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ABSTRACT

SURFACE AND BULK PASSIVATION OF MULTICRYSTALLINE SILICON SOLAR CELLS BY SILICON NITRIDE (H) LAYER: MODELING AND EXPERIMENTS

by Chuan Li

The objective of this dissertation is to study passivation effects and mechanisms in Si solar cells, specifically, the surface and bulk passivation by hydrogen-rich PECVD silicon nitride (SiN_x :H) antireflection layer on multicrystalline silicon (mc-Si) solar cells.

The passivation of silicon surface can be achieved in two ways: by field-effect passivation and/or by neutralization of interface states. In other words, the deposition should result in a high value of fixed charge, Q_f and /or a low value of interface state density, D_{it} . The surface recombination velocity can be described by Shockley-Read-Hall (SRH) statistics.

Current SRH formalisms have failed to explain the surface recombination mechanism in terms of injection level dependence as has been observed by lifetime measurements. Previous SRH modeling result shows that very high Q_f (up to several 10^{12} /cm²) on the surface of Si wafer, induced by SiN_x:H layer, leads to no injection level dependence of surface recombination velocity (SRV), which is in contradiction to experimental results. An alternative approach is needed to address this problem.

A modified SRH formalism which includes the carrier recombination in the space-charge region was developed in this thesis to evaluate the recombination mechanism at SiN_x :H-Si interface. Numerical modeling results indicate that, at low injection-levels, carrier recombination in the damaged layer is the dominant mechanism

as compared to surface recombination. The majority of surface damage can be healed by rapid thermal annealing (RTA). Therefore, less minority-carrier recombination in the SCR is expected after the firing treatment of Si solar cells.

Based on the damaged layer and trapping/detrapping theory, a semi-quantitative hydrogen transportation model of H migration from SiN_x :H layer into Si is presented. The model is verified by secondary ion mass spectrometry (SIMS) measurements of H in Si solar cells before and after annealing. The redistribution of H deep inside the cells can lead to excellent bulk passivation and high device performance.

Experimental results of the reproducibility of minority-carrier life measurement using QSSPCD technique indicate that wafer preparation requires a well-cleaned wafer and high quality surface passivation. In this study, a novel laboratory procedure for wafer preparation is proposed.

Theoretical and experimental studies on the influence of defect clusters on the performance of mc-Si solar cell have been performed. In a typical cell, the defect clusters produce an efficiency loss of 3 to 4 percent.

SURFACE AND BULK PASSIVATION OF MULTICRYSTALLINE SILICON SOLAR CELLS BY SILICON NITRIDE (H) LAYER: MODELING AND EXPERIMENTS

by

Chuan Li

A Dissertation Submitted to the Faculty of New Jersey Institute of Technology in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy in Materials Science and Engineering

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APPROVAL PAGE

SURFACE AND BULK PASSIVATION OF MULTICRYSTALLINE SILICON SOLAR CELLS BY SILICON NITRIDE (H) LAYER: MODELING AND EXPERIMENTS

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CHAPTER 1

INTRODUCTION

1.1 Solar Cells-A Perspective

As the world becomes more concerned about the environmental effects of burning fossil fuels, and as fossil fuels become scarcer, we need to develop alternate energy technologies. One of the most promising is photovoltaic (PV) or solar cells that are already in use in many places.

Solar photovoltaic energy conversion is a one-step conversion process which generates electrical energy from light energy. The explanation relies on ideas from quantum theory. Light is made up of packets of energy, called photons, whose energy depends on the frequency of light. The energy of photons in visible wavelengths is sufficient to excite electrons to higher energy levels where they are freer to move.

Photovoltaic technology actually dates back over 160 years. The PV effect was first discovered and reported in 1839 by French physicist A.E. Becquerel [1] when he observed that certain materials would produce a small current when exposed to light. About 55 years later, in 1883, the first solar cell was built by Charles Fritts [2], an American inventor, by coating selenium wafers with an ultrathin, nearly transparent layer of gold to form a metal-semiconductor junction. Fritts's devices were very inefficient, transforming less than 1 percent of the absorbed light into electrical energy. In 1918, a Polish scientist, Jan Czochralski [3] discovered a method for monocrystalline silicon production, which enabled the production of monocrystalline silicon solar cells. In 1941, the first silicon solar cell was invented by Russell Ohl [4]. Silicon proved to be a much better semiconductor and is the predominant material that is used today in solar cells. Ohl was able to obtain energy conversions of less than one

percent; however, soon, more advances were made in order to increase PV energy conversion efficiencies.

In 1954, a silicon solar cell capable of 6% energy conversion efficiency with direct sunlight was invented by three American scientists, Gerald Pearson, Calvin Fuller and Daryl Chapin [5]. They created the first solar panel by putting several strips of silicon p-n junctions together to form an array and placed it in sunlight. The first field trial of the Bell Solar Battery in actual service began on a telephone carrier system in October, 1955 [6]. The first sun-powered automobile was demonstrated in Chicago, Illinois in August 1955 [7]. In 1958, Hoffman Electronics achieved 9% efficient PV cells. Vanguard I, the first PV-powered satellite, was launched in cooperation with the U.S. Signal Corp. The satellite power system operated for eight years [7, 8]. The first telephone repeater powered by solar cells was built In Americus, Georgia [7]. In 1959, Hoffman Electronics achieved 10% efficient, commercially available PV cells. Hoffman Electronics also learned to use a grid contact, reducing the series resistance significantly [7]. On August 7th 1959, the Explorer VI satellite was launched with a PV array of 9600 solar cells. On October 13th 1959, Explorer VII was launched [7]. In 1960, Hoffman Electronics introduced yet another solar cell with 14% efficiency [7]. In 1963, Sharp Corporation developed the first usable photovoltaic module from silicon solar cells [9]. In 1985, researchers at the University of New South Wales in Australia constructed a solar cell with more than 20% efficiency [10]. By the late 1980s, silicon solar cells, as well as those made of gallium arsenide, with efficiencies of more than 20 % had been fabricated [11, 12]. In 1989, a concentrator solar cell, a type of device in which sunlight is concentrated onto the cell surface by means of lenses, achieved an efficiency of 37% due to the increased intensity of the collected energy [13]. In general, solar cells of widely

varying efficiencies and costs are now available. In 2006, Spectrolab's cells achieved 40.7% efficiency in lab tests [14]. Scientists at the National Renewable Energy Laboratory (NREL) have set a world record of 48% efficiency on an inverted metamorphic triple-junction solar cell. This is the highest confirmed efficiency of any photovoltaic device to date [15].

The deployment of solar cells was transferred from space to terrestrial applications in the early 70s. So far, solar cells have been developed to serve many applications. They work in remote area power systems, earth orbiting satellites, handheld calculators, remote radio telephones and water pumping applications. Solar cell manufacturing is a vital and rapidly growing industry, enjoying over 30% annual growth during the last 10 years. The annual production of solar modules has increased ten-fold every decade. Figure 1.1 shows the growth of world solar module manufacturing from 1980 to 2000 [16].



Figure 1.1 World solar module productions 1980-2000 [16].

1.2 How Does A Solar Cell Work

The most commonly known solar cell is configured as a large-area p-n junction made from semiconductors. The electric field established across the p-n junction creates a diode that promotes current to flow in only one direction across the junction. The diode is made from a semiconductor with a band gap defined by $E_c - E_v$ (see Figure 1.2). When the energy of the incident photon is larger than the band gap, the photons can be absorbed by the semiconductor p-n junction to create electron-hole pairs. The electrons and holes are then driven by the internal electric field in the diode to produce a photocurrent (light-generated current). In Figure 1.2, a schematic of the photogeneration process in a semiconductor is depicted.



Figure 1.2 A schematic of photogeneration effect.

In order to produce a solar cell, the semiconductor has to be contaminated or doped. Pure semiconductors (also called "intrinsic") do not conduct electricity at room temperature and are thus not useful for the fabrication of electronic devices. Semiconductors conduct electricity if they are doped with a small amount of impurity atoms. In the case of silicon (Si), these would be atoms from group III and group V of the periodic table. Impurities in semiconductors are divided into two broad categories: donors and acceptors. A donor is an element with typically one more valence electron than the group IV semiconductor. Each Si atom has four electrons in its outermost shell; these electrons are involved in forming chemical bonds with the neighboring Si atoms. For example, an arsenic (As) atom has five electrons in its outermost shell. The extra electron in As can be easily removed from the As donor on which it was originally localized. If this happens, the electron can move freely in the semiconductor material and conduct electric current. A semiconductor doped with donors is known as *n*-type material. An acceptor is an element with typically one fewer valence electron than the element that forms the semiconductor. A boron (B) atom has three electrons in its outermost shell. The missing electron in the chemical bond is called a hole. It too can be easily removed from the vicinity of the B atom and move freely in the semiconductor material. A semiconductor doped with acceptors is known as *p*-type material. As the two types of semiconductors are brought together, a *p*-n junction is formed and the concentration gradient of carriers near the metallurgical junction leads to a carrier flow. As the junction region gets "depleted" of carriers, the ionized dopant cores left behind build up an electric field across the junction, which introduces drift current that is opposite to the diffusion current. An equilibrium situation will be arrived at as the two currents match. In the dark, the equilibrated *p*-n junction should have a spatially uniform Fermi level and no net macroscopic current flow is observed.

When a p-n junction is illuminated, excess electron-hole pairs are generated by light throughout the cell. This disturbs the equilibrium state of carriers everywhere. The excess electrons (holes) in *n*-type (*p*-type) region diffuse towards the junction and are quickly pulled across the depletion region by the electric field. This is the photovoltaic effect.

A simplified solar cell model is usually illustrated as a current source in parallel with a diode and, a shunt resistance and a series resistance component as well are added. The resulting equivalent circuit of a solar cell is shown in Figure 1.3. Notice that the current generated by the photons is represented by an independent source. The two resistors shown in Figure 1.3 represent two of the losses in a solar cell. R_s is a series resistance loss due, primarily, to the ohmic loss in the surface of the solar cell. The shunt resistance, $R_{\rm sh}$, is used to model leakage currents. A shunt resistance of a few hundred ohms does not reduce the output power of the solar cell appreciably. In reality, $R_{\rm sh}$ is much larger than a few hundred ohms and can in most

cases be neglected. The series resistance, however, can drastically reduce output power.



Figure 1.3 An electrical equivalent circuit of a solar cell.

Figure 1.4 is a plot of a typical current-voltage (I-V) characteristics of a solar cell. A solar cell mainly consists of a diode, whose ideal forward current-voltage relationship (i.e., I-V curve) can be expressed as:

$$I = I_0(e^{\beta V} - 1),$$

where I_0 is the dark current;

 $\beta = (q/kT)$, q is the elementary charge, k is Boltzmann's constant, T is the absolute temperature, and V is voltage.



Figure 1.4 The *I-V* characteristic of a solar cell with maximum power point [17].

In solar cell applications, this characteristic is usually drawn inverted about the voltage axis, as shown above. The cell generates no power in short-circuit (when current is I_{sc}) or open-circuit (when cell generates voltage V_{oc}). The cell delivers maximum power, P_{max} , when operating at a point on the characteristic at which the product IV is maximum. J_{sc} , V_{oc} , and fill factor FF are related by:

$$FF = [P_{max} / (V_{oc} \times I_{sc})]$$

 $J_{\rm sc}$, $V_{\rm oc}$, and fill factor FF are the three key parameters characterizing solar cell performance. The maximum limit for J_{sc} is given by the photogenerated current density, $J_{\rm ph}$. $V_{\rm oc}$ cannot exceed $E_{\rm gap}/q$ (q is the charge of an electron) and is, in general, quite a bit lower due to recombination.

For open-circuit conditions, all photogenerated carriers recombine within the solar cell. Thus, if recombination can be minimized, V_{oc} can more closely approach the limit (E_{gap}/q) . However, from thermodynamic considerations of the balance

between radiation and generation, one finds that recombination cannot be reduced below its radiative component, yielding a lower basic limit for V_{oc} .

Considering that FF is calculated as a function of V_{oc} by assuming that the *I-V* characteristics of a diode are, in an ideal case, an exponential function, calculations show that FF is limited by E_{gap} .

The optimum value of E_{gap} for the total energy conversion efficiency (including charge separation) is ~1.5 eV, with a "limited" efficiency approaching 30%. Gallium arsenide (GaAs), indium phosphide (InP), and cadmium telluride (CdTe) are semiconductor materials that have bandgap energies very near the optimum value. However, the first two are too costly for large-scale terrestrial applications, and CdTe has toxicity problems. With crystalline silicon, laboratory cells have been produced that are near the corresponding efficiency "limit" of 29%-30% [18, 19]. However, such record cells are based on sophisticated designs and are not suited for large-scale commercial utilization. Unlike the small-size, expensive laboratory facilities, various additional losses must be considered for commercial PV-Si cells and compromises between performance and cost often end up with module efficiencies that are, in the best cases, $15\% \sim 20\%$ [20].

1.3 Silicon Solar Cells

1.3.1 Three Generations of Solar Cells

Solar cells can be conveniently classified into three generations regarding their history, research and applications, even though, in reality, these generations are concurrently present in commercial production [21].

First generation cells consist of large-area, high quality and single junction devices. First generation technologies involve high energy and labor input which prevents any significant progress in reducing production costs. Single junction silicon devices are approaching the theoretical limiting efficiency under concentrated sunlight [22] and achieve cost parity with fossil fuel energy generation after a payback period of 5-7 years [23].

However, first-generation cells are expensive to produce because of the high costs of purifying, crystallizing and sawing the single silicon wafer. Secondgeneration solar cells are aimed at reducing costs by using thin films of silicon and other compound semiconductors, such as gallium arsenide (GaAs), cadmium telluride (CdTe), copper indium diselenide (CIS) and copper indium gallium selenide (CIGS) mounted on steel, plastic or glass substrates in order to reduce material mass and, therefore, production costs [24]. However, second-generation devices suffer from structural defects that make them less efficient than their single-crystal counterparts, thus making commercialization of these technologies difficult. In 2007, First Solar produced 200 MW of CdTe solar cells making it the fifth largest producer of solar cells in 2007 and the first ever to be in the top ten companies for production of solar cells using second generation technologies alone [25]. Wurth Solar commercialized its CIS technology in 2007 with production capacities of 15 MW [26]. Nanosolar commercialized its CIGS technology in 2007 with a production capacity of 430 MW for 2008 in the United States and Germany [27]. In 2007, the total market share was as follows: 4.7% for CdTe, thin film silicon at 5.2% and CIGS at 0.5% [25].

Third generation technologies are targeting higher conversion efficiencies of up to 30-60% as compared to the poor performance of second generation while retaining low cost materials and manufacturing techniques [21]. The following are the examples of third generation technologies: multijunction photovoltaic cells, quantumwell or other nano-structure solar cells, dye-sensitized solar cells, organic/polymer solar cells, concentration systems and excess thermal generation approaches to enhance voltages or carrier collection [24].

1.3.2 Silicon Solar Cells

The work presented in this dissertation focuses on problems relating to methods to improve efficiencies of crystalline silicon solar cells. Silicon is not only the material used in the earliest successful PV devices, but continues to remain as the most widely used PV material. Over 95% of all the solar cells produced worldwide are composed of Si. As the second most abundant element in the earth's crust, silicon has the advantage of being available in sufficient quantities.

