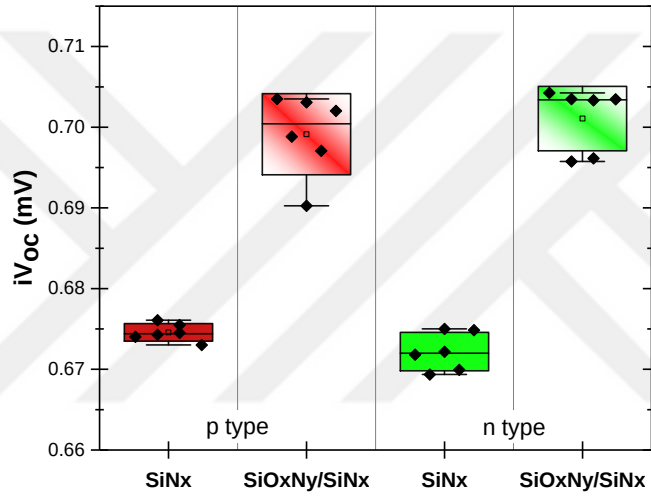


Figure 3.9. iV_{oc} values of the SiN_x and $\text{SiO}_x\text{N}_y/\text{SiN}_x$ passivation samples on p-type and n-type textured Si wafers after firing process.

3.2 Aluminum Oxide Film Optimizations

Atomic Layer Deposition (ALD) is recently becoming the most preferred aluminum oxide (Al_2O_3) deposition technique due to its high uniformity, conformity, and precise thickness control at the angstrom scale, at lower deposition temperatures. This section of the thesis focuses on the optimization studies that have been carried out to enhance the passivation performance of the Al_2O_3 layer. All of the information that is presented in this section may also be found in the paper that was written by

Kökbudak, G. et al. [81]. This contribution aims to improve the passivation performance of the PER'X' (Passivated Emitter and Rear Cell 'PERC'-based architectures) and carrier-selective passivating contact (CSPC) solar cells [82] by utilizing ultra-thin (2-5 nm) Al_2O_3 deposited using industrially feasible tools and processing steps. PERC-based architectures include passivated emitter rear locally diffused (PERL) and passivated emitter rear totally diffused (PERT).

The ALD tool used in this thesis study is manufactured by the SoLayTec Company and located in the GÜNAM Photovoltaic Line (GPVL) is a pilot-size tool having throughput capacity of 100 wafer/hour. Al_2O_3 films are deposited on p-type Cz-Si wafers by spatial ALD tool using trimethylaluminum (TMA) as the aluminum precursor, water (H_2O) as oxidant, and N_2 as the purge gas. In the Fast-ALD Process Development Tool (PDT) (Figure 3.10), the wafer is periodically subjected to two precursor gases, namely nitrogen (N_2) carrying trimethylaluminum (TMA) and nitrogen (N_2) carrying water vapor (H_2O). The precursor gases originate from a liquid source, which is delivered into the system via canisters. The wafer is inserted into and removed from the system through the use of cassettes.

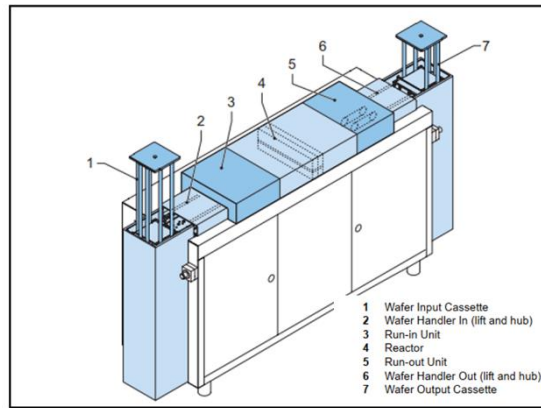


Figure 3.10. Overview of the Fast-ALD process development tool [83].

Several thicknesses and post-anneal conditions for the Al_2O_3 layer are considered to evaluate $\text{Al}_2\text{O}_3/\text{SiN}_x$ stack passivation performance after the high-temperature firing process. Thin films of Al_2O_3 known to be excellent passivation material to suppress

defects, especially on p-type c-Si surfaces, are currently the most extensively explored and implemented in the solar cell industry thanks to their superior chemical and field-effect passivation properties [84,85]. Chemical passivation is realized by the formation of an unintentional SiO_x amorphous layer at the interface, which forms effective passivation to Si surface bonds, resulting in a reduced D_{it} [84,86]. On the other hand, high density of negative fixed charges (Q_f) of the Al_2O_3 provides field effect passivation which repels photogenerated minority charge carriers (electrons) away from the rear interface [87]. Post-annealing of Al_2O_3 further enhances the passivation performance due to the overall improvement of Q_f and D_{it} [85,87]. Post-annealing can activate the negative Q_f [88] and enhance the growth of interfacial SiO_x formed at the $\text{Al}_2\text{O}_3/\text{Si}$ interface during the ALD process. Hydrogen from the Al_2O_3 bulk could also diffuse to the $\text{Al}_2\text{O}_3/\text{Si}$ interface and saturates the dangling bonds there. The SiO_x and H passivation together are considered to contribute to the substantial reduction in D_{it} [85,87]. Post-annealing conditions, usually in a tube furnace, under different ambient such as N_2 [85,89–91], forming gas (FG, 5% H_2 , 95% N_2) [89,92,93] and atmosphere (ATM) [89] in the 300-750 °C temperature range have been extensively studied in recent years.

SiN_x capping layer on Al_2O_3 , commonly used as a barrier layer against rear metallization, assists in optimizing rear side reflectivity when used under the metal layer on the rear side [94,95]. However, during the firing process of metal contact formation, usually at elevated temperatures, the $\text{Al}_2\text{O}_3/\text{SiN}_x$ stack may be delaminated, due to the well-known blistering phenomena [96,97]. Blistering deteriorates passivation quality and reduces the optical benefits of the rear stack. Post-annealing thermal treatment of the Al_2O_3 layer, before SiN_x deposition, was found to eliminate the markers arising from blistering by the process called “out-gassing” [90,91]. Al_2O_3 thickness has also been found to be crucial for this blistering effect. It was shown that blistering occurs due to the thick enough Al_2O_3 layer acting as a gas barrier and hence leading to bubble formation upon thermal treatments above a certain critical temperature. It is reported that a thick enough Al_2O_3 layer without an annealing step at temperatures up to 700 °C prior to SiN_x capping leads to

blistering [90]. It has also been demonstrated that fired stacks of spatial ALD deposited Al_2O_3 and PECVD deposited SiN_x suffer from blistering for Al_2O_3 layer thicknesses > 6 nm, if no annealing step is applied between Al_2O_3 and SiN_x layer depositions. Recent studies have shown that the effect of SiN_x capping layer thickness and firing temperature on passivation quality is rather weak for the considered SiN_x thickness in the 70-110 nm range and peak firing temperature in the 750- 870 °C range [96]. Hence, in this section of the thesis, the capping SiN_x layer thickness and processing conditions, together with the firing temperature of the $\text{Al}_2\text{O}_3/\text{SiN}_x$ stack layer, are kept constant to examine the influence of Al_2O_3 thickness on the firing stability and passivation performance of the $\text{Al}_2\text{O}_3/\text{SiN}_x$ stack layers.

3.2.1 Symmetrical Sample Preparation for Passivation Optimizations

P-type (100) Cz mono c-Si wafers, with the size of $156.75 \times 156.75 \text{ mm}^2$, the resistivity of 1-3 $\Omega\cdot\text{cm}$, and thickness of 190 μm , are employed. The wafers are pyramidally textured and cleaned using ozone (O_3) based cleaning in one single tool. Afterward, HF dip is performed to remove silicon oxide from the surfaces. As it was reported in an earlier study [98] that when using $\text{AlO}_x/\text{SiN}_x$ passivation stacks, small polishing removals are sufficient to obtain high solar cell efficiencies, within the scope of this study, passivation research is being carried out with symmetrically textured samples. For the purpose of measuring iV_{oc} values via QSSPC measurement technique using Sinton WCT-120 lifetime tester [99], symmetrical samples (Figure 3.11) are manufactured.

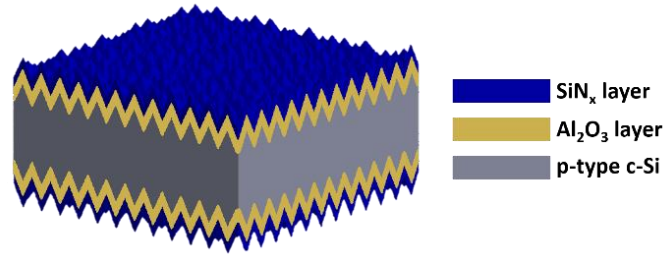


Figure 3.11. 3D representation of the symmetrical $\text{Al}_2\text{O}_3/\text{SiN}_x$ passivation sample.

Since the samples with a single Al_2O_3 layer and the $\text{Al}_2\text{O}_3/\text{SiN}_x$ stack have different optics, especially the reflectivity, optical constants during the iV_{oc} measurements via Sinton lifetime tester are regulated accordingly. Additionally, all the measurements are done similarly, i.e., after storing the samples in the dark boxes in non-degraded state and carefully measured under the light. All the reported iV_{oc} and effective surface recombination velocity (SRV) values belong to 1-sun measurement and calculations. Effect of post-annealing conditions on the single Al_2O_3 layer and on the $\text{Al}_2\text{O}_3/\text{SiN}_x$ stack is examined using the same ALD recipe shown in Table 3.2 below. The number of cycles has been adjusted based on the desired thickness.

Table 3.2 Constant Parameters Used for Al_2O_3 Fabrication.

	<i>Temperature (T)</i>	<i>Speed (m/s)</i>	<i>TMA Flow (slm)</i>	<i>H₂O Flow (slm)</i>
Recipe	200	0.75	5	5

3.2.2 Effect of Post-Annealing Conditions of Al_2O_3

Since high surface passivation levels could be obtained by post-deposition annealing of ALD grown Al_2O_3 thin films, different annealing conditions are examined in this section. Post-annealing not only causes reconstruction of the Al_2O_3 layer at the interface but also triggers hydrogen diffusion from Al_2O_3 to the c-Si/ Al_2O_3 interface [96,100]. The former increases negative built-in charges which enhance field-effect

passivation on the p-type c-Si surface, while the latter provides chemical passivation of the Si surface.

Following symmetrical Al_2O_3 film deposition on both sides of the wafers, the effects of thermal treatments have been investigated to tune the passivation quality of the layer. To reach the best passivation performance after Al_2O_3 deposition, samples are prepared by depositing 20 nm thick Al_2O_3 films symmetrically. Afterward, N_2 or FG annealing is utilized at 425 °C, 510 °C, and 550 °C for 10 and 30 minutes. Each set consists of a total of 4 different samples, to avoid misinterpretations that may otherwise arise from bulk resistivity variations of different wafers. Figure 3.12 shows the comparison of one-sun iV_{oc} values of 20 nm symmetrical Al_2O_3 -coated and activated samples. Except for the set annealed under FG at 550 °C, the passivation performance of all samples is enhanced with increasing annealing time from 10 to 30 minutes. The highest iV_{oc} of 692 mV is obtained from the sample with FG anneal at 425 °C. For 30- minute annealing, the passivation performance of the samples annealed under N_2 seems independent from the annealing temperature whereas samples that experienced FG annealing at elevated temperatures, of 510 and 550 °C, have lower iV_{oc} as compared to that obtained from 425 °C anneal. The dependence of iV_{oc} on the annealing temperature under FG is mainly due to the dehydrogenation effect which becomes pronounced at temperatures ≥ 450 °C [94]. On the other hand, the dehydrogenation effect is not detected for samples annealed under N_2 , for different temperatures, as supported by the independence of iV_{oc} values on the annealing time of N_2 annealed samples.

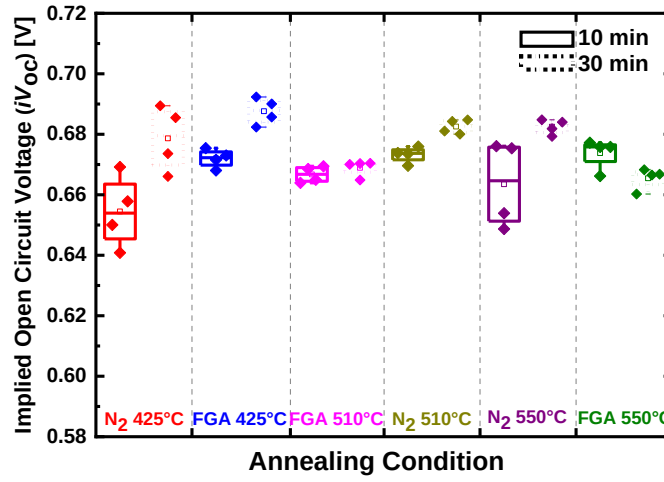


Figure 3.12. Measured implied V_{oc} of the 20 nm Al_2O_3 -coated passivation samples and activated under different annealing conditions for 10 and 30 minutes.

Hsu et al. [94] have shown that annealing under oxygen, at 600 °C, results in improved field-effect passivation due to the induced high fixed charge density while the hydrogen supplied during FG annealing (at moderately high temperatures, < 450 °C, Figure 3.12) hydrogenates the Si surface and thus improves the chemical passivation. Hence, combining both annealing scenarios leads to improved chemical and field-effect passivation on moderately thick Al_2O_3 of Al_2O_3/SiN_x stacks and thus improves overall passivation quality. Based on these findings, a new set of samples is prepared including those prepared with our best annealing conditions obtained from the previous set (Figure 3.12), referred to as one-step (N_2 or FG), and two-step annealed samples experienced O_2 (600 °C) + FG (425 °C) annealing. To keep the total annealing time fixed at 30 minutes, one-step annealing is done for 30 minutes while two-step annealing is done for 15 minutes for each sub-step. Hsu et al. [94] have demonstrated that two-step annealing can provide good passivation only if O_2 annealing is applied first and followed by FG annealing. Otherwise, dehydrogenation of Al_2O_3/Si may occur, and exposure to oxygen results in the replacement of Si-H bonds with the Si-O bonds [94,101]. Figure 3.13 shows one-sun iV_{oc} values belonging to this set together with the samples experiencing two-step annealing conditions. O_2 ambient (10000 sccm) and atmosphere anneal (ATM) are utilized as

O₂ sources. Two-step annealing improves surface passivation compared to single gas (N₂ or FG) annealing processes for the 20 nm Al₂O₃-coated samples and shows an average iV_{oc} value of 702 mV with a peak value of 708 mV.

