

Ion beam-induced Surface Modification of PVC: A simulation Study

Hawzhin T. Ahmed¹ Salah R. Saeed² Omed Gh. Abdullah²

¹ Department of General Science, College of Education and Language, Charmo University, Chamchamal, Sulaimani, Kurdistan Region, 46023, Iraq

² Advanced Materials Research Lab., Department of Physics, College of Science, University of Sulaimani, Kurdistan Region, 46001, Iraq

^{*}Corresponding Author E-mail: <u>hawzhin.taha@charmouniversity.org</u>

ARTICLE INF.

Article history: Received: 4 AUG., 2023 Revised: 26 NOV., 2023 Accepted: 28 NOV., 2023 Available Online: 28 DEC. 2023

Keywords:

Polymer TRIM Recoil Atom Stopping power Sputtering

A B S T R A C T

The investigation of PVC surface characteristics involved the utilization of Monte Carlo simulation software, TRIM, to replicate the interaction between ion beams and the PVC surface. TRIM is a widely employed tool for examining surface structure. The analysis centered on the interactions between PVC surfaces and ions of hydrogen, helium, argon, and krypton. The ion beam irradiation was carried out at varying angles 0°, 15°, 30°, 45°, 60°, and 75° relative to the sample's surface normal, and it encompassed two distinct incident ion energies 1 keV and 1 MeV. The interplay between ions and the PVC surface can result in diverse processes, including sputtering, emission, and ionization, contingent upon the mass, incident energy, and angle of incidence of the ions. The calculation of stopping power (both nuclear and electronic) and the range of projectiles can also be determined using the same set of incident ions (H, He, Ar, and Kr) but within different energy spectrums (from 10 eV to 10 MeV). The stopping range is contingent on the incident energy and mass of each incident ion, a crucial factor in the process of implantation. This procedure finds applications in doping semiconductors or other materials, with potential uses in catalysis, gas sensing, and various chemical applications.

DOI: https://doi.org/10.31257/2018/JKP/2023/v15.i02.13046

تعديل سطح بولي كلوريد الفينيل بفعل شعاع الأيون: دراسة محاكاة

ئوميد غريب عبدالله

صلاح رضا سعيد `

هاوزين طه احمد

خلاصة

لا قسم العلوم العامة، كلية التربية واللغات، جامعة جرموو. لا قسم الفيزياء، كلية العلوم، جامعة السليمانية.

الكلمات المفتاحية:

وليمر TRIM ذرة اندفاع قدرة الأيقاف تضمن هذه الدراسة فحص في خصائص سطح بولي كلوريد الفينيل (PVC) باستخدام برمجيات المحاكاة مونت كارلو، TRIM، لتكرار التفاعل بين شعاع الأيون وسطح بولي كلوريد الفينيل. يعتبر TRIM أداة الترذيذ

مستخدمة على نطاق واسع لفحص هيكل السطح. تمحور التحليل حول التفاعلات بين سطوح بولي كلوريد الفينيل وأيونات الهيدروجين والهيليوم والأرجون والكربتون. تم إجراء تشعيع شعاع الأيون بزوايا متغيرة (0°، 15°، 30°، 45°، 60°، و 75°) بالنسبة للسطح العينة، وشمل طاقتين مختلفتين للأيونات الواردة (1 كيلو إلكترون فولت و1 ميجا إلكترون فولت). يمكن أن يؤدي التفاعل بين الأيونات وسطح بولي كلوريد الفينيل إلى عمليات متنوعة، بما في ذلك الاخرق، والانبعاث، والتأين، اعتمادًا على كتلة الأيون، وطاقته الساقطة، وزاوية سقوط الأيونات. يمكن أيضًا تحديد حساب قوة التوقف (النووية والإلكترونية) ونطاق المشروعات باستخدام نفس مجموعة الأيونات الساقطة الهيدروجين والهيليوم والأرجون والكربتون ولكن في طيف طاقة مختلف (من 10 إلكترون فولت إلى 10 ميجا إلكترون فولت). يعتمد نطاق التوقف على الطاقة الواردة وكتلة كل أيون وارد، وهو عامل حاسم في عملية الزرع. تجد هذه الإجراءات تطبيقات في تطعيم أشباه الموصلات أو غيرها من المواد، مع استخدامات محتملة في عمليات التحفيز، واستشعار التوقف على الطاقة الواردة وكتلة مختلف (من 10 الكترون فولت إلى 10 ميجا إلكترون فولت). يعتمد نطاق التوقف على الطاقة الواردة وكتلة مختلف (من 10 الكترون فولت إلى 10 ميجا إلكترون فولت). يعتمد نطاق التوقف على الطاقة الواردة وكتلة مختلف من مامواد، مع المات الماقطة الهيدروجين والهيليوم والأرجون والكربتون ولكن في طيف طاقة مختلف من المواد، مع عامل حاسم في عملية الزرع. تجد هذه الإجراءات تطبيقات في تطعيم أشباه الموصلات منوعيرها من المواد، مع استخدامات محتملة في عمليات التحفيز، واستشعار الغاز، وتطبيقات كيميائية

1. Introduction

Recent applications in materials science involve simulations computer to investigate the deceleration and deflection of high-energy ions within materials. These simulations have been valuable in the examination of ion implantation, radiation-induced damage. sputtering phenomena, ion reflection, and ion transmission. The Monte Carlo method stands out as a potent technique, numerous simulation offering advantages compared to conventional analytical methods [1]. Notably, it excels in considering surface and interface phenomena, aspects often overlooked conventional analytical by techniques. Moreover, it enables precise modeling of elastic scattering events, a crucial factor in numerous practical applications. Additionally, the Monte Carlo method readily provides insights into the energy and angular distribution of particles, facilitating various research endeavors [2].

