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Calculation of Ion Irradiation Damage for Defective Tin Oxyhydroxide

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1. Introduction

Metal oxyhydroxides have similar material properties to metal oxides or hydroxides but generally have a layered structure. They are widely used in various electrochemical applications, for example, catalysts, supercapacitors, semiconductors, and secondary batteries, due to their unique structural stability, interlayer conductivity, multiple redox states, electrocatalytic activity, and electrochemical properties [1,2].

In particular, it has been reported that when crystal defects are properly present in metal oxyhydroxides, their electrochemical activity can be greatly enhanced to exhibit better performance [3]. To create defects in materials, there are methods such as hydrogen annealing, plasma treatment, flame treatment, and laser ablation, which are mostly high-temperature or high-pressure processes, as well as time-consuming and inefficient.

Diverse defects can also be generated by irradiating the target material with ions. Ion irradiation can not only achieve a high density of defects compared with other methods but also has a relatively short process time and is employed at room temperature. Additionally, it is versatile because the incident ion source can be easily altered.

In this study, we calculated ion irradiation damages (displacement per atom, dpa) to form defects in the metal oxyhydroxide using the Stopping Range of Ions in Matter (SRIM) code. SRIM code is an intuitive tool that can simulate the transport of ions in a matter. The matter selected was tin oxyhydroxide, which is a very promising material due to its electrochemical superiority and environmental benignity. The incident ions were adopted as ions of inert gases to focus on vacancies among various types of defects. We try to derive the optimal conditions for generating significant vacancies in tin oxyhydroxide after calculations.

2. Method

2.1 Irradiation Information

$Sn_6O_4(OH)_4$ (density: 4.902 g/cm^3) was chosen as the tin oxyhydroxide medium, and the incident ions were determined to be helium, neon, argon, krypton, and xenon ions. The direction in which the ions were incident was perpendicular to the medium, and the energy was set to various values as appropriate for each ion as a monoenergy. Before the ions are incident on the $Sn_6O_4(OH)_4$ matter, they first collide with the 10 μm thin polyethylene (PE) film (density: 0.93 g/cm^3) surrounding the $Sn_6O_4(OH)_4$.

2.2 SRIM Simulation

The simulation was performed using the SRIM-2008 code developed by James F. Ziegler. For Layer 1, “Polyethylene” was selected from the “Compound Dictionary” tab, and for Layer 2, H, O, and Sn were input and then assigned an atomic ratio of 4:8:6. The displacement damage of H, C, O, and Sn was set to 10, 28, 28, and 25, respectively. The depths of the two layers were designed to be 10 and 100 μm, respectively. The total number of ions was input as 10000 to identify the approximate distribution. “Ion Distribution and Quick Calculation of Damage” and “Ion Distribution with Recoils projected on Y-Plane” were selected as the damage type and basic plots respectively. The angle of incidence was set to 0. As output files, ion ranges, backscattered ions, and transmitted ions/recoils were adopted. The damage (dpa/fluence) was calculated as in Eq. 1 [4].

$$\frac{dpa}{fluence} = \frac{total\ vacancies}{atom\ density} \quad (1)$$

where, total vacancies are the sum of vacancies by ions and vacancies by recoils in the unit of vacancies/cm·ions, atom density is the number of atoms present in a unit volume of a matter in the unit of atoms/cm^3. Therefore, the unit of dpa/fluence is cm^2/ions.

3. Results and Discussion

A concise illustration depicting the irradiation of tin oxyhydroxide with ions is presented in Fig. 1. It is essential that minimum damage should take place in the PE layer and much damage should be induced in the tin oxyhydroxide layer. First, when He ions of 5 MeV energy are incident on the matter, little damage occurs in the PE layer as shown in Fig. 2. However, as soon as it reaches the tin oxyhydroxide layer, it reacts with atoms in the matter, and the energy of the He ions is lost, resulting in displacement. As the ions progress deeper, the energy loss increases exponentially, showing a maximum dpa at about 24 μm. Also, the range of the ion increases as the energy becomes high and is 57 and 102 μm at 10 and 15 MeV, respectively. Nevertheless, it is difficult to achieve even damage distribution in tin oxyhydroxide due to the presence of the Bragg peak, and a fluence of at least 1.00×10^{17} ions/cm^2 is required to obtain a reasonable dpa of 1 to generate a large number of defects [5].

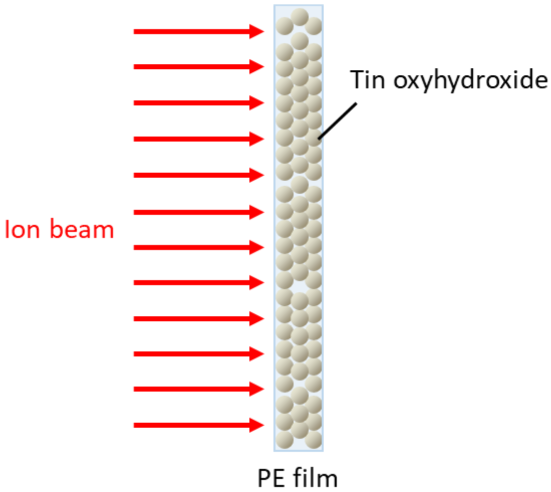

Fig. 1. Simple illustration depicting ion irradiation on tin oxyhydroxide.

