Modulation of Characteristics of Si Solar Cells by Luminescence-Downshifting Zn-Based Nanoparticles with Mn doped

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***Abstract*— We deposit Mn-doped Zn-based nanoparticles (NPs) on Si solar cells using the drop casting and layer-by-layer methods and measure their current-voltage and spectral response characteristics. The solar cells covered by the NPs show higher conversion efficiencies due to the interference of the layered NPs. We also observe enhancement of internal quantum efficiency (IQE) of Si cells, which is due to the luminescence downshifting (LDS) of deposited NPs. A model for describing effects of LDS on IQE is also provided.**

I. Introduction

Characteristics of solar cells are sensitive to the optical properties of their surfaces such as anti-reflection films and textures. We previously synthesized nanoparticles (NPs) of compound semiconductors such as CdTe [1], ZnSe [2][3] and ZnSe:Mn [4] and investigated their optical properties. We also deposited them on substrates using the layer-by-layer (LBL) method [5][6]. We experimentally conformed that luminescent-downshifting (LDS) occurred in these NPs [4][7]. On the assumption that the characteristics of solar cells might be improved by forming layers of such NPs on surfaces of their emitters, we previously coated the emitter surfaces of Si cells with CdS NPs and observed that the contribution of NPs was apparent in the reflectance spectra [8]. In this work, we examined effects of layered Zn-based NPs on characteristics of Si cells with emphasis on their spectral response.

II. EXPERIMENTAL

We performed ion implantation of boron and phosphorous species to p-Si (100) substrates and annealing so as to form p+-base and n+-emitter layers. The contacts to the p+-base were formed by evaporating Al/Ni/Au multilayers and annealing. We fabricated n-on-p Si cells by forming emitter contacts by Ti/Au evaporation and dicing. The area of emitters was 2 mm by 2 mm. We measured their current-voltage (I-V) characteristics under the solar irradiance of AM1.5G/one sun as well as reflectance and quantum efficiency characteristics at room temperature. We prepared ZnSe:Mn/ZnS core/shell (core-doped) and ZnSe/ZnS:Mn/ZnS core/shell (shell-doped) NPs by using the hydrothermal synthesis method. These NPs absorb photons at a wavelength $\lambda < 400$ nm. We previously observed photo emission from core-doped NPs at 563 nm [7]. The emission was attributed to doped Mn as emission center [7]. We assume that shell-doped NPs reveal higher luminescence efficiency in comparison with core-doped ones.

Using the drop casting (DC) and LBL methods [5], we coated the surfaces of emitters of the Si cells with these NPs. The DC and LBL processes are schematically shown in Figs. 1 and 2, respectively. In the DC method, substrates were dipped by solutions of poly vinyl alcohol doped with core-doped NPs. In the LBL process, the surfaces of Si cells were alternately dipped by a solution of positively-charged poly diallyl-dimethyl ammonium-chloride and a solution of negatively-charged poly acrylic acid and NPs. The Si cells were rinsed by water between dipping [8].

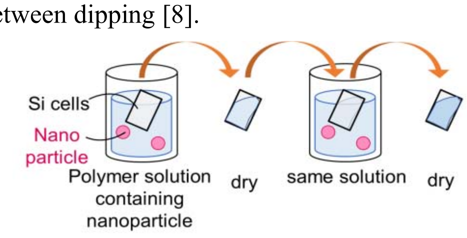

Fig. 1. Schematic process flow of the drop casting method. Substrates were dipped by solutions of poly vinyl alcohol doped with core-doped NPs.

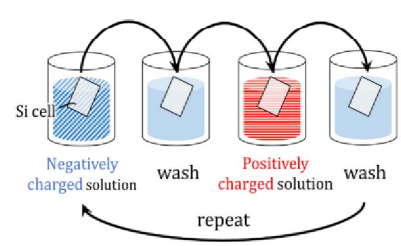

Fig. 2. Schematic process flow of the layer-by-layer (LBL) method. Substrates were alternately dipped by solutions of positively charged and negatively charged molecules. Substrates were rinsed by wafer between dipping.

