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Farsad Imtiaz Chowdhury¹, Aesha Alnuaimi¹, Sabri Alkis², Bülend Ortaç², Selçuk Aktürk³, Mustafa Alevli⁴, Nikolaus Dietz⁵, Ali Kemal Okyay⁶ and Ammar Nayfeh¹

¹ Institute Center for Future Energy Systems(iFES), Department of Electrical Engineering and Computer Science(EECS), Masdar Institute of Science and Technology, 54224, Abu Dhabi, United Arab Emirates

² Institute of Materials Science and Nanotechnology(UNAM), Bilkent University, Ankara, 06800, Turkey

³ Physics Engineering Department, Istanbul Technical University, 34469, Istanbul, Turkey

⁴ Department of Physics, Marmara University, 34722, Istanbul, Turkey

⁵ Department of Physics, Georgia State University, 3965, Atlanta, USA

⁶ Department of Electrical and Electronics Engineering, Bilkent University, Ankara, 06800, Turkey

E-mail: fchowdhury@masdar.ac.ae

The following addition should be made to the caption of figure 1:

‘Reproduced with permission from Electrochem. Soc. Trans., 66 (40) 9–16 (2015). Copyright 2015, The Electrochemical Society.’ The figure in ECS Transactions is showing a schematic of n-i-p a-Si:H solar cell structure which is modified to show a schematic of c-Si HIT solar cell structure in this work.

The following addition should be made to the caption of figure 2:

‘Reproduced with permission from Electrochem. Soc. Trans., 66 (40) 9–16 (2015). Copyright 2015, The Electrochemical Society.’ The figure in ECS Transactions is only showing TEM image of InN nanoparticles and in this work information about nanoparticle size distribution has been added to the TEM image as inset.

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PAPER

Enhancement in c-Si solar cells using 16 nm InN nanoparticles

Farsad Imtiaz Chowdhury¹, Aesha Alnuaimi¹, Sabri Alkis², Bülend Ortaç², Selçuk Aktürk³, Mustafa Alevli⁴, Nikolaus Dietz⁵, Ali Kemal Okyay⁶ and Ammar Nayfeh¹

¹ Institute Center for Future Energy Systems (iFES), Department of Electrical Engineering and Computer Science (EECS), Masdar Institute of Science and Technology, 54224, Abu Dhabi, United Arab Emirates

² Institute of Materials Science and Nanotechnology (UNAM), Bilkent University, Ankara, 06800, Turkey

³ Physics Engineering Department, Istanbul Technical University, 34469, Istanbul, Turkey

⁴ Department of Physics, Marmara University, 34722, Istanbul, Turkey

⁵ Department of Physics, Georgia State University, 3965, Atlanta, USA

⁶ Department of Electrical and Electronics Engineering, Bilkent University, Ankara, 06800, Turkey

