SYNTHESIS AND CHARACTERIZATION OF METHYLAMMONIUM LEAD BROMIDE PEROVSKITE BASED PHOTOVOLTAIC DEVICE[†]

^{(D}Shaily Choudhary^a, ^{(D}Shalini Tomar^a, ^{(D}Depak Kumar^b,

[©]Sudesh Kumar^c, [©]Ajay Singh Verma^{d,*}

^aDepartment of Physics, Banasthali Vidyapith, Banasthali, Rajasthan 304022, India ^bDepartment of Chemical Engineering, Banasthali Vidyapith, Banasthali 304022, India ^cDepartment of Physics, Banasthali Vidyapith, Banasthali, Rajasthan 304022, India ^dDepartment of Natural and Applied Sciences, Glocal University, Saharanpur 247232, India *Corresponding author: ajay_phy@rediffmail.com Received April 17, 2021; accepted August 5, 2021

Hybrid electronic devices give a reasonable path for feasible power sources and other further applications due to its easy arrangement, preparation, producing, ease of materials, and less environmental impact. In this paper, we have discussed electrical properties of hybrid bromide perovskite nanoparticles and current progressions in perovskite photovoltaic devices have also been discussed. In order to fabricate, low-temperature solution-processed devices using one-step spin coating methods play a key role in producing uniform thin films. The spin coating technique has been used for the deposition of the precursor solution including methylammonium bromide (MABr) and lead bromide (PbBr2) with molar ratio (3:1) to prepare the thin films onto FTO-substrate. One-step solution processes has been used for deposition of the CH₃NH₃PbBr₃ absorber layers and have explained an overview of material composition, deposition technique and the architecture of the device, the selection of charge transport layer and electrode.

Keywords: metal halide perovskites; charge carrier mobility; resistance; capacitance; electrochemical impedance spectroscopy **PACS:** 61.30.Hn; 61.41.+e; 61.46.Df; 61.82.Fk; 68.37.Hk; 73.21.-b; 73.30.+y; 73.40.Lq; 73.50.Gr

The speed up world population expansion and post industrialized period bring to consideration a unexpected requirement of energy, answerable for environment dilemma, sustainable growth concerns with financial challenges [1-3]. Presently, finite sources of energy like fossil fuels are the resource for greater than 85% of the world main power and accountable in support of most of the green house gas emission. Wind, sun, hydraulic, biomass and geothermal have been studied for the technologies that take benefit of renewable energy sources. Sunbeams has an huge potential as energy resource among an irradiance 1.8×10^{14} kW at earth's outside, which can be convert in electrical energy as well as heat with negligible natural impact. Photovoltaic devices are one of the great hopeful mechanization for producing electricity from sunlight [4-6].

Kojima et al. [7] have demonstrated that organometal halide perovskites as light absorber with 3.8% power conversion efficiency. The organometalic hybrid halide perovskite material used, with the nonspecific structure of CH₃NH₃PbX₃, quickly proved to have an amazing high efficiency as light absorber displaying also very strong hole and electron conductivity. This disrupting result led to the appearance of a new thin film photovoltaic family– in today's world one of the most investigated families of photovoltaic devices are Perovskite photovoltaic devices [8]. The rapid attention on the perovskite photovoltaic devices has correlated to the great enhance on energy conversion efficiency, this technology experienced in the last 7 years, from 3.8% in 2009 to 22.1% in 2017 [9]. The essential property of Hybrid organic-inorganic Perovskites is their phase complexity from cubic, tetragonal, orthorhombic and monoclinic polymorphs (orthorhombic (space group -Pna21) to tetragonal (space group- P4/mmm) transition at 161.4 K and tetragonal to cubic (space group- Pm_3m) at 340.4 K). The main reason for phase transitions is a change in temperature, pressure, and applied field [10]. Theoretically number of first principles calculations for CH₃NH₃PbI₃ has been reported in recent years, for instance, Li Lang et. al and Yuan Ye et. al. reported that band gap and lattice constant depends upon A, B and X in ABX₃ they reported that as A increases from Cs to CH₃NH₃⁺ or NH₃CHNH₃⁺ and X changes from Cl to Br to I lattice constant increase and B varies from Sn to Pb band gap increase [11-12]

