

New ion desorption mechanism from rare gas solids by multiply charged ion impacts

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This study measured the absolute ion desorption yield from the surface of solid Ne and Ar by low-energy Ne^{q+} ($q = 1-4$), Ar^{q+} ($q = 1-6$), and Kr^{q+} ($q = 2-6$) ion impacts. Results revealed the dependence of ion desorption yield on the potential and the kinetic energies of the incident ions, as well as its linear proportionality with the former. Present results could not be explained by existing models for ion desorption from insulator surfaces. We proposed a new mechanism of ion desorption that considers the contribution of both energy types to ion desorption.

Keywords: potential sputtering, ion desorption, rare gas solids.

1. Introduction

The potential sputtering phenomenon [1,2] widely observed on the surfaces of insulators, such as alkali-halides [3] and oxides [4], is a desorption mechanism induced by the transfer of potential (internal) energy from incident multiply charged ions to the solid surface. Several models of potential sputtering processes, including the Coulomb explosion [5–8] and defect-mediated sputtering [3], have been proposed based on the experimental results of the desorption (sputtering) yields. Another model, the kinetically assisted potential sputtering [9], has been employed to explain MgO_x sputtering yields due to the impact of slow multiply charged Xe ions. In this model, lattice and electronic defects are produced, respectively, by the kinetic and potential energies of the incident ion contributing to the desorption process.

Dynamic processes of desorption induced by electronic transitions can ideally be studied using rare gas solid (RGS) [10], as it has the simple electronic structure similar to isolated atoms, along with very unique characteristics, such as small cohesive energy (e.g., 0.02 eV/atom for Ne), large band gap energy (e.g., 21.6 eV for Ne), and long diffusion length of excitons (e.g., ~ 200 nm for Ne), which set it apart from the other materials [11].

In our previous study, we discussed the relative ion yields of potential sputtering from solid Ne by Ar^{q+} ($q = 1-7$) impact [12], and demonstrated the proportionality of the sputtering ion yields to the potential energy of the incident ion. Herein, we describe the experimental results of *absolute* sputtering yields from RGSs by multiply charged ion impacts, and propose a new ion desorption mechanism.

2. Experimental

Details of the experimental apparatus have been described elsewhere [12–14]. Briefly, multiply charged ions were generated by an electron cyclotron resonance (ECR) type ion source (NANOGAN, Pantechnik). Extracted ions were mass-selected by an analyzing magnet and were focused onto the sample surface at the center of the main chamber. Incident ion current was reduced to about a few nA in order to prevent the charge-up effect. The main chamber was evacuated by a series of turbo-molecular pumps and a Ti-getter pump, resulting in a pressure of $\sim 2 \cdot 10^{-8}$ Pa.

RGSs were condensed onto a polycrystalline Cu substrate cooled to 4.5 K by a mechanical cryostat. The sample film was condensed onto the Cu disk by filling the chamber with gaseous Ne to a pressure of 10^{-6} – 10^{-4} Pa. The film thickness was estimated from the exposure by assuming

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the condensation coefficient to be unity, and was 1000 atomic monolayers throughout this work. The sample film was evaporated and re-deposited after each run of the measurement. Annealing of the sample to 7 K for solid Ne and 25 K for solid Ar did not change the experimental results within our experimental uncertainty.

Absolute ion desorption yield Y_{ion} was estimated from the number of desorbed ions per second N_{des}^i and the number of incident ions per second N_{in} using the following equation:

$$Y_{\text{ion}} = \frac{N_{\text{des}}^i}{N_{\text{in}}} = N_{\text{des}}^i \frac{qe}{I_{\text{in}}}$$

where I_{in} and q are the current and charge state of the incident ion, respectively. N_{des}^i was estimated by a procedure as follows: (i) I_{in} was measured at the Cu substrate and a movable Faraday cup just in front of the substrate (Fig. 1(a)); (ii) the sample solid (RGS) was condensed on the Cu substrate and; (iii) the current flowing into the substrate I_s was measured (Fig. 1(b)). If RGS was not condensed on the substrate, then I_s would be the same as I_{in} ; otherwise, if RGS was formed on the substrate, then I_s would decrease by the amount of I_{des} (desorbed ion current). Most of the desorbed ions were known to be singly charged ions [14]. Using the variables just discussed, the absolute desorption yield Y_{ion} could be rewritten as

$$Y_{\text{ion}} = I_{\text{des}} \frac{q}{I_{\text{in}}} = \frac{I_{\text{in}} - I_s}{I_{\text{in}} / q}$$

