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ORIGINAL RESEARCH

Development of Lead-Free Germanium based Photovoltaic Cells using Low Dimensional Materials as Charge Carriers

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Abstract

Introduction: The energy sector poses one of the greatest challenges in most nations as it influences economic growth. Decades of neglect of renewable energy sources has resulted in over dependence on hazardous fossil-fuel.

Aims: In this study, we reported the development of high-performance lead-free methyl ammonium germanium halide ($CH_3NH_3GeI_3$) based Perovskite Photovoltaic cells using computational method.

Materials and Methods: The optical property of two dimensional (2D) graphene and mxenes nanocomposites as hole and electron transporters were incorporated to optimize the device performance using SCAP 1D software. The effect of several parameters on the solar cell performance were investigated such as thicknesses of perovskite, hole-transporting materials (HTMs), defect density, hole mobility, and metal electrode work function on the charge collection.

Results: Ge-based PSCs with graphene and mxenes (Ti_3C_2) and TMDCs (NiS_2/$NiTe_2$) as alternating HTMs exhibited a remarkable power conversion efficiency (PCE) reaching 21% and a 62.01V; 0.60 $mAcm^{-2}$; 80.10% as open-circuit voltage, current density and fill factor respectively.

Conclusion: Our results advocate for a simple and safe design of HTMs for highly efficient and stable solar cells at low cost.

Keywords: Lead-free, Germanium halide, based Perovskite Photovoltaic cells, optical property, graphene, mxenes, defect density, hole mobility, work function.

All co-authors agreed to have their names listed as authors.

1. INTRODUCTION

The energy sector directly influences economic growth of any nation. Implementation of renewable energy strategy has been on the rise due to recent global initiatives on sustainable development. One of the greatest challenges is its utilization and decades of neglect has resulted in over dependence on imported fossil-fuel which overburdened the annual national budget (Al-Mhairat and Al-Quraan[1]; and Saleh et al.[2]). Solar and wind energy has become the world's most renewable energy sources. They are cheap, affordable and clean without producing greenhouse gas emissions (Mas'ud et al.[3]).

Studies on improving the performance of solar cells are on the increase and thin films Perovskite solar cells (PSCs) in particular has received significant attention. The PSCs, copper indium gallium diselenide (CIGS) and cadmium telluride (CdTe) based heterojunction SCs are being worked upon since single junction silicon SCs have a laboratory scale efficiency ~ 25% achieved as a result of the over 60 years of research. In the absence of non-radiative recombination, the Shockley-Queisser limit for a single p-n junction solar cell with energy bandgap (E_g) between 1.1 and 1.4 eV is ~33%. This shows that ~70% of the entire energy coming from the sun does not contribute to the generation of solar electricity. The two phenomena that are main sources of loss are (i) transmission of photons with energies lower than the E_g of the material without absorption and (ii) the loss of energy by photons of energy higher than the E_g of the material via phonon emission at the rotational and vibrational energy levels which lie at the continuum band. In PSCs, their stability and efficiency can be improved to withstand atmospheric hazards due to heating, humidity, and rain (Iqbal et al.[4]; and Ladan and Buba[5]). Two-dimensional (2D) titanium carbide (Ti_3C_2) was the first mxene reported at Drexel University, USA while Ti_2C, Nb_2C, V_2C, Ti_3CN, Mo_2C, and Ta_4C_3 have been prepared successfully among the several theoretically predicted mxenes (Rahman et al.[6]).