E-mail: fchowdhury@masdar.ac.ae

Keywords: solar cells, photoluminescence, downshifting, scattering

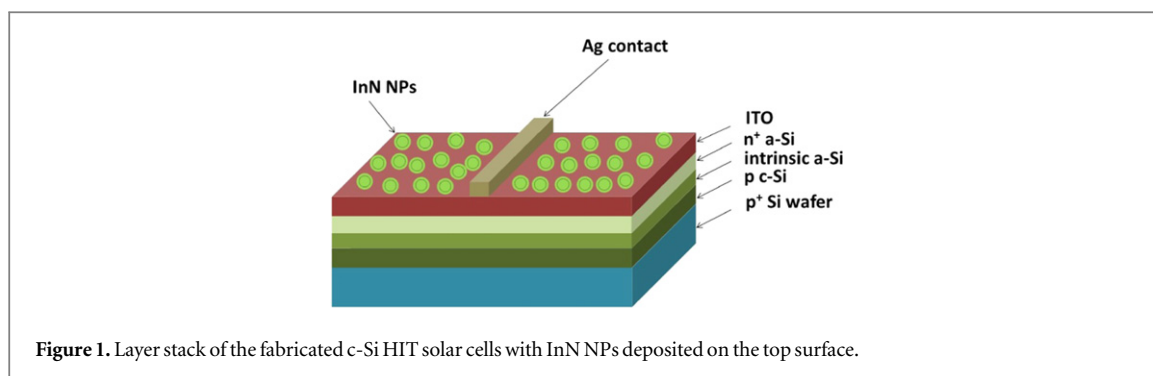
Abstract

In this work, 16 nm indium nitride (InN) nanoparticles (NPs) are used to increase the performance of thin-film c-Si HIT solar cells. InN NPs were spin-coated on top of an ITO layer of c-Si HIT solar cells. The c-Si HIT cell is a stack of 2 μm p type c-Si, 4–5 nm n type a-Si, 15 nm n^+ type a-Si and 80 nm ITO grown on a p^+ type Si substrate. On average, short circuit current density (J_{sc}) increases from 19.64 mA cm^{-2} to 21.54 mA cm^{-2} with a relative improvement of 9.67% and efficiency increases from 6.09% to 7.09% with a relative improvement of 16.42% due to the presence of InN NPs. Reflectance and internal/external quantum efficiency (IQE/EQE) of the devices were also measured. Peak EQE was found to increase from 74.1% to 81.3% and peak IQE increased from 93% to 98.6% for InN NPs coated c-Si HIT cells. Lower reflection of light due to light scattering is responsible for performance enhancement between 400–620 nm while downshifted photons are responsible for performance enhancement from 620 nm onwards.

1. Introduction

A heterojunction with intrinsic thin layer (HIT) structure is found to be a promising structure for future thin-film solar cells. Panasonic recently reported 25.6% energy conversion efficiency; a world record for HIT cell [1]. This type of cell combines the high efficiency of c-Si and low temperature deposition technology of a-Si, which leads to a sufficient cost reduction. This is one of the main reasons HIT cells have gained a lot of attention as they can be an alternative to conventional thick c-Si solar cells [1–7]. Finding new ways to reduce the reflection of the incoming light is vital to further improve the performance of thin-film HIT solar cells. For thin-film solar cells, this is normally done by using an anti-reflection coating (ARC) layer such as indium tin oxide (ITO), aluminum doped zinc oxide (AZO), etc [8–14]. Studies have been conducted to improve the performance of ARC layers such as texturing ARC for light trapping, multilayer ARCs, etc [15–19]. Use of nanoparticles [20–25] is a cheap alternative which promotes light scattering and would help to reduce the reflection further from ARC layer if deposited on top of it.

Recently, semiconductor nanoparticles have received great interest for their photoluminescence property that enhances solar cell performance. Due to this property, a high energy photon is absorbed by a material which then re-emits a photon with lower energy. Detailed reviews of luminescence downshifting and its application in different types of solar cells can be found in [21, 26–39] which include some of our previous works focusing on the effect of semiconductor nanoparticles on solar cells. Several mechanisms are believed to have contributed towards this enhancement, including wavelength down conversion from higher energy to lower energy, which is due to radiative recombination of photoexcited excitons that allows solar cells to absorb more light, separation of excitonic charge and transport of charge in the film (top solar cell), or improved light coupling and



propagation (ARC) [35, 40–43]. In this work, we have combined the standard ITO ARC layer with InN NPs for better light coupling in c-Si HIT solar cells. Namely, 16 nm InN NPs were spin-coated on top of an ITO layer of the solar cells and wavelength dependent reflectivity, internal/external quantum efficiency (IQE/EQE), as well as current–voltage characterizations were done to study the enhancement in solar cell performance.

2. Experiment

2.1. Indium nitride nanoparticles fabrication

Fabrication of InN NPs was carried out using a nanosecond pulsed ND:YLF laser. The operated wavelength, pulse duration and pulse repetition of this laser were 527 nm, 100 ns and 1 kHz, respectively. High-pressure chemical vapor deposition (HPCVD) was used to grow InN samples [44, 45] which were kept in 20 ml pure ethanol and a plano-convex lens with a focal length of 50 mm was used to focus the laser beam on to the sample. More details on the deposition process and optical properties of the HPCVD grown InN layers can be found elsewhere [46]. The InN target was kept 5 mm below the surface of the liquid layer and laser ablation was carried out for 5 min [44]. Optical and spectroscopic properties of these InN NPs have been reported in detail elsewhere [44]. Raman spectroscopy of these InN NPs showed an E_2 peak at 496.76 cm^{-1} and the full width at half maximum (FWHM) value was 5.36 cm^{-1} which is also consistent with the experimental spectrum [44]. UV-Vis measurement of InN NPs showed an absorption between 200–1200 nm with prominent shoulders at 260 nm and an absorption edge that starts around 500 nm [44].