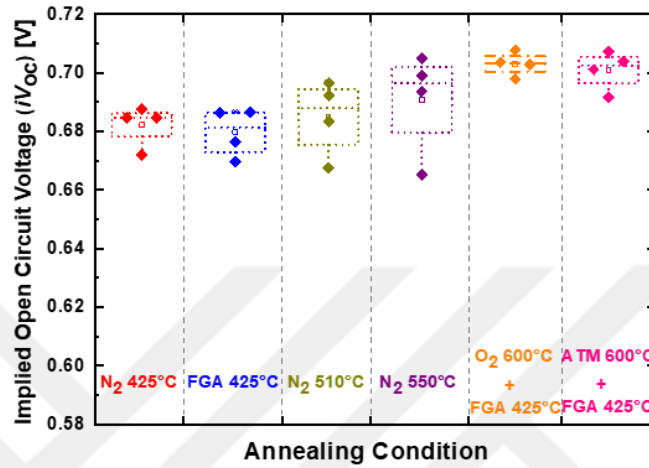


Figure 3.13. Measured iV_{oc} of the 20 nm Al₂O₃-coated passivation samples and activated under different annealing conditions for 30 minutes in total.

3.2.3 Passivation Performance of Al₂O₃/SiN_x stack layer

Nonetheless, thus far, all passivation sets discussed do not reflect the real rear side passivation of the common PERC architectures. To imitate the actual PERC structure which features the rear side passivation layer of Al₂O₃ capped by SiN_x, that will experience high temperature firing step during metal contact formation, a new set is fabricated by depositing the passivation structure of Al₂O₃/SiN_x (20/120 nm). Reference batches with only the SiN_x layer (120 nm), only the Al₂O₃ layer (20 nm) as activated, and the stack layer (20/120 nm) without Al₂O₃ activation are also included in this set, for comparison. For the annealed ones, annealing is applied immediately after Al₂O₃ deposition. Implied V_{oc} values are measured before and after the firing step, carried out at the set temperature of the belt furnace of 910 °C; and the real measured peak temperature of 800 °C.

A total of 6 different anneal conditions are implemented to activate the Al_2O_3 layer before capping by PECVD SiN_x . It can be seen from x that only the SiN_x layer, deposited on the bare c-Si wafers, results in a modest passivation quality with iV_{oc} in the range of ~ 640 mV. Annealing 20 nm Al_2O_3 layer under N_2 at 425°C for 30' (Anneal A) has no significant impact on the passivation performance of the $\text{Al}_2\text{O}_3/\text{SiN}_x$ stack layer and notably leads to the same iV_{oc} values of as-deposited $\text{Al}_2\text{O}_3/\text{SiN}_x$ stack, before and after firing step. This suggests that the thermal treatment associated with the PECVD process has the same effect as 'Anneal A' conditions. Al_2O_3 -coated samples that experienced annealing under FG, for 30 minutes, and capped by SiN_x , show better passivation performance, before and after firing, than those that experienced N_2 annealing for the same duration. Furthermore, iV_{oc} of 15 minutes annealed (Anneal C) samples under FG are slightly less than that of 30 minutes annealed (Anneal B) ones. O_2 annealing performance does not seem to be time-dependent since 15- and 30-minute (Anneal E and Anneal D) annealing results in similar iV_{oc} values. Samples experienced 'Anneal F' comprising of two-step annealing for a total of 30 minutes, show higher iV_{oc} values and fair firing stability. The highest iV_{oc} value of 693 mV is recorded from the two-step annealed batch, with a 20 nm Al_2O_3 /120 nm SiN_x stack passivation layer, after the firing step. Implied V_{oc} of the samples with only Al_2O_3 , experienced two-step annealing (Al_2O_3 + Anneal F), reduced after capping by SiN_x . After firing, Al_2O_3 +Anneal F capped by SiN_x shows similar iV_{oc} values as compared to Al_2O_3 +Anneal F, yet with narrower deviations. It is worth mentioning that the presence of SiN_x , in PERC design, is a prerequisite for better firing stability, improved rear side reflectivity (reduced rear parasitic absorption), and avoiding direct Al_2O_3 damage by subsequent aluminum deposition and firing.

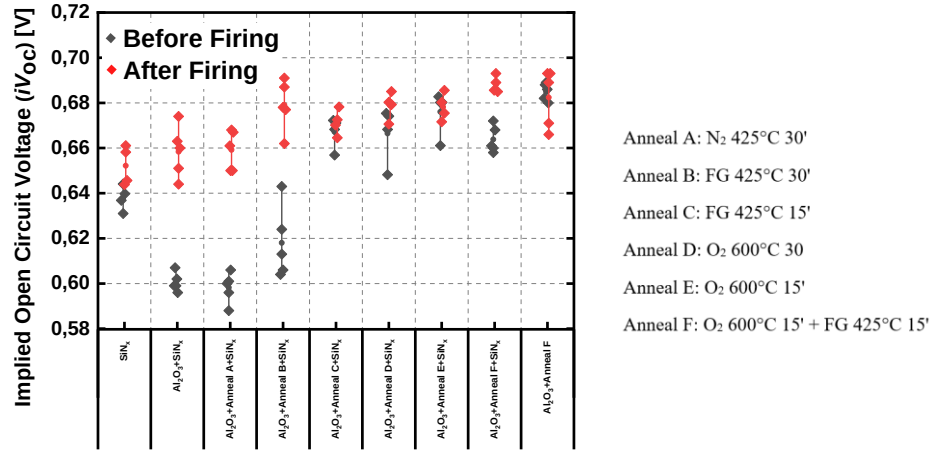


Figure 3.14. Measured implied V_{oc} of the passivation samples before and after firing.

3.2.4 Effect of Al₂O₃ layer thickness

Dependence of Al₂O₃ thickness on the Al₂O₃/SiN_x passivation performance after firing has been widely investigated by several groups [85,89,93,96]. Al₂O₃ with thicknesses of <10 nm capped by PECVD SiN_x or SiO_xN_y layers is known to improve passivation after activation or firing steps because of the hydrogen diffusion from hydrogenated layers through thin Al₂O₃ towards the Si/Al₂O₃ interface, promoting the chemical passivation. As mentioned before, blistering becomes detectable for spatial ALD grown Al₂O₃ layers with thicknesses above 6 nm if no annealing step is performed before SiN_x capping. Interestingly, in any of the samples produced in the scope of this thesis study, the blistering is not detected after any step of deposition, post-deposition annealing, or firing processes. This is because all deposited Al₂O₃ layers experienced the activation annealing step, out-gassing of the films [91], before SiN_x capping.

It is known that in this industrial ALD tool, a single pass deposits an Al₂O₃ layer with a thickness of 13.5 Angstroms (Å). In order to reach the appropriate thickness, the pass value within the device has been modified. In order to determine the optimal

thickness of the Al_2O_3 layer for the $\text{Al}_2\text{O}_3/\text{SiN}_x$ stack passivation structure, a series of samples are fabricated with five distinct Al_2O_3 thicknesses ranging from 2 to 30 nm as shown in the Figure 3.15. All Al_2O_3 layers are activated by the best-performed annealing condition, ‘Anneal F’, (Figure 3.14), for the 20 nm Al_2O_3 case. Two sets of samples are considered, the first one consists of only as-activated Al_2O_3 before and after firing. In the second set, the as-activated Al_2O_3 is capped by 120 nm thick SiN_x . Here 2 nm and 30 nm thick Al_2O_3 correspond to 15 and 220 ALD passes, respectively. For samples with only Al_2O_3 experienced two-step annealing, iV_{oc} is almost the same for all thicknesses above 5 nm (Figure 3.15) with iV_{oc} well above 680 mV, on average. As-activated 2 nm thick Al_2O_3 resulted in modest iV_{oc} with an average of 622 mV and increased to 649 mV after firing. After the SiN_x capping of 2 nm-thick activated Al_2O_3 , an average iV_{oc} of 650 mV is obtained before the firing process. The lower iV_{oc} value of the 2 nm $\text{Al}_2\text{O}_3/\text{SiN}_x$ stack than the stacks including thicker Al_2O_3 layers can be attributed to insufficiently negative Q_f values for extremely thin Al_2O_3 layers under SiN_x coatings, according to the study reported by Schuldis et al. [92]. Moreover, the low iV_{oc} obtained for Al_2O_3 with thickness < 5 nm is likely due to poor chemical passivation, which arises from the incomplete reaction of TMA molecules for a few ALD cycles. An interesting improvement in the passivation quality is recorded for 2 nm thick Al_2O_3 , which may be due to improved chemical passivation together with the increased negative fixed charge density at the $\text{Al}_2\text{O}_3/\text{Si}$ interface. This can be explained by the induced oxygen atoms, during firing, at the $\text{Al}_2\text{O}_3/\text{Si}$ interface resulting in even higher oxygen to aluminum atomic ratio. However, for 5 and 10 nm bare Al_2O_3 , iV_{oc} decreases after firing, still with values higher than those obtained from 2 nm layers. Degradation in the passivation quality of these layers is presumably due to hydrogen loss at the $\text{Al}_2\text{O}_3/\text{c-Si}$ interface due to the absence of a capping layer during firing, which alters the chemical passivation. The maintained high passivation levels of 20 and 30 nm thick Al_2O_3 are because layers with large thicknesses can themselves provide the hydrogen necessary to achieve decent chemical passivation of the Si surface [102]. Capping with SiN_x seems to have a miniature effect on iV_{oc} recorded from only Al_2O_3 with

thicknesses above 5 nm before firing, while capping 2 nm thick Al_2O_3 with SiN_x improves the corresponding passivation quality. Firing 2 nm Al_2O_3 /120 nm SiN_x stack further improves iV_{oc} to 676 mV on average. At this point, it is important to mention that this pronounced improvement is because hydrogen diffusion from SiN_x to the $\text{Si}/\text{Al}_2\text{O}_3$ interface is more feasible through 2 nm layer, improving chemical passivation. On the other hand, firing drastically deteriorates the passivation quality of 5 and 10 nm Al_2O_3 . The degradation of passivation at these thicknesses after capping with SiN_x and firing is in line with the observed decrease in iV_{oc} before SiN_x capping and after firing. While firing bare Al_2O_3 with these thicknesses resulted in hydrogen loss at the $\text{Al}_2\text{O}_3/\text{Si}$ interface, these thicknesses may be thick enough to partially hinder hydrogen diffusion from SiN_x to the $\text{Si}/\text{Al}_2\text{O}_3$ interface. For thicknesses above 20 nm, the films provide field-effect passivation, which, along with the decent diffused hydrogen from Al_2O_3 itself [102], reduced interface state density, results in excellent and maintained iV_{oc} values after firing. Finally, the stack with 30 nm thick $\text{Al}_2\text{O}_3/\text{SiN}_x$ resulted in the highest iV_{oc} .

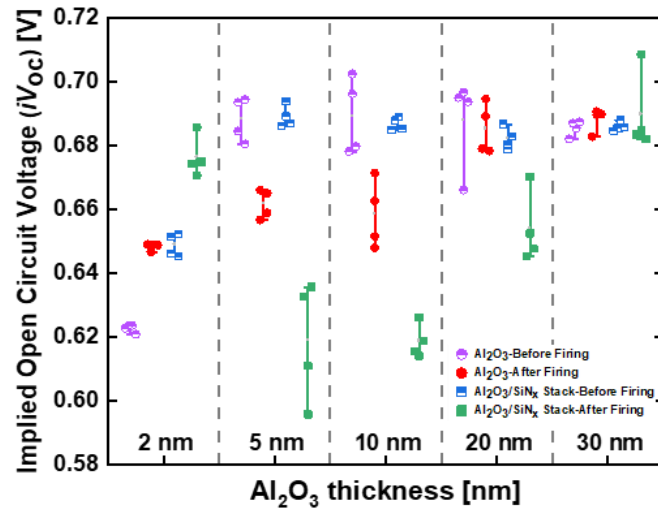


Figure 3.15. Measured iV_{oc} values depending on the Al_2O_3 thickness (2-30 nm).

As seen from Figure 3.15, the impressively high iV_{oc} values obtained from below 5 nm Al_2O_3 /120 nm SiN_x stacks after firing aroused interest in the Al_2O_3 thicknesses

between 2 and 5 nm. Despite various treatments of 30 nm Al_2O_3 , iV_{oc} maintained high values; however, the focus is held on ultra-thin layers to reach more cost-effective and mass-production-compatible processes. Hence, Al_2O_3 thicknesses of < 5 nm are examined in detail. SiN_x capping thickness kept fixed again at 120 nm and all aluminum oxide layers are two-step annealed (Anneal F) after Al_2O_3 film deposition. The corresponding iV_{oc} obtained from Al_2O_3 and $\text{Al}_2\text{O}_3/\text{SiN}_x$ stacks before and after firing are depicted in Figure 3.16. For passivation layers with these thicknesses, without the capping layer, the limiting factor is their reduced chemical and field effect passivation levels, which become more pronounced for extremely thin layers. Especially the $\text{Al}_2\text{O}_3/\text{SiN}_x$ stacks where Al_2O_3 is ultra-thin, around 1 nm, can demonstrate zero or even positive Q_f values, which are attributed to the SiN_x capping layer, according to the study reported by Schuldis et al. [92]. Increasing the thickness of as-activated Al_2O_3 increases iV_{oc} before firing. Further firing steps improve the iV_{oc} of 1.2 and 2 nm-thick Al_2O_3 , while no change in iV_{oc} is recorded for 2.8 and 3.6 nm. These values indicate that for 1.2 and 2 nm layers, the field-effect and partially the chemical passivation levels are improved due to an increased oxygen to aluminum atomic ratio and thus an increased negative fixed charge density. For 2.8 and 3.6 nm, the passivation performance improvement is not detected, which may suggest that the Si/ Al_2O_3 interface is not altered by possible oxygen diffusion to the interface. This indicates that layers with these thicknesses start to hinder the feasible diffusion of oxygen to the Si/ Al_2O_3 interface. The film with 4.5 nm Al_2O_3 experienced a reduction in iV_{oc} after firing as compared to the values obtained from the as-activated layer. A similar reduction is also observed for the 5 nm as-activated thick layer (Figure 3.15). Nevertheless, all Al_2O_3 films with thicknesses between 1.2 and 5 nm resulted in similar average iV_{oc} after firing. A similar trend to that observed for as-activated Al_2O_3 is seen for stack $\text{Al}_2\text{O}_3/\text{SiN}_x$ with increasing Al_2O_3 thickness before firing. After firing, all ultra-thin $\text{Al}_2\text{O}_3/\text{SiN}_x$ stacks resulted in improved iV_{oc} with different degrees for different Al_2O_3 thicknesses except for 4.5 nm.