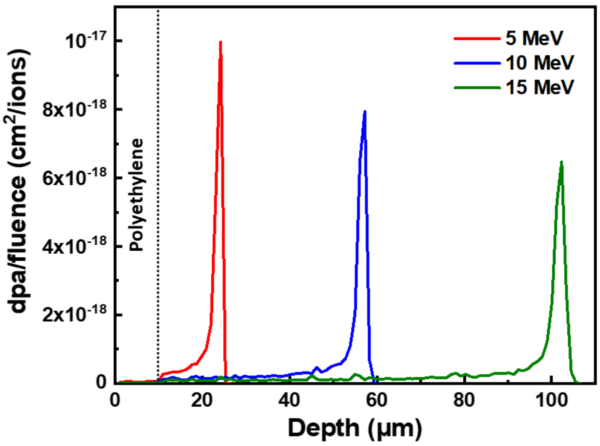

Fig. 2. Damage distribution calculated using SRIM code for tin oxyhydroxide irradiated by He ions.

Ne ions were irradiated onto tin oxyhydroxide to attain higher damage. Fig. 3 shows the dpa profile of tin oxyhydroxide by Ne ions. Higher energy is required to pass through the PE layer than for He ions. A significant dpa was calculated on the tin oxyhydroxide surface due to the short range of ~13 μm when the Ne ion energy was 20 MeV. In the case of 40 MeV, the range was about 21 μm, and dpa/fluence of 2.26×10^{-16} cm^2/ions was obtained. At higher energy of 60 MeV, the range increased to about 30 μm, but the maximum dpa decreased. The calculated fluence at 40 MeV to obtain 1 dpa is about 4.42×10^{15} ions/cm^2, which is 22.6 times less than when using He ions. As in the case of the He ion, prominent Bragg peaks can be observed.

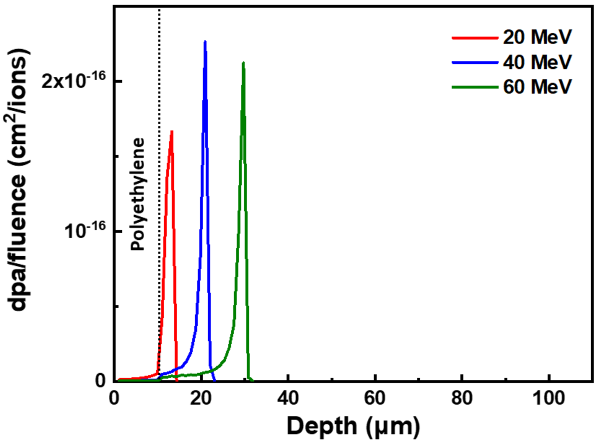

Fig. 3. Damage distribution calculated using SRIM code for tin oxyhydroxide irradiated by Ne ions.

The effect of heavier ions is also shown in Fig. 4. All ions were incident on the medium with an energy of 50 MeV. There is almost no damage to the PE layer in Ar ion irradiation, but slight damages are seen in Kr and Xe ion irradiation. Therefore, it implies that Kr and Xe ion irradiation is not very effective. The range of the three types of ions is 15, 13, and 12 μm, respectively, indicating that most reactions take place on the surface of tin oxyhydroxide. The damage through Ar ion irradiation was calculated to be about 5.48×10^{-16} cm^2/ions, and a considerably higher defect creation than He and Ne ions can be expected from the surface to a depth of about 18 μm. The minimum fluence for 1 dpa of Ar ion irradiation is obtained as approximately 1.82×10^{15} ions/cm^2.

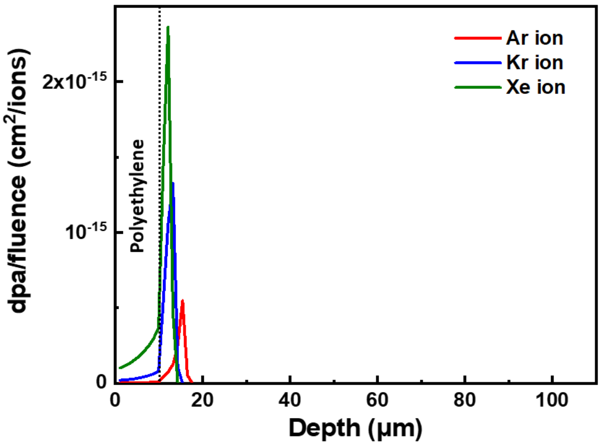

Fig. 4. Damage distribution calculated using SRIM code for tin oxyhydroxide irradiated by 50 MeV Ar, Kr, and Xe ions.

Accordingly, two cases can be considered for creating defects in tin oxyhydroxide. The first is to irradiate about 50 MeV of He ions to the constructed tin oxyhydroxide with a thickness of about 20 μm. This makes it easier to prepare the tin oxyhydroxide sample for ion irradiation, but it is relatively limited in giving uniform damage in the depth direction. The next one is to use Ar ions of about 50 MeV as well, but this approach has a difficulty in preparing tin oxyhydroxide within about 8 μm. Nevertheless, it is clear that, if prepared, it can induce considerable defects in the overall region.

4. Conclusions

The damage of tin oxyhydroxide by inert gas ion irradiation was investigated using SRIM simulation. A significant level of fluence was required to generate sufficient defects for He ion irradiation. In the case of Ne ion, high dpa could be achieved within about 18 μm, but there was an inconvenience of having to prepare a thin tin oxyhydroxide. When 50 MeV heavier ions were used, a high degree of damage was observed on the surface of tin oxyhydroxide, and impairment of the PE film, which serves to fix the sample, also occurred. Consequently, defective tin oxyhydroxide can be obtained by distributing tin oxyhydroxide very thinly and irradiating 50 MeV Ne or Ar ions at a fluence level of around 10^{15} ions/cm^2.

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