

PCCP

Accepted Manuscript



This article can be cited before page numbers have been issued, to do this please use: Z. Purohit, D. Verma and B. Tripathi, *Phys. Chem. Chem. Phys.*, 2018, DOI: 10.1039/C8CP02703J.



This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the [author guidelines](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the ethical guidelines, outlined in our [author and reviewer resource centre](#), still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.

1 **Electro-analytical investigation of potential induced degradation** 2 **in mc-silicon solar cells: sodium ions induced inductive loop**

3 Zeel Purohit^a, Deepak Verma^b, Brijesh Tripathi^{a,*}

4 ^a*Department of Science, School of Technology, Pandit Deendayal Petroleum University,*
5 *Gandhinagar – 382007 India.*

6 ^b*School of Engineering and Applied Science, Ahmedabad University, Ahmedabad – 380009*
7 *India.*

8 *Corresponding Author: Ph. +91 79 2327 5455, Fax. +91 79 2327 5030, E-mail.
9 brijesh.tspv@gmail.com

10

11 **Abstract**

12 Potential induced degradation of shunt type (PID-s) in multi-crystalline silicon (mc-
13 Si) solar cells is becoming critical for performance reduction of solar panels in large scale
14 photovoltaic (PV) power plants. In this article PID-s has been investigated by applying high
15 voltage stress on mc-Si solar cell for their degradation and recovery and results have been
16 explained on the basis of DC and AC characterization. The efficiency decreases drastically
17 from 15.7% to 2.9% due to the high voltage stress of -800V at 85°C for 48 hours, which is
18 attributed to reduction in shunt resistance and increase in depletion and diffusion
19 capacitances. Reduction in electrical performance due to PID-s has been further explained by
20 morphological, structural and elemental analysis. Observed negative capacitance behaviour in
21 impedance spectra of mc-Si solar cells after PID-s has been attributed to structural
22 deformation caused by potential induced migration of sodium ion (Na⁺) into mc-Si. The
23 structural deformation induced by potential induced migration of Na⁺ ion has been confirmed
24 by using non-destructive and lattice strain sensitive micro-Raman spectroscopy. The obtained

25 experimental results have been correlated with existing theoretical understanding of p-n
26 junction solar cells to explain consequences of the PID-s.

27

28 **Keywords:** reliability, crystalline silicon solar cells, potential-induced degradation (PID),
29 impedance spectroscopy (IS).

30

31 **1 Introduction**

32 In megawatt-scale solar photovoltaic (PV) power plants, multi-crystalline silicon (mc-
33 Si) solar modules are connected in series and parallel combination in order to enhance the
34 voltage and current outputs of an array respectively. The solar cells inside the encapsulated
35 PV modules experience significant voltage stress with respect to the aluminium frame. This
36 high voltage stress is responsible for adverse effects on the power output of solar PV module,
37 which is known as potential-induced degradation (PID) [1-5]. In recent times, PID has been
38 given more attention as the major reliability issue due to frequent mid-life failures of modules
39 in larger scale power plants [5]. For the developing countries like India, with an aggressive
40 target of 100 GW by 2022 [6], it becomes important to consider reliability issues associated
41 to mid-life failures. The PID-s affected modules have an enormously declined power output
42 over a period of time under harsh environmental conditions [7]. Several studies have been
43 done towards the identification and investigation of PID-s affected modules under various
44 climatic and potential conditions [8-11]. Further, solar PV modules subjected to PID-s are
45 also influenced by the properties of anti-reflection coatings (ARCs) [12, 13], encapsulating
46 materials [14-17], covering glass [18, 19] and system topologies [12, 13, 20, 21].

47 In recent years, various PID experiments have been performed on different types of
48 solar cell technologies and also, many efforts have been made in order to evaluate the origin
49 of the PID-s phenomena [22-25]. The migration of sodium ions (Na^+) under strong electric

50 field has been considered as a major factor causing PID [23]. Moreover, the PID of mono-
51 crystalline silicon solar cells has been studied with respect to the different orientations of
52 crystal planes [26]. In addition, atomic modelling using first principle density functional
53 theory (DFT) calculations for Na accumulation has been performed to envisage the effect of
54 Na impurities on the electronic structure of silicon material [27, 28]. The reduction in the
55 electrical output parameters under the influence of PID-s in relation to the micro-structural
56 defects in the material through electro-analytical method has not been well explored.

57 Impedance spectroscopy (IS) is an alternating current (AC) characterization
58 technique, which is widely used for characterization of solid-state electrolytic device such as
59 solar cell [29-32]. This technique helps to investigate the dynamic behaviour of electro-
60 analytical parameters of solar cell under small amplitude sinusoidal perturbing AC signal
61 superimposed on a suitable direct current (DC) voltage. The response of the solar cell can be
62 used to calculate the overall impedance (Z , a complex number) as a function of frequency (f).
63 Various electronic processes in the solar cell occur on different time scales, which result in
64 semicircles of different sizes in the complex plane referred as Nyquist plot (Z' - Z''). Nyquist
65 plot consists of a number of semicircles depending on physical processes happening at
66 various interfaces in the solar cell [30]. Each semicircle represents particular physical process
67 described in terms of series or parallel combination of Voigt elements (a combination of a
68 resistor (R) and capacitor (C) or an inductor (L)). IS has been widely used to investigate
69 electronic processes in the solar cell such as surface transport, diffusion and recombination
70 associated to the bulk and the interface [29-36]. Moreover, IS has been also used to study PID
71 phenomenon by Opera et al. [35], however in-depth analysis and explanation has yet to be
72 thoroughly discussed.

73 This article explains the electrical performance output of mc-Si solar cells subjected
74 to PID-s with a better understanding of the physical processes behind the reduction in open-

75 circuit voltage (V_{OC}) and maximum output power (P_{max}). The experimental DC current
76 density-voltage (J-V) characteristics before and after PID-s have been theoretically fitted
77 using two-diode model and a drastic reduction in the electrical output of solar cells has been
78 further explained using IS. This article reports various physical processes associated to the p-
79 n junction deterioration caused by migrated Na^+ impurity concentration. In addition, an
80 increased recombination through micro-structurally deformed grain boundaries due to Na^+
81 movement has been found responsible for the reduction in the efficiency (η) of commercially
82 available mc-Si solar cell.

83

84 2 Experimental details

85 Encapsulated commercially available mc-Si solar cells of 1 cm^2 area were used for
86 study, marked as 'CS-1', 'CS-2' and 'CS-3'. The mc-Si cells (n^+ -p-p $^+$), typically contain
87 aluminium (Al) back surface field (BSF) structure with a phosphorus-doped n^+ emitter, a
88 boron-doped p-type base, and an Al-doped p $^+$ BSF, with Ag and Al metalized contacts at the
89 front (emitter) and back (base) surfaces, respectively with SiN_x ARC layer on top. The 'CS-1'
90 represents the fresh solar cell, 'CS-2' represents degraded solar cell after subjecting 'CS-1' to
91 an applied voltage of 800V for 48 hours in a configuration as shown in Fig. 1. 'CS-3'
92 represents the recovered solar cell by applying reverse polarity voltage of 800 V for 240
93 hours to the 'CS-2'. The solar cells were embedded in sandwich structure of tempered cover
94 glass as the front window material; ethylene vinyl acetate (EVA) as front and back
95 encapsulation material and polyvinyl fluoride (PVF) is used as the encapsulating back sheets.
96 The PID tests were carried out by applying a high voltage stress of 800 V (at a temperature of
97 $85\text{ }^\circ\text{C}$ and relative humidity of 65 %RH) across the encapsulated solar cell by connecting the
98 positive electrode to the aluminium foil placed on the front cover glass and negative electrode
99 to the shorted terminals (Fig. 1). To evaluate the J-V characteristics, CS-1', 'CS-2', and 'CS-

100 3' were measured under standard test conditions (25°C, 1000 Wm⁻², AM1.5G spectrum)
 101 using solar simulator (SS80AAA, Photoemission Tech., USA) equipped with AM1.5G filter
 102 and source measuring unit (U2722A, Agilent). The surface morphological and elemental
 103 analyses were carried out using field emission scanning electron microscope (FESEM, Carl
 104 Zeiss, Ultra-55, 1-20 kV) equipped with energy dispersive X-ray spectrometry (EDX, Oxford
 105 Instruments). IS and capacitance-voltage (C-V) measurements were carried out under dark
 106 conditions using a three electrode potentiostat (660D, CH Instruments) equipped with a
 107 frequency response analyser with 5 mV AC perturbation signal in the frequency range of 0.1
 108 Hz to 1 MHz. Micro-Raman measurements were carried out using (Renishaw inVia system)
 109 with an excitation laser beam of 532 nm.