2.2. Solar cell structure and fabrication

In order to study the effect of an InN NPs coated ITO ARC layer, a-Si:H (n^+)/a-Si:H (i)/c-Si (p) HIT solar cells were fabricated. Figure 1 shows the layer stack of the fabricated a-Si:H (n^+)/a-Si:H (i)/c-Si (p) HIT solar cell. For a-Si:H (n^+)/a-Si:H (i)/c-Si (p) HIT solar cells, a Si wafer with doping concentration (p^+) of approximately $1 \times 10^{19}\text{ cm}^{-3}$ was used as substrate. 2 μm epitaxial Si layer was grown on the p^+ substrate using low-pressure chemical vapor deposition (LPCVD) with nominal boron concentration of $1 \times 10^{16}\text{ cm}^{-3}$. An undoped a-Si layer of 5 nm and n^+ doped a-Si layer of 15 nm were grown afterwards. The p^+ type Si substrate serves as a back contact and does not contribute significantly to electron–hole pair generation. In addition, 80 nm ITO was deposited using plasma-enhanced chemical vapor deposition (PECVD) [47]. InN NPs were then spin-coated on top of ITO. After the coating of NPs, silver (Ag) was deposited using an electron-beam evaporator tool and a lift off technique was used to form the contacts. More details on the solar cell fabrication can be found elsewhere [7, 48–50]. Three different cell area-sizes were fabricated, i.e. $1\text{ cm} \times 1\text{ cm}$, $0.5\text{ cm} \times 0.5\text{ cm}$ and $0.25\text{ cm} \times 0.25\text{ cm}$. Solar cells of size $0.25\text{ cm} \times 0.25\text{ cm}$ are presented in this work unless stated otherwise.

For the current–voltage characteristic study, a J – V curve testing system (Model IV5) of PV Measurement, Inc. was used. Before the measurement the system was calibrated using a light meter to set the intensity of the light such that the irradiance equals one sun under AM1.5G. The spectral response of the fabricated device was measured using a solar cell spectral response measurement system (Model QEX7) of PV Measurement, Inc. Before the measurement this system was also calibrated using a silicon photodiode for the whole calibration range at room temperature (23 ± 2) $^\circ\text{C}$.

3. Results and discussion

A transmission electron microscopy (TEM) image of the laser synthesized InN NPs in ethanol solution is shown in figure 2. This image shows that InN NPs exhibit spherical-like geometries without any aggregation in organic solution. To obtain information about the size distribution, 150 particles seen in the TEM image were counted.

