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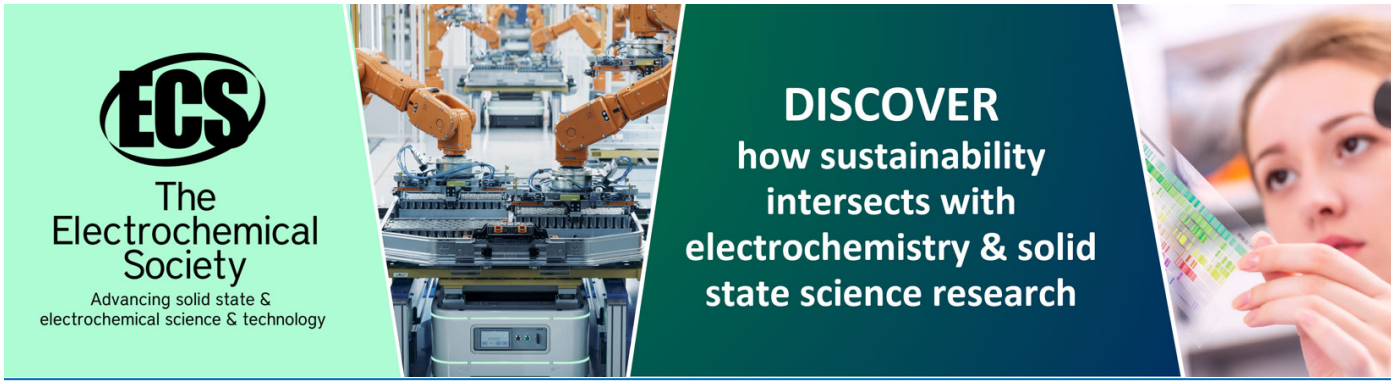

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Analytical Form of Sputtering in Relation to Surface Binding Energy for Different Types of Perovskites

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Abstract. In recent years, perovskite materials have been the focus in solar cell fabrication industry. Herein, an investigation was conducted on the effect of ion-solid interactions on factors are responsible for differences in the properties of these perovskite materials by using a Monte Carlo simulations of ion beam surface sputtering. A connection was established between the experimental efficiencies of solar cells of these materials and both projected yield and sputter yield of these structurally alike perovskite materials.

Keywords: PV cells; Sputtering; MC Simulations, Perovskites; Sputter yield; Range of ions.

1. Introduction

Solar cells have evolved from a restricted application for powering space vehicles [1&2] to a commercially viable and indispensable clean and renewable terrestrial energy source [2] Efficiency of solar cells and ways of increasing it are of paramount interest. Far back in the early stages of solar cell research, the efficiency of real silicon solar cells (SSC) were found to have a maximum achievable efficiency (~16%) that was short of the ideal SSC maximum achievable efficiency of 22% for Air Mass 0 (AM0) in which case sunlight undergoes no scattering processes [1], which is way below the

thermodynamic (theoretical) limit of 31% established in the theoretical analysis of Shockley and Queisser [3]. Things have improved significantly with a laboratory best efficiency of 25% (18% commercially) recorded for single crystal SSC and 32% for multi-junction solar cell [4].

Organo-metal halide perovskites have a lot of potential over silicon for achieving higher power conversion efficiencyy (PCE) solar cells [5, 6]. They have, therefore, engendered an intense research interest one of the aims of which is to achieve higher solar cell PCEs [7-13]. For instance, advanced device engineering techniques aimed at controlling morphology, its makeup and interface properties of the thin films from perovskite can enhance efficiency and are active research interests [13]. In particular, the quantum dots of these perovskites have a potential to increase PCE in photovoltaic operation and have attracted a lot of focus in recent years [14].