110

111 3 Theoretical details

112 3.1 Theory of DC equivalent circuit

113 The two-diode based equivalent circuit of the solar cells is shown in Fig. 2. The
 114 reverse saturation current densities of the first and second diodes are denoted as J_{01} and J_{02}
 115 and ideality factors of the first and second diode are represented as n and m , respectively. The
 116 parallel/shunt resistance (R_{sh}), and series resistance (R_s) are included to quantify the
 117 deviation of the current density-voltage (J-V) characteristics from the ideal behaviour. The
 118 two-diode model equation for illuminated solar cell can be expressed as [33]:

$$119 \quad J = J_{PH} - J_{01} \left(\exp \frac{q(V_j + JR_s)}{nk_B T} - 1 \right) - J_{02} \left(\exp \frac{q(V_j + JR_s)}{mk_B T} - 1 \right) - \frac{V_j + JR_s}{R_{sh}} \quad (1)$$

120 where, V_j represents bias voltage, J_{PH} represents light generated current density, q represents
 121 the charge of an electron, k_B represents the Boltzmann constant, and T represents the absolute
 122 temperature. The two-diode model is used to fit experimental data using the
 123 MATLAB/Simulink code to estimate R_s , R_{sh} , n and m of the solar cell subjected to PID-s.
 124 The performance parameters of the silicon solar cell namely, short-circuit current density

125 (J_{sc}), V_{oc} , the fill factor (FF) represent the extent of pseudo rectangular shape for the non-
126 linear J-V curve, are related to η as per following expression:

$$127 \quad \eta = \frac{V_{oc} \times J_{sc} \times FF}{(A \times P_{in})} \quad (2)$$

128 Here, P_{in} represents the power input through the incident light radiation per unit area and A
129 represents the area of solar cell.

130

131 3.2 Theory of AC equivalent circuits

132 Electro-analytical IS technique has been extensively used as the powerful probing
133 characterization to manifest the physical fundamental processes in the devices, (e.g.
134 crystalline silicon solar cell) with linear sweep voltammetry [31, 32]. Furthermore, it serves
135 the understanding associated to charge carrier transport kinetics, which is mainly governed by
136 minority carrier diffusion and recombination. The p-n junction space charge layer of mc-Si
137 solar cell is mainly governed by two circuit elements: junction resistance (R_j) and junction
138 capacitance (C_j). The effective junction resistance (R_j) is approximately equal to the sum of,
139 R_{sh} and diffusion resistance (R_d). The R_d can be extracted from the voltage dependence of
140 current density under intermediate and strong forward bias and governed by diode ideality
141 factor and reverse saturation current as given by following expression [33]:

$$142 \quad R_d = \frac{mk_B T}{q \cdot \exp\left(\frac{qV_j}{mk_B T}\right)} \left[\frac{1}{J_{0e}} + \frac{1}{J_{0b}} \right] \quad (3)$$

143 where, V_j represents the junction voltage, J_{0e} and J_{0b} represent the current density of the
144 emitter and the base, respectively. The effective junction capacitance (C_j) is approximately
145 equal to the sum of capacitance of depletion layer (C_{dl}), which is also known as transition
146 capacitance (C_T) and diffusion capacitance (C_μ). For the case of depletion layer width much
147 greater than Debye length, which is the case under reverse and low forward bias, C_{dl}^{-2} varies
148 linearly with respect to bias as given by following equation [32]:

$$149 \quad C_j = \frac{\epsilon_r \epsilon_0}{w_0 V_j^{1/2}} \quad (4)$$

150 where, w_0 represents depletion width, $w = w_0 V_{sc}^{1/2}$, ϵ_r and ϵ_0 represent the relative and
 151 absolute permittivity respectively. The w_0 is equal to $\left(2\epsilon_r \epsilon_0 / qN\right)^{1/2}$ where, N represents the
 152 charge concentration. At intermediate and strong forward bias the capacitance associated with
 153 the homogenous layer thickness L (thickness of solar cell) is known as diffusion capacitance
 154 or chemical capacitance (C_{LH}), which depends on the minority carrier concentration and
 155 effective density of states in the conduction band, as expressed by following equation [29, 30,
 156 32]:

$$157 \quad C_{LH} = \frac{q^2 L n_0}{k_B T} \exp\left(\frac{qV_j}{k_B T}\right) \quad (5)$$

158 The sign of V_j is positive or negative, depending on whether the diode junction is forward
 159 ($+V_{FB}$) or reverse ($-V_{RB}$) biased. Holes from the p^+ side of the low-high (LH) interface (p - p^+
 160 BSF) diffuse into the p side to form a hole-accumulation layer. The electric field of p - p^+
 161 prevents diffusing electrons from the n^+ - p junction back into p layer. The physical terms of
 162 AC circuit elements (used in Eq. (6)) for fresh solar cell can be described as: R_s represents
 163 series resistance to photo-generated charge carriers while they flow out of the solar cells to
 164 the external contacts, R_j represents junction resistance, R_{LH} represents p - p^+ diffusion
 165 resistance, C_j represents the junction capacitance, C_{LH} represents the p - p^+ capacitance offered
 166 by the high low. If the electrode is non-polarizable, then the system can be modelled by
 167 introducing a resistance R_j parallel to the capacitance C_j , which is known as simplified
 168 Randle's circuit [34]. Eventually, the circuit consists of a series connection of a material
 169 resistance R_s with a parallel combination of a charge transfer resistance R_j and a double layer
 170 capacitance C_j (Fig. 3(a)). The impedance of the system can be written as:

$$171 \quad Z(\omega) = R_s + \frac{R_j}{1 + \omega^2 R_j^2 C_j^2} - j \frac{\omega R_j^2 C_j}{1 + \omega^2 R_j^2 C_j^2} + \frac{R_{LH}}{1 + \omega^2 R_{LH}^2 C_{LH}^2} - j \frac{\omega R_{LH}^2 C_{LH}}{1 + \omega^2 R_{LH}^2 C_{LH}^2} \quad (6)$$

172 The impedance spectra of CS-2 and CS-3 solar cells can be explained by Eq. (7). Further, the
 173 inductive part can be understood in terms of negative capacitance described recently in
 174 reference [36] and shown in Fig. 3(b). As described earlier, a negative capacitance represents
 175 the inductive behaviour of a device with the frequency which is expected to have capacitive
 176 response [37]:

$$177 \quad Z(\omega) = R_s + \frac{R_j}{1 + \omega^2 R_j^2 C_j^2} - j \left(L\omega + \frac{\omega R_j^2 C_j}{1 + \omega^2 R_j^2 C_j^2} \right) + \frac{R_{LH}}{1 + \omega^2 R_{LH}^2 C_{LH}^2} - j \left(L\omega + \frac{\omega R_{LH}^2 C_{LH}}{1 + \omega^2 R_{LH}^2 C_{LH}^2} \right) \quad (7)$$