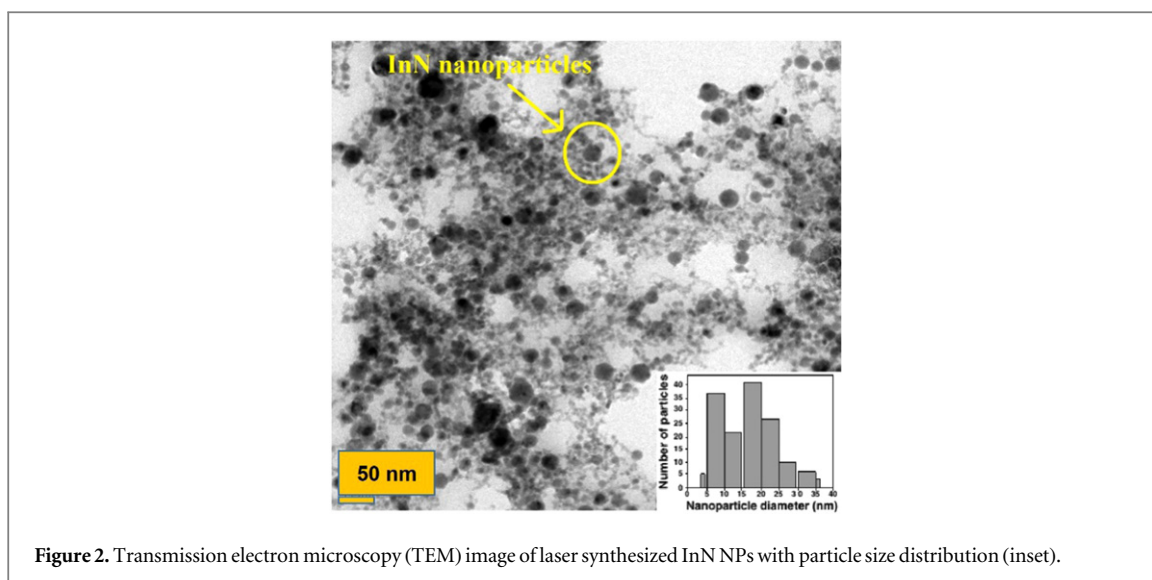


Figure 2. Transmission electron microscopy (TEM) image of laser synthesized InN NPs with particle size distribution (inset).

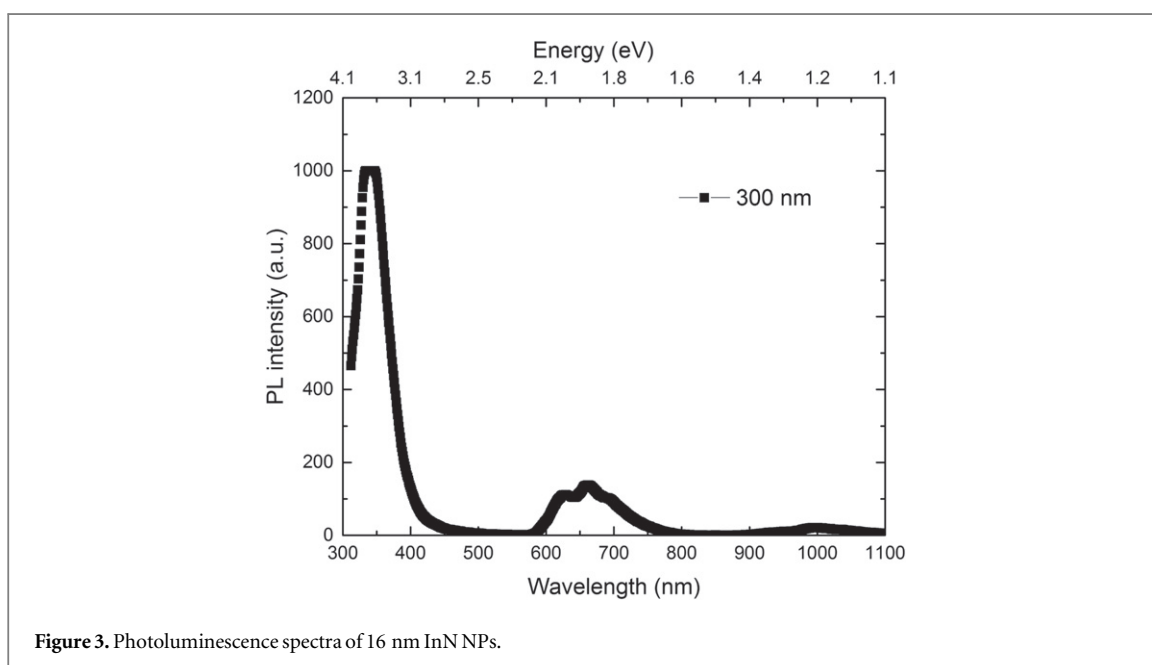


Figure 3. Photoluminescence spectra of 16 nm InN NPs.

The sizes of InN NPs range from 3.24–36 nm with an average size of 16 nm (inset, figure 2). Figure 3 shows the photoluminescence spectra of InN NPs under 300 nm excitation. For this excitation, two emission peaks were recorded, one in the UV spectrum and the other one in the near-infrared spectrum. Similar excitation in the near-infrared region was also observed by Sardar *et al* [51] which is characteristic of InN. Figure 4 shows the transmission and reflection spectra of InN NPs coated on glass. Both the curves show an absorption edge around 320 nm which is related to the property of the glass. InN NPs coated on the top of glass substrate would scatter incoming light which will eventually increase the propagation of light in the forward direction (better light coupling). Reduced reflection and increased transmission from the InN NPs coated glass substrate verify this argument. Maximum enhancement due to the presence of InN NPs was detected around 380 nm and it gradually decreases as the wavelength increases in both curves.