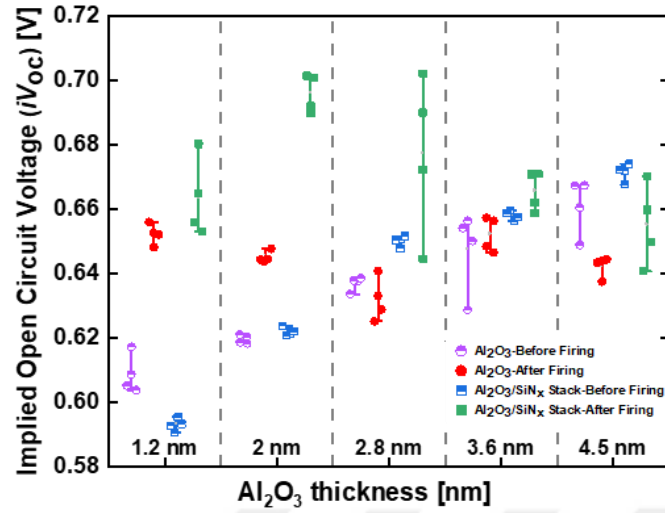


Figure 3.16. Measured iV_{oc} values for Al_2O_3 thicknesses below 5 nm.

The Al_2O_3/SiN_x stacks have shown an increasing trend in iV_{oc} with increasing Al_2O_3 thicknesses, before firing. This behavior can be attributed to the insufficient negative Q_f values due to the SiN_x capping of ultra-thin Al_2O_3 layers as already mentioned [92]. Taking these into consideration, the observed trend in Figure 3.16 further demonstrates that ultra-thin Al_2O_3 allows hydrogen diffusion from SiN_x to Si/Al_2O_3 interface, improving the chemical passivation level, after firing. The level of hydrogen diffusion through these layers is more pronounced for 1.2 and 2 nm layers. This further proves the explanation of the improvement of the passivation levels of these layers, with no SiN_x capping, after firing and is attributed to oxygen diffusion to the interface. Higher iV_{oc} of Al_2O_3/SiN_x stacks with 2 nm Al_2O_3 as compared to 1.2 nm may be attributed to ultra-thin (around 1 nm) Al_2O_3/SiN_x stacks demonstrating insufficient negative Q_f values, especially after SiN_x capping [92]. For the 2.8 and 3.6 nm layers, a slight increase, on average, in the passivation level is observed. This increase is due to hydrogen, supplied from SiN_x , that partially diffuses to the interface during firing and due to negative Q_f formation after firing. On average, the highest iV_{oc} of 695 mV, with a peak of 701 mV is recorded from only 2 nm thick Al_2O_3 and capped by SiN_x .

So far, all p-type wafers used have a resistivity of $\sim 1.2 \Omega\cdot\text{cm}$. To investigate the effect of the used wafer resistivity on the passivation quality of Al_2O_3 and $\text{Al}_2\text{O}_3/\text{SiN}_x$, two sets of p-type wafers with ~ 1.2 and $\sim 1.5 \Omega\cdot\text{cm}$ are prepared, by considering three different Al_2O_3 thicknesses of 2, 5, and 30 nm (Figure 3.17). The overall iV_{oc} trend is identical for wafers with different resistivities. Yet the record iV_{oc} of 709 mV is obtained from wafers with $\sim 1.5 \Omega\cdot\text{cm}$ resistivities, after firing of $\text{Al}_2\text{O}_3/\text{SiN}_x$ stack with Al_2O_3 thickness as thin as 2 nm.

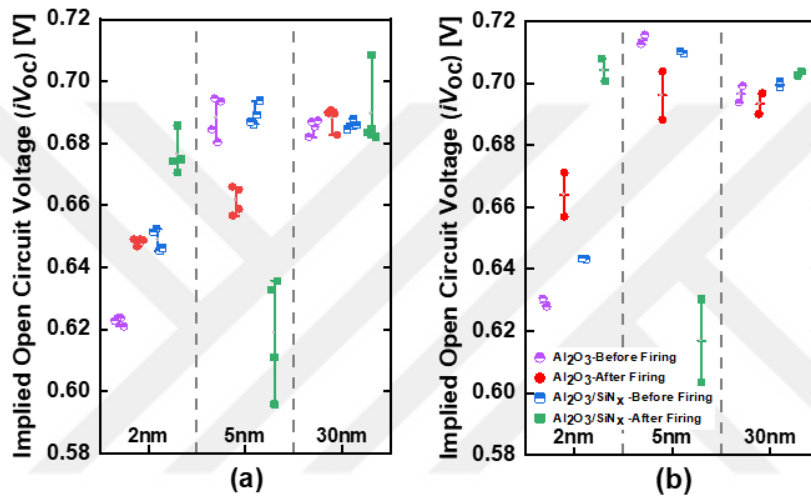


Figure 3.17. Measured iV_{oc} values for a) Wafers with the resistivity of $1.2 \Omega\cdot\text{cm}$, b) Wafers with the resistivity of $1.5 \Omega\cdot\text{cm}$.

Since still there might be a potential for the various post-deposition annealing treatments to have different impacts depending on Al_2O_3 thickness, especially regarding hydrogen diffusion, different annealing treatments applied to the 2 nm thick Al_2O_3 film and $\text{Al}_2\text{O}_3/\text{SiN}_x$ stacks using p-type wafers with a resistivity of $\sim 1.2 \Omega\cdot\text{cm}$ (Figure 3.18).

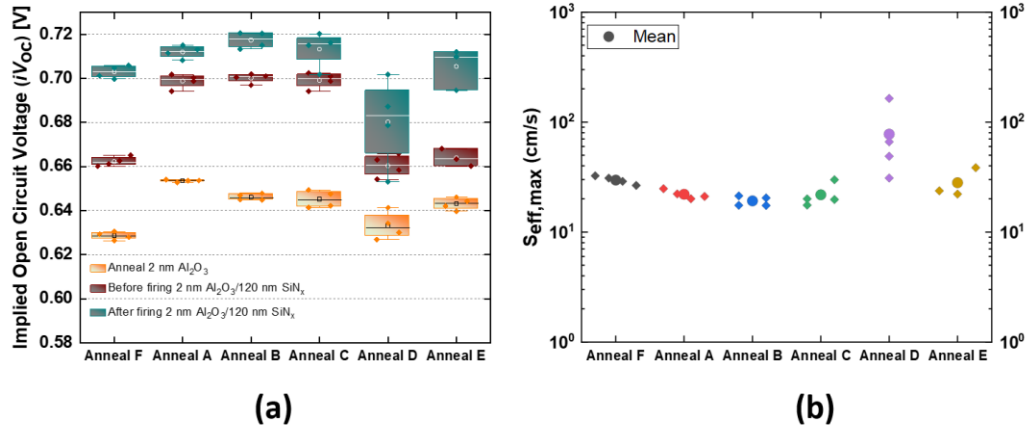


Figure 3.18. (a) Measured iV_{oc} values for 2 nm Al_2O_3 layers after activation and Al_2O_3/SiN_x stacks before and after firing b) Calculated $S_{eff,max}$ values.

For the samples activated with Anneal A, B and C, the iV_{oc} improvement with the capping SiN_x addition is greater than the samples activated with Anneal D, E and F. Anneal D, E and F includes O_2 annealing at higher temperatures (600 °C), differently from Anneal A, B and C. According to the ellipsometry and C-V analyses done by Rafi et al.[103], the effect of a high temperature anneal depends on the initial thickness of the films. For the thicker Al_2O_3 layers, the higher temperature annealing lead to a decrease in thickness due to the densification of the films, as already shown to occur [104] for TMA and H_2O -based ALD-deposited Al_2O_3 layers exposed to high-temperature conditions. On the other hand, in the case of ultra-thin films, an increase in thickness occurs when subjected to high-temperature annealing treatments due to the oxidation of the interface. Rafi et al. [103] have already shown that higher temperature treatments alter either the thickness of the ALD film, the interfacial SiO_x layer, or both. For the treatments including oxygen (ATM or O_2 annealing), SiO_x layer thickness at the interface was found to vary, while this is not the case for the FG or N_2 annealing due to the absence of oxygen [89]. Thicker interface SiO_x and ALD Al_2O_3 layers may start to block the possible hydrogen diffusion to the Si surface. This may be the reason for the decrease in passivation performance of the thin Al_2O_3 layers annealed under the oxygen involving

environment, in contrast to the high performance of 20 nm Al₂O₃ layers activated under the oxygen involving environment.

After firing of 2 nm Al₂O₃ (as-activated by anneal B)/120 nm SiN_x stack, an impressive 720 mV iV_{oc} value was measured from the p-type industrial Cz c-Si samples which were treated symmetrically.

In Figure 3.18(b), the level of surface passivation is quantified by effective surface recombination velocity (SRV). $S_{eff,max}$ corresponds to the upper limit of the effective surface recombination velocity and was calculated from effective lifetime at 1-sun (τ_{eff}) by Equation 3.3, assuming an infinite bulk lifetime [105].

$$S_{eff,max} = \frac{d}{2\tau_{eff}} \quad (\text{Eq. 3.3})$$

$S_{eff,max}$ value for the p-type Cz c-Si sample with 2 nm Al₂O₃ (as-activated by anneal B)/120 nm SiN_x stack that gives 720 mV iV_{oc}, was calculated as ~20 cm/s. Thus, these results demonstrate that activated ultra-thin spatial ALD deposited Al₂O₃ layer is well suited for industrial fabrication of PER'X' solar cells if capped by PECVD films and fired.

3.3 Magnesium Oxide Film Optimizations

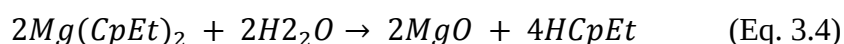
Magnesium oxide thin films have been studied and fabricated in a different ALD system from the one utilized for aluminum oxide depositions. The equipment is the Savannah S100 research-scale ALD tool manufactured by Veeco Company. This system is situated within the UNAM facility, located at Bilkent University in Ankara. This ALD device allows for the deposition of a single sample at a time, with the sample size limited to a maximum of 4 inches. Precursors are stored in separate precursor cylinders, fed into the chamber by their own vapor pressure, and can be

heated if required. ALD stop valves control the pulsing, which is timed in milliseconds. Nitrogen is the system's continuous carrier gas throughout all operations. In order to maintain the chamber's low vacuum pressure, the output pipe is connected to a vacuum pump. Depending on the specific deposition conditions, the reactor chamber may be heated to temperatures ranging from 100 to 250 °C and is designed for the deposition of films on substrates up to 100 mm in diameter.

This section provides an elucidation of the stoichiometry research of the MgO_x film as well as the subsequent optimization of its thickness according to the contact resistivity values. The examination of the passivation characteristics of the MgO_x film, conducted through an analysis of finished solar cells, is addressed in Chapter 5.

3.3.1 Stoichiometry Optimizations

In this thesis study, an investigation into the production of MgO_x layers using a water-based ALD process using bis(ethylcyclopentadienyl) magnesium (Mg(CpEt)₂) as the precursor is employed. The deposition temperature and Mg(CpEt)₂ precursor temperature are systematically varied within the ranges of 200-250 °C and 25-90 °C , respectively, in an attempt to identify the optimal process parameters. The range of parameters employed is given below in Table 3.3. Stoichiometric MgO_x production is given initial emphasis in this investigation, monitored through XPS measurements conducted within UNAM facility. X-ray photoelectron spectroscopy (XPS). This is motivated by the well-known insulating properties and wide energy band gap exhibited by stoichiometric MgO_x (x=1) [106]. The projected ALD MgO_x reaction using Mg(CpEt)₂ and H₂O may be represented as shown in the Equation 3.4 [107].



The optimization of the stoichiometric MgO_x layer thickness is achieved through the utilization of X-ray reflectivity (XRR) measurement, which is a non-destructive method used to determine the thickness of a thin films ranging from 2 to 200 nm [108]. By combining multiple experimental procedures, precise control over the stoichiometry and thickness of the MgO_x layers is successfully achieved.

Table 3.3 Parameter Set Used for Optimization of MgO_x Layer

<i>Parameters</i>	<i>Range</i>
Temperature (° C)	200-250
Mg(CpEt) ₂ Pulse (s)	1-2
Mg(CpEt) ₂ Temp. (° C)	25-90
H ₂ O Pulse (s)	0.015-0.2
Purge Mg(CpEt) ₂ (s)	5-10

The deposition process for magnesium oxide is developed and executed on a 2-inch polished silicon wafer, employing a series of treatments including acetone, alcohol, water, and a 5% hydrofluoric acid (HF) solution. The initial experiments involve the use of the Mg(CpEt)₂ precursor at ambient temperature. However, the lack of expected pressure pulse peaks seen during the procedure led to doubts over the effectiveness of the deposition. Subsequent XPS analysis of these samples revealed the absence of MgO_x-indicative signals. Next, an exploration of relevant literature highlighted the requirement to elevate the Mg(CpEt)₂ precursor temperature to a range of 80–90 °C (delivery temperature) [107]. Concurrently, a series of

incremental precursor temperature adjustments were performed in various experimental runs, incrementally raising the temperature to 50, 65, 70, 85 and 90 °C.

In the process where the operating temperature remains constant at 250 °C and the durations of the $\text{Mg}(\text{CpEt})_2$ and H_2O pulses are 2 and 0.2 seconds, respectively, the precursor temperature is established at 85°C. After allowing for a one-hour interval, apparent changes in pressure peaks are noticed, indicative of the presence of $\text{Mg}(\text{CpEt})_2$ flow. This implication is further validated by the observable alteration in color on the surface of the sample. Surface and subsurface XPS measurements were conducted on this silicon sample (Figure 3.19). The XPS results obtained from both the surface and the depth profile (Table 3.4) reveal that the deposited film is rich in oxygen and that the 'x' value deviates from unity.

