

Nanoscale charge transport properties of perovskite solar cells with WSe₂ flakes as protective layer for stable performance

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ABSTRACT

Organic-inorganic perovskite solar cells have become a promising technology for next generation solar cells due to their superior optoelectronic properties such as tunable low bandgap, long charge diffusion length, low exciton binding energy and balanced charge transport. The power conversion efficiency (PCE) of perovskite solar cells prepared from low temperature solution processing have been improved drastically. However, perovskite solar cells suffer from poor stability in presence of moisture inhibiting its commercialization. We report the use of WSe₂ flakes as protective and charge transport layer in heterostructure devices. The synthesis of WSe₂ was done by liquid exfoliation method and by chemical vapor deposition (CVD) technique. It is found that an atomically thin layer of WSe₂ can improve the charge transport properties in perovskite solar cell due to its higher mobility and conductivity.

Keywords: Perovskite solar cell, Charge transport, 2D materials,

1 INTRODUCTION

Perovskite is a promising organo lead halide material in photovoltaic solar cell technology [1-3]. In the short time span of five years, perovskite based solar cells have shown drastic increase in power conversion efficiency. Due to higher efficiency, perovskite solar cells have shown greater promise than dye sensitized solar cells, polymer solar cells, CdTe and CZTSSe solar cells [4]. Organo lead halide perovskite materials have been used as a photoabsorber layer in light emitting devices and photo-detectors [5, 6]. However, fundamental understanding of effects of hole transport layer (HTL) and its interfaces with adjacent layers is limited. One of the major hinderance for commercialization of organo lead halide perovskite solar cells is due to its poor stability with water and low hole mobility of the hole transport layer despite its promising efficiency.

The degradation mechanism of perovskite solar cells due to moisture and limited charge transport due to low mobility of HTL has opened the door for debate [7, 8]. Several reports have provided insight to better understand the effect of moisture with post treatment of perovskite film by exposing it in controlled moisture conditions [1, 2, 9-12]. According to a literature, it is reported that moisture decomposes the perovskite in to lead iodide and methyl

ammonium iodide lowering the device efficiency. Niu et al. showed further breakdown of methyl ammonium iodide into methylamine (CH_3NH_2) and hydrogen iodide (HI), leading to the formation of I_2 (solid) and H_2 (gas) after exposure to ambient atmosphere (i.e. oxygen and sunlight) [13]. It was shown experimentally that perovskite forms transparent monohydrate ($\text{MAPbI}_3 \cdot \text{H}_2\text{O}$) and dehydrate phase ($(\text{MA})_4\text{PbI}_6 \cdot 2\text{H}_2\text{O}$) when exposed to moisture [14]. It is clear that experiments are providing an increasingly clear picture of the degradation, an alternate hole transport layer with hydrophobic property and high mobility can solve the process of degradation of perovskite materials from moisture.

It is also reported that the interface between perovskite and Spiro-Ometad plays critical role in device stability and charge transport [15]. This is due to the ion migration from perovskite to Spiro-Ometad which degrades the cell efficiency. In addition, the direct contact between perovskite and electrode results in decrease in short circuit current density and open circuit voltage. Therefore, the complete coverage of perovskite by HTL is required. The thickness of the HTL layer should be thin in order to minimize the series resistance. Here, we report the use of few layers of Tungsten Diselenide(WSe₂) as an additional HTL layer with Spiro-Ometad in order to overcome this problem. Since, two-dimensional (2D) materials beyond graphene such as transitional metal dichalcogenides (TMDCs), Tungsten Diselenide(WSe₂) and Tungsten Disulfide (WS₂) have attracted significant attention due to their superior opto-electronic properties. These 2D materials possess weak interlayer interaction and strong intralayer covalent bonds, high mobility, tunable bandgap and can be exfoliated to few layers or single layer. This property makes them inherently flexible and good candidates for photovoltaic applications. The primary purpose of adding WSe₂ as additional hole transport layer is to increase the hole mobility towards the metal electrode and suppress the water penetration to perovskite layer. We have also studied the interface between WSe₂/Si for application in heterostructure devices.

2 EXPERIMENTAL PROCEDURE

Liquid-Phase and CVD growth of monolayer and few layers of WSe₂: Bulk WSe₂ was exfoliated in NMP by dissolving WSe₂ flakes. WSe₂ was dispersed in 10 mL of NMP and ultrasonicated for 6 hrs. The obtained dispersion was ultracentrifuged at 10,000 rpm for 15 min, to separate

bulk WSe₂. Supernatant was collected by pipetting after the exfoliation process. WSe₂ was also prepared by CVD method: Se powders (10 mg, Alfa Aesar, 99.999%) were placed in the first zone at upstream which reached 270°C during the growth and 24 mg mixture of WO_{2.9} (Alfa Aesar, 99.99%) /NaCl (Alfa Aesar, 99.99%) was placed at the center of the furnace in order to grow WSe₂ flakes.