The effect of InN NPs coating was evaluated by comparing InN NPs coated ITO cells with reference cells containing an ITO ARC layer only. For electrical (J - V under one sun, i.e. AM1.5G) measurements four solar cells were measured before and after NPs deposition. Figure 5 shows the J - V curves of the best performing solar cell (ITO only and ITO + InN NPs). For this cell, J_{sc} increases from 19.21 mA cm^{-2} to 22.4 mA cm^{-2} and efficiency increases from 6.27% to 7.22%.

Table 1 summarizes the result of the effect of the InN NPs + ITO ARC layer on c-Si HIT cells. On average, J_{sc} and efficiency increase from 19.64 mA cm^{-2} to 21.54 mA cm^{-2} and 6.09% to 7.09% respectively. Compared to

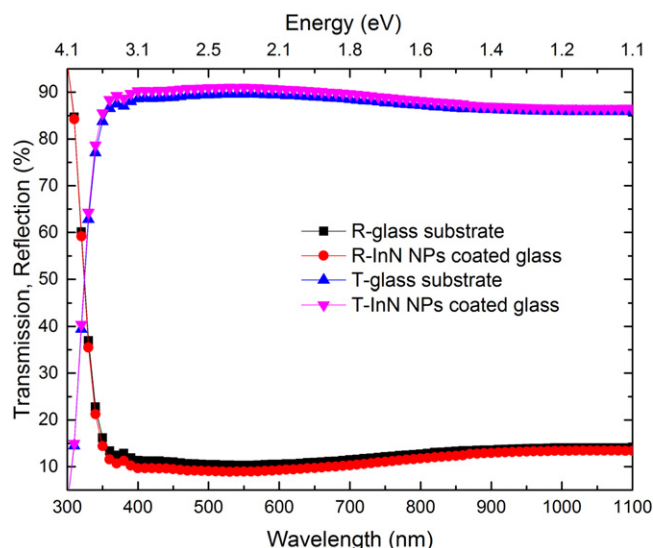


Figure 4. Transmittance and reflectance of an InN NPs coated glass substrate.

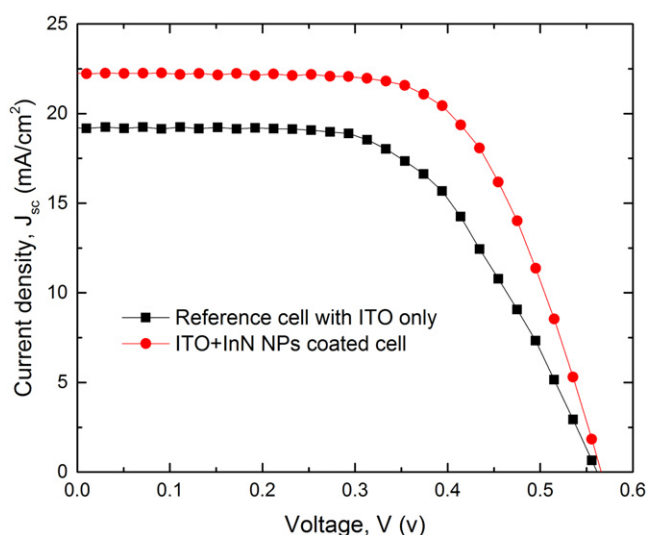


Figure 5. J - V characteristics of the c-Si HIT reference cell with ITO and the cell with ITO + InN NPs under one sun, i.e. AM1.5G.

Table 1. Summary of results.