Graphene is 2D sp^2 hybridised carbon atom in a hexagonal pattern. 2D transition metal dichalcogenide (TMDCs) MX_2 are mostly layered structures and in Co, Rh, Ir and Ni based TMDCs, NiS_2 forms a pyrite structure and $NiTe_2$ is layered pattern. MoS_2, WS_2, $MoSe_2$ and WSe_2 have been identified as semiconductors. 2D materials are of atomic thickness. They have excellent optical, electrical and thermal conductivities at room temperature and about 90% transmittance to solar rays making them suitable for optoelectronic and energy conversion devices (Geim and Novoselov,[7]; Paulchamy et al.[8]). Their properties can be tailored to suit different applications due to the large surface area above 3000 m^2/g and are capable of absorbing solar radiation in the UV-visible region (Alam et al.[9]; Chou et al.[10]). There is huge flux of photons from the Sun on the earth and if properly harnessed can solve the energy crisis.

There is need for the development of high-performance lead-free methyl ammonium germanium halide ($CH_3NH_3GeI_3$) PSCs using 2D graphene, Mxenes and TMDCs nanocomposite as hole and electron transporters to optimize the device performance using SCAP 1D software. Integration of carbon

based material in designing optoelectronic devices can improve efficiency, reduced cost and enhanced life time.

2. MATERIAL AND METHODS

Numerical modeling were performed using SCAPS-1D software under AM 1.5 solar spectrum at 100 mW/cm^2 light intensity to obtain the photovoltaic performance. The thin film PSCs is modelled in layers characterized by the thickness, doping level, carrier density, charge mobility and other physical properties using 2D HTMs. Table 1 shows the parameters that were collected from recent studies. SCAPS 1D is based on coupled differential equations Poisson's equation and the continuity equations for electrons and holes. They are solved self-consistently by iteration technique to simulate the electric field distribution, current density, transport properties, and recombination profile (Burgelman et al.[11]; and Kumar et al.[12]).

The Poisson equation relates the static electric field ε to the space-charge density ρ. The electron and hole transport equations 2 and 3 are coupled by the electric field ε, a set of coupled differential equations.

$$\frac{d^2\emptyset(x)}{dx} = -\frac{d\,\varepsilon(x)}{dx} = -\frac{\rho(x)}{\epsilon_0\epsilon_s} \qquad (1)$$

where $\emptyset$ is the electrostatic potential, ϵ_0 is the permittivity of free space and ϵ_s is the relative permittivity of the medium.

$$D_e\frac{d^2n}{dx^2} + \mu_e\varepsilon\frac{dn}{dx} + n\mu_e\frac{d\varepsilon}{dx} - R_e(x) + G_e(x) = 0 \qquad (2)$$

$$D_h\frac{d^2p}{dx^2} + \mu_h\varepsilon\frac{dn}{dx} + p\mu_h\frac{d\varepsilon}{dx} - R_h(x) + G_h(x) = 0 \qquad (3)$$

Where e and p are electron and hole densities, μ_e and μ_p are the electron and hole mobilities, D_e and D_h are the electron and hole diffusion constants, $R(x)$ and $G(x)$ are the recombination and photo-generation rates, respectively.

Table 1: Material property for each layer

	ITO	**PEDOT: PSS**	**$MAPbI_3$**	**$MAGeI_3$**	**PCBM**	**Graphene 2D**
Thickness, nm	500	200	450	WR	200	WR
E_g(eV)	3.65	1.60	1.55	1.90	2.0	2.7
x (eV)	4.80	3.40	3.75	3.98	3.9	4.5
N_c(cm^{-3})	5.8 x10^{18}	10^{22}	2.20	10^{16}	2.5 x 10^{21}	3.10 x 10^{19}
N_v (cm^{-3})	10^{18}	10^{22}	2.20	10^{15}	2.5 x 10^{21}	3.10 x 10^{19}
N_d (cm^{-3})	10^{20}	10^{22}	10.0	10^{9}	2.93 x 10^{17}	
N_A (cm^{-3})	0	0	5x10^{16}	10^{9}	0	0
ε_r	8.90	3.0	6.50	10	3.9	3.3
μ_n (cm^{2}c^{-1}s^{-1})	10.0	4.5 x 10^{-4}	2.0	16.20	0.02	15,000
μ_h (cm^{2}c^{-1}s^{-1})	10.0	9.9 x 10^{-5}	2.0	10.10	0.02	15,000
Defect density	-	2.5 x 10^{15}	1.5 x10^{16}	10^{14}	1 x 10^{15}	1 x 10^{15}
Work	-	-	-	-	-	4.0

function						
References	Kumar et al. [12]	Kanoun et al. [13]	Li et al. [14]	Lakhdar et al. [15]	Zhao et al. [16]	Wang et al. [17]