Advanced microelectronic manufacturing relies on the utilization of process simulation software to anticipate the results of diverse procedures, including oxide laver development, ion implantation characteristics, photoresist etching exposure, and surface features.

Numerous process simulation applications exist, yet their effectiveness hinges on a thorough comprehension of the fundamental physical phenomena inherent to these procedures [3]. Furthermore, the inspiration behind this research stems from the noteworthy observation that ion bombardment can induce beam profound alterations in the surface characteristics of PVC. To emulate this process, the Monte Carlo method, specifically the 'Transport of Ions in Matter' (TRIM), was employed. It's worth noting that TRIM is a constituent module within a suite of programs known as 'Stopping and Range of Ions in Matter' (SRIM), a creation attributed to Ziegler et.al. [4].

PVC ranks as the second most extensively utilized polymer in terms of worldwide consumption, boasting annual global an production exceeding 25 million tons. Its primary application lies within the medical sector, where it constitutes approximately 28% of the total plastic consumption [5]. PVC belongs to the category of thermoplastic materials, which implies that it can be softened through heating and subsequently molded into various exhibits configurations. Furthermore, it remarkable resistance to both oxidation and degradation. The composition of PVC consists of 57% chlorine, obtained from industrial salt, and 43% carbon, sourced from oil or gas via ethylene production. Notably, its production is less reliant on crude oil when compared to other polymers, thanks to chlorine being considered a naturally occurring resource. Nonetheless, PVC encounters certain challenges owing to the hydrophobic nature of its polymer surface. Chemical structure of PVC (C_2H_3Cl) is illustrated in Figure 1 [6].



Figure 1: The chemical structure of the PVC molecule.

PVC has found extensive applications in various fields, including coatings, adhesives, composite materials, biomaterials, medical devices, microelectronics, and thin-film technology. However, PVC does face challenges related to biocompatibility, undesired poor protein adsorption, and bacterial attachment [7]. To mitigate these issues, various approaches have been employed. Particularly noteworthy are strategies centered on surface modification, which has seen significant advancements over the past three decades [8]. These advancements aim to enhance surface properties and reduce plasticizer migration [6]. It's worth noting that vinyl is an environmentally sustainable product that offers energy efficiency, cost-effectiveness, flexibility, and practicality [9]. When employing ion beams for surface alteration of a polymer, two concurrent processes take place: polymer ablation and modification. Polymer ablation occurs as ions displace atoms from the polymer surface, resulting in the formation of smaller, readily desorbable molecules, a phenomenon known as sputtering. Simultaneously, polymer modification transpires as ions generate free radicals within the polymer surface [10]. These free radicals subsequently partake in various reactions. thereby altering the chemical composition of the polymer surface. Distinguishing the precise demarcation between these two processes poses a challenge since the treated surface undergoes gradual sputtering [2,11-12].

Conversely, ions also penetrate beyond the surface layer, instigating altered further transformations. During the ion bombardment of polymers, a pivotal phenomenon revolves around the energy transfer from incoming ions to the target material. The energy dissipated by an ion as it traverses through a substance is defined by the ion's energy loss per unit distance $\left(\frac{dE}{dx}\right)$, which is contingent upon the ion's velocity. These energy dissipation mechanisms are categorized into two primary types: nuclear-stopping power and electronic-stopping power. Additionally, crucial parameters include ion penetration depths and, consequently, the distribution of damage attributed to sputtering. This process induces ionphonon interactions and creates vacancies, both

of which can be most readily ascertained through the utilization of the (TRIM) method [13-16].

2. Ion-Polymer Interaction:

When high-energy ions interact with solid materials, they can induce a range of physical and chemical transformations. In polymers, ion irradiation can lead to irreversible alterations, notably main-chain scission, which entails the breaking of the polymer molecule's primary chain. This process can result in the formation of smaller molecular weight compounds and a subsequent decline in mechanical properties. Moreover, ion irradiation can generate lightweight molecules, some of which may be released or sputtered from the polymer's surface. Additionally, ion irradiation can give rise to secondary electrons, photons, vacancies, and free radicals. These free radicals can engage in various reactions, thereby altering the chemical composition of the polymer surface, as depicted in Figure 2. In cases where there is no external source of reactive elements and a higher concentration of primary radicals exists, the polymeric bonds that are cleaved during the scission process may have the opportunity to react with each other, initiating processes such as cross-linking, branching, or the creation of double bonds. In such instances, the molecular weight of the polymer increases [17-19].