		V_{oc} (V)	J_{sc} (mA cm^{-2})	Efficiency (%)	FF (%)
Reference cell with ITO	Average	0.56	19.64	6.09	55.30
	Median	0.56	19.72	6.23	56.41
	Standard deviation	0.00	0.27	0.27	2.97
ITO + InN NPs coated cell	Average	0.56	21.54	7.09	58.54
	Median	0.56	21.40	7.05	57.43
	Standard deviation	0.00	0.59	0.27	2.89

the reference cell that has ITO only, the cell consisting of the InN NPs coated ITO ARC layer shows 9.68% and 16.53% relative increase in J_{sc} and efficiency. V_{oc} remains 0.56 V and does not change significantly after NPs incorporation. The fill factor (FF) of the cells also increases on average from 55.30% to 58.54%.

The reflectivity of the cells was also measured to see the effect of the InN NPs coated ITO ARC layer. Figure 6 shows the reflection of the c-Si HIT cells, one consisting of ITO and one consisting of ITO + InN NPs. The

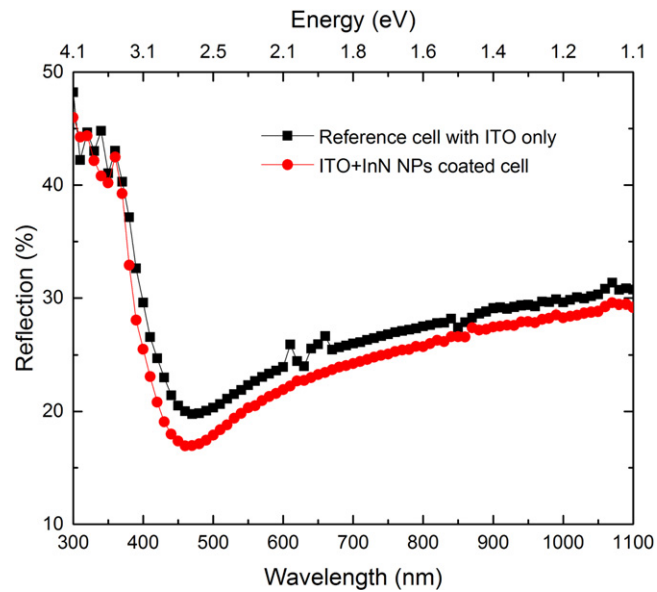


Figure 6. Reflectance of the c-Si HIT reference cell with ITO and the cell with ITO + InN NPs.

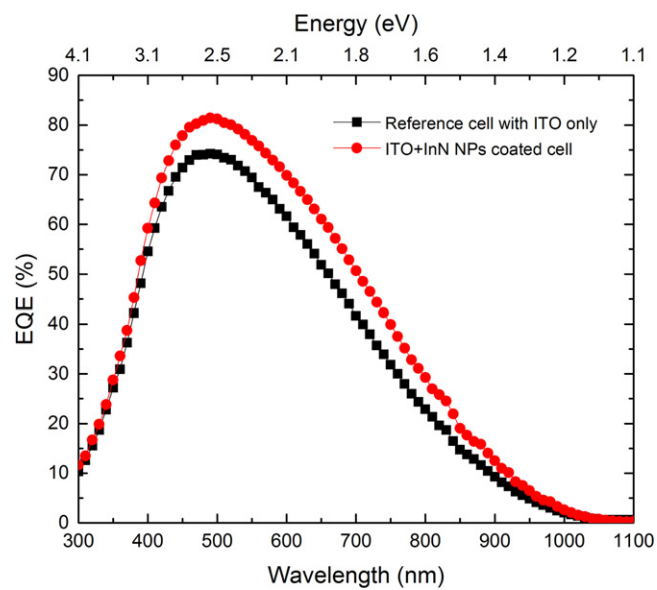


Figure 7. External quantum efficiency of the c-Si HIT reference cell with ITO and the cell with ITO + InN NPs.

reflection reduction in the spectral region $> \sim 370$ nm verifies better coupling of light due to the presence of InN NPs.