178

179 4. Results and discussion

180 4.1 DC analysis of PID-s affected solar cell

181 Figure 4(a) shows the J-V characteristics of mc-Si solar cells for the cases CS-1, CS-2
 182 and CS-3 and corresponding data has been listed in Table 1. A drastic reduction in J-V
 183 performance has been observed for CS-2 as compared to CS-1 due to PID-s, where η
 184 decreases from 15.7% to 2.9% after 48 hours of PID-s. The value of η depends on the I_{sc} , V_{oc}
 185 and FF, although J_{sc} has not been affected much by PID-s as compared to V_{oc} . The V_{oc}
 186 decreases significantly from 0.59 V to 0.25 V, which is governed by the value of R_{sh} in Eq.
 187 (1). Under PID-s, R_{sh} has decreased from 3000 Ω to 8.7 Ω indicating a higher level of leakage
 188 path across the junction restricting minority charge carrier accumulation in QNR, which
 189 explains drastic reduction in V_{oc} under PID-s. Moreover, ideality factors n and m have been
 190 obtained from two-diode model (Eq. (1)) for CS-1 as 1.5 and 2.2 respectively. For CS-2 the
 191 values of n and m increased to 2.5 and 3.5, which indicate the increase in recombination in
 192 SCR and QNR regions and degradation in p-n junction. The explanation of increase in
 193 ideality factor is in accordance with Lausch et al. [38]. In the recovered solar cell (CS-3), the
 194 V_{oc} and R_{sh} have increased from 0.25 V to 0.43 V and from 8.7 Ω to 17 Ω respectively,
 195 which can be explained by decrease in leakage path across p-n junction during recovery.
 196 Decrease in reverse saturation current density from $9.42 \times 10^{-5} \text{ mAcm}^{-2}$ to $1.57 \times 10^{-5} \text{ mAcm}^{-2}$

197 further supports the decrease in leakage path. The V_{OC} is related to reverse saturation current
198 density by, $V_{OC} \approx (k_B T/q) \ln(J_{PH}/J_0)$ [39], which indicates that V_{OC} would increase with
199 decrease in J_0 . Figure 4(b) illustrates the junction resistance, R_j with respect to bias voltage.
200 The decrease in shunt resistance, R_{sh} by two order of magnitudes has been observed for CS-2
201 and CS-3 as compared to CS-1. The recombination flux governs the R_j beyond the knee
202 voltage (≈ 0.4 V) as per following expression: $R_j = (dJ_{rec}/dV_j)^{-1}$, where J_{rec} represents
203 recombination current density [29, 33]. The main reason behind higher recombination in
204 CS-2 is the increase in leakage path due to defects, whereas in CS-3 the recombination is
205 lower as compared to CS-2 due to improvement in junction quality due to partial recovery.
206 The nature and distribution of positive ions has been explored in detail through elemental
207 analysis of degraded solar cells.

208

209 **4.2 Correlation of morphological and elemental analysis with electrical characterization**

210 To investigate the effect of PID-s on the surface morphology of mc-Si solar cells at
211 the micro-scale, the PID-s affected solar cells have been characterized by using FESEM.
212 Figure 5 shows the surface morphology and the EDX analysis of mc-Si solar cells after
213 PID-s. It is observed from FESEM image that there are micro-structural defects on the
214 surface of PID-s affected solar cell due to high voltage stress. Moreover, EDX analysis of
215 degraded solar cell reveals that there is a significant amount of sodium impurities with 10
216 at.% of elemental composition (the marked defected region of Fig. 5). The defected region
217 has been further investigated by the EDX mapping of Si, Na, O, N elements as shown in Fig.
218 5. There are three dark spots in Si mapped image, which signifies the absence of Si atoms in
219 that region. By mapping sodium element it is revealed that there is high concentration of
220 sodium atoms at the dark spots. The elemental mapping of O and N shows their uniform
221 presence within the allowed limits. This sodium impurity plays a key role towards the

222 progression of PID-s [23-25]. The micro-structural defects are responsible to initiate the
223 stacking faults through grain boundaries and allow Na^+ to drift through SiN_x layer and finally
224 get a path to penetrate into n^+ -p junction. After entering into n^+ -emitter layer, the Na^+ ions are
225 neutralized by free electrons and their further motion in the stacking fault is governed by
226 diffusion process rather than drift process [40]. In order to explore the effect of sodium
227 impurity on the electrical performance of solar cell, electro-analytical investigation has been
228 carried out using AC IS as detailed in next section.

229

230 4.3 AC impedance analysis of PID-s affected solar cell

231 Figure 6 shows the impedance measurement results of CS-1, CS-2 and CS-3. Figure
232 6(a) demonstrates the Nyquist plots of CS-1 in the bias range from -1 V to +0.3 V. The
233 dotted curve represents the experimental data, which has been fitted with the theoretical AC
234 equivalent circuit governed by Eq. (6) as shown by solid curve. The diameter of impedance
235 spectra (nearly semicircle) increases with the reverse bias due to increase in the width of
236 depletion region, which offers high impedance, whereas, under forward bias, impedance is
237 decreasing due to decrease in the width of depletion region. The R_j increases from 2795 Ω to
238 3607 Ω while increasing reverse bias from 0 V to -1 V and decreases to 350 Ω with forward
239 bias value of 0.3 V. The junction capacitance, C_j of CS-1 varies from 9.79 μF to 1.2 μF for
240 +0.3 V to -1 V. Figure 6(b) shows the AC impedance spectra of PID-s affected solar cell, i.e.
241 CS-2. The R_j increases from 6.15 Ω to 15 Ω while increasing reverse bias and decreases to
242 2.32 Ω with a value of forward bias equal to +0.3 V. The junction capacitance offered by
243 CS-2 varies from 10.9 μF to 0.16 μF for an applied bias of +0.3 V to -1 V. The R_j has
244 decreased for CS-2 as compared to CS-1 due to presence of Na^+ ions creating shunt path
245 across the n^+ -p junction at the deformed regions as confirmed by elemental analysis of
246 defected area shown in Fig. 5. Similar observation has been obtained from DC analysis

247 indicating the increased leakage current across the n^+p junction. Further, the negative
248 capacitance has been observed at higher frequency for bias voltage in the range from 0 V to
249 +0.3 V, which has been attributed to inductive behaviour of n^+p junction originated after
250 PID-s. In general, inductive behaviour occurs when excess charge carriers are injected in a
251 small nanoscale dimension into the material, which gives rise to a negative capacitance.
252 Considering the present work, there are two possible interpretations of negative capacitance
253 for Na^+ contaminated stacking faults under PID-s: (1) The Na^+ impurity injection through
254 stacking faults modulates the bulk conductivity of solar cells, which may yield the inductive
255 nature [41, 42], (2) The presence of excessive Na^+ impurities delocalize the minority charge
256 accumulation process and further leads to an abrupt change in junction capacitance values.
257 This charge delocalization effect may give rise to the occurrence of inductive behaviour [43,
258 44]. The negative capacitance indicates the presence of parasitic inductance and the overall
259 contribution is taken care by a series inductor L as shown in Fig. 6(b). The value of L
260 increases from 0.062 μH to 0.116 μH for CS-2 for applied bias from -1 to +0.3 V. The
261 negative capacitance is attributed to the presence of Na^+ ions across the p-n junction, which
262 creates defects and trap states leading to charge delocalization [36, 45]. Under forward bias
263 condition, electrons fill-up the empty trap states at the interface. Consequently overall charge
264 at interface decreases with increasing bias leading to negative equivalent capacitance. Figure
265 6(c) demonstrates the Nyquist curve for CS-3, the R_j increases from 7.9 Ω to 31.4 Ω for the
266 range of applied bias from +0.3 V to -1 V. The inductance values remain in the range from
267 0.28 μH to 0.46 μH for CS-3, which is high as compared to CS-2. The possible reason behind
268 the increment in R_j as compared to CS-2 is the decrease in leakage path due to reverse
269 migration of Na^+ ions across the junction, but some significant structural deformation has still
270 been contributing towards the irreversible charge dislocation process, which is represented by
271 high value of L in CS-3. Figure 6(d) shows the frequency dependent impedance of CS-1, CS-

272 2 and CS-3 for comparison purpose. The change in R_j and C_j is clearly evident from the
273 values of impedance and slope of the curves for CS-1, CS-2 and CS-3 respectively.