The promising organic-inorganic hybrid halide perovskite photovoltaic device (PPVs) represent one of the lifechanging technology, just like organic photovoltaic devices (OPVs), and DSSCs, Perovskite also potentially can be converted into light-weight, adjustable and low in cost power sources throughout the high-throughput solution fabrication [13-15]. Perovskite photovoltaic devices have therefore acquired the exhaustive efforts in research from both academic world and industry. It fundamentally benefits from the outstanding electrical properties of semi-conducting organic– inorganic hybrid perovskite, such as the strong optical absorption coefficient, a long carrier life time, diffusion length, direct band gap, and high electron/hole mobility in crystalline state [16-17]. Most prominently, organic-inorganic lead halide perovskite produces loosely bonded exciton with truly little bonding energy, which facilitates the manufacture of free charge carriers within the Perovskite by the cost of negligible dynamic force [18].

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EXPERIMENTAL METHODS

The heterojunction device has been fabricated onto coated glass-substrate. The zinc powder and hydrochloric acid (HCl) (2.0 M) have been used to etch the fluorine-doped tin oxide (FTO) substrate to acquire the required electrode pattern. After that the substrate was cleaned. The cleaning process of FTO substrate has been displays in Fig. 1.



Figure 1. Illustration of method to clean FTO coated glass-substrate before fabrication of device.

Synthesis of CH₃NH₃PbBr₃ precursor solution. CH₃NH₃Br has been synthesized at 0° C by reacting aqueous hydrobromic acid (HBr) under continuous stirring of 2 hr. After that to remove the solvent the solution has evaporated for 45 min at 60. Through this process the solution transforms into white powder crystals that have washed three times by diethyl ether attend by overnight drying at 60 in vacuum oven. The field emission scanning electron microscopy (FESEM) image of methylammonium lead bromide (CH₃NH₃PbBr₃) perovskite precursor solution onto glass-substrate has been prepared by the deposition of one-step spin coating technique and displays in Fig 2. This image exhibits large domain size of perovskite material with uniform grains distribution and complete surface coverage.



Figure 2. FESEM image shows the surface morphology of perovskite precursor solution.

Photovoltaic device fabrication. The fabrication procedure is following as,



Figure 3. (a) Layout of fabricated device heterostructure, (b) Energy diagram of corresponding device with charge carrier transportation from perovskite to respective electrodes in illumination.

Firstly, the FTO coated glass-substrate has been cleaned as shown in Fig. 1 and then giving it an ozone treatment for 15 minutes for the better deposition. After that, the CH₃NH₃PbBr₃ Perovskite layer (photoactive layer) has been directly coated onto FTO substrate by 2500 rpm for 40 sec and then heated up-to 110 for 5 minutes. A layer of Phenyl-

 C_{61} -butyric acid methyl ester (PC₆₁BM) has been deposited onto perovskite layer by 3000 rpm for 40 sec and then heated for 2 min. Now, the Bathocuprione (BCP) buffer layer has coated onto PC₆₁BM layer by 4500 rpm for 40 second and annealed the device for 5 min. All the layers have been deposited by spin-coating technique inside the glove box under nitrogen gas. Finally, the device has been completed by thermal evaporation of Al to make the top electrode (cathode). The fabrication steps and architecture of the planer perovskite photovoltaic device has displayed in Fig. 3(a). The resultant device is composed of Al/BCP/PCBM/Perovskite/FTO and the energy level diagram of the device has shown in Fig. 3(b) with transportation of the charge carriers excited from Perovskite layer in illumination and then transport to their respective electrodes.

RESULT AND DISCUSSIONS

The surface morphology of perovskite precursor solution characterized by field emission scanning electron microscopy (FESEM) which grown on glass-substrate has displayed in Fig 2. The top view of FESEM image exhibits large grain size of perovskite material with uniform grain distribution and complete surface coverage without agglomeration. We have used band gap value is 2.3 eV, which is investigated in our previous paper [19]. I-V characteristics of the fabricated perovskite (photoactive layer) based device in dark and illumination condition have shown in Fig. 4 (-10V to \pm 10V). We have seen from the figure that in forward biasing current increases exponentially, on the other hand the current vary slowly in dark with the applied voltage. By interpretation of current-voltage curve, applying Shockley model we have acquired the main diode characteristics. The photocurrent is calculated by using following formula:

$I = I_{\circ} \left[exp(qV/nkT) - 1 \right]$

Where, e is electron charge; K is Boltzmann constant; V is ideality voltage; T is absolute temperature; I₀ is reverse saturation current. The value saturation current can be described from the intercept at V = 0 can be obtained from the slope of the linear portion of forward bias region of the semi-logarithmic J-V characteristic shown in Fig. 4(a) as shown in Fig. 4(b), the saturation current (I_s) has been calculated in the value of 1.02×10^{-4} mA by intercept at V=0 using semi-logarithmic scale of I-V curve.



