Sol-gel ZnO Nanoparticles as a Selective Electron Layer in low-Temperature Solution-Processed Perovskite Solar Cells.

Ahmed. H. Kurda 1
Department of Physics, College of Science Salahaddin University
Erbil, Kurdistan of Iraq.
Email: ahmedkurdaj69@gmail.com

Yuosif M. Hassan 2
Department of Physics, College of Science
Salahaddin University
Erbil, Kurdistan of Iraq.

Naser M. Ahmed 3
School of Physics, University Sains Malaysia, Nano optoelectronics Research &Technology (NORT)
11800, Penang, Malaysia

Abstract: The sol-gel ZnO nanoparticles were found to form a relatively compact film without sintering steps throw low temperature process (<1200°C) to perform perovskite solar cells using a spin coating technique. The perovskite layer was sandwiched between zinc oxide (ZnO) nanoparticles thin film as a selective electron transport layer (ETL) and organic hole selective poly (3,4-ethylenedioxythiophene): poly (styrenesulfonate) PEDOT:PSS layer. A methylammonium lead iodide (CH$_3$NH$_3$)PbI$_3$ active layer was deposited on the ZnO nanoparticles modified ITO substrate. X-Ray Diffraction (XRD), field effect scanning electron microscope (FESEM) were employed to characteristic structure and morphology of the samples. Photoluminescence (PL) spectroscopy used for optical band gap energy for ZnO nanoparticles, methyl ammonium lead iodide (CH$_3$NH$_3$)PbI$_3$ perovskite were calculated to be 3.27, 1.62 eV respectively. The crystalline ZnO nanoparticles 15 nm in diameter were determined by transmission electron microscope (TEM). The whole device could be fabricated under mild conditions with relatively low temperature and solution process. Devices based on modified (ETL) could achieve high power conversion efficiency (PCE) 7.41 on rigid and 4.65 on flexible substrates with improved device stability. These results imply that interface engineering provides a promising approach to simplify device configuration and reduce the fabrication cost for perovskite solar cells.

Keywords: ZnO, nanoparticles, low-temperature, Spin Coating, perovskite, solar cells.

I. INTRODUCTION

Low-temperature solution process able hybrid solar cells are becoming more attractive as they offer a viable alternative to conventional solar cells fabricated via vacuum-based or high-temperature processes for large-scale, and cost-effective manufacturing on flexible plastic substrates. Organic-inorganic an interesting class of materials is extremely studied as the hybrid, which are required to combine the attractive feature of organic materials and inorganic materials within a single molecule-scale composite.

In the past two decades the organic inorganic hybrid perovskite have arisen as a new functional material and have grown great attention and research effort when deposited by spin coating. These compounds are self-assembled system; they form a multi-quantum well structure spontaneously and exhibit excellent optical and electronic properties at room temperature. The optical properties of these materials can be finely tuned thanks to molecular engineer on the organic part or on the inorganic part. Furthermore, the preparation of these materials is a very simple compared to the deposition techniques for inorganic semiconductors such as PECVD (Plasma Enhanced Chemical Vapour Deposition), MBE (Molecular Beam Epitaxy), and MOCVD (Metalorganic Chemical Vapour Deposition).

Recently organic in organic perovskite have been used in many optoelectronic devices such as surface Plasmon’s [1, 2], LEDs [3], solar cells [4-6], and Microcavities [7-9]. The
 Investigate the optical properties and characterization. The optical properties of perovskite solar cells were measured from the peak of the characteristic absorption of a perovskite structure of CH$_3$NH$_3$PbI$_3$. ZnO nanoparticles were dispensed in the chloroform to form the precipitace was washed twice with methanol. Finally, ZnO nanoparticles were dispersed in the chloroform to form a ZnO nanoparticle solution. The solution was stable for more than a month. The optical properties of the samples were investigated using photoluminescence (PL) spectroscopy (model: JobinYvon 800 UV) with a wave length range 200-1100 nm and the optical band gap was measured from the peak of photoluminescence spectrum.

**EXPERIMENTAL SECTION**

ZnO nanoparticles were prepared according to literature procedures [20] Zinc acetate dehydrate (Zn (COOH)$_2$·2H$_2$O, Sigma Aldrich) 2.95 g was dissolved in methanol (125 ml) with stirring at 65 °C. A solution of potassium hydroxide (KOH) 1.48 g in methanol (65 ml) was then added drop wise at 60-65 °C over a period of 15 min. The reaction mixture was stirred for 2.5 h at 65 °C. After cooling to room temperature, the supernatant was decanted and the precipate was washed twice with methanol. Finally, ZnO nanoparticles were dispersed in the chloroform to form a ZnO nanoparticle solution. The solution was stable for more than a month.