274 Figure 7 shows variation in the time constant with respect to applied bias. The time
275 constant represents the effective life time of charge carriers in the solar cell and has been
276 extracted from the product of R_j and C_j values at maxima of Nyquist plot shown in Fig. 6(a-
277 c). The minority carrier lifetime has been calculated at the voltage of 0.3 V for CS-2 and
278 CS-3 as 0.73 μs and 0.89 μs , which is lower as compared to 4.15 ms for CS-1, thus indicating
279 a higher recombination under the influence of defects created by Na^+ ions.

280

281 4.4 C-V analysis of PID-s affected solar cell

282 Figure 8 shows the Mott-Schottky plot for CS-1 (CS-2 and CS-3 in the insert),
283 governed by following expression: $C_j^{-2} \approx 2(V_{bi} - V_j)/q\epsilon N_A$ [46], where V_{bi} represents the
284 built-in potential, N_A represents the base doping concentration and ϵ represents product of the
285 permittivity of free space and dielectric constant of silicon. The Mott-Schottky curve slope
286 and intercept represents the build-in potential and base doping concentration. The slope

287 $(2/q\epsilon N_A)$ and intercept $(2V_{bi}/q\epsilon N_A)$ of the fitted lines gives a value of V_{bi} and N_A

288 respectively for CS-1, which has been obtained as 0.61 V and $1.13 \times 10^{16} \text{ cm}^{-3}$. Similarly, the
289 V_{bi} and N_A for CS-2 and CS-3 are obtained as 0.26 V, $1.74 \times 10^{17} \text{ cm}^{-3}$ and 0.45 V, 1.20×10^{17}
290 cm^{-3} respectively. The increase in N_A for CS-2 as compared to CS-1 has been attributed to
291 migration of Na^+ ions into the base material. The effect of partial recovery is clearly seen
292 through the reduction of N_A for CS-3 as compare to CS-2, which indicates out diffusion of
293 Na^+ ions during recovery process. The out diffusion also improved V_{bi} as reflected from
294 increase in V_{OC} from 0.25 V to 0.43 V.

295

296 4.5 Raman analysis

297 Raman spectrometry has been proven as the highly efficient characterization
298 technique to probe the lattice defects [47-49], doping concentration [50, 51] and impurities
299 evaluation corresponding to lattice vibrational modes in the materials. The shift and
300 broadening of phonon peaks indicate the lattice strain induced by defects [49]. To investigate
301 Na^+ induced lattice disorder in mc-Si solar cell, the micro-Raman signals have been analysed.
302 Figure 9 depicts the Raman spectra obtained for Initial and PID-s affected cells (taken at
303 different PID-s affected regions named as the PID-1, PID-2 and PID-3 as schematically
304 shown by 1, 2 and 3 in the insert of Fig. 9). A significant variation has been observed for all
305 characteristic peaks over the wide range of wavenumbers from 100 cm^{-1} to 1500 cm^{-1} for
306 PID-s affected solar cell as compared to Initial. First order transverse optical phonon peak
307 (1TO) located at 520 cm^{-1} has been obtained for initial mc-Si solar cells, whereas for PID-s
308 affected solar cells intensity of 1TO strongly decreases and slightly shifts towards higher
309 frequency. The decreasing intensity and shift is mainly attributed to Na^+ induced localized
310 defects in PID-s affected solar cells, which is more evident for PID-3 (most defected/dark
311 region) as compared to initial. This observation has a strong correlation with EDX analysis
312 (see Fig. 5) which is showing a higher concentration of Na^+ defects for PID-3 and
313 correspondingly reflects the decrease in order of crystallinity of Si material [47]. In addition,
314 optical phonons are strongly affected by the presence of Na^+ impurities due to their small
315 coherence length which gives information about local environment. Whereas, large coherence
316 length of acoustic phonons gives an ease to investigate deeply buried lattice delocalization
317 caused by Na^+ induced defects. The broad peaks at 302 and 940 cm^{-1} correspond to the
318 second order transverse acoustic phonon mode (2TA) and transverse optical phonon mode
319 (2TO) for the initial and PID-s affected regions. Similar observations have been found for
320 second order overtone peaks with decrease in intensity at the PID-s affected regions (302 and

321 940 cm^{-1} in Fig. 8). Moreover, at higher frequency other characteristic peaks have been
322 observed for highly affected region, PID-3. These peaks are mostly influenced by higher
323 concentration of Na^+ impurities located at deformed region that causes a significant
324 deterioration in local crystallinity of solar cell due to PID-s.

325

326 5. Conclusions

327 In this article, PID-s has been investigated by applying high voltage stress on mc-Si solar cell
328 and results have been explained using electrochemical analysis by DC and AC
329 characterization. Reduction in electrical performance due to PID-s has been explained by
330 morphological, structural and elemental analysis. Furthermore, observed negative capacitance
331 behaviour in impedance spectra of mc-Si solar cells after PID-s has been attributed to
332 structural deformation caused by potential induced migration of Na^+ into mc-Si. The Na^+ ion
333 migration has been analysed using non-destructive and lattice strain sensitive micro-Raman
334 spectroscopy. The decrease in efficiency from 15.7% to 2.9% due to the applied voltage of
335 -800V at 85°C for 48 hours has been explained through the reduction in shunt resistance,
336 increase in depletion and diffusion capacitances and lattice disorder.

337

338 Conflicts of interest

339 There are no conflicts of interest to declare.

340

341 Acknowledgements

342 The authors acknowledge Solar Research and Development Centre (SRDC), PDPU for
343 providing the facilities and support.

344

345 References

- 346 1. G. Mon, L. Wen, R. Ross and D. Adent, Proceedings of the 18th IEEE Photovoltaic
347 Specialists Conference, Las Vegas, NV, USA, 1985, pp. 1179–1185.
- 348 2. S. Pingel, O. Frank, M. Winkler, S. Daryan, T. Geipel, H. Hoehne and J. Berghold,
349 Proceedings of the 35th IEEE Photovoltaic Specialists Conference, Honolulu, HI, USA, 2010,
350 pp. 2817–2822.
- 351 3. S. Pingel, O. Frank, M. Winkler, S. Daryan, T. Geipel, H. Hoehne and J. Berghold,
352 Proceedings of the 35th IEEE Photovoltaic Specialists Conference, Honolulu, HI, USA,
353 2010, pp. 2817–2822.
- 354 4. P. Hacke, K. Terwilliger, S. Glick, D. Trudell, N. Bosco, S. Johnston and S. Kurtz,
355 Proceedings of the 35th IEEE Photovoltaic Specialists Conference, Honolulu, HI, USA, 2010,
356 pp. 000244–000250.
- 357 5. M. Köntges, S. Kurtz, C.E. Packard, U. Jahn, K. Berger, K. Kato, T. Friesen, H. Lui and
358 M.V. Iseghem, Review of Failures of Photovoltaic Modules, Performance and Reliability of
359 Photovoltaic Systems, External final report IEA-PVPS, March 2014.
- 360 6. Government announces Trajectory to achieve its targets of commissioning 100 GW of
361 Solar generating capacity and 60 GW of Wind power by 2022.
362 <http://pib.nic.in/newsite/PrintRelease.aspx?relid=173830> (accessed on 22-06-2018).
- 363 7. J. Berghold, S. Koch, S. Pingel, S. Janke, A. Ukar, P. Grunow and T. Shioda, Proceedings
364 of SPIE, San Diego, CA, USA, 2015, vol. 9563, pp. 95630A.
- 365 8. P. Hacke, R. Smith, K. Terwilliger, G. Perrin, B. Sekulic and S. Kurtz, Prog. Photovoltaics,
366 2014, 22, 775–783.
- 367 9. P. Hacke, K. Terwilliger, R. Smith, S. Glick, J. Pankow, M. Kempe, S. K. I. Bennett and
368 M. Kloos, Proceedings of the 37th IEEE Photovoltaic Specialists Conference, Seattle, WA,
369 USA, 2011, pp. 000814–000820.