Perovskite films were fabricated on fluorine doped tin oxide (FTO) coated substrates (1.5 cm × 1.5 cm). FTO substrates were etched using zinc powder and diluted in hydrochloric acid (0.1 ml HCl in 1 ml DI water by volume). All etched substrates were subsequently cleaned by detergent water, DI water, acetone and isopropanol by sonication for 25 min each. Substrates were then dried using nitrogen gas followed by plasma cleaning for 20 min in presence of oxygen.

Compact layers of TiO₂ were spin coated onto cleaned substrates at 4500 rpm for 30 sec from their precursor (titanium diisopropoxide bis(acetylacetone), 75 wt.% solution in 2-propanol) solutions at a concentration of 0.15 M and 0.3 M, respectively. The compact layers of TiO₂ were then annealed at 450 °C for 30 min. The substrates were then cooled down to room temperature. 1 g of mesoporous TiO₂ (Dyesol 18NRT with particle size 20 nm) was diluted with 4.436 ml of ethanol and the mixed solution was spin coated at 3000 rpm on top of the compact layers of TiO₂. The mesoporous TiO₂ layer was then annealed at 450 °C for 30 min, and cooled down to room temperature. The mesoporous TiO₂ layers were then immersed in TiCl₄ (25 mM) solution for 30 min at 70 °C, followed by rinsing with DI water, ethanol and then again annealed at 450 °C for 30 min.

PbI₂ solution (462 mg/ml in DMF) was prepared by overnight stirring at 70 °C. The solution was then spin coated on top of a mesoporous TiO₂ layer at 4500 rpm for 40 sec followed by annealing at 70 °C for 30 min. To form perovskite layer, the PbI₂ films were dipped in CH₃NH₃I solution (10 mg/ml in IPA), followed by immediately spin coating at 5000 rpm for 10 sec. Perovskite films were then annealed at 100 °C for 15 min. Spiro-OMeTAD was used as hole transport layer, prepared by mixing 72.3 mg of (2,2',7,7'-tetrakis(N,N-di-p-methoxyphenylamine)-9,9'-spirobifluorene) (spiro-MeOTAD), 28.8 μL of 4-tert-butylpyridine, 17.5 μL of a stock solution of 520 mg/mL lithium bis-(trifluoromethylsulfonyl)imide in acetonitrile in 1 mL of chlorobenzene. Spiro-OMeTAD was spin coated on top of Perovskite layer at 2000 rpm for 40 sec. An additional layer of WSe₂ was spin coated at 1000 rpm for 45 sec followed by annealing at 100°C for 30 min on top of spiro-OMeTAD as hole transport layer. Finally, Silver (Ag) was then deposited as top electrode in a high vacuum chamber using thermal evaporation.

3 CHARACTERIZATION

The surface topography was obtained with optical microscopy. Capacitance-frequency measurement was done with B1500A semiconductor analyzer coupled with Lake shore cryogenic probe station. Surface potential was measured by using Kelvin probe microscopy.

4 RESULT AND DISCUSSIONS

Figure 1. (a) and (b) shows the optical image of WSe₂ prepared by liquid exfoliation method and low pressure chemical vapor deposition method . The surface topography of WSe₂ film shows smooth ,compact and uniformly deposited film. The smooth and compact film helps to reduce the shunt path for current and decreases the contact losses. Monolayer to few layers of WSe₂ (fig. 1b) were obtained with chemical vapor deposition method. It is found that the CVD growth of WSe₂ results in less defects which are useful for transport layer in heterostructure devices.