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We prepared three types of NP-coated Si cells. The first type of Si cells was prepared by coating them with core-doped NPs using (a) the DC and (b) the 10-times-repeated LBL methods. We also coated Si cells with shell-doped NPs by repeating the LBL process (c) 20 and (d) 30 times, respectively. The nominal thickness of NP layer was 300 nm and 21.9 μm by DC and 30-times LBL methods, respectively. We observed Mn-related photo emission at ≈580 nm from these NP-coated cells when they were irradiated with a 325-nm Xe lamp (not shown).

III. Results and Discussion

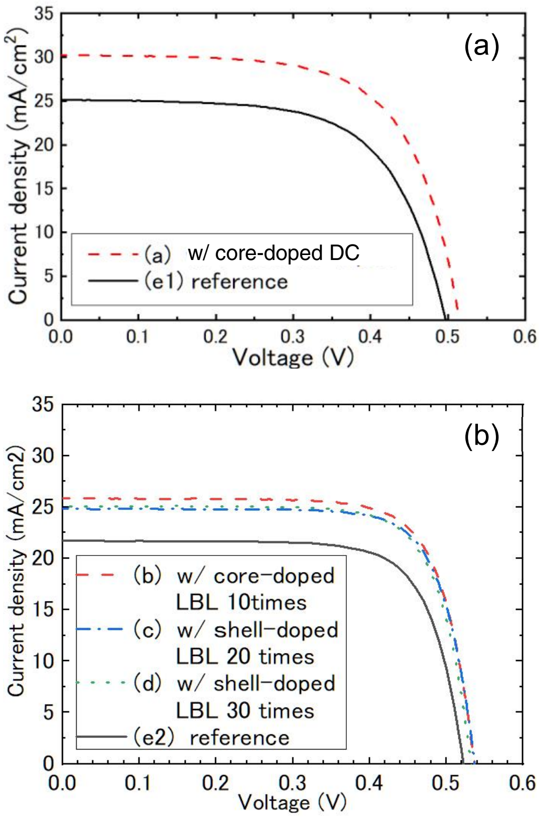

Fig. 3. I-V characteristic of cells under the solar irradiance with the AM 1.5G / 1SUN after coating NPs using (a) the DC process (a) and (b) the LBL process (b-d). I-V characteristics of uncoated cells are also shown for comparison (e1, e2).

TABLE 1

Parameters of Si cell characteristics.

	(a)	(b)	(c)	(d)	(e1)	(e2)
J_{sc} (mA/cm2)	30.3	25.8	24.8	25.0	25.1	21.7
V_{oc} (V)	0.51	0.54	0.54	0.53	0.50	0.52
Fill Factor	0.65	0.75	0.76	0.75	0.64	0.74
R_s (Ω·cm)	1.73	4.77	5.44	4.41	2.36	5.38
R_{sh} (Ω·cm)	2.17 E+4	1.31 E+5	1.13 E+6	5.65 E+5	6.15 E+3	1.66 E+5
Conversion efficiency (%)	10.2	10.4	10.1	10.0	7.99	8.41

The I-V characteristics of cells prepared using the LBL and DC methods are shown in Figs. 3 (a) and 3(b), respectively. Characteristics of uncoated cells are also shown for comparison in the respective figures (e1 and e2). Parameters extracted from the respective curves are summarized in Table I. We obtained a larger short-circuit current (J_{SC}) and a higher conversion efficiency in (a)-(d).

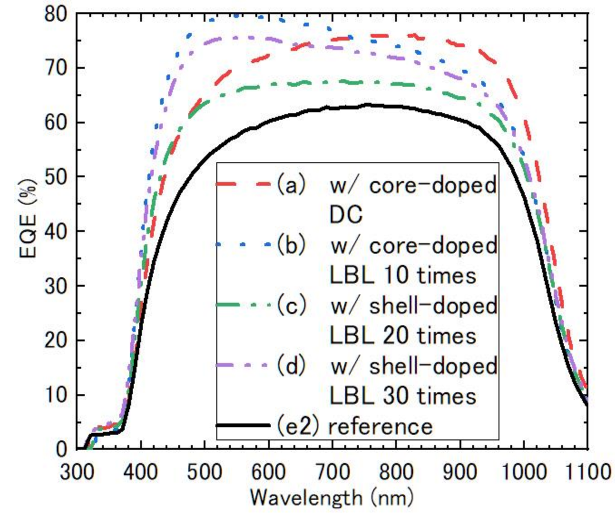

Fig. 4. EQE spectra of cells after coating process by core-doped NPs (a, b) and by shell-doped NPs (c, d). The EQE for an uncoated cell is also shown for comparison (e2).