The current I_s was stable for about 30–60 s after the ion irradiation and then decreased probably due to the charge-up effect, therefore the current measured within about 10 s after the ion incidence was used for the determination of Y_{ion} .

The uncertainty of Y_{ion} was estimated at approximately $\pm 30\%$, the largest source of which was the instability of the ion beam; ammeter accuracy had no influence as both I_{in} and I_s were measured with the same ammeter (Keithley, 6485).

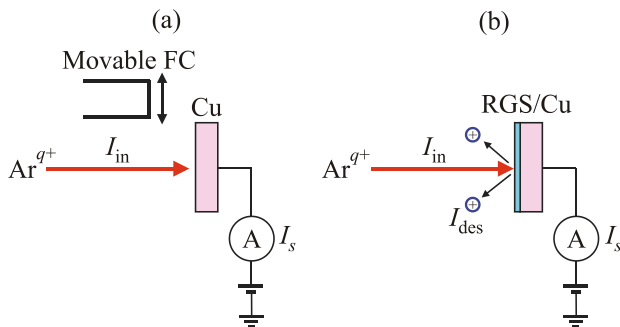


Fig. 1. (Color online) Measurement of the incident ion current (I_{in}) and the desorbed ion current (I_{des}). See text for details.

The absolute total desorption yield Y_{total} was estimated from the number of desorbed atoms per second N_{des}^t as expressed by [15]

$$Y_{\text{total}} = \frac{N_{\text{des}}^t}{N_{\text{in}}} = \frac{S\Delta P}{kT} \frac{qe}{I_{\text{in}}}$$

where S , ΔP , k , and T indicate the pumping speed of the pumping system for each gas, partial pressure change in the main chamber during the irradiation of the ion beam, Boltzmann constant, and ambient temperature, respectively. The total pumping speed of the turbo-molecular pump and cold surfaces was measured at $(0.14 \pm 0.01) \text{ m}^3/\text{s}$ for Ne, and $(0.21 \pm 0.02) \text{ m}^3/\text{s}$ for Ar, as determined by the pressure measured by a Bayard-Alpert type ionization gauge installed in the main chamber, and from the flow rate calibrated volumetrically using a reference volume and a Baratron pressure gauge as a reference. Partial pressure rise during irradiation, typically within 10^{-8} to 10^{-6} Pa, was detected by a quadrupole mass spectrometer which was calibrated against the ionization gauge for each run of the experiment. Ne partial pressure in the main chamber during the bombardment of 1 keV Ne^+ as a function of time is shown in Fig. 2. The target was solid Ne and the incident Ne^+ current was 2.7 nA. When the ions were incident on the sample at $t = 0$, the pressure increased from $3 \cdot 10^{-8}$ Pa to $\sim 10^{-6}$ Pa and was constant during about 600 s, then gradually decreased to the order of 10^{-8} Pa, indicating that most of the sample atoms were desorbed. The partial pressure change ΔP was estimated as a difference between the pressure before and after the ion bombardment as shown in Fig. 2.