Table 3.4 XPS Results from Non-stoichiometric MgO_x layer

	<i>Surface Profile</i>	<i>Depth Profile</i>
<i>Spectrum</i>	<i>Atomic Percentage (%)</i>	<i>Atomic Percentage (%)</i>
C1s	19.71	4.19
Si2p	-	0.42
O1s	56.69	58.69
Mg1s	23.6	36.7

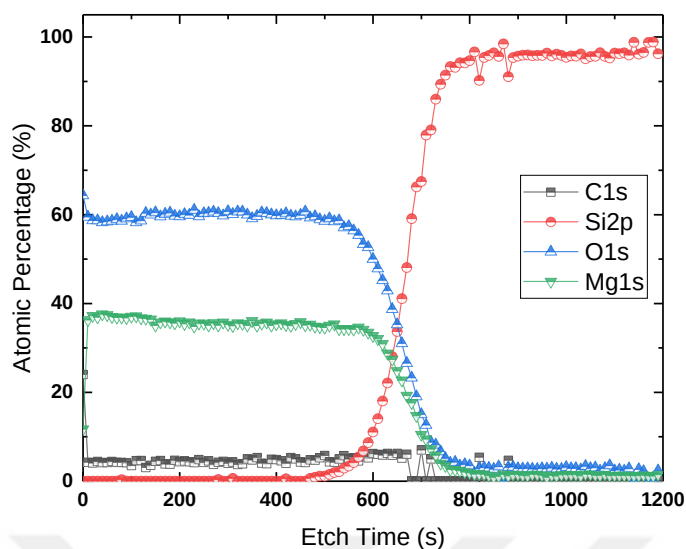


Figure 3.19. XPS depth profile from non-stoichiometric MgO_x layer.

Based on the analysis results of the oxygen-rich MgO_x film, modifications were applied to the recipe, aiming for a stoichiometric MgO_x coating. As a result of these modifications, the $\text{Mg}(\text{CpEt})_2$ precursor temperature is elevated to 90 °C, and the H_2O and $\text{Mg}(\text{CpEt})_2$ pulse durations are reduced to 0.015 and 1 second respectively. The XPS result of the MgO_x structure, which was produced using this new recipe, is provided in Table 3.5 below. The mentioned modifications have resulted in a modest decrease in the atomic proportion of oxygen, enabling the development of a MgO_x layer recipe that closely approximates a stoichiometric composition. Using this recipe, thickness analysis of the 300-cycle layer deposited on the polished Si surface was performed through X-ray Reflectivity (XRR). According to the XRR results, the 300-cycle coating resulted in a MgO_x layer with a thickness of 33.7 nm, indicating an approximate deposition rate of 0.112 nm/cycle. This is notably close to the

reported value of 1.26 Å/cycle at 250 °C provided by the manufacturer, and variations can be predicted based on modified process parameters.

Table 3.5 XPS Results from Stoichiometric MgO_x Layer

<i>Spectrum</i>	<i>Depth Profile</i>
	<i>Atomic Percentage (%)</i>
O1s	45.82
Mg1s	54.18

In light of these results, the decision has been made to deposit the MgO_x layer, which will be employed in the solar cells to be produced within the framework of this thesis research, utilizing the aforementioned optimized deposition parameters.

3.3.2 Thickness Optimizations for Contact Resistivity

Due to the inherent trade-off between achieving high-quality passivation and minimizing contact resistivity (ρ_c), the incorporation of the MgO_x layer into the solar cell structures presents a significant challenge. Consequently, the investigation of contact resistivity is conducted by varying the thickness of the MgO_x layer, yielding information about the electrical properties of the n-type Si/MgO_x/Al interface in order to find the optimal layer thickness for the solar cells employing MgO_x as the rear carrier selective contact. Using the same substrate as the solar cells produced, contact resistivity measurements were carried out by the transmission line method (TLM) [109,110]. The schematic representation of the sample structure used for contact resistivity measurements using the TLM method is presented in Figure 3.20. Careful attention was given to ensuring the utilization of the same wafer and rear surface architecture as that employed in the cell structure. Deposition of MgO_x layers with different thicknesses was carried out on the surface of n-type Cz c-Si. Then, using a shadow mask and an e-beam evaporator, 2-μm-thick Al contacts with a width

of 0.25 mm were thermally evaporated onto the MgO_x layer, maintaining a distance of 1.25 mm between each contact.

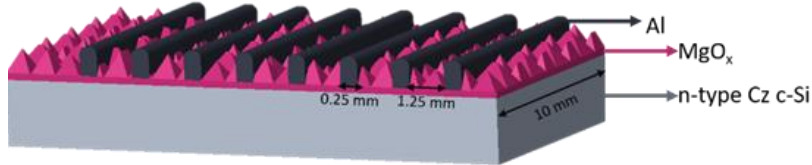


Figure 3.20. Schematic representation of the samples used for TLM contact resistivity measurements.

TLM measurements were conducted using the PV-Tools TLM-Scan device (Figure 3.21). To ensure accurate analysis of TLM results, multiple TLM structures were fabricated for measurements.

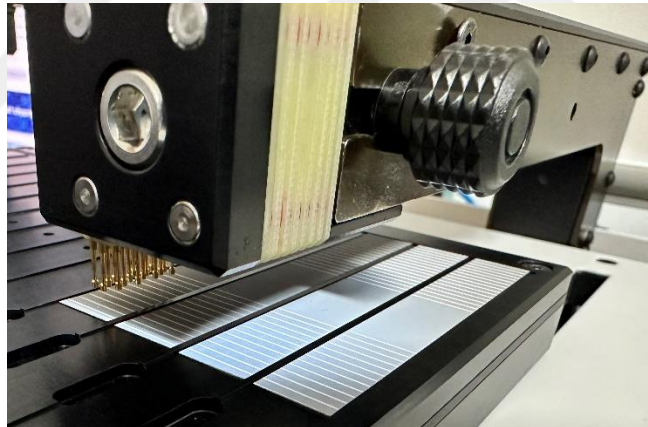


Figure 3.21. TLM measurement by PV-Tools TLM-Scan device.

The performances of MgO_x films deposited with thicknesses of 1.5, 3, and 10 nm, along with a reference without a MgO_x layer, on textured n-Si wafers were assessed by TLM measurements. In order to see the electrical contact characteristics of the reference solar cell, samples without any MgO_x layer (0 nm) are also introduced to the contact resistivity analysis. The selection of these particular thicknesses made it possible to conduct a thorough analysis of how MgO_x thickness affects the electrical

contact properties of $\text{MgO}_x/\text{c-Si}$. In the context of this thesis work, the utilization of the TLM was more suitable than the Cox and Strack method [111] in terms of the process applicability. Consequently, it is worth considering that the contact resistivity values might have been overestimated as a result. Therefore, it is advisable to conduct the evaluation of these values, both in relation to established reference values and in a comparative analysis amongst themselves.

Figure 3.22 illustrates the contact resistivity values of samples with and without a nanoscale MgO_x film between the Al electrode and the n-type c-Si substrate. Without MgO_x , the contact resistivity averages at $2.7 \Omega\cdot\text{cm}^2$, indicating a high resistance or rectifying behavior due to the significant surface potential barrier at the Al/n-type c-Si interface [112]. In contrast, the inclusion of a thin MgO_x film (approximately 1.5 nm) greatly enhances the contact behavior by supporting electron transport from c-Si to electrode, resulting in an average contact resistivity of $0.66 \Omega\cdot\text{cm}^2$ at the Al/n-type c-Si interface. The reduced resistance and enhanced electron transport can be attributed to the high conductivity and electron concentration as well as the passivation of the gap states between the Al metal and silicon substrate [113].

The contact resistivity for the 1.5 nm MgO_x -coated sample was significantly reduced compared to the sample without MgO_x coating. Beyond this point, when examining the average ρ_c values for the thicknesses of 1.5 and 3 nm, they appear to be quite similar. However, it is worth noting that the minimum value achieved corresponds to the 1.5 nm thickness, which is significantly lower compared to the minimum value for the 3 nm case. Figure 3.22 (a) clearly illustrates that a comprehensive dataset was obtained by conducting extensive measurements across a wide area of the TLM samples. Consequently, the large distribution observed in the 1.5 nm case may be attributed to the commonly reported island growth phenomenon associated with such ultra-thin thicknesses [114]. Subsequently, the contact resistivity exhibits a considerable increase if the thickness exceeds 3 nm and approaches 10 nm. The rise in ρ_c observed for thicker films can be attributed to the bulk resistivity of the MgO_x material. When a 10 nm thickness of MgO_x is used, it has been observed that the

contact resistivity values increase and vary within a wide range. The reason for having such a wide range could be the potential disruption of the homogeneous deposition as the thickness increases. Hence, the addition of a 1.5 nm MgO_x layer results in a very low contact resistivity of only $0.66 \Omega.\text{cm}^2$. This presents a significant opportunity for the production of high-efficiency silicon solar cells with MgO_x rear electron contacts.

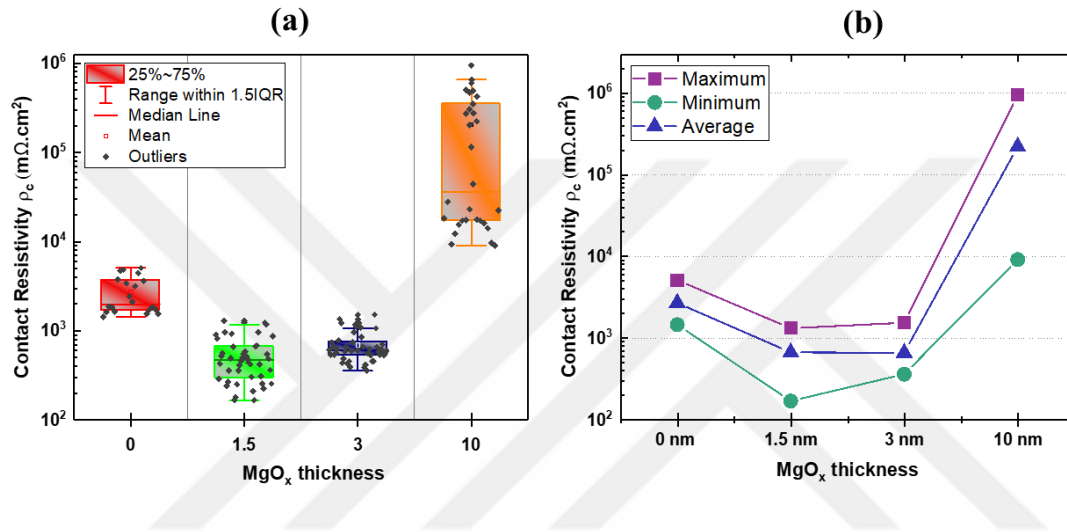


Figure 3.22. ρ_c as a function of MgO_x thickness. (a) Distribution of all measurement results, (b) Representation of max., min., and average values.

In addition, a hot plate annealing study was performed on the finished TLM samples to investigate the effect of temperature on the contact resistivity. The samples were annealed at 100°C and 200°C for 5 and 10 minutes, respectively, followed by re-measurement of the contact resistivity values. The contact resistivity values exhibited a notable increase with temperature for all MgO_x thicknesses, indicating a potential degradation of the MgO_x layer when exposed to prolonged high temperatures.

CHAPTER 4

PASSIVATED EMITTER AND REAR CONTACT CELL

The concept of passivated emitter and rear contact cell (PERC) was initially developed by the University of New South Wales (UNSW) in 1983 and subsequently achieved world-record efficiency in 1989 [115]. The transmission of this technology to the industry occurred 25 years after its first appearance. Currently, it comprises the largest portion of photovoltaic production lines. Prior to the introduction of PERC solar cells, the dominant technology in the industry was the utilization of aluminum (Al) for full screen printing on the rear side of silicon solar cells (aluminum back surface field, Al-BSF), which constituted around 90% of the market share. In the world of photovoltaics, the primary motivation for transitioning to PERC lies in its superior efficiency compared to the already utilized Al-BSF cell. While the Al-BSF does mitigate recombination losses to some extent, the presence of a complete aluminum layer leads to excessive recombination of photo-generated carriers at the rear surface. Hence, local contact designs successfully reduce these losses. Additionally, the utilization of a dielectric layer offers benefits in terms of light management. This is due to the ability of the dielectric layer to reflect infrared light at the back surface, which is generally absorbed by aluminum. As a result, the key advantages of PERC over the Al-BSF cell are enhanced rear-surface reflectivity and reduced rear-surface recombination. Exceptional rear side passivation is responsible for the elevated open circuit voltage (V_{oc}). Furthermore, the increased rear-side reflection and diminished parasitic absorption contribute to the potential for a high short circuit current (I_{sc}).

In order to evaluate the effectiveness and impact of the developed and optimized passivation layers, first, the passivated emitter and rear contact (PERC) solar cell structure is studied in detail. This study spans from the initial PERC solar cell structure produced at GÜNAM GPVL facility to the most recent and highest

efficiency PERC solar cell structure achieved over the years. The GÜNAM GPVL, Turkey's first pilot photovoltaic production line, was opened by the GÜNAM in 2017. The facility is comprehensively equipped with the necessary machinery to manufacture PERC structures, having an overall processing capacity of 100 wafers per hour.

With only minor adjustments to the standard Al-BSF process flow, the PERC architecture provides existing and future commercial cells with efficiencies ranging from 21% to 24% [116]. This allows for the continued utilization of industrial equipment, materials, and procedures.

4.1 Experimental Details

The PERC solar cells with the architecture shown in Figure 4.1 are fabricated with different dielectric stacks on the front and rear side.

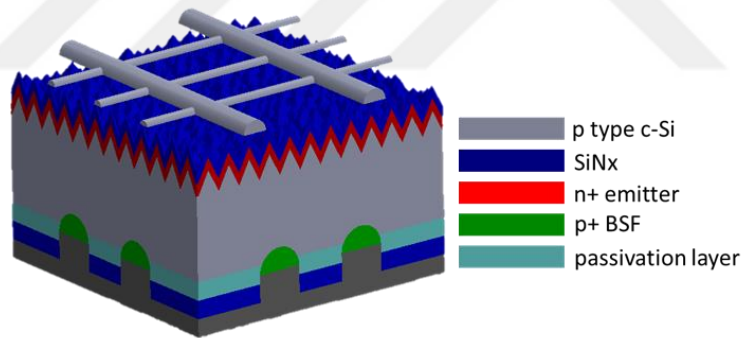


Figure 4.1. Schematic drawing of the p-type mono c-Si PERC solar cell.