A roadmap of solar cell production and capacity is shown in Figure 1.5 [28].



Figure 1.5 Solar cell production and capacity [28].

The statistics and predictions indicate that crystalline silicon solar cells were, are and will be the dominant influence in the PV industry.

Basically, materials for manufacturing silicon solar cells can be distinguished according to the type of crystal into three categories: monocrystalline, polycrystalline and amorphous. In order to produce a monocrystalline silicon cell, absolutely pure semiconductor material is necessary. Monocrystalline rods are extracted from melted silicon and then sawed into thin plates. This production process guarantees a relatively high level of efficiency. The production of polycrystalline cells is more cost-efficient. In this process, liquid silicon is poured into blocks that are subsequently sawed into plates. During solidification of the material, crystal structures of varying sizes are formed, at whose borders defects emerge. As a result of this crystal defect, the solar cell is less efficient. If a silicon film is deposited on glass or another substrate material, this leads to the so-called amorphous or thin layer cell. The layer thickness amounts to less than 1µm; so the production costs are lower due to the low material costs. However, the efficiency of amorphous cells is much lower than that of the other two cell types. Because of this, they are primarily used in equipment that require low power (watches, pocket calculators) or as facade elements.

Silicon solar cell technology has greatly advanced in the past three decades. Crystalline silicon is the dominant material in today's photovoltaic industry, and is expected to remain so in the coming decades ($\sim 80\%$ of solar cells produced at present are crystalline silicon solar cells and the remaining 20% are mostly non-silicon solar cells) [28].

1.4 Structure of A Crystalline Si Solar Cell

Crystalline silicon is the primary example of a homojunction solar cell. A single crystal silicon is altered so that one side is p-type, dominated by positive holes, and the other side is n-type, dominated by negative electrons. The p/n junction is located

so that the maximum amount of light is absorbed near it. The free electrons and holes generated by light in the p/n junction are separated to produce a current. As shown in Figure 1.6, typical crystalline silicon solar cell consists of a glass or plastic cover or other encapsulate, an antireflection layer, a front contact to allow electrons to enter a circuit, a back contact to allow them to complete the circuit, and the semiconductor layers in which the electrons begin and complete their journey [29].



Figure 1.6 An illustration of a typical crystalline Si solar cell [29]

1.5 Defects and Impurities in Si Solar Cells

Commercial Si solar cells are fabricated on low-cost wafers that contain high concentrations of impurities and defects which adversely affect the minority carrier lifetime and consequently conversion efficiencies of the final products.

Defects are generally categorized point, line, area or volume defects depending on their spatial characteristics. Some examples of each type are shown in Figure 1.7 [30].



Figure 1.7 A pictorial representation of various types of point, line, area and volume defects: (a) foreign interstitial; (b) dislocation; (c) self-interstitial; (d) precipitate; (e) extrinsic stacking fault and partial dislocation; (f) foreign substitutional; (g) vacancy; (h) intrinsic stacking fault surrounded by a partial dislocation; (i) foreign substitutional [30].

Examples of point defects are self-interstitials, vacancies and foreign substitutions or interstitial atoms [(c), (g), (l), (f), and (a) above, respectively]. Vacancies, interstitials and vacancy-interstitial pairs can be easily introduced during crystal growth. The most important factor controlling the grown-in point defect and micro-defect is the ratio γ /G [31, 32], where, γ is the pulling rate and G is the nearsurface axial temperature gradient. On further cooling, supersaturated vacancies (interstitials) may agglomerate into D-void-defects (A/B-swirl-defects), which are micro-volume defects. Growth of PV multicrystalline (mc) Si materials usually requires a high pulling rate, so they contain a higher level of vacancies than interstitials [33].

Dislocations are an example of line defects [(b) above]. Dislocations represent boundaries between slipped and unslipped regions of a crystal. The formation of dislocation lowers the total free energy to relieve the tension caused by the temperature gradient during crystal growth and cooling. Dislocations in silicon may be dissociated into glide and be involved in the deformation behavior of silicon [34]. As a result of elastic distortions associated with a dislocation, band bending occurs in its vicinity. Dangling bonds are also created along the core of the dislocation and introduce energy levels in the bandgap.

Stacking faults [(e) and (h) above], grain boundaries and twin planes are examples of area defects. Stacking faults arise from excess silicon self-interstitials generated during oxidation. Grain boundaries are formed during crystal growth. In polycrystalline silicon material grown by casting process, a large amount of grain boundaries can be induced. Grain boundaries may be treated as an assemblage of dislocations whose properties depend on the crystallography of the boundary; and, their electrical activities are connected with the set of dislocations and constitute a boundary.

Precipitates [(d) above] and impurity clusters are examples of volume defects. During processing, contamination by metallic impurities is also present. Unlike the intentional doping of shallow level impurities, metallic impurities may be incorporated without notice due their high solubilities in silicon. Transition atoms, such as Fe, Co, Cr, Ni, Cu, in the silicon lattice are believed to introduce energy levels in the bandgap [35]. Multicrystalline silicon (mc-Si) solar cells can tolerate iron, copper, or nickel in concentrations up to 10^{14} – 10^{15} cm⁻³ [36] because metals in mc-Si are often found in less electrically active inclusions or precipitates at structural defects (e.g., grain boundaries) rather than being atomically dissolved.

Within the crystal, impurities can act in isolation as recombination centers or can be precipitated at crystallographic defects, with the combined defect acting as an efficient recombination site. Once precipitated, it is generally considered more difficult to remove the impurity.

In order to achieve high device efficiency, cell fabrication processing must include steps that can remove as-grown impurities and defects as much as possible and passivate the remaining impurities and defects. However, to maintain cost effectiveness, these processes must be included as a part of a typical cell-fabrication sequence without increasing the number of process steps.

1.6 Impurity Gettering in PV-Si

The performance of solar cells would be quite poor if the concentration of impurities in the device is as high as in the as-grown PV-Si. Some of the impurities are removed during device processing. This mechanism, called gettering, has been used in microelectronic devices to trap impurities away from the active region of the device by oxygen precipitates.

The general mechanism of gettering can be described by the following steps: 1) the impurities are released into solid solution from whatever precipitate they are in; 2) they undergo diffusion through the silicon; 3) they are trapped by defects such as dislocations or precipitates in an area away from device regions.

There are two general classifications of gettering, namely, extrinsic, and intrinsic. Extrinsic gettering refers to gettering that employs external means to create

damage or stress in the silicon lattice in such a way that extended defects needed for trapping impurities are formed. These chemically reactive trapping sites are usually located at the wafer backside.

Solar cells are minority-carrier devices and use nearly the entire bulk of the device. It is more attractive to apply external gettering techniques to clean up the bulk of the material. Phosphorous diffusion and Al alloying are some of the processes that have worked well for efficient gettering of solar cells. Because these processes are used extensively in solar-cell manufacturing for junction and contact formation, all Si solar cells experience a certain degree of gettering.

1.7 Passivation of Residual Impurities and Defects

It should be noted that not all impurities can be completely gettered during solar-cell processing. Even impurities which are readily getterable remain in the solar cell at significant levels and introduce detrimental effects on solar-cell performance. In addition to the residual impurities, many crystallographic defects are stable at the processing temperatures. It is often observed that defect concentrations remain essentially unaltered by solar-cell processing. Therefore, it is important to identify methods of dealing with residual impurities and defects.

It is known that the hydrogen passivation yields very good results in terms of passivation. One of the most promising methods is application of the hydrogenated amorphous silicon nitride layers (a-SiN_x:H) deposited by plasma-enhanced chemical vapor deposition (PECVD). These layers are used as very effective antireflective coatings [37]. The major interest in these films, however, is attributed to the bulk and surface defect passivation of silicon. It has been shown that hydrogen released from
the SiNx:H layer during the thermal treatment of a solar cell can passivate silicon defects [38].

1.8 Dissertation Outline

Chapter 1 is an introduction to silicon solar cells, its history, status, and trends in the photovoltaic industry. The physics of solar cells, specifically Si solar cells and limiting factors of cell performance are discussed.

Chapter 2 is an overview of silicon nitride layer as a multi-functional component in Si solar cells. PECVD hydrogen-rich silicon nitride (SiN_x:H) films, not only act as desirable AR coatings in PV industry, but are also capable of providing excellent passivation of surface defects as well as bulk passivation of impurities and defects.

Chapter 3 gives a brief overview of numerical modeling of surface recombination velocity (SRV) based on the so-called extended SRH formalism, which calculates SRV at the SiN_x:H-Si interface as a function of injection level. In order to overcome the discrepancy generated by the existing model, a modification is presented, which includes both the carrier recombination on the Si surface and the recombination across the space-charge-region (SCR) which is related to the charge and defects distribution in a damaged layer caused by ion bombardment during the PECVD process. A semi-quantitative model for H evolution mediated by SiN_x:H layer together with process-induced-damage is established based on the theory of H transport across SiN_x:H medium and H trapping-detrapping mechanisms. The results of these models are used to establish properties of SiN_x:H for the purpose of optimum passivation. Chapter 4 addresses the experiments relating to the minority-carrier lifetime measurements using Quasi-Steady-State Photo-Conductance-Decay (QSSPCD) technique. The experiments indicate that wafer preparation for meaningful lifetime measurements requires a clean wafer and high quality surface passivation as well. A novel laboratory procedure for wafer preparation is proposed.

Chapter 5 is a combination of theoretical and experimental studies of defect clusters in mc-Si and their adverse effects on solar cell performance. In a typical cell, network model is employed to analyze the correlation between defect clusters and cell performance. Experimental studies of cells fabricated on wafers from the same ingot before and after firing facilitate a comparison and discussion of the impact of the defect clusters.

Chapter 6 focuses on conclusions based on the above studies and some possible future directions.

CHAPTER 2

SILICON NITRIDE LAYER FOR SOLAR CELL APPLICATIONS: AN OVERVIEW

2.1 Antireflection Coating

Until recently, the objective of using an antireflection coating (AR) on a solar cell has been to minimize the reflectance losses due to the cell and maximize the light trapping ability to obtain highest photocurrent for the incident solar photons.

Silicon is a shiny gray material and, therefore, acts as a mirror, reflecting more than 30% of the light that is incident on it. In order to improve the conversion efficiency of a solar cell, it is necessary to minimize the amount of light reflected so that the semiconductor material can capture as much light as possible to generate charge carriers. Maximum absorbance of the incident light is preferred to achieve ideal conversion efficiency.

A technique to reduce the reflectance loss is to texture the top surface. Chemical etching creates a pattern of cones and pyramids, which capture and trap light rays that might otherwise be deflected away from the cell. Reflected light is redirected down into the cell, where it has another chance to be absorbed.

In Si solar cells, a pseudoperiodic roughness is generated by chemical etching in a NaOH or KOH-based solution. Figure 2.1 shows the surface morphology of a typical texturized silicon surface using conventional NaOH texturization bath [39]. The etching also serves to remove the surface damage produced when ingots are sawn into wafers. A rough or textured surface typically has a much lower reflectance than that of a planar surface—a feature particularly useful in the case of high refractive-index semiconductors.

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Figure 2.1 SEM picture of a typical texturized silicon surface using conventional NaOH texturization bath [39].



Figure 2.2 The calculated reflectance spectra of a bare Si wafer for different surface conditions: (a) polished and (b) (100) textured. Wafer thickness =300 μm [40].

Figure 2.2 summarizes the reflectance spectra of Si for two surface conditions: double-side polished and double-side textured [40], respectively, which shows that the

reflectance of polished Si can be greatly lowered by texturing. For a well-textured surface of a (100)-oriented wafer, the reflectance can be as low as 0.1.

The other approach is to deposit thin coatings of a material on top of the surface of a photovoltaic cell that reduces the light reflection and increases light transmission. These coatings are called antireflection (AR) coatings. The materials include SiO_2 , TiO_2 , ZnO₂, MgF and Si_3N_4 . A single layer of the antireflection material is usually several hundred nanometers thick.

The most common method for broadbanding in optical applications is to use multilayer coatings that exhibit reflectance nulls at several wavelengths [41]. If the nulls are located close to each other, it can result in a very low reflectance surface. This approach has been successfully applied in other optical devices, such as beam splitters, architectural glass windows, and optical instruments. But, because of cost considerations, a conventional multilayer approach is not suitable for solar cells. However, the broadband anti-reflection features in solar cells are obtained through the use of rough surfaces, in conjunction with a single-layer of AR coating.

In the past, the PV industry has used materials, such as SiO_2 and TiO_2 for AR coatings. SiO_2 is not an ideal material for AR coating of Si because its refractive index (n=1.45) is too low. However, it offers the advantage of providing surface passivation. On the other hand, TiO_2 is better matched optically with Si, but does not contribute to surface passivation. SiN offers a better match as an AR coating for Si, but the cost of depositing nitride layers is generally high and is not warranted for low-cost solar cells. However, the nitridation process can save other process steps and contribute to significant improvement of the cell efficiency, making it a viable option [42].



Figure 2.3 The calculated reflectance spectra of a Si wafer coated with SiN (n=2 and α =5.0): double-sided polished (solid line) and (100) double-sided textured (dotted line). Wafer thickness = 350 µm [42].

Figure 2.3 shows the reflectance spectra of Si coated with a non-absorbing (absorption coefficient α =0) dielectric coating of SiN_x with a refractive index (n) of 2. The thickness (t) is 75 nm. Figure 2.3 also shows that the minimum reflectance of the polished surface occurs at wavelength λ =4×n₁×t, where, n₁ is the refractive index of the dielectric layer. If n₁ = (n₀×n₂)^{1/2}, the minimum reflectance is reduced to zero (n₀ and n₂ are the refractive indices of the medium in which the cell is embedded and Si, respectively). Figure 2.3 shows that texturing results in a very broad null condition- a feature highly desirable for solar applications. Because an AR coating must be designed to maximize the performance of the cell for the incident spectral range, device performance optimization requires that the internal response of the solar cell and the spectrum for which the solar cell is to be operated be known. In most cases, this

information is application-oriented and may not be known at the time of cell design. A generalized approach used by most solar-cell manufacturers is to design the AR coating to provide a minimum reflectance corresponding to the peak in the solar spectrum [42].

For the AM1.5 spectrum, as shown in Figure 2.4 [42], the energy distribution peak occurs at $\lambda \cong 0.6 \,\mu\text{m}$, yielding a required thickness of 75 nm for the AR coating on a PV-Si cell to be directly operated in air (typically used for laboratory testing). For practical operation, the AR coating is designed for use in an encapsulated module. Here, the cell is encapsulated in ethylene vinyl acetate (EVA)—a medium of n \cong 1.5. Thus, it is necessary to have an AR coating with n \cong 2.2 for optimal device operation.



Figure 2.4 The spectrum of AM1.5 radiation [43].

2.2 Processing of Silicon Nitride Films for Si Solar Cells

Currently hydrogen containing silicon nitride (SiN_x:H) layers deposited by plasma enhanced chemical vapor deposition (PECVD) method have been extensively employed as AR coatings for multicrystalline Si solar cells. This is because of its capability to accomplish multiple functions and eliminate several additional process steps that are required in the fabrication of high-efficiency Si solar cells [42].