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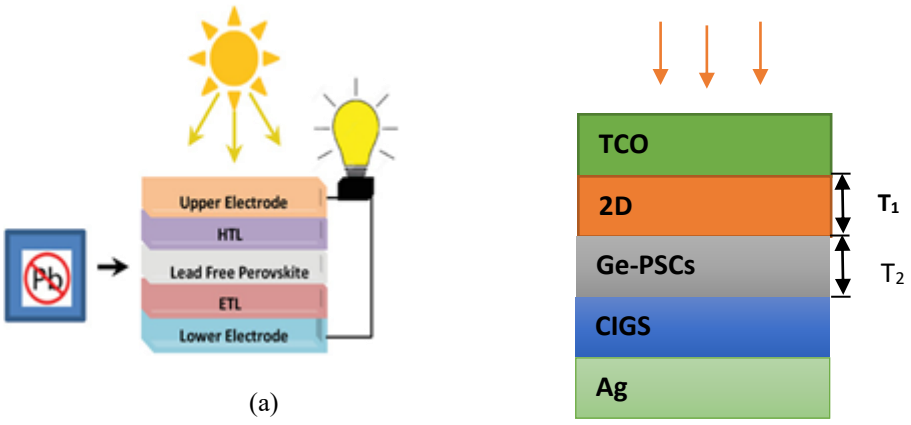
Where E_g (eV) is the band gap energy, χ (eV) is the electron affinity, N_c (cm^{-3}) is effective density of states at CB, N_v (cm^{-3}) is the effective density of states at VB, N_d (cm^{-3}) is the donor density /density of p-type doping, N_A (cm^{-3}) is the acceptor density/ density of n-type doping, ε_r is the relative dielectric permittivity, μ_n ($cm^2c^{-1}s^{-1}$) is the mobility of electron, μ_h ($cm^2c^{-1}s^{-1}$) is the mobility of electron, N_{te} (cm/s) is the electron thermal velocity, N_{th} (cm/s) is the hole thermal velocity.

Table 2: Photovoltaic parameters of the solar cells

Structure	**J_{sc} (mA/cm^2)**	**V_{oc} (V)**	**FF (%)**	**PCE (%)**	**References**
Cu_2O /$CH_3NH_3PbI_3$/n-cSi	0.67	48.58	90.0	19.50	This study
2D/Ti_3C/$CH_3NH_3GeI_3$/Ag	0.60	62.01	80.10	21.02	This study
P-graphene/$CH_3NH_3PbI_3$/n-cSi	30.87	0.6879	84.31	17.90	Gagadeep et al. [18]
$mTiO_2$+G/perovskite/GO/spiro-OMeTAD	22.48	1.08	75.12	18.19	Lakhdar et al. [15]
$CH_3NH_3PbI_3$-based solar cell Simulation, TiO_2	23.44	0.93	60.75	13.30	Agresti et al. [19]



(a)

(b)