Figure 2: Schematic diagram of the ion-solid surface interactions [20].

When polymers are exposed to radiation, two distinct processes can transpire ion-induced chain scission and cross-linking. Chain scission entails the fracture of the primary polymer molecule's main chain, while cross-linking involves the establishment of bonds between adjacent polymer chains. Both of these processes have the potential to bring about permanent modifications in the polymer and its mechanical properties. If chain scission predominates, the polymer will eventually deteriorate, leading to the failure of the irradiated layer. Conversely, if cross-linking prevails, adhesion failure can transpire between the strongly cross-linked regions of the polymer and the underlying, unirradiated polymer. In cases where polymers are irradiated with oxygen or nitrogen ions, the free radicals generated react with reactive species, promoting the formation of carbon-oxygen and/or carbon-nitrogen functional groups [17,19].

Furthermore, in our current study involving PVC as the target material, the response to the ion beam is notably influenced by various factors. These factors encompass the beam current, incident ion energy, the geometry of trenches or features, the raster pattern, the milling angle, and the structural configuration of the target material, whether it is amorphous or crystalline [20,21]. Notably, the crystalline structure of the target material has a substantial impact on the stopping power and, consequently, on the range profiles, differentiating them from each other [22,23]. In the case of an amorphous structure, atoms are arranged randomly without any preferred direction. This implies that the ion's stopping power remains independent of the direction of ion movement. Consequently, the range profile of ions exhibits symmetry and follows a Gaussian distribution, with its peak at the mean range [22]. Interactions between the incident ions and the solid material result in a loss of the ion's initial kinetic energy. A small fraction of these ions are backscattered to the target surface through collisions, and these backscattered particles can consist of positive ions, negative ions, and neutral atoms. Consequently, if an ion is not backscattered from the target surface, it ultimately comes to rest, becoming implanted within the target material at a specific depth beneath the specimen surface, denoted as Rp, as depicted in Figure 2 [20].

When ions impinge upon the surface of a target material, they instigate a variety of alterations, including the creation of vacancies and interstitials, adjustments in stoichiometry, the release of electrons (commonly referred to as secondary electrons), and the emission of photons. However, the predominant portion of incident ions that penetrate the surface undergo deceleration through interactions with the atoms and electrons residing beneath the surface of the target material. The energy imparted to these target atoms can set in motion a collision cascade, potentially resulting in the expulsion of surface atoms or clusters of target atoms, a phenomenon known as sputtering [21,24].

3. Computer Simulation Method:

The Binary Collision Approximation (BCA) is a computational method employed for modeling the trajectories of particles within a solid material. In BCA, the interactions between these particles and the atoms within the solid are simplified into a sequence of independent binary collisions. This approximation employs the universal Biersack-Ziegler-Littmark (BZL) potential to describe the interaction potential between the incoming projectile and the atoms within the material. The cumulative elastic and inelastic energy losses of the particles are tracked along their respective paths [25]. Sputtering phenomena have been simulated, with the angle of incidence of primary ions measured from the surface of the target. Both the incoming ions and the recoiling atoms are meticulously monitored throughout their process of deceleration, wherein their energy gradually diminishes.

In this research, we employed the TRIM program to investigate the sputtering process that takes place when a rigid PVC surface is subjected to bombardment by various incident ions (H, He, Ar, Kr). Our simulations encompassed the bombardment of 10,000 ions across a range of energy levels (1 keV to 1 MeV) and incident angles (0° to 75°). The objective was to ascertain how these parameters influence the generation of backscattered atoms (sputtering), secondary electron emission, the formation of vacancies, and the emission of photons resulting from ion interactions. We also assessed the nuclear and electronic stopping power of each incident ion upon interaction with the PVC surface.

In the context of our sputtering analysis, our primary focus was on sputtering and the quantity of vacancies produced by each incident ion at varying angles. Sputtering transpires when an incident ion is deflected out of the target material, either directly or through a sequence of collisions. This phenomenon bears a resemblance to backscattering observed in electron-solid interactions. As depicted in Figure 3, the sputtering yield of the incident ion escalates with the angle of incidence. In addition, we conducted a comparative analysis of the sputtering yields for hydrogen (H) and krypton (Kr) ions. The findings revealed a direct correlation between the sputtering yield and two key factors: the mass ratio of the incident ion to the target atom (M_2/M_1) and the incident ion energy [20]. Essentially, this implies that the higher the mass of the incident ion and its energy level, the greater the likelihood of ejecting an atom from the surface. As illustrated in Figure 3, it becomes evident that the sputtering yield of Kr and H ions is lower when the incident energy is 1 MeV and the incident angle is 75° (resulting in 744-3 particles sputtered) compared to the conditions of an incident energy of 1 keV and an incident angle of 75° (resulting in 2014-3966 particles sputtered). This indicates that the sputtering yield is contingent on the incident angle. The substantial mass and energy possessed by Kr ions lead them to interact with the PVC surface atoms, causing them to become entrapped or accumulate within the solid. This phenomenon is known as ion implantation and is extensively employed for modifying material properties, including conductivity and hardness. In the context of semiconductor materials, ion implantation serves to 'dope' the material, signifying the introduction of impurities to alter its electrical characteristics. This technique is commonly employed in the manufacturing of integrated circuits.