Methylammonium iodide (CH$_3$NH$_3$I) was synthesized by reacting 27.86 ml methyamine (40% in methanol, Sigma-Aldrich) and 30 ml of hydroiodic acid HI (57% in water, Sigma-Aldrich) in 250 ml round bottomed flask at 0 °C for 2 h with stirring. The precipitate was recovered by evaporation at 50 °C for 1h. The product, methylammonium iodide (CH$_3$NH$_3$I) was washed with diethyl ether by stirring the solution for 30 min, which was repeated three times, and finally dried at 60 °C in a vacuum oven for 24 h [21].

Solar cell fabrication: figure 1 shows the device architecture of the perovskite Solar cells were fabricated on rigid (glass/ITO, glass/FTO) and flexible polyethylene terephthalate (PTE/ITO) substrates with a sheet resistances of 8 Ω sq$^{-1}$ and 30 Ω sq$^{-1}$ respectively. first, a ZnO nanoparticle layer was spun coated onto the substrate at 3000 rpm for 20 s. The procedure was repeated three times to obtain a continuous smooth film. (CH$_3$NH$_3$I) PbI$_3$ was deposited on top of ZnO layer using a two-step method [21]. A 1 M lead iodide PbI$_2$ (Sigma, Aldrich) solution was prepared by dissolving 2.33g of PbI$_2$ in 5 ml of N, N-Dimethylformamid (DMF, Sigma Aldrich). The solution was kept at 70 °C for 2 h. A (CH$_3$NH$_3$I) solution was prepared by dissolving 0.05 g of (CH$_3$NH$_3$I) in 5 ml of 2-propanol (0.063M). A100µL portion of pbI$_2$ solution was dropped on the cleaned ITO (FTO) glass 2.5 × 2.5 cm$^2$ substrate; the substrate was spun immediately at 3000rpm for 20s and dried at 100 °C for 10 min. After cooled a 200µL of (CH$_3$NH$_3$I) solution was dropped on the substrate; a wait time of 20 s was observed, and the sample was spun at 2000rpm for 20 s and dried at 100 °C for 10 min. The hole transport layer was formed by spin –coating the PEDOT: PSS (37% in H$_2$O, Sigma Aldrich) at 3000rpm for 30 s and annealed at 120 °C for 10 min. Finally, a thick silver Ag layer was deposited by thermal evaporation at a base pressure of 4×10$^{-5}$ mbar.

From the optical and electrical properties of perovskite solar cells, the hydrothermal method used for preparation ZnO nanoparticles, with a nanoparticle size and the current verses voltage (I-V) characteristics of device with different substrates were taken under Am1.5G (100 mW cm$^{-2}$) illumination.
III. RESULTSAND DISCUSSIONS:
A. Optical Properties of device
Figure 2a Shows the photoluminescence spectrum for ZnO nanoparticles. The samples are excited by a light source which is the 325 nm line of a He-Cd laser and the PL emission signal is then collected by a (spectrometer coupled to a CCD camera). The maximum intensity of the luminescence is observed at 378.315 nm corresponds the optical band gap $E_g = 3.27$ eV of ZnO nanoparticles. The small intensity peak is due to the same defects, in fact the values of band gap depend on many factors, e.g. the granular structure, the nature and concentration of precursors, the structural defects and the crystal structure of the films. Figure 1b shows the photoluminescence (PL) spectrum of the $(\text{CH}_3\text{NH}_3)_2\text{PbI}_3$ perovskite film, the sharp and smooth peak range from 700 nm to 800 nm with intensity over than 2000 c/sec appeared. The PL intensity is proportional to the number of the emitting photons on the perovskite surface. The maximum intensity of the luminescence is observed at wavelength 765.032 nm corresponds the optical band gap 1.62 eV for $(\text{CH}_3\text{NH}_3)_2\text{PbI}_3$ perovskite.

