Chalcogenide As Inorganic Transport Layer in Perovskite Solar Cell

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Research Article

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Abstract

Fill factor (FF) deficit and stability is a primary concern with the perovskite solar cell. Resistance values and band alignment at junction interface in perovskite are causing low fill factor. Moisture sensitivity of methylammonium lead halide perovskite is causing a stability issue. We tried to solve these issues by using inorganic hole transport layer (HTL). FF is sensitive to the band offset values. We study the band alignment/band offset effect at the Perovskite /HTL junction. Inorganic material replacing Spiro-MeOTAD can enhance the stability of the device by providing an insulation from ambient. Our simulation study shows that the earth abundant p-type chalcogenide materials of SnS as HTL in perovskite is comparable to Spiro-MeOTAD efficiency.

Introduction

Terawatt scale Perennial supply of pollution-free energy at a competitive cost is a desirable for sustainable growth. Photovoltaic is potential solution subjected to availability of low cost, nontoxic material, and fabrication technology. Perovskite Methylammonium Lead Halide (CH$_3$NH$_3$PbI$_3$ or MAPbI$_3$) is the material with ideal properties of light absorption, defect-free bandgap, high mobility and diffusion length. In a short span of time perovskite has achieved high power conversion efficiency of 22.1% [1]. The organic component in the perovskite solar cell device structure has the challenge of stability due to moisture, thermal and photosensitivity [2, 3]. The sensitivity of the organic MA (methylammonium) toward polar solvent like water leads to their dissociation in presence of moisture. A moisture resistant perovskite material or suitable passivation from moisture is probable stability solution. Better insulation from thermal and ambient can be provided by encapsulation using inorganic layers. TiO$_2$ as electron transport layer (ETL) on one side and another inorganic material as hole transport layer (HTL) can better shield the perovskite layer. Low mobility of holes, unstable (thermal, Photo and moisture stability) issues in polymer HTL like Spiro-MeOTAD, PEDOT: PSS etc. could be overcome by using inorganic layers. Inorganic materials which are tried for HTL in literature are listed in Table. 1. On this line we explored inorganic Chalcogens materials (CIGS, CZTS, SnS, Cu$_2$S, PbS, Sb$_2$S$_3$, FeS$_2$) for HTL, where all the elements are nontoxic, abundant [4] and can be economically processed for solar cell application. The p-type nature of these chalcogens with high acceptor density and hole mobility can be exploited for HTL. Inorganic layer with low thermal conductivity and resilient to the ambient condition can enhance the lifetime of perovskite by encapsulating them from outside environment. In order to discuss and gain some insight into the feasibility of inorganic HTL here, we performed simulation study with inorganic hole transport layer in perovskite.

Chalcogens

Chalcogens we selected here (CIGS, CZTS, SnS, Cu$_2$S, PbS, Sb$_2$S$_3$, FeS$_2$) are prominent p-type absorber material with high absorption coefficient ($\sim 10^5$cm$^{-1}$) and bandgap lying invisible region (0.5-1.5eV). Their material properties are listed in Table 2. These are all abundant material available enough for terawatt scale energy generation, nontoxic and cost-effective. Solution-processed fabrication techniques make them strong for the low-cost application. These are Multifunction material with application ranging from (i) prominent absorber layer in inorganic and hybrid solar cells, (ii) counter electrode in DSSC and batteries, (iii) as a
photocatalyst, (iv) as a gas sensor (v) Counter electrode in quantum dot solar cell, (vi) Thermoelectric (vii) ultra-fast photo-detector and optoelectronic applications. All the selected chalcogens material binary (SnS, Cu₂S, PbS, Sb₂S₃, FeS₂) and quaternary (CIGS, CZTS) have higher hole mobility than Spiro-MeOTAD.

