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Projected Range and Sputter Yield of Ne^+ and Ar^+ in the Sputtering of Lead and Tin Perovskites

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Abstract. Metal halide perovskites have been the subject of intense theoretical and experimental research in recent years due to their huge potential over their silicon based counterparts for tunable optoelectronic applications in high-tech device innovation. The current best perovskite for solar cell applications, with a power conversion efficiency of 22%, methyl ammonium lead iodide ($\text{CH}_3\text{NH}_3\text{PbI}_3$), is toxic due to the presence of lead and is therefore harmful in solar cell applications despite its low concentration in solar cells. Hence, research exploits are geared towards perovskites without lead. Unfortunately, this has taken back the gains in PCEs by about 15%, and a lot is being done for improvement. In this paper, we performed molecular dynamics and Monte Carlo simulations of ion-beam sputtering of lead and tin perovskites to determine differences between the sputtering characteristics of lead perovskite and a lead-substituted perovskite (tin perovskite). Our results show that they both exhibit similar sputtering characteristics of linear projected ion range, and maximum yield around 78° ion incidence.

Keywords: Solar cells; Sputtering; Perovskites; Sputter yield; Range of ions.

1. Introduction

Lead halide perovskites have huge potential for applications in solution-based photovoltaics (e.g. solar cells) with greater power conversion efficiencies (PCEs) than silicon-based photovoltaics [1]. However, they suffer a large setback in these applications due to the toxicity of lead and its solubility in water. There has therefore been an intense research interest with promising results in recent years on non-toxic metal replacements [2 - 6]. One advantage of perovskite based photovoltaics over their silicon based counterparts is their low-cost fabrication due to the possibility of producing them in a variety of ways, including the use of vacuum techniques [7].

A vacuum processing and fabrication technique is ion-beam sputtering of materials, which is an area of current intensive research as a cost-effective method of surface analysis, processing and fabrication of self-organized nanostructures for optoelectronic applications [8 – 14]. A new radio-frequency-sputtering method of production of lead-iodide perovskite was proposed in Ref. 15. This



comprises of a deposition of thin films of lead sulphide, their conversion to perovskites by placement in an iodine atmosphere, and subsequent immersion into a solution of methyl ammonium (i.e. solution based). Whereas in Ref. 16, a non-solution based method of perovskite film fabrication by sputtering was proposed. They confirmed that sputter processed perovskite films showed similar characteristics as their solution-processed counterparts and produced perovskite solar cells with higher PCEs.

In a sputtering process, an incoming ion collides with an atom of the target material and sets off secondary collision cascades leading to kinetic and thermal agitations of the targets atoms. Noble gas ions are commonly used in sputtering experiments due to their inert nature and low reactivity with the sputtered targets. By virtue of the nature of the sputtering process and the need for kinetic details within the earliest impact times, molecular dynamics simulation can be exploited. A number of enquiries have taken this approach, focusing on specific sputtering conditions (e.g. [17- 20]). However, statistical collisional data is also required and this is obtained by statistical physics Monte Carlo simulations.

A molecular dynamics simulation suite developed by Ziegler and Biersack [21 – 23], Stopping and Range of Ions in Matter (SRIM), and its more extended counterpart, TRansport of Ions in Matter (TRIM), which includes SRIM and statistical simulation and calculation of some sputtering parameters with Monte Carlo techniques, are versatile tools in this regard [24]. They are reference and very popular simulation software packages with a large number of scientific citations to them every year [23]. Signatures of the ion-target interaction are the collision cascade parameters and sputter yield. These can be drastically changed by minute changes in the target composition. It is therefore of interest to know the effect of lead replacement on the sputter characteristics of metal halide perovskites. This has not yet been studied, to the knowledge of the authors of this article.

The most suitable material for this comparison is $\text{CH}_3\text{NH}_3\text{SnI}_3$ which is a metal halide perovskite with similar characteristics as $\text{CH}_3\text{NH}_3\text{PbI}_3$ but with a reportedly much lower PCE of 6.4% [2]. It, nonetheless, has the highest PCE among all the lead-substituted perovskites [7]. However, Sn or Pb are good occupants of the B-site of a perovskite ABX_3 structure, where the monovalent organic cation (e.g. methyl ammonium, CH_3NH_3^+) occupying the position A, or the halide counter-ion (e.g. iodine, I) occupying the X-site of the perovskite structure, can be changed to tune the properties of the perovskite.