Figure 3: The TRIM calculations showing sputtering yield for H and Kr on the PVC as a function of incidence angle at 1 keV and 1 MeV.

When a particle attempts to undergo sputtering, it diminishes the likelihood of successful transmission. This is due to the sputtering process removing surface atoms, creating defects that can impede the penetration of subsequent ions. As depicted in Figure 4, when low-energy H and Kr ions (in the keV range) traverse through the PVC target, a significant portion of the incident ions backscatter, and no transmitted ions are observed. This outcome arises because low-energy ions lack the necessary energy to penetrate the PVC surface effectively. However, when high-energy H and Kr ions (in the MeV range) traverse through the PVC target, a substantial portion of the H ions are transmitted, regardless of the incident angle. This is because H ions possess lower mass and, consequently, lower momentum compared to Kr ions. The different incident angles have a limited impact on H ions. On the contrary, Kr ions are more prone to backscatter at higher incident angles. This is due to the elevated incident angles imparting greater momentum to the Kr ions, making them more susceptible to interactions with PVC atoms. The transmission of Kr ions demonstrates an inverse relationship with the incident angle.



Figure 4: The TRIM calculation for H and Kr ions transmission at 1 keV and 1 MeV.

Another crucial parameter that can be computed using the TRIM program is the number of vacancies. When an incident ion interacts with a solid, there is a probability of creating vacancies and interstitials. This probability is contingent on several factors, including the type of incident ion (mass of the ion bombardment), incident energy, and the properties of the target material, as elucidated in Table 1. From the data presented in Table, it becomes evident that an increase in the mass of the incident ion and the incident ion's energy leads to the formation of a larger quantity of vacancies. This trend is observed because H ions, due to their lower energy, do not induce significant distortion within the material, resulting in fewer vacancies compared to Kr ions.

Ion Angle	Vacancies by	Vacancies by H	Vacancies by	Vacancies by
in degrees	H in kev	in Mev	Kr in kev	Kr in Mev
0	3.8	0.2	12	5390.8
15	3.9	0.2	12	5545.4
30	3.8	0.3	12	5935
45	3.7	0.4	12	6227.2
60	3.4	0.4	12	6271.7

Table 1 The TRIM measurement vacancies by H and Kr in 1 keV and 1 MeV.

75 2.9 0.6 11.8 6126.8

When a high-energy incident ion collides with the solid surface of PVC, it engages in interactions with the surface atoms, resulting in energy loss through processes such as ionization, vacancy formation, and photon emission. The TRIM program is capable of accurately quantifying these parameters, as illustrated in Figure 5. For ions like H, He, Ar, and Kr with 1 MeV energy, a significant portion of their energy loss occurs through ionization as they traverse the absorbing material. This ionization leads to the loss of energy by the incident ion, which is subsequently transferred to the material in the form of phonons and vacancies. The percentage of energy loss decreases with the increase in mass of the incident ion, particularly for H and He, where nearly 99% of their energy loss occurs

directly through collision, without the formation of vacancies and phonons. This implies that H and He ions lack the necessary energy and ability to create vacancies and phonons, instead predominantly transferring their energy to the PVC surface atoms through ionization. In contrast, for Ar and Kr ions, the energy loss decreases to 67% and 30%, respectively, indicating that they possess sufficient energy to undergo collisions, form vacancies, and generate phonons (0.37% and 0.41% for Ar and Kr, respectively, at 1 MeV). This leads to localized heating, a phenomenon that can find applications in specific surface treatment processes. Ion radiation is widely employed for purposes such as ion implantation in the top surface layer or the deposition of coatings [26].



Figure 5: The different percent energy loss for the incident H, He, Ar, and Kr ions with 1 MeV calculated by TRIM.

4. Slowing Down of Ions in Materials (Stopping Power):

When an ion is implanted into a target material, it undergoes collisions with the target's atoms, resulting in the gradual dissipation of its energy. This process continues until the ion reaches a specific depth within the material, referred to as the projected range (R_p) , as depicted in Figure 6. The factors governing the loss of the ion's energy throughout its penetration depth are collectively known as the stopping power $\left(\frac{dE}{dx}\right)$, which represents the energy lost per unit length as a charged particle traverses through a medium. Stopping power can be categorized into two components: nuclear stopping power and electronic stopping power. Consequently, the overall stopping power (S), often referred to as the slowing-down force, can be expressed

mathematically as presented in Equation (1) [4,27].

$$S = \left(\frac{dE}{dx}\right)$$
$$= \left(\frac{dE}{dx}\right)_{nuclear}$$
$$+ \left(\frac{dE}{dx}\right)_{electronic}$$
(1)

The theory regarding the deceleration of ions can be traced back to Niels Bohr's groundbreaking paper published in 1913 [28]. Since that time, there has been a continuous evolution of stopping theories spanning nearly a century, aided by advancements in microelectronics and techniques for atomic-scale analysis [29].



