

**GROWTH AND OPTIMIZATION OF DOPED HYDROGENATED
AMORPHOUS AND NANOCRYSTALLINE
SILICON LAYERS FOR SILICON HETEROJUNCTION SOLAR
CELLS FABRICATION**

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INDIAN INSTITUTE OF TECHNOLOGY DELHI

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SILICON LAYERS FOR SILICON HETEROJUNCTION SOLAR
CELLS FABRICATION**

by

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Submitted

In fulfillment of the requirements of the degree of Doctor of Philosophy

to the



INDIAN INSTITUTE OF TECHNOLOGY DELHI

APRIL 2025

Dedicated to my parents...

CERTIFICATE

This is to certify that the thesis entitled “**Growth and Optimization of Doped Hydrogenated Amorphous and Nanocrystalline Silicon Layers for Silicon Heterojunction Solar Cells Fabrication**” being submitted by Ms. Shrestha Bhattacharya to Indian Institute of Technology Delhi is ethical of consideration for the award of the degree of Doctor of Philosophy and is a record of the original and bonafide research work carried out by her under my guidance and supervision. The results obtained in the thesis have not been submitted in part or full to any other University or Institute for award of any degree/diploma.

Date:

Place: New Delhi

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ABSTRACT

The hydrogenated amorphous/crystalline silicon (a-Si:H/c-Si) heterojunction (SHJ) solar cells emerge as a promising alternative to the traditional Al-BSF homojunction solar cells fulfilling the photovoltaic industry demands. A key feature of the SHJ technology is the application of a hydrogenated intrinsic amorphous silicon (i-a-Si:H) layer, which effectively passivates the c-Si surface, enabling higher open-circuit voltage as compared to the conventional c-Si solar cells. Doped hydrogenated amorphous silicon layers are used as charge-selective layers along with the transparent conductive oxide (TCO) layer, which facilitates lateral charge transport.

This thesis work explores various strategies aimed at enhancing the power conversion efficiency of SHJ solar cells by initially optimizing the c-Si surface through wet chemistry followed by doped hydrogenated amorphous and nanocrystalline silicon layer grown by plasma enhanced chemical vapour deposition (PECVD) tool. The c-Si/a-Si:H interface is quite crucial, so proper surface conditioning, including the formation of the random pyramids, is the first priority. Another significant challenge faced by SHJ solar cells is transport losses, which have been analyzed and minimized through the optimization of charge carrier selective contacts.

The first part of the thesis emphasizes silicon surface conditioning, which affects the SHJ's device performance. Achieving a uniform textured c-Si surface becomes crucial, which can be managed either through the initial saw damage removal (SDR) step or during the texturing stage. This study investigates the influence of the SDR process on the as-cut raw c-Si wafers in controlling the textured silicon morphology. On varying the NaOH concentration of the SDR solution, a direct correlation is observed in the pyramidal surface morphology after texturization. An appropriate concentration of NaOH helped to initially control the silicon surface resulting in reduced arithmetic average reflectance of ~12% and better c-Si/a-Si:H passivation of ~1 ms. A 30 wt.% NaOH solution produced uniform square-shaped pits,

resulting in a homogeneous distribution of pyramids. SHJ solar cells were fabricated using wafers processed with the optimized SDR technique, achieving a power conversion efficiency of $\sim 18.2\%$ and an open-circuit voltage (V_{oc}) of ~ 701 mV.

The next part of the thesis focuses on the development of a phosphorous-doped hydrogenated nano-crystalline silicon layer as an electron-selective contact via the PECVD tool to replace the n-doped hydrogenated amorphous layer (n-a-Si:H) to take advantage of higher conductivity and optical bandgap of the nanocrystalline layer. The impact of varying power densities on the dissociation of precursor gases (SiH_4 , PH_3 and H_2) is examined through optical emission spectroscopy and the crystalline fraction in n-nc-Si:H films are analyzed in relation to their dark conductivity. At an optimal power density of 122 mW/cm² and $\sim 2\%$ phosphorus doping, n-nc-Si:H film exhibited a Raman crystallinity of 53%, a high dark conductivity of 43 S/cm, and an activation energy of ~ 23 meV. The textured c-Si surface passivation improved by 2 folds to ~ 2 ms with the n-nc-Si:H layer in contrast to the n-a-Si:H layer. An improvement in the V_{oc} and the external quantum efficiency (EQE) >650 nm is observed due to better passivation from unintentional hydrogen plasma treatment incorporating the n-nc-Si:H layer in the rear side. Also, an improvement in the fill factor (FF) from $\sim 71\%$ to $\sim 75\%$ due to better charge carrier transport and reduced electron-selective contact resistivity (ρ_c) from 271 m Ω -cm² to 61 m Ω -cm². By balancing the passivation and carrier selectivity with an optimized parameter of the n-nc-Si:H electron selective layer, a power conversion efficiency of $\sim 20\%$ is achieved on the front emitter SHJ structure.