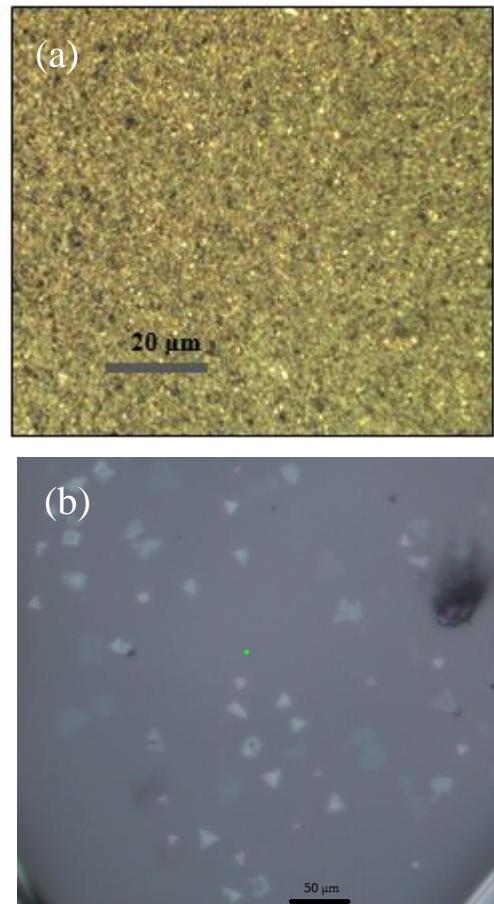


Figure 1. Optical image of WSe₂ prepared by (a) liquid exfoliation method (b) Chemical vapor deposition method

Figure 2 shows the surface potential line profile of WSe₂ on n-silicon substrate. The back recombination

barrier between the electrons from silicon to holes from WSe₂ is nearly 350meV which is sufficient to suppress recombination. This shows that the CVD grown WSe₂ can be used as hole transport layer with silicon to make inorganic heterostructure solar cell devices. The separated electrons and holes can be collected using suitable metal electrodes as shown in figure 2. It is required to minimize the carrier losses to achieve high device efficiency. Therefore, the electron transprt and hole transport layer should have less defects, high mobility and proper energy band alignment with adjacent layers. Surface potential line profile between WSe₂/Si gives the energetics difference of the position of valence band and conduction band. Kelvin probe force microscopy (KPFM) measures the difference between work function of the tip and sample and gives the average position of the fermi level of the silicon and WSe₂. It is observed that the WSe₂ flakes prepared from CVD can be used as electron transport layer with silicon to make hetero structure solar cells. Tertiary metal dichalcogenide shows ambipolar property, which makes them suitable for either electron or hole transport layer in normal or inverted type solar cells.

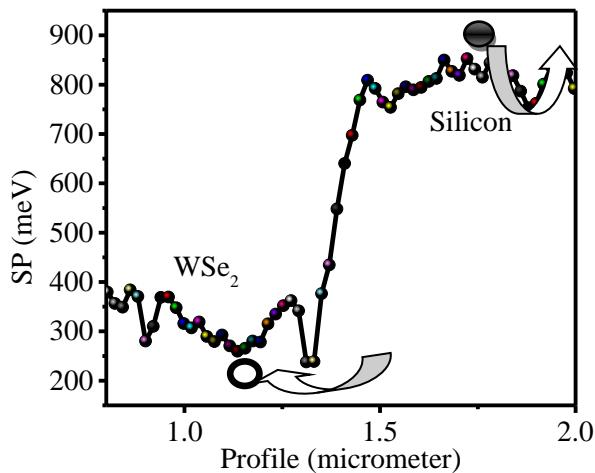


Figure 2. Surface potential line profile of CVD grown WSe₂ on silicon

Figure 3 shows the capacitance-freuecny (CF) measurement of perovskite solar cells prepared by using WSe₂ as an additional hole transport layer on top of the Sprio-ometad. An ac signal of 100 mv and varying frequency from 1KHz to 5 MHz was used to perturb the interfaces within perovsktie solar cell. The CF curve shows that the capacitance is constant above 100 KHz suggesting that the trap energy level lying mid within the bandgap and can not respond to high frequency. Since, the emission-rate of trap states depends on their location in the bandgap with slower trap responding to high frequecny range.

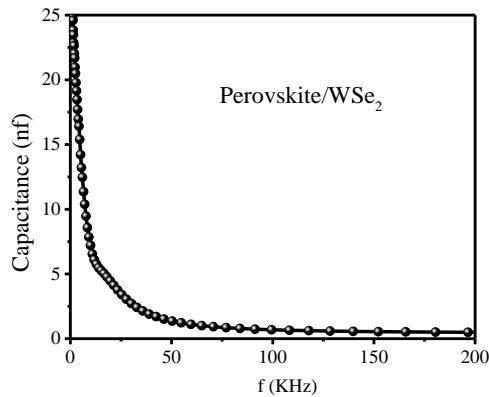


Figure 3. C-F curves of perovskite solar cells with WSe₂ on top of Spiro-Ometad

5 CONCLUSIONS

The synthesis of WSe₂ was done successfully by liquid phase exfoliation and chemical vapor deposition method. Compact and dense tungsten diselenide film was obtained by soluiton processed technique. It is found that an atomically thin layer of WSe₂ can improve the charge transport properties in perovsktie solar cells. It has shown potenital hole transport material to overcome the limitation imposed by the widely used Spiro-Ometad. CVD grown tungstein diselenide shows appropriate band alignment with silicon with promising application in inorganic heterostructure devices.

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