Figure 6: Illustration of the slowing down of a single ion in solid material.

The investigation of stopping power holds significant importance as it enables the prediction of range profiles for ions implanted within materials and facilitates the determination of absolute depth scales. Furthermore, techniques like Rutherford Backscattering Spectrometry (RBS) and Elastic Recoil Detection Analysis (ERDA) find utility in the analysis of target structures [29].



Figure 7: A schematic of the behavior of the nuclear and electronic stopping as a function of

particle energy.



Figure 8: The TRIM result to calculate the nuclear-stopping power for Ar and Kr.

4.1 Nuclear Stopping Power $\left(\frac{dE}{dx}\right)_n$:

In the context of nuclear stopping, the energy loss experienced by a moving ion primarily arises from its elastic collisions with the nuclei of the target material. This mechanism is

predominantly applicable to ions with low velocities. The energy lost by the incident ion during these interactions is converted into heat within the decelerating material, as atoms disperse kinetic energy through a sequence of collisions, known as collision cascades. A common characteristic shared by all ions is that nuclear stopping, in relation to ion energy, exhibits a peak at relatively low energies, typically around 1 keV/amu. Additionally, nuclear stopping diminishes as the energy of the ion increases [29].

4.2 Electronic Stopping Power $\left(\frac{dE}{dx}\right)_e$:

Electronic stopping power is a commonly used term that encompasses the energy loss attributed to all electronic processes. It involves the deceleration of incident ions due to inelastic collisions occurring between the bound electrons of the target atoms and the passing ions. This phenomenon originates from various contributions, depending on the nature of the interaction [29,30].

Electronic stopping power, in the form of energy loss, becomes prominent when incident ions are

moving at speeds greater than 1 keV/amu, indicative of high-energy levels [31-32]. The term 'inelastic' denotes that such collisions may result in the excitation of the target atom's electrons as well as the excitation of the electron clouds surrounding the incident ions. As part of these energy loss processes, the impact of the ion beam also leads to the ejection of secondary electrons and photons, in addition to the sputtering of the solid material, which involves the expulsion of atoms, ions, and molecular particles [29].



Electronic Stopping Power for H

Figure 9: The TRIM result to calculate the electronic stopping power for H and He.

5. TRIM Calculation Stopping Power Results:

Figures 8 and 9 depict the energy losses as a function of incident ion energy for various incident ion types (H, He, Ar, Kr), calculated using simulations from the SRIM code. The results underscore that the primary energy loss mechanism varies between light ions and heavy ions. In the case of light ions such as H and He, the dominant contributor to energy loss is electronic, and this electronic energy loss increases as the ion energy rises. Conversely, for heavy ions like Ar and Kr, nuclear loss emerges as the primary contributor.

Our analysis allows us to extract the nuclear and electronic stopping power for each incident ion, and Figure 10 visually demonstrates that, for lighter incident ions, electronic stopping power predominates and is more significant. Figure 10 illustrates a noteworthy trend where ion energy losses grow in tandem with the mass of the ion. This phenomenon occurs because heavier ions possess greater momentum, enabling them to engage with a larger number of electrons within the target material. For example, in the case of H ions, we observe that as the incident energy the electronic stopping increases. power, represented as $\left(\frac{dE}{dx}\right)_{e}$, rises until it reaches a peak at around 450 keV. Beyond this point, the electronic stopping power experiences a steep exponential decline as ion energy further escalates. The maximum electronic stopping power, approximately $(1.02 \times 10^{+1} \text{ eV/Å})$, imposes limitations on the penetration of ions into the rigid PVC material, as depicted in Figure 10. The penetration depth increases with rising ion energy

up to its maximum value, after which it starts to decrease.



Figure 10: The TRIM calculation of the electronic stopping power for H, He, Ar, and Kr.

When we compare H and He ions, it's evident that their mass difference plays a significant role in determining their stopping power ranges. This distinction is clearly visible in Figure 10, where He ions shift upwards in the graph. For He ions, the maximum $\left(\frac{dE}{dx}\right)_e$ is approximately 2.387×10⁺¹ eV/Å at 900 keV. It's worth noting that the maximum nuclear loss of energy is dependent on the ion's mass and shifts to lower energy levels for lighter ion species.

Furthermore, the TRIM calculations reveal a pronounced presence of nuclear-stopping power with the increase in the mass of the incident ions, as demonstrated in Figure 11. From the graph, it is evident that nuclear-stopping power denoted as $\left(\frac{dE}{dx}\right)_n$ for Ar ions, exhibits an upward trend as the ion energy increases, reaching its peak at approximately $4.269 \times 10^{+1} \text{ ev/A}^{\circ}$ at an energy of 30 keV. Subsequently, the nuclear-stopping

power experiences a steep exponential decline with further increases in ion energy.