Figure 1: Outline (a) Lead Free PVCs with (b) 2D inter layer 100-1000 nm

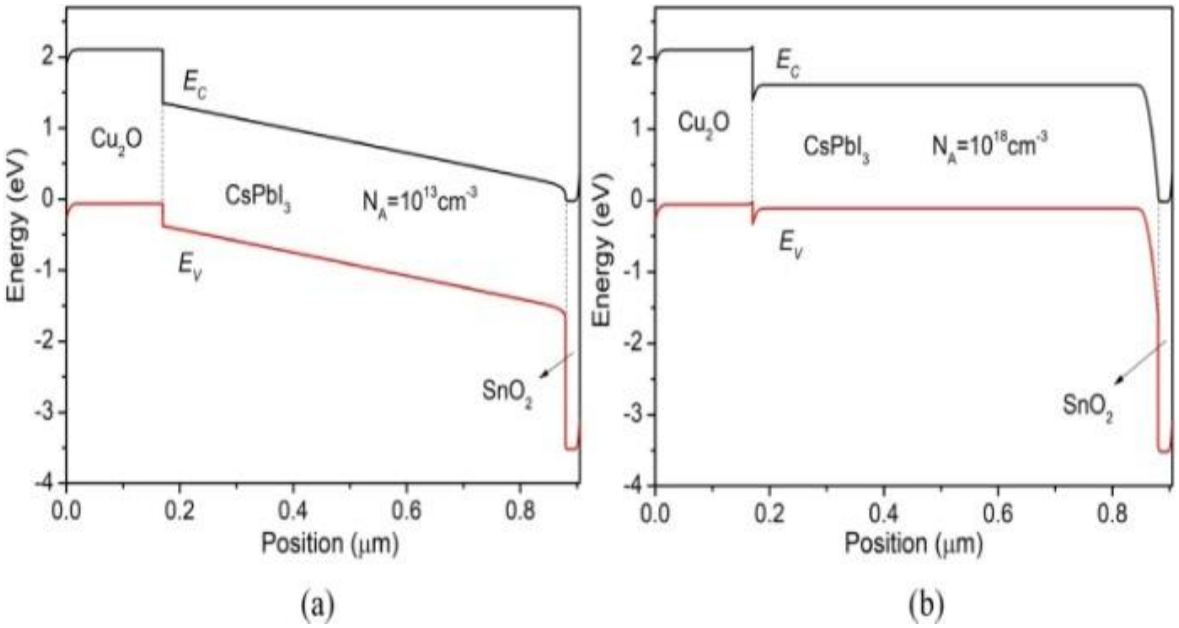


Figure 2: Energy band diagrams of the device with different doping density (a) NA= 10^{-13} cm^{-3} and (b) NA = $10^{-}18$ cm^{-3}.

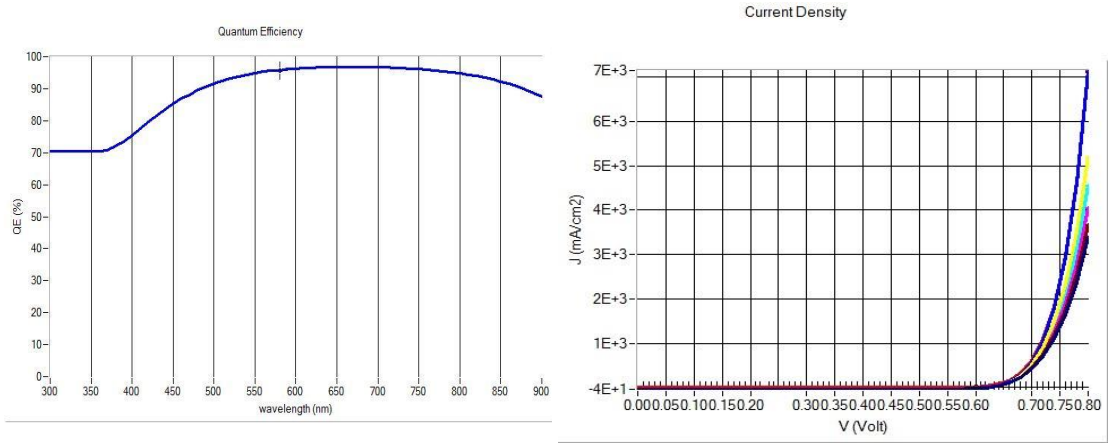


Figure 3 (a) Quantum efficiency of PSCs without 2D HTL (b) J-V of the PSCs with Graphene-TiO_2 at 2.5μm