Simulation Detail

Solar cell capacitance simulator SCAPS-1D version 3.3.0.2 is used for the theoretical study. SCAPS model semiconductor and electrostatic equation in 1D environment to simulate a thin film solar cell. Using Newton Raphson and Gummel iteration it solves 1D Poisson equation and continuity equation for heterostructures. To begin with, we have modeled a p-i-n structure FTO/TiO₂/MAPbI₃/Spiro-MeOTAD and simulated the performance of the solar cell. The reported material parameters of perovskite as thickness 350 nm, bandgap 1.55 eV, the dielectric constant of 10, a value of N_A of ~10¹³/cm³, the diffusion length of electrons in perovskite, L_p~1000 nm, we used similar values of L_n, the electron mobility of ~10 cm²/Vs, radiative recombination coefficient (cm³/s) 10⁻¹³. Neutral defects density of 10¹⁴ at the center of the bandgap with a Gaussian distribution and characteristic energy of 0.1eV; and the capture cross-section of electrons and holes of 2×10⁻¹⁴ cm⁻². The absorption constant A (1/cm eV^(1/2)) was assumed to be 10⁵. The device is illuminated from FTO layer side with AM1.5 spectrum using relevant SCAPS option at temperature 300 K. Front contact is from the FTO layer and a back contact is taken from metal contact with work function taken to be 5.1eV. For the series resistance (R_s) and shunt resistance (R_sh), we have used typical values of 5Ω-cm² and 5k Ω-cm². The schematic of the device is shown in Fig. 1a.

The relevant material parameters used in the simulation were obtained from the literature and are listed in Table 3 [23-25]. Quantum efficiency (QE) curve shows maximum light absorption is within perovskite region. The simulated output parameter (V_OC=1.08V, J_SC=24.5mA/cm², FF=75.5%, Efficiency=20.02%) as shown in Fig. 1b are closely matching with the experimentally reported values of V_OC, J_SC, FF and efficiency [26]. The bandgap of perovskite is 1.55eV the corresponding SQ limiting parameter are (V_OC 1.287V, FF 90.32%, J_SC 26.37mA/cm², Efficiency 30.68%).

Results And Discussion

Design of the solar cell does affect the mechanism of the photovoltaic action and efficiency. The structure should be optimized for efficient separation and collection of photogenerated generated charge carrier. (a) Built-in Electric field, (b) effective force field (work function difference), (c) discontinuity at an energy level at the interface, are some of the design related options implemented for better performance of the photovoltaic device. The interface at heterojunction, control voltage generation and current flow, potential variation, the electric field at either side of the junction. Perovskite configuration of FTO/TiO₂/Perovskite/HTL is p-i-n type. p-i-n structures is suitable for large built-in potential across absorber layer. Built-in potential depends on the carrier density of p and n layer. The effective force field can be induced by the appropriate choice of the contacts work function. For design point of view, an HTL should be having a high hole to electron mobility ratio so that it acts as a selective contact. To gain large built-in voltage charge density should be higher in n and p region of a pin. Higher charge density will also shift the space charge layer into the intrinsic layer an
advantageous situation for charge drift. Figure 2a shows the higher built-in voltage resulting from higher
density of carrier in p and n layer of pin structure. The slope of band energy level in i layer (absorber) also
increases with the carrier density in p and n, as shown in figure 2a. A spike to be present at the valence band
offset to lower the interfacing recombination between \( E_{V,HTL} \) and \( E_{C,Perovskite} \)\textsuperscript{[23,27]. The reason for the low
recombination at slightly positive valence band offset is the low value of \( \Delta \). The \( \Delta \) is the energy difference
\( E_{C,Perovskites} - E_{V,HTL} \) as shown in the Fig. 2. The cliff at the perovskite/HTL junction lowered the \( \Delta \) shown in
figure 2b, enhancing the chances of recombination of an electron from perovskite to hole from HTL. The
presence of spike at the junction increases the \( \Delta \) value shown in Fig. 2c and thus lower the chances of
recombination of an electron from perovskite and hole from HTL. The high Spike value will impede hole
transfer from perovskite to HTL. The slightly positive values of VBO are advantageous and their optimum
value can be ascertained by simulation. Device optimization by simulation for an HTL (p layer) in p-i-n the
optimizing conditions are

i) A positive VBO at the p-i junction.

ii) High hole density in p,n layer ( p\textsuperscript{+}-i structure),

a) High built-in voltage

b) Lead to the higher field in absorber (i) layer.