- 370 10. M. Schütze, M. Junghänel, M. Koentopp, S. Cwikla, S. Friedrich, J. Müller and P. Wawer,
371 Proceedings of the 37th IEEE Photovoltaic Specialists Conference, Seattle, WA, USA, 2011,
372 pp. 000821–000826.
- 373 11. N. G. Dhere, N. S. Shiradkar and E. Schneller, IEEE Journal of Photovoltaics, 2014, 4,
374 654–658.
- 375 12. J. Berghold, O. Frank, H. Hoehne, S. Pingel, B. Richardson and M. Winkler, Proceedings
376 of the 25th European Photovoltaic Solar Energy Conference and Exhibition, Valencia, Spain,
377 2010, pp. 3753–3759.
- 378 13. S. Pingel, O. Frank, M. Winkler, S. Daryan, T. Geipel, H. Hoehne and J. Berghold,
379 Proceedings of the 35th IEEE Photovoltaic Specialists Conference, Honolulu, HI, USA,
380 2010, pp. 2817–2822.
- 381 14. J. Berghold, S. Koch, B. Frohmann, P. Hacke and P. Grunow, Proceedings of the 40th
382 IEEE Photovoltaic Specialists Conference, Denver, CO, USA, 2014, pp. 1987–1992.
- 383 15. S. Yamaguchi, A. Masuda and K. Ohdaira, Sol. Energy Mater. Sol. Cells, 2016, 151,
384 113–119.
- 385 16. M. López-Escalante, L.J. Caballero, F. Martín, M. Gabás, A. Cuevas and J. Ramos-
386 Barrado, Sol. Energy Mater. Sol. Cells, 2016, 144, 691–699.
- 387 17. J. Kapur, A. Bennett, J. Norwood, B. Hamzavytehrany and I. Kueppenbender,
388 Proceedings of the 28th European Photovoltaic Solar Energy Conference and Exhibition,
389 Paris, France, 2013, pp. 476–479.
- 390 18. M. Kambe, K. Hara, K. Mitarai, S. Takeda, M. Fukawa, N. Ishimaru and M. Kondo,
391 Proceedings of 42nd IEEE Photovoltaic Specialist Conference, Tampa, FL, USA, 2013, pp.
392 3500–3503.
- 393 19. J. Oh, S. Bowden and G. TamizhMani, IEEE Journal of Photovoltaics, 2015, 5, 1540–
394 1548.

- 395 20. M.B. Koentopp, M. Krober and C. Taubitz, *IEEE Journal of Photovoltaics*, 2016, 6, 252–
396 257.
- 397 21. S. Pingel, S. Janke and O. Frank, *Proceedings of the 27th European Photovoltaic Solar*
398 *Energy Conference and Exhibition*, Frankfurt, Germany, 2012, pp. 3379–3383.
- 399 22. P. Hacke, K. Terwilliger, R. Smith, S. Glick, J. Pankow, M. Kempe, S.K.I. Bennett and
400 M. Kloos, *Proceedings of the 37th IEEE Photovoltaic Specialists Conference*, Seattle, WA,
401 USA, 2011, pp. 000814–000820.
- 402 23. V. Naumann, D. Lausch, S. Großer, M. Werner, S. Swatek, C. Hagendorf and J. Bagdahn,
403 *Energy Procedia*, 2013, 33, 76–83.
- 404 24. V. Naumann, D. Lausch, A. Graff, M. Werner, S. Swatek, J. Bauer, A. Hähnel, O.
405 Breitenstein, S. Großer and J. Bagdahn, *Phys. Status Solidi RRL*, 2013, 7, 315–318.
- 406 25. P. Hacke, R. Smith, K. Terwilliger, S. Glick, D. Jordan, S. Johnston, M. Kempe and S.
407 Kurtz, *Proceedings of the 38th IEEE Photovoltaic Specialists Conference*, Austin, TX, USA,
408 2012, pp. 1–8.
- 409 26. S. Yamaguchi, A. Masuda and K. Ohdaira, *Jpn. J. Appl. Phys.*, 2016, 55, 04ES14.
- 410 27. B. Ziebarth, M. Mrovec, C. Elsässer and P. Gumbsch, *J. Appl. Phys.*, 2014, 116, 093510.
- 411 28. J. Parka, M. Chan, *J. Appl. Phys.*, 2018, 123, 161560.
- 412 29. J.E. Garland, D.J. Crain, J.P. Zheng, C.M. Sulyma and D. Roy, *Energy Environ. Sci.*,
413 2011, 4, 485–498.
- 414 30. J.E. Garland, D.J. Crain and D. Roy, *Sol. Energy*, 2011, 85, 2912–2923.
- 415 31. R.A. Kumar, M.S. Suresh and J. Nagaraju, *IEEE Trans. Power Electron.*, 2006, 21, 543–
416 548.
- 417 32. I. Mora-Sero, G. Garcia-Belmonte, P.P. Boix, M.A. Vazquez and J. Bisquert, *Energy*
418 *Environ. Sci.*, 2009, 2, 678–686.

- 419 33. P. Yadav, B. Tripathi, K. Pandey and M. Kumar, *Phys. Chem. Chem. Phys.*, 2014, 16,
420 15469.
- 421 34. D.J. Crain, S. E. Rock, J. E. Garland and D. Roy, *Curr. Appl. Phys.*, 2013, 13, 2087–
422 2097.
- 423 35. M.I. Oprea, *Proceeding of the 43rd IEEE Photovoltaic Specialists Conference (PVSC)*,
424 Portland, OR, 2016, pp. 1575-1579.
- 425 36. J. Panigrahi, Vandana, R. Singh, N. Batra, J. Gope, M. Sharma, P. Pathi, S.K. Srivastava,
426 C.M.S. Rauthan and P.K. Singh, *Sol. Energy*, 2016, 136, 412–420.
- 427 37. M. Ershov, H.C. Liu, L. Li, M. Buchanan, Z.R. Wasilewski and A.K. Jonscher, *IEEE*
428 *Trans. Electron Devices* 1998, 45, 2196–2206.
- 429 38. D. Lausch, V. Naumann, O. Breitenstein, J. Bauer, A. Graff, J. Bagdahn and C.
430 Hagendorf, *IEEE Journal of Photovoltaics*, 2014, 4, 834–840.
- 431 39. C.S. Solanki, *Solar Photovoltaics: Fundamental, technologies and applications*, Prentice
432 Hall, India, 2nd ed., 2011.
- 433 40. W. Luo, Y. Khoo, P. Hacke, V. Naumann, D. Lausch, S. P. Harvey, J. P. Singh, J. Chai,
434 Y. Wang, A. G. Aberle and S. Ramakrishna, *Energy Environ. Sci.*, 2017, 10, 43-68.
- 435 41. J.J.H. Van den Biesen, *Solid-St. Electron.*, 1990, 33, 1471-1476.
- 436 42. M.A. Green and M.W. Gunn, *Phys. Status Solidi (a)*, 1973, 19, K93.
- 437 43. I. Mora-Sero, J. Bisquert, F. Santiago and G. Belmonte., *Nano Lett.*, 2006, 6, 640-650.
- 438 44. A. Zohar, N. Kedem, I. Levine, D. Zohar, A. Vilan, D. Ehre, G. Hodes and D. Cahen,
439 *Phys. Chem. Lett.* 2016, 7, 191–197.
- 440 45. X. Wu, E.S. Yang, and H.L. Evans, *J. Appl. Phys.*, 1990, 68, 2845.
- 441 46. A. Goetzberger, J. Knobloch and B. Voss, *Crystalline silicon solar cells*, J. Wiley, New
442 York, 1998.

