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Wide optical gap B-doped nc-Si thin films of advanced crystallinity and conductivity on transparent flexible substrates for potential low-cost flexible electronics including nc-Si superstrate $p$-$i$-$n$ solar cells

Debajyoti Das* and Chandralina Patra

Current boost in the flexible energy harvesting devices demands fabrication on non-rigid, light-weight and cheap substrates to enable roll-to-roll process technology economically viable. The B-doped nc-Si films of $\sim$82.5% crystallinity with $\sim$9.63 nm average grain size, $\sim$1.836 eV optical band gap and $\sim$2.02 $S$ cm$^{-1}$ electrical conductivity are grown from SiH$_4$ without deliberate H$_2$-dilution, on optically transparent flexible PET-substrates at around 30–100 $^\circ$C, facilitated by the inherent high electron-density of the low pressure plasma in inductively coupled (ICP) plasma-CVD and strain-induced nanocrystallization kinetics at the incubation-layer originating from substrate surface-bending via plasma-heating. It is appraised that a better compliance is attained on the flexible PET substrate by means of its surface deformation that provides efficient intrinsic stress relaxation during growth of the film network via energy transfer across the film-substrate interface and that triggers prompt crystallization in the film network, compared to that on glass substrate and also at relatively low growth temperature. Films are of significant characteristics suitable for low-cost flexible electronics and exclusively for using as window layers in nc-Si superstrate $p$-$i$-$n$ solar cells even at ambient temperature.

Introduction

Crystalline silicon wafers and transparent glasses are the two commonly used rigid substrates for the fabrication of conventional devices. Currently, the flexible devices produced on plastic substrates are of significant interest because of its advantages in assembling, role-to-role industrial manufacturing, convenience in transportation and above all being cost-effective. However, lower melting point of the plastic substrates limits its compatibility in producing device grade semiconductor nanostructures of good opto-electronic properties and stability, and makes it challenging in state-of-the-art device manufacturing, in general.

Silicon is the backbone of semiconductor engineering, however, within the family of Si-species nanocrystalline silicon (nc-Si) is the unique two-phase photovoltaic material, accommodating high carrier-mobility, better dopability and significantly reduced light-induced-degradation compared to its a-Si counterpart, and simultaneously providing lower production cost compared to its c-Si complement. Combining superior electrical conductivity with the wide optical band gap together, B-doped nc-Si films are exclusively used as both emitter-layer in heterojunction solar cells and window-layer in nc-Si solar cells with $n$-$i$-$p$ structure and $p$-$i$-$n$ superstrate configuration, in particular, by facilitating essential lattice-matching at the intrinsic nc-Si interface, apart from its many other applications in flexible electronics.

Current boost in the flexible energy harvesting devices demands fabrication of solar cells on non-rigid, light-weight, and cheap substrates, e.g., different polymers like, PET, PEN, PI films and various cellulose papers, including photo-paper (PP). For flexible solar cell fabrication, low temperature growth of nc-Si films in MOS-technology compatible plasma processing is essentially pursued via using high H$_2$-dilution to the SiH$_4$-precursors or applying high electrical power and/or substrate bias. However, elevated H$_2$-dilution adversely reduces the growth-rate that enhances the device fabrication-cost in turn, and high electrical power and/or substrate bias cause damage on the front face of the substrate and affect the substrate-film interface, being particularly harmful for the films grown on flexible substrates.

In the present work B-doped ($p$-type) nc-Si films delivering significant crystallinity, superior electrical conductivity as well as broad optical band gap are developed at around 30–100 $^\circ$C on optically transparent and physically flexible substrates compatible for manufacturing of nc-Si superstrate $p$-$i$-$n$ solar cells. A single-step processing in spontaneous RF-plasma (13.56 MHz) of SiH$_4$, without deliberate H$_2$-dilution, was employed at a low pressure (~mTorr) in planar inductively coupled plasma (ICP) CVD with its inherent high electron-density retaining intense atomic-H population at the vicinity of the growth zone.
Experimental