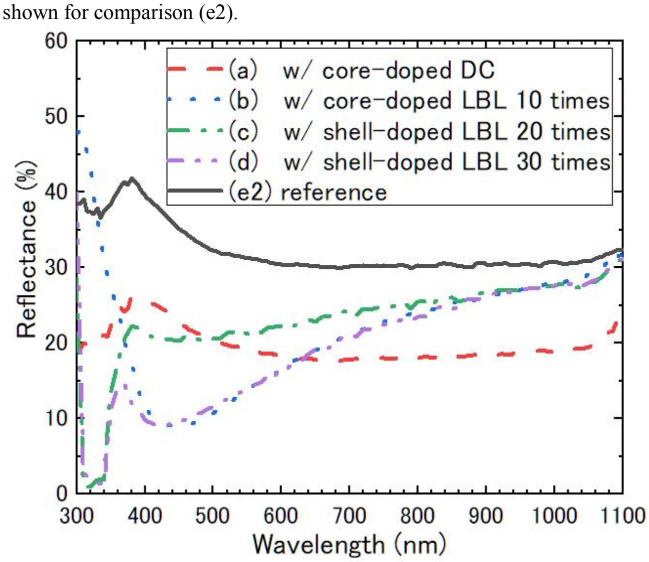

Fig. 5. Reflectance spectra of Si cells after coating process by core-doped NPs (a, b) and by shell-doped NPs (c, d). The spectrum for an uncoated cell is also shown for comparison (e2).

Figures 4 and 5 show the external quantum efficiency (EQE) and the reflectance spectra of (a)-(d) for λ between 300 and 1100 nm. The internal quantum efficiency (IQE) extracted using the EQE and reflectance is shown in Fig. 6. In accordance with higher J_{SC}, the coated cells (a)-(d) revealed a markedly larger EQE. (a)-(d) had higher IQE for λ between 400 and 1000 nm. The difference in the IQE spectra among cells was not as apparent as that observed in the EQE spectra. As is shown in the inset of Fig. 6, we observed IQE enhancement in (a)-(d) for λ between 300 and 400 nm.

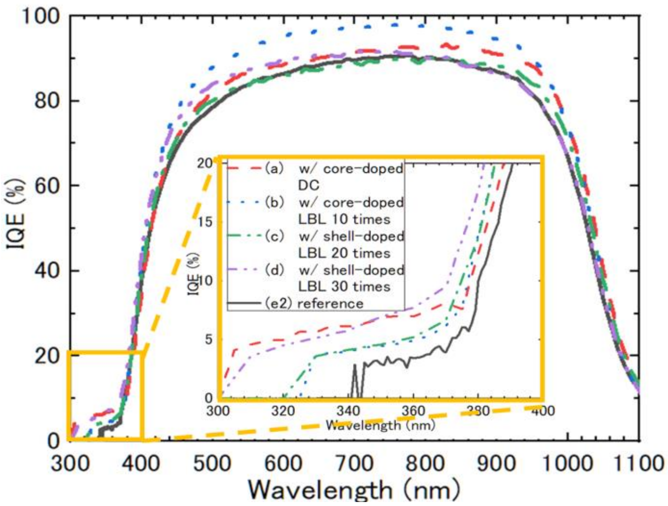

Fig. 6. IQE spectra of Si cells after coating process by core-doped NPs (a, b) and by shell-doped NPs (c, d). IQE spectra of uncoated cells are also shown for comparison (e2).

We deposited NPs on transparent glass plates and measured their optical density (OD) (not shown). Figure 7 shows relationship between IQE of coated cells at 350nm and OD of NP layers on glasses. We find that IQE of cells coated by shell-doped NPs with OD = 0.06 almost agrees with IQE of cells coated by core doped NPs with OD = 0.13.