PECVD is a method of forming a thin solid film on a substrate by reaction of vapor phase chemicals which contain the required constituents. The reactant gases are activated by plasma energy and react on a temperature-controlled surface to form the thin film. The reactive species, energy, rate of chemical supply and substrate temperature largely determine the film properties.

The first publication specifically aimed at plasma-enhanced deposition for semiconductor processing appeared in 1963 [44]. Two years later, PECVD technique was invented [45]. This technique was soon utilized in IC technology and, in the mid-1970s, in photovoltaic (PV) technology, when the first PECVD amorphous silicon (a-Si) thin film solar cell was fabricated in RCA Laboratories by Carlson and Wronski in 1976 [46]. In 1981, for the first time, plasma SiN was applied to single-crystalline silicon metal-insulator-semiconductor inversion-layer (MIS-IL) solar cell cells as a promising dielectric [47, 48]. The first commercial cast mc-Si solar cell process with SiN AR coating was developed using available commercial equipment [49].

Since then, plasma SiN has been used by several large Si solar cell venders. To name a few, Mobil Solar (now ASE America) incorporated plasma SiN into edge-defined film fed growth (EFG) ribbon silicon solar cells. An overview of the history of the PECVD SiN can be found in the literature [50].

Silicon nitride deposition by PECVD was described by Sterling and Swann in 1965 [51]. For the photovoltaic application, SiN_x :H film is usually made from a gas mixture of SiH₄ and NH₃. Silane acts as a source of silicon and hydrogen. Ammonia, in addition to being a source of nitrogen, has a tendency to deposit SiN with a high ratio of incorporated hydrogen. Deposition is performed in a reactor operating at a pressure from a few hundred mTorr to a few Torr. Silane and ammonia or nitrogen react in a plasma at temperatures in the range of 200 to 400°C.

The kinetic energy of the plasma is used to dissociate the input gas leading to the following species:

$$SiH_4+e \rightarrow SiH$$
, SiH_2 , SiH_3 , Si , $H+e$,

$NH_3+e \rightarrow NH_2$, HN, N, H+e.

The reaction between the nitrogen- and hydrogen-containing species in the plasma results in an amorphous solid deposit commonly denoted as a-SiN_X:H or simply SiN.

The overall deposition reaction is written as:

$$SiH_4 + NH_3 (or N_2) \xrightarrow{(200-400^\circ C, rf)} Si_x N_y H_z + H_2$$

The deposition rate depends strongly on rf power, gas flow, chamber pressure and frequency.

Fundamentally, two kinds of PECVD methods are used: direct PECVD and remote PECVD (see Figure 2.5). In direct PECVD, all processing gases in the reactors are excited by an electromagnetic field and the samples are located within the plasma. The electromagnetic field has a frequency of either 13.56 MHz (high-frequency method) or in the 10-500 kHz range (low-frequency method). In the remote PECVD method, ammonia or a nitrogen-hydrogen mixture is excited outside the deposition chamber and silane is injected into the plasma. The plasma excitation is usually made by means of microwaves. Compared with direct RF plasmas, remote plasmas provide independent control on plasma production and surface conditioning, plasma transport and deposition. High deposition rate is intrinsically possible [50].

a)





Figure 2.5 Deposition of SiN_x:H fim in (a) a direct-plasma reactor and (b) a remoteplasma reactor[50].

Use of silane and nitrogen as reaction gases in a PECVD system typically yields silicon-rich films that exhibit low breakdown strengths. This behavior can be overcome by substituting NH_3 for N_2 . Depositions are normally carried out at pressures of 0.2-3 torr, which yield growth rates of 200–500 Å/min. These films contain up to 15-40% of hydrogen bonded to either silicon or nitrogen.

One of the advantages of SiN as an AR coating is that the refractive index of the film can be customized by controlling the deposition conditions, such as temperature, gas flow rates, chamber pressure etc., to produce Si-rich or N-rich films. The Si-rich films have a higher refractive index, whereas N-rich films have a lower index. On the other hand, Si-rich films have higher absorption. Optical and electrical properties of SiN films are controlled by the structure and chemistry of Si–H, N–H, Si–N bond densities, Si-to-N

b)

ratio, and the amount of unbound H. As a result, a wide range of properties can be obtained by managing these structural and chemical properties by manipulating the deposition parameters [42].

Optical properties, such as absorption, reflection and refractive index of the SiN AR coating, depend significantly on the concentration and chemical distribution of hydrogen, silicon and nitrogen in the film, i.e., on the deposition conditions, which are controlled by the N/Si ratio (x) in the films. For small x, the hydrogen-bonding configuration consists of isolated Si–H bonds, with no adjacent Si–N bonds. As x increases, multi-N-bonded Si–H bonds dominate the structure. For x>1, N–H bonds start to form and increase with x. Thus, a means of controlling the material properties of the SiN_x films consists of simply adjusting the x value by changing the nitrogen content.



Figure 2.6 The refractive index as a function of N/Si ratio for SiN_x:H films [52]. A line is drawn through the data for visual guidance only.

Figure 2.6 shows the dependence of the refractive index of SiN_x :H films on the N/Si ratio [52]. It is seen that the refractive index can be adjusted between about 1.9 and 2.2. A Si-rich, high-density, non-stoichiometric film has a high refractive index and a higher absorption loss, whereas a low Si-content film can have a low refractive index with a low optical loss.

Typically, a v-shaped Si solar cell is coated with 750-Å SiN_x:H/100-Å SiO₂ to achieve optimal AR effect and light absorption. Figure 2.7 shows the reflectance spectrum (thick dotted line) and the absorbance spectrum of a typical Si solar cell (thick solid line) that is 350 mm thick with an Al back contact. These calculations use a refractive index of 2.0 for SiN_x:H to maximize the cell performance (measured in air). However, for a solar cell operating in a module, the refractive index must be close to 2.2. Figure 2.7 also shows the reflectance spectrum (thin dotted line) and absorbance spectrum (thin solid line) of a solar cell encapsulated in a glass module. These calculations show excellent characteristics of the AR coating both for air and module operations. The photocurrent densities achievable by the optimized coatings are 40.97 mA/cm² and 39.74 mA/cm² for air and module operation, respectively [42].



Figure 2.7 The calculated reflectance and absorbance spectra of a Si solar cell operating in air (thick lines) and in an encapsulated module (thin lines). The nonabsorbing nitride is assumed to have n=2 for air and n=2.2 for module operation [42].

2.3 SiN_x-Si Interface Structure

The microscopic origin of interfacial defects in SiN_x -Si structures has been investigated by many researchers. Stemans reported the $\bullet Si \equiv Si_3$ defect in Si/Si_3N_4 interface, i.e., the surface Si dangling bond [53], which was also described by Garcia et al. as the unpaired hybrid pointing out of the Si surface [54].

It is reported that, during the SiN_x deposition, the SiO_x film is converted into an oxynitride film [52, 55]. Hence, it can be expected that the actual interfacial region on a silicon wafer covered by a PECVD SiN_x film possesses some similarity to the one found at the thermally grown Si-SiO₂ interface. Due to the presence of nitrogen and oxygen

atoms, the interface states are silicon dangling bond defects back bonded with Si, N and O atoms [56].

2.4 Surface Passivation of Si by PECVD SiN_X:H Films

Thermally grown silicon dioxide films have been studied to passivate silicon surfaces since 1960, allowing the development of integrated circuits [57]. The oxide grows into the wafer by consuming the underlying silicon. Because of this oxide growth, the oxygen must diffuse through the SiO₂ film and this generates a new interface within the wafer. This displacement of the interface to clean regions within the wafer is one of the main reasons for the excellent quality of thermally grown Si-SiO₂ interfaces, which exhibit a few interface state densities. On high resistivity silicon (>100 Ω cm) *p*-type Si wafers, this method is capable of providing extremely low surface state densities , $D_{it} \cong 10^9$ cm⁻² eV⁻¹, as demonstrated by surface recombination velocity (SRV) values below 10 cm/s [58]. For low substrate resistivities ($\cong 1 \Omega$ cm), the passivation quality depends on the doping type: *n*-Si surfaces can be more efficiently passivated than *p*-Si, but both are poorer [59].

During the last few decades, it has become increasingly clear that PECVD nitride produces excellent surface passivation of silicon solar cells. Very low SRV were obtained on silicon wafers (Mäckel and Lüdemann reported S_{eff} as low as 4-6 cm/s [60], while Lauinger et. al. achieved 4 cm/s [61, 62]).

Surfaces and interfaces can be regarded as severe discontinuities of the crystalline lattice of a semiconductor and consequently, high densities of allowed energy levels occur in the forbidden gap. At the present time, the thermally grown Si-SiO₂ interface is the best characterized silicon-insulator interface. It is well-known that the interface states of this system are mainly related to silicon dangling bond defects with a very broad energy distribution due to the inherent variation in the bond angles and the distances of the next neighbor atoms [63, 64].

Post-deposition anneals of PECVD layers on silicon are important in order to obtain passivated surfaces. Hezel et al. have shown that such an anneal can decrease interface state density of SiN_x -Si by two orders of magnitude [65], which agrees with the measured results of strong reduction of S_{eff} due to post-deposition that was observed by Leguijt et al. [66]. However, other authors have expressed different opinions. Boehme and Lucovsky reported hydrogen loss during anneal of SiN [67].

The deposition of SiN_x layers on silicon substrate leads to the formation of a space charge region at the interface characterized by a Q_f of the order of 10^{12} cm⁻². In *p*-type Si, a depletion/inversion layer is formed, while in *n*-type Si, the positively charged insulator attracts majority carriers and repels minority carriers. Hence, an accumulation layer is formed.

Low S_{eff} of PECVD SiN-passivated Si surface is attributed to the combination of moderately low density of interface states and a high positive charge density. Both parameters are given in Table 2.1 for as-deposited and thermally treated silicon nitride films [68].

 Table 2.1 Positive Fixed Charge and Interface-Trap-Density of As-Deposited and

 Annealed SiN-Si Interface [68]

Silicon nitride condition	$Q_{\rm f}({\rm cm}^{-2})$	$D_{\rm it} ({\rm cm}^{-2}/{\rm eV})$
As-deposited	3×10 ¹²	2×10 ¹¹
Thermally treated	1×10^{12}	1×10 ¹¹

2.5 Bulk Passivation of Si by SiN_x:H Films

It is believed that the bulk passivation effects are achieved by hydrogen passivating the impurities and defects in bulk Si and hence increasing the minority carrier lifetime. For PECVD SiN_x deposited with silane and ammonia as reactants, the hydrogen concentration in the as-deposited layer can be as high as 40% [68].

2.5.1 The Mechanism of H Transport

The mechanism of PECVD SiN_x :H-assisted H diffusion or transportation has been continuously evoking the interest of many research scientists. Robertson believes that a chemical equilibrium is formed between Si dangling bonds and weak Si-Si bonds that are controlled by Si-H bonds, which is thermally activated and acts over a long range. The higher defect density leads to H diffusion from the SiN bulk to the SiN-Si interface and passivates Si dangling bonds. The diffusion of hydrogen in nitrogen rich nitride is hindered by the increased activation energy [69]. This can also be used to explain why good passivation can be achieved if the SiN_x has a high density of Si-H bonds.

Lucovsky et. al. have proposed a model for defect generation at the SiN_x/Si interface. In this model, Si-H and N-H bonds and atomic hydrogen are the precursors of defects or are generated in a passivation pathway of Si dangling bonds. Hydrogen is locally displaced by the hopping of electrons and holes and by the breaking of weak bonds [70].

Mäckel and Lüdemann have developed a combined model to describe the stoichiometric dependent reaction pathways during PECVD for defect generation and neutralization [60]. A high SiH₄ gas flux during PECVD is proposed to be responsible for

the passivation of dangling bonds at the SiN-silicon interface with the following possible reaction pathways:

(i) A hydrogen radical in the plasma gas attaches to a Si dangling bond and forms a Si-H bond:

 \equiv Si⁰ + •H $\rightarrow \equiv$ Si—H

(ii) Silane radicals react with the surface:

 $\equiv Si^{0} + \bullet Si - H_{2} \rightarrow \equiv Si - Si - H_{2}$

(iii) A Si— H^+ ion from the plasma attaches to a Si dangling bond by forming a weak bridging Si— H^+ —Si bond. One of the Si atoms then forms a Si—Si bond with a neighboring Si dangling bond at the silicon surface by hopping of an electron:

$$\equiv Si - H^{+} + \equiv Si^{0} \rightarrow \equiv Si - H^{+} - Si \equiv,$$
$$\equiv Si - H^{+} - Si \equiv + \equiv Si^{0} + e^{-} \rightarrow \equiv Si - Si \equiv + \equiv Si - H$$

From the above model, it can be seen that •H radical plays a fundamental role in the formation of complexes.

2.5.2 Hydrogen Passivation Effect

Although the mechanism of bulk passivation of c-Si solar cells by SiN_x :H films is not yet completely known, the passivation effect has been experimentally proved. Chen et. al. [71] studied PECVD of SiN_x films (~600 Å) on top of PECVD-grown SiO_2 (~100 Å) on both surfaces of samples followed by photo-assisted anneal at 350°C in forming gas

combination of internal quantum efficiency (IQE) measurements and computer modeling.

ambient. The bulk and surface passivation effects were quantified and decoupled by a

It was found that the bulk lifetime of PECVD passivated solar cells increased by 30% - 70% and the effective lifetime improved by a factor of 2.6 - 9.5 [71].

By using electron spin resonance (ESR) method, Fukui, et. al. [72] measured a decrease in unpaired electron-spin density from 4×10^4 spins/cm³ to 2×10^4 spins/cm³ as a result of deposition of PECVD SiN_x films onto three different mc-Si substrates. Hence, they pointed out that PECVD SiN_x film has bulk passivation effect and the effect is larger when the quality of substrate is lower [72].

According to Sopori and Zhang et. al. [42, 73], PECVD of SiN during solar cell fabrication serves as a step for H incorporation. The majority of the hydrogen atoms are trapped and "stored" in process-induced traps (PITs) in the surface damaged layer produced by the plasma process during the nitride deposition. It should be noted that there is a diffusion of H, but because of the traps, the H is primarily confined to the vicinity of the surface. In rapid thermal anneal (RTA) step, H is released from the surface and redistributed into the bulk region. Three steps are involved during the hydrogen diffusion: 1) release of hydrogen from the damaged layer, 2) bulk diffusion, and 3) if bulk trap level is high, the diffusion is stalled and controlled by trapping and detrapping in the vicinity of the diffusion front. The bulk H may also be released from the chemical bonds in the SiN films, but is less important compared to the strong release of hydrogen from the surface.

However, some researchers have questioned whether bulk hydrogenation from SiN occurs at all. Boehme and Lucovsky reported only 10-20 nm diffusion of deuterium (D) [67] into silicon from SiN. This degree of passivation is too small for improvement of solar cell emitter regions. They attribute the H loss during anneal to H migration out of the nitride and not into the Si area thus resulting in the effectiveness of the hydrogenation from the post-deposition annealing of SiN layers to be questionable.

