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Optimization of TiO_2/ZnO bilayer electron transport layer to enhance efficiency of perovskite solar cell

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ABSTRACT

In the present study, TiO_2/ZnO bilayer as electron transport layer is optimized and used to design a perovskite solar cell. This bilayer helps in high electron extraction and low interfacial recombination. TiO_2 films are prepared using spray pyrolysis techniques on fluorine doped tin oxide substrate. The deposition parameters are optimized using parametric study as well as using the Taguchi optimization technique. ZnO is used as other part of electron transport bilayer to reduce the charge recombination. The thickness of prepared TiO_2 film obtained at Taguchi optimum condition (103 nm) is lower than that of obtained at parametric optimum condition (147 nm). At optimum conditions, the optical band gaps are in the range of 3.20–3.25 eV. The prepared TiO_2 films are consequently applied in perovskite solar cell preparation. 4-tert-butylpyridine is used with PbI_2 to increase the stability of the perovskite solar cell. In addition, spiro-OMeTAD and Pt- fluorine doped tin oxide are used as hole transport material and counter electrode, respectively. The power conversion efficiency of the device at optimum conditions (parametric (D_5) and Taguchi (D_9)) has been found as 5.59% and 6.51%, respectively. The power conversion efficiency of the device using 4-tert-butylpyridine as stabilizer has been found as 7.39% (D_{11}), which is highest among all devices. Current density (J_{sc}), open circuit voltage (V_{oc}) and the fill factor obtained for the device (D_{11}) are 17.87 mA cm^{-2}, 0.65 V, and 64%, respectively.

1. Introduction

TiO_2 thin films have various advantages over other n-type semiconductor materials as it has excellent optical and electrical property, perfect chemical stability, oxidizing properties, and a wide band gap [1]. It is an excellent material to be applied in many fields such as sensors [2], photocatalysis [3], light emitting diode [4], anti-reflecting coating [5], and solar cells [6]. TiO_2 has different crystalline phase; rutile, anatase, and brookite [7]. When the deposition temperature is kept between 350 and 700 °C, anatase phase is observed whereas at the higher temperature it leads to the growth of rutile phase [8]. However, complex preparation promotes the formation of brookite phase. Brookite phase is unstable phase and it has never been found as single phase. Anatase phase is more photocatalytic active than the rutile and brookite phases [9]. Spray pyrolysis technique is a solution based technique and therefore the quality of films can be tuned easily by altering the synthesis parameters [10]. In the present work, spray pyrolysis technique is selected for TiO_2 film preparation. In this technique, the major process parameters influencing the properties of the deposited film are precursor concentration, substrate temperature, and solution flow rate. To identify the optimized conditions, it is necessary to understand the effect of each of the important process parameter on responses. One can also identify the most influencing operating parameter. Optimization of output based on input data using parametric study requires a large number of experiments. To reduce the number of experiments and to optimize the output based on input parameters, Taguchi and Komesh have developed a statistical method [11]. This technique is used to identify and optimize the deposition parameters which affect the performance of a process significantly. However, to the best of Author's knowledge; study on the simultaneous effect of each of the three major parameters is yet to be reported. The effect of substrate temperature and the flow rate is reported by Azizi and Mohagheghi in detail [12]. The effect of temperature and precursor concentration is reported in detail by Dhanapandian [13]. The effect of only precursor concentration is reported by Fugare and Lokhande in detail [14]. The effect of only solution flow rate has reported by Naffouti et al. in detail [15]. So, there is a need of this study.

Hybrid perovskite materials have received much attention and applied in the fabrication of low-cost and high-efficiency solar cells solar cells because of their excellent properties [16–18]. The power conversion efficiency (PCE) of perovskite solar cell (PSC) is increased from 3.9% [19] to 22.1% [20]. The typical structure of PSC is composed of a

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conductive substrate, a compact layer of electron transport material, a mesoporous layer (optional), a photo-active hybrid perovskite layer, hole-transporting material (HTM), and a metal electrode [21]. The perovskite layer absorbs photons to generate electron–hole pairs. The generated electrons and holes are injected through the electron transport layer (ETL) and hole transport layer, respectively, to separate the charges [22]. Compact layer is one of the most important layers in the structure of PSC because it is used to block the flow of electrons from fluorine doped tin oxide (FTO) to HTM or the flow of holes from HTM to FTO. This reduces the recombination of charges [23]. Most of the reported perovskite solar cells are composed of blocking layer and the mesoporous TiO_2 layer [24–29] and achieved good efficiency. Mesoporous layer helps to form pin-hole free blocking layer that increases the efficiency of the solar cell. Doping of blocking layer with aluminium iodide salt and with an element of the fifth group can be used to enhance the PCE of PSC [30,31]. A compact layer is crucial to prevent interfacial charge recombination at the photoanode/electrode interface of a PSC. To reduce the interfacial charge recombination and improve the PCE of PSC, Duan et al. has used TiO_2/ZnO/TiO_2 sandwich multilayer films as a hole blocking layer and achieved an efficiency of 12.8% [32]. Xu et al. [33] and Yin et al. [34] have applied TiO_2/ZnO multilayer ETL to make highly efficient PSC. The reported PSC [24–33] contains Au/Ag as a metal electrode to complete the device structure. Deposition of a metal electrode (Ag/Au) requires very high temperature that increases the processing cost of solar cell. So, the present study is focused on the use of ZnO as a part of bilayer ETL to reduce the interfacial charge recombination. Further, Pt-FTO has been used as metal electrode to make low cost solar cell.