In this paper, we studied the range and sputter yield of ions in $\text{CH}_3\text{NH}_3\text{PbI}_3$ (lead) and $\text{CH}_3\text{NH}_3\text{SnI}_3$ (tin) perovskites for different ion energies and incidence angles by molecular dynamics and Monte Carlo simulations using SRIM and TRIM. We used ions of inert gases Ne and Ar in the sputtering of these perovskites. The rest of the paper is organized as follows. In the next section we elaborate on the methods we have used to obtain our results. For reproducibility, we provide details of the simulation set-up on the SRIM and TRIM graphical user interface and the values used for all other parameters. We present and discuss our results in section 3, and provide our conclusions in section 4.

2. Methodology

In this section we provide the specific details of our simulation. Details of the theoretical background for the calculations and simulation algorithms embedded in the TRIM and SRIM packages are discussed in the papers by Ziegler and Biersack [21, 25]. SRIM was used to perform molecular dynamics simulations of the range of inert gas ions Ne^+ and Ar^+ , with energies varied from 1 keV to 10 keV, at normal incidence on the two targets, namely, lead perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$ and tin perovskite $\text{CH}_3\text{NH}_3\text{SnI}_3$. While TRIM was used to perform molecular dynamics and Monte Carlo simulations for the number of each component of the perovskites yielded as a result of bombardment of the perovskite by an incident ion, for varied incidence angles from 0° to 89° , and for ion energies 1 keV and 5 keV.

In both SRIM and TRIM set-ups we used perovskite wafer thickness of 35 nm, and built up the lead perovskite from its composites in the stoichiometric ratio 1:3:1:3:1:3 for C, H, N, H, Pb/Sn, I,

respectively, and densities 4.16g/cm^3 [26] and 3.51g/cm^3 [27] for the lead and tin perovskites, respectively. We also used 1000 ions for each simulation. A detailed calculation with full damage cascade was performed for each simulation (i.e. each complete run of TRIM or SRIM for a particular set-up).

3. Results and discussion

The results of our simulations are presented and discussed in this section. We observed the same trends for the two ions (Ne^+ and Ar^+), though with higher values for Ar^+ , and therefore present the results for only Ne ion here. Figure 1 shows the results of the projected range of the ions in the perovskites for different ion energies varied from 1 keV to 10 keV. These exhibitions of almost the same values of the linear range of the ions for the different perovskites indicate that the two materials are remarkably similar as regards their stopping power to energetic particle irradiation.

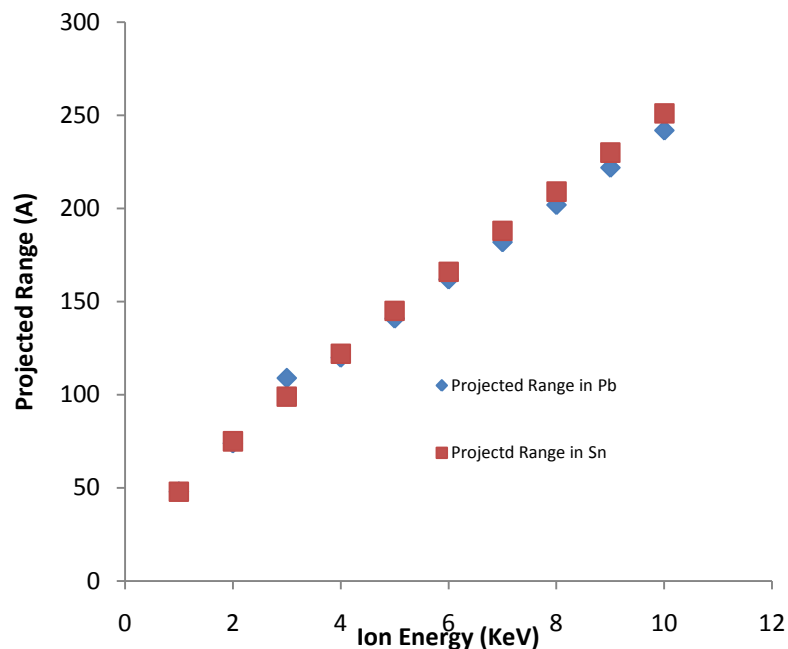


Figure 1: Projected range of Ne^+ ion lead (diamond symbol) and tin (square) perovskite targets for differentiation energies from 1 keV to 10 keV.