In order to increase the sensitivity of the detection of H, Jiang and Stavola et. al. used vibrational spectroscopy, coupled with the use of Pt marker impurities in Si to probe the H that is assumed to be introduced into Si by post-deposition annealing of SiN_x:H AR coatings [74]. Their experiments indicated that hydrogenation of Si from the nitride layer yielded a modest H concentration, which is less than ~ 10^{14} cm⁻³. A five minute anneal at 600°C resulted in ~ 500 µm depth of H penetration into Si, which surprisingly suggested a H diffusion constant that is a factor only ~ 2 smaller than an extrapolation of the classic results of Wieringen and Warnmoltz [75].

The above approach is a promising method to introduce H into c-Si solar cells to passivate bulk defects by post-deposition annealing of H-rich SiN_x layers. However, from the studies in the literature, a thorough understanding of the mechanisms involved in hydrogen passivation is still lacking.

CHAPTER 3

MODELING OF SURFACE RECOMBINATION VELOCITY - ROLE OF THE DAMAGED LAYER

3.1 Background

3.1.1 Recombination Mechanisms in Silicon

Illumination of a semiconductor junction with photons of sufficient energy creates electron-hole pairs ('generation'). Hence, the charge carrier concentration is higher under illumination than the dark (thermal equilibrium). Upon termination of illumination, the carrier concentrations return to their thermal equilibrium values. The responsible processes are called recombination.

The recombination process occurs via defect levels (surface states) in the forbidden bandgap of the semiconductor. Three fundamental recombination processes are often addressed in semiconductors:

- Band-to-band recombination

- Trap-assisted recombination

– Auger recombination.

. . .

3.1.1.1 Band-to-band Recombination. Band-to-band recombination is the inverse process to the absorption of light in a semiconductor. An electron in the conduction band falls into a non-occupied state (a hole) in the valence band; the excess energy is released in the form of a photon. Band-to-band recombination in a direct band-gap semiconductor is shown schematically in Figure 3.1[76].



Figure 3.1 Band-to band recombination in a direct band-gap semiconductor [76].

Band-to-band transition is typically also a radiative transition in direct-bandgap semiconductors such as GaAs and is technically exploited in light-emitting diodes (LEDs).

3.1.1.2 Trap-Assisted Recombination. Trap-assisted recombination occurs when an electron falls into a "trap" – i.e., an energy level within the bandgap caused by the presence of a foreign atom or a structural defect. Once the trap is filled, it cannot accept another electron. The electron occupying the trap, in a second step, moves into an empty valence band state, thereby completing the recombination process. One can envision this process as a two-step transition of an electron from the conduction band to the valence band or as the annihilation of the electron and hole, which meet each other in the trap. This process is often referred to as Shockley-Read-Hall (SRH) recombination [77, 78].

Figure 3.2 shows the forbidden gap of a semiconductor that has several types of impurity levels. Those near the midgap position, E_i , are labeled as recombination centers. Also shown are levels that are designated as electron traps and hole traps. These lie near the conduction band and the valence band, respectively.



 E_R — Recombination center E_n — Electron Trap E_p — Hole Trap

Figure 3.2 Schematic diagram of impurity-related energy levels within the forbidden gap of a semiconductor. Levels are labeled as to whether the defect is likely to be a trap or a recombination center according to the SRH model.

3.1.1.3 Auger Recombination. Auger recombination is a process in which an electron and a hole recombine in a band-to-band transition, but now the resulting energy is given off to another electron or hole instead of emitting a photon. Hence, this recombination process involves three charge carriers. The third excited carrier returns to its initial energy state by emitting phonons.

3.1.2 Surface Recombination

3.1.2.1 Fundamentals. Recombination at surfaces and interfaces can have a significant impact on the behavior of semiconductor devices. This is because surfaces and interfaces typically contain a large number of recombination centers. These centers are due to the abrupt termination of the semiconductor crystal, which leaves non-saturated ('dangling') bonds resulting in a large density of defects (surface/interface states). In addition, the

surfaces and interfaces are more likely to contain impurities since they are exposed during the device fabrication process.

As discussed above, the trap-assisted recombination is described by the SRH theory. In order to calculate the recombination rate, a number of simplifying assumptions are made [79]:

(a) no radiative recombination or Auger recombination;

(b) the semiconductor is not degenerate;

(c) the energy level of the defects does not change with charge condition;

(d) the relaxation time of the charge carriers caught by the defect is negligibly small compared to the average time between two emission processes;

(e) the defect concentration is very small compared to the doping density;

(f) Fermi-Dirac statistics apply;

(g) the defects do not interact with each other (i.e., an electron cannot make a transition from one defect level to another).

Based on these assumptions, the SRH theory predicts the following recombination rate U_t (unit cm⁻³/s) for a single –level defect located at an energy E_t [79] :

$$U_t = \frac{v_{th}N_t(np-n_i^2)}{\frac{n+n_1}{\sigma_p} + \frac{p+p_1}{\sigma_n}} = \frac{np-n_i^2}{\tau_{p0}(n+n_1) + \tau_{n0}(p+p_1)}$$

with
$$n_1 \equiv n_i exp(\frac{E_t - E_i}{kT}), p_1 \equiv p_i exp(\frac{E_i - E_t}{kT})$$

$$n_1 p_1 = n_i^2$$

and

$$au_{p0}\equivrac{1}{\sigma_{p}v_{th}N_{t}}$$
 , $au_{n0}\equivrac{1}{\sigma_{n}v_{th}N_{t}}$

 $\sigma_{\rm n}$ and $\sigma_{\rm p}$ are the capture cross sections of electrons and holes, $v_{\rm th}$ is the thermal velocity of the electron or hole. The electron and hole concentrations are *n* and *p*, respectively. $N_{\rm t}$ is the volume density of deep levels and $E_{\rm t}$ is the energy level of the traps, $\tau_{\rm n0}$ and $\tau_{\rm p0}$ are the so-called capture time constant of electrons and holes. Typical values for the capture cross sections of bulk defects in silicon are in the range of $10^{-12} \sim 10^{-18} \text{ cm}^2$. The recombination rate is proportional to the thermal velocity and the defect concentration. The driving force for this recombination process is the term $np - n_i^2$, which describes the deviation of carrier concentration from the thermal equilibrium values.

The SRH recombination rate has been derived in most semiconductor textbooks (Grove and Fitzgerald, 1966; Sze, 1981) and is shown to be [80, 81]:

$$R_{SRH} = \frac{\sigma_p \sigma_n v_{th} N_t [pn - n_i^2]}{\sigma_n [n + n_i e \frac{E_t - E_i}{kT}] + \sigma_p [p + n_i e \frac{E_i - E_t}{kT}]}$$

For a doped semiconductor, one has either $n_0 >> p_0$ (*n*-type) or $p_0 >> n_0$ (*p*-type). First, taking the case of an *n*-type material, one can derive the recombination rate for holes at a single energy level, E_t , in the forbidden gap. This case is completely symmetrical to that of electron recombination in p-type material. In this expression, $n_0 =$ N_D and $p_0 \sim 0$. Therefore,

$$R_{SRH} = \frac{\sigma_p \sigma_n v_{th} N_t [\rho N_D + \rho^2]}{\sigma_n [N_D + \rho + n_i e \frac{E_t - E_i}{kT}] + \sigma_p [\rho + n_i e \frac{E_i - E_t}{kT}]}$$

where, ρ is injection level.

In 1988, Girisch et. al. [82] introduced an extended SRH formalism, which included the effects of band bending due to fixed insulator charges and charged interface states.

In Figure 3.3, an illustration of the dielectric-semiconductor system under nonequilibrium conditions is presented. Figure 3.3 shows that, as a result of positive fixed charge (Q_f), the energy bands bend down and a space charge region is formed.



Figure 3.3 Charge distribution and band diagram at the dielectric-semiconductor interface under non-equilibrium conditions. The non-equilibrium conditions are indicated by the separation of electron and hole quasi-Fermi levels ϕ_n and ϕ_p . Note that the surface potential ψ_s is positive when the energy bands bend down.

 $Q_{\rm Si}$ — charge density induced in the silicon

- $Q_{\rm it}$ interface state charge density
- $Q_{\rm f}$ density of dielectric-induced fixed charges
- ψ electrostatic potential
- $\psi_{\rm s}$ surface potential
- ϕ_n , ϕ_p quasi-Fermi potential of electrons and holes, respectively

For a continuum of noninteracting surface states, U_S is obtained by an integration over the band gap:

$$U_{S} = (n_{S} \cdot p_{S} - n_{i}^{2}) \cdot v_{th} \cdot \int_{E_{\nu}}^{E_{c}} \frac{D_{it}(E_{t})}{(n_{S} + n_{1})} + \frac{p_{S} + p_{1}}{\sigma_{n}(E_{t})} dE_{t}$$

with

$$n_1 = n_i \exp(\frac{E_i - E_i}{kT})$$
 and $p_1 = n_i \exp(\frac{E_i - E_i}{kT})$

where, n_s and p_s are the electron and hole concentration at the surface, n_i represents the intrinsic carrier concentration, E_i is the intrinsic Fermi level, E_c is the bottom of the conduction band, E_v is the top of the valence band, E_t is the interface trap energy level, k is the Boltzman constant, T is the absolute temperature, σ_n , σ_p are the capture cross sections for electrons and holes, respectively, D_{it} is the interface state density and v_{th} is the carrier thermal velocity.

Thus, the effective surface recombination velocity, S_{eff} , at the edge of the surface space charge region can be calculated:

$$S_{eff} = \frac{U_S}{\Delta n}$$

where, Δn is the injected carrier concentration.

A schematic of the complete numerical algorithm, proposed by Girisch, allowing for the calculation of surface velocity rates under the assumption of flat quasi-Fermi levels in the depletion region and for given values of $Q_{\rm f}$, Δn and V is shown in Figure 3.4 [82].

This formalism was later adopted by Aberle et. al.[83] who used this theory successfully to explain the measured injection level dependence of surface recombination velocity (S_{eff}) for the Si-SiO₂ interface.

Low S_{eff} of the PECVD SiO₂-passivated Si surfaces is attributed to the combination of moderately low density of interface states at midgap $(D_{it}=(1-10)\times10^{10}\text{ cm}^{-2}\text{eV}^{-1})$ and a high positive oxide fixed charge density $Q_{\text{ox}}=[(1-10)\times10^{11} \text{ cm}^{-2}]$ [84]. The presence of a positive charge leads to a downward band banding (Ψ_s) at the Si/SiO₂ interface. The large Ψ_s lowers surface hole concentration for recombination and consequently reduces the S_{eff} . Therefore, even for a moderately high D_{it} , it is possible to get low S_{eff} with higher Q_{ox} . Modeling results of the dependence of S_{eff} on Q_{ox} for different interface-state densities are shown in Figure 3.5 for an injection level of $(a)10^{14}\text{ cm}^{-3}$ and $(b)10^{16}\text{ cm}^{-3}$ respectively [84].



V

 $n_S = nd.exp(+q/kt. \psi_S)$

 $p_S = pd.exp(-q/kt. \psi_S)$

V

U_S,S_{eff}

diagram of a numerical algorithm for the calculation of surface recombination rates at the Si-insulator interface for given excess concentration at the edge of surface space region [82].





Figure 3.5 The calculated dependence of effective SRV (S_{eff}) on the fixed positive charge density (Q_{ox}) for different interface-state densities. The results are shown for two injection levels: (a) 10^{14} cm⁻³ and (b) 10^{16} cm⁻³ [84].

3.2 Modeling of Surface Recombination Velocity at SiN_x-Si Interface

It was discovered that the surface passivation of PECVD-deposited SiN_x films showed a pronounced injection-level dependence of the effective surface recombination velocity $(S_{eff} (\Delta n))$, which is similar to that for thermal oxides [83, 85, 86]. This property implies a similar recombination mechanism for the SiN_x -Si interface, although it is known that D_{it}

and Q_f at SiN_x-Si interface are approximately one order in magnitude higher than that for the Si-SiO₂ interface.

Similarly, the deposition of SiN_x layers on silicon substrates lead to the formation of a space charge region at the interface characterized by a fixed positive charge density (Q_f) of the order of 10^{12} cm⁻². In *p*-type Si, a depletion/inversion layer is formed, while in n-type Si, the positively charged insulator attracts majority carriers and repels minority carriers. Hence, an accumulation layer is formed.

3.2.1 Program for SRV Calculations

Based on the extended SRH formalism, a program is written to calculate the SRV at dielectric film-Si interface. A brief description of the algorithm and methodology of this program is as follows:

There are only two differences in the programs between the *n*-Si and *p*-Si:

1. The *p*-type uses the Na input parameter while the *n*-type uses the Nd input parameter;

2. The p and n types use slightly different equations to determine the bandbending (phi_s), recombination rate (Us), surface recombination velocity (Se) values.

It is the same exact numerical method for both types.

The method:

1. The programs asks for input parameters (see note below);

2. The programs have an outer and inner loop: the outer loop is controlled by the m value while the inner loop is controlled by the n value; together, these m, n parameters control the energy at which the phi_s, Us and Se will be calculated; the formula is delta_n

* 10 ^ m; m is in a range from m1 to m2 and is set by the input parameters; n is in a range from 1 to <10 and is determined by the fine tune parameter;

3. Once delta_n is determined, various other constants are calculated: nd, pd, phi_n and phi_p;

4. Then a list of values are calculated into the following 1-dimensional arrays: phi_s(i), E(i), ns(i), ps(i), where i goes from 0 to N, where N is 1 / step size (step size is an input parameter);

5. Then fa and fd are calculated into 2-dimmensional arrays fa(i, j) and fd(i, j); again i and j range from 0 to N where, N is 1 / step size (step size is a decimal therefore 1 / step size will be greater than 1);

6. Then the A and B parameters (both 1-dimmensional arrays) are found by performing a simple integration of fa and fd respectively; these A and B parameters are required only to simplify the mathematics used later;

7. Then the Qit(i), F(i), Qsi(i) and Qo(i) 1-dimmensional arrays are calculated from A and B and other values either inputted or calculated earlier;

8. At this point, the program has calculated an array of values for Qo(i) that cover various possible phi_s values; the program then reads through all Qo(i) values to find the smaller Qo(i) value; this Qo(i) value corresponds to the proper phi_s(i); this is a simple comparison test;

9. Now that the programs determined the phi_s that lead to the smallest Qo, it then ends by calculating Us and Se for that phi_s;

10. The program outputs two files: a text (txt) file readable by user and a prn (prn) file readable by mathcad (to plot graphs).

The programs have shortcut functions that are used to calculate:

nt(E), pt(E), LINT and Lx (LINT is an integral required to find Us, Lx is the function within the integral); the functions are just computational shortcuts and do not affect the idea behind the method.