3.1.1 HTM layer parameter

For the simulation of inorganic HTL, we inserted an interface defect layer (IDL) at HTL perovskite junction.
The width and defect density of IDL is taken to be 10nm and \( 10^{17} \) cm\(^{-3}\). High defect density in IDL is used to
simulate the interfacial recombination caused by lattice mismatching and defect state. CZTS have bandgap
tail state of multivalent defect near to conduction band and valence band. We have assumed multivalent
defect of charge state \{3+/2+, 2+/+, +/0\} in CB at \( E_t = 1.40 \text{eV} \) with characteristic energy of 0.05eV. Acceptor
defects of charge state \{0/-, -/2-, 2-/3-\} at VB. The defect density of \( 5 \times 10^{14} \) cm\(^{-3}\), capture cross section of \( 10^{-13} \) cm\(^2\). To model SnS defects we have used a neutral defect of density \( 10^{17} \) cm\(^{-3}\), capture cross section of \( 10^{-15} \) cm\(^2\). The parameter of the CZTS, CIGS,
Cu2S, Sb2S3, PbS, FeS2, SnS are taken from literature and are listed in Table 2.

These inorganic material are p-type with 2-4 order high hole density than perovskite and have a similar
bandgap. Simulation is run for these sulfide as HTL in Perovskite solar cell. HTL parameter of thickness, hole
density are simulated. Fig. 3 shows the dependence of inorganic HTL device performance on hole density,
thickness. The hole density in the HTL is varied from \( 10^{14} \) to \( 10^{18} \) cm\(^{-3}\) to simulate the effect on efficiency.
Efficiency rises with hole density for all HTL. As doping concentration in HTL increases, the resistivity of HTL
layer reduces. This increases the \( V_{OC} \) and FF whereas the current remains constant. Carrier (hole)
concentration will affect the bend banding and potential distribution at the junction. Perovskite has a low
doping thus higher doped HTL will induce banding in Perovskite absorber layer thus creating a potential
distribution across perovskite layer. Higher carrier concentration will cause higher built-in voltage in the
device and is favorable until limiting diffusion length at high carrier density, Auger and Radiative
recombination effect supersedes. All the binary sulfides layers have shown 0.1µm optimum thickness after which efficiency becomes constant. Quaternary CZTS and CIGS have shown a 0.2µm as optimum thickness. With thickness, FF grows initially and then all the parameter becomes constant. Rau et. al. estimated critical mobility for achieving 90% of efficiency in the solar cell [28]. The critical mobility values remain less than 1 cm²V⁻¹s⁻¹. The HTL material under consideration here are well known p-type material with mobilities higher than critical mobilities as required by Rau et al. The optimum value of thickness, hole density as obtained by simulations can be easily attainable in given HTL materials. These parameters are highly dependent on growth condition and stoichiometry. We have used the value of these parameter forms the experimental data reported in the literature and listed in Table 2.

3.1.2. Band diagram and IV

The band structure of all the HTL/Perovskite solar cell is simulated and shown in Fig. 4. The band alignment at the HTL/perovskite junction is observed in all structure. The CZTS, CIGS showed bending in HTL layer energy level as they have hole density of 10¹⁶ cm⁻³. SnS showed band bending at the back metal contact. Simulated IV curve of all the structure is shown in the Fig. 5. The junction of HTL/perovskite is changing. PbS, FeS₂ are showing low efficiency of 11.1% and 10.9% due to a large negative VBO at HTL/perovskite junction. CIGS and CZTS show a moderate value of efficiency 16.5% and 18.4% respectively. They have a positive VBO of 0.25 and 0.15 eV. SnS, Cu₂S, Sb₂S₃ are showing comparable efficiency to Spiro-MeOTAD perovskite solar cell at 20.88%, 20.6%, 20.2% respectively. The comparable efficiency of SnS could be further optimized and could replace Spiro organic HTL. The difference in electron affinity (X_{HTL}) of the HTL layer and perovskite (X_{Abs}) is causing the valence band offset (VBO) at the junction. For hole transport valence band offset (VBO) the alignment of the valence band level E_V of HTL and E_V of perovskite is important. Also at this HTL junction, an interface defect density is assumed. A 10 nm thick layer is inserted at this junction to simulate any defect density arising from electrical or mechanical dissimilarity.