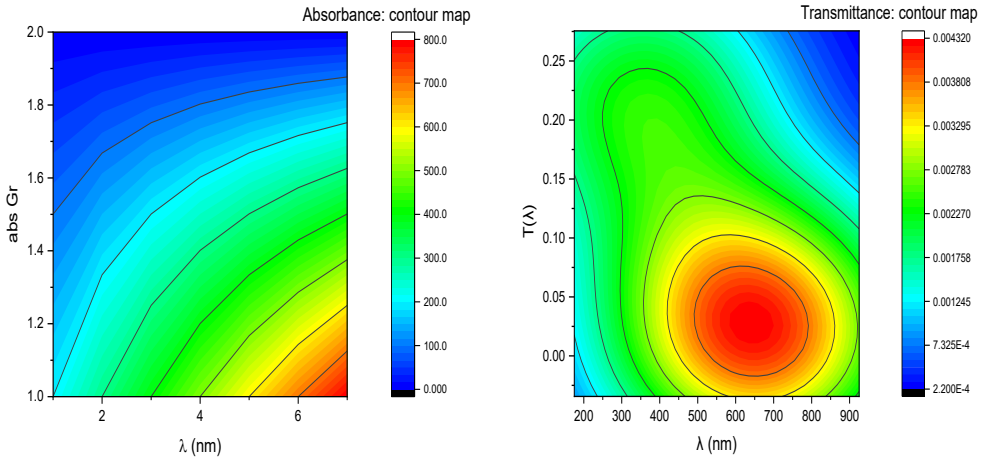


Figure 4: Contour Map of the absorbance and transmittance against wavelengths

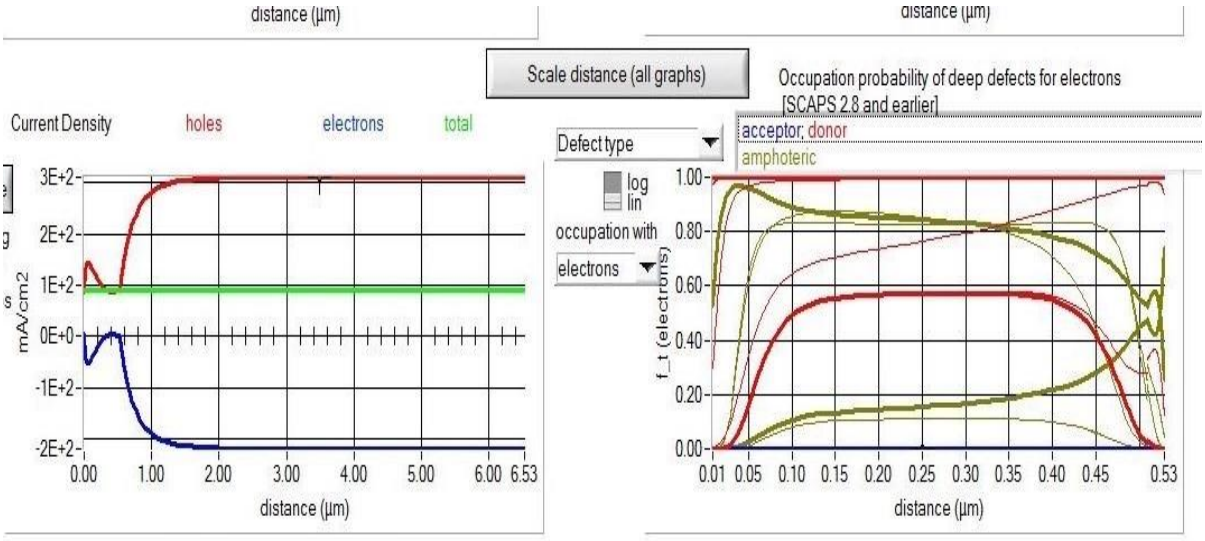


Figure 6: The occupation probability of deep defect for electrons and the carrier density