In short, the method calculates an array of all possible Qo(i) values, and, by a simple value by value search, finds the smallest Qo(i), and the phi_s(i) that corresponds to that Qo(i), then from that, it calculates Us, Se (Seff)

Inputs:

for n and p type:

output file name: eight characters maximum, no extension

the program creates two files with a .txt and a .prn

extension

the .prn is comma delineated and can be read by Excel and

Mathcad

delta n 10^x range: enter x, y (with the comma)

where, x is the 10^x of the lowest delta_n and y is the 10^y

of the

	highest delta_n
Qf, Dit, vth:	enter x.xxxxeyy, x.xxxxeyy, x.xxxxeyy (with the commas)
	note the eyy is how the program understands scientific
notation	

where $eyy = 10^{yy}$

note the eyy is how the program understands scientific

where $eyy = 10^{yy}$

note! Na could be Nd if you 're using a different type, the

idea is the same

notation

step size, fine-tune: enter x.xxxx, x.xxxx (with the comas)

a typical stepsize is 0.001, but it can be made smaller for

more

accuracy.

a typcial fine tune is 1, .1, .2, .25, .5 etc.

the program will calculate different delta_n's by using the

fine-tune

example: if it's at 1x10^7 and the fine-tune is .1 then 1.00x10^7 1.10x10^7 1.20x10^7 etc

.

3.2.2 Modeling Results and Discussion

As can be seen from the extended SRH surface recombination model, the effective SRV depends in a complex manner on the energy dependent interface state density $D_{\rm H}(E)$, the capture cross sections for electrons $\sigma_{\rm H}(E)$ and holes $\sigma_{\rm P}(E)$, the dielectric-induced charge density $Q_{\rm f}$, the substrate doping concentration $N_{\rm dop}$, and the bulk injection level Δn .

3.2.2.1 S_{eff} dependence on $D_{\text{it.}}$ Low S_{eff} of the PECVD SiN_x:H-passivated Si surface is attributed to the combining of moderately low density of interface states, and a high positive charge density. Both parameters are given in Table 2.1 for as-deposited and thermally treated silicon nitride films [68].

According to the SRH formalism, S_{eff} will decrease by reducing the interface state density D_{it} . In Figure 3.6, the dependence of S_{eff} on D_{it} is shown for 1 Ω -cm *p*-Si wafer.



Figure 3.6 Calculated effective surface recombination velocity S_{eff} for *p*-Si surface as a function of the injection level Δn in the quasi-neutral bulk for different values of interface state density D_{it} . Input parameters: Doping concentration = 1×10^{16} cm⁻³; $\sigma_n = 1 \times 10^{-14}$ cm², $\sigma_p = 1 \times 10^{-16}$ cm²; $Q_f = 1.3 \times 10^{11}$ cm⁻².

Experimental results are consistent with this prediction. As can be seen from Figure 3.7, SiN_x :H films prepared by remote plasma or direct PECVD at high frequency (HF) provide much better surface passivation than nitride layers prepared at low frequency (LF). This is achieved by avoiding heavy ion bombardment during the deposition process, and consequently much lower D_{it} [56].



Figure 3.7 Measured $S_{\text{eff}}(\Delta n)$ dependence at the SiN_x-passivated surfaces of three 1.5 Ω cm FZ *p*-Si wafers. The SiN_x films were fabricated by three different PECVD methods: low-frequency(100 kHz) direct PECVD, high-frequency (13.56 MHz) direct PECVD, and remote PECVD [56].

3.2.2.2 S_{eff} dependence on resistivity. Figure 3.8 shows the calculated S_{eff} as a function of the injection level Δn in the quasi neutral bulk for different wafer resistivities (1, 2, 3 and 5 Ω -cm) and *p*- and *n*-type silicon, respectively.

For model calculations, a typical set of parameters for the dielectric-Si interface has been used. An interface state density, D_{it} of 5×10^{10} cm⁻² eV⁻¹, a positive fixed charge Q_{f} of 1×10^{11} m⁻² and capture cross-sections for electrons and holes of 10^{-14} and 10^{-16} cm², respectively, were taken from measurements reported in the literature [83]. Furthermore, an assumption was made that the interface states were uniformly distributed across the bandgap and that all states below midgap were donor-like states whereas all states above
midgap were acceptor-like states. It was also assumed that the capture cross-sections were energy independent.



Figure 3.8 Calculated dependence of S_{eff} for *n*-Si and *p*-Si surfaces as a function of injection level (Δn) for different wafer resistivities. $D_{\text{it}}=5\times10^{10} \text{ cm}^{-2} \text{ eV}^{-1}$, $Q_{\text{f}}=1\times10^{11} \text{ cm}^{-2}$.

From Figure 3.8, the following observations can be drawn: i) The beneficial effect on S_{eff} due to band bending, or field effect passivation depends strongly on the resistivity (doping concentration) of the Si wafers. If other parameters remain the same, the higher the resistivity (the lower doping concentration) of the Si wafers, the smaller the corresponding SRV. 2) A clear difference in S_{eff} between *p*- and *n*-type silicon under lowlevel injection conditions can be seen whereas, at high-level injection conditions, the curves converge to a single value. In low level injection, the recombination process is dominated by the capture rate of minority carriers.

3.2.2.3 S_{eff} dependence on Q_{f} . The modeling results of surface recombination velocity, S_{eff} , as a function of the excess carrier density, Δn , are shown in Figure 3.9 (a) for *n*-Si and Figure 3.9 (b) for *p*-Si for different fixed positive charge densities and interface state densities. In *n*-Si, the positively charged insulator attracts majority carriers and repels minority carriers, producing an accumulation layer. In *p*-Si, a depletion/inversion layer is formed. If other input parameters remain the same, the higher the Q_{f} , the lower the corresponding S_{eff} (S_{S} in Figure 3.9). For example, a variation of Q_{f} from 1×10^{12} to 2×10^{12} cm⁻² results in a decreasing S_{eff} by about a factor of 7.



(a)



Figure 3.9 Calculated dependence of surface recombination velocity (S_S) for (a) *n*-Si and (b) *p*-Si surfaces as a function of injection level (Δn) for different fixed positive charge densities and interface state densities, $\sigma_n = 10^{-14}$ cm⁻² and $\sigma_p = 10^{-16}$ cm⁻².

Figure 3.9 shows that: (i) the SRV for *n*-Si is lower than that for *p*-Si, which is expected because the existence of Q_f causes the minority carriers in *n*-Si to be repelled from the surface; (ii) in *p*-Si, a depletion/inversion layer is formed; and (iii) S_{eff} decreases with the injection level, and the low values of S_{eff} can occur at injection levels that are produced in a solar cell under 1-sun illumination. An increase in S_{eff} beyond an injection level of 10^{16} cm⁻³ occurs because, at these high-injection levels, band bending begins to disappear.

Some reported experimental measurements of SRV, in the literature, show that the dependence of SRV on the injection level deviates from those shown in Figure 3.9a and b [87, 88]. Figure 3.10 shows experimental data reported by Dauwe et. al. [89]. It is seen that, initially S_S decreases with an increase in the injection level and then increases at $\Delta n > 1 \times 10^{16}$ cm⁻³.



Figure 3.10 Measured effective SRV showing dependence on excess carrier density [89].

According to this model calculation, very high $Q_f (1 \sim 3 \times 10^{12} \text{ cm}^{-2})$ will lead to no injection level dependence of the effective surface recombination velocity for *p*-type Si wafer, which is in contradiction to experimental results as shown in Figure 3.10 [89]. This discrepancy is assumed to be caused by carrier generation and recombination in the depletion region [87]. It is implied that a complete model of surface recombination at SiN_x-Si interface should also consider other recombination mechanisms.

3.2.3 A Modified Model including Recombination in Damaged Region

As mentioned above, the existing SRH formalism fails to obtain a reasonable agreement between experiment and theory in terms of injection level dependence. It is due to the more complicated properties of SiN_x :H-Si interface compared to SiO_2 -Si interface. In order to solve this problem, a "deeper" insight of SiN_x :H-Si interface is needed.

It has been found that, during the nitridation procedure, a damaged layer is formed [90 - 92], which is not only critical for H storage and subsequent bulk passivation after firing, but also is crucial for surface passivation. Figure 3.11 is an XTEM image which shows the existence of the surface damage between PECVD SiN_x :H layer and Si wafer.



Figure 3.11 High-resolution cross-sectional TEM of Si-SiN_x:H interface before firing showing process-induced damage by plasma [92].

A large distribution of traps or recombination centers results in a large carrier density across the damaged layer. This suggests that a complete surface recombination model should go beyond the current SRH formalism to a deeper extent.

The recombination is evoked in the damaged region that is formed by processinduced defects in the vicinity of the surface. Hence, there is an increased minoritycarrier recombination within the damaged layer, which occurs within the SCR. Based on this, one must include recombination in the SCR. A similar conclusion was arrived at by Schmidt [93], but his reasoning did not include the surface damage. However, one can follow his approach to calculate the effect of increased recombination near the damaged surface. Once SCR exists beneath the surface of the wafer, its detailed characteristics are uniquely determined by the shape of the potential barrier. A full derivation of approximate solutions to the recombination velocity in SCR can be found in the literature [94, 95]. The surface potential distribution across the space charge region is given by:

$$\psi(z) = \psi_s \cdot e^{-z/L}$$

where, z is the vertical distance from the surface, and Ψ_s is the surface potential at the surface or at one end of SCR (z = 0), which can be found by an iterative approach of Shockley-Read-Hall (SRH) formalism. L is the extrinsic Debye length and is defined as:

$$L \equiv \sqrt{\frac{k\varepsilon_0\varepsilon_b KT}{q^2(n_b + p_b)}}$$

where, n_b , p_b denote carrier density of electrons and holes in the bulk, respectively, and e_b is the dielectric constant of the semiconductor.

In the SCR, the carrier densities are functions of the position z:

$$n(z) = n_b e^{\beta \psi}, \ p(z) = p_b e^{-\beta \psi}$$

The definition and parameterization of recombination rate in the SCR, $U_{SCR}(z)$ parameterization can be found in the literature [96]. The recombination velocity in the SCR is calculated by:

$$S_{SCR} = \frac{1}{\Delta n} \int^{L} U_{SCR}(z) dz$$

Hence, the effective SRV is given by:

$$S_{eff} = S_S + S_{SCR}$$

A modified SRV model calculation is proposed based on current SRH formalism and recombination in SCR.

Figure 3.12 shows the calculated results for S_{eff} as a function of injection level. S_{eff1} (when there is a damaged layer) has a more pronounced injection-level dependence compared to S_{eff2} (when there is no damage layer). S_{SCR1} and S_{SCR2} denote the intrinsic recombination in the SCR, with or without the damaged layer, respectively. S_S is the recombination at the surface. Figure 3.12 also demonstrates this at low injection levels;



Figure 3.12 Calculated recombination velocity components S_s and S_{SCR} (dotted lines), and the total S_{eff} (solid lines) at SiN_x :H/Si interface as a function of injection level. Assumptions: *p*-Si, 1.5 Ω -cm, $Q_f = 2 \times 10^{12}$ cm⁻², $D_{it1} = 1 \times 10^{12}$ eV⁻¹ cm⁻², $D_{it2} = 1 \times 10^{11}$ eV⁻¹ cm⁻².

recombination in the SCR influences the magnitude of S_{eff} , whereas, at high injection levels, S_{eff} is mostly determined by the recombination at the surface.

After plasma deposition, there is damage beneath the Si surface up to about 20 nm deep [97, 98], which agrees well with the calculated L. Note that the major amount of surface damage can be healed by the RTA process so that the width of the SCR will subsequently be reduced. Therefore, a reduction of minority-carrier recombination in the SCR is expected after the firing step for metallization of Si solar cells.

3.3 H Transportation Mediated by SiN_x:H Layer

Based on the damaged layer and trapping/detrapping theory, a semi-quantitative hydrogen transportation model is proposed which can be simply described in the following steps:

(i) A large amount of the hydrogen atoms are trapped and "stored" in processinduced traps (PITs) across the damaged region produced by the plasma process during the nitride deposition.

(ii) In a rapid thermal annealing (RTA) step, H is released from the surface and redistributed into the bulk region. Also, because the concentration of H in the damaged region is higher than that in the SiN_x :H layer, some of the H may migrate into the nitride layer.

(iii) H evolution from SiN_x :H layer thus occurs both ways: into the air and into Si. The diffusion process of H into the bulk region and the out-diffusion into the ambient occur simultaneously. As the H diffuses deeper into Si, it saturates the traps and other defects, requiring less H for passivation. At the same time, the damage at the surface is being healed. Eventually, all the traps in the bulk of the Si are filled with H, the surface damage is healed and the H transport mediated by SiN_x :H reaches a steady state. Outflow of H across the SiN_x :H/Si interface stops accordingly [97].



An illustration of hydrogen transport is shown in Figure 3.13.

Figure 3.13 A schematic illustration of H transport from SiN_x :H layer to bulk Si (the black dots represent H atoms, and the brown dots represent defects/impurities in the bulk Si).

Figure 3.13 shows that: 1) after the firing, the majority of the surface damage is healed; 2) Simultaneously, H migrates into bulk Si and interacts with defects and impurities.

A verification of H "storage" during nitridation and its subsequent diffusion is seen in Figure 3.14 [98]. This figure is a secondary ion mass spectrometry (SIMS) plot of H in a Si solar cell before and after annealing. Figure 3.14 clearly shows that the H is temporarily stored at the surface, and is then redistributed (limited by the detection sensitivity of H in the SIMS measurement) after annealing.



Figure 3.14 The SIMS profiles of H in a solar cell introduced during a PECVD SiN coating before (red line) and after annealing (black line) [98].

The redistribution of H deep inside the cell can lead to excellent passivation and high device performance. Figure 3.15 shows the difference in the poly-Si solar cell performance with and without a PECVD SiN coating [99]. This exemplifies a significant increase in efficiency. A good hydrogenation process can improve the cell efficiency ranging from about 12% to about 16%. Currently, H passivation is extensively applied in mc-Si solar cell manufacturing.



Figure 3.15 Effect of PECVD on the internal quantum efficiency of the cell [99].

CHAPTER 4

MINORITY-CARRIER LIFETIME MEASUREMENTS

4.1 Quasi-Steady-State Photoconductance Decay

One of the fundamental physical properties of a silicon solar cell is the minority-carrier lifetime. In practice, measurements on wafers yield an effective lifetime which can then be interpreted as a combination of bulk and surface recombination components. In order to do this correctly, the measurements of the effective lifetime must have a strong physical basis. Currently, there are three methods being deployed by the PV-Si industry for lifetime measurements: quasi-steady state photoconductance decay (QSSPCD), photoluminescence mapping and microwave reflection. In this thesis, QSSPCD was used to measure the minority-carrier lifetime of PV-Si.

For long-lifetime wafers, the transient method (measurement after the light is extinguished) is preferred since it does not require knowledge of the photogeneration in the sample (reflection and absorption of photons in the sample) or the excitation wavelength. The QSS method has been found to be useful for lower-lifetime materials that are often used in the production of PV cells. The QSSPCD technique has been developed by Sinton [100]. This award-winning technique uses inductive coupling between a small coil that is placed under the sample platform and the sample under test. The frequency used is 10 MHz, and the light source is a very long duration (several milliseconds) flash lamp. The setup involves a zeroing procedure that accounts for the dark conductivity of the sample. The user also inputs the estimated carrier concentration.