Figure 4. (a) Current-voltage curve of heterojunction devices under the dark and illumination, (b) I-V curve reporting in semilogrithmic scale of corresponding device.



Figure 5. Log-Log scale of I-V curve; m represents the slope of the curve

By analyzing the double logarithmic I-V plots as shown in Fig. 5 the charge transport properties of the device were studied.

General power law dependence of J-V^m exhibit from the curve, where m represents the slope of the curve, a important quantity to define voltage dependent charge transport regions. Number of charge carriers at low applied voltage is miner. The injected charge carriers relatively high as applied voltage is increased beyond the ohmic region. Therefore, the density of injected carriers inside the organic layer reaches to the maximum value. Here the current is limited by the space charge and increased quadratically with the voltage as shown in region m = 2 in the curve. This characteristic represent the trap free space charge limited conduction phenomenon. Therefore, within the band gap presence of traps influence the conduction mechanism, distribution and location of the trap centers governs the current conduction.

SUMMARY AND CONCLUSIONS:

In this paper, we have synthesized and characterized of methylammonium lead bromide perovskite and prepared a thin film. This film has strong surface coverage and negligible pin holes represented by FESEM image. In I-V characteristics, we have shown that the perovskite thin film exhibit rectification behavior. The calculated saturation current is 1.02×10^{-4} mA. We believe that this study will be beneficial in the developments of CH₃NH₃PbBr₃ based devices, mainly for photodetectors and solar cells.

ORCID IDs

Shaily Choudhary, https://orcid.org/0000-0003-4211-0921;
Shalini Tomar, https://orcid.org/0000-0001-7385-3061
Depak Kumar, https://orcid.org/0000-0002-2958-8309;
Sudesh Kumar, https://orcid.org/0000-0002-7507-4712
Ajay Singh Verma, https://orcid.org/0000-0001-8223-7658

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СИНТЕЗ І ХАРАКТЕРИСТИКА ФОТОЕЛЕКТРИЧНОГО ПРИСТРОЮ НА ОСНОВІ ПЕРОВСКИТНОГО МЕТІЛАММОНІЙНОГО БРОМІДУ СВИНЦЮ

Шайлі Чоудхарі^а, Шаліні Томар^а, Депак Кумар^а, Судеш Кумар^с, Аджай Сінгх Верма^d

^аФізичний факультет, Банастхалі Відьяпітх, Банастхалі, Раджастан, 304022, India

^bDepartment of Chemical Engineering, Банастхалі Відьяпітх, Банастхалі 304022, Індія

^сФізичний факультет, Банастхалі Відьяпітх, Банастхалі, Раджастан, 304022, Індія

^dФакультет природничих та прикладних наук, університет Глокал, Сахаранпур, 247232, Індія

Гібридні електронні пристрої дають прийнятний підхід до можливих джерел живлення та інших подальших застосувань завдяки простоті розташування, підготовки, виробництва, легкості використання матеріалів та меншому впливу на навколишнє середовище. У цій роботі було розглянуто електричні властивості гібридних бромідних наночастинок перовскіта, а також обговорювався шлях розвитку перовскітних фотоелектричних пристроїв. Для виготовлення пристроїв, що обробляються низькотемпературним розчином, ключову роль у виробництві однорідних тонких плівок відіграє використання одноетапних методів спінового покриття. Технологія спінового покриття була використана для нанесення розчину попередника, включаючи бромід метиламмонію (MABr) та бромід свинцю (PbBr2) з молярним співвідношенням (3:1) для нанесення тонких плівок на FTO-підложку. Одноетапний процес розчину був використаний для нанесення шарів поглинача CH₃NH₃PbBr₃ та відобразив загальне уявлення щодо складу матеріалу, техніки нанесення та архітектури пристрою, вибір шару транспортування заряду та електрода.

Ключові слова: перовскітні металогалогеніди; мобільність носія заряду; опір; ємність; спектроскопія електрохімічного імпедансу