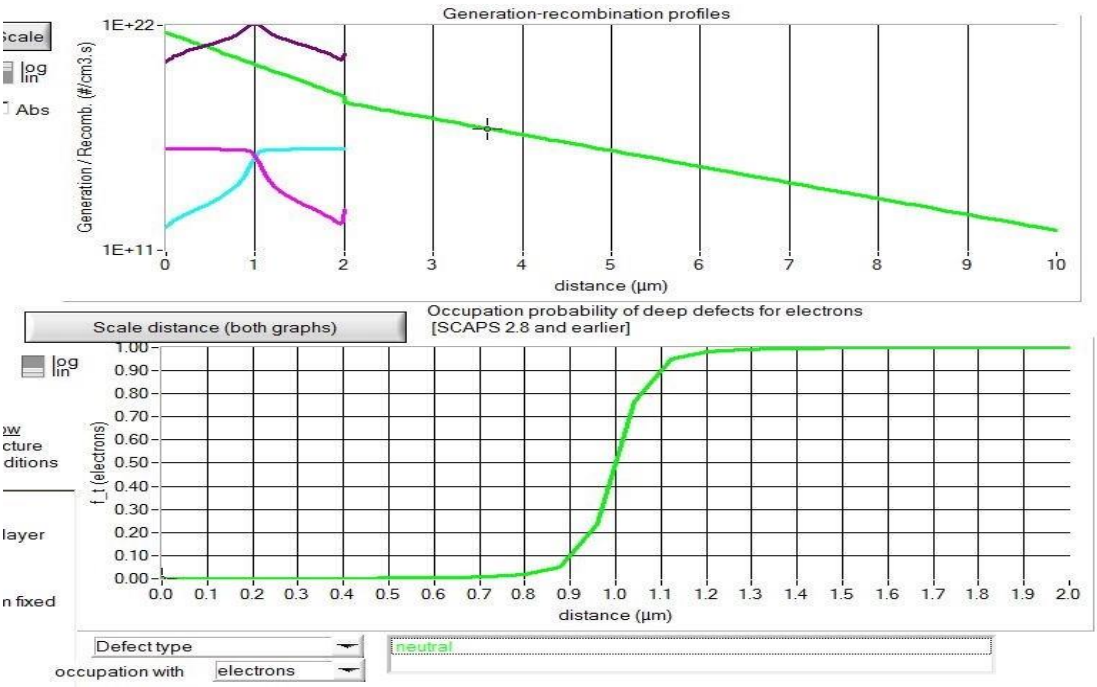


Figure 8: Generation and recombination profile

3. RESULTS AND DISCUSSION

In the solar cell, the absorber plays a crucial role on the performance and is composed of Ge-based perovskite photo-absorber. The thickness is such that it equilibrates the photo-generated electrons and holes with reduced absorption and recombination profile. By optimizing the absorbers thickness, band gap energy (1.9 eV), in perovskite device, the open circuit voltage (V_{oc}), short circuit current (J_{sc}), fill factor (FF) and power conversion efficiency (PCE) for the various 2D HTMs were obtained at 21% and a 0.52V; 60.50 $mAcm^{-2}$; and 80.07% respectively (Ladan and Buba [5]).

The J_{sc} increases with the increase in the absorber layer thickness and reaches the maximum. It has revealed that the thinner the absorber, the more photons and excess carrier concentration with longer wavelength and generation of improved electron-hole pairs are produced. V_{oc} slightly decreases as absorber layer thickness increases due to more carrier recombination. It showed V_{oc} is depended on photo generated J_{sc}, dark saturation current of the cell depends on the recombination profile which is a measure of the amount of recombination in the device. The FF of 80% with the absorber thickness changing from 50 nm to 250 nm is due to the high series resistance and shunt conductance of the device, a measure of the carrier's mobility (Lin et al. [20]; and Gagadeep et al. [18]).

