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Enhancing Optoelectronic Properties of Multicrystalline Silicon Using Dual Treatments for Solar Cell Applications

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Abstract: Surface texturing is vital for enhancing light absorption and optimizing the optoelectronic properties of multicrystalline silicon (mc-Si) samples. Texturing significantly improves light absorption by minimizing reflectance and extending the effective path length of incident light. Furthermore, porous silicon treatment on textured mc-Si surfaces offers additional advantages, including enhanced carrier generation, reduced surface recombination, and improved light emission. In this study, a dual treatment combining porous silicon and texturing was employed as an effective approach to enhance the optical and optoelectronic properties of mc-Si. Both porous silicon and texturing were achieved through a chemical etching process. After these surface modifications, the morphology and structure of mc-Si were examined using Atomic Force Microscopy (AFM), Scanning Electron Microscopy (SEM), UV-Vis-IR spectroscopy, photoluminescence (PL), WCT-120 photo-conductance lifetime measurements, and Two-Internal Quantum Efficiency (IQE) analysis. The results reveal a substantial improvement in the material's properties. The total reflectivity dropped from 35% to approximately 5%, while the effective minority carrier lifetime increased from 2 µs for bare mc-Si to 36 µs after treatment. Additionally, the two-dimensional IQE value rose from 35% for the untreated sample to 66% after treatment, representing an enhancement of around 31%. These findings highlight the potential of surface engineering techniques in optimizing mc-Si for photovoltaic applications.

Keywords: silicon; texturization; porous silicon; reflectivity; lifetime; two-dimensional IQE

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1. Introduction

Multicrystalline silicon (mc-Si) is widely used in solar cells for its cost-efficiency [1–4]. Recent processing advancements aim to enhance its light absorption and electronic properties to improve its performance [5–8]. Among these techniques, double treatments, which combine two different processing methods, have shown significant promise. The ability of silicon to absorb light increases with wavelength. Techniques such as texturing and anti-reflection coatings [9,10] have been explored to enhance the absorption characteristics of mc-Si. Surface modifications using chemical etching [11] or plasma treatments [12] can significantly reduce light reflectance, increasing the amount of light absorbed by the solar cell. Recent studies have investigated various combinations of treatments to optimize the light absorption and electronic performance of mc-Si. These double treatments typically include texturing and antireflective coatings. Surface texturing enhances light trapping

by creating a rough surface that reduces reflectance. For instance, alkaline etching followed by acidic etching has been shown to produce optimal textures. Materials such as silicon nitride and titanium dioxide [13,14] are commonly used as antireflective coatings to further minimize reflection losses. Combining texturing with ARC has been found to improve optical absorption and overall cell efficiency. The optoelectronic properties of mc-Si, including charge carrier lifetime, mobility, and junction quality, are crucial for device performance. Double treatments have been shown to improve these properties. Enhanced optical properties often correlate with improved carrier lifetimes. For example, studies report that double treatments can lead to lifetimes exceeding 1 ms, significantly boosting efficiency. Optimizing surface conditions through double treatments can reduce recombination losses at the surface and within the bulk material, enhancing the overall device performance. Silicon used in commercial solar cell fabrication typically contains impurities and defects that negatively impact minority carrier lifetime, thereby reducing cell efficiency. As a result, the photovoltaic (PV) industry is seeking processes that can provide both surface and bulk passivation in c-Si solar cells. Surface texturing plays a critical role in enhancing the optical path length of incident light and reducing surface reflections, and has become a key feature in solar cell technology. In silicon solar cells, surface texturing is traditionally achieved through chemical etching methods, including both anisotropic and isotropic etching [15,16]. Porous silicon (PS) can be easily formed using the stain etching (SE) technique by immersing crystalline silicon in a solution of HF (40 wt%)/HNO_3 (65 wt%)/H_2O for an optimized duration [17]. The combination of texturization and PS is a new approach to enhancing the optical and optoelectronic properties of crystalline silicon. The present work aims to demonstrate mc-Si's optic and optoelectronics properties, which can be achieved using a combination of two treatments: texturization and porous silicon. Elaborated samples were characterized to investigate the material's structure, optics, and optoelectronic properties by measuring the reflectivity, infrared (IR) absorption, PL, effective lifetime, and two-dimensional internal quantum efficiency.