Using only 2 sccm SiH₄ and 10 sccm B₂H₆ (1% in H₂) gases in 13.6 MHz RF powered planar ICP-CVD reactor maintained at 40 mTorr, B-doped nc-Si thin films were deposited on Corning Eagle 2000™ rigid glass, photo-plate (Kodak Company, USA) as well as polyethylene terephthalate (PET) (EM6, Garware polyester limited, India) polyester-film flexible substrates maintained at temperature (Tₛ) varying from 30 (RT) to 150 °C. The glass as well as flexible substrates were cleaned by ultrasonication in ethanol for 10 minutes, followed by N₂ gas blow-drying. The thickness of the grown films was measured by Dektak stylus 6 M profilometer and also from the transmission measurement. For structural characterization, Renishaw inVia micro-Raman spectrophotometer was used with excitation source 514 nm Ar+ laser of power ~2 mW cm⁻² in a back-scattering geometry. The crystallographic orientations were monitored using a Cu-Kα X-ray radiation (~1.5418 Å) source with a Bragg refraction arrangement (Seifert 3000P). Structural studies in terms of various bonding of Si and H was performed via Fourier transformed infrared absorption of the films deposited on p-type <111> c-Si polished substrates and using Nicolet Magna-IR 750 FTIR spectrometer. The high-magnification transmission electron microscope (JEOL JSM 2010) functioning at 200 kV was used to obtain the TEM images in ~30 nm thin films grown on Cu micro-grids pre-coated by carbon. The surface morphology was studied by field-emission scanning electron microscope (FE-SEM, JEOL-JSM-6700F) and further by atomic force microscope (AFM; Bruker AXS). The elemental composition (B/Si ratio) of the films was estimated using Omicron X-ray (Mg Kα) photoelectron spectrometer. The UV–vis optical data was acquired from double-beam spectrophotometer (Hitachi 330). Co-planer parallel Al electrodes with a gap of 1 mm were deposited on the films by thermal evaporation, for measuring the dc electrical conductivity in a high vacuum (~5 x 10⁻⁵ Torr) system and by a Keithley 6517A electrometer.

Results

The Raman spectra of p–nc-Si thin-films prepared on Corning Eagle 2000™ glass, polyethylene terephthalate film (PET) and photo-plate (PP) substrates at different temperature (Tₛ), shown in Fig. 1(a–c), identify an analogous asymmetric distribution with a dominant Lorentzian-peak at ~520 cm⁻¹ related to transverse-optical (TO) vibration-mode of c-Si. The spectral line-width gradually broadened accompanied by a red-shift of the peak on lowering of Tₛ, which might occur due to miniaturization of the nanocrystals or via strain-relaxation at the network. However, a dominant Gaussian component-peak at 480 cm⁻¹ in case of photo-plate substrate demonstrates substantial presence of a-Si fraction in the network that gradually increased at lower Tₛ. Considering an ultra-nanocrystalline Si (size of nanocrystals < 3 nm) component-peak at 510 cm⁻¹ as part and portion of the network crystallinity, the proportional strength of crystalline volume fraction (χc) in each case was assessed via conventional procedure followed earlier:24

\[
\chi_c = \frac{I_{nc-Si}}{I_{nc-Si} + I_{a-Si} + I_{c-Si}}
\]

where, Iₙₙ stands for the integrated area under each individual satellite component x in corresponding deconvoluted spectrum, as shown in a typical deconvolution in Fig. 1(d).

As plotted in Fig. 1(e), the network crystallinity (χc) of B-doped nc-Si films reduced from the lowest, only 80.2% at Tₛ= 150 °C, and that further reduced very fast at lower Tₛ, attaining ~69.1% at Tₛ= 30 °C; while it reduced only marginally in other two cases. On glass substrate crystallinity (χc) of the p–nc-Si films reduced from 82.2 to 78.9%, and interestingly, on PET-substrates the crystallinity was marginally higher all along and that reduced from ~83.6 to only 80% on lowering in Tₛ from 150 to 30 °C. The nanocrystalline size (D_Raman) was evaluated from the shift of nc-Si peak, using standard process,25 following:

\[
D_{Raman} = 2\pi \frac{\sqrt{\Delta\omega}}{\sqrt{20}}
\]

where, Δω presents the nc-Si peak-shift with reference to the c-Si peak positioned at 520.8 cm⁻¹ and β= 2 nm² cm⁻¹. On flexible substrates, in general, nanocrystals were of larger size, ~16.7 nm on PET and ~82.2% at Tₛ= 150 °C [inset of Fig. 1(d)] that reduced sharply to 9.6 nm at lower Tₛ ~100 °C and further to 6.5 nm at Tₛ= 30 °C. On photographic plate the nanocrystals, however, attained virtual saturation in size, ~5±0.2 nm at Tₛ < 100 °C; while on glass-substrate it remained virtually unchanged at ~±0.3 nm over the entire temperature range 30 °C ≤ Tₛ ≤ 150 °C. Apart from due to changes in grain size, the shift of the Raman peak occurred via generation of stress within the network,25 which might be the reasons for obtaining grossly increased size of the nanocrystals in general on flexible substrates, particularly at Tₛ > 100 °C, once mechanical deformation seems feasible than on glass, and also due to increased dopant incorporation at elevated Tₛ.26
corresponding to each crystallographic orientation was estimated from the FWHM ($\beta$) of the XRD peaks, using Scherrer’s equation $^{23,25}$

$$D_{XRD} = 0.9 \lambda / \beta \cos \theta$$

(3)

and are plotted in Fig. 2(f), along with $D_{Raman}$, as a function of growth temperature. The crystallite size estimated from the Raman data, $D_{Raman}$, presents the average size of crystals of different orientations, which closely matches with those of the <220> $D_{XRD}$ and <311> $D_{XRD}$ data. However, <111> $D_{XRD}$ appears larger in magnitude. Similar deviation from the Raman data as well as TEM estimation was also evident in earlier report, particularly for growth temperatures ($T_s$) $\leq$ 200 $^\circ$C. $^{31}$