Sputter yield results are presented in the figures that follow, one for each element in the perovskite, namely, C, H^1 (H of the methyl molecule), N, H^2 (H of the ammonium molecule), Pb/Sn, I. Figure 2 shows the result for the number of C atoms ejected per incident Ne^+ ion on the lead and tin perovskites at different angles of incidence varied from 0° to 89° , and for Ne^+ energy of 1 keV and 5 keV. The same variables apply to Figs. 3 – 7, but for the other elements, respectively. For all results the yield is expectedly higher for higher ion energy, and a maximum yield occurs at the same $\theta \sim 78^\circ$ for both energies. Also, for 5 keV the yield obtained from the sputtering of tin perovskite is lower than that of the sputtering of lead perovskite for normal incidence, and then increases with angle of incidence, relative to the yield on lead perovskite, until it becomes higher around the angle of incidence at which maximum yield occurs.

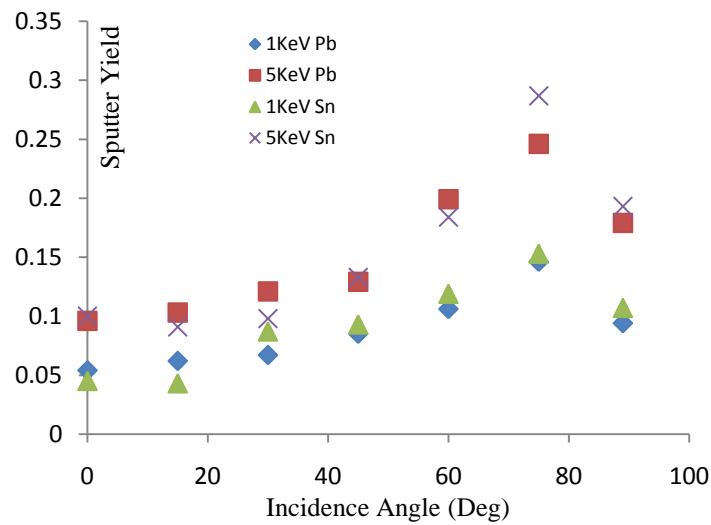


Figure 2: Sputter yield (C atoms/ion) for the ejection of C atoms from Ne^+ bombardment of the perovskites at different angles of incidence and ion energy 1 keV and 5 keV.

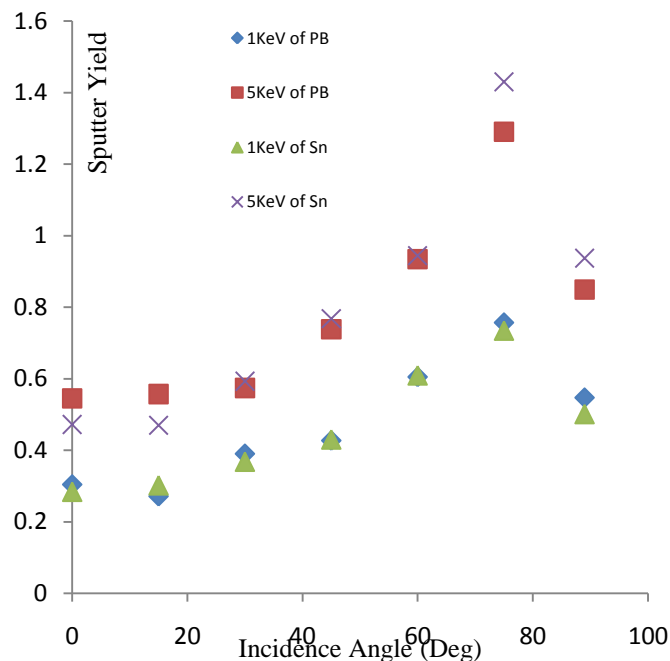


Figure 3: Sputter yield (H^1 atoms/ion) for the sputter erosion of H atoms of the methyl molecule from Ne^+ bombardment of the perovskites at different angles of incidence and ion energy 1 keV and 5 keV.