The sensor coil detects the photoconductivity produced by the flash lamp, and the interfaced computer processes the data. A highly calibrated on-board silicon cell, that is

interfaced with the measurement apparatus, monitors the instantaneous flash intensity. The quasi-steady state lifetime is monitored as function of the instantaneous photon density. The QSSPCD method uses the classic expression for steady state photoconductivity:

$$\Delta \mathbf{n} = G_L \tau_{eff}$$

where, Δn is the phtogenerated electron/hole density, $G_{\rm L}$ is the optical generation function, and $\tau_{\rm eff}$ is the effective carrier lifetime. The physical quantity, which is measured by the inductive sensor system, is the photoconductivity, $\sigma_{\rm L}$:

$$\Delta \sigma_L = q \Delta n (\mu_n + \mu_p) W$$

Where μ_n , μ_p are the electron and hole mobilities respectively, Δn is the excess electron/hole density and W is the sample volume. The associated computer program calculates the carrier mobilities, based on the doping density, and excess carrier density. The reference cell measures the instantaneous generation rate, G, and therefore, the average lifetime is computed and displayed. This technique works at any injection level, and the display shows lifetime versus injection level as the intensity of the flash decays from the maximum value to zero. Figure 4.1 is a snap shot of a QSSPCD apparatus and user interface at NREL.



Figure 4.1 A photograph of QSSPCD apparatus at NREL.

4.2 Wafer Preparation and Passivation Procedure for Producible Minority Carrier Lifetime Measurements

4.2.1 Objective

Measurement of the bulk minority carrier lifetime (τ_b) by QSSPCD is strongly influenced by surface recombination. A number of techniques are known to lower the effective surface recombination velocity. These include use of oxidation, floating N/P junction, SiN_x:H layer, HF immersion, and use of iodine in ethanol or methanol (I-E or I-M solution) [101-107]. Use of I-E (or I-M) solution appears to be very simple and this technique does not require any high temperature treatment such as oxidation, diffusion, or nitridation processes that can change τ_b [101].Yet, this is not a preferred procedure within the photovoltaic community because it is a common experience that it is difficult to obtain same τ_b -values reproducibly, particularly when the silicon wafer lifetime is long. The objective for studying lifetime measurements using I-E passivation is two-fold:

- (i) to apply it to compare lifetimes of wafers (having different τ_b) by various techniques such as QSSPCD and transient PCD using short laser pulses of different light intensity;
- (ii) to make minority-carrier diffusion length (L) measurements by surface photovoltage (SPV) technique, and to use τ_b and L data to determine diffusivity (D) values for various impurity and defect concentrations, using the relationship

 $L = \sqrt{D\tau_b}$ [103,106,107]

There are various reasons which can make lifetime measurements irreproducible using I-E solution passivation, such as the influence of the strength of iodine in ethanol solution, wafer cleaning procedures, influence of wafer container during lifetime measurements, and stability of the I-E solution. Although some of these studies were also performed by other researchers, they only examined individual parameters [102]. The objective of this study was to examine interdependencies between these parameters.

4.2.2 Influence of Wafer Cleaning

The initial cleaning procedure ("ICP") in this study was similar to those used by others, and consisted of the following: removal of organics by solvent clean followed by DI water rinse, piranha (H₂SO₄:H₂O₂ 2:1) clean at 80°C, dilute HF rinse, DI water rinse and nitrogen drying.

Following this cleaning by "ICP", the sample was placed in a petri dish or polyethylene bag. It was found that zip-lock bags provided an excellent way to passivate the samples. A variety of bags of different quality and thicknesses were utilized in this work. The most convenient is 1 mil polyethylene bag. A well cleaned sample is placed in a polyethylene bag and covered on both sides with I-E solution (typically the molarity of 0.1). Excess solution from each surface is squeezed out to leave a thin uniform layer of the solution on the surface. In the measurements performed in this study, the molarity of the solution (within a range of 0.01 and 0.1) did not influence the measurements. Figure 4.2 shows a typical measured lifetime using QSSPCD technique with Sinton apparatus, as a function of time (curve A). The wafer was a semiconductor grade, p-type Si, with a resistivity of 12.8 Ω -cm.



Figure 4.2 τ_b of a *p*-type Si wafer measured by QSSPCD as a function of time. The sample was cleaned by "ICP" and passivated in IE solution. (A) after ICP; (B) dilute HF dip after (A); (C) dilute HF dip after (B); (D) after oxide removal [108].

The lifetime values correspond to injection level of 10¹⁶ cm⁻³. The wafer was prepared using the above described ICP and the measurements were made every 5 minutes. Following these measurements, the sample was dipped in dilute HF and dried, and measured (curve B). The curve C was obtained after dipping the sample once again following measurement B.

These and similar other results indicated that the sample surface was progressively loosing cleanliness resulting in longer time to reach final lifetime. This indicated that the surface was not properly cleaned and that near-surface region influences the passivation characteristics of I-E/Si interface [104].



Figure 4.3 Time dependence of τ_b after including oxidation in the cleaning procedure, for sequential cleaning steps [108].

Figure 4.2 also indicates that the presence of a very thin passivation layer near the surface can have a strong influence on the passivation. In order to confirm this, the wafers were cleaned and a thin layer of native oxide was permitted to grow on the silicon wafer surface. The oxide was then etched off. Curve D, in Figure 4.2, shows the time dependence of the minority carrier lifetime, using I-E passivation. This curve shows that the lifetime maximum was reached much faster and the maximum is higher than previous values. It is clear that it is necessary to remove the native oxide surface (in this case by oxidation and dilute HF dip). In order to determine the depth of the native oxide surface, oxidation was performed in steps.

Figure 4.3 shows the time dependence of the lifetime measurements for first three steps. The sample was cleaned and oxidized after each set of measurements. Further oxidation only increased the slope of the curves while the τ_{max} remained the same.

4.2.3 Influence of Illumination

It was also observed that, if the measurements were performed at shorter intervals, the slope of the curves increased. This is an interesting phenomenon indicating that the I-E surface passivation has a light-activated component. To evaluate this effect, a wafer was cleaned (using the new oxidation procedure), placed in an I-E bag, and exposed to about 0.5 sun intensity from a solar simulator for 15 minutes.

It was found that the lifetime after exposure to light yielded τ_{max} immediately after the exposure; furthermore, there was a slow decrease (as shown in Figure 4.4) in τ . This decrease occurs for all wafers after the measured lifetime reaches a maximum. Figure 4.5 shows a short-term variation of τ_b for a long lifetime wafer.



Figure 4.4 τ_b decay after light exposure (no rise time was observed) [108].



Figure 4.5 Short-term variation of τ_b for a long lifetime wafer. The wafer was cleaned with the new procedure [108].

It was tempting to assume that light-induced passivation occurred from dissociation of I-E solution (presumably to ionize I), which might be induced by UV light. When the wafer in I-E bag was exposed to UV light, the lifetime did not reach τ_{max} . The exposure of the wafer in I-E bag caused it to heat. Again, heating did not produce any change in the lifetime. Figure 4.6 elucidates the influence of various treatments on time dependence of the lifetime measured immediately after the treatment.





4.2.4 Discussion

The experiments seem to indicate that wafer preparation for a good passivation requires two essential steps:

1. Wafer cleaning, which includes removal of about 200-300 Å of Si from each surface. A procedure was outlined to yield a very clean surface. The use of fresh chemicals (piranha, HF, and other acids) for each batch of wafers minimizes surface quality variations. These chemicals have propensity to acquire impurities from ambient and, in some cases, leach them from the containers if very high quality containers are not used. The use of optical oxidation following piranha clean is recommended. Although piranha process also produces a thin layer of a suboxide, it requires multiple steps of piranha clean to remove the desired thickness. Kimerling et. al. [102] observed improvement in measured τ_b following multiple cleaning. However, they did not attribute this to surface removal. It should be noted that similar cleaning is also demanded for obtaining high quality oxide or nitride passivation. In this regard, wafer preparation for I-E passivation is similar.

2. Activation of surface passivation seems to require establishment of a steady state between I-E solution and Si surface. One can expect two mechanisms to participate in this process:

(a) Formation of a steady state at the I-E and Si interface in which I-ions produce a surface field. This field is influenced by the parameters (such as resistivity and lifetime) of the Si wafers. It is expected that a surface layer of the order of a Debye length plays an important role. Because a wafer typically has contamination at the surface layer, which may extend to 200-300 Å, it is necessary to remove this layer to create a high quality passivation. This mechanism can also explain sensitivity of passivation to light and perhaps dependence on resistivity and lifetime. Unfortunately, experimental data on a variety of wafers are not consistent. For example, wafers from a lot (with similar resistivities and lifetime) do not have same dependence of lifetime on the light exposure. However, it was consistently seen that lower lifetime wafers had less dependence on the light exposure (i.e. they stabilize faster). Further investigations are being done to understand the observed time dependence of the measured lifetime.

Based on these results, a simple model for wafer preparation was proposed as shown in Figure 4.7.



Figure 4.7 A wafer with a shallow (200-300 Å) contaminated surface layer (a), after cleaning (b) and surface passivation (c) [108].

CHAPTER 5

EFFICIENCY LIMITATIONS CAUSED BY DEFECT CLUSTERS

5.1 Background

One of the approaches to reduce the cost of commercial Si solar cells is to use lower-cost, multicrystalline Si (mc-Si) substrates instead of single-crystal wafers. This approach has gained increasing acceptance by the photovoltaic (PV) industry and, as a result, the use of mc-Si has grown steadily to about 60% of the total Si-based solar cell production. The success of mc-Si as a cost-effective solar cell material is due primarily to the fact that advanced processing techniques, such as impurity gettering and hydrogen passivation, which are used in current solar cell fabrication, have worked very well in enhancing cell performance. These processing methods have led to efficiency of mc-Si solar cells exceeding 14%, which is slightly below that of commercial crystalline Si (c-Si) solar cells. However, further improvement in cell efficiency has proven difficult to achieve. Recent research has found that, in spite of using extensive gettering and passivation, mc-Si solar cells exhibit regions of low photoresponse and concomitant poor material quality. These local, low-response regions have a crystal structure that is not amenable to gettering, and constitute a new performance-limiting mechanism. By analysis of the structure of these regions, a new type of defect configuration was found, now called a defect cluster [109].

5.2 Objective

An electronic model is utilized to understand the nature of defect clusters, their formation mechanism, their effects on solar cell performance and to assess the limitation on cell performance posed by defect clusters. New gettering/passivation techniques to achieve further improvements in cell efficiency and effectively getter defect clusters are evaluated.

5.3 Characterization of Defect Clusters

Multicrystalline Si used for commercial solar cells is grown either as ribbons or cast in a crucible and then sliced into wafers by wire sawing. The PV industry has accepted two basic measures to lower the cost of mc-Si substrates. The first is to utilize substrates with high impurity content, which result from the use of cheaper, lower-grade feedstock (consisting of tops and tails, off-spec rejects from the microelectronic industry). The PV industry has compromised cleanliness of the growth process. Typically, the as-grown material has high concentrations of C and/or O. It also contains transition metal impurities (such as Fe, Cr) in levels reaching 10^{14} cm⁻³, which are detrimental to the minority-carrier lifetime. Typically, the average minority-carrier lifetime of as-grown material is < 10 µs. The second measure involves the use of much higher crystal growth speeds as compared to conventional crystal growth, resulting in higher thermal stresses accompanied by high densities of defects in as-grown form. Typically, the as-grown material has an average defect density of about 5×10^5 cm⁻². A unique feature of current mc-Si wafers is that they contain "defect clusters"— crystal defects that clump together forming extended defect regions, which remain separated from each other.

Clustering of defects can be seen from the defect map of a commercial 4.25-in x 4.25-in mc-Si wafer as shown in Figure 5.1. This map was generated by a commercial instrument called GT-PVSCAN, and shows that the majority of the wafer has a low (and much of it nearly zero) dislocation density [110]. The average value of the dislocation density is about 4 x 10^5 cm⁻². However, the presence of defect clusters can be seen as dark regions in this otherwise very low defect density material. These regions can have defect density as high as 10^7 cm⁻². An inset in the figure shows a magnified region of a large defect cluster (identified in the defect map by arrows). A detailed structure of a defect cluster can be seen after etching the wafer [111].



Figure 5.1 A defect map of a commercial mc-Si wafer showing clustering of defects as dark regions. The inset shows a magnified region indicated by arrows [112].

Figure 5.2 is a photograph of a defect-etched, cast mc-Si wafer showing dislocation pile-up in a defect cluster, which extends over several grains [112]. Similar clustering is seen in ribbon material. Typically, the fractional area of the wafer covered by defect clusters is about 5% -10% for a high-quality material; lower-quality material may have a higher-percentage area covered by defect clusters.



Figure 5.2 A defect cluster region showing etch pits produced by defect etching [112].



Figure 5.3 An XTEM image of a defect cluster showing metallic precipitation [112].

Defect clustering occurs during crystal growth when local thermal stress exceeds yield stress of some preferred grain orientations causing the stress relief through local generation of defect networks. Defect clusters also serve as internal gettering sites for metallic impurities, and often result in impurity precipitation at these sites. Figure 5.3 is a cross-sectional TEM image of such precipitates in a defect cluster region; other researchers have also observed similar precipitates [113].

Precipitation of impurities at defect clusters is of particular concern, because it is now known that precipitated impurities are difficult to getter by the techniques used in the PV industry (viz, P diffusion for junction formation and Al alloying for back-contact formation). Hence, defect clusters have an important bearing on the development of new impurity-gettering methods which must dissolve the precipitates during a gettering process.

5.4 Influence of Defect Clusters on Solar Cell Performance

Defect clusters constitute regions of high carrier recombination resulting in low photocurrent generation, which can be easily observed by performing light beam induced current (LBIC) mapping. However, their dominant effect occurs through a voltage-degradation mechanism. Defect cluster regions develop a lower voltage compared to defect-free regions during the cell operation. Because the entire cell is connected through a common junction, the defect cluster regions exert a shunting influence on the entire cell. Unfortunately, the shunting behavior of the defect clusters cannot be evaluated through experimental measurements alone. It requires a combination of theoretical modeling to include the distributed nature of the cell and experimental measurements pertaining to local characteristics of the cell. The next section briefly describes the use of a network model to evaluate the efficiency loss due to defect clusters. This model was developed previously to describe a non-uniform solar cell. The detailed discussion of original model can be found in the literature [114].

5.4.1 Theory

A conventional approach in defect modeling for calculating the influence of defects on the material quality is to estimate the "average" carrier recombination and express it in terms of an average minority-carrier lifetime or diffusion length. However, such a procedure will not work for device modeling, because a solar cell is a distributed device in which each region "communicates with" all other regions and the entire device "is sensitive to" the presence of each defect cluster. Hence it is necessary to calculate the characteristics of each local device using its local properties, and then calculate the influence of each local device on the entire device. This approach permits the calculation of the influence of any defect distribution on the total device performance, and can be applied to calculate the performance of the device without any defects, to determine losses introduced by various defect distributions. This formalism can be easily incorporated into the Network Model developed for an inhomogeneous solar cell [114]. The network model builds a large-area solar cell from an array (40x40) of small-area, local cells that are interconnected through a common junction and a bus. Each small-area cell is assigned a defect density corresponding to that in the actual wafer for the corresponding location. Figure 5.4(a) illustrates this model.