As the device efficiency increases with thickness of the Ge and saturates at 600 nm, it means more light absorption and more excess carrier concentration leads J_{sc} increase. Ge has very high absorption coefficient up to 105 cm^{-1}, it implies that it can reach high values of J_{sc} and PCE in a very thin

absorber thickness of about 450 nm. High defect densities in the device can limit the performance of the solar cells. It induces carrier recombination and lifetime reduction, using 2D HTMs alternatively increases the efficiency due to minimized defect and less resistance by enhancing hole (+) mobility. On doping the absorber layer with 2D materials, it was recorded that when the dopant concentration is larger than 1000 cm^{-3}, the J_{sc} decreases, whereas the efficiency and V_{oc} increases. The effect of the metal electrode work function W (Pt: 5.65 eV, Pd: 5.3 eV, Ag: 4.7 eV, Cu: 4.65 eV, Au: 5.1 eV, Ni: 5.0 eV) on the output of the device were explored. The PCE increases with increase in the W of the contact metal agreement with similar studies. With the 2D materials, noble metals Au, Ni and Ag indicated better improvement compared to other metals. The high W of the metal produced a higher barrier for electron transfer from the 2D HTMs to metal contact (Lin et al. [20]; Gagadeep et al. [18]; Dadashbeik et al. [21]).

The transmitted light, contour map (fig. 5) for the absorbance versus the wavelength of the radiation indicated peak heat generation at 700 nm/tr between 0.5 and 0.25 above violent region at the same projection to achieve maximum absorbance and transmittance at 550.5 nm[5].

The operation of the device in generating power can be affected by changes in atmospheric temperature, as a result, the variation of photovoltaic parameters as a function of temperature for all 2D HTMs considered were simulated. It is clear that J_{sc} slightly increased along with temperature increase, while V_{oc} decreases. This can be attributed to reduction in energy band gap. The effect of temperature on the electron and hole mobility, and carrier density on the device needs further investigation due to the dynamic nature of the HTMs (fig 6-7). 2D graphene, mxenes and TMDCs, as HTM as contact layer in thin films solar cell reduces the optical and energy losses. They improved the absorption of radiation since they are about 97.7% transparent to solar rays and reflection losses at interface decreases J_{sc} by 9% (Kumar et al. [12]; Gagadeep et al. [18]; Kosyanhenko et al. [22]).

4. CONCLUSION

Using SCAPS-1D Solar simulating software, we have studied the effect of absorber thickness, defect density, carrier mobility, operating temperature and metal work function of $CH_3NH_3GeI_3$ based PSCs. The study indicated an optimum absorber thickness of about 600 nm for improved efficiency of the device. An increase in the PCE exceeding 20% using high surface area 2D HTMs (graphene, Mxene and TMDCs) due to improved area of exposure, transparency, thickness, and excellent optical, electrical and thermal conductivities. They have higher hole mobility and decreased defect density. The photovoltaic parameters of 2D layered HTM obtained using SCAPS simulation for the first time will lead to more investigations on their applications for improved efficiency, stability and life span. The introduction of the novel materials enhance the interaction between the layers which is beneficial for electrical conductivity and efficiency of solar cells, charge transport, and suppressed recombination of electron-hole pair.

Graphene and its analogue, mxenes and TMDCs exhibit unique optoelectronic properties. Rational assembly of individual monolayers into bilayers or heterostructures provides a means for the realizations

of a wide range of novel quantum materials and devices with tunable electrical, mechanical, optical and transport phenomena based on unique spin-valley degrees of freedom and strong electron correlations.

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AUTHOR CONTRIBUTIONS:

Ladan H.M.A: Conceptualization, Methodology, Writing original draft.

Buba A.D.A /Adamu A.S: Methodology, Writing & correction

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