However, for N erosion of Fig. 4, a first instance of the higher value of the sputter yield of the ion on Sn perovskite occurs at a lower angle of about 45° and then a second instance at the angle for maximum yield. Though, this could be a mere statistical fluctuation, it is noteworthy as it is exhibited in the H^1 result of Fig. 3. Note that in Fig. 6 only two sets of data are available for each (Pb or Sn) since Pb is not available in tin perovskite or vice versa. The values of I atom yields are the highest Fig. 7, followed by H atom, Pb/Sn atom, N atom, and the lowest yields are those of the C atom.

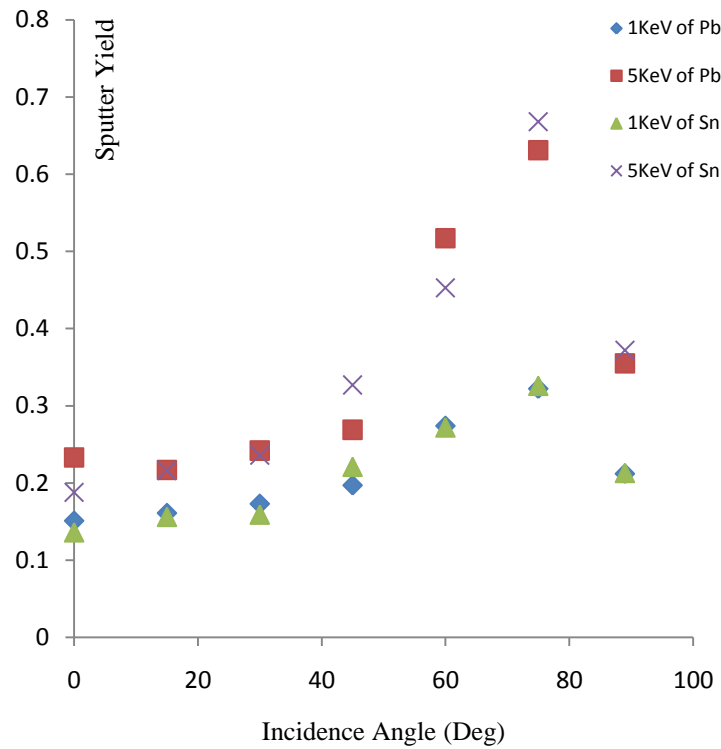


Figure 4: Sputter yield (N atoms/ion) for the erosion of N atoms from Ne^+ bombardment of the perovskites at different angles of incidence and ion energy 1 keV and 5 keV.

The two H atom yields are similar, with the yield of H^1 being slightly higher (about 1.4) than that of H^2 (about 1.3).

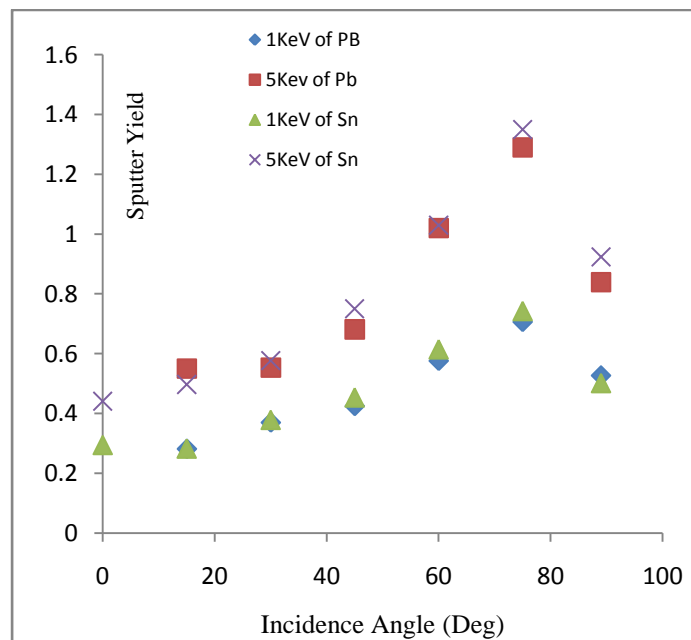


Figure 5: Sputter yield (H^2 atoms/ion) for the ejection of H atoms of the ammonium molecule from Ne^+ bombardment of the perovskites at different angles of incidence and ion energy 1 keV and 5 keV.