In the present analysis, a defect cluster is considered as a localized, large defect that propagates through the entire cell (crossing both the base and the emitter regions of the cell), as illustrated in figure 5.4(b). Because of very high recombination and large size, one can ignore internal carrier transport and band bending associated with each defect cluster. The defect region acts as a "poor" device in the spatial distribution of the total cell.

The modeling requires two steps. First, each device is represented in terms of the recombination properties associated with its defect density, which yields values of photogenerated current density (J_{ph}), a minority-carrier lifetime (τ), and dark saturation-current components J_{01} and J_{02} , corresponding to the bulk and the junction recombination, respectively. Next, the diode array is interconnected using resistive components corresponding to the sheet resistance of the junction and the metallization pattern. The network is solved to yield the terminal characteristics of the device, as well as distribution of local currents and voltages for any given terminal voltage. In this model for defect clusters, there are basically two kinds of diodes-a defect-free diode and a diode with defects.



Figure 5.4 (a) A schematic of a defect cluster, and (b) a network model of a solar cell showing voltage and current sources corresponding to dark (indicated by subscript d) and illuminated (indicated by subscript L) conditions, and the resistive components due to the sheet rho of the junction [112].

The characteristics of each cell can be expressed in terms of the J_{ph} and two exponential components of the dark current in a standard form as:

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$$J_{dark}(V) = J_{01i} \exp\{(-eV/kT) - 1\} + J_{02i}\{\exp(-eV/2kT) - 1\}$$

The saturation currents J_{01} and J_{02} can be written in standard forms for a P/N junction. The total current, J, is given by:

 $J = J_{phi} - J_{darki}(V)$

where J_{phi} and J_{darki} (V) are the photogenerated and the dark-current densities, respectively, and i corresponds to either a defect-free cell element or a cell element with defects [115, 116]. The values of J_{phi} , J_{01i} , and J_{02i} can be estimated from experimental measurements. For example, we select one cell and make an estimate of J_{ph} values for defect-free cells and cells with defects based on LBIC (long wavelength) responses and cell *I-V* plots. However, J_{01} and J_{02} cannot be determined from the cell itself. A library of J_{01} and J_{02} values for a variety of materials and for different defect densities is available. It uses a diode array technique that has been described in the literature [117]. Edgepassivated, mesa diode arrays are fabricated on wafers and their electrical characteristics are probed. The device characteristics and their defect data are compiled and used as input in the model. The output of the model generates terminal I-V characteristics of the total cell and spatial distribution of cell voltages and currents for any terminal voltage. These sets of data result in excellent agreement between calculated and actual terminal characteristics of the large-area cell (as seen in next section). It should be pointed out that the network model assumes no internal carrier transport-the communication between the devices occurs via a highly conducting emitter region and the bus bar.

5.4.2 Experimental Approach

The major objective of the experimental work is to fabricate solar cells on wafers of known distribution of defect clusters and compare the cell characteristics with theoretical

modeling. Wafers were selected from different regions of a mc-Si casting and separated into two "sister" groups of adjacent wafers. Wafers from one group were defect-mapped using a commercial machine, GT-PVSCAN 5000, to determine distributions of defect clusters, and C and O measurements were performed [110]. These distributions were simplified in order to convert this information into easily useable distributions of the defect clusters for the Network model. As an example, Figure 5.5(a) shows a sketch of defect clusters obtained from the defect maps for a wafer. These distributions were also compared with the LBIC maps after fabricating cells on sister wafers.

Figure 5.5(b) shows the long-wavelength LBIC response of the cell fabricated on the sister wafer of Figure 5.5(a). A pattern similar to the defect pattern of Figure 5.5(a) can be seen in the LBIC map. The LBIC map also shows ratio of J_{ph} in defect cluster and defect-free regions.

A comparison of maps in Figures 5(a) and (b) shows important distinctions. First, it is clear that the LBIC map (compared to defect map) exhibits additional defects in the bulk of the cell. However, these additional defects have densities below the cut-off for a defect cluster. The second feature is that the defect clusters in the LBIC map appear to be "thinned" compared to the defect map. These are the results of a lower resolution for the PVSCAN in a defect-mapping mode as compared to the LBIC mode. The third feature seen in the LBIC map is square patterns of low photoresponse; these correspond to Ag pads on the back of the cell that are used for making solder contacts to the backside of the cell. These pads appear in the LBIC image because (a) the cell has a long minority-carrier diffusion length, and (b) the back Ag-Si contact has a higher recombination compared to rest of the back contact. The defect-clustered regions were TEM analyzed to determine the nature of the precipitations. The precipitates contain a multitude of impurities such as Fe, Cr, C, and O. All solar cells were characterized for their *I-V* characteristics and LBIC maps. The LBIC map identifies J_{ph} values in defect and defect-free regions.



(a)



Figure 5.5 A comparison of (a) defect-cluster distribution in a wafer and (b) longwavelength LBIC image of the solar cell on a sister wafer.

5.4.3 Results

The typical experimental results of material and cell parameters are summarized in Table 5.1 for six cells and their corresponding sister wafers. Column 4 in Table 5.1 shows cell parameters, open-circuit voltage (V_{oc}), short-circuit current (J_{sc}) and external fill factor (FF) of solar cells fabricated using commercial processing. The calculated cell parameters of these cells are shown in column 5. These calculations were performed using actual defect distributions and the following values of the network parameters:

$$J_{ph}(undefected) = 34.00 \text{ mA cm}^{-2}, J_{ph}(defected) = 23.8 \text{ mA cm}^{-2}$$
$$J_{01}(undefected) = 3.6 \times 10^{-9} \text{ A cm}^{-2}, J_{01}(defected) = 3.6 \times 10^{-8} \text{ A cm}^{-2}$$
$$J_{02}(undefected) = 4.5 \times 10^{-13} \text{ A cm}^{-2}, J_{01}(defected) = 4.5 \times 10^{-11} \text{ A cm}^{-2}$$

Cell #	$ \begin{array}{c} <\!\!\mathrm{Nd} \\ (\mathrm{x} \ 10^{\ 6} \\ \mathrm{cm}^{\ 2}) \end{array} $	<lbic> 0.63/0.98 بالس</lbic>	Measured (V _{oc} , J _{sc} , FF, Eff.) (mV, mA cm ⁻² . %)	Calculated (V _{oc} , J _{sc} , internal FF, Eff.).(A _d) (mV, mA cnr ² , %)
107	0.75	21.04/17.4 3	604.7, 30.3, 70.05, 12.8	601,30.517,78.72, 14.437 , (0.07)
108	1.277	20.86/18.4 2	604.7. 30.13, 69.07. 12.6	606,30.65,78,23, 14.528 , (0.07)
102	1.02	22.72/23.1 6	590.5, 27.8, 73, 12.0	598, 30.505, 79.04, 14.418, (0.1)
103	0.98	22.73/23.0 7	585.4, 27.4, 70.17, 11.2	598,30.505,79.04, 14.418 , (0.1)
112	0.638	21.85/16.3	581.2, 23.85, 72.8, 10.1	580,29.87,78.33, 13.570 , (0.15)
113	0.725	23.45/17.8 5	580.6, 27.8, 69.7, 11.2	581,29.87,78.56, 13.633, (A0.15)
No defect clusters			633, 31.3, 82.5, 16.3 A realistic external FF (of 0.75) for a defect-free cell with otherwise the same material quality will have efficiency of 15%.	

Table 5.1 A Summary of Measured and Calculated Results for Two Typical Solar Cells

 of Three Groups

It is seen that the calculated values of V_{oc} and J_{sc} are in close agreement with the measured values. However, it should be pointed out that the calculated value of FF is internal to the cell (i.e., it does not take into account the metallization effects). However, the measured FF is external and includes the effect of metal shadowing as well as the additional series resistance due to metallization. These features are not included in the model at this time. Based on these results, this theory can be used to calculate the performance of defect-free cells (using the same material quality). Figure 5.6 shows the calculated I-V curve for a defect-free device using the same material quality. Again, the calculated FF is an internal value. Using a corrected FF of 0.72, the expected efficiency of the defect-free cell is 16%. It is interesting to note that there is a significant increase in cell voltage and FF for defect-free cell. This indicates that defect clusters have a strong influence in degrading the cell performance by shunting. In practice, the FF of a mc-Si solar cell is strongly controlled by the cell processing, in particular by the metal firing, and is typically lower than that of a single-crystal cell. The major reason for this is that

alloying results in metallization "spikes," which are formed at the defect-cluster site. They result in increased shunting (lower shunt resistance) of the cell. Thus, the calculated FF in Table 5.1 is higher than the measured FF.

The entire I-V plot of each cell can also be calculated by this theory. Figure 5.6 compares calculated I-V characteristics of cells A, C, and the one without defects. It is seen that a dominant effect of defect clusters is in degrading the voltage-related parameters [112].



Figure 5.6 A comparison of calculated *I-V* characteristics of three cells—cell #113, cell #107, and cell having no defects [112].

This model can also be used to provide an in-depth understanding of the cell operation, because it provides complete spatial distribution of voltage and currents for any terminal voltage. As an example, Figure 5.7 shows the current flow in various regions of cell #108 at different voltages. Here, the light (green) color implies a current generation and the dark (red) color, a current flow in the opposite direction, depicting an internal dissipation. Notice that the device is generating current until it reaches a voltage
of 0.5 V. At a terminal voltage of 0.505 V and above, the device is actually dissipating power in the regions of defect clusters. A comparison of Figure 5.7 with Figure 5.5 shows that the dissipation regions correspond to the defect clusters.





Terminal voltage 0.525V

Figure 5.7 The current flow in various regions of cell #108 at different voltages [112].

A combination of theory and experiment was used to determine the loss in the efficiency of a mc-Si solar cell due to defect clusters. Several salient results of this analysis are:

(i) Defect clusters are the primary sites of impurity precipitation, and hence are not gettered by conventional gettering treatments of P diffusion and Al alloying.

(ii) Defect clusters act as shunts, creating "internal sinks," which dissipate power within the cell.

(iii) The loss depends on several factors: the nature of the impurity precipitates, distribution and total area of defects compared to the cell area, quality of the base material (the regions with no defects, in which cell performance is limited by the dissolved impurities only), and cell processing technology.

(iv) In a typical cell, the defect clusters produce an efficiency loss of 3 to 4 percent. In order to reduce the influence of defect clusters, techniques for dissolving the precipitates during impurity gettering must be developed. These techniques must be cost-effective. Concomitantly, it is of major interest to determine the achievable improvement in the cell efficiency. An intuitive approach to mitigating the influence of defect clusters would be to dissolve the precipitates by a high-temperature treatment prior to, or during gettering. A new approach to dissolution of impurity precipitates has recently been developed at NREL, which uses vacancy injection to lower the temperature needed for precipitate dissolution.

CHAPTER 6

CONCLUSIONS AND FUTURE DIRECTIONS

6.1 Conclusions

Extended Shockley-Reed-Hall (SRH) calculations across the space charge region was applied to evaluate recombination effects in the SiN_x :H-Si interface. Modeling results show that the overall recombination that is occurring at this interface should consider the charge-induced electric fields both at the edge of and across the space charge region. This is especially required in order to explain the injection-level dependence of the effective surface (interface) recombination velocity (S_{eff}).

Previous extended SRH modeling results successfully addressed the surface (interface) recombination mechanism at the SiO₂-Si interface. Low S_{eff} of the PECVD SiO₂-passivated Si surface is attributed to a combination of moderately low density of interface states at midgap $[D_{it} = (1-10) \times 10^{10} \text{ cm}^{-2} \text{ eV}^{-1}]$ and a high positive oxide charge density $[Q_{ox} = (1-10) \times 10^{11} \text{ cm}^{-2}]$. The presence of a positive charge leads to a band bending at the SiO₂-Si interface and will result in separation of electrons and holes, thus reducing carrier recombination.

Similarly, the deposition of SiN_x:H layers on the silicon substrate leads to the formation of a space charge region at the SiN_x:H/Si interface and is characterized by a fixed positive charge density (Q_f) of the order of 10^{12} cm⁻². In *p*-type Si, a depletion/inversion layer is formed, while in *n*-type Si, the positively charged insulator attracts majority carriers and repels minority carriers. Hence, an accumulation layer is formed. However, according to this model calculation, very high $Q_f (1~3 \times 10^{12} \text{ cm}^{-2})$, for

 SiN_x induced charge density on the Si surface will lead to no injection level dependence of the effective surface recombination velocity, which is in contradiction to experimental results. This discrepancy implies that, perhaps, other recombination mechanisms are missing in the previous SRV modeling.

A modified SRH formalism, which includes the carrier recombination in the damaged region that is caused by ion bombardment onto the Si wafer during PECVD step, was developed in this study to evaluate the recombination at the SiN_x:H-Si interface. Modeling results indicate that, at low injection-levels, carrier recombination in this damaged layer can be the dominant mechanism as compared to the surface recombination. The calculated results seem to be in agreement with the experimental results reported by other research groups. It should be noted that the majority of surface damage can be healed by the rapid thermal annealing process. Therefore, less minority-carrier recombination in the SCR is expected after the firing treatment of Si solar cells.

Minority-carrier life measurements, using QSSPCD technique, indicate that the measurements are very sensitive to wafer preparation and surface passivation. A simple laboratory procedure for wafer preparation was proposed in this study.

A combination of theoretical and experimental study indicates that, in a typical cell, the defect clusters produce an efficiency loss of 3 to 4 percent in efficiency. In order to reduce the influence of defect clusters, techniques for dissolving the precipitates during impurity gettering must be developed.

6.2 Future Directions

The future work may consider the following:

1. Although the damaged region at the SiN_x :H-Si was experimentally identified, additional research is needed to: (a) understand the types of defects/traps in this region and (b) the charge distribution which dominates the surface (interface) recombination at low injection levels. Deep level transient spectroscopy (DLTS) is the technique that can lead to quantifying the interface traps.

2. The previous model of SiN_x :H-Si interface recombination was modified in this work. In order for the recombination in Si solar cells to be studied in detail, a thorough study of the SiN_x -Si interface and the N+/P junction is required.

3. More lifetime measurements and surface recombination velocity calculations need to be performed to support the modeling results.

4. Detailed analyses, such as the process of vacancy injection in rapid thermal anneal step, H transport and evolution from the nitride layer to the bulk Si region, etc, are necessary to determine the optimum process for PECVD-SiN_x:H-assissted H passivation of Si solar cells.