2. Results

The structural characterization of multicrystalline silicon (mc-Si) is crucial for understanding the impact of NaOH texturization and porous silicon (PS) formation. Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM) offer valuable insights into the surface morphology of mc-Si following these treatments. Chemical texturing modifies the surface morphology to enhance light trapping and minimize reflectivity. In this study, Atomic Force Microscopy (AFM) in tapping mode was used to characterize the surface of multicrystalline silicon (mc-Si) before and after treatment. A 20 μm × 20 μm area was scanned to obtain high-resolution topographical data, enabling precise analysis of surface roughness and morphology. As shown in Figure 1b, the textured surface significantly increases the effective area that interacts with incoming light compared to the reference sample (Figure 1a). This texturization plays a crucial role in improving light absorption in solar cells by inducing multiple internal reflections within the material, thereby increasing photon absorption in silicon. Additionally, textured surfaces capture light at various angles, enhancing absorption under different lighting conditions, including direct sunlight and diffuse light. The rough surface scatters incoming light instead of reflecting it away, promoting diffused reflection and reducing optical losses. During the texturing process, the alkaline solution etches the silicon, resulting in a nanoscale pyramidal structure, as shown in Figure 1b. These structures enhance light scattering and trapping, thereby increasing light absorption in silicon by reducing reflectivity compared to a flat silicon surface. This, in turn, leads to increased generation of electron–hole pairs. As illustrated in Figure 1b, the micro-sized pyramids significantly increase the effective surface area available for light

absorption. Their geometry allows for improved light capture at various angles, which is particularly advantageous under varying lighting conditions. Additionally, the textured surface scatters incoming light, minimizing direct reflection that would otherwise occur on smooth surfaces. The pyramidal structures effectively act as a natural anti-reflective coating, reducing optical losses and enhancing overall light absorption.

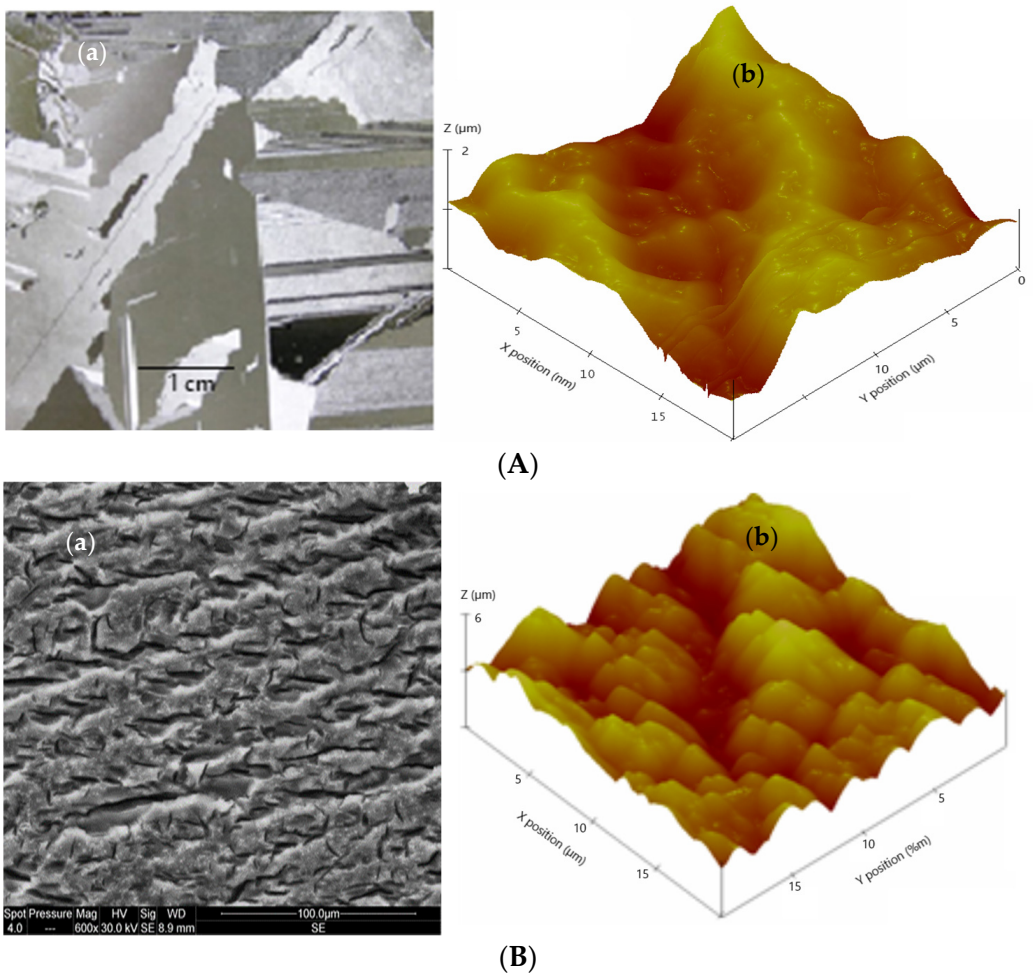


Figure 1. (**a**) SEM and (**b**) AFM images of (**A**) bare and (**B**) textured mc-Si.