From this graph, it becomes evident that for heavy ions such as Ar, an increase in incident energy leads to a corresponding increase in $\left(\frac{dE}{dx}\right)_n$, reaching its peak at 30 keV. Beyond this point, Ar ions tend to come to rest, resulting in a steep exponential decline in nuclear-stopping power. At this juncture, the maximum nuclear-stopping power, approximately $4.269 \times 10^{+1} \text{ eV/Å}$, significantly limits penetration through the PVC surface. This occurs because, at 30 keV, Ar ions engage in more frequent collisions and ionization events, requiring higher energy levels to sustain motion through the PVC surface.

Furthermore, when we examine krypton, which possesses the highest atomic mass among the ions under study (83.912 amu), we find it exhibits the highest nuclear-stopping power. This relationship is attributable to the fact that nuclear-stopping power increases in tandem with the mass of the incident ion. For Kr ions, the nuclear-stopping power attains its peak value, approximately $8.864 \times 10^{+1} \text{ ev/A}^{O}$, at incident ion energy of 70 keV. This notable increase in nuclear-stopping power has a significant impact on the penetration of Kr ions through the PVC surface. The high collision rate arising from ionization and excitation processes causes Kr ions to rapidly lose energy, preventing them from penetrating deeply into the PVC surface. This consideration holds particular importance in implantation applications, where it is desirable for ions to achieve maximum penetration into the target material.



Figure 11: The TRIM calculation of the nuclear-stopping power for H, He, Ar, and Kr.

Up to an energy level of 10 keV, the interactions between the ion beam and the target can be effectively analyzed as a sequence of isolated binary collisions. The overall rate of energy loss $\left(\frac{dE}{dx}\right)$ within the PVC target is attributed to a combination of nuclear and electronic losses, as illustrated in Figure 12.

When an ion penetrates a target material, it engages in interactions with both the nuclei and electrons of the target substance. As a result of these interactions, the ion experiences a loss of energy and gradually decelerates along a stochastic trajectory. Ultimately, the ion reaches a point of rest at a specific depth within the target material. The distance traveled by the ion, known as the 'projected range'. is defined as the cumulative path length covered by the ion within the target [33,34]. The projected range of the ion is contingent upon factors such as the incident ion energy, the ion's mass, and the mass of the target material. This relationship can be mathematically expressed as follows:



Figure 12: The TRIM illustration for electronic and nuclear $\left(\frac{dE}{dx}\right)$.

$$R_p = \int_{E_f}^{E_o} \left(\frac{dE}{dx}\right)^{-1} \tag{2}$$

Here, E_o represents the initial energy of the incoming projectile, while E_f denotes the final energy of the projectile ion. The final energy of the projectile ion corresponds to the energy level at which it has expended sufficient energy to no longer possess the capability to surmount the potential barrier existing between the target atoms. Consequently, it comes to a complete halt and ceases its motion.

In scenarios involving heavy ions at low energies, where electronic stopping has minimal impact, the total range and projected range are connected through a function dependent on the mass ratio between the projectile (M_1) and the target material (M_2) [11]:

$$R_p^p$$

$$=\frac{R_p}{1+\frac{M_2}{3M_1}}$$

When R_p^p represents the principal projected range along the initial path of the projectile, it is equivalent to the average depth of penetration, but specifically for normal incidence.



Figure 13: The total range R_p , projected range R_p^p , and depth of penetration of a projectile.

The projected range can be easily determined through TRIM simulations, as depicted in Figure 14 and summarized in Table 2. As illustrated in Figure 14, the H ion, being the lightest among the ions considered, exhibits the highest projected range, measuring 21.11 μ m at an energy of 1 MeV. In contrast, for the same energy value, He, Ar, and Kr ions demonstrate projected ranges of 4.48 μ m, 1.29 μ m, and 0.8504 μ m, respectively. These results align with theoretical expectations, indicating that H ions can penetrate up to 21.21 μ m, while Kr ions are only able to penetrate 0.8504 μ m into the PVC surface due to their significantly higher mass

compared to H ions. Table 2 demonstrates that the projected range (R_p) is contingent on both the incident energy and the specific type of incident ion. Across each ion type, elevating the incident energy leads to an augmentation in the projected range toward the PVC surface. This, in turn, contributes to greater distortion. It is noteworthy that the choice of polymer material is a crucial factor to take into account when examining this phenomenon, as different polymers exhibit distinct chemical compositions and structures.

Energy (keV)	R_p Angstrom
1	291
10	1918
100	10900
1	163
10	1414
100	8820
	Energy (keV) 1 10 100 1 10 10 10 10 10 100 100 100

Table 2 The TRIM calculation to determine R_p for rigid PVC polymer at different ion and ion energies.

	1	48
Ar	10	201
	100	1424
	1	53
Kr	10	173
	100	887



Figure 14: The TRIM illustration to determine the projected range for H, He, Ar, and Kr as a function of incident ion energy.

Conclusion:

PVC stands out as one of the most extensively used polymers worldwide due to its energy efficiency, cost-effectiveness, and flexibility. Investigating its surface properties holds significant importance in enhancing and achieving desired characteristics. While numerous methods exist for studying these properties, low-energy ion beam irradiation has emerged as a viable technique for modifying both the chemical and physical attributes of polymer surfaces.