In a new Monte Carlo simulation study of ion beam surface sputtering of potential perovskite materials, it was found that sputtering characteristics of the materials, such as the ion yield and range had some correspondence to the reported efficiencies of solar cells based on the materials [7]. These simulations were performed using the Monte Carlo simulation package which is made by Biersack and Ziegler [15-18], SRIM (Stopping and Range of Ions in Matter), and its further extended counterpart TRIM (TRansport of Ions in Matter), which comprises SRIM and some sputtering calculation factors using MCarlo techniques[18]. The SRIM and TRIM codes, while being versatile simulation tools in this regard, are far much faster and computationally less demanding than an alternative, albeit standard and detailed, simulation route.

This alternative is a combination of density functional theory calculations of electronic properties, molecular dynamics simulations equilibrium (optimised and stable) structures and of light-irradiation of the optimised structures of the perovskite solar cells to calculate their efficiencies. Hence, if a proper (e.g. analytical) correspondence can be established between the physical sputtering factors and PCEs, one has a readily available, very fast and easy method of comparative assessment of the potential of a set of materials for solar cell efficiency. Consequently, this research aimed to relate the sputter characteristics of the perovskite materials to some existing material property that is independent of the sputtering process and to obtain the analytic form of such a relation.

In the seminal Sigmund ion sputtering theory, classical scattering theory was used to arrive at analytic expressions for the sputter yield as a function of target-target collision cross-sections, ion target and atomic binding energy [19]. In addition, the spatial distribution of the energy of the incident ion was given as a function of the ion energy and material-dependent collision cascade parameters. Feix *et al.* performed molecular dynamics simulations of the sputtering of copper crystals, in the binary collision approximation, and found similar qualitative properties of the ion yield and energy distribution [20]. Quantitatively, they found significant deviations from Sigmund's energy distribution, such as an exponential, rather than Gaussian, decrease of deposited energy with increasing distance of surface atom from ion trajectory. However, their focus was on the effect of this deviation in shifting the form of the analytic continuum equations of the evolution of surface height with position and time, from the expected Bradley-Harper form. Which led to a non-monotonous dependence of the yield on incidence angle being inferred. Hobler *et. al. r*ecently used Monte Carlo

simulations to investigate the sphere of application of the Sigmund model in detail by testing the validity of its three core assumptions and studying the reason for its deviation from reality under some conditions, and breakdown at grazing incidence [21].

Although Sigmund's model has been remarkably successful, with the Bradley-Harper theory of ion beam surface sputtering and its many extensions based on the model [22], it fails for some observed aspects of sputtering [20-21]. Bradley and Hofsäss modified the Sigmund energy distribution equation, for it to be in accord with realistic molecular dynamics simulations of energetic ion sputtering [23], and inferred the properties of the yield for different sputtering scenarios [22]. Effects of self-organised behaviour and other interesting phenomena, under prolonged sputtering, manifest at timescales of the order of minutes, which is way beyond the realm of application of molecular dynamics. Monte Carlo simulation is thus indispensable for such studies. MC simulation suites made by Ziegler and Biersack [15-18] SRIM, and its more extended counterpart, TRIM, which includes SRIM and deduction of some sputtering parameters with MC techniques, are versatile tools in this regard [18].

Bearing in mind that our interest in the sputter characteristics lie not in the topographical evolution of perovskite surfaces, but in the correspondence between the differences in their light harvesting and conversion efficiencies, and their sputter characteristics, there is the need to obtain a governing equation of the yield instead of the usual morphology-based approach of interest in the continuum equations of the surface height. Therefore, in this paper, we used SRIM Monte Carlo simulation codes to study the Ar ion sputtering of perovskites of interest [8] and used it to deduce the analytic equation of the yield.

The remaining part of the research paper is arranged as follows; in the next part, the methods used in obtaining the results discussed in this research work were elaborated. The set-up of the simulation details on the TRIM and SRIM Graphical User Interface, GUI and the values used were provided. Section 3 shows the presentation and discussion of results, and in section 4, we concluded.

