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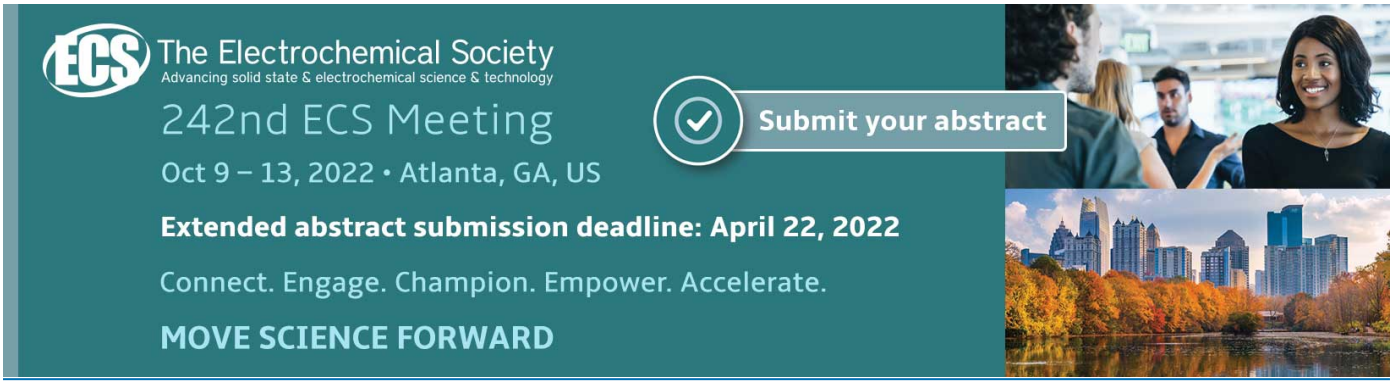

Relative straggle of sputtering parameters as a potential measure of power conversion efficiency of Perovskite materials

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Abstract. The growing demand for electricity necessitates the development of time-efficient computational methods in search of better solar energy-harvesting materials. One challenge has been ways to improve the power conversion efficiencies (PCEs) of potential harvesters.In this paper, an ion sputtering approach was used to study the problem of estimation of the power conversion efficiencies (PCEs) of perovskite solar device materials through their surface sputtering signatures. This rests on a hypothesis that the similarity between the phenomenon of photon excitation from light-sensitive absorbers, leading to electricity generation, and ejection of energetic particles from sputtered surfaces, could be exploited to estimate PCE. Hence, a Monte Carlo (MC) simulation of the sputtering of surfaces of perovskite materials with energetic ions was performed; and a number of quantities that could be used for the estimation of PCE were calculated. The results indicated that the relative straggle of surface sputtering parameters of the materials could be an effective measure of the theoretical maximum power conversion efficiencies of these materials. In particular, the relative straggle of the projected range of the ions in the respective materials was found to be close to reported experimental results of PCEs in the literature.

Keywords: Average Sputter Yield, Perovskites, Power Conversion Efficiency, Relative Straggle, Surface Sputtering.

1. Introduction

The research efforts aimed at meeting the ever-increasing energy demand of the world population most efficiently and cost-effectively have occupied scientists for decades. With increased human population comes the electricity demand. According to [1-2], approximately 70% of the global surge in energy demand, and the 80% for electricity in the future lies in

emerging markets and developing economies. A 4.5% increase in 2021 is the fastest growth in over ten years. In particular, the data above suggested that the solar photovoltaic (PV) electricity generation is set to reach 1000 terawatts hour this year.

For years, silicon has been the archetypical semiconductor material for photovoltaic solar energy applications [3-4]. It is the commonest solar module in the market with industrial power conversion efficiency between 18 to 22% under standard test conditions [4]. Crystalline silicon PV cells also have laboratory PCE of over 25% [3]. But in recent times, attention has shifted to perovskites [5]. Perovskites are a group of materials that crystallize in the ABX_3 structure after $CaTiO_3$ [6].