To further study the effect of the InN NPs coated ITO ARC layer on c-Si HIT cells, EQE and IQE were measured. Figure 7 shows EQE versus the wavelength of c-Si HIT cells. This figure shows that c-Si HIT cells with InN NPs coated ITO ARC layer have a better spectral response compared to cells that have only ITO. Peak EQE of the cells increases from 74.2% to 81.4% at 490 nm. The expected short circuit current and overall increase in short circuit current have also been calculated from the measured EQE using the relation [52]:

$$J_{sc} = q \int bs(E) QE(E) dE \quad (1)$$

$$\Delta J_{sc} = \text{Equation(1)}_{(\text{InN NPs coated})} - \text{Equation(1)}_{(\text{reference})} \quad (2)$$

where q is the charge of the electron, $bs(E)$ is the incident spectral photon flux density and $QE(E)$ is the measured EQE versus wavelength. The solar spectrum AM1.5G was considered during the calculation. Using these two

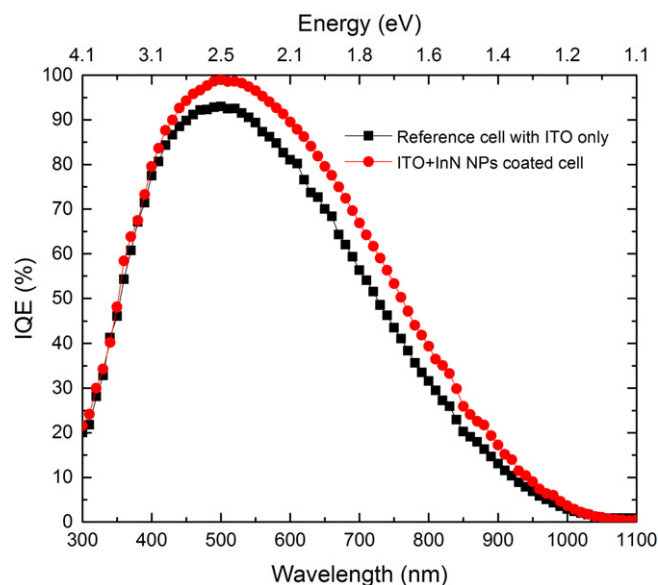


Figure 8. Internal quantum efficiency of the c-Si HIT reference cell with ITO and the cell with ITO + InN NPs.

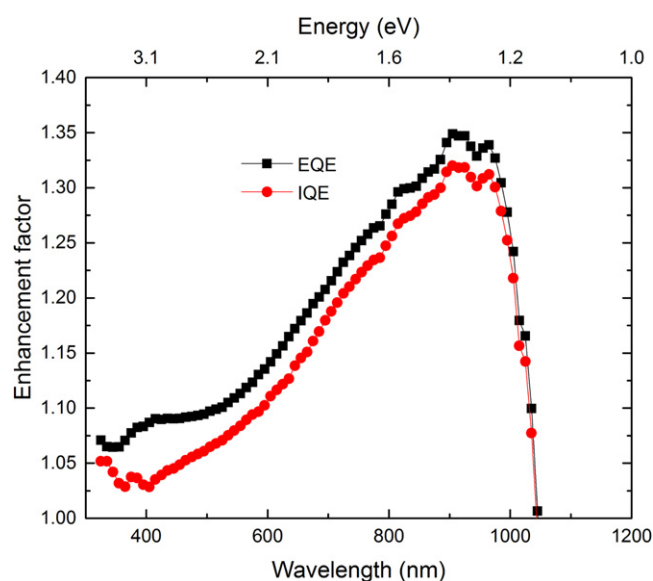


Figure 9. Enhancement factor of external and internal quantum efficiency of c-Si HIT cells due to the addition of InN NPs.

equations and figure 6, a J_{sc} increase of 2.41 mA cm^{-2} has been found due to the spin-coating of InN NPs on top of ITO. This increase is in good agreement with the results found during electrical characterization of the cells.

Figure 8 plots IQE versus wavelength of the reference cell consisting of ITO and the cell consisting of ITO + InN NPs. This plot shows an enhancement due to InN NPs incorporation where the peak increases from 93% at 500 nm to 98.6% at 510 nm.