3.1.3. VBO and contact optimization of HTL layer

VBO is the discontinuity in the energy level at the junction shown by a vertical line in Fig. 3. VBO is given by (E_{gHTM}+X_{HTL})- (E_{gPerov}+ X_{Perov}), E_g is the bandgap, X is electron affinity. The simulated band diagram of the device Inorganic HTL/Perovskite shows valence band offset. The High negative offset introduces a cliff, favorable path way for hole transport from perovskite to HTL case shown in Fig. 2b for Perovskite /SpiroMeOTAD. High positive offset (X_{HTL}+E_{gHTL}>X_{Abs}+E_{gAbs}) introduces a spike forming a barrier for hole transfer from the absorber to HTL as the shown in Fig. 2c. At zero Valence band offset make continuity at the junction. The Δ (as shown in the figure should be large to avoid interfacial recombination between E_{V HTL} and E_{C Perovskite}. The positive value of VBO will be suitable to increase Δ. However large VBO will inhibit the hole transfer from absorber to HTL. The height of spike should be less than the built-in voltage in absorber. SnS show comparable efficiency to Spiro, therefore, we optimized SnS for further efficiency enhancement. The electron affinity of the HTL layer is varied to vary the VBO and the band alignment. The band alignment is simulated for positive and the negative and zero valence band offset. SnS/perovskite has a E_{VBO} of 0.15eV shown in band diagram Fig. 4. The effect of Spike and Cliff on device performance is studied. The
simulation is run for range of VBO from negative to positive value. The defect at the junction of perovskite/HTL is simulated by inserting a IDL (interface defect layer) with a defect density of $10^{17}$ cm$^{-3}$.

The dependence of cell efficiency on valence Band offset at interface is shown in Fig. 6. For VBO values from -0.05 to .3eV the efficiency increases and peaks at a value of 0.15eV. Interface defect density at the junction highly affects the negative valence band. Recombination current dependence on valence band offset is shown in the inset of Fig. 4. Recombination current is minimum at the slightly positive band offset region. The efficiency maximizes at VBO where recombination current is minimum. Interface defect density is assumed to be high ($10^{17}$ cm$^{-3}$). Recombination current depends upon the defect density at the interface. High positive VBO is detrimental for performance as simulated results shows. Slightly positive band offset of 0.05eV to 0.1eV is yielding the highest efficiency irrespective of high defect density for SnS. The reason for the low recombination current at slightly positive valence band offset is the low value of $\Delta$. Efficiency abruptly decreases for higher VBO values as seen in the simulation Fig. 6. Interfacial recombination within the HTL/Perovskite junction can be lowered by a positive band offset. The slightly positive values of VBO are advantageous and their optimum value can be ascertained by simulation. The prominent effect of VBO is on the fillfactor of the device. Table 4 summaries the VBO resulting by variation of the electron affinity of SnS. FF maximize at the slightly positive VBO (0.1eV) the similar trend followed by efficiency.

The band diagram of SnS/perovskite in the figure shows abrupt band bending at back contact. This suggests at Schottky at the back contact with the assumed metal contact of work function 5.1eV in the simulation. The barrier at the back contact can be sorted by optimizing back contact work function. The effect of work function ($\phi_m$) of metal contact at HTL layer is simulated for contact optimization. Fig. 7 shows the efficiency improvement with the work function ($\phi_m$) of back contact. Simulation results show that $V_{OC}$ and efficiency rise initially with work function and then becomes constant for both the HTL shown in Fig. 7. This increase in $V_{OC}$ is due to improved built-in voltage [29,30]. We have a metal/semiconductor back contact acting as Schottky barrier for majority carrier. The barrier is required to be low to make it near ohmic. The band diagram is simulated for increasing work function values. For higher work function there is rise in energy level of the HTL at the back contact. This rise in energy level at back contact improves built-in voltage in HTL and perovskite layer. The simulated band diagram is shown work function in the inset of Fig. 7. The bending in $E_V$ and $E_C$ level at rear contact is eliminated with metal contact of high work function as shown in the simulated diagram.