The formation of the porous silicon layer on the texturized mc-silicon surface was realized by the stain etching method. This process results in a network of pores that further enhances the material's properties (see Figure 2). The formed pores increase the surface area even further, allowing for better light trapping and absorption. The porous structure can reduce reflectivity even further than what is achieved by texturing alone, as the irregular surface structure scatters light more effectively. The combination of texturing and porous silicon results in a synergistic effect, where each method enhances the benefits of the other. The textured surface provides a foundation for effective light trapping, while the porous layer further minimizes reflectivity and improves charge carrier lifetime. The obtained results have shown that mc-Si substrate treated with both chemical texturing and porous silicon layers can achieve significantly higher electronic quality compared to untreated or only textured substrate.

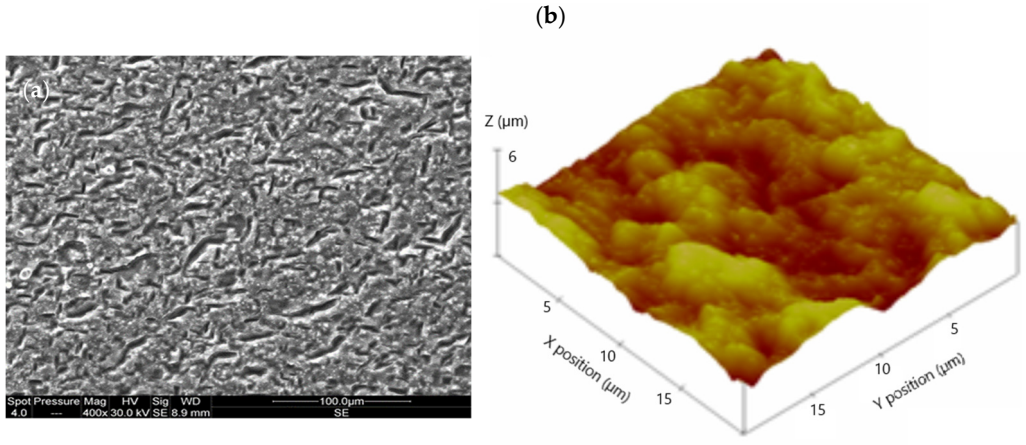


Figure 2. (**a**) SEM and (**b**) AFM images of a texturization mc-Si with PS.

This dual treatment enhances light trapping, reduces surface reflectivity, and provides passivation, all of which collectively contribute to the greater quality of mc-Si. Optical characterization is essential for evaluating the effectiveness of treatments such as chemical texturing and the addition of a PS layer on the mc-Si wafer. This characterization helps assess light absorption, reflectivity, and overall material quality for solar cell applications. Figure 3 shows optical characterization after different texturization times. First, we carried out an optimization of the surface texturing and measured the reflectivity each time. For untreated mc-Si, the average reflectivity is about 50–55% in the range of (400–1000 nm). For textured mc-Si, the average reflectivity ranges from approximately 25% to 15% across the same wavelength range, with sharp decreases at specific wavelengths due to enhanced light trapping. The reflectivity spectrum indicates that the optimal etching time to reduce surface reflectivity to 15% is 3.5 min. The rise in reflectivity beyond 1100 nm is due to the reduced absorption of silicon for photon energies below its indirect bandgap (~1.12 eV). At these longer wavelengths, photons lack the energy to excite electrons across the bandgap, resulting in increased reflection rather than absorption. In the next step, a porous silicon layer was added to this textured surface, resulting in a significant decrease in reflectivity. As shown in Figure 4, textured mc-Si with a porous silicon layer further reduces surface reflectivity to approximately 5–10%, this result is a better result than that reported in [18,19]., thereby improving light absorption. This substantial reduction in reflectivity is attributed to the combined effects of texturing and porosity, particularly in the UV spectrum, due to the formation of a nano-porous morphology.