The process flow of the fabricated PERC type solar cells within this thesis study is depicted in Figure 4.2. P-type (100) Czochralski (Cz) mono c-Si wafers, with a size of $156.75 \times 156.75 \text{ mm}^2$, a resistivity of $1\text{-}3 \text{ }\Omega\cdot\text{cm}$, and a thickness of $190 \text{ }\mu\text{m}$ are used. First, a random pyramid texture structure is generated on both sides of the wafers utilizing potassium hydroxide (KOH) texturing with organic additives, which decreases reflection and promotes light trapping. After cleaning with ozone (O_3) to get rid of organic and metallic contaminants, removal of oxide with hydrofluoric

acid, rinsing, and hot nitrogen (N_2) drying are performed. After being cleaned, the wafers underwent a solid-state diffusion procedure to create an n-type emitter. This process occurred within an atmospheric solid-state diffusion furnace employing phosphorus oxychloride ($POCl_3$) as the phosphorous precursor. Following the diffusion step, further cleaning and isolation of the junction were executed using an industrial-scale single side etching tool to eliminate the phosphosilicate glass (PSG) and the emitter on the back side. Subsequently, a rear passivation layer of Al_2O_3 was applied using the spatial ALD, varying in thickness between 2 and 5 nm across the entire duration of the thesis research. In an open-tube furnace, the Al_2O_3 layer was subsequently activated. In the industrial PECVD tool, passivation was followed by rear SiN_x or SiO_xN_y/SiN_x capping layers and front SiN_x or SiN_x/SiO_xN_y anti-reflective coatings. Upon passivating both surfaces, the surface underwent preparation for the employment of a local back surface field (BSF) and ohmic contacts. This preparation involved conducting a backside local contact opening (LCO) on the rear surface utilizing a 532 nm, picosecond laser. Screen printing was used to metalize the Ag finger and busbars on the front side and the full Al contacts on the back side. Rapid firing was then used in the last phase to create a local Al:BSF on the rear side and make it easier to fire through the front Ag on PECVD-deposited layers.

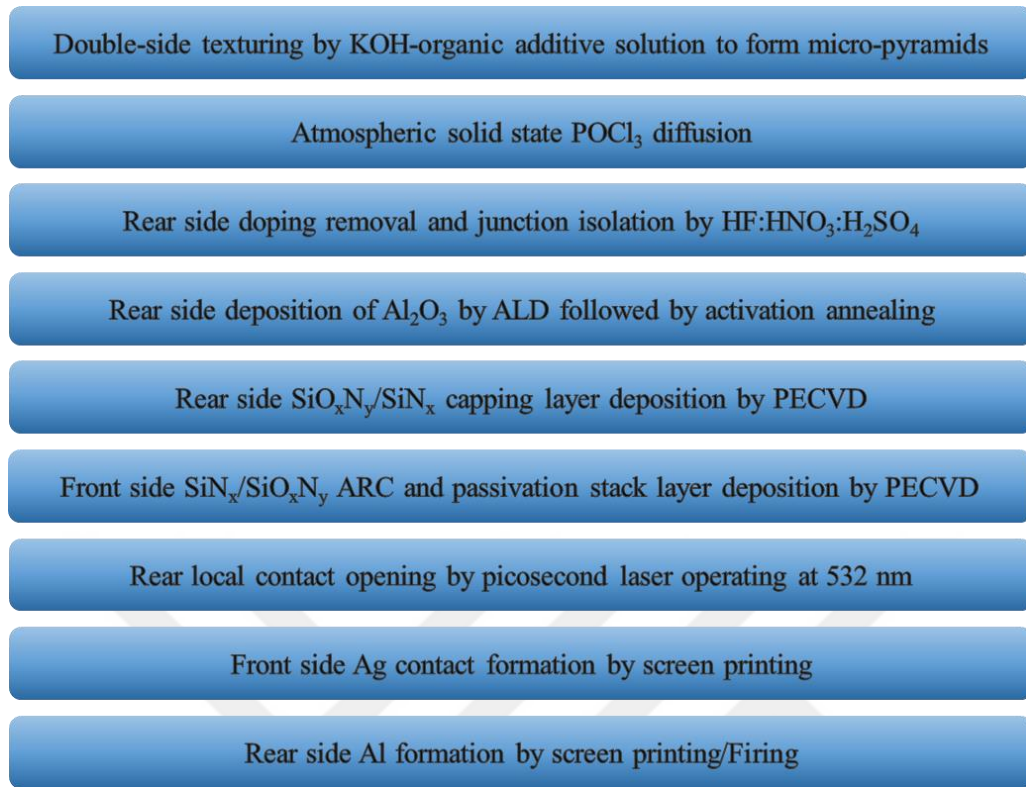


Figure 4.2. Experimental process flow of the PERC solar cell.

4.2 Results and Discussion

In Figure 4.3, solar cell efficiency values achieved by the large area of industrially feasible PERC cells produced at the GPVL facility are depicted, organized chronologically from the initial production of the first PERC solar cell up to now. In her thesis at the GPVL facility, Genç, E. (2018) [117], delved into the investigation of the optimization of laser processing parameters. This endeavor resulted in the attainment of a first PERC solar cell efficiency of 19.04%, utilizing the optimized laser parameters in conjunction with passivation layers that were not fine-tuned. Subsequently, Es et al. (2019) [73] documented the first production process and outcomes of Al_2O_3 -integrated PERC solar cells at the GPVL. In this fabrication, a 5 nm thick Al_2O_3 rear passivation layer was utilized and then activated at around 550 °C in an open tube furnace under N_2 flow. In the PECVD, rear silicon nitride (SiN_x) capping and front SiN_x antireflective coatings with thicknesses of 120 nm and 75

nm, respectively, were deposited. Supplementary loss analysis was also utilized to demonstrate how the initial optimization can be readily attained, resulting in notable improvements. Comprehensive characterizations were conducted to address the losses, and their combined impacts were assessed using the synergetic efficiency gain analysis (SEGA) approach. Hence, PERC solar cells achieving the highest efficiency of 19.21% were successfully produced. Based on the loss analysis conducted concurrently with the solar cell manufacturing, it is evident that the primary efficiency setbacks for the 19.21% efficient cell are attributed to recombination at the front surface and emitter. These factors were considered in the upcoming solar cell fabrication processes.

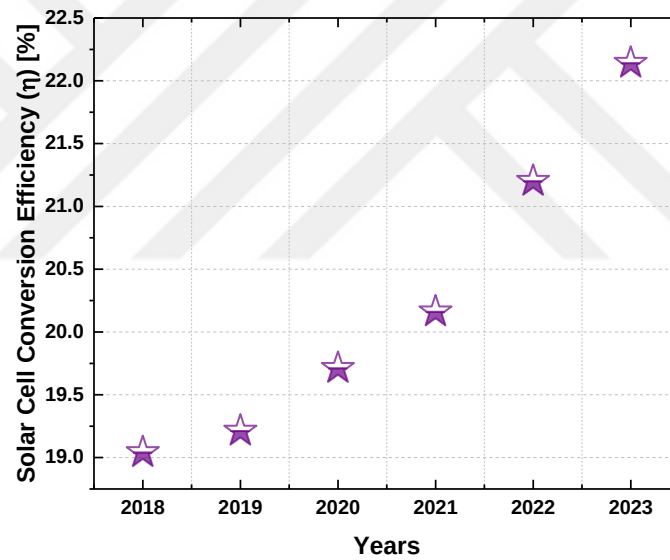


Figure 4.3. Efficiency evolution of industrially feasible large-area PERC solar cell structure produced at GÜNAM GPVL facility over the years.

Drawing from the preceding PERC solar cell fabrication outcomes and analyses, the Al_2O_3 thickness and annealing optimizations conducted in 2020, as elaborated in Section 3.2, have been concluded within the scope of this thesis study. In addition to the comprehensive Al_2O_3 passivation study detailed in Section 3.2, supplementary p-type passivation investigations were conducted for the PERC solar cell. Within the scope of these additional studies, various oxide layers were introduced beneath SiN_x

and Al_2O_3 structures to observe their passivation performances. These oxide structures can be categorized into thermal oxide and wet chemical oxide. Thermal oxide is produced in a diffusion furnace and can be deposited at different thicknesses by varying the temperature and duration parameters. On the other hand, wet chemical oxide can be produced in diverse ways [118,119]. In this study, wet chemical oxide was generated using ozone (O_3) in the RENA BatchTex tool. Symmetrical p-type structures were fabricated using different combinations of passivation layers, and iV_{oc} values were measured using the Sinton WCT-120 lifetime tester (Figure 4.4). Ultimately, it was concluded that none of the combinations including oxide layers could passivate the rear side of the p-type PERC solar cell better than the optimized $\text{Al}_2\text{O}_3/\text{SiN}_x$ structure. From these measurements, it has been calculated that the $J_{0,\text{rear}}$ value of the $\text{Al}_2\text{O}_3/\text{SiN}_x$ structure applied to the p-type wafer falls within the range of 28.7 to 31.1 fA/cm^2 .

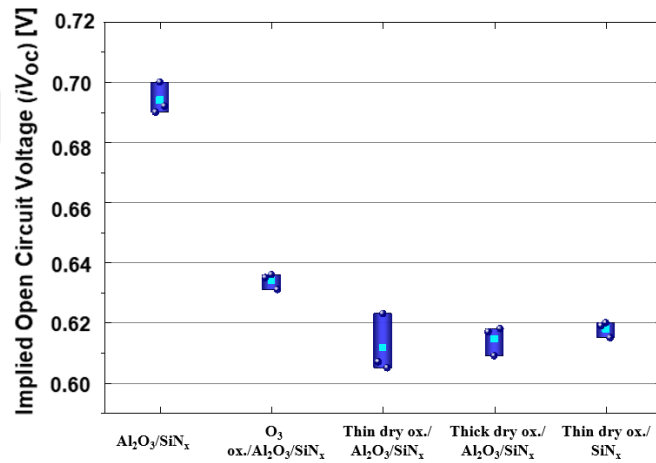


Figure 4.4. iV_{oc} results of p-type symmetrical passivation samples including silicon dioxide, aluminum oxide and silicon nitride combinations.

In conclusion, utilizing industrial tools, a PERC solar cell was fabricated by applying the optimized 2 nm Al_2O_3 /120 nm SiN_x stack on the rear surface along with the two-step annealing procedure. This led to an efficiency value of 19.71%, in 2020. Contact resistivity analysis using the TLM method has also been directly performed across the entire front surface of this large-area solar cell and the resulting distribution is

illustrated in Figure 4.5. From this figure, it can be observed that the contact resistivity values remain below 7 mΩ.cm² across the entire front surface.

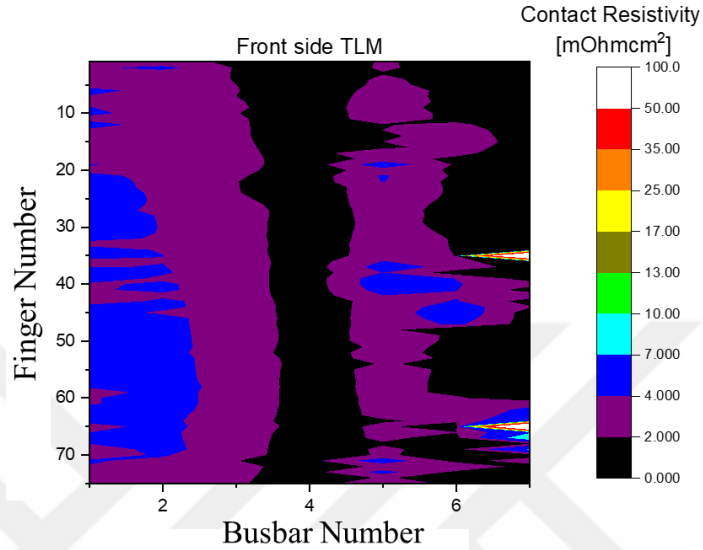


Figure 4.5. TLM distribution of the fabricated PERC solar cell.

In order to further advance the efficiency of this PERC structure, an investigation was undertaken to examine the rear local contact patterns within the previously fabricated structure [120]. Various types of rear local contact opening patterns, including lines and dashes, are created on the rear surfaces of PERC solar cells, using an industrial-grade picosecond laser with a fixed laser contact opening (LCO) width. The rear dielectric passivation layer is subjected to ablation using four distinct LCO patterns. This is achieved by altering the rear local contact pitches within the range of 900 μm to 1200 μm, with an increment of 100 μm. The line pattern employed in this study serves as the reference pattern, with a line pitch of 1500 μm and uniform contact width. In this investigation, it was observed that the rear contact pattern with a metal content of around 3% and a pitch of 1000 μm exhibited comparatively higher efficiency compared to the other contact patterns examined. Through the utilization of this particular framework, the efficiency of PERC solar

cells has overcome the critical threshold of 20%, facilitating the development of large-scale PERC solar cells that exhibit efficiencies beyond 20%.

In addition to the comprehensive $\text{Al}_2\text{O}_3/\text{SiN}_x$ passivation study conducted within the scope of this thesis, Canar et al. (2022) [72,121] focused on improving the rear surface passivation of PERC solar cells produced in the GPVL facility further. Various stoichiometries of SiN_x and SiO_xN_y films were fine-tuned for the enhancement of the PERC solar cell. The impact of SiN_x stoichiometry on both the Al_2O_3 layer and the $\text{SiO}_x\text{N}_y/\text{Al}_2\text{O}_3$ stack was examined through experiments. Furthermore, optimization of the front surface ARC layer was pursued to achieve optimal passivation and anti-reflective properties. The combination of a SiO_xN_y film deposited using PECVD along with a SiN_x film was considered as an ARC stack due to its beneficial characteristics such as a greater optical band gap and negligible absorption. By evaluating various combinations of SiN_x and SiO_xN_y structures with different stoichiometries on the front and rear surfaces of the PERC solar cell, the efficiency values have been successfully elevated to beyond 21%. Utilizing the optimized front and rear passivation layers, as well as the ARC layers, the carrier-selective solar cell structure was fabricated which will be mentioned in the subsequent chapter. On the other hand, it's noteworthy that in GPVL facilities, standard PERC solar cells achieved an efficiency value surpassing 22% on the large scale in 2023. This accomplishment was attributed to specific fine-tuning modifications applied to the emitter sheet resistance and base doping.