In general, it was reported in earlier works $^{32-35}$ that depending on different parametric changes when the grain size reduces, the crystalline volume fraction in the network deteriorates. However, it was also demonstrated for the Si-nc growth in nc-Si/a-SiC and nc-Si/a-SiO$_2$ mixed phase network $^{36,37}$ that in spite of reducing grain size, the crystallinity could improve via rapid increase in the number density of even smaller crystallites. In the present case, on gradual lowering in growth temperature, the crystalline volume fraction of the p-nc-Si network reduces systematically, however, the nature of changes seem to grossly vary on the substrate materials characteristics. In addition, comparing the data relating the changes in crystalline volume fraction in Fig. 1(e) and the corresponding grain size at the inset in Fig. 1(d) it is apparent that the number density of crystallites are, in general, lower on flexible photo-plate substrates than that on glass, and the number density further reduces very fast at $T_s$ $<$ 75$^\circ$C, altogether revealing inferior crystallinity in the p-nc-Si network all along, compared to that on glass substrates. While, superior crystallinity is attained in the p-nc-Si network grown on PET substrates by virtue of larger size of the nanocrystallites along with their non-dimining number density at reduced growth temperature.

Changes in the chemical structure of the films in terms of different Si–H bonding configurations and the amount of bonded-H $(C_H)$ in film network had been investigated via infrared vibrational studies on films deposited on p-type <111>-c-Si substrates. Fig. 3(a-b) presents the Si–H wagging and Si–H stretching vibration modes of the films prepared at different $T_s$, along with their deconvolutions into various satellite components of Si–H wagging and rocking modes, their mono-, di- and tri-hydrde stretching modes, along with the Si–H–Si platelet like configurations present in the matrix. The amounts of bonded-H $(C_H)$ in the films were estimated using the equation: $^{37,38}$

$$C_H = \frac{A_H}{N_{Si}} \frac{\alpha^2}{\beta} \int \frac{d\omega}{\omega} \times 100 \text{ at.\%}$$

(4)

where, $N_{Si} = 5 \times 10^{22}$ cm$^{-3}$ presents the atomic density of c-Si, $A_H = 1.6 \times 10^{13}$ cm$^{-2}$, the oscillator strength and $\int \frac{d\omega}{\omega}$ corresponds to the integrated absorption by the Si-H wagging mode component around 620 cm$^{-1}$.

Furthermore, from the deconvoluted stretching mode absorption components, the microstructure factor ($R$), related to the poly-hydrde fraction of the network, $R = (I_{SiH3} + I_{SiH2})/(I_{SiH3} + I_{SiH2} + I_{SiH} + I_{Si-H-Si})$ (5) and the surface passivation index ($\delta$), identified by the Si–H–Si platelet like component present in the matrix, $^{38-39}$

Fig. 2. XRD spectra of p-nc-Si thin-film on (a) glass and (b) PET-substrate. Zoomed-in spectrum of (c) virgin PET substrate and (d) nc-Si film on PET substrate. (e) Intensity difference of XRD signal, identifying presence of <220>-nc-Si peak as the sample response, removing the substrate effect. (f) Variation of the size ($D_{Raman}$) of nanocrystallites of different crystallographic orientations with $T_s$, and its comparison with that ($D_{XRD}$) estimated from the Raman data, for the p-nc-Si films deposited on glass substrates.