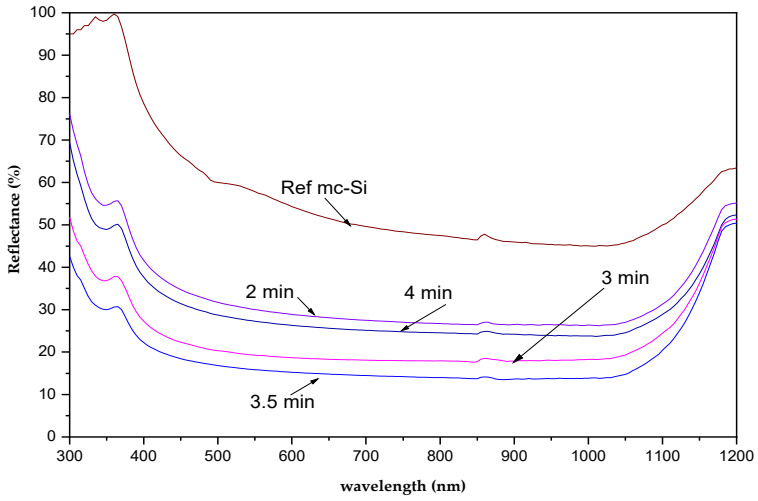


Figure 3. Variation in the surface reflectivity of mc-Si for different texturization times.

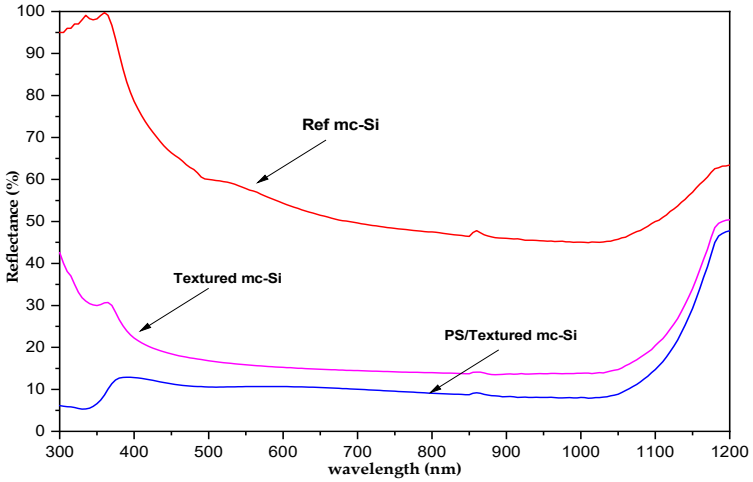


Figure 4. Surface reflectivity of Textured mc-Si and PS/Textured mc-Si compared to ref mc-Si.

It is important to investigate the potential of using PS treatment on textured silicon wafers for photovoltaic applications. To quantify the variation in the electronic quality of the mc-Si before each treatment, we assessed the surface quality of the textured and PS/textured samples by measuring the effective carrier lifetime of mc-Si before and after each treatment (Ref, texturized, and PS/texturized mc-Si wafers). The optoelectronic characterization (lifetime measurement) highlights a significant improvement in the performance of multicrystalline silicon due to the combination of chemical texturing and porous silicon treatment. Figure 5 and Table 1 illustrate the effective lifetimes at an injection level of 10^{15} cm^{-3}, measured using a photoconductivity system (WCT-120). We observed that the effective lifetime of the bare mc-Si wafer was 5 µs, which increased to 10 µs after texturization and 36 µs after PS formation on the textured mc-Si, which is higher than that obtained by HF/HNO_3 solutions [20]. The formation of PS appears to remove damage caused by chemical texturing, which eliminates some surface impurities and reduces related surface defects, thus enhancing the effective carrier lifetime. These results suggest a correlation between the increased lifetime value and hydrogen passivation. As shown in Figure 6, the freshly prepared PS exhibits well-defined silicon-hydrogen absorption bands at 905–910 cm^{-1} and 2087–2106 cm^{-1} [21], which are associated with groups adsorbed at the extended porous silicon surface. Additionally, Si–O modes at 1065 and 1150 cm^{-1} can be observed [22]. It is believed that both surface and bulk passivation effects are achieved through hydrogen, which passivates impurities and defects in the surface and bulk silicon [23], thereby increasing the minority carrier lifetime, as demonstrated in Figure 5 and Table 1. Carrier lifetime measurements before and after treatment quantitatively assessed defect density reduction, enabled correlation with PS characteristics, and validated hydrogen passivation, as evidenced by the improved carrier lifetimes post-treatment.