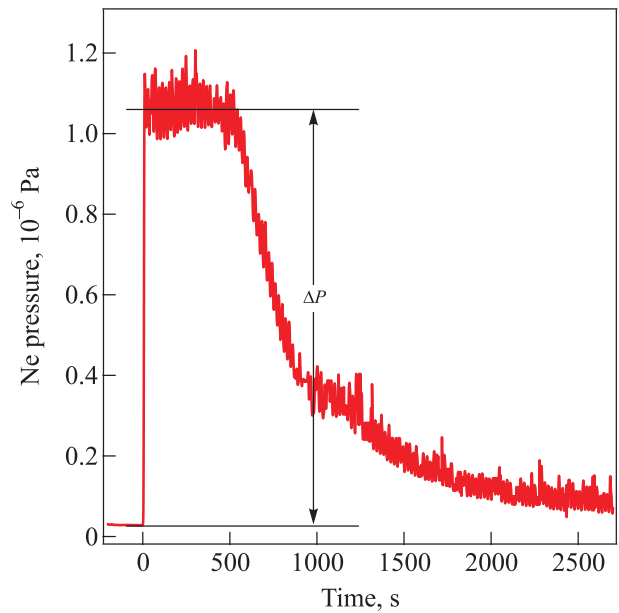


Fig. 2. (Color online) Ne partial pressure during the bombardment of 1 keV Ne^+ to a solid Ne surface as a function of time. The thickness of the solid Ne was 1000 atomic layers.

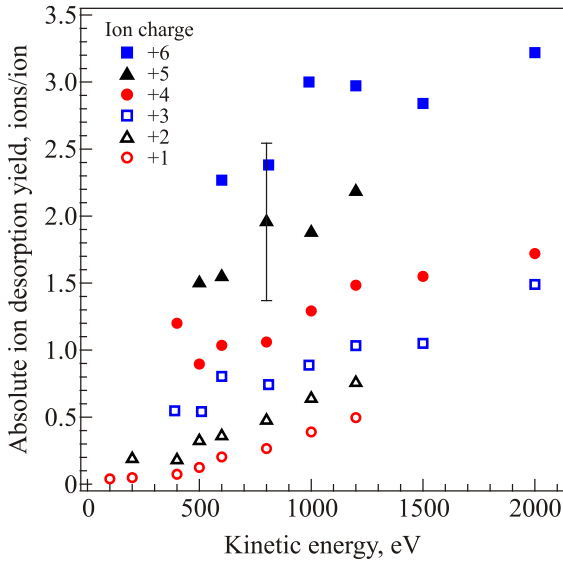


Fig. 3. (Color online) Absolute ion desorption yield Y_{ion} from solid Ne by Ar^{q+} ($q=1-6$) impact as a function of the kinetic energy of the incident ions.

The uncertainty of Y_{total} was estimated at approximately $\pm 40\%$, the largest source of which was the absolute pressure measured by the ionization gauge. It should be noted that the uncertainty of the relative sensitivity of the ionization gauge was canceled in determining desorption rate by the present method.

The sample substrate was biased to +15 V for suppression of secondary electrons.

3. Experimental results

Figures 3 and 4 show the plot of Y_{ion} from solid Ne by Ar^{q+} ($q=1-6$) impact as a function of the kinetic and potential energies of the incident ions, respectively, which clearly indicated Y_{ion} dependence on both energies. Specifi-

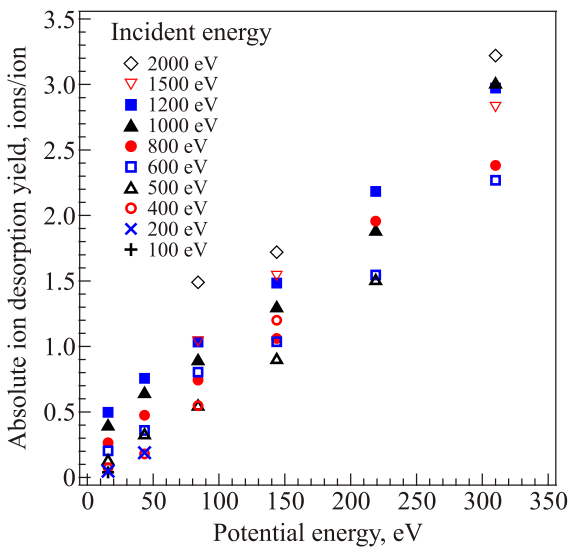


Fig. 4. (Color online) Absolute ion desorption yield Y_{ion} from solid Ne by Ar^{q+} ($q=1-6$) impact as a function of the potential energy of the incident ions.