The pioneering research that demonstrated their rich prospect for solar energy conversion was carried out by Kojima *et* al. [7]. Researches supporting their potentials highlighted their low-cost fabrication techniques, higher charge carriers mobility, great absorbance coefficient, long carrier diffusion length, easy to modify bandgap, controllable thermalisation among other interesting optoelectronic behaviours [5] [8]. It is implied that commercialising perovskite photovoltaic devices would rival the adoption of silicon-based devices whose fabrication processes demand a lot of energies [9].

In the drive to optimise perovskite-based solar cells (PSC) performance, different approaches have been used. Some of them involved substituting tin, germanium, bismuth for the not so environmentally-friendly lead in the B site of the metal halides, and Monte Carlo simulation [10-11]. In addition to this compositional engineering approach, the stability of the resultant perovskite has been a major challenge [12]. To stabilise the material and at the same time increase its power conversion efficiency, special materials have been employed to reduce charge recombination in the light harvester. The majority of the mostefficient PSCs have utilised TiO_2, spiro-OMeTAD, P3HT, CuSCN to do this. But in recent times, oxides of some metals are better substitutes. More so, Copper Indium (CuI) and tungsten disulphide (WS_2) have been reported to be excellent holes and electrons extracting materials respectively [13]. WS_2 is a transition metal dichalcogenide (TMDC) like molybdenum disulphide (MoS_2). TMDCs are reported to demonstrate good conductivity and optical properties [14].

A faster way to predict the theoretical maximum efficiency of these materials as they are being synthesised becomes important. This has the advantage of knowing what material has the better prospect for higher energy conversion and what to look up in the space of competing candidate materials as we engineer them for higher efficiencies. From the foregoing, there is the need to develop a flexible and faster means of predicting the power conversion efficiency of solar cell materials.

Sputtering refers to the removal of materials (atoms, electrons, ions) from the surface of solids when irradiated with particles having suitable energies. It has been widely used in the semiconductor industries for deposition, etching, and surface erosion [15-16]. In this study, there are reasons to think that it could provide some information about the PCE of solar device materials. Since in these cells, surfaces sensitive to photons or particles of light generate electricity, it was argued that there is no reason to not think that a similar phenomenon will not take place in surfaces sputtered by ions. Prince and Loferski, as reported

by Schockey and Queisser [17], attempted these predictions based on energy gap-dependence. Rühle [18] also made some contributions in this regard in a method influenced by [17].

The question has been whether one can determine the power conversion efficiency of solar cell materials from their Monte Carlo Simulation of sputtering behaviours. To the extent of the literature reviewed, this study extends the work of [11]. By way of numerical computation through SRIM/TRIM simulation programme, predictions of the theoretical maximum of the PCEs of the materials under study were made.

2. Methodology

To carry out this study, ten materials with known experimental power conversation efficiencies were selected from the literature. Among the materials studied are formamidinium lead tri-iodide ($FAPbI_3$); formamidinium lead tri-bromide ($FAPbBr_3$); methylammonium lead tri-iodide ($MAPbI_3$); methylammonium tri-bromide ($MAPbBr_3$); methylammonium tin tri-iodide ($CH_3NH_3SnI_3$); methylammonium germanium tri-iodide ($CH_3NH_3GeI_3$); Cesium lead tri-iode ($CsPbI_3$); cesium lead tribromide ($CsPbBr_3$); rubidium antimony iodide ($Rb_3Sb_2I_9$), butylammonium copper bromate ($(CH_3(CH_2)_3NH_3)_2CuBr_4$ and silicon.

The software used for the simulation was the Stopping and Range of Ions in Matter (SRIM), alongside the TRansport of Ions in Matter (SRIM/TRIM version 2013.00) [27]. It is a Monte Carlo Simulation suite developed by Ziegler and Biersack. Google Sheet and the OriginPro (version 8.5.0) by OriginLab were used for statistical analysis and graphing.