The final parameters of the Perovskite with inorganic HTL layer are summarized in the Fig. 8. The inorganic HTL (CZTS, Sb$_2$S$_3$, Cu$_2$S, SnS) have higher FF and SnS have higher efficiency than the standard perovskite cell with organic Spiro HTL. The $V_{OC}$, FF, $J_{SC}$ and Efficiency are compared with Spiro-MeOTAD and the SQ limit. The SQ limit gap in $V_{OC}$, $J_{SC}$, FF for Spiro-MeOTAD is shown. Among them FF has the largest deficit this may be due to suboptimal band alignment at the perovskite/HTL, perovskite/ETL and the high value of series resistance and low shunt resistance values in perovskite solar cell. The efficiency of the SnS is higher than Spiro-MeOTAD. The stability of SnS and low thermal conductivity is advantageous over organic HTL like PEDOT: PSS, Spiro-MeOTAD etc. Apart from high efficiency they can provide stable encapsulation to organic-inorganic perovskite from outer moisture and temperature gradient.
Conclusion

Earth-abundant inorganic HTL are used to provide insulation to perovskite layer for enhanced stability and replacing costly, unstable organic HTM (Spiro-MeOTAD, PTAA etc). Simulation points out HTL property (a) small positive VBO at the HTL/perovskite junction and (b) high doping density. The inorganic chalcogenides are well-known p-type material exploiting them for hole transport applications. These materials are well suited for their availability, material stability and processability. Perovskite with inorganic HTL (Cu$_2$S, Sb$_2$S$_3$, SnS, CZTS, CIGS, FeS$_2$, PbS) are simulated shows high efficiency. A slightly positive VBO matching is showing to give efficiency to 20% which can be further improved with the flat band at the back contact. SnS can replace organic Spiro-MeOTAD HTL effectively with improved performance and stable perovskite cell.

Declarations

Declaration of interest

Author declare that he has no conflict of interest

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### Tables

Table 1: The reported inorganic HTL in perovskite solar cell in literature.

| Material   | $V_{oc}$ (V) | $J_{sc}$ (mA/cm$^2$) | FF (%) | Eff. (%) |
|------------|--------------|-----------------------|--------|----------|
| Cu$_2$O[5] | 0.952        | 17.5                  | 66.2   | 11.03    |
| NiO[6]     | 1.01         | 21                    | 76     | 16.1     |
| CuI[7]     | 0.55         | 17.8                  | 62     | 6        |
| CuInS$_2$[8]| 0.878        | 16.6                  | 45.1   | 6.57     |
| CuSCN[9]   | 1.020        | 19.2                  | 58     | 11.4     |
| CIGS[10]   | 0.94         | 17.66                 | 54.88  | 9.15     |
| CZTS[11]   | 1.06         | 20.54                 | 58.7   | 12.75    |
| PbS[7]     | 0.86         | 12.1                  | 72     | 7.5      |

Table 2: Some of the material property of selected Chalcogenide for the inorganic hole transport layer.
| Parameters                             | CIGS[12] | CZTS[12-13] | SnS[14] | Cu$_2$S[16-17] | PbS[18,19] | Sb$_2$S$_3$[20] | FeS$_2$[21,22] |
|---------------------------------------|----------|-------------|---------|----------------|-------------|----------------|----------------|
| Hall mobility (cm$^2$/Vs)             | ~35      | 6-30        | 100     | 25             | 80          | 10             | 10             |
| Thermal conductivity (Wm$^{-1}$K$^{-1}$)| 4.44[15] | 1.69 [15]   | 1.25    | .3-5           | 2.19        | -              | 45             |
| Band gap (eV)                         | 1.13     | 1.5         | 1.5     | 1.2            | 0.92        | 1.7            | 0.95           |
| Hole density (cm$^3$)                 | $\sim10^{16}$ | $\sim10^{14-17}$ | $\sim10^{17}$ | $\sim10^{19}$ | $10^{15}10^{17}$ | $\sim10^{16}$ | $\sim10^{18}$ |
| Conductivity type                     | p        | p           | p       | p              | p           | p              | p              |
| Electron Affinity (eV)                | 4.58     | 4.2         | 3.9-4.2 | 4.25           | 3.95        | 3.95           | 3.9            |