443 47. C. Villeneuve, V. Paillard, K.K. Bourdelle, I. Cayrefourcq, A. Boussagol and M.
444 Kennard, Nuclear Instruments and Methods in Physics Research Section B: Beam
445 Interactions with Materials and Atoms, 2006, 253, 182-186.

446 48. N. M. Johnson, F. A. Ponce, R. A. Street and R. J. Nemanich, Phys. Rev. B, 1987, 35,
447 4166.

448 49. G. Popovici, G. Y. Xu, A. Botchkarev, W. Kim, H. Tang, A. Salvador and H. Morkoç, R.
449 Strange and J. O. White, J. Appl. Phys., 1997, 82, 4020.

450 50. H. Q. Ni, Y. F. Lu, Z. Y. Liu, H. Qiu, W. J. Wang, Z. M. Ren, S. K. Chow and Y. X. Jie,
451 Appl. Phys. Lett., 2001, 79, 812.

452 51. M. Becker, U. Gösele, A. Hofmann and S. Christiansen, J. Appl. Phys., 2009, 106,
453 074515.

454

455

456

457

458

459

460

461

462

463

464

465

466

467

468 **Table 1:** Performance parameters of solar cells extracted from DC characterization

Parameters	J_{SC} (mA)	V_{OC} (V)	J₀₁ (mA cm⁻²)	J₀₂ (mA cm⁻²)	R_s (Ω)	R_{sh} (Ω)	n	m	FF (%)	η (%)
CS-1	38.06	0.59	8.48 ×10 ⁻⁹	3.88 ×10 ⁻⁶	0.8	3000	1.5	2.2	70	15.7
CS-2	38.31	0.26	9.42 ×10 ⁻⁵	5.33 ×10 ⁻⁴	1.5	8.7	2.5	3.5	29	2.9
CS-3	37.66	0.42	1.57 ×10 ⁻⁵	1.46 ×10 ⁻⁴	1.5	17	2.5	3.5	34	5.4

469

470

471

472 **Figure captions:**

473

474 **Figure 1:** Cross-sectional schematic diagram of PID setup.

475 **Figure 2:** Two-diode model DC equivalent circuit.

476 **Figure 3:** (a) J-V characteristics of measured CS-1, CS-2 and CS-3 solar cells, with two-
477 diode model fitted curves, (b) Junction resistance with respect to DC bias voltage.

478 **Figure 4:** AC equivalent circuits of PID-s affected solar cells (a) CS-1 and (b) CS-2.

479 **Figure 5:** FESEM analysis of PID-s affected solar cell with EDX mapping.

480 **Figure 6:** Nyquist curves of (a) CS-1 (b) CS-2 and (C) CS-3 solar cells, (d) Comparative
481 frequency-impedance behaviour of three cases.

482 **Figure 7:** Effective minority carrier lifetime versus applied voltage bias.

483 **Figure 8:** Mott–Schottky response of mc-Si solar cell for CS-1, CS-2 and CS-3.

484 **Figure 9:** Micro-Raman spectra of initial (CS-1) and PID-s affected solar cell (PID-1, PID-2
485 and PID-3 represent data obtained from PID-s affected regions as marked by 1, 2 and 3 in the
486 insert).