The combination of texturing and porous silicon results in a synergistic effect, where each method enhances the benefits of the other. The textured surface provides a foundation for effective light trapping, while the porous layer further minimizes reflectivity and improves charge carrier dynamics. The obtained results have shown that mc-Si substrate treated with chemical texturing and porous silicon layers can achieve significantly higher electronic quality than untreated or only textured substrate. The porous silicon layer also serves a crucial role in passivating defects on the silicon surface. The porous structure helps reduce surface states' density, which can trap charge carriers and lead to recombination losses. By passivating the surface, the porous silicon layer enhances the lifetime of charge carriers, leading to improved solar cell efficiency.

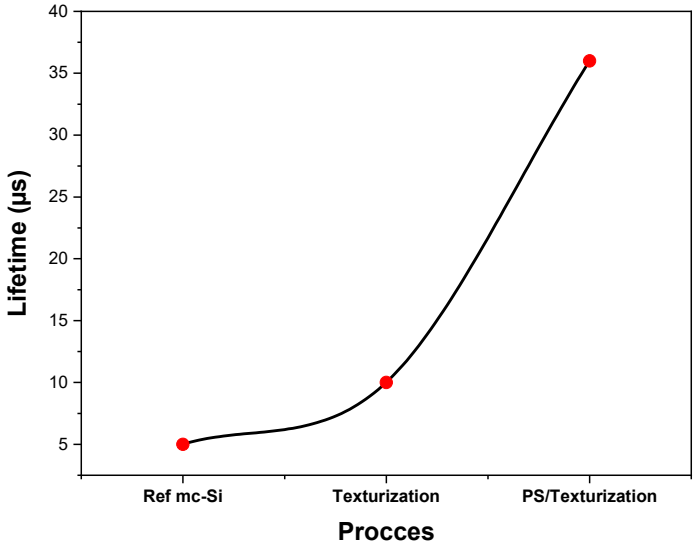


Figure 5. Evolution of mc-Si lifetime for various processes.

Table 1. Evolution of mc-Si lifetime after various treatments at an injection level of 10^{15} cm^{-3}.

Process	Bare mc-Si	Texturized mc-Si	Texturized/PS
Lifetime (µs)	2	10	36

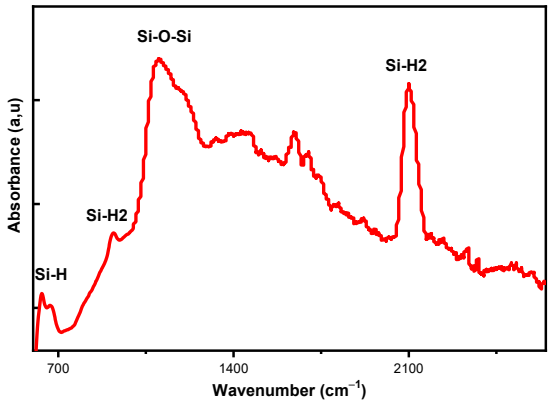


Figure 6. FTIR spectra of PS prepared by the SE method.

The obtained results enable us to correlate the increase in lifetime values with the total reflectivity, as shown in Figure 7. The improvement in lifetime can be attributed to hydrogen passivation, as revealed by the FTIR analysis, as well as the enhanced surface area resulting from both texturization and porous silicon (PS) treatment.

Figure 8 demonstrates the photoluminescence spectra of both textured mc-Si and porous silicon layers at room temperature. The maximum PL peak between 600 and 650 nm displays an intense, Gaussian-like spectrum. An important increase in PL intensity is seen after the PS elaboration. This enhancement is attributed to surface passivation by hydrogen and chemical oxidizing agents, which reduce non-radiative recombination and improve emission efficiency. A PL peak detected at 500 nm can be related to the silicon defective oxide layer, which forms as a result of the wet ambient conditions. Lifetime measurements further confirm this result. At room temperature, PL spectra provide valuable insights into the thermally activated processes within the material. The intensity and position of the peaks offer information about carrier dynamics and recombination mechanisms. Additionally, variations in excitation power during PL measurements can

influence peak intensity, revealing differences in carrier generation and recombination between the textured and PS layers.