Moreover, the study of ion beam irradiation can be conducted through computer simulations, notably employing the TRIM program. This approach offers several advantages over analytical formulations based on transport theory. It enables a comprehensive consideration of surface and interface effects, provides precise treatment of elastic scattering, and facilitates the determination of energy and angular distributions. In our research, we have employed this simulation program to investigate the interaction of ion beams with rigid PVC polymer. This interaction has direct implications for altering its mechanical and chemical properties, which are crucial in various applications, including ion implantation or introducing impurities to target surfaces.

We can conclude that the majority of observed phenomena during the ion bombardment of polymers stem from the energy deposited by incoming ions into the target material. This deposition can result in various energy outcomes, including the remove of atoms from the surface (known as sputtering), the generation of secondary electrons, photons, vacancies, and free radicals. Our findings indicate that different incident ion characteristics, such as energy, mass ratio, and incident angle, lead to varying collision events, including ionization and excitation, which, in turn, result in distinct levels of distortion. Furthermore, the number of generated phonons and vacancies is influenced by the mass of the incident ion. We observed that as the mass of the incident ion increases, the sputtering process becomes more intense and inflicts greater damage on the surface. In particular, our study showed that Kr ions, which possess significantly greater mass than H ions, exhibit higher levels of sputtering and lower transparency. Additionally, we noted that as the increases, incident energy the sputtering decreases, and this relationship is directly proportional to the increase in the incident angle. For H and He ions, approximately 99% of their energy loss occurs through direct collision with PVC surface atoms, as they lack the requisite energy and ability to generate vacancies and phonons. Conversely, for Ar and Kr ions, the energy loss through collision is lower. accounting for 67% and 30%, respectively.

The energy loss per unit length $\left(\frac{dE}{dx}\right)$ of the projectile is a fundamental parameter that characterizes the transfer of energy from ions to target materials. It can be divided into two components: nuclear and electronic stopping power. Electronic stopping power predominates when dealing with lighter ions, such as hydrogen (H) and helium (He), while nuclear-stopping power becomes more significant for heavier ions like argon (Ar) and krypton (Kr). The projected range, which denotes the distance an ion can travel within a material, is influenced by both

incident energy and projectile mass. It is directly proportional to the incident energy, meaning that as the incident energy increases, the projected range also increases. Conversely, the projected range is inversely proportional to the mass of the projectile. For instance, when considering Ar ions with incident energies of 1, 10, and 100 keV, the projected ranges within PVC are measured at 48, 201, and 1424 Å, respectively. Furthermore, the type of incident ion plays a role in determining the projected range. Taking He ions with the same incident energies as an example, their projected ranges within PVC are calculated as 163, 1414, and 8820 Å, respectively. This difference can be attributed to He ions being lighter compared to Ar ions, allowing them to penetrate more deeply into the PVC surface.

References

[1] Rymzhanov, R.A., Medvedev, N. and Volkov, A.E. (2021) Damage kinetics induced by swift heavy ion impacts onto films of different thicknesses, *Applied Surface Science* 566, 150640. DOI: 10.1016/j.apsusc.2021.150640

[2] Biersack, J. and Haggmark, L. (1980). A Monte Carlo computer program for the transport of energetic ions in amorphous targets. *Nuclear Instruments and Methods* 174(1-2), pp. 257-269. DOI: 10.1016/0029-554x(80)90440-1

[3] Biersack, J., Berg, S. and Nender, C. (1991). T-DYN Monte Carlo simulations applied to ion assisted thin film processes. *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms*, 59-60, pp. 21-27. DOI: 10.1016/0168-583x(91)95167-c

[4] Ziegler, J., Biersack, J. and Littmark, U. (1985). *The stopping and ranges of ions in matter*. New York: Pergamon Press. ISBN: 008021603X [5] Wilkes, C., Summers, J. and Daniels, C. (2005). *PVC handbook*. München: Hanser

[6] Asadinezhad, A., Lehocký, M., Sáha, P. and Mozetič, M. (2012). Recent progress in surface modification of polyvinyl chloride. *Materials* 5(12), pp. 2937-2959. DOI: 10.3390/ma5122937

[7] Williams, D.F. (1982). *Biocompatibility in Clinical Practice; CRC Press: Boca Raton, FL, USA*.

[8] Leveneur, J., Zhang, Y., Fiedler, H., Prabakar, S., Le Ru, E.C. and Kennedy, J. (2023) Surface modification of collagen using lowenergy noble gas ion implantation, *Surface and Coatings Technology* 468, pp. 129768. DOI: 10.1016/j.surfcoat.2023.129768

[9] Markarian, J. (2007). PVC additives – What lies ahead?. *Plastics, Additives and Compounding,* 9(6), pp. 22-25. DOI: 10.1016/s1464-391x(07)70153-8

[10] Dias, F.G.A., Souza, L.S.G., Veiga, A.G., Andreopoulou, A.K., Kallitsis, J.K. and Rocco, M.L.M. (2023) From orthophosphate to phosphine-based groups: The effects of argon ion sputtering on doped polyethersulfone films, *Surface and Interface Analysis* 55(9) pp. 677-682. DOI: 10.1002/sia.7222

[11] Fink, D. (2004). *Transport processes in ionirradiated polymers*. Berlin: Springer.