Firstly, simulation parameters maintained their laboratory experimental values where possible. The densities of materials used were extracted from pieces of literature [11] and [20], respectively. Where the experimental value was not readily available, the values were estimated by TRIM. Similarly, the average perovskite wafer thickness of 35 nm [11] was adopted. This was supported by literature to be within the optimal thickness for sputter experiments [19]. One thousandions of Neon each on the different target materials, one at a time, were used to simulate a practical timescale [11][16].

Secondly, Monolayer Collision Step/Surface Sputtering [27]was done to compute the sputter yield. Detailed Calculation with full Damage Cascades was carried out to compute the projected range of ions in the target materials at normal incidence. Calculations of the yield of atoms for each material at ions energies of 5 KeV for different sputter angles from 0 degrees; and in steps of 5 degrees until 89 degrees were made. For the range of ions, the energies were varied from 1 KeV to 10 KeV. This was justified by the fact that ion energies in sputtering experiments fall within this limit. Only low-energy sputtering experiments adopt ion energies around 500 eV [11]. Furthermore, all targets were built from their composites according to their chemical formulae and stoichiometry.
The data calculated were collected and presented in tabular format in Google Sheet for visual inspection of any trend before further analysis was done. Firstly, a plot of Projected Range against energies was made for all materials. Plot of the Sputter Yields against the angles of the sputter was made. To test further the initial observations, the average sputter yield of the ten materials over all angles (0 – 89 degrees) was calculated to arrive at a single value; it was also

repeated for each angle. Similar calculations were made for the linear projected range of ions in the materials. The calculations were repeated for each material separately for all angles.

The straggle was calculated using the equation (1):

$$Straggle = \sqrt{\left\langle \left(Y(\theta) - \left(Y(\theta)\right)\right)^2 \right\rangle} \quad (1)$$

While the PCE was calculated using the equation (2):

$$PCE = \frac{Straggle}{Mean\ range} \times 100 \quad (2)$$

where $Y(\theta)$ is the angle-dependent sputter yield. This can be replaced by the range, $R(E)$, a function of energy to calculate the straggling on the projected range of ions for each material.

3. Results and Discussion

In this section, simulation results are presented and discussed. Sputter yields results for the perovskites are presented in Figure 1. Overall, the trends for the materials are similar with an average peak of around 78 degrees. This region corresponds to the points of maximum yield for each material, and is in agreement with the results in [11]. For $FAPbI_3$, the average yield is least at 0 deg. (0.4924), peaks at 80 deg. (1.3470), then it dropped to 0.7940 at 89 deg. $MAPbI_3$ has 0.5423 at 0 deg., 1.0464 at 80 deg., then 1.0282 at 89 deg. $MAPbBr_3$ has 0.4886, 1.0888 at 80 and 0.8704 89 deg. $MASnI_3$ has 0.4398 and 0.8099. $MAGeI_3$ has 0.5174 and 0.8298. $CsPbI_3$ has 0.6990, 1.7153 at 75 and 1.0150 at 89 deg. $CsPbBr_3$ has 0.9983, 2.3580 at 75, 1.3593 at 89 deg. Rb_3Sb2I_9 has 1.3700, 3.1430 at 70 and 1.4787 at 89 deg. $(CH_3(CH_2)_3NH_3)_2CuBr_4$ has 0.1969, 1.1060 at 80, 0.6721 at 89 deg. and silicon has 1.220, 7.070 at 75 and 3.980 at 89 deg., respectively.The figure shows that Sn^{2+} can replace the toxic lead in $MAPbI_3$ and the same is true for Ge^{2+}. It is also evident that silicon is not a perovskite material going by its unique curve. In addition the similarity in the behaviour of $CsPbIr_3$ and $CsPbBr_3$ is reflected by the closeness of their curves.