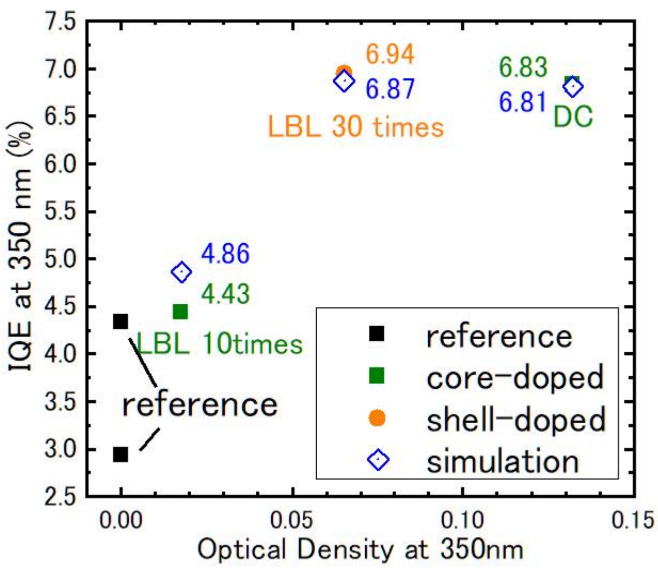

Fig. 7. Relationship between IQE of coated cells at 350nm and OD of NP layers. Calculated IQE is also shown for comparison.

The IQE enhancement at 300-400nm observed for NP-coated cells suggests that the incident light at these wavelengths is converted to a longer-wavelength light, i.e., the Mn-related luminescence downshifting occurs. The light with a longer wavelength is assumed to penetrate into a deeper part of cells so that the IQE should be improved. It is notable that shell-doped NP layers with a smaller OD (0.06) brought about an IQE enhancement almost equal to that due to core-doped NP layers with a larger OD (0.13), which indicates that shell-doped NPs are more effective in improving characteristics of solar cells. The increase in J_{SC} and EQE due to deposited NP layers are mainly attributable to the changes in reflectance due to the interference inside of the NP layers that act as optical thin films [8].

With reference to research of another group [9], we assume that IQE of NP-coated cells at 350 nm is the sum of contributions of incident 350-nm photons and downshifted photons emitted from NPs. On this scheme, IQE of NP-coated cells at 350 nm, $IQE_{350,NP}$, is expressed as follows:

$$IQE_{350,NP} = (1-T) \times LQE \times \alpha \times IQE_{580,ref} + T \times IQE_{350,ref}$$

In this expression, T and LQE are the transmission probability of incident 350 nm photons across the NP layers ($T=10^{-OD}$) and the luminescence efficiency of NPs, respectively. It is notable that (1-T)×LQE provides the ratio of the number of downshifted photons emitted from NPs to the number of incident photons. $IQE_{350,ref}$ and $IQE_{580,ref}$ stand for IQE of reference (uncoated) cells at 350 and 580 nm, respectively. We assume that the contribution of downshifted photons to IQE is represented by that at 580 nm, the peak wavelength of photoluminescence spectrum of NP layers. The coefficient α ($0<\alpha<1$) gives a loss due to escape of downshifted photons from top surface or sides of NP layers [10].

We calculated IQE of the respective cells at 350 nm by assuming that α=0.7. The obtained IQE values are also shown in Fig. 7. We obtained an agreement between calculated and experimental results. The model described above predicts that higher IQE values are achieved by decreasing T, i.e., by increasing the optical density of NP layers.

IV. CONCLUSION

The surfaces of Si solar cells were coated with Zn-based nanoparticles (NPs) with Mn doped in their cores and shells. The drop casting and LBL methods were used in coating process. We found improvement of IQE of Si solar cell by doped Mn-related downshifting of luminescence. The observed relationship between the enhancement of IQE and OD of NP layers indicated that the shell-doped NPs are more efiicient in enhaning quantum efficiencies of solar cells in comparision with the core-doped ones. For further improvement of IQE, increasing NPs concentration in LDS layer is efficient.

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