CHAPTER 5

MAGNESIUM OXIDE PASSIVATING ELECTRON CONTACT ION IMPLANTED SOLAR CELL

In recent years, there has been significant progress in the development of crystalline silicon (c-Si) solar cells featuring carrier-selective passivating contacts. Outstanding benefits have been demonstrated, such as more straightforward configurations and greater potential efficiencies, compared to conventional c-Si solar cells that rely on highly doped emitters. Because of their outstanding separation and collection capabilities on photogenerated carriers, carrier selective contacts (CSCs) with favorable energy band alignment have recently caught the interest of researchers working with crystalline silicon (c-Si) solar cells [28,122]. Furthermore, a combination of CSCs with other solar cell architectures has the potential to enhance solar cell efficiency by leveraging the critical features of the materials, which opens up promising pathways in advancing photovoltaic research for designing more efficient and innovative solar cells.

One of the primary benefits of carrier-selective layers is their ability to reduce recombination losses, which is a significant factor limiting solar cell performance. These layers can be designed to create an electric field that aids in the separation of photo-generated charge carriers. Carrier-selective layers enable electrons and holes to travel with minimal resistance toward their respective electrodes by creating a favorable energy gradient, thereby increasing V_{oc} and improving charge collection efficiency [28]. Utilizing carrier selective contacts using dopant-free materials as a charge carrier extraction method has been elaborated in greater detail in Section 2.1.3.

In order to reduce the contact resistivity (ρ_c), the barrier height (Φ_B) needs to be decreased. One direct method to enhance electron transport is introducing a metal layer with a sufficiently low work function, for example, calcium [123] or

magnesium [124]. This results in a moderately minor barrier height of approximately 0.35 eV on n-type crystalline silicon. Another method is adding an interfacial layer between the silicon and the metal electrode and pinning the Fermi level.

The most fundamental idea behind how energy bands are arranged at the interface of a metal and a semiconductor (M/S) is that the bands naturally align with one another while keeping the energy difference of each band from the vacuum level fixed at the interface. This phenomenon is referred to as the Mott-Schottky rule. Although, there is a strong tendency for the metal's Fermi level to coincide with the Fermi level of the semiconductor. As a result, the work function of the metal has no impact on the Schottky barrier height (SBH). "Fermi level pinning" is the term used to describe this phenomenon at the metal-semiconductor interface [125].

Besides acting as a passivation layer, the interlayer between the absorber and the metal also needs to lower the density of states at the interface. It should also be sufficiently conductive to allow efficient carrier transport. With this interlayer, it is possible to lower the work function of the external metal layer and achieve low contact resistivity by having the minimal conduction band offset to c-Si and minimal bulk resistivity [113].

In light of the implications discussed above, significant efforts have been made to investigate materials that can make electron-selective connections on n-type c-Si wafers without intentional dopants. Various materials, including alkali/alkaline earth metal salts, carbonates, and transition metal oxides, have been documented to enhance the ohmic contact of aluminum to n-type c-Si significantly. Magnesium oxide (MgO_x) is a further candidate that has shown potential in light-emitting diodes [126] but has yet to make much progress in photovoltaics.

Demonstrating well-developed, highly performing contacts to c-Si has become an important research focus, particularly for high-performance electron selective contacts (ESCs). Figure 5.1 presents the alkali/alkaline earth metal contact film work functions including MgO_x [28]. Through XPS secondary electron cut-off analysis of a MgO_x/Al stack, a work function of around 4.1 eV is evident [113]. This value is in

line with the work function of the Al metal itself which is reported as 4.2 eV [127]. The essential contribution of the increased conductivity and electron concentration in the bulk MgO_x film is vital for enabling the ohmic contact behavior between the Al contact and the n-type silicon substrate.

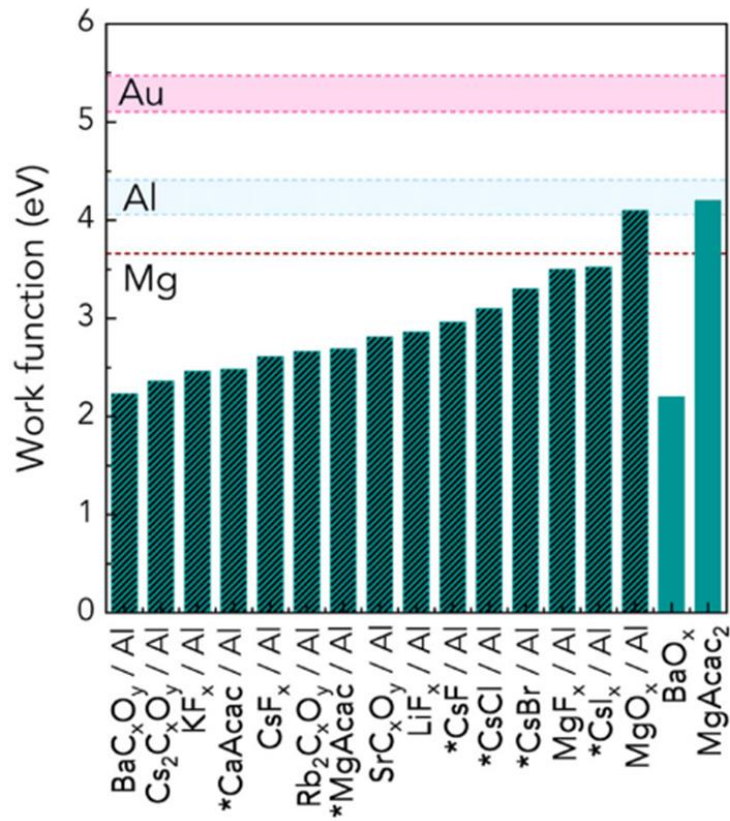


Figure 5.1. Alkali/alkaline earth metal contact film work functions [28].

Although the work function of aluminum (Al) and the electron affinity of silicon have a slight difference of 0.1-0.2 eV, and this leads to a low barrier height as per the Schottky-Mott rule, when Al is directly deposited on n-type c-Si, the resulting contact has a rectifying behavior and exhibits high resistance. Fermi-level pinning commonly explains the observed behavior and produces a relatively high Schottky barrier height (Φ_B) of 0.65 eV, which blocks electron flow from the n-type silicon wafer [112,113,128]. As mentioned, one simple method for reducing Φ_B for electron transport is to use low-work function metal oxides between the external metal electrode and the internal silicon absorber. Low work function metal oxides, which

have a small conduction band offset with n-Si, e.g., titanium oxide [36,37], zinc oxide [38], and tantalum oxide [40] have recently been investigated as ESCs for n-Si solar cells.

In this section of the thesis, it is demonstrated that thin films of magnesium oxide (MgO_x) deposited using the ALD tool can serve as a highly effective electron-selective passivating contact for n-type crystalline silicon (c-Si) solar cells. Moreover, the ion implantation technique is employed to form the emitter, further simplifying the process flow by enabling doping on a single side and offering precise control over the doping level. Due to the inherent trade-off between achieving high-quality passivation and minimizing contact resistivity (ρ_c), incorporating the MgO_x layer presents a significant challenge. Consequently, the investigation of contact resistivity and passivation is conducted together by varying the thickness of the MgO_x layer in order to find the optimal layer thickness. The optimization study of contact resistivity has been summarized in the preceding Section 3.3.2.

Bulk MgO_x exhibits a bandgap ranging from 7.3 eV to 7.83 eV [129,130] offering the potential to create substantial band offsets that can effectively reduce leakage currents [130,131]. To enable efficient electron transport, low work function MgO_x material is chosen as a layer that selectively allows electrons to pass through, leading to reduced contact resistivity. Figure 5.2 illustrates the estimated energy band diagram of the “Ag&Al metal/ p^+ /n c-Si/ MgO_x /Al metal” structure.

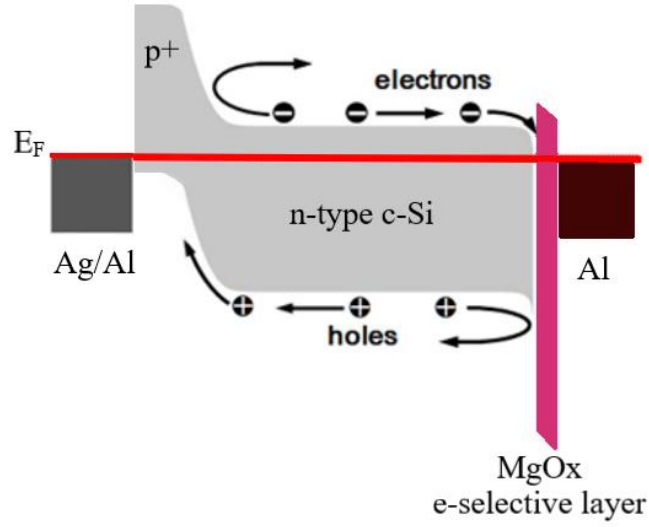


Figure 5.2. The energy band diagram of “Ag&Al metal/p⁺/n c-Si/MgO_x/Al metal”.

As supported by the results in Section 3.3.2, literature findings show that at the n-Si/Al interface (without the MgO_x interlayer) characteristic behavior of Schottky diodes is displayed [132]. This can be attributed to the Fermi-level pinning effect due to the considerable density of metal-induced gap states (MIGS) and unpassivated defects existing between the Al and Si substrates [133]. When a thin MgO_x was introduced, the nature of the contact switches from Schottky to ohmic contact behavior, yielding low contact resistivity values. Using the low work function MgO_x interlayer mitigates the Fermi level pinning effect and decreases the energy barrier for electron movement. Hence, the thin MgO_x layer enhances electron transportation from silicon to the corresponding metal due to the improved interfacial states.

Consequently, the combination of aluminum (Al) with a thin layer of magnesium oxide (MgO_x) offers a viable solution for efficient electron collection in n-type crystalline silicon (c-Si) solar cells. Such an option will pave the way for Ag-free solar cell manufacturing, which is highly desirable for industrial applications. Driven by this motivation, this section of the thesis study focused on exploring the utilization of ALD-deposited MgO_x layers in the fabrication of c-Si solar cells with a simplified cell structure and an easily controlled fabrication procedure.

5.1 Literature Review

Due to its high dielectric constant and good electrical insulation properties, magnesium oxide (MgO_x) has also started to be considered as an appropriate material for electron contact in c-Si based devices with the work function of 4.22 eV [43,134,135]. Thin layers of MgO_x have recently been successfully used as electron transport layers for dye-sensitized solar cells [136,137], perovskite solar cells [138], CIGS solar cells [139], and n-type c-Si solar cells [43,113,132,134]. There have been studies of solar cells that utilize electron-selective contacts made of thin MgO_x layers, prepared either by e-beam [43,132] or thermal evaporation methods [113]. To mitigate the high-temperature requirements of physical vapor deposition (PVD) methods, atomic layer deposition has been identified as a potential alternative for depositing highly uniform layers while maintaining their properties and cost-effectiveness. In a recent study, ALD deposited MgO_x was utilized as an electron-selective layer in silicon heterojunction solar cells [41]. However, the researchers combined i-aSi:H and MgO_x layers to form a passivation/electron transport layer stack to advance passivation properties instead of investigating the stand-alone MgO_x layer.

The particular focus of this thesis study is on understanding the performance of solar cells with a stand-alone MgO_x layer without the additional use of a dedicated silicon-based passivation layer such as aSi:H. The low thermal budget of the emitter and rear metal formation, its dopant-free nature, the simplicity of the cell fabrication, and, more importantly, less Ag usage while fabrication of solar cells offers a new low-cost route for industrial solar cell manufacturing. Additionally, to the best of our knowledge, the size of the solar cells with a MgO_x layer produced in this study is larger than the size of similar solar cells that have been published in the literature which shows the potential of the ALD deposited MgO_x to be applied for industrial-size Si solar cells.

5.2 Experimental Details

The industrial-grade n-type Czochralski silicon (Cz-Si) wafers, with a size of 43.50 cm², bulk resistivity of 1-3 Ω cm, and thickness of 180 ± 20 μ m, experienced a series of processes for the fabrication of ion-implanted c-Si solar cells with atomic layer deposited magnesium oxide as a passivating electron contact. The limiting factor for the sample size here is the chamber size of the ALD device used for depositing the MgO_x layer.

In this part of the thesis study, three sets of solar cells were fabricated, each following a specific process sequence. The sequential steps employed during the fabrication of these solar cells are visually presented in Figure 5.3, while Figure 5.4 provides schematic representations of the resulting structures. It is noteworthy that the front side structure remains identical among all the solar cells produced within the study. In the "full rear" configuration, the rear side of the solar cells utilized a MgO_x layer as the electron collector without any additional passivation layer. The MgO_x layer was entirely deposited beneath the Aluminum (Al) metal layer. On the other hand, in the "local rear" configuration, solar cells have a silicon oxynitride/silicon nitride (SiO_xN_y/SiN_x) stack as the passivating layer on the rear side. Before the deposition of MgO_x, a picosecond laser operating at a 532 nm (green) wavelength was employed to ablate the rear passivation layer locally, creating specific regions of contact openings in the form of dashed lines. This ablation process resulted in removing approximately 3% of the rear stack passivation layer. The reference solar cell, sharing the same front side structure as the other configurations, solely features the Aluminum (Al) metal layer on the rear side, without any additional layers.

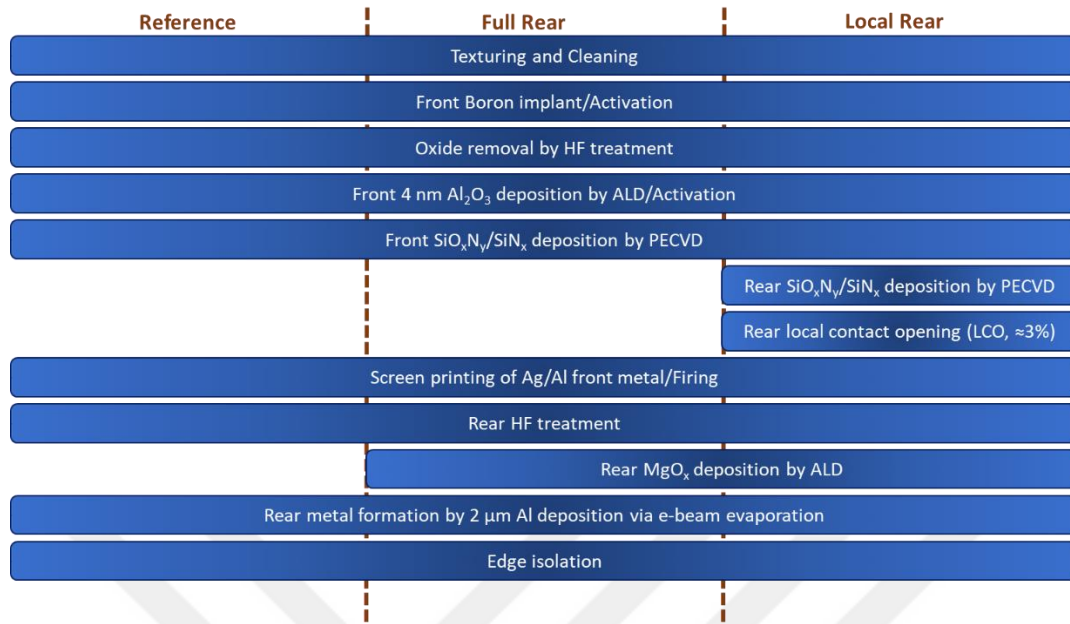


Figure 5.3. Process flow of Reference, Full Rear and Local Rear MgO_x solar cells.