B. Structural Analysis for device
Figure 3a depict the x-ray diffraction (XRD) pattern of the crystal structure and orientation of the ZnO nanoparticles on glass substrate using spin-coating 3000rpm and anneled at 120°C for 10 min. From the XRD pattern, one can clearly observe a diffraction peak at 20 =34.34. strong preferential growth is observed along c-axis i.e. (002), suggesting that the prepared ZnO nanoparticles have the wurtzit structure. Figure 3b depicts the X-ray diffraction (XRD) pattern perovskite film deposited on glass substrate using two-step solution deposition by spin-coating at 3000rpm and 2000rpm, and then annealed in air at 100°C (Fig. 3(c) ). The XRD pattern of $(\text{CH}_3\text{NH}_3)_2\text{PbI}_3$ perovskite shows a set of strong diffraction peaks at 20 = 26.2611, 40.4942, and 50.4667 degree corresponding to the (110), (211), and (213) planes of the $(\text{CH}_3\text{NH}_3)_2\text{PbI}_3$ perovskite crystal. These indicate a tetragonal crystal structure of halide perovskite with high crystallinity using facile and attractive two-step deposition[22]. According to the literature [23], there is often a tiny signature peak at 20 = 34.2680 is corresponding to a low level impurity of PbI$_2$ and 20 = 43.9415, 44.2250 are corresponding to $(\text{CH}_3\text{NH}_3)I$. The absence of a PbI$_2$ peak in the present perovskite film suggests complete consumption of PbI$_2$. XRD patterns could be ascribed comparable to the most reliable methods of vacuum deposition or vapour deposition processing [23].

C. Morphological analysis of device
Figure 4 shows the transmission electron microscopy (TEM) of ZnO nanoparticles synthesized as electron selective contacts by hydrolysis method. The process produces a relatively compact ZnO layer and crystalline ZnO nanoparticles that are average 15 nm in diameter. The thickness of which can be varied systematically by repeating the spin coating process several times.
IV. I-V CHARACTERIZATION OF DEVICE

Figure 6a presents the current - voltage (I-V) curves of the perovskite solar cells consisting of ZnO(nanoparticle)/(CH$_3$NH$_3$)PbI$_3$/PDOT:PSS/Ag on different (rigid glass /ITO, FTO and flexible PET/ITO substrates) under 1 sun Am 1.5 simulated solar irradiation. The photovoltaic parameters of the devices are summarized in Table 1. As shown in figure 6b, the incident photon to electron conversion spectrum indicates that the device shows a spectral response in the region from the visible to near infrared (300 – 800 nm).

Table 1 Device parameters for solar cells prepared with varying substrates

<table>
<thead>
<tr>
<th>substrates</th>
<th>$I_{sc}$ (mA)</th>
<th>$V_{oc}$ (Volt)</th>
<th>Fill factor %</th>
<th>PCE %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass/ITO</td>
<td>12.8</td>
<td>0.83</td>
<td>70.0</td>
<td>7.41</td>
</tr>
<tr>
<td>Glass/FTO</td>
<td>10.85</td>
<td>0.8</td>
<td>68.5</td>
<td>5.94</td>
</tr>
<tr>
<td>PET/ITO</td>
<td>8.7</td>
<td>0.77</td>
<td>69.5</td>
<td>4.65</td>
</tr>
</tbody>
</table>

V. CONCLUSION

In this work, we have synthesized ZnO nanoparticles as a selective electron layer in (CH$_3$NH$_3$)PbI$_3$ perovskite solar cells on rigid and flexible substrates using two-step solution processed spin-coating technique. The structure, morphological and optical properties of the films were investigated. The two-step solution is a simple technique, and there are many factors which affected the quality of the films. We have optimized different parameters such as time formation and full spin-coating deposition to obtain a good crystalline structure of (CH$_3$NH$_3$)PbI$_3$ perovskite film with intense and sharp (PL) peak. According to XRD results, the as-deposited films exhibited a tetragonal structure with (003) preferential orientation after annealing at 100 in air.
ambiance for 10 min. The XRD pattern consists of two (003), (112) peaks which occurred due to (CH$_3$NH$_3$)PbI$_3$ crystals and grows along the c-axes. The grain size and thickness of the films are estimated to be 5.83 nm and 350 nm. FESEM of (CH$_3$NH$_3$)PbI$_3$ perovskite film shows that the medium grains made a smooth and opaque surface. The maximum photoluminescence (PL) spectrum intensity is observed at wavelength 378.315 nm, 765.032 nm corresponds to the optical band gap 3.27 eV for ZnO nanoparticles and 1.62 eV for (CH$_3$NH$_3$)PbI$_3$ perovskite film. A novel low-temperature approach to fabricated perovskite films, based on the kinetically favourable reaction between the as-deposited film of PbI$_2$ and CH$_3$NH$_3$I. The perovskite film derived from this approach exhibits full surface coverage, uniform grain structure with grain size up to nanometres, and 100% precursor transformation completeness. Two-step deposition presents a simple, controllable, and versatile approach to the pursuit of high-quality perovskite film and the resulting high-performance efficiency (PEC) 7.41 on rigid and 4.65 on flexible perovskite solar cells.

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