Table 1 presents some parameters calculated from the average sputter yields, taken over the atoms. It is observed that the relative straggle of $FAPbI_3$ is 37.63% (max. PCE 22.10%); $MAPbI_3$ gave 24.35% (max. PCE 22.70%); $MAPbBr_3$ gave 29.51% (max. PCE 10.40%); $MASnI_3$ gave 20.96% (max. PCE 7.78%); $MAGeI_3$ gave 19.88% (max. PCE 0.20%); $CsPbI_3$ was 31.85% (max. PCE 2.90%); $CsPbBr_3$ was 32.35% (max. PCE 6.20%); Rb_3Sb2I_9 gave 30.56% (max. PCE 0.66%) and $(CH_3(CH_2)_3NH_3)_2CuBr_4$ gave 60.97% (max. PCE 0.63%) and silicon was 60.09% (max. 26.1% and its theoretical max. PCE 30% [17]).

Why the calculated PCE values of Silicon and $(CH_3(CH_2)_3NH_3)_2CuBr_4$ are the outliers at about 60% is notimmediately clear. However, the average PCEs over the materials is 34.82 ± 13.84%. This appears to suggestthat the Schockley - Queisser limit may be exceeded, andthat the solar cell PCEs could be improvedup to about50%.

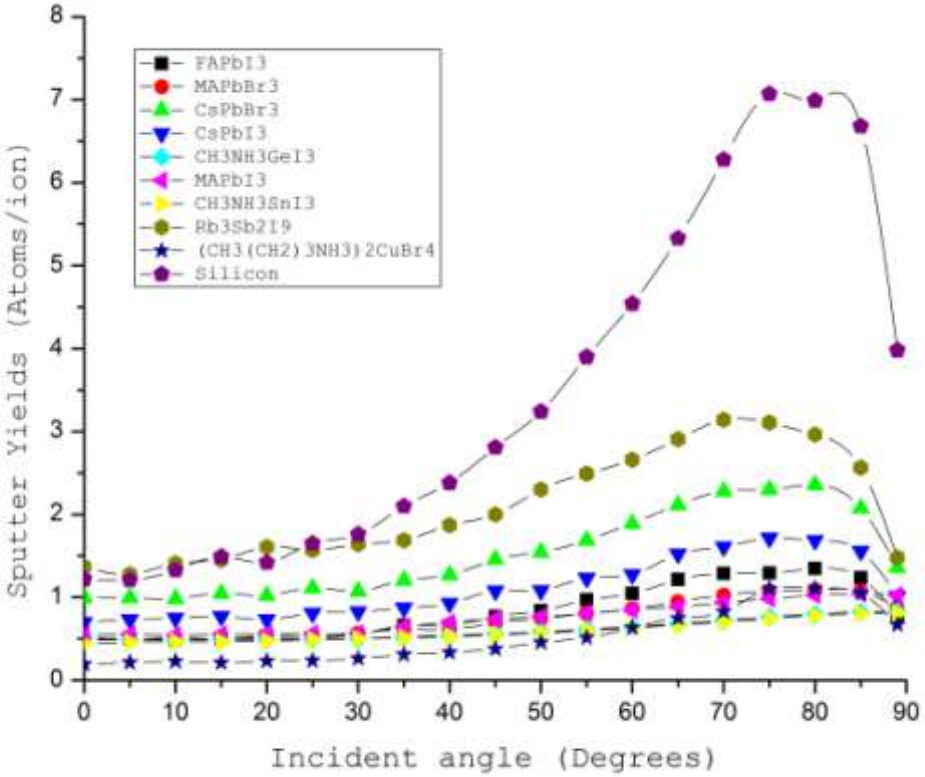

Figure 1: Average sputter yield across ABX atoms of perovskite absorber materials from 0 – 89 degrees, and Ne^{+} energy 5 KeV.

In Table 2, a side-by-side comparison of the relative straggles calculated on the projected range of the ions to their highest experimentally achieved PCEs is presented. It is observed that $FAPbI_3$ has 26.44% (with max. PCE 22.10%); and $MAPbI_3$ has 23.07% (with max. PCE 22.70%). $FAPbI_3$ shows a difference of 4.34 from its highest improved reported value while there is a difference of 0.37 for $MAPbI_3$.

On the contrary, the rest of the materials demonstrated significant deviation from their current experimental values. This difference could be explained by insufficient and slow-paced research efforts towards enhancing their photon absorbance characteristics, unlike $MAPbI_3$ and $FAPbI_3$. Therefore, it is expected that over time, they would be improved to attain higher comparable PCEs.