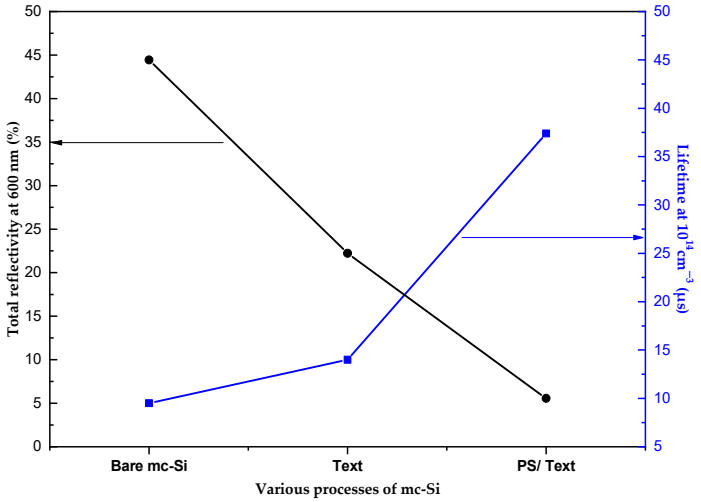


Figure 7. Correlation between the effective lifetime versus total reflectivity for various processes of mc-Si.

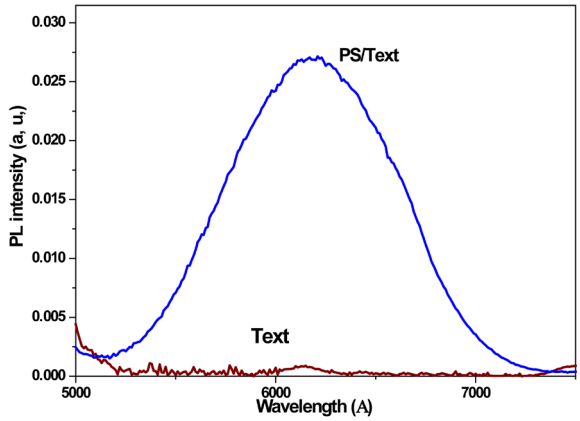


Figure 8. PL spectra of the texturized mc-Si sample before and after PS treatment.

To evaluate the effectiveness of the investigated surface passivation methods in high-efficiency silicon solar cells, a simplified passivated emitter structure was fabricated on multicrystalline silicon (mc-Si) substrates, as depicted in Figure 9. The metallization process was designed with a front contact coverage of 2%, ensuring minimal shading losses, while the back surface was entirely metalized (100%) to optimize charge carrier collection. Among the key performance indicators of a solar cell, internal quantum efficiency (IQE) is particularly sensitive to recombination processes within the device. Therefore, our analysis primarily focuses on this parameter.

Our study primarily focuses on quantum efficiency measurements for local characterization. In particular, the internal quantum efficiency (IQE) technique enables high-resolution mapping of spatial variations in photo-response before and after porous silicon (PS) treatment. This approach is especially important for multicrystalline silicon (mc-Si), where grains and grain boundaries often exhibit significantly different electrical and optical properties.

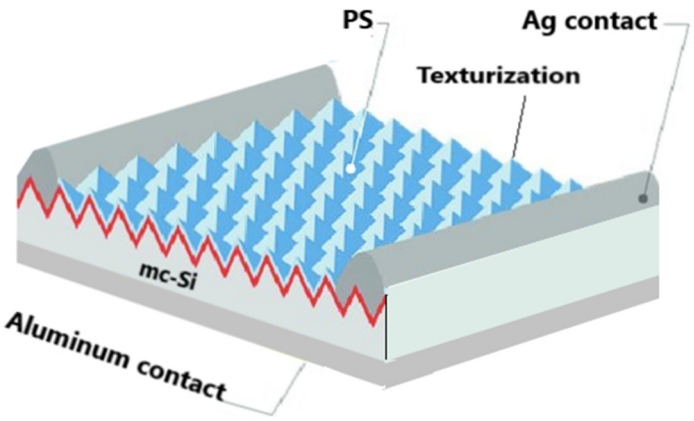


Figure 9. Schematic diagram of a textured mc-Si solar cell with PS layer.