APPENDIX I

PROGRAMS TO CALCULATE SRV USING SRH FORMALISM

N-TYPE

defsng a-z

٤.

```
declare function nt(E)
declare function pt(E)
declare function Lx(smin, E)
declare function LINT(smin)
```

```
dim shared Qf, Dit, vth, Nac, Ndc, mun, mup, po, no, stepsize, ft
dim shared phis(10000), ns(10000), ps(10000), fa(10000, 10000), fd(10000)
dim shared A(10000), B(10000), E(10000), F(10000), Qit(10000),
Qsi(10000), Qo(10000)
```

```
const q = 1.602e-19

const k = 1.381e-23

const T = 300

const beta = q / k / T

const eo = 8.85e-14

const eox = 3.9

const esi = 11.7

const ni = 1.5e10

const dE1 = -.55

const dE2 = .55

const dE2 = .55

const Ei = (dE1 + dE2) / 2

const D = (2 * k * T * ni * eo * esi) ^.5

const TOL = .001
```

```
input "output file name {xxxxxx} : "; fl$
open fl$ + ".txt" for append as #1
open fl$ + ".prn" for output as #2
print
print #1, ""
```

```
input "delta_n 10^x range {low, high} : "; m1, m2
print #1, using "delta n 10x range : ## ##"; m1, m2
print
```

```
print #1, ""
input "Qf, Dit, vth {x.xxxeyy} : "; Qf, Dit, vth
print #1, using "Qf Dit vth
                                         : #. ####^^^^
                                                      #. ####^
#.####*^^^"; Qf, Dit, vth
print
print #1, ""
Qf = Qf * q
input "Nd, sigman, sigmap {x.xxxeyy} : "; Ndc, mun, mup: Nac = 0
print #1, using "Nac num nup
                                      : #. ####^^^^ #. #####^^^^
#.####*^^^"; Ndc, mun, mup
print
print #1, ""
no = Ndc
po = ni * ni / no
input "stepsize, fine-tune {x.xxx} : "; stepsize, ft
                                  : #.####^^^^
print #1, using "stepsize fine-tune
                                                      #. ##":
stepsize, ft
print
print #1, ""
print
print #1, ""
print "<RUN DATA>"
print #1, "<RUN DATA>", time$, date$
print
print #1, ""
print "n.nn * 10 mm phi_s Qoverall Us
                                                     Se″
print #1, " n.nn * 10<sup>°</sup>mm phi_s
                                  Qoverall Us
                                                        Se"
print "-----
print #1, "-----
---"
for m = m1 to m2
 for n = 1 to (10 - ft) step ft
   deltan = n * 10 \hat{} m
   nd = no + deltan
   pd = po + deltan
```

```
phin = -Ei - 1 / beta * log(nd / ni)
    phip = -Ei + 1 / beta * log(pd / ni)
    for i = 0 to (1 / stepsize)
      phis(i) = 0 + stepsize * i
      E(i) = -.55 + 1.1 * stepsize * i
      ns(i) = ni * exp(beta * (phis(i) - phin))
      ps(i) = ni * exp(-beta * (phis(i) - phip))
    next i
    for i = 0 to (1 / stepsize)
      for j = 0 to (1 / stepsize)
        fa(i, j) = (100 * ns(i) + pt(E(j))) / (100 * (ns(i) + nt(E(j))))
+ (ps(i) + pt(E(j))))
        fd(i, j) = (100 * nt(E(j)) + ps(i)) / (100 * (ns(i) + nt(E(j))))
+ (ps(i) + pt(E(j))))
      next j
    next i
    for i = 0 to (1 / stepsize)
      A(i) = 0
      B(i) = 0
      for j = 0 to (1 / stepsize)
        A(i) = A(i) + fa(i, j) * 1.1 * stepsize
        B(i) = B(i) + fd(i, j) * 1.1 * stepsize
      next i
    next i
    for i = 0 to (1 / stepsize)
      Qit(i) = -q * Dit * (A(i) - B(i))
      F(i) = (\exp(beta * (phip - phis(i))) - \exp(beta * phip) + exp(-
beta * (phin - phis(i))) - exp(-beta * phin) + beta * phis(i) * (Nac -
Ndc) / ni) ^.5
      Qsi(i) = -D * F(i)
      Qo(i) = log(abs(Qit(i) + Qsi(i) + Qf) / q) / log(10)
    next i
    qmin = Q_0(0)
    smin = 0
    for i = 1 to (1 / stepsize)
```

```
if Qo(i) < qmin then qmin = Qo(i): smin = i
    next i
    Us = (ns(smin) * ps(smin) - ni * ni) * vth * LINT(smin)
    Se = Us / deltan
                                #. ####^^^^ #. ####^^^^ #. ####^
    print using " #. ## ##
#.#####^^^~"; n, m, phis(smin), exp(qmin * log(10)), Us, Se
    print #1, using " #. ## ## #. #####^^^^ #. #####^^^^
                                                              #. ####
#.#####^^^~"; n, m, phis(smin), exp(qmin * log(10)), Us, Se
    write #2, n * 10 ^ m, phis(smin), exp(qmin * log(10)), Us, Se
  next n
  print
  print #1, ""
next m
close 1, 2
end
function nt(E)
  return ni * exp(beta * (E - Ei))
end function
function pt(E)
 return ni * exp(-beta * (E - Ei))
end function
function Lx(smin, E)
  tpl = (ns(smin) + nt(E)) / mup
 tp2 = (ps(smin) + pt(E)) / mun
 return Dit / (tp1 + tp2)
end function
function LINT(smin)
 nmax = (dE2 - dE1) / TOL
 iter1 = Lx(smin, dE1)
 iter2 = Lx(smin, dE2)
```

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```
iter3 = 0
for xi = 1 to nmax / 2 - 1
E3 = dE1 + TOL * (2 * xi)
iter3 = iter3 + Lx(smin, E3)
next xi
iter4 = 0
for xi = 1 to nmax / 2
E4 = dE1 + TOL * (2 * xi - 1)
iter4 = iter4 + Lx(smin, E4)
next xi
```

.

return (TOL / 3) * (iter1 + iter2 + 2 * iter3 + 4 * iter4) end function

APPENDIX II

PROGRAMS TO CALCULATE SRV USING SRH FORMALISM

```
P-TYPE
```

```
defsng a-z
declare function nt(E)
declare function pt(E)
declare function Lx(smin, E)
declare function LINT(smin)
dim shared Qf, Dit, vth, Nac, Ndc, mun, mup, po, no, stepsize, ft
dim shared phis(10000), ns(10000), ps(10000), fa(10000, 10000), fd(10000,
10000)
dim shared A(10000), B(10000), E(10000), F(10000), Qit(10000),
Qsi(10000), Qo(10000)
const q = 1.602e-19
const k = 1.381e-23
const T = 300
const beta = q / k / T
const eo = 8.85e-14
const eox = 3.9
const esi = 11.7
const ni = 1.5e10
const dE1 = -.55
const dE2 = .55
const Ei = (dE1 + dE2) / 2
const D = (2 * k * T * ni * eo * esi) .5
const TOL = .001
```

```
input "output file name {xxxxxx} : "; fl$
open fl$ + ".txt" for append as #1
open fl$ + ".prn" for output as #2
print
print #1, ""
input "delta_n 10^x range {low, high} : "; m1, m2
print #1, using "delta n 10x range
                                   : ## ##"; m1, m2
print
print #1. ""
input "Qf, Dit, vth {x.xxxeyy} : "; Qf, Dit, vth
print #1, using "Qf Dit vth
                                      : #. ####^^^^ #. ####*^^^^
#.####^^^^"; Qf, Dit, vth
print
print #1, ""
Qf = Qf * q
input "Na, sigman, sigmap {x.xxxeyy} : "; Nac, mun, mup: Ndc = 0
print #1, using "Nac num nup : #. #####^^^^ #. #####^^^^
#. ####<sup>^^^</sup>; Nac, mun, mup
print
print #1, ""
po = Nac
no = ni * ni / po
input "stepsize, fine-tune {x.xxx} : "; stepsize, ft
print #1, using "stepsize fine-tune : #. ####*^^^
                                                       #. ##":
stepsize, ft
print
print #1, ""
print
print #1, ""
print "<RUN DATA>"
print #1, "<RUN DATA>", time$, date$
print
print #1, ""
print "n.nn * 10 mm phi_s Qoverall Us
                                                      Se"
print #1, " n.nn * 10<sup>^</sup>mm phi_s Qoverall Us
                                                          Se″
print "-----
```

```
print #1, "-
__″
for m = m1 to m2
  for n = 1 to (10 - ft) step ft
    deltan = n * 10 m
    nd = no + deltan
    pd = po + deltan
    phin = -Ei - 1 / beta * log(nd / ni)
    phip = -Ei + 1 / beta * log(pd / ni)
    for i = 0 to (1 / stepsize)
      phis(i) = 0 + stepsize * i
      E(i) = -.55 + 1.1 * stepsize * i
      ns(i) = ni * exp(beta * (phis(i) - phin))
      ps(i) = ni * exp(-beta * (phis(i) - phip))
    next i
    for i = 0 to (1 / stepsize)
      for j = 0 to (1 / stepsize)
        fa(i, j) = (100 * ns(i) + pt(E(j))) / (100 * (ns(i) + nt(E(j))))
+ (ps(i) + pt(E(j))))
        fd(i, j) = (100 * nt(E(j)) + ps(i)) / (100 * (ns(i) + nt(E(j))))
+ (ps(i) + pt(E(j))))
      next j
    next i
    for i = 0 to (1 / stepsize)
      A(i) = 0
      B(i) = 0
      for j = 0 to (1 / stepsize)
        A(i) = A(i) + fa(i, j) * 1.1 * stepsize
        B(i) = B(i) + fd(i, j) * 1.1 * stepsize
      next j
    next i
    for i = 0 to (1 / stepsize)
      Qit(i) = -q * Dit * (A(i) - B(i))
```

```
F(i) = (\exp(beta * (phip - phis(i))) - \exp(beta * phip) + exp(-
beta * (phin - phis(i))) - exp(-beta * phin) + beta * phis(i) * (Nac -
Ndc) / ni) ^.5
      Q_{si}(i) = -D * F(i)
      Q_0(i) = \log(abs(Qit(i) + Qsi(i) + Qf) / q) / \log(10)
    next i
    qmin = Q_0(0)
    smin = 0
    for i = 1 to (1 / stepsize)
      if Qo(i) < qmin then qmin = Qo(i): smin = i
    next i
    Us = (ns(smin) * ps(smin) - ni * ni) * vth * LINT(smin)
    Se = Us / deltan
    print using " #.##
                           ##
                                  #.####^^^ #.####^^^ #.####^^^
#.#####^^^~"; n, m, phis(smin), exp(qmin * log(10)), Us, Se
                                      #.####**** #.####****
    print #1, using " #.##
                              ##
                                                               #. ####
#.#####^^^^"; n, m, phis(smin), exp(qmin * log(10)), Us, Se
    write #2, n * 10 m, phis(smin), exp(qmin * log(10)), Us, Se
  next n
  print
  print #1, ""
next m
close 1, 2
end
function nt(E)
  return ni * exp(beta * (E - Ei))
end function
function pt(E)
  return ni * exp(-beta * (E - Ei))
end function
function Lx(smin, E)
  tpl = (ns(smin) + nt(E)) / mup
  tp2 = (ps(smin) + pt(E)) / mun
```

```
return Dit / (tp1 + tp2)
end function
function LINT(smin)
 nmax = (dE2 - dE1) / TOL
 iter1 = Lx(smin, dE1)
  iter2 = Lx(smin, dE2)
  iter3 = 0
  for xi = 1 to nmax / 2 - 1
   E3 = dE1 + TOL * (2 * xi)
   iter3 = iter3 + Lx(smin, E3)
  next xi
  iter4 = 0
  for xi = 1 to nmax / 2
   E4 = dE1 + TOL * (2 * xi - 1)
   iter4 = iter4 + Lx(smin, E4)
  next xi
  return (TOL / 3) * (iter1 + iter2 + 2 * iter3 + 4 * iter4)
```

end function

APPENDIX III

COMPUTATIONAL METHOD FOR RECOMBINATION VELOCITY IN SCR

Units: CGS is applied throughout the calculations

k=1.381×10 ⁻²³	Boltzmann constant	
T=300	Absolute temperature	
$n_i = 1.5 \times 10^{10}$	Intrinsic carrier concentration	
q=1.602×10 ⁻¹⁹	Magnitude of electronic charge	
E _i =0	Intrinsic Fermi level	
$\epsilon_0 = 8.85 \times 10^{-14}$	permittivity of vacuum	
ε _s =7.5	Dielectric constant of silicon nitride	
$\varepsilon_{Si}=11.7$	Dielectric constant of silicon	

$$\beta \equiv \frac{q}{kT} = 38.668$$

Assumptions: *p*-type silicon, $N_A = 10^{16}$ cm⁻³ and $Q_f = 10^{12}$ cm⁻²

Injection level in the bulk $\Delta n_b = 10^{12} \text{ cm}^{-3}$

The mobile carrier densities in the neutral bulk of the silicon is given by:

$$n_b = n_0 + \Delta n_b \tag{1}$$

The equilibrium carrier densities n_0 and p_0 can be easily calculated from the doping concentration;

or

$$n_{b} = n_{i}e^{-\beta\Phi_{n}}$$

$$p_{b} = n_{i}e^{\beta\Phi_{n}}$$
(2)

where, Φ_n , Φ_p denote the quasi-Fermi levels for electrons and holes respectively, n_i is the intrinsic carrier density of the silicon.

In the space charge region, the carrier densities are:

$$n(z) = n_b e^{\beta \psi}$$

$$p(z) = p_b e^{-\beta \psi}$$
(3)

where, z denotes the position in the space charge region, Ψ denotes the corresponding position-dependent potential in the space charge region.

$$z = \beta \lambda_D \int_{\psi_s}^{\psi} \mu \frac{1}{F} d\psi$$
(4)

where Ψ_s is the surface potential, and with the steady-state extrinsic Debye length

$$\lambda_D = \sqrt{\frac{\varepsilon_o \varepsilon_s}{\beta q(n_b + p_b)}} \tag{5}$$

and the function,

$$F(\Psi, \phi_p, \phi_n) = \sqrt{\frac{2}{p_b + n_b}} \{ p_b (e^{-\beta \Psi} + \beta \Psi - 1) + n_b (e^{\beta \Psi} - \beta \Psi - 1) \}$$
(6)

The recombination rate in the space charge region is :

$$U_{SCR}(z) = \frac{(n(z)p(z) - n_i^2)}{\tau_{p_0}(n + n_i) + \tau_{n_0}(p + n_i)}$$
(7)

With the capture time constant for electrons $\tau_{n0} = (\sigma_n \upsilon_{th} N_t)^{-1}$ and for holes, $\tau_{p0} = (\sigma_p \upsilon_{th} N_t)^{-1}$

Hence, the recombination velocity in the space-charge region is given by:

$$S_{SCR} = \frac{1}{\Delta n} \int_{0}^{d_{scr}} U_{SCR}(z) dz$$
(8)

where, d_{scr} is the width of the space-charge region:

$$d_{scr} = \beta \lambda_D \int_{\psi_s}^0 \mu \frac{1}{F} d\psi$$
(9)

Approach:

- 1. Find $\mathcal{\Psi}_s$ by the iterative calculation proposed by Girisch et al.
- 2. Solve Eq. (1)
- 3. Solve Eq. (5)
- 4. solve Eq.(4) numerically

APPENDIX IV

SUMMARY OF DIFFUSION PARAMETERS OF H IN Si, Si₃N₄ AND SiO₂

Medium	$D_0 (cm^2/S)$	E _a (eV)
Si	8.3×10 ⁻¹¹ [1]	0.48 (atom), 0.78 (molecule) [1]
Si ₃ N ₄	5×10 ⁻⁸ [2]	1.0 [2]
SiO ₂	3×10 ⁻¹⁶ [3]	0.73 [3]

 $D = D_0 \exp\left(-\frac{E_a}{kT}\right)$

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