The XRD spectra in Fig. 2(a), for samples on glass-substrates, identify the <111>, <220> and <311> planes of c-Si, corresponding to sharp peaks at 2$\theta$ ~ 28.3°, 47.2° and 57.2°, respectively, demonstrating good crystallinity of the network grown even at a low $T_s$ ~ 60 $^\circ$C. For the PET-substrate XRD peak at around 20 ~ 27° was so intense that other two peaks at ~47° and 55° appeared imperceptible [Fig. 2(b)]. However, careful analysis via subtraction of the zoomed-in spectrum of virgin-substrate [Fig. 2(c)] from sample-on-substrate data [Fig. 2(d)] clearly identify, in Fig. 2(e), the presence of sharp <220>-diffraction peak of Si nanocrystallites on flexible PET-substrate, $^{38-39}$ generated via thermodynamically favoured growth. $^{22,38}$ For the PP substrate, the sample signature could not been separated because of the very high intrinsic XRD-response of the substrate itself. The average size ($D_{XRD}$) of the nanocrystals $\beta$ for P-type Si(111)$^{32,33}$ with some absorption components, the microstructure factor ($R$), related to the poly-hydrde fraction of the network, $R = (I_{SiH3} + I_{SiH2})/(I_{SiH3} + I_{SiH2} + I_{SiH} + I_{Si-H-Si})$ (5) and the surface passivation index ($\delta$), identified by the Si–H–Si platelet like component present in the matrix, $^{38-39}$

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were estimated, where, $I_x$ corresponds to the integrated absorption under each satellite component $\text{SiH}_2$, $\text{SiH}_3$, $\text{SiH}_4$ and $\text{SiH}_-\text{Si}$, as shown in \( \text{Fig. 3(b)} \). It has been revealed from \( \text{Fig. 3(c)} \) that the $C_H$ reduced from 6.74 at.% to 4.45 at.% for increase in $T_S$ from 30 to 150 °C. Similar reducing nature of the surface passivation index ($S$) with its low magnitude of ~0.125 and the concomitant elevation in the microstructure factor ($R$) to a high magnitude of ~0.87, together acknowledge a gradual increase in crystallinity within the Si network at elevated $T_S$. A significantly high crystallinity in the film network was obtained on c-Si substrate at $T_S$ = 150 °C, as obtained on all other variety of substrates also, as shown in \( \text{Fig. 1(c)} \). Furthermore, it has been noted that sharp changes in all the parameters, e.g., $C_H$, $S$ and $R$ occurred most prominently within a temperature zone of 60–100 °C where a transition in the rate of change in crystallinity of the Si:H network, particularly on the photo-plate substrate, was demonstrated in \( \text{Fig. 1(d)} \).

\[ S = \frac{I_{\text{Si-H-Si}}}{I_{\text{SiH}_2} + I_{\text{SiH}_3} + I_{\text{SiH}_4} + I_{\text{Si-H-Si}}} \]  

\( (6) \)

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**Fig. 3.** IR absorption spectra in (a) wagging mode vibration with Si–H wagging and Si–H$_n$ (n ≥ 2) rocking components, (b) Si–H stretching mode vibration with different SiH$_n$ (n = 1, 2, 3) components including Si–H–Si platelet like component. (c) Variations of bonded hydrogen content ($C_H$), microstructure factor ($R$) and the surface passivation index ($S$) with growth temperature ($T_S$) of the doped nc-Si films.

**Fig. 4.** SEM images of p–nc-Si films on (a) glass, $T_S$ = 150 °C, and on PET-substrate at (b) $T_S$ = 150 °C and (c) $T_S$ = 100 °C.
The SEM images of B-doped nc-Si films grown at the highest $T_S \sim 150$ °C on glass and PET substrates, in Fig. 4(a-b), demonstrate that on glass the sample has a compact and granular structure with homogeneous surface-distribution of tiny and unique size grains with sharp grain boundaries, while on PET the sample-surface possesses an inhomogeneous morphology, comprising of a variety of larger-sized clusters (as identified by areas enclosed by white borders) and irregular cracks with black lines of wide separations. In general, larger average-size (~16.7 nm) of the grains on PET substrate, compared to that (~5.3 nm) on glass substrate, were also determined by the Raman data [Fig. 1(d)]. For sample on PET grown at 100 °C [Fig. 4(c)], however, the cluster size is smaller and the cracks are narrower.

The atomic force microscope images of the B-doped nc-Si films grown on glass and PET substrates at different temperatures are shown in Fig. 5(a-b). For each type of substrate, the surface of the film deposited at low temperature (30 °C) seems to possess an inhomogeneous texture containing a lot of voids and consequently a relatively high surface roughness. The void density and the surface inhomogeneity sharply reduced at elevated $T_S$. Comparing the individual effect induced by the nature of the substrate, it seems from the consistent lower average surface roughness, in Fig. 5(c), that the PET substrate facilitates a better coalescence of the material and hence an increased overall crystallinity in the $p$–nc-Si network, as evident from the Raman studies as well [Fig. 1(e)]. Similar observation was reported earlier from both AFM and Raman studies that second to $c$-Si wafer substrate, the PET substrate propagates improved crystalline network of the film than on glass substrate. On further elevated $T_S \sim 150$ °C, however, a relatively higher surface roughness is consistent with the formation of surface cracks on the sample on PET substrate, as evident from the SEM data in Fig. 4(b).