Table 3: List of material parameters used in the simulation.

| Parameters                             | TiO$_2$ | SpiroMeOTAD | Perovskite |
|---------------------------------------|---------|-------------|------------|
| Thickness(nm)                         | 100     | 190         | 350        |
| Bandgap(eV)                           | 1.5     | 3           | 1.55       |
| Electron affinity(eV)                 | 3.6     | 2.2         | 3.9        |
| Dielectric permittivity               | 10      | 3           | 10         |
| CB effective density of state N$_e$(cm$^{-3}$) | $2.2x10^{18}$ | $2.8x10^{19}$ | $2.2x10^{18}$ |
| VB effective density of state N$_v$(cm$^{-3}$) | $1.8x10^{19}$ | $1.0x10^{19}$ | $1.8x10^{19}$ |
| Electron thermal velocity(cm/s)       | $10^7$  | $10^7$      | $10^7$     |
| Hole thermal velocity(cm/s)           | $10^7$  | $10^7$      | $10^7$     |
| Electron/hole mobility(cm$^2$/Vs)     | 10      | .0001/.0039 | 10/10      |
| Donor/ Acceptor density, N$_D$/N$_A$ (cm$^{-3}$) | $10^{17}$ | $10^{18}$  | $10^{13}$  |
Table 4: FF variation with band alignment (VBO) at the SnS/perovskite junction.

| Electron affinity (eV) | VBO (eV) | FF (%) |
|------------------------|----------|--------|
| 3.8                    | -0.01    | 75.33  |
| 3.9                    | 0.0      | 76.98  |
| 4                      | 0.1      | 77.67  |
| 4.1                    | 0.2      | 77.24  |
| 4.15                   | 0.25     | 76.14  |

Figures

Figure 1
(a) Schematic of the Perovskite solar cell. (b) Simulated IV and QE of Perovskite solar cell.

Figure 2

(a) The pin junction shows a large built in voltage and slope of band level in absorber increases with higher density in p and n layer. (b) The Schematic of HTM/Perovskite band diagram. It shows $\Delta$ for the case of (b) Cliff and (c) Spike at HTM/perovskite junction. Line in red shows the interfacial recombination. For reduced recombination value of $\Delta$ must be larger i.e. the case with the spike.
Figure 3

(a) Efficiency vs thickness of the HTM layer is simulated. To obtain optimum HTM layer width of the various HTM/Perovskite solar cell. (b) Efficiency vs Hole density is plotted for all the HTL/perovskite cell. Higher hole density in HTL layer is preferred for high efficiency of Inorganic HTM/perovskite cell.
Simulated band diagram showing energy level with respect to layer widths. a) Perovskite solar cell with the Spiro MeOTAD and inorganic HTL. The structure is identical for the TCO, TiO2, Perovskite layers. With different HTL range of Valence band offset at perovskite/HTL junction is observed. The band bending in HTL and at back contact is observed in some HTL/perovskite cells.
Figure 5

IV curve of the all inorganic HTL/perovskite solar cell.
Figure 6

VBO effect on the efficiency for the HTM(SnS)/Perovskite solar cell is plotted. Interface defect density 1017 cm⁻³ is used for SnS/perovskite case. Inset curve is showing the recombination current with respect to VBO. Efficiency is maximum and Recombination current is (Jrec) is minimum for the slightly positive value of VBO.
Figure 7

Efficiency of the device with respect to the work function of the back metal contact. Band diagram at work function ($\phi_m$) of the back metal contact is shown in the inset graph.
The performance parameter of the Perovskite with Spiro-MeOTAD, chalcogenide HTM and SQ limit are compared. It shows the gap in SQ limit and present efficiency is primarily due to low FF factor and current of perovskite solar cells. Our suggested HTL layer has higher FF values than Spiro-MeOTAD.