In the last part of the thesis work, the hole-selective contact is explored for reducing contact resistance (ρ_c) and charge carrier recombination. The impact of varying diborane doping in the p-a-Si:H layer and its thickness is explored to reduce the series resistance (R_s) and the FF of the device. With an optimal doping level of $\sim 3\%$, dark conductivity of $\sim 2 \times 10^{-5}$

S/cm and ρ_c of $\sim 432 \text{ m}\Omega\text{-cm}^2$ was obtained. Lower contact resistivity ensures proper band bending and effective carrier transport. A breakdown of the R_s components revealed that the hole-selective contact (i+p/ITO) accounts for around 49% of the device's total R_s of $\sim 860 \text{ m}\Omega\text{-cm}^2$. With the abovementioned optimization the front-emitter SHJ cell exhibits a V_{oc} of $\sim 725 \text{ mV}$, an FF of $\sim 79.20\%$, and a power conversion efficiency of $\sim 22.16\%$. TCAD simulations elucidated the impact of p-layer doping and thickness on carrier screening length and energy band bending at device interfaces, establishing a theoretical correlation for the experimental findings.

सार

हाइड्रोजनीकृत अमॉर्फस/क्रिस्टलाइन सिलिकॉन (a-Si:H/c-Si) हेटरोजंक्शन (SHJ) सोलर सेल पारंपरिक Al-BSF होमोजंक्शन सोलर सेल की तुलना में फोटोवोल्टिक उद्योग की आवश्यकताओं को पूरा करने वाला एक आशाजनक विकल्प बनकर उभर रहा है। SHJ तकनीक की एक मुख्य विशेषता यह है कि इसमें हाइड्रोजनीकृत इन्ट्रिंसिक अमॉर्फस सिलिकॉन (i-a-Si:H) परत का उपयोग किया जाता है, जो प्रभावी रूप से c-Si सतह को पैसिवेट करती है और पारंपरिक c-Si सोलर सेल की तुलना में अधिक ओपन-सर्किट वोल्टेज सक्षम बनाती है। चार्ज-चयनात्मक परतों के रूप में डोप की गई हाइड्रोजनीकृत अमॉर्फस सिलिकॉन परतों का उपयोग किया जाता है, और साथ ही पारदर्शी कंडक्टिव ऑक्साइड (TCO) परत चार्ज के पार्श्व परिवहन को आसान बनाती है।

यह शोध कार्य SHJ सोलर सेल की पावर कन्वर्शन एफिशिएंसी (पीसीई) को बढ़ाने के लिए विभिन्न रणनीतियों की जांच करता है। इसमें प्रारंभ में वेट केमिस्ट्री के माध्यम से c-Si सतह का अनुकूलन किया गया है, जिसके बाद प्लाज़्मा एन्हांसड केमिकल वेपर डिपोज़िशन (PECVD) तकनीक द्वारा डोप्ड हाइड्रोजनीकृत अमॉर्फस और नैनोक्रिस्टलाइन सिलिकॉन परतों को तैयार किया गया है। c-Si/a-Si:H इंटरफेस अत्यंत महत्वपूर्ण होता है, इसलिए उचित सतह कंडीशनिंग, जिसमें रैंडम पिरामिड की संरचना शामिल है, पहली प्राथमिकता होती है। SHJ सोलर सेल द्वारा सामना की जाने वाली एक और महत्वपूर्ण चुनौती ट्रांसपोर्ट लॉसेज़ (वाहक परिवहन हानि) है, जिसे चार्ज कैरियर सिलेक्टिव कॉन्टैक्ट्स के अनुकूलन के माध्यम से विश्लेषित और न्यूनतम किया गया है।