![AFM images](image-url)

Fig. 5. AFM images, with 2D and 3D views, of $p$–nc-Si films deposited on (a) glass and (b) PET substrates. (c) Comparison of the RMS roughness of $p$–nc-Si films on glass and PET-substrates at different $T_S$. 

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**J. Name., 2013, 00, 1-3 | 5**

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The TEM images of the samples prepared on C-coated Cu-microgrids at two different $T_S \sim 30$ °C and 100 °C, are represented in Fig. 6(a) and 6(b), respectively. At the lowest $T_S \sim 30$ °C, the TEM image reveals the dispersion of tiny-crystallites within amorphous-network in Fig. 6(a-i). In the high-resolution image in Fig. 6(a-ii), individual nanocrystals containing distinctly separated lattice planes corresponding to the $<111>$ and $<220>$ crystal orientation are evident which are further supported by the corresponding diffraction pattern in Fig. 6(a-iii). At a moderate $T_S \sim 100$ °C, the TEM micrograph in Fig. 6(b-i) and the high-resolution image in Fig. 6(b-ii) reveal the prominent distribution of high density and comparatively large size nanocrystallites dispersed in the amorphous matrix. The TED-pattern in Fig. 6(b-iii) consists of very bright and sharp circular rings wherein, in addition to the $<111>$ and $<220>$ planes, $<311>$ nanocrystalline orientations are distinctly observed, as also in Fig. 6(a-iii).23

![TEM images of p-nc-Si films grown at (a) $T_S \sim 30$ °C and (b) 100 °C, in (i) moderate and (ii) high-resolution, and the corresponding (iii) SAED patterns.](image)

The optical properties of B-doped nc-Si films grown on transparent rigid-glass and flexible-PET substrates were studied via UV-vis absorption. Figure 7(a) represents the transmission spectra of two films grown at 100 °C on two transparent substrates, glass and PET. Apart from the mechanical measurement by stylus, the film thickness was also optically assessed from the waves in the transmission spectra, using Swepneol method.28 It is apparent from the spectral distribution that on the same run the grown films are

![Transmission spectra of p-nc-Si films on glass and PET substrates grown at $T_S = 100$ °C, and their absorption data in Tauc’s plot.](image)

Fig. 7. (a) Transmission spectra of p-nc-Si films on glass and PET substrates grown at $T_S = 100$ °C, and their (b) absorption data in Tauc’s plot. (c) Comparison of Tauc’s plot of p-nc-Si films deposited at different $T_S$ on PET substrates, and (d) comparison on the variations of $E_g$ with $T_S$ for samples on glass and PET substrates.
thicker on glass than on PET. At $T_S=100$ °C the B-doped nc-Si films grew on glass at a deposition rate ~14.9 nm/min, while on PET it came down to ~7.5 nm/min. The optical band-gaps were estimated from the intercept of linear slope of the Tauc’s plot ($\sqrt{\alpha h\nu}$ vs. $h\nu$) to $\alpha=0$ [Fig. 7(b)], following standard process using Tauc’s equation:

$$ (\alpha h\nu)^{1/2} = B(h\nu - E_g) $$

(7)

where, $\alpha$ is absorption coefficient, and $B$ is the Tauc’s constant. The slope of the plots i.e., the Tauc’s constant $B$ became grossly different for the $p$-nc-Si films deposited on two different types of substrates at the same run, as shown in Fig. 7(b). The magnitude of $B$ being higher in case of the rigid glass substrate than that of the flexible PET substrate, the optical band gaps ($E_g$) of $p$-nc-Si films demonstrated higher magnitudes when deposited on glass. In general, the optical band gap of B-doped nc-Si films reduced monotonically at lower $T_S$, as shown in Fig. 7(c), for the set of films grown on PET substrate. The slope of the plots i.e., the Tauc’s constant $B$ remained very close, identifying a limited change in crystallinity within the span of variation in $T_S$, (30 – 150) °C, wherein the crystalline volume fraction increased from 80 to 83.6% only, as estimated from the Raman data. Within a temperature range (30 – 150) °C, the ($E_g$)$_{glass}$ increased from 1.814 to 1.875 eV, while the relatively lower ($E_g$)$_{PET}$ = 1.792 eV at $T_S=30$ °C increased to ~1.869 eV at $T_S=150$ °C, which was pretty close to that of corresponding ($E_g$)$_{glass}$, as shown in Fig. 7(d).