487

488

489

490

491

492

493

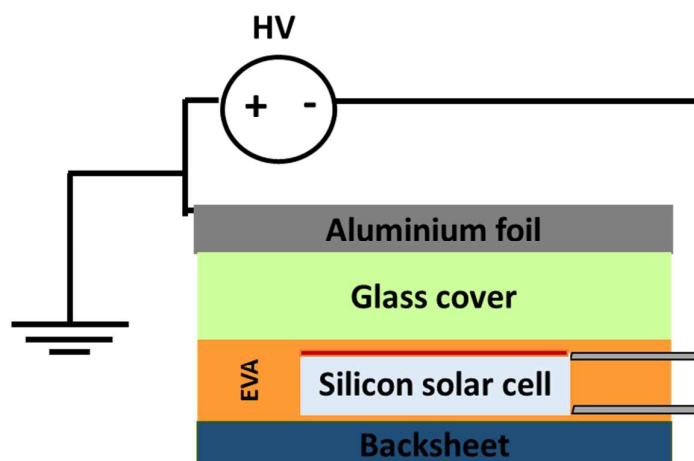
494

495

496

497

498

499 **Figure 1:**

500

501

502

503

504

505

506

507

508

509

510

511

512

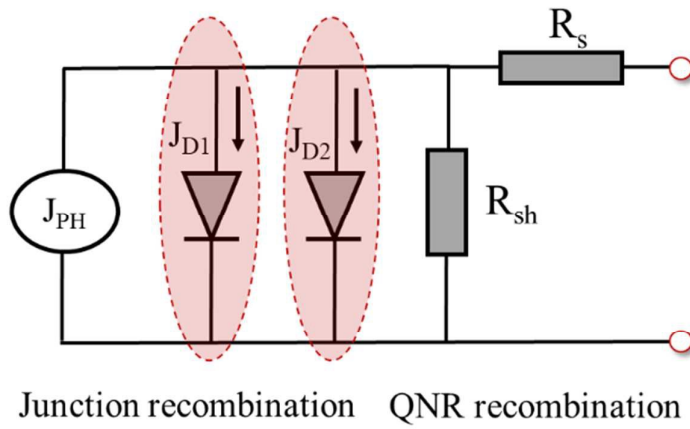
513

514

515

516

517

518 **Figure 2:**

519

520

521

522

523

524

525

526

527

528

529

530

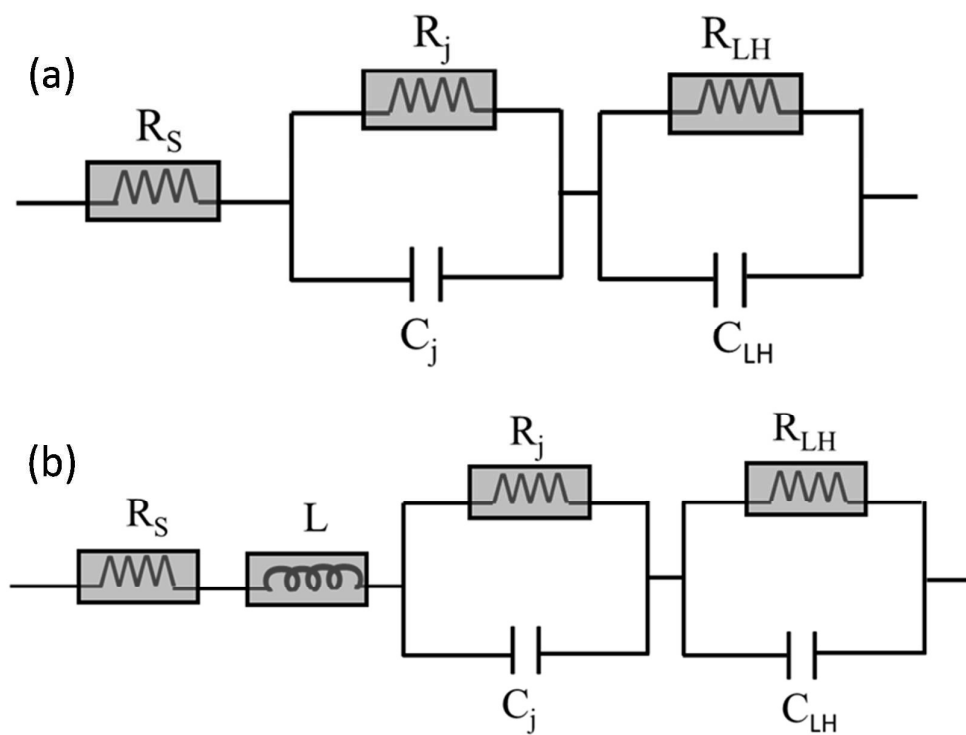
531

532

533

534

535

536 **Figure 3:**

537

538

539

540

541

542

543

544

545

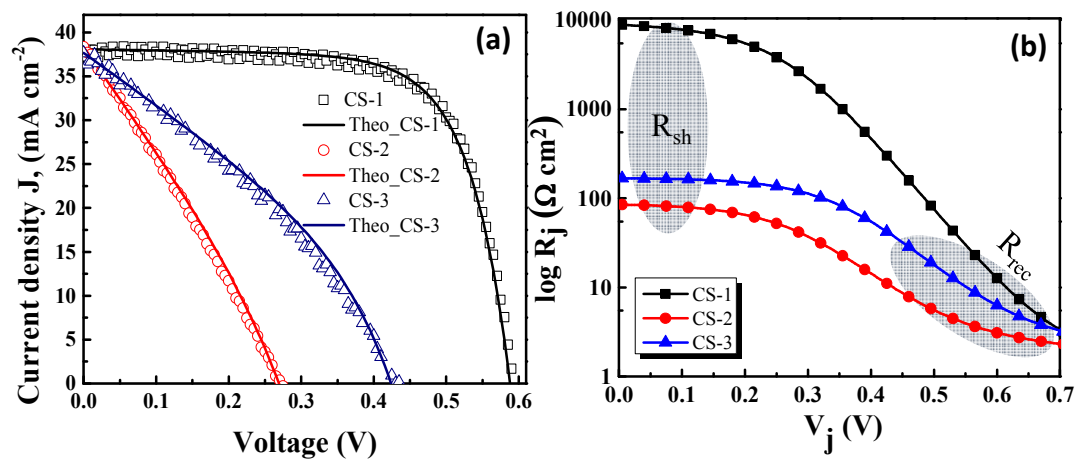
546

547

548

549

550

551 **Figure 4:**

552

553

554

555

556

557

558

559

560

561

562

563

564