2. Methodology

We provide the details of our simulation and the details of the theoretical background for the simulation algorithms and calculations implanted in the TRIM and SRIM tool are discussed in Ziegler and Biersack works [24, 25]. Molecular dynamics simulations of the range of inert gas ions Ne^+ and Ar^+ was performed by SRIM and energies ranged from 1 keV to 10 keV, at incidence which is normal on the perovskites targets, namely, lead (Pb) perovskite $CH_3NH_3PbI_3$ and tin perovskite $CH_3NH_3SnI_3$, Germanium perovskite $CH_3NH_3GeI_3$, $(CH_3(CH_2)_3NH_3)_2CuBr_4$, $Rb_3Sb_2I_9$ and $Cs_3Bi_2I_9$

In SRIM set-up perovskite wafer thickness of 35 nm was used, and built up the lead, Tin and Germanium perovskites from its composites in the stoichiometric ratio 1:3:1:3:1:3 for C, H, N, H, Pb/Sn, I, respectively, and densities of 4.16g/cm^3 [26] and 3.51g/cm^3 [27] and 3.32g/cm^3 [7]for the

lead, tin and germanium perovskites, respectively. While we used 1.87 g/cm^3, 7.43 g/cm^3 and 8.30 g/cm^3 for $(CH_3(CH_2)_3NH_3)_2CuBr_4$, Rb3Sb2I9 and Cs3Bi2I9 respectively[7].

3. Results and discussion

We discovered identical trends for Ne^+ and Ar^+ ions, but with higher values for Ar^+ ion, the results of the projected range of the ions in lead perovskite $CH_3NH_3PbI_3$, tin perovskite $CH_3NH_3SnI_3$, Germanium perovskite $CH_3NH_3GeI_3$, $(CH_3(CH_2)_3NH_3)_2CuBr_4$, $Rb_3Sb_2I_9$ and $Cs_3Bi_2I_9$ for different ion energies varied from 1 keV to 10 keV is shown in Figure 1. Figure 2 shows the results of the projected range of the ions in the lead perovskite $CH_3NH_3PbI_3$, tin perovskite $CH_3NH_3SnI_3$, Germanium perovskite $CH_3NH_3GeI_3$, $(CH_3(CH_2)_3NH_3)_2CuBr_4$, $Rb_3Sb_2I_9$ and $Cs_3Bi_2I_9$ for different ion energies ranged from 1 keV to 10 keV. These displays of almost similar values of the linear range of the ions for the various perovskites point towards that the two materials are amazingly related as regards their stopping power to energetic particle irradiation.

These results indicate that the projected range follows a trend governed by the equation

$$\frac{d^2R}{dE^2} + k\frac{dR}{dE} = q; k, q \in \Re$$

Where the values of the constants vary with the type of perovskite.