![Graph showing the comparison of $\sigma_p$ as a function of $T_S$ for $p$-nc-Si films on glass, photo-plate and PET substrates.](image)

The room temperature dark electrical-conductivity ($\sigma_p$) as a function of growth-temperature ($T_S$) in Fig. 8 identifies that ($\sigma_p$)$_{glass}$ at each temperature had trivially higher magnitude than ($\sigma_p$)$_{PET}$, along with their similar nature of variation within 30 ≤ $T_S$ (°C) ≤ 100, above which formation of significant surface-cracks on sample-on-PET may obstruct regular $T_S$-induced promotion of electrical transport, leading to relatively larger difference in $\sigma_p$. While ($\sigma_p$)$_{PET}$ at 150 °C was lower than the others, that was further reduced by more than two orders-of-magnitude on lowering of $T_S$ to 30 °C, the deterioration being faster at $T_S$ below 75 °C. The B-doped nc-Si films having

![Graph showing the XPS data of $p$-nc-Si films on PET and glass substrates.](image)

Fig. 9. XPS data of $p$-nc-Si films on (a) PET and (b) glass substrates, and (c) estimated B to Si ratio in the doped nc-Si films grown at different substrate and at different $T_S$, presented in bar-diagram.

![Graph showing the comparison of $\sigma_p$ as a function of $T_S$ for $p$-nc-Si films on glass, photo-plate and PET substrates.](image)
the plasmonic component, as shown in the insets in Fig. 9(a–b).

The content of B in the doped nc-Si films was estimated from the ratio of integrated area under the B-Si peaks, e.g., Si-2p and Si-2s. Based on the analysis, B concentrations was estimated to be around 2.99, 3.25 and 3.45 at.% on PET substrate, and 3.2, 3.55 and 3.95 at.% on glass substrate for samples prepared at \( T_s = 30^\circ \text{C}, 100^\circ \text{C} \) and 150°C, respectively, as presented by a bar-diagram in Fig. 9(c).

Discussion

In general, the photo-plate substrate provides a lesser crystallinity to nc-Si film, which may be attributed to very different chemical nature and roughness of the substrate, controlling the surface reactions. The emulsion layer containing silver-halide grains dispersed in a gelatine matrix on photo-plate substrate makes the surface rough, inhomogeneous and unstable that encourage random-growth. At elevated \( T_s \), rapid removal of humidity from the gelatine-latex emulsion-layer of photo-plate substrate resumes degree of crystallization, (\( \chi \)pp), closer to other substrates, along with similar elevation in (\( \sigma_d \)pp). Significantly high (\( \chi \)Glass \( \approx 78.9\% \)) and remarkable (\( \sigma_d \)Glass \( \approx 1 \text{ S cm}^{-1} \)) of p–nc-Si film deposited at room-temperature (\( T_s = 30^\circ \text{C} \)) from SiH\(_4\) without additional H\(_2\)-dilution, are the consequences of unique high electron-density (\( \approx 10^{12} \text{ cm}^{-3} \)) plasma of ICP-CVD, which demonstrates a very special route for high-yield nanocrystalline growth.

During nanocrystallization, formation dynamics of the incubation-layer at the substrate-surface dominantly controls the subsequent growth-kinetics and that, in turn, sensitively depends on the substrate material and morphology, apart from parameters like temperature, electrical-bias, etc. Undoped poly-Si thin films grown on PET substrate using SiH\(_4\) in 99.5% H\(_2\)-dilution in conventional RF PE-CVD demonstrated maximum conductivity (\( \sigma \approx 8 \times 10^5 \text{ S cm}^{-1} \)), corresponding to its maximum crystallinity (\( \approx 71.5\% \)) and the narrowest optical band gap (\( \approx 1.66 \text{ eV} \)), at a substrate bias of \(-100 \text{ V}\). At a very high –ve bias applied to the substrate, band gap increased significantly due to nanocrystallization in the network, corresponding to a phase transition from high crystallinity towards amorphous dominated structure. Using extremely high H\(_2\)-dilution to the SiH\(_4\) plasma in a capacitive-coupled RF PE-CVD, crystalline volume fraction up to 68.8% was reported\(^{26}\) for B-doped nc-Si sample grown on PET substrate at \(-120 \text{ V}\) bias, revealing the maximum magnitude of dark conductivity (\( \approx 1.94 \text{ S cm}^{-1} \)). Further increase in bias, however, caused high-energy H\(_2\) ions bombardment and subsequent degradation of crystallinity. In doped \( \mu \text{c-Si}:\text{H} \) films deposited at \( T_s = 100^\circ \text{C} \), higher crystalline volume fraction, (\( \chi \)c \( \approx 72\% \)) on PET substrate, compared to that on glass substrate (\( \chi \)c \( \approx 65\% \)), although the conductivity of the samples on PET (\( \sigma_d \approx 2.6 \times 10^1 \text{ S cm}^{-1} \)) was lower than that on glass (\( \sigma_d \approx 8.9 \times 10^1 \text{ S cm}^{-1} \)).