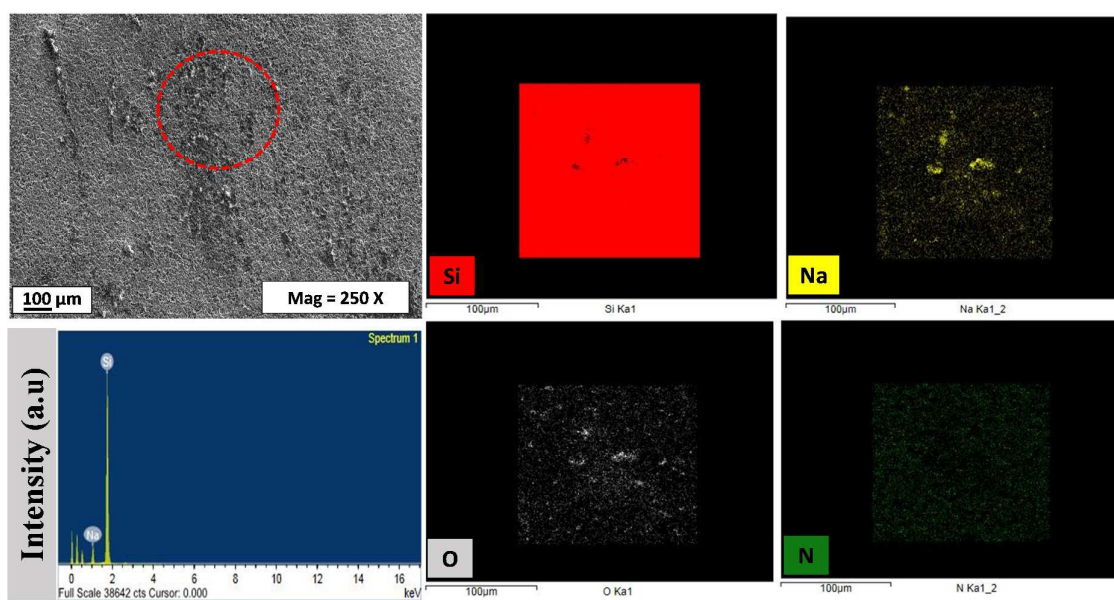
565

566

567

568

569

570 **Figure 5:**

571

572

573

574

575

576

577

578

579

580

581

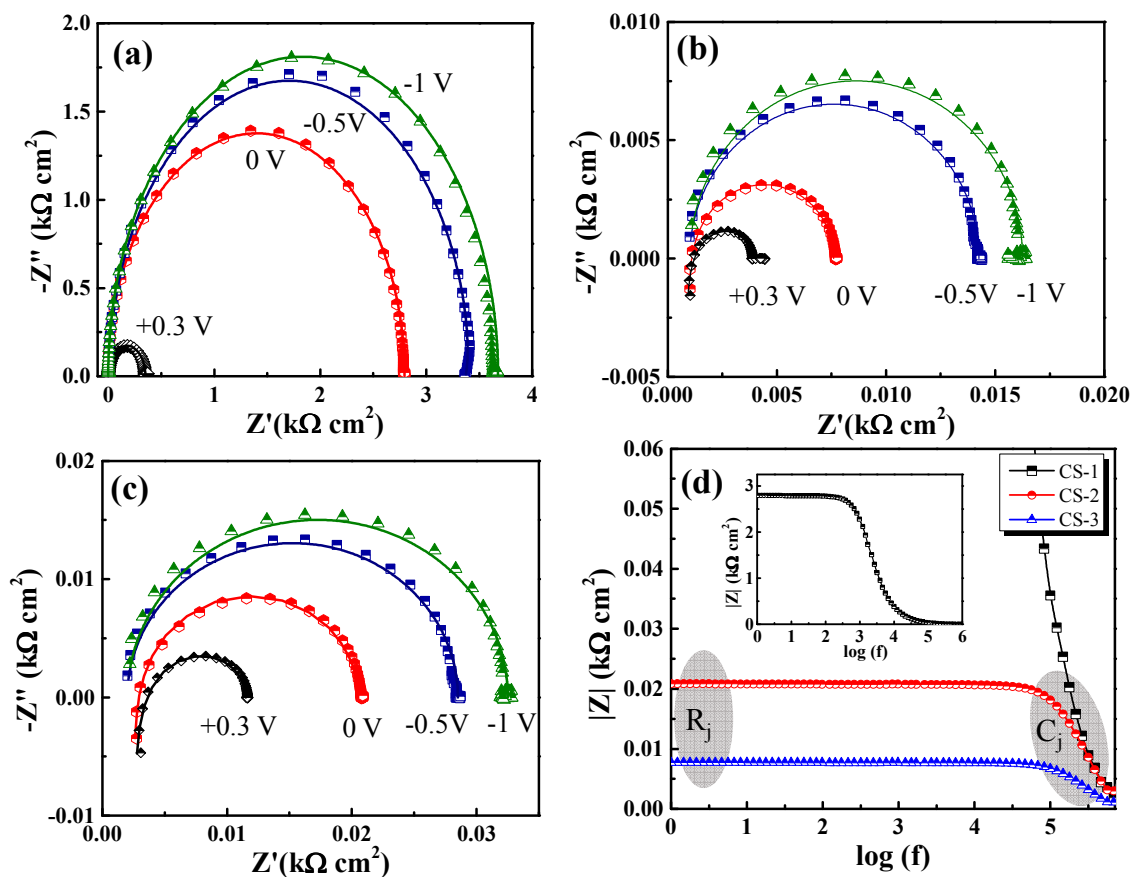
582

583

584

585

586

587 **Figure 6:**

588

589

590

591

592

593

594

595

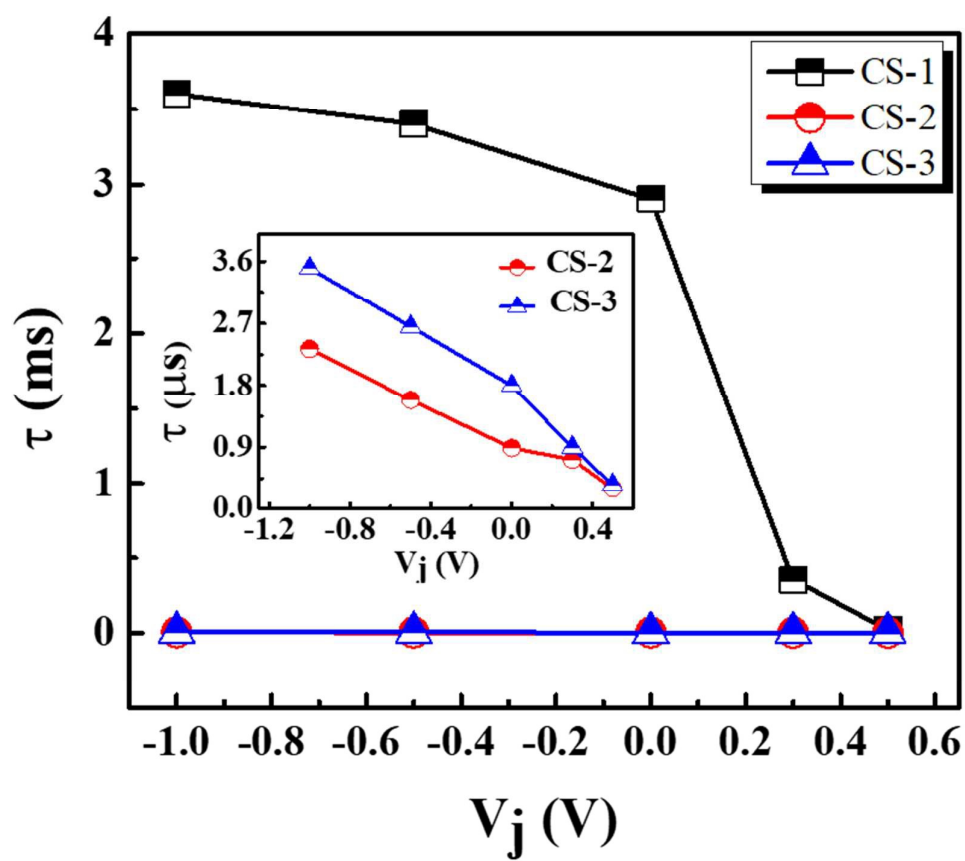
596

597

598

599

600 Figure 7:



601

602

603

604

605

606

607

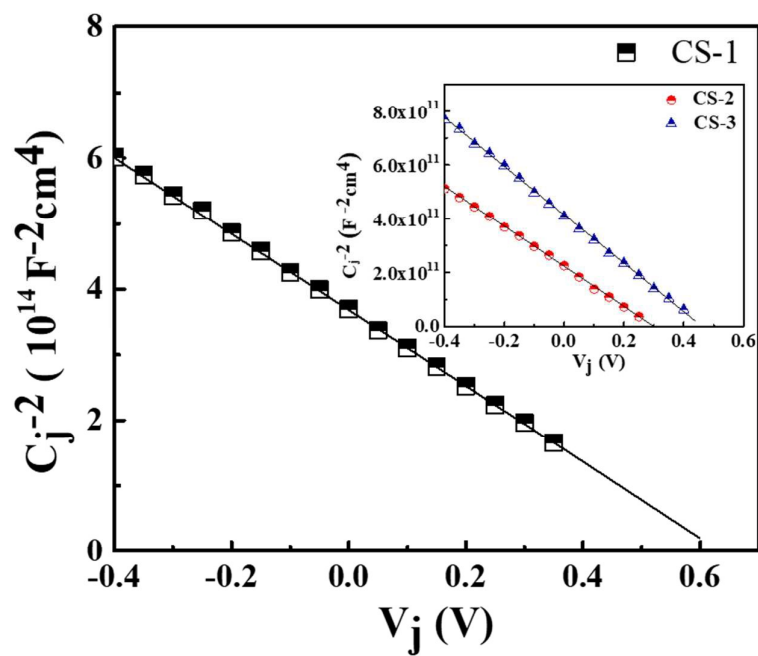
608

609

610

611

612

613 **Figure 8:**

614

615

616

617

618

619

620

621

622

623

624

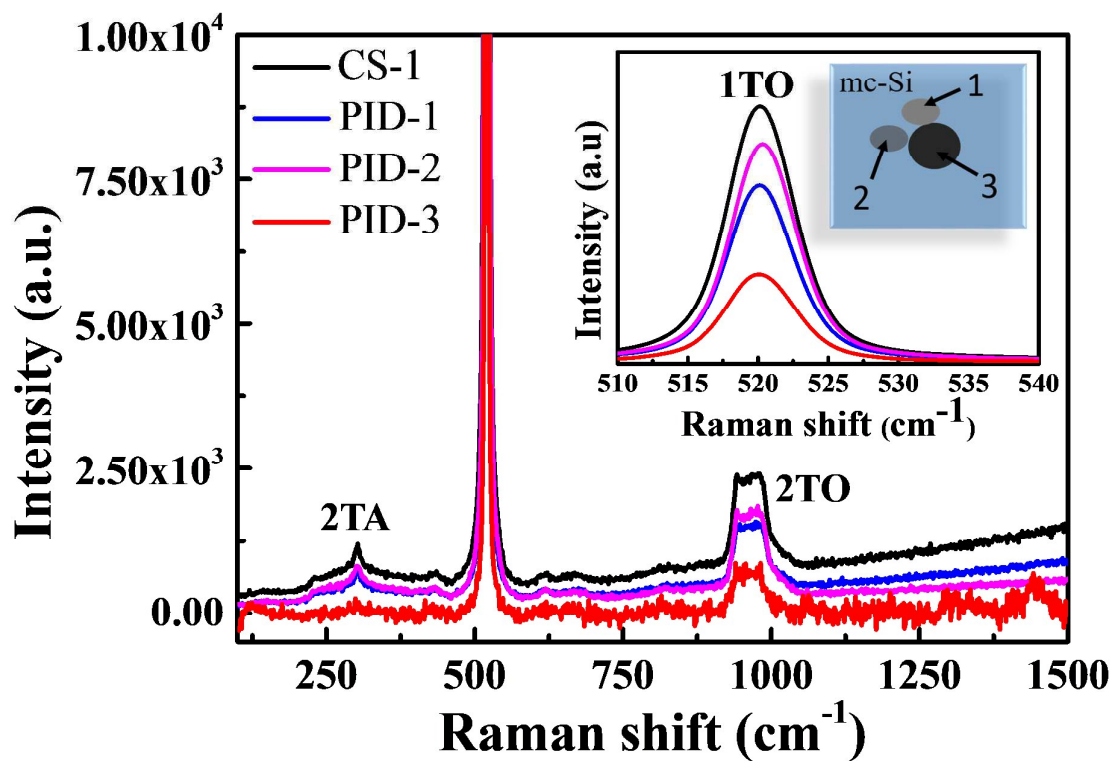
625

626

627

628

629

630 **Figure 9:**

631

632