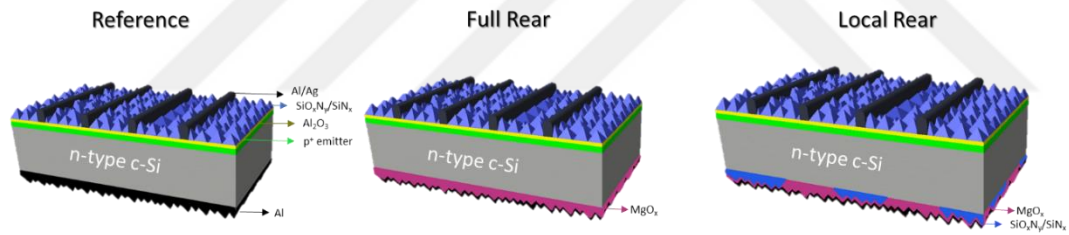


Figure 5.4. Schematic representations of Reference, Full Rear and Local Rear MgO_x solar cells.

In this part of the thesis study, all the fabricated solar cells underwent a double-sided texturing process using potassium hydroxide (KOH) to induce the formation of randomized pyramids on the surface of the wafer using the RENA BatchTex tool. An ozone (O_3) cleaning procedure was employed to effectively remove organic and metallic contaminants from the solar cell substrates. The front side of the samples were then subjected to boron (B) ion implantation utilizing the Dong Guan Plasma Ltd.'s Bosphorus ion-implantation system. The implanted samples were subjected to an annealing process in an atmospheric furnace, where they were heated to a

temperature of 1050 °C for 30 minutes in a nitrogen (N₂) gas environment to activate the dopants. The doping characteristics of the boron implantation and the sheet resistance (R_s) of the layer were assessed on the wafers using the ECV and 4PP techniques, respectively. The mean sheet resistance of the boron-implanted layer on n-Si wafers is determined to be around 100 $\Omega/\square$. The associated ECV graph is presented in Figure 5.5. The active dopant dosage for boron was computed from the ECV graph as $1.17 \times 10^{15} \text{ cm}^{-2}$ [24,140].

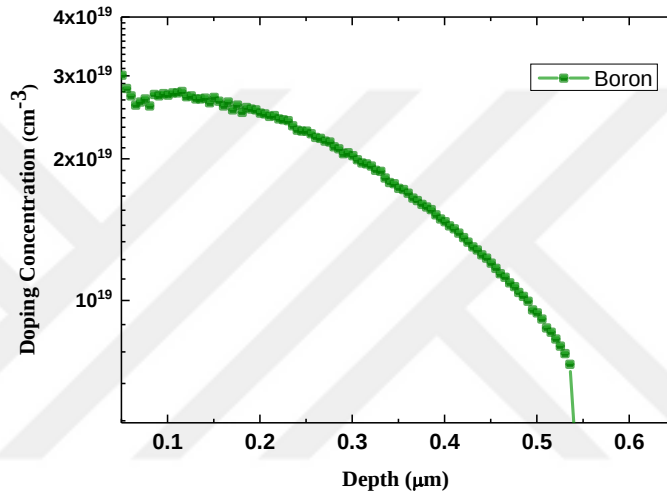


Figure 5.5. ECV profile of Boron implanted emitter.

Subsequently, a hydrofluoric acid (HF) treatment was applied to remove the thin SiO₂ layer that formed during the dopant activation process. The front side of the solar cells was coated with a 4 nm Al₂O₃ layer using ALD, followed by activation. Additionally, a capping layer of SiO_xN_y/SiN_x stack layer was deposited using plasma-enhanced chemical vapor deposition (PECVD) at front surfaces with a total thickness of 90 nm, regarding the optimum ARC and passivation property [72,141,142]. Afterward, for the “full rear” and “local rear” sets, the rear SiO_xN_y/SiN_x stack layer was deposited by PECVD with a 90 nm thickness, followed by the rear contact opening process. All the process details and characterizations of these depositions, including Al₂O₃, SiN_x, SiO_xN_y, and MgO_x, are provided in Section 3. Then, for all the sets, front metallization of the cells was achieved using the screen-printing method. Silver (Ag)/Aluminum (Al) metal paste was screen-printed on the

front side. Finally, a fast-firing process was performed to enable Ag/Al penetration through the passivation and anti-reflective coating layers at the front side. Before proceeding to the next step, possible native oxide on the rear surface was removed by applying a one-sided HF treatment. Subsequently, the rear surfaces of the samples, excluding the reference samples, were coated with the MgO_x layer using thermal ALD. Before the edge isolation process, a 2 μm thick Aluminum (Al) metal was deposited on the rear side using electron beam evaporation.

The passivation performance of the MgO_x/Al film stack was studied by measuring implied open circuit voltage (iV_{oc}) values using finished solar cells by Sinton Suns V_{oc} measurements. In conjunction with the production of solar cells, a supplementary set of samples was fabricated to measure contact resistivity, ρ_c , as mentioned in Section 3.3.2. These additional samples allowed for a detailed analysis of contact resistivity as well as solar cell performance, yielding information about the electrical properties of the n-type Si/ MgO_x/Al interface on the rear side.

5.3 Results and Discussion

In the Section 3.3, magnesium oxide film optimizations were explained detailly including the stoichiometry optimizations and the contact resistivity analysis. Therefore, it has been established that adding a 1.5 nm MgO_x layer results in the lowest contact resistance value of 0.66 $\Omega\cdot\text{cm}^2$. This provides an important opportunity for producing high-efficiency silicon solar cells with a thin MgO_x rear electron contact.

Figure 5.6 illustrates the iV_{oc} values of solar cells with and without a MgO_x interlayer of two different thicknesses. The observed significant variation in the iV_{oc} results of the reference solar cell can be attributed to differences between batches since not all of the solar cells represented, despite being identical, were manufactured within a single batch. It is observed that the iV_{oc} values of all other combinations utilizing MgO_x between Al and Si surface are significantly higher compared to all the

reference samples. iV_{oc} value remains unchanged for the "full rear" structure with 1.5 and 3 nm thick MgO_x layers, indicating the same level of passivation. While the MgO_x layer plays a crucial role in reducing surface recombination, if factors such as bulk recombination or front surface passivation are dominant compared to the MgO_x layer, the MgO_x thickness variation may not significantly impact the iV_{oc} . In both "full rear" and "local rear," a higher degree of iV_{oc} variation within the set is noticed in the case of 1.5 nm MgO_x thickness. This observation can be attributed to the phenomenon of island growth, which is associated with extremely thin layers. Additionally, the execution of the HF treatment carried out immediately before applying MgO_x on the rear surface might be inadequate and may have a notable impact, particularly in the "local rear" samples. This might have resulted in uneven coverage on the local contacts relative to the full rear contacts.

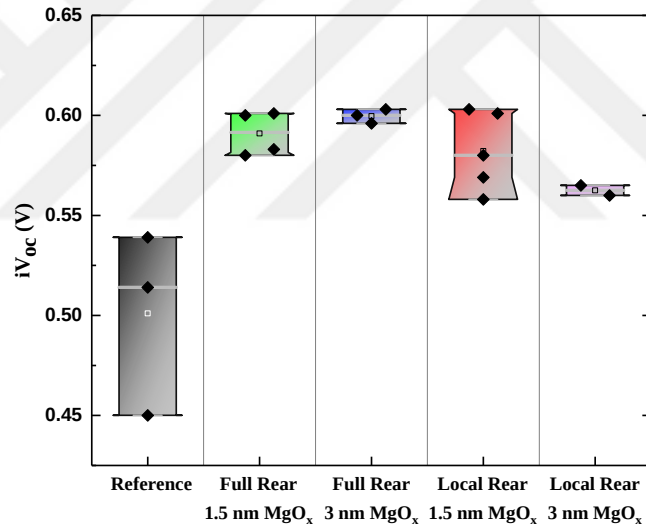


Figure 5.6. Implied V_{oc} (iV_{oc}) results of different sets.

It is essential to highlight that the solar cells were exposed to ambient air for one month before re-measuring their iV_{oc} values to assess the stability of the device since this is a critical factor in module encapsulation and overall device longevity. Notably, the iV_{oc} performance of the cells has remained unchanged throughout this period.

Table 5.1 presents the photovoltaic characteristics of the best efficient solar cells fabricated on n-type c-Si wafer, from one specific batch. The findings suggest that,

considering the observed differences among the batches, a more accurate approach is to compare batches within their own group rather than comparing them collectively. The table includes various types of solar cells, namely those with only a rear aluminum (Al) layer (without MgO_x) as a reference, solar cells with an entire rear layer of 1.5 and 3 nm MgO_x , and solar cells with a local rear layer of 1.5 nm MgO_x .

Comparing the full rear MgO_x solar cell performances with different MgO_x thicknesses, the effect of contact resistivity becomes noticeable when the thickness of MgO_x is increased from 1.5 nm to 3 nm (if only the best efficient solar cells are considered). The short-circuit current density (J_{sc}) and fill factor (FF) both experience a slight decrease as a result of this increase in MgO_x thickness, whereas V_{oc} slightly increases. The solar cell with a 3 nm MgO_x layer achieves an efficiency value of 16.14% at best, while the 1.5 nm MgO_x counterpart reaches 16.34%. Despite a minor increase in open-circuit voltage (V_{oc}), the solar cell's overall power conversion efficiency (PCE) decreases due to the well-known trade-off between passivation quality and contact resistance. The best efficient reference solar cell, without a MgO_x layer, demonstrates an efficiency value of 13.93%, accompanied by a V_{oc} of 548 mV and a fill factor of 70.25%. Regardless of the relatively small difference (approximately 0.1-0.2 eV) between the work function of aluminum (Al) and the electron affinity of n-type crystalline silicon (c-Si), when Al is directly deposited on c-Si, the resulting contact exhibits rectifying behavior and shows a high contact resistance. The widely accepted explanation for this phenomenon is the Fermi-level pinning effect, induced by a high density of bandgap states or defects at the interfaces between the metal and semiconductor. This Fermi-level pinning leads to a relatively high Schottky barrier height (Φ_B), impeding the flow of electrons out of the n-type silicon wafer [112,113,128]. It can be inferred that there is a correlation between the V_{oc} values of the produced solar cells and the observed trend in implied V_{oc} values. A considerable improvement was observed when comparing PERC-like local rear cells with a 3% area ratio to full-area 1.5 nm MgO_x contacts (100% area ratio). The open-circuit voltage (V_{oc}) increased from 591 to 604 mV and the power

conversion efficiency (PCE) improved from 16.34% to 16.83% from a 43.50 cm² solar cell area. These enhancements in PCE were primarily attributed to reduced recombination losses and series resistance, resulting in improved charge carrier collection.

Table 5.1 The Photovoltaic Parameters of the Best Efficient Solar Cells Fabricated Incorporating the ALD-Grown MgO_x Layers

Sample Type (MgO _x thickness)	V_{oc} (V)	J_{sc} (mA/cm ²)	FF (%)	PCE (%)
Reference (0 nm)	0.548	36.18	70.25	13.93
Full Rear (1.5 nm)	0.591	36.78	75.15	16.34
Full Rear (3 nm)	0.597	36.01	75.08	16.14
Local Rear (1.5 nm)	0.604	36.83	75.71	16.83

Introducing a local thin MgO_x layer together with the passivation layers into the reference cell resulted in a noteworthy enhancement of 56 mV in the open-circuit voltage (V_{oc}). This improvement can be attributed to mitigating charge carrier recombination and eliminating rectifying contact behavior. As a consequence, the incorporation of this MgO_x layer facilitates superior charge transport and leads to overall enhanced electrical characteristics. Additional remarkable advancement observed was the enhancement of the FF by an absolute 5.46%. This improvement can mainly be attributed to the reduction in rear contact resistivity, as indicated by the ρ_c values in Figure 3.22. The decrease in resistivity indicates an enhancement in the efficiency of charge carrier transport at the rear contact, which can be attributed to the presence of the MgO_x interlayer. Remarkably, the Si/Al junction exhibited the most significant energy barrier for electron transport at the rear side, leading to comparatively poor device performance in the reference cells. On the other hand, the lowest contact resistivity emerged from the thin MgO_x/Al sample, resulting in the most favorable device performance among the all types of devices. The MgO_x/Al contact solar cell demonstrated a respectable V_{oc} and a high FF, which indicate its

advantageous electron-selective properties. These findings show that the MgO_x/Al contact efficiently encourages the desired electron movement within the cell, which helps to improve performance. Moreover, the slightly lower J_{sc} observed in the control cell, compared to the 1.5 nm MgO_x/Al cell, aligns with the notion of higher recombination losses at the c-Si/Al rear interface. This finding further emphasizes the superior performance achieved by utilizing the c-Si/ MgO_x/Al interface, where recombination losses are reduced, and overall cell efficiency is enhanced.

The reference solar cells were fabricated by thoroughly coating c-Si bulk with Al metal. In order to make accurate comparisons, solar cells with full 1.5 nm MgO_x/Al coating on c-Si bulk in the "full rear" configuration were compared with reference solar cells having a c-Si/Al rear structure using the EQE method (Figure 5.7). The external quantum efficiency response at longer wavelengths (around 900–1200 nm) experiences a substantial improvement due to incorporating the MgO_x interlayer. The carrier recombination could be suppressed by the n-Si/ MgO_x/Al rear-side contact design. This outcome again signifies that the MgO_x interlayer effectively provide passivation on the silicon wafer, aligning with the enhanced V_{oc} . This enhancement is also in accordance with the observed low contact resistivity. The response from the front side and the bulk of the solar cells appears to be similar in both configurations, as expected.