Figure 9 plots the enhancement factor (value of InN NPs coated cell/value of reference cell) of EQE and IQE as a function of wavelength. This figure shows that the enhancement in EQE is always higher than IQE which suggest that forward scattering of light has been playing the major role in performance improvement of these solar cells. EQE curves in figure 7 shows an increase in EQE from 400 nm onward due to the addition of InN NPs and a lower reflection from the InN NPs coated cell between 390–1100 nm in figure 6 confirms that forward scattering of light is occurring. Now IQE curves shown in figure 8 suggest an enhancement from 400 nm onwards, though photoluminescence spectra of InN NPs shows an emission peak between 310–400 nm. Figure 9 also shows little enhancement of IQE in this range which increases gradually and reaches to its peak value around 870 nm ($\sim 1.43 \text{ eV}$). From the reflection and transmission curves of InN NPs coated glass (figure 4)

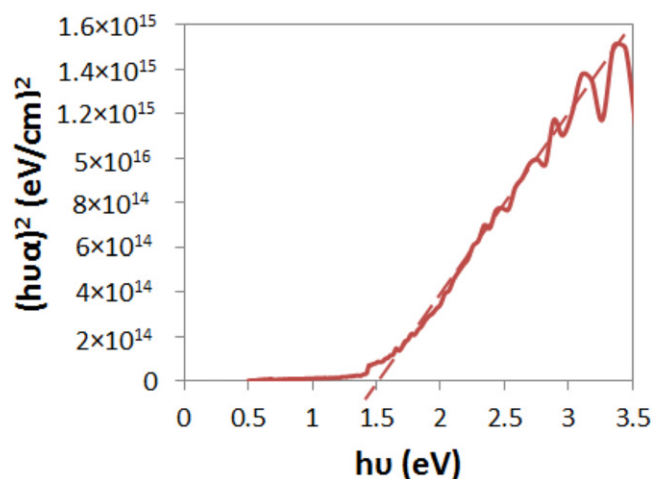


Figure 10. InN NPs band gap calculation using Kubelka–Munk function.

and using the Kubelka–Munk function, the band gap of the InN NPs was found to be ~ 1.5 eV (shown in figure 10) which is close to the peak of enhancement seen in figure 9. We believe that effect of downshifting becomes more prominent at a wavelength closer to the band gap of InN NPs which was also found while studying other semiconductor NPs like Si NPs [36]. Solar cells coated with Si NPs show broader IQE enhancement with two different peaks. The increase between 360–530 nm had been attributed to the efficient charge separation and collection from Si NPs to ITO which happens due to favorable positioning of the conduction bands of Si NPs and ITO (electron affinity of Si NPs is 2.8 eV and ITO is 4.2 eV) and enhancement between 530–610 nm was due to downshifting of electrons with energy close to the band gap energy of Si NPs (2.03 eV) [36]. For InN NPs, we do not see such enhancement in the shorter wavelength range due to the presence of a barrier between the conduction bands of InN NPs and ITO (electron affinity of InN NPs is 4.6 eV and ITO is 4.2 eV) which prevents charge separation and collection. But close to the band gap of InN NPs radiative recombination becomes more prominent and hence we see a large enhancement in IQE near the band gap of InN NPs.

From a physics perspective, the scattering and downshifting of light due to NPs will occur regardless of the quality of the underlying cell. With higher quality, the scattering and downshifting may be more significant since the lifetime of the layer will be higher which could theoretically generate more electron–hole pairs. In fact, InN NPs of 230 nm diameter have already been studied for commercially available polycrystalline solar cells [21]. It was found that spin-coating polycrystalline solar cells with InN NPs will increase J_{SC} from 34.38 mA cm^{-2} to 35.06 mA cm^{-2} and efficiency from 12.50% to 13.98%. For InN NPs coated polycrystalline solar cells, the spectral response also improved between 300–1000 nm which shows the ability of InN NPs to scatter and downshift light for a wide range of wavelengths. This shows the excellent prospect of InN NPs for commercially available solar cells as this can be added without making any major change in the current fabrication steps by using techniques like spin-coating, spray-coating, dip-coating, drop-casting, etc.

4. Conclusion

In summary, InN NPs coated on top of an ITO ARC layer are proposed to improve the performance of c-Si HIT cells. Exploiting the optical properties of InN NPs, short circuit current density and efficiency have been improved. Compared to the reference cell consisting only of ITO, the average improvement of short circuit current density and efficiency are 9.67% and 16.42% respectively for the InN NPs coated c-Si HIT cells. In addition, the spectral response also improves due to the coating of InN NPs on top of ITO. Finally, these results highlight a simple use of nanotechnology to improve the performance of c-Si solar cells.

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