The internal quantum efficiency (IQE) performance was evaluated using Light Beam-Induced Current (LBIC) measurements [24,25]. This technique involves scanning a focused laser beam (638 nm) across the surface of the multicrystalline silicon (mc-Si) while measuring the local IQE at each point. The resulting data are used to generate a spatially resolved map that reveals variations in carrier collection efficiency and identifies electrically active defects. These maps are essential for assessing the electronic quality and uniformity of mc-Si. By comparing IQE distributions before and after surface treatment, the effectiveness of passivation processes can be quantitatively assessed. In this study, the laser beam was systematically scanned over a surface area of 1.5×1.5 cm^2 to obtain detailed insight into the spatial performance of the treated and untreated regions. Figure 10 presents the IQE surface mapping using the LBIC technique for mc-Si solar cells, both with and without PS/textured passivation treatment. Before PS treatment (Figure 10a), the IQE ranges from 8% to 35%. After PS treatment (Figure 10b), the minimum IQE increases to 54%, and the maximum value reaches 66%, reflecting a 31% improvement. This enhancement confirms the effectiveness of the passivation technique in reducing surface recombination and improving device performance [26]. This significant improvement is attributed to the combined effects of surface texturization, which reduces reflectivity, and chemical passivation through Si-O and Si-H bonds in the porous silicon layer, and this result is good compared to that of porous aluminum–silicon nanostructures [27]. The increase in internal quantum efficiency correlates with a rise in effective lifetime from 5 to 36 µs, driven by hydrogen passivation and chemical oxidizing agents., which reduce surface states' density, trap charge carriers, and lead to recombination losses. This result is confirmed by lifetime and PL measurements. The findings presented in this study confirm that the PS/textured surface passivation technique significantly enhances the performance of mc-Si solar cells by improving front surface passivation and reducing recombination losses. These results demonstrate the strong potential of PS/textured passivation as an advanced strategy for achieving higher-efficiency mc-Si solar cells.

Based on Figure 10, we constructed the histogram shown in Figure 11, which illustrates the IQE mapping frequency as a function of IQE for the same sample before and after PS/texturization treatment on mc-Si. For the PS-treated texturized sample (b), the histogram shifts to higher IQE values. The IQE range increases from 47 to 48% for the bare mc-Si to 46–64% for the PS-treated texturized sample, highlighting the significant improvement in the treated mc-Si sample's electronic quality.

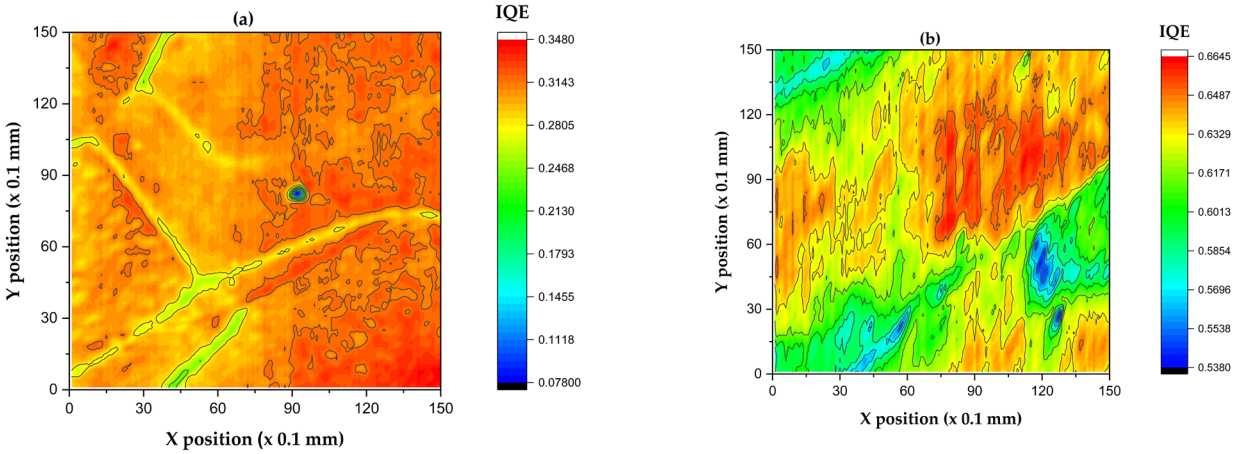


Figure 10. Two-dimensional distribution of IQE) (**a**) before and (**b**) after treatment.