Because of similar reasons in facilitating device fabrication, besides Si in its different structural configurations e.g., amorphous, nanocrystalline, microcrystalline and polycrystalline thin films, various other semiconductor thin films e.g., CdS,\(^{51}\) ZnO,\(^{52,53}\) In-doped ZnO (IZO),\(^{54}\) Al-doped ZnO (AZO),\(^{55}\) etc., were deposited simultaneously on flexible PET and rigid glass substrates and studied with their differences in opto-electronic properties. It was identified that, in general, these films possessed higher crystallinity, however, simultaneous narrower optical band gap and mostly lower electrical conductivity, when deposited on PET than on glass substrate.

In the present investigation a superior crystallinity on flexible PET-substrate arises from strain-induced crystallization at the incubation-layer due to substrate-bending via plasma-heating. Stress generated at substrate/incubation-layer interface provides the activation energy for nanocrystallization and favours the formation of larger-nanocrystals at elevated \( T_s \) and also leads to a gradually increased difference in crystallinity, although trivially, compared to that on glass substrate.\(^{57,58}\) Although having a higher (\( \chi \)PET \( \approx 80\% \)), the (\( \sigma_d \)PET \( \approx 6.0 \times 10^1 \text{ S cm}^{-1} \)) of the p–nc-Si film prepared at ambient temperature (\( T_s = 30^\circ \text{C} \)) appears slightly lower than (\( \sigma_d \)Glass \( \approx 9.95 \times 10^1 \text{ S cm}^{-1} \)) and the deviation increases at \( T_s > 100^\circ \text{C} \), which indicate that the surface strain/bending may not be favorable for electrical transport in samples on flexible PET- substrates, which becomes more stringent at higher \( T_s \), due to the formation of micro-cracks on the sample-surface. Although better network-ordering corresponding to higher crystallinity consequences wider optical band-gap (\( E_g \)) of the p–nc-Si films at elevated \( T_s \) over 30–150°C on both flexible PET and rigid glass substrates, fundamentally \( E_g \) always pursues a lower magnitude in PET than on glass.

The optical band gap of Si:H network, in general, depends on two major factors, the intrinsic network structure and the amount of bonded H-content (\( C_H \)) including its nature of bonding as mono, di- or poly-hydride. In case of Si:H network with moderate crystallinity (containing significant amount of amorphous component) and lower \( \sigma_d \), normally with increasing deposition temperature, \( C_H \) reduces and the SiH\(_4\) bond becomes gradually less poly-hydride in configuration and those together lead to systematic lowering in the optical band gap.\(^{59}\) By scavenging H attached to the Si-network via atomic F and H together, on ECR-CVD grown Si:H films normally possessing a huge hydrogen content, relatively non-rigid network containing significant amount of voids and subsequently an wide optical gap, it was demonstrated that the optical band gap changed proportionally with the bonded H-content.\(^{60}\) Furthermore, in Si:H films possessing low H-content, prepared by repetition of growth interruption and subsequent increasing dose of H-plasma treatment in both ECR-CVD and capacitively coupled PE-CVD, systematic widening of optical band gap had been obtained by virtue of gradual increase in poly-hydrogenation of the network and significant network ordering, even with simultaneous significant elimination of bonded H from the network.\(^{56,62}\) It has
been endorsed by Mahan el al. that the intrinsic optical band gap of the SiH network in medium range order, $(E_g)_{MRO}$, follows the empirical relation: $E_g = (E_g)_{MRO} + 0.0135 \cdot C_H$, where $(E_g)$ is the experimentally determined optical band gap and $C_H$ is the bonded H-content of the network. Furthermore, they have demonstrated that the magnitude of $(E_g)_{MRO}$ increases linearly with the increased network ordering. In case of the present sets of B-doped nc-Si films deposited on glass and PET substrates, the amount of H bonded to the network is very low by virtue of high crystallinity of the network and simultaneous unavailability of surplus atomic-H in the plasma because of using SiH$_4$ plasma without deliberate H$_2$-dilution in ICP-CVD, both. Within such network the escalating experimentally determined optical band gap $(E_g)$ on removal of H and simultaneous increase in the microstructure factor (R) at elevated growth temperature $(T_g)$ [Fig. 3(c)] essentially signifies the systematic widening of the intrinsic optical band gap, $(E_g)_{MRO}$ or rather $(E_g)_{SRO}$, due to temperature mediated gradual improvement of the network towards short-range ordering (SRO). This phenomenon applies equally for films grown on glass as well as flexible PET substrates where virtually identical linear elevation of optical band gap has been revealed on growth temperature mediated elevated network crystallinity (Fig. 10).