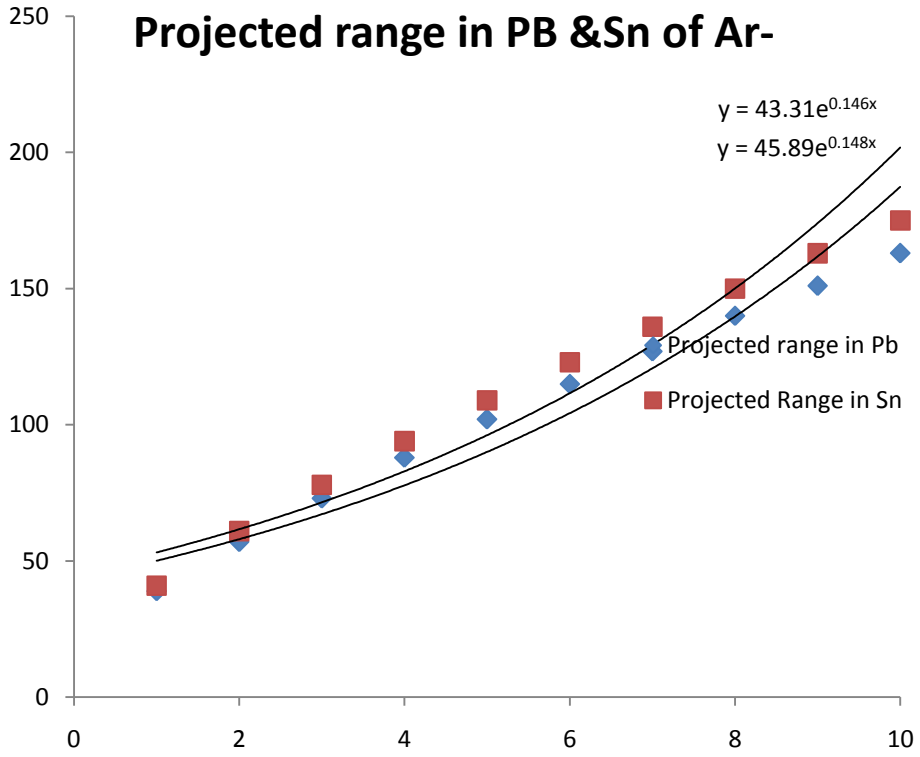

Figure 1: Projected range of Ar^+ ion in lead and tin perovskite targets for different ion energies from 1 keV to 10 keV.

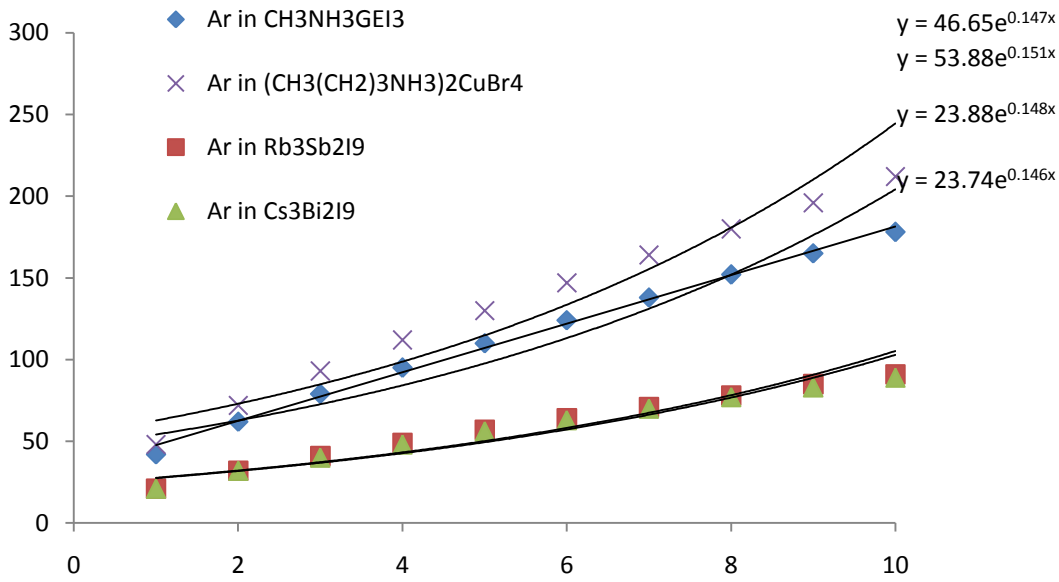

Figure 2: Projected range of Ar^+ ion in other selected perovskite targets for different ion energies from 1 keV to 10 keV.

4. Conclusion

Monte Carlo simulations of the ion beam sputtering of organo-metal halide perovskites which are potential substitutes for toxic lead perovskite has been done. These perovskites are tin perovskite $CH_3NH_3SnI_3$, Germanium perovskite $CH_3NH_3GeI_3$, $(CH_3(CH_2)_3NH_3)_2CuBr_4$, $Rb_3Sb_2I_9$ and $Cs_3Bi_2I_9$. Currently, there is a much lower PCE by these substitutes perovskites lead perovskite. However, an understanding of the physical factors that correspond to the efficiency of their solar cells would greatly impact increase in their efficiencies. Our analysis of the simulations performed here revealed an analytical form of connection between the solar cell efficiencies of the projected range and sputter yield in the perovskites which can be utilised in further studies.

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