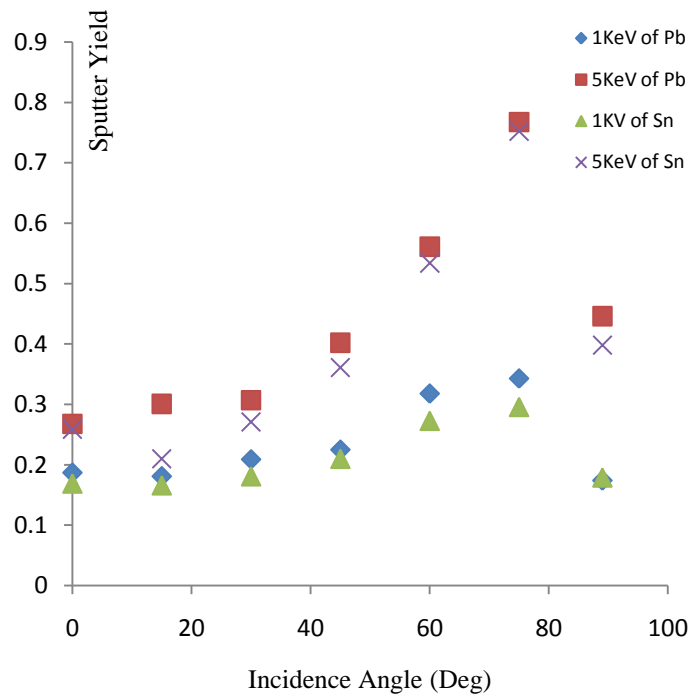


Figure 6: Sputter yield (Pb/Sn atoms/ion) for the erosion of Pb/Sn atoms from Ne^+ bombardment of the perovskites at different angles of incidence and ion energy 1 keV and 5 keV.

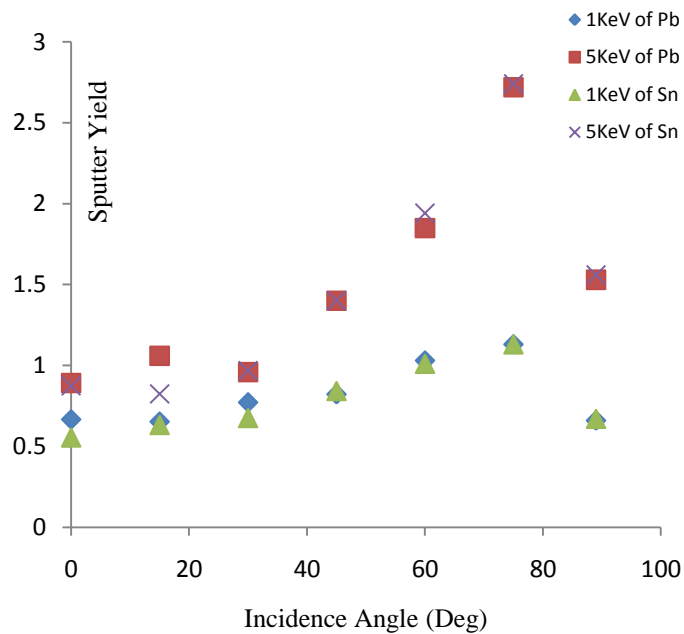


Figure 7: Sputter yield (atoms/ion) for the erosion of I atoms from Ne^+ bombardment of the perovskites at different angles of incidence and ion energy 1 keV and 5 keV.

4. Conclusion

We performed molecular dynamics and Monte Carlo simulations of the ion sputtering of methyl ammonium lead iodide (lead perovskite) and its lead-substituted counterpart, methyl ammonium tin iodide (tin perovskite), as a new perspective of understanding and improving upon the desired physical properties of safer perovskite materials that are based on the possible substitutes for lead.

Currently, these substitutes give perovskites with a much lower PCE than lead perovskite. In our studies, reported in this paper, we found the sputtering results of lead perovskite and its best substitute so far, tin perovskite, to be very similar. In fact, so similar as to serve as another reason why the quest to improve upon the properties of tin perovskites, towards the desired better PCE in tin halide perovskite based solar cell applications, should not be abandoned despite its current very poor PCE.

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