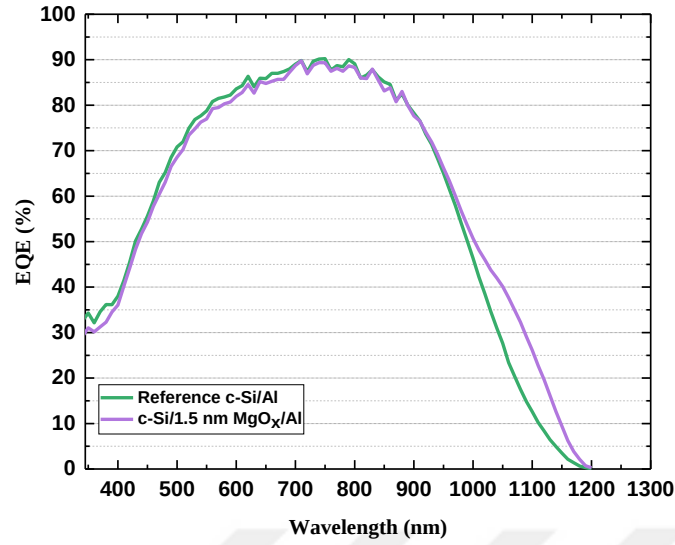


Figure 5.7. EQE comparison of the solar cells having c-Si/Al and c-Si/1.5 nm MgO_x/Al rear architecture.

Figure 5.8 shows a complete picture of the overall results of all photovoltaic devices fabricated, including those with the most outstanding efficiency shown in Table 5.1. Consequently, a more discernible illustration of the distribution within the sets becomes attainable. When examining the V_{oc} , FF, and efficiency values of the reference cells, it is observed that the results exhibit a wide range of variation across the samples within the dataset, which was already observed in the iV_{oc} pattern in Figure 5.6. Regardless of the MgO_x thickness in full rear samples, narrower distributions are observed within the set. However, it can be observed that in the local rear samples with 1.5 nm MgO_x, the distribution of the parameters, especially FF and efficiency, is significantly wider. This might be due to the one-sided HF treatment on the locally ablated rear side, which may not be implemented effectively enough because of the low open area ratio. Due to its significant area coverage on the back surface, the SiO_xN_y/SiN_x layer may have effectively mitigated the passivation effect, resulting in a minimal variation in the cell V_{oc} . Similar J_{sc} values are obtained from the all types of solar cells due to the similar optical designs they have. Although the highest FF value was obtained from the local rear samples with a 1.5 nm MgO_x layer, the FF distribution within the set remained significantly high. If further developments are carried out in cell production to enable better coverage

of the local openings with a MgO_x layer, solar cell efficiency would be further improved.

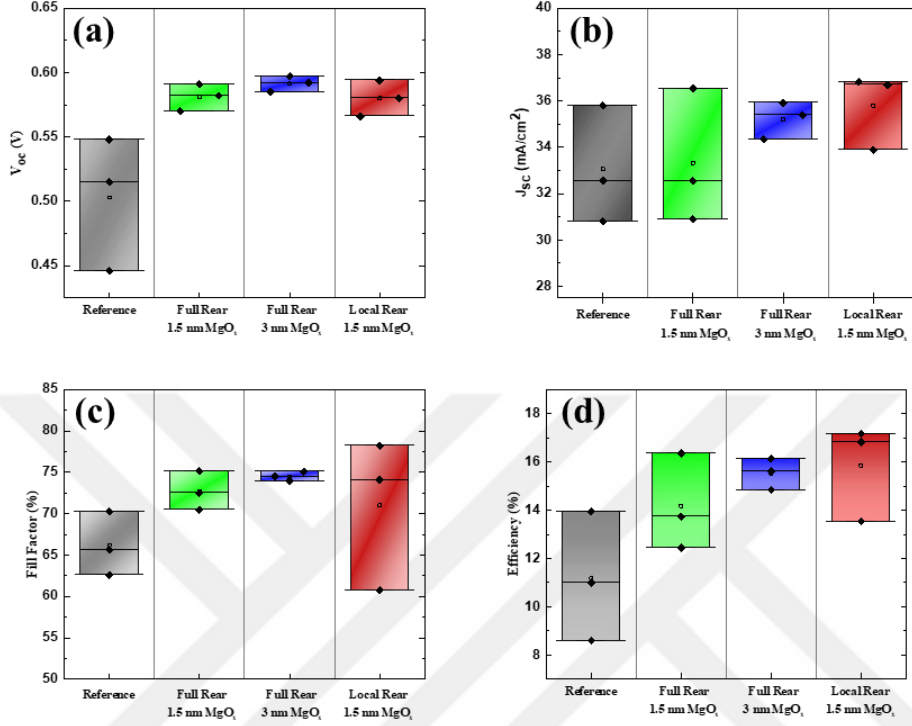


Figure 5.8. (a) V_{oc} , (b) J_{sc} , (c) FF and (d) efficiency comparison of different types of solar cells.

Figure 5.9 shows the J-V photovoltaic characteristic curve for the best efficient solar cells from the specific batch (Table 5.1) under one sun standard illumination. Incorporating a MgO_x layer, whether in the full or local rear configuration, significantly enhances all parameters of the solar cells. It is evident that adding a MgO_x interlayer results in a more significant increase in V_{oc} compared to J_{sc} compared to the reference cell without the MgO_x interlayer. This can be attributed to the provided passivation of the MgO_x/Al stack on the rear silicon surface and the elimination of the rectifying contact behavior. The persistent high fill factor (FF) observed in all solar cells with the MgO_x layer, in contrast to the reference solar cell, provides further evidence of the favorable electron-selective characteristics conferred by the MgO_x layer. Additionally, the slightly lower short-circuit current

(J_{sc}) in the reference cell suggests increased recombination losses at the c-Si/Al rear interface compared to the Si/MgO_x/Al interface.

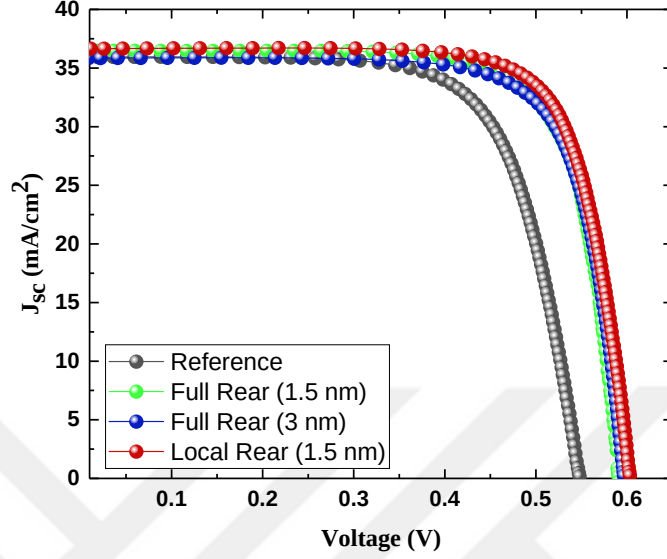


Figure 5.9. J_{sc} -V graph of the best efficient solar cells in each set.

As previously noted, variations between different batches have already been observed due to ongoing optimizations in n-PERT front metallization, rear HF treatment, and uncontrollable island growth. Consequently, the fabrication of the solar cell architecture giving the highest efficiency has been repeated, incorporating a local 1.5 nm thick MgO_x layer. This configuration has yielded the highest solar cell efficiency, achieving 17.17% from a 43.50 cm²-sized solar cell area. Figure 5.10 shows the J_{sc} -V graph, along with the PV parameters of this most efficient solar cell.

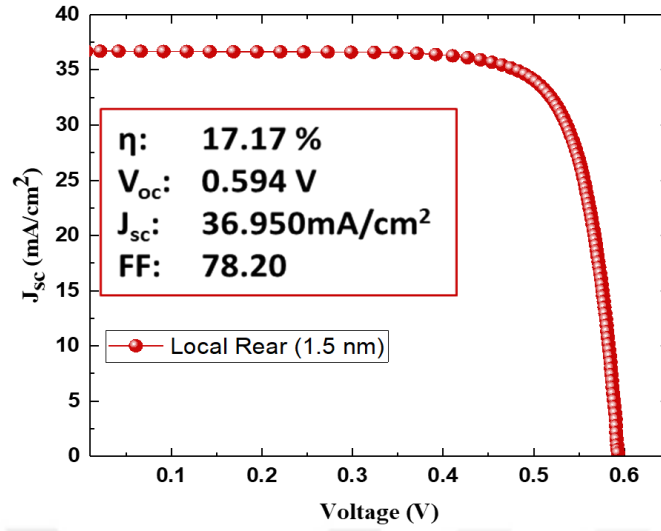


Figure 5.10. J_{sc} -V graph and the PV parameters of the best efficient local MgO_x rear solar cell.

Utilizing a low-temperature MgO_x deposition technique, combined with the simplified one-sided emitter formation through ion implantation, enables the fabrication of a MgO_x carrier-selective solar cell structure, serving as a proof-of-concept in this thesis study.

The contact scheme utilized in the fabricated solar cells resulted in a significant reduction in contact resistivity compared to the reference solar cells, where direct deposition of Al onto n-type c-Si was employed. Consequently, our ALD MgO_x layers can be considered a suitable building block for further development in c-Si-based devices. As a result, Al combined with a thin MgO_x layer can be used to collect the electrons in the n-type c-Si solar cells. This approach can potentially eliminate silver (Ag) use in solar cell manufacturing, which is highly desirable for industrial applications. The insertion of the MgO_x layer significantly improved rear contact quality, leading to a remarkable efficiency of 17.17% from a device area of 43.50 cm^2 .

Utilizing supplementary passivation interlayers, employing advanced light-trapping designs and the optimization of the metal contact and the interfaces may be the routes to boost the potential in open-circuit voltage and short-circuit current density further.

CHAPTER 6

CONCLUSION AND OUTLOOK

This thesis aimed to demonstrate the feasibility of integrating the novel magnesium oxide (MgO_x) electron-selective (hole-blocking) layer into crystalline silicon solar cells. The goal is to explore alternative solutions for the development of PER'X' (Passivated Emitter and Rear Cell 'PERC'-based architectures) and carrier-selective passivating contact (CSPC) solar cells to attain high-efficiency values while reducing the overall cost/kWh ratio. The initial efforts towards this objective were focused on optimizing the passivation and anti-reflective layers in standard p-type PERC solar cells. These optimized layers were subsequently employed on the front and rear surfaces of n-type PERC-like solar cells. It is apparent that, within the past five years, the efficiency values of industrial-scale PERC solar cells produced at the GPVL facility have surpassed 22%, up from 19.04%, owing to the optimization of passivation layers in conjunction with other crucial enhancements.

The atomic layer deposition (ALD) technique is used to deposit MgO_x layers at low temperatures, around 250 °C, using bis(ethylcyclopentadienyl)magnesium ($\text{Mg}(\text{CpEt})_2$) and H_2O as precursors. High-uniformity film deposition and accurate thickness control at the monolayer scale are both provided by ALD deposition. By combining multiple experimental procedures, precise control over the stoichiometry and thickness of the MgO_x layers was successfully achieved. Furthermore, the ion implantation method is utilized for emitter formation to simplify the process flow by enabling single-side doping and having precise doping control.

The introduction of MgO_x layers presents a notable difficulty due to the inherent trade-off between the quality of passivation and the resistivity of contacts. The passivation performance of the MgO_x/Al film stack was studied by measuring

implied open circuit voltage (iV_{oc}) values using finished solar cells. In conjunction with the production of solar cells, a supplementary set of samples was fabricated to measure contact resistivity, ρ_c .

Upon examining the average iV_{oc} and V_{oc} values of the solar cells fabricated, a significant enhancement is evident when 1.5 nm of MgO_x is introduced, whether a 'full rear' or 'local rear' configuration is utilized in the n-type cSi solar cells. Specifically, the introduction of full rear 1.5 nm of MgO_x results in a noteworthy increase in the average iV_{oc} value, compared to the reference solar cell, rising from 0.501 to 0.591 Volts. Moreover, when the MgO_x layer is locally applied on the rear side in conjunction with the SiN_x/SiO_xN_y stack, the enhancement is further amplified, achieving an average iV_{oc} value of 0.599 Volts.

Considering the average V_{oc} values, it can be observed that the average V_{oc} value of the reference sample, which is initially 0.503 V, increases to 0.581 V upon the full integration of 1.5 nm MgO_x . Furthermore, with the local addition of 1.5 nm MgO_x , the average V_{oc} value rises to 0.591 V. Furthermore, the implementation of a 1.5 nm MgO_x layer substantially enhances the quality of the rear contact, leading to one order of magnitude reduction in the average contact resistivity to a value of 0.66 $\Omega.cm^2$.

The mentioned enhancements ultimately resulted in a remarkable solar cell efficiency of 17.17% from the 43.50 cm^2 "local rear" designed novel carrier selective MgO_x integrated PERC-like solar cells. According to our current knowledge, the solar cells created in this thesis using a MgO_x layer are larger in size compared to the similar solar cells discussed in the literature. This highlights the possibility of utilizing MgO_x deposited through atomic layer deposition (ALD) for producing industrial-scale silicon solar cells. Additionally, this approach can potentially eliminate silver (Ag) use in manufacturing of n-type c-Si solar cells, a highly coveted development for industrial solar cell applications. These findings collectively indicate a promising avenue for producing high-efficiency, cost-effective, dopant-free heterojunction solar cells. Looking ahead, an alternative approach worth

exploring involves depositing MgO_x onto an intentionally ultra-thin oxide layer rather than an HF-last Si surface. This alternative route holds promise for achieving improved contact properties and enhanced passivation.



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EDUCATION

Degree	Institution	Year of Graduation
MS	METU Micro and Nanotechnology	2017
BS	METU Physics Education	2015
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WORK EXPERIENCE

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2021-Present	ASELSAN	Lead Engineer
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FOREIGN LANGUAGES

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PUBLICATIONS

Journal Articles

1. Altuntepe A., Olgar M.A., Erkan S., Hasret O., Keçeci A.E., Kökbudak G., Tomakin M., Seyhan A., Turan R., Zan R. "Hybrid transparent conductive electrode structure for solar cell application", Renewable Energy, (2021), vol. 180, pp. 178-185. doi: 10.1016/j.renene.2021.08.061.

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