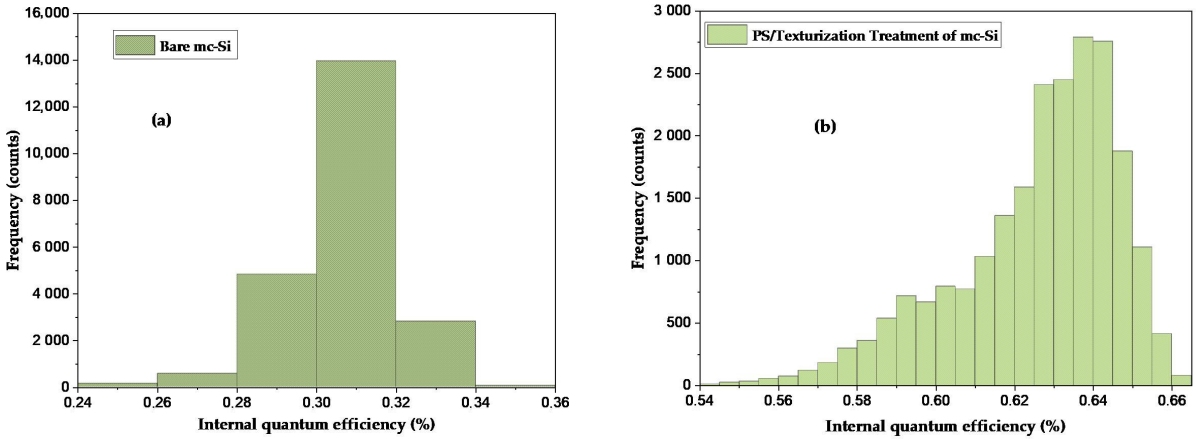


Figure 11. IQE histograms (**a**) before and (**b**) After PS/texturization treatment of mc-Si.

3. Materials and Methods

This experimental method aims to enhance the optical and optoelectronic properties of mc-Si by combining texturization and porous silicon (PS) formation. The approach seeks to improve light absorption and reduce surface recombination in the mc-Si wafer. The material used is a p-type mc-Si wafer with resistivity of 0.5–2 Ω·cm and an area of 1 cm × 1 cm. First, organic contaminants are removed by cleaning the mc-Si wafers in hydrochloric acid (HCl) and hydrogen peroxide (H_2O_2) for 10 min, followed by thorough rinsing with deionized water and drying with nitrogen. The mc-Si substrate is then texturized by immersing it in a 1 M NaOH solution at 80 °C for varying etching times. The etching time was selected based on reflectivity spectrum analysis to optimize the texturization process. After NaOH texturization, the mc-Si substrate undergoes PS formation using the stain etching (SE) method. PS is formed on the texturized mc-Si by dipping the wafer in a 1:3:5 mixture of HF (48 wt%), HNO_3 (65 wt%), and H_2O for 20 min. After etching, the PS-treated sample is washed with deionized water and dried under a nitrogen gas. The composition of the PS on the texturized mc-Si surface is analyzed using FTIR (Nicolet MAGNA-IR 560ESP FT-IR, Madison, WI, USA). Photoluminescence (PL) measurements are performed with an argon laser (4765 Å). Photo-carrier lifetimes are measured using the WCT-120 photoconductivity system (in the range 10 ns to 10 ms). Surface morphology is analyzed by Atomic Force Microscopy (AFM) and Scanning Electron Microscopy (SEM). Reflectivity spectra are obtained using a LAMBDA 950 UV/Vis/NIR (Perkin-Elmer Lambda 950, Springfield, IL, USA) Spectrophotometer with an integrating sphere (in the range

350–1100 nm). Finally, two-dimensional internal quantum efficiency (IQE) distribution is measured with the LBIC technique.

4. Conclusions

This study demonstrates that stain etching-based porous silicon (PS) formed on textured multicrystalline silicon (mc-Si) enhances surface lifetime, photoluminescence, and reduces reflectivity.

In summary, optical and optoelectronic characterization of mc-Si with a combined porous silicon/texturized layer reveals significant improvements in electronic quality. Chemical texturing and PS formation effectively reduce reflectivity from 35% to 5%, significantly increasing light absorption across the visible spectrum. Additionally, the porous silicon layer enhances passivation through hydrogen incorporation, leading to an increase in carrier lifetime from 2 to 36 µs at a minority carrier density (Δn) of 10^{15} cm^{-3}, while the internal quantum efficiency (IQE) improves from 35% to 66%, reflecting a 31% improvement. These findings highlight the potential of surface engineering techniques in optimizing mc-Si for photovoltaic applications, paving the way for more efficient and cost-effective solar energy solutions. Future research should focus on refining these treatments and integrating them into commercial solar cell manufacturing.

Author Contributions: All authors contributed to the study's conception and design. Conceptualization, M.B.R., Y.Z. and A.E.H.; methodology, A.M.; software, K.C.; validation, M.A.A., W.D. and M.B.R.; formal analysis, A.E.H. and Y.Z.; investigation, A.M.; resources, K.C.; data curation, M.A.A.; writing—original draft preparation, W.D.; writing—review and editing, M.B.R.; visualization, K.C.; supervision, M.B.R.; project administration, K.C.; funding acquisition, K.C. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: The datasets generated during and/or analyzed during the current study are available from the corresponding author upon reasonable request.

Conflicts of Interest: The authors declare no conflicts of interest.

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