Table 1: Calculated Parameters on Sputter Yields for Each Material

Material	**PCE (Experimental)%**	**Average sputter yields (atoms/ion)**	**Straggle**	**Calculated PCE (Relative Straggle)%**
$FAPbI_3$	22.10[22] 19.70[22] 14.20[25]	0.8267	0.3110	37.63
$MAPbI_3$	22.70[21] 21.09[26] 16.10[23]	0.7533	0.1834	24.35
$MAPbBr_3$	10.40[23]	0.7382	0.2178	29.51
$MASnI_3$	7.78[24] 6.00[23]	0.5899	0.1237	20.96
$MAGeI_3$	0.20[11]	0.6096	0.1212	19.88
$CsPbI_3$	2.90[23]	1.0995	0.3502	31.85
$CsPbBr_3$	6.20[23]	1.5158	0.4903	32.35
$Rb_3Sb_2I_9$	0.66[11]	2.0790	0.6353	30.56
$BACuBr_4$	0.63[11]	0.5122	0.3122	60.97
Silicon	26.10[3]	3.4411	2.0679	60.09

MA= methylammonium ($CH_3NH_3^+$); FA = formamidinium [$HC(NH_2)_2^+$)];

BA = butylammonium [$(CH_3(CH_2)_3NH_3)_2^+$]