[12] Behrisch, R. (1981). *Sputtering by particle bombardment*. Berlin: Springer-Verlag.

[13] Jeong J.W. and Song Y.S. (2023) Surface characteristics of metal-like composites fabricated with aliphatic polyketone, *Korea-Australia Rheology Journal* 35, pp. 169–178. DOI: 10.1007/s13367-023-00061-2

[14] Behrisch, R. (1981). *Sputtering by Particle Bombardment I*. Berlin: Springer-Verlag.

[15] Behrisch, R. and Wittmaack, K.(1991). *Sputtering by particle bombardment*.Berlin: Springer-Verlag.

[16] Fink, D. (2004). *Transport processes in ion-irradiated polymers*. Berlin: Springer.

[17] Calcagno, L. and Foti, G. (1991). Ion irradiation of polymers. *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms*, 59-60, pp.1153-1158. DOI: 10.1016/0168-583X(91)95784-B

[18] Li, S., Fan, Y., Chen, H., Nie, J., Liang, Y., Tao, X., Zhang, J., Chen, X., Fu, E. and Wang Z.L. (2020) Manipulating the triboelectric surface charge density of polymers by low-energy helium ion irradiation/implantation, *Energy Environ. Sci.* 13, pp. 896-907. DOI: 10.1039/C9EE03307F

[19] Fragalà, M., Compagnini, G., Torrisi, L. and Puglisi, O. (1998). Ion beam assisted unzipping of PMMA. *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms*, 141(1-4), pp. 169-173. DOI: 10.1016/S0168-583X(98)00087-1

[20] Giannuzzi, L., Prenitzer, B. and Kempshall,B. (2005). *Introduction to focused ion beams*.New York: Springer. ISBN: 978-0-387-23116-7

[21] Sigmund, P. (1969). Theory of sputtering. I. Sputtering yield of amorphous and polycrystalline targets. *Physical Review* 184(2), pp. 768-768. DOI: 10.1103/physrev.187.768

[22] Ruge, I. and Graul, J. (1971). *Ion implantation in semiconductors*. Berlin: Springer-Verlag.

[23] Tian, S. (2003). Predictive Monte Carlo ion implantation simulator from sub-keV to above 10 Mev. *Journal of Applied Physics*, 93(10), pp. 5893-5904. DOI: 10.1063/1.1565690 [24] Sigmund, P. (2005) Sputtering by ion bombardment theoretical concepts, Sputtering by Particle Bombardment, 47, pp. 9-71. DOI: 10.1007/3540105212_7

[25] Dzhurakhalov, A. (2004). Sputtering of binary crystal surface under grazing ion bombardment. *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms*, 216, pp. 202-205. DOI: 10.1016/j.nimb.2003.11.035

[26] Totten, G. and Hong, L. (2004). *Surface modification and mechanisms*. New York: Marcel Dekker.

[27] Srinadhu, E.S., Shyam, R., Kumar, J., Thanu, D.P.R., Keswani, M. and Zhao M. (2019) Adhesion enhancement of polymer surfaces by ion beam treatment: A critical review, *Reviews of Adhesion and Adhesives* 7(2) pp. 169-194.

[28] Bohr, N. (1913). I. On the constitution of atoms and molecules. *The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science*, 26(151), pp. 1-25. DOI: 10.1080/14786441308634955

[29] Peltola, J. (2003). *Stopping power for ions and clusters in crystalline solids*. Helsinki: University of Helsinki, pp.5-11. ISBN: 95210-0939X

[30] Zhang, Y. and Weber W.J. (2020) Ion irradiation and modification: The role of coupled electronic and nuclear energy dissipation and subsequent nonequilibrium processes in materials featured, *Appl. Phys. Rev.* 7, 041307. DOI: 10.1063/5.0027462

[31] Schwartz, K., Trautmann, C. and Neumann, R. (2003). Electronic excitations and heavy-ioninduced processes in ionic crystals. *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and* *Atoms*, 209, pp.73-84. DOI: 10.1016/s0168-583x(02)02013-x

[32] Moro, M.V., Bauer, P. and Primetzhofer, D. (2020) 'Experimental electronic stopping cross section of transition metals for light ions: Systematics around the stopping maximum', *Physical Review A*, 102(2). doi:10.1103/physreva.102.022808.

[33] Kantre, K.A., Moro, M.V., Paneta, V. and Primetzhofer D. (2021) Assessing electronic energy loss of heavy ions detected in reflection geometry, *Surf Interface Anal.* 53, pp. 650-657. DOI: 10.1002/sia.6951

[34] Arnold, G. and Mazzoldi, P. (1987). *Ion Beam Modification of Insulators*. Amsterdam: Elsevier, pp.1-648.