In our previous study [35], we have optimized ZnO thin films using spray pyrolysis technique. In the present study, spray pyrolysis technique has been used for TiO_2 preparation. All the major parameters are varied to optimize the processing parameters. Further, the Taguchi optimization technique has been also used to optimize the process parameters for TiO_2 film preparation. TiO_2 films prepared at optimized conditions with ZnO film [35] have been used as bilayer ETL for perovskite solar cell preparation. Spiro-OMeTAD and Pt-FTO have been used as hole transport material and counter electrode respectively. In addition, 4-tert-butylpyridine (TBP) has been used as the stabilizer with the perovskite layer to enhance the stability of the device.

2. Materials and methodology

2.1. Material

Fluorine doped tin oxide glass, titanium isopropoxide (TIP), lead iodide (PbI_2), methyl amine iodide, Spiro-MeOTAD, chlorobenzene, 4-tert-butylpyridine, lithium-bis-(tri-fluoro methane sulfonyl) imide (Li-TFSI), acetonitrile, and hexachloroplatinic acid (H_2PtCl_6) were purchased from Sigma Aldrich. Iso-propyl alcohol (IPA) was purchased from S.D. fine chemical; Vadodara, India. All chemicals were of analytical grade and used without further purification.

2.2. Methodology

2.2.1. Deposition of TiO_2 films

TiO_2 thin films have been prepared by the spray pyrolysis method using TIP precursor. TIP was dissolved in IPA-HCl to make precursor solution. The precursor solution was sprayed on FTO to deposit TiO_2 thin film. Air was used as carrier gas to assist the spray nozzle. The experimental setup was same as used in our previous study [35]. The influence of various control parameters has been studied in detail to find optimum conditions. Precursor concentration (0.05–0.15 M); substrate temperature (350–550 °C); and the solution flow rate (3–6 mL min^{-1}) were varied. The carrier gas pressure was fixed at 1.5 bar throughout the study.

2.2.2. Deposition of ZnO film

ZnO layer of thickness 79 nm was coated further on FTO/TiO_2 layer according to the method reported in our previous study to make electron transport bilayer [35].

2.2.3. Perovskite solar cell fabrication

First, a blocking layer of TiO_2 is coated on etched FTO and then ZnO layer was coated on FTO/TiO_2 to form electron transport bilayer using the method mentioned in the methodology section. Then a layer of $CH_3NH_3PbI_3$ was coated on FTO/TiO_2/ZnO layer according to the method reported by Mukta et al. [36]. Change in colour was observed from yellow to black, which confirmed the proper formation of perovskite layer. Spiro-MeOTAD (2,2′,7,7′-tetrakis (N,N-di-p-methoxyphenylamine)-9,9′-spirobifluorene) was used as a source of the HTM. The solution of the HTM was made and a layer was coated on FTO/TiO_2/ZnO/$CH_3NH_3PbI_3$ substrate using the method reported by Saliba et al. [37]. For the counter electrode, hexachloroplatinic acid (H_2PtCl_6) was used as a precursor of the platinum electrode. A 5 mM, H_2PtCl_6 was made in IPA and it was coated on other FTO using the spin coating method, and then sintered at 400 °C for 15 min [38] to get the platinised counter electrode. The platinised FTO was sandwiched with the prepared FTO/TiO_2/ZnO/$CH_3NH_3PbI_3$/Spiro-MeOTAD film to complete the device structure [39]. In order to measure the PCE of PSC, a solar simulator under 100 mW cm^{-2} incident light was used. The active area used for efficiency measurement was kept at 0.09 cm^{-2} and rest of the area was masked with a black tape [40].

2.3. Characterization

Structural and surface morphology have investigated with X-ray diffraction (XRD; Rigaku D/Max 2200) and scanning electron microscopy (SEM; Nova Nanosem 450, FEI limited), respectively. Optical properties of the films were measured by UV–Vis–NIR spectrophotometer (Hach-DR6000). The film thickness was measured using MProbe thickness monitor (SemiconSoft, USA). The PCE of PSC was measured using SS150 solar simulator (ScienceTech, Canada) connected to the keithley (2401) source-meter.

3. Results and discussion

3.1. Optimization of TiO_2 using the parametric study

3.1.1. Effect of substrate temperature

The influence of substrate temperature on (a) the thickness of the prepared TiO_2 film and (b) the PCE of PSC was studied in detail. The precursor concentration (0.15 M) and solution flow rate (4 mL min^{-1}) were kept constant and the substrate temperature was varied from 350 to 550 °C to find the optimum condition. The XRD pattern of prepared TiO_2 film at various substrate temperatures is shown in Fig. 1. It was obtained in the scanning range (2θ) of 20–60° using a copper radiation source (λ_{max} = 1.5406 Å). The X-ray tube was operated at 30 kV and 25 mA. The major peak is obtained at 25.54°, which is corresponding to the (101) plane. This confirms the proper formation of the TiO_2 film (JCPDS NO. 21-1272). From Fig. 1, it is clear that with the decrease in the substrate temperature from 450 °C to 350 °C, the amorphous nature of the film is observed. A similar result was observed by Dhanapandian et al. [13]. Additionally, the thickness of prepared TiO_2 was observed to be increased (see Table 1, D_1-D_4) below the temperature 450 °C. This might be attributed to the less amount of thermal energy available to convert TIP into TiO_2 at low temperature. However, with the increase in the temperature from 450 °C to 550 °C, the height of the major peak reduces (see Fig. 1). A similar result was reported by Azizi and Mohagheghi [12]. This might be attributed to the evaporation of solvent at the higher temperature before reaching to the substrate. Further, the films obtained at 350 °C, 450 °C, 475 °C, and 550 °C were applied in PSC fabrication (D_1, D_2, D_3, and D_4, respectively). The PCE of the device