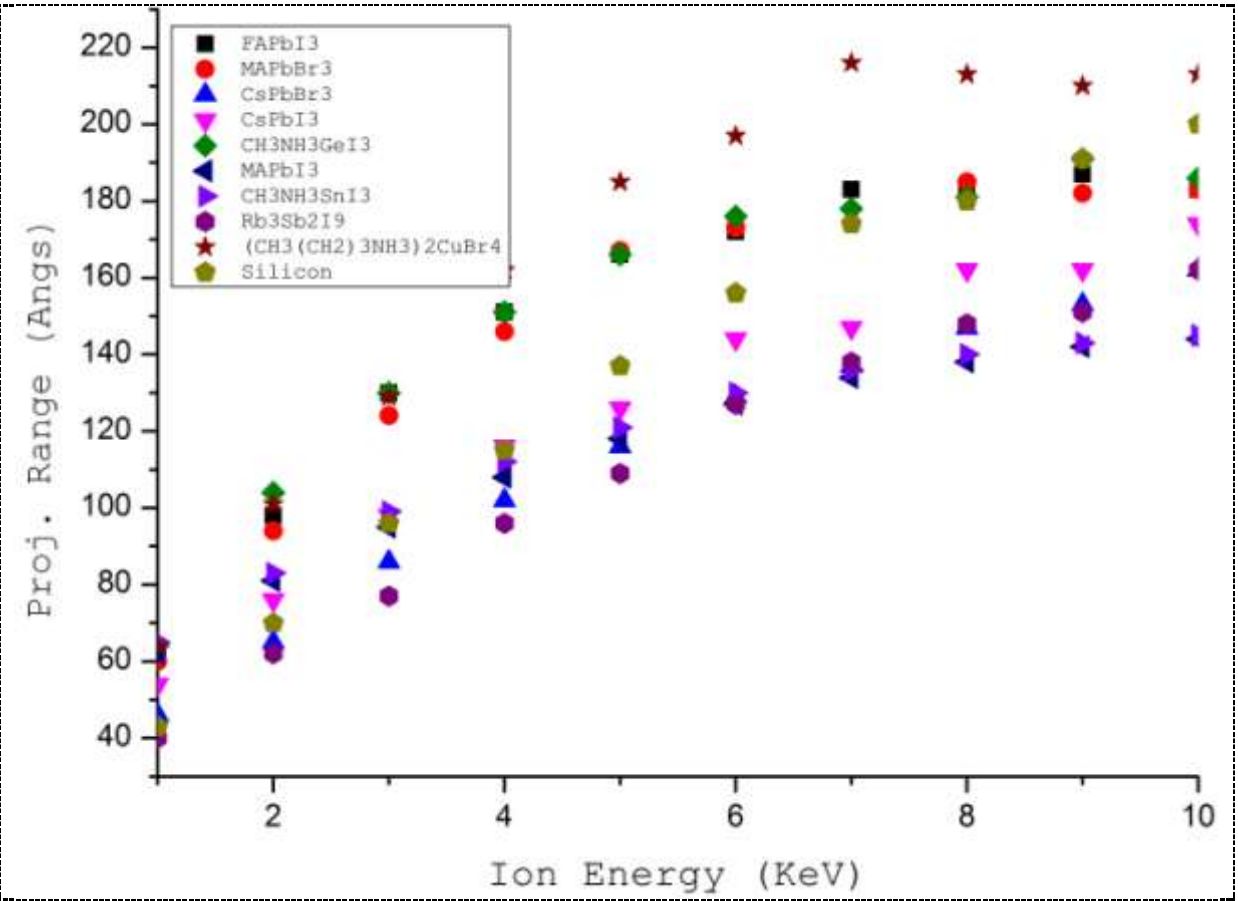

Figure 2: Projected range of Ne+ ions in some perovskites target materials for different ion energies from 1 KeV to 10 KeV.

For the mono-crystalline silicon, Schockley and Queisser had reported a 30% theoretical maximum for the PCE. They assumed that all the photons impinging on the semiconductor were absorbed completely. But in the case of only 90% absorption, the theoretical maximum dropped to 26%. Going by the former assumption, a deviation of 7.99 from the ideal theoretical maximum for silicon has been obtained. This may be attributed to some factors not yet determined. Overall, the calculated PCE values on the projected range of ions average to 29.06% and to within 5.12 standard deviation of the Schockley - Queisser limit. From these results, it could be inferred that the relative straggle of the projected range of ions in PSC materials is a potential measure of the PCEs of these light-absorbers. Nevertheless, the results from the average sputter yield seem to be pushing the maximum attainable PCE to about 50% for a single junction cell.

Table 2: Calculated Parameters on Projected Range Data for Each Material

Material	**PCE (Experimental)%**	**Mean Range (Å)**	**Straggle**	**Calculated PCE (Relative Straggle)%**
$FAPbI_3$	22.10[22] 19.70[22] 14.20[25]	151.7	40.11	26.44
$MAPbI_3$	22.70[21] 21.09[26] 16.10[23]	114.9	26.51	23.07
$MAPbBr_3$	10.40[23]	148.8	40.79	27.42
$MASnI_3$	7.78[24] 6.00[23]	117.4	25.97	22.12
$MAGeI_3$	0.20[11]	152.7	39.36	25.78
$CsPbI_3$	2.90[23]	125.7	37.72	29.96
$CsPbBr_3$	6.20[23]	114.3	36.91	32.29
$Rb_3Sb_2I_9$	0.66[11]	111.0	39.22	35.33
$BACuBr_4$	0.63[11]	169.0	51.09	30.23
Silicon	26.10[3]	136.2	50.94	37.99

MA= methylammonium ($CH_3NH_3^+$); FA = formamidinium [$HC(NH_2)_2^+$)];

BA = butylammonium [$(CH_3(CH_2)_3NH_3)_2^+$]

4. Conclusion

This study aimed at devising a means to arrive at some theoretical predictions of power conversion efficiencies of solar device materials using their surface sputter characteristics. It has been demonstrated that it is possible to arrive at the theoretical maximum of PSC using a faster method of the SRIM/TRIM Monte Carlo suite.

From the analyses of results presented in this paper, it was found that the relative straggle of surface sputtering parameters of perovskites, via ion-beam bombardment could be an effective measure of the theoretical maximum power conversion efficiencies of these materials. In particular, the relative straggle of the projected range of the ions in the respective materials was found to be close to reported experimental results of PCEs in the literature.

Acknowledgment

The authors appreciate the Covenant University Centre for Research, Innovation and Discovery (CUCRID) for her support.

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