थीसिस के पहले भाग में सिलिकॉन सतह की कंडीशनिंग पर जोर दिया गया है, जो SHJ डिवाइस के प्रदर्शन को प्रभावित करती है। एक समान टेक्सचरयुक्त c-Si सतह प्राप्त करना अत्यंत महत्वपूर्ण होता है, जिसे प्रारंभिक सॉ डैमेज रिमूवल (SDR) चरण या टेक्सचरिंग चरण के दौरान नियंत्रित किया जा सकता है। यह अध्ययन SDR प्रक्रिया का असर कच्चे कटी हुई c-Si वेफर पर टेक्सचर सिलिकॉन की बनावट को नियंत्रित करने में जांचता है। SDR घोल में NaOH की सांद्रता को परिवर्तित करने पर, टेक्सचरिंग के बाद बनने वाली पिरामिडीय सतह संरचना में सीधा संबंध देखा गया। NaOH की उपयुक्त सांद्रता ने प्रारंभ में सिलिकॉन सतह को नियंत्रित करने में मदद की, जिससे औसत परावर्तन ~12% तक कम हुआ और c-Si/a-Si:H पैसिवेशन ~1 मिलीसेकंड तक बेहतर

रहा। 30 wt.% NaOH घोल ने एकसमान चौकोर आकार के गड्ढे बनाए, जिससे पिरामिडों का समान वितरण संभव हुआ। अनुकूलित SDR तकनीक से तैयार किए गए वेफरों का उपयोग करके SHJ सोलर सेल बनाए गए, जिनसे ~18.2% की पावर कन्वर्शन एफिशिएंसी और ~701 mV का ओपन-सर्किट वोल्टेज (V_{oc}) प्राप्त हुआ।

थीसिस के अगले भाग में फॉस्फोरस-डोप्ड हाइड्रोजनीकृत नैनोक्रिस्टलाइन सिलिकॉन परत के विकास पर ध्यान केंद्रित किया गया है, जिसे PECVD उपकरण के माध्यम से इलेक्ट्रॉन-सिलेक्टिव कॉन्टैक्ट के रूप में विकसित किया गया है। इसका उद्देश्य n-डोप्ड हाइड्रोजनीकृत अमॉर्फस सिलिकॉन (n-a-Si:H) परत को प्रतिस्थापित करना है ताकि नैनोक्रिस्टलाइन परत की उच्च कंडक्टिविटी और ऑप्टिकल बैंडगैप का लाभ उठाया जा सके। इस भाग में, प्रीकर्सर गैसों (SiH_4 , PH_3 और H_2) के विघटन पर विभिन्न पावर डेंसिटी के प्रभाव का अध्ययन ऑप्टिकल एमिशन स्पेक्ट्रोस्कोपी के माध्यम से किया गया है, और n-nc-Si:H फिल्मों में क्रिस्टलाइन अंश को उनकी डार्क कंडक्टिविटी के संबंध में विश्लेषित किया गया है। 122 mW/cm^2 की आदर्श पावर डेंसिटी और लगभग 2% फॉस्फोरस डोपिंग पर, n-nc-Si:H परत ने 53% रमन क्रिस्टैलिनिटी, 43 S/cm की उच्च डार्क कंडक्टिविटी और लगभग 23 meV का एक्टिवेशन एनर्जी दर्शाया। n-a-Si:H परत की तुलना में n-nc-Si:H परत के उपयोग से टेक्सचरयुक्त c-Si सतह का पैसिवेशन लगभग दोगुना होकर ~2 मिलीसेकंड तक सुधर गया। रियर साइड में n-nc-Si:H परत के समावेशन से अनायास हाइड्रोजन प्लाज़्मा ट्रीटमेंट के कारण बेहतर पैसिवेशन हुआ, जिससे V_{oc} और 650 nm से अधिक तरंगदैर्घ्य पर एक्सटर्नल क्वांटम एफिशिएंसी (EQE) में सुधार देखा गया।

साथ ही, बेहतर चार्ज कैरियर ट्रांसपोर्ट और इलेक्ट्रॉन-सिलेक्टिव कॉन्टैक्ट रेजिस्टिविटी (ρ_c) को $271\text{ m}\Omega\text{-cm}^2$ से घटाकर $61\text{ m}\Omega\text{-cm}^2$ करने के कारण फिल फैक्टर (FF) में ~71% से बढ़कर ~75% तक सुधार हुआ। n-nc-Si:H इलेक्ट्रॉन सिलेक्टिव परत के अनुकूलित मापदंडों के माध्यम से पैसिवेशन और कैरियर सिलेक्टिविटी के बीच संतुलन स्थापित कर, फ्रंट एमिटर SHJ संरचना पर लगभग 20% की पावर कन्वर्शन एफिशिएंसी प्राप्त की गई।

थीसिस कार्य के अंतिम भाग में होल-सिलेक्टिव कॉन्टैक्ट का अध्ययन किया गया है, जिसका उद्देश्य कॉन्टैक्ट रेजिस्टेंस (ρ_c) और चार्ज कैरियर रिकॉम्बिनेशन को कम करना है। p-a-Si:H परत में डाइबोरेन डोपिंग और इसकी मोटाई को बदलने के प्रभावों का विश्लेषण किया गया, ताकि डिवाइस की सीरीज़ रेजिस्टेंस (R_s) और