The electrical conductivity of B-doped nc-Si films has been found to have a direct one-to-one co-relation with the network crystallinity. Under the chosen parametric condition, the crystalline volume fraction in the network grown on both the flexible substrates (PP and PET) from the SiH$_4$ plasma undiluted by additional H$_2$ in the ICP-CVD, follow a single straight-line relation, as shown in Fig. 10. At very high crystallinity, $\chi_C > 82.5\%$, the p–nc-Si film deposited on PET at $T_g > 100$ °C shows little deviation in the straight-line relation of $\sigma_D$ which might arise because of the formation of surface cracks on the sample that hinders the usual transport of charge carriers across the network. In addition, improved $\sigma_D$ of the films on glass substrate may occur from the higher carrier density by virtue of increased dopant activation (Fig. 8), as an individual effect arising from the particular chemical nature of the substrate, however, the similar linear relation with identical slope between $\chi_C$ and $\sigma_D$ is maintained all along, as demonstrated in Fig. 10. Elevated dopant incorporation could originate increased distortion in the tiny host crystallites, and thereby, cause reduced crystallization in the network grown on glass substrate than on PET substrate.

In the process of film growth by PECVD, adsorption of the plasma precursors onto the substrate, their temperature mediated diffusion across the substrate surface and finally sticking at some low energy site via making chemical bonds with the substrate, at an early stage, are the different sequential steps involved. In the elementary adsorption process the chemical affinity between the substrate and the precursors, therefore, plays a major role. The SiH$_4$ precursors easily make bonds with the similar Si element of the glass substrate via its abundant dangling bond and results in a higher deposition rate compared to that on PET substrates where C is the major bonding element with various functional groups like –COOH, –OH, –C=O. In the course of onward process, evolution of substrate surface roughness and creation of voids, at the interface between substrate and the incubation area of the growth zone, initiated by inhomogeneous etching of the weak Si–Si bonds by atomic H of the plasma causes a structural reorientation and formation of islands, the first set of nuclei; and the nucleation becomes predominant for slower network formation during silicon nanocrystallization. At the early stage of growth of the nanocrystalline network, the deposition continues typically via the development of the already existing nuclei because of the lower energy requirement and form a columnar growth morphology. However, new nuclei are formed simultaneously and the growth continues along the lateral dimension. Gradual coalescence of the columnar structures via lateral extension produces a compact and rigid network. Hence, the initial formation of nuclei controls the subsequent growth dynamics and determines the final network structure. Here lies the importance of the substrate. The structural morphology and the chemical composition of the substrate, along with the growth parameters, determine the nucleation, columnar configuration and amalgamation of the growth species. Better compliance via surface deformation on flexible PET substrate, compared to rigid glass substrate, affords intrinsic stress relaxation and promotes spontaneous crystallization in Si-network.
Conclusion:
It has been assessed that compared to the rigid glass, better compliance by means of deformation of the flexible polyethylene terephthalate (PET) substrate provides plausible intrinsic stress relaxation during evolution of the film network via energy transfer across the film-substrate interface, which facilitate improved network crystallinity within sustainable temperature limit up to 100 °C. Inherent high electron-density of the ICP-CVD providing surplus atomic-H within the low pressure SiH4 plasma without additional H2-dilution and favorable strain-induced nanocrystallization-kinetics at the incubation layer arising from surface-bending via plasma-heating on flexible PET-substrate promote high-yield advanced crystallinity even at ambient temperature. The B-doped nc-Si films on PET substrate possess high electrical conductivity and wide optical band gap by virtue of functional dopability and high crystallinity and retain overall optoelectronic properties closely at per with that on glass substrates. Superior crystallinity (ξC ~82.5%) with average grain size D_Raman ~9.63 nm, wide band-gap \( E_g \sim 1.836 \text{ eV} \) and high electrical-conductivity \( \sigma_p \sim 0.2 \text{ S cm}^{-1} \) of the low temperature (\( T_S \sim 100 \text{ °C} \)) deposited B-doped nc-Si film on transparent and flexible PET-substrate seems ideal for window layer in nc-Si solar cells in p-i-n superstrate configuration and also amply suitable for low-cost flexible-electronics. For large scale device fabrication involving process automation, flexible polycrystalline substrates are uniquely suitable and the present work identifies an essential low temperature (\( \sim 100 \text{ °C} \)) avenue, for growing device grade p–nc-Si film via CMOS compatible plasma-processing of SiH4 without deliberate H2-dilution, with the advent of low-pressure high-density planar inductively coupled plasma.

Author Contributions
The authors declare that they have equal contributions in this publication.

Conflicts of interest
The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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