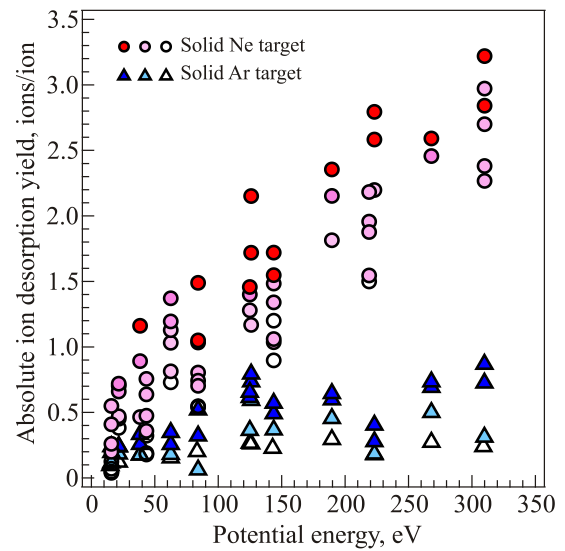


Fig. 5. (Color online) Absolute ion desorption yield Y_{ion} from the surface of solid Ne and solid Ar by Ne^{q+} ($q=1-4$), Ar^{q+} ($q=1-6$) and Kr^{q+} ($q=2-6$) impact as a function of the potential energy of the incident ions. Color depth indicates the kinetic energy of the incident ions: 100–500 eV (open marks), 600–1200 eV (thin marks), and 1500–2000 eV (solid marks).

cally for Fig. 4, Y_{ion} increased linearly with the potential energy, which was consistent with our previous results [12].

Figure 5 illustrates the plots of Y_{ion} from solid Ne and solid Ar by Ne^{q+} ($q=1-4$), Ar^{q+} ($q=1-6$), and Kr^{q+} ($q=2-6$) impacts; color depth represents the kinetic energy of the incident ion: open marks indicate 100–500 eV, thin marks 600–1200 eV, and solid marks 1500–2000 eV.

Absolute total desorption yield Y_{total} from the surface of solid Ne and solid Ar by Ne^+ , Ar^+ and Kr^+ impacts as a function of the incident energy is shown in Fig. 6. Data for the Ar^+-Ne solid were taken from our previous paper [13].

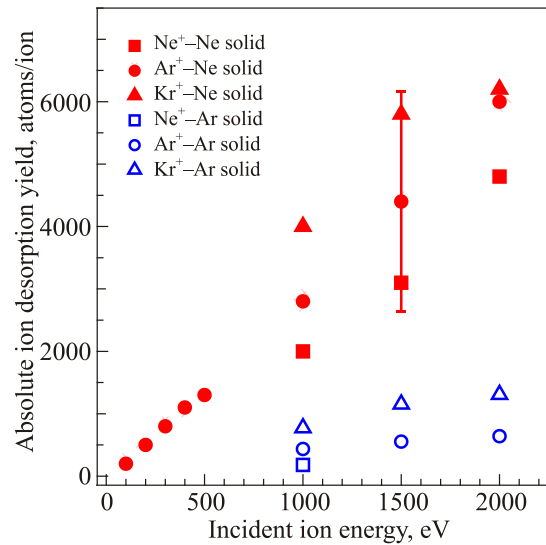


Fig. 6. (Color online) Absolute total desorption yield Y_{total} from the surface of solid Ne and solid Ar by Ne^+ , Ar^+ and Kr^+ impacts as a function of the incident energy. Data for Ar^+-Ne solid obtained from our previous paper [13].

4. Discussion

Results in Figs. 3, 4, and 5 represented the linear increase of Y_{ion} with the potential energy of the incident ions, for both solid Ne and solid Ar targets; additionally, the Y_{ion} of the former was a few times larger than of the latter.