फिल फैक्टर (FF) को बेहतर किया जा सके। लगभग 3% के आदर्श डोपिंग स्तर पर $\sim 2 \times 10^{-5}$ S/cm की डार्क कंडक्टिविटी और ~ 432 m Ω -cm² की ρ_c प्राप्त की गई। कम संपर्क रेजिस्टिविटी (ρ_c) बेहतर बैंड बैंडिंग और प्रभावी कैरियर ट्रांसपोर्ट सुनिश्चित करती है। R_s के घटकों के विश्लेषण से यह पाया गया कि होल-सिलेक्टिव कॉन्टैक्ट (i+p/ITO) डिवाइस की कुल R_s (~ 860 m Ω -cm²) का लगभग 49% योगदान करता है। उपरोक्त अनुकूलन के साथ, फ्रंट-एमिटर SHJ सोलर सेल ने ~ 725 mV का V_{oc} , $\sim 79.20\%$ का FF और $\sim 22.16\%$ की पावर कन्वर्शन एफिशिएंसी प्रदर्शित की। TCAD सिमुलेशनों के माध्यम से p-परत की डोपिंग और मोटाई का प्रभाव कैरियर स्क्रीनिंग लंबाई और डिवाइस इंटरफेस पर ऊर्जा बैंड बैंडिंग पर स्पष्ट किया गया, जिससे प्रयोगात्मक परिणामों के लिए एक सैद्धांतिक संबंध स्थापित किया गया।

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ABBREVIATIONS

PV	Photovoltaics
c-Si	Crystalline silicon
Al-BSF	Aluminum diffused back surface field.
PERC	Passivated Emitter Rear Contact
TOPCon	Tunnel oxide passivating contact
SHJ	Silicon heterojunction
ARC	Anti-Reflection Coating
SHJ	Silicon heterojunction
BSF	Back surface field.
V _{OC}	Open circuit voltage
FF	Fill Factor
Poly-Si	Polycrystalline Silicon
TCO	Transparent conducting oxide
ITO	Tin doped indium oxide
PECVD	Plasma Enhanced Chemical Vapour Deposition
J _{SC}	Short circuit current density
Al	Aluminium
Ag	Silver
FBC-SHJ	Front/back-contacted silicon heterojunction
IBC	Interdigitated Back Contact
MPP	Maximum Power Point
SRH	Shockley-Read-Hall
DI	De-ionized
SEM	Scanning Electron Microscopy
OH ⁻	Hydroxyl ion
SDR	Saw Damage Removal
Na ₂ SiO ₃	Sodium Metasilicate
NaOH	Sodium Hydroxide
KOH	Potassium Hydroxide

TMAH	Tetramethylammonium Hydroxide
Na ₃ PO ₄	Trisodium orthophosphate
NaHCO ₃	Sodium Bicarbonate
IPA	Isopropyl Alcohol
HNO ₃	Nitric acid
HF	Hydrofluoric acid
CH ₃ COOH	Acetic acid
RCA	Radio Corporation of America
RF	Radio Frequency
OES	Optical Emission Spectroscopy
TCAD	Technology Computer-Aided Design
FZ	Float Zone
HNA	Hydrofluoric acid, Nitric acid and Acetic acid
SSC	Sampling Setting Chamber
LLC	Load Lock Chamber
VASE	Variable angle spectroscopy ellipsometry
SSP	Single Side Polished
PCD	Photoconductance Decay
DB	Dangling bonds
iV _{oc}	Implied open circuit voltage.
ToF-SIMS	Time-of-Flight Secondary Ion Mass Spectrometry
UV-Vis-NIR	Ultraviolet Visible Near Infrared
PTM	Photomultiplier Tube
InGAs	Indium Gallium Arsenide
PbS	Lead Sulphide
STC	Standard Test Conditions
OC	Open-circuit points
QE	Quantum Efficiency
EQE	External Quantum Efficiency
IQE	Internal Quantum Efficiency

PERX	Passivated Emitter Technologies
MoO _x	Molybdenum Oxides
MCL	Minority Carrier Lifetime
TO	Transverse Optical
ASD	As Deposited
TLM	Transfer Length Method
HPT	Hydrogen Plasma Treatment
<i>p</i> FF	Pseudo-Fill Factor
HMS	Hall Measurement System
V ₂ O ₅	Vanadium (V) oxide
NiO _x	Nickel oxide