In RGSs it is known that the creation of excitons and holes plays an important role in the desorption process. The contribution of exciton induced processes to the present results can be negligibly small if we consider the absolute desorption yields by the creation of excitons and holes [10,15,16]. It is also known that the exciton-induced defects and holes created by VUV photons [17] and low-energy electrons [18] can be accumulated in RGSs, which can affect the ion desorption process. The contribution of these effects to our results can also be ruled out because our desorption signals were stable during the yield measurements as stated above, and we used a new sample solid for each measurement.

In the traditional Coulomb explosion model, ions created along the ion track and/or on the solid surface were desorbed from the surface by Coulomb repulsion. In this case, Y_{ion} should be proportional to the number of ions created in the solid, i.e., charge changing (ionization and charge exchange) cross section σ_{cc} by ion impact. This model can not explain larger Y_{ion} for Ne solid than for Ar solid if we refer to σ_{cc} data by Cocke *et al.* and Justiniano *et al.* [19,20]. This model has already been ruled out for the potential sputtering process of insulating surfaces, such as oxides and alkali-halides [21], and now can be ruled out for molecular solids.

We used a model based on our previous study on the desorption of Ne cluster ions Ne_n^+ from solid Ne by 1 keV Ar^+ impact [14], which measured the kinetic energy distribution of desorbed cluster ions and the thickness dependence of the cluster ion desorption yields. Based on the experimental results of this model and another gas flow model [22–24], a new model of ionic cluster growth characterized by the following was proposed:

(1) A high-pressure, high-temperature spike region is created in the solid by an incident ion,

(2) atoms and ions in the spike volume erupt from the surface, and

(3) a desorbing ion can grow into a cluster ion by three-body collisions with surrounding neutral atoms, during the outflow of a large number of bulk atoms into the vacuum.

In this model, ions created in the solid desorb together with a large number of surrounding neutral atoms, therefore Y_{ion} should be proportional not only to σ_{cc} but also to the Y_{total} , i.e., $Y_{\text{ion}} \propto \sigma_{\text{cc}} Y_{\text{total}}$.

As a side note, the charge state dependence of Y_{total} was not observed within the experimental uncertainty [13], which makes the results of the singly charged ion impact in Fig. 6 applicable for all charge states of the incident ion.

To the best of our knowledge, the σ_{cc} of the incident ion with the target atoms in the solid was unavailable. As earlier stated, our targets were van der Waals solids, in which the collision process of the incident ion with the target atom in the solid is similar to that with an isolated atom in a gas phase; therefore, we employed the gas phase data. Charge changing cross section σ_{cc} was estimated by a simple scaling law proposed by Kimura *et al.* [25], derived for the charge transfer cross sections in slow collisions of highly charged ions ($q \geq 5$) with atoms, based on the extended classical over-barrier model by Niehaus [26]. The scaling law predicts the total charge transfer cross section σ_{CT} in atomic units as

$$\sigma_{\text{CT}} = 4\pi q / E_{\text{IP}}^2,$$

where q is the charge state of the incident ion and E_{IP} is the ionization potential of the target atom. As the direct ionization cross section was very small compared to the charge transfer cross section in this energy range, we assumed $\sigma_{\text{cc}} \simeq \sigma_{\text{CT}}$. Finally a proportionality

$$Y_{\text{ion}} \propto \frac{q}{E_{\text{IP}}^2} Y_{\text{total}}$$

could be expected.

Figure 7 shows Y_{ion} as a function of $\Gamma \equiv (q / E_{\text{IP}}^2) Y_{\text{total}}$. Data points included Y_{ion} of the solid Ne (solid circles) and Ar (open circles) targets, incident ions of Ne^{q+} ($q = 1-4$) (\square), Ar^{q+} ($q = 1-6$) (\times), and Kr^{q+} ($q = 2-6$) ($+$), and incident energies of 1000, 1500, and 2000 eV. Because Kimura *et al.* claimed that their scaling law is valid for $q \geq 5$, the data points of $\text{Ar}^{5+,6+}$ and $\text{Kr}^{5+,6+}$ projectiles are plotted with large marks, while those of $q = 1-4$ projectiles with small marks. The error bar shown in the figure corresponds to the

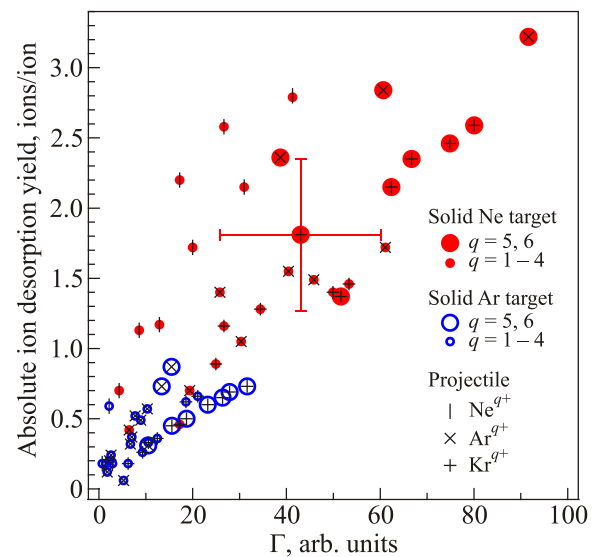


Fig. 7. (Color online) Absolute ion desorption yields Y_{ion} as a function of $\Gamma \equiv (q / E_{\text{IP}}^2) Y_{\text{total}}$. See text for details.

experimental uncertainty of Y_{total} (x axis) and Y_{ion} (y axis). Although the scatter was large, our data of Y_{ion} showed a linear correlation with Γ .

It is found that the slope depends on the projectile, i.e., heavier projectile has a smaller slope. This could be attributed to the larger volume of the spike region than that of the ion creation region. This was plausible as the Y_{total} , which corresponds to the spike volume, was very large for heavier projectiles, as shown in Fig. 6. Rough estimation from the charge transfer cross section from Ref. 19 and an assumption that the crater is a semi-spherical shape as Fig. 1 in Ref. 23 supports this possibility.

5. Summary

Our absolute ion desorption yield measurements from the surfaces of solid Ne and Ar by multiply charged ion impacts indicated that (i) ion desorption yields were linearly proportional to the potential energy, and (ii) dependent on both potential and kinetic energies of the incident ions. These findings were qualitatively validated by a new desorption model, in which the ions were created in the solid by the potential energy of the incident ions and desorbed together with surrounding neutral atoms erupting from the spike region in the solid. A linear correlation between the ion desorption yield and a parameter based on this model was found indicating the validity of our simple model.

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Новий механізм десорбції іонів з поверхні інертних газів при дії багатозарядних іонів

K. Ban, M. Akiwa, H. Ueta, T. Tachibana,
T. Hirayama

Експериментально вивчено абсолютну десорбцію іонів з поверхні твердих Ne і Ag при низькоенергетичному бомбардуванні іонами Ne^{q+} ($q = 1-4$), Ar^{q+} ($q = 1-6$) та Kr^{q+} ($q = 2-6$). Показано, що десорбція іонів залежить від потенційної і кінетичної енергії іонів, що падають, і лінійно пропорційна потенційній енергії. Отримані результати неможна пояснити існуючими моделями десорбції іонів з поверхні діелектрика. Запропоновано новий механізм десорбції іонів, що враховує внесок обох типів енергії.

Ключові слова: потенційне розпилення, десорбція іонів, твердий газ.

Новый механизм десорбции ионов с поверхности инертных газов при воздействии многозарядных ионов

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T. Hirayama

Экспериментально изучена абсолютная десорбция ионов с поверхности твердых Ne и Ag при низкоэнергетической бомбардировке ионами Ne^{q+} ($q = 1-4$), Ar^{q+} ($q = 1-6$) и Kr^{q+}

($q = 2-6$). Показано, что десорбция ионов зависит от потенциальной и кинетической энергии падающих ионов и линейно пропорциональна потенциальной энергии. Полученные результаты не могут быть объяснены существующими моделями десорбции ионов с поверхности диэлектрика. Предложен новый механизм десорбции ионов, учитывающий вклад обоих типов энергии.

Ключевые слова: потенциальное